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A mechanistic study of certain cyclopropylidene and cyclopropylidenoid rearrangements

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A MECHANISTIC STUDY OF CERTAIN CYCLOPROPYLIDENE AND CYCLOPROPYLIDENOID REARRANGEMENTS

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A mechanistic study of certain cyclopropylidene and cyclopropylidenoid rearrangements

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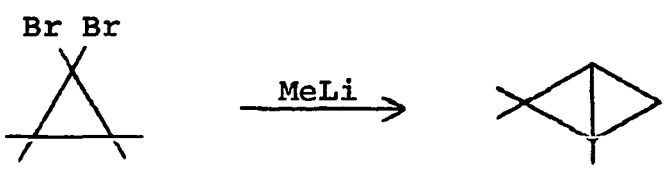
INTRODUCTION

In recent years, the reaction of gem-dihalides with alkyllithiums to produce carbenoid intermediates has been widely studied.[1] In the case of simple 1,1-dibromocyclopropanes, the α-bromocyclopropyllithium intermediate or the cyclopropylidene derived therefrom can afford allenes[2] (Eq. 1) or insertion products[3] (Eq. 2), result in electrophilic addition to olefins[4] (Eq. 3), or if a suitably positioned double bond is available, lead to rearrangement[5] (Eq. 4, Table I).

(1)



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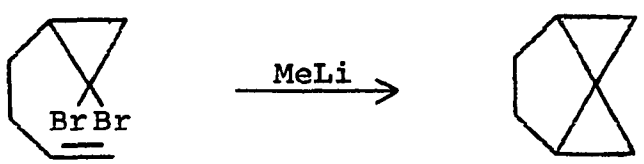

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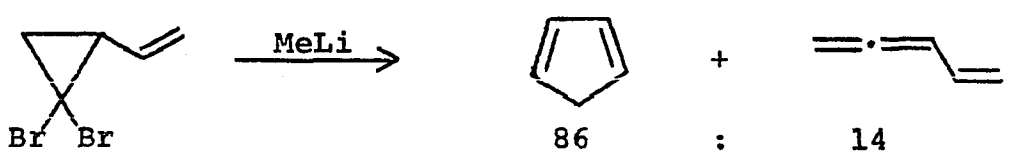
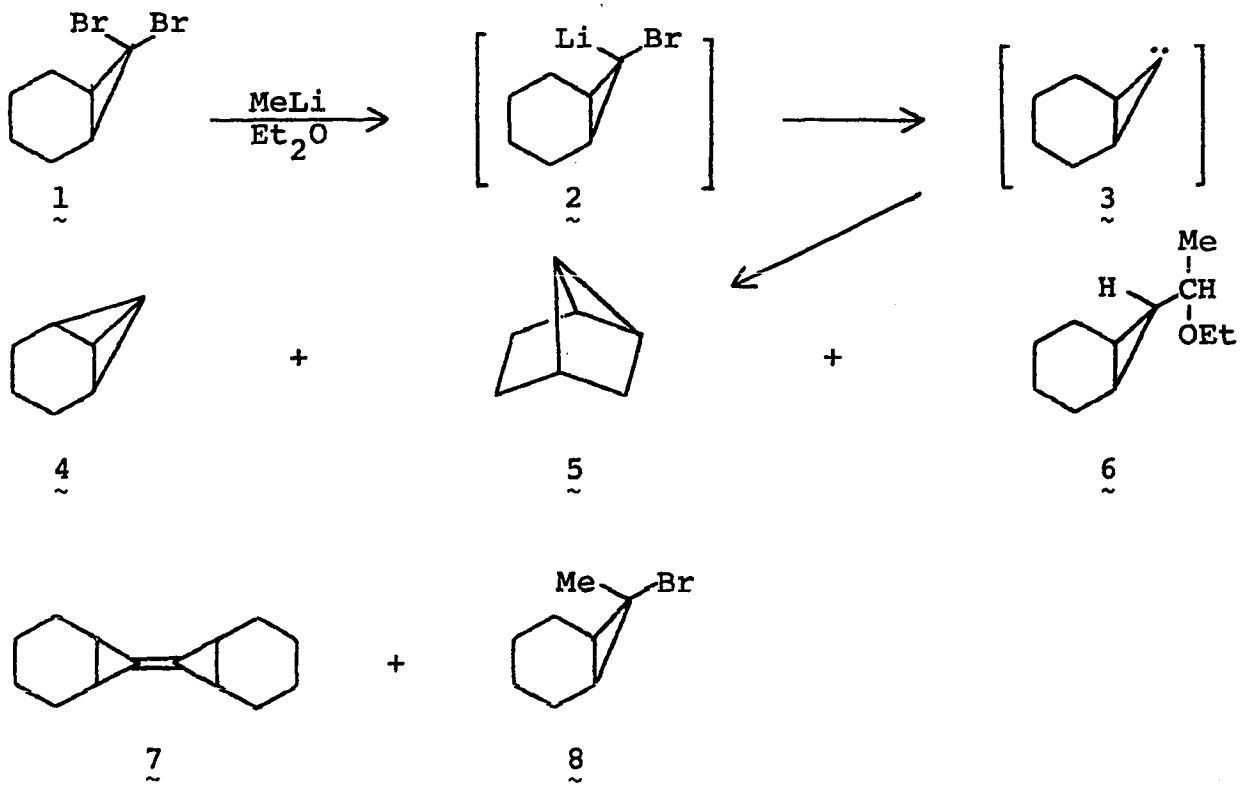


(4)

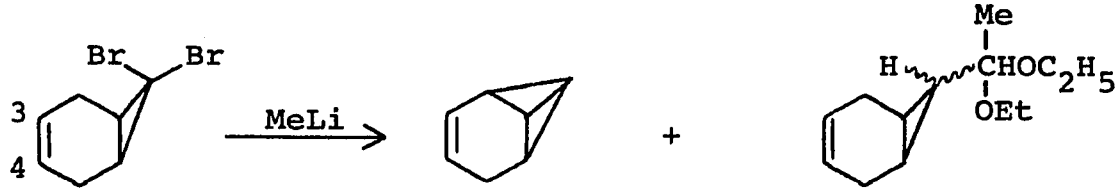
In systems where ring size imposes restrictions on the formation of cyclic allenes, intramolecular C-H insertion becomes kinetically dominant.[2a,6] Reaction of 7,7-dibromobicyclo[4.1.0]heptane (1) with MeLi generates the carbenoid 2, and/or the related carbene 3, which undergoes intramolecular insertion into C-H bonds to produce 4 and 5, intermolecular C-H insertion into the solvent to produce 6, overall dimerization to give 7, and net alkylation to yield 8.[7]



1 2 3 4 5 6 7 8

When a double bond is placed in the 6-membered ring (9, 10), two different types of reaction occur depending upon

the position of the double bond. In the case of 9[8] where the double bond is $\Delta^{3,4}$, the reaction occurs similarly to that of 1 to afford C-H insertion products (Eq. 5). However, when the double bond is in conjugation with the cyclopropane ring (10)[5b], a rearrangement takes place to give 11 in 80% yield.



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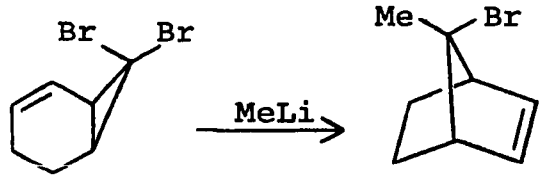
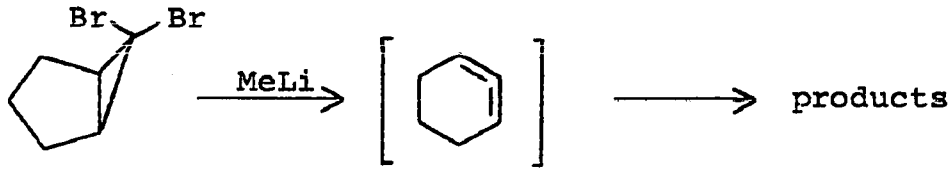
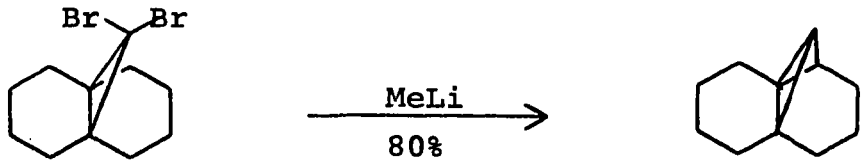


10 11 (6)

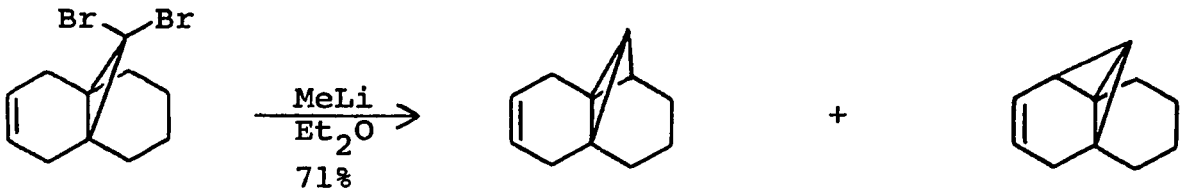
Moore and Moser[9] have found that a more strained system, 6,6-dibromobicyclo[3.1.]hexane, reacts with MeLi to give exclusively dimers and tetramers which apparently emanate from 1,2-cyclohexadiene.



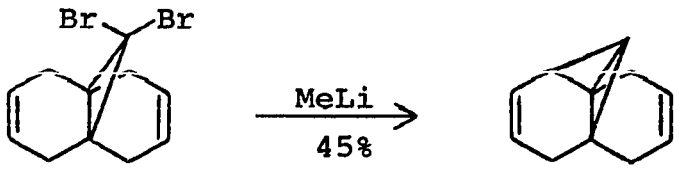
11,11-Dibromotricyclo[4.4.1.$0^{1,6}$]undecane reportedly reacts with MeLi to give an intramolecular C-H insertion product.[10,11] In the unsaturated systems, 12 and 13, reac-



tion with MeLi leads to insertion products only[11a]; no allenes were observed.



12 13 : 1

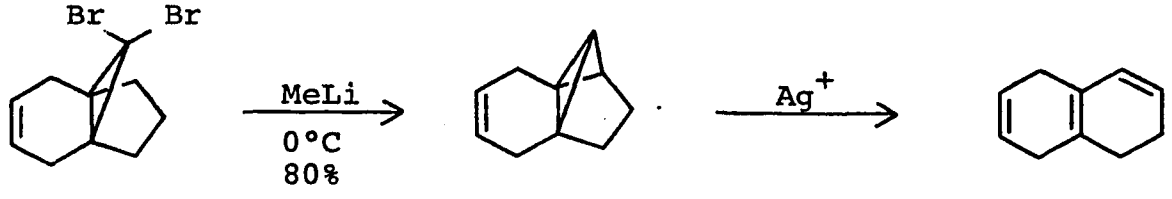


13

Moore et al.[11b] also investigated the reaction of 10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (14) with MeLi. The

14

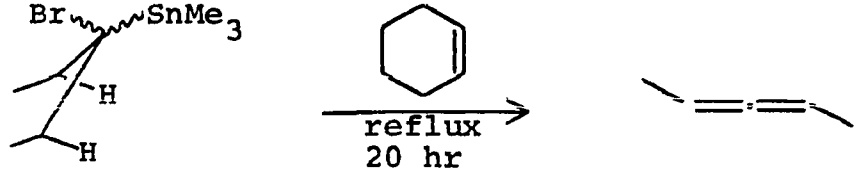
products were characterized as primarily resulting from intramolecular C-H insertion; no ring opening was observed. Paquette et al.[11c,11d] also treated 15 with MeLi at 0°C, and



15 16

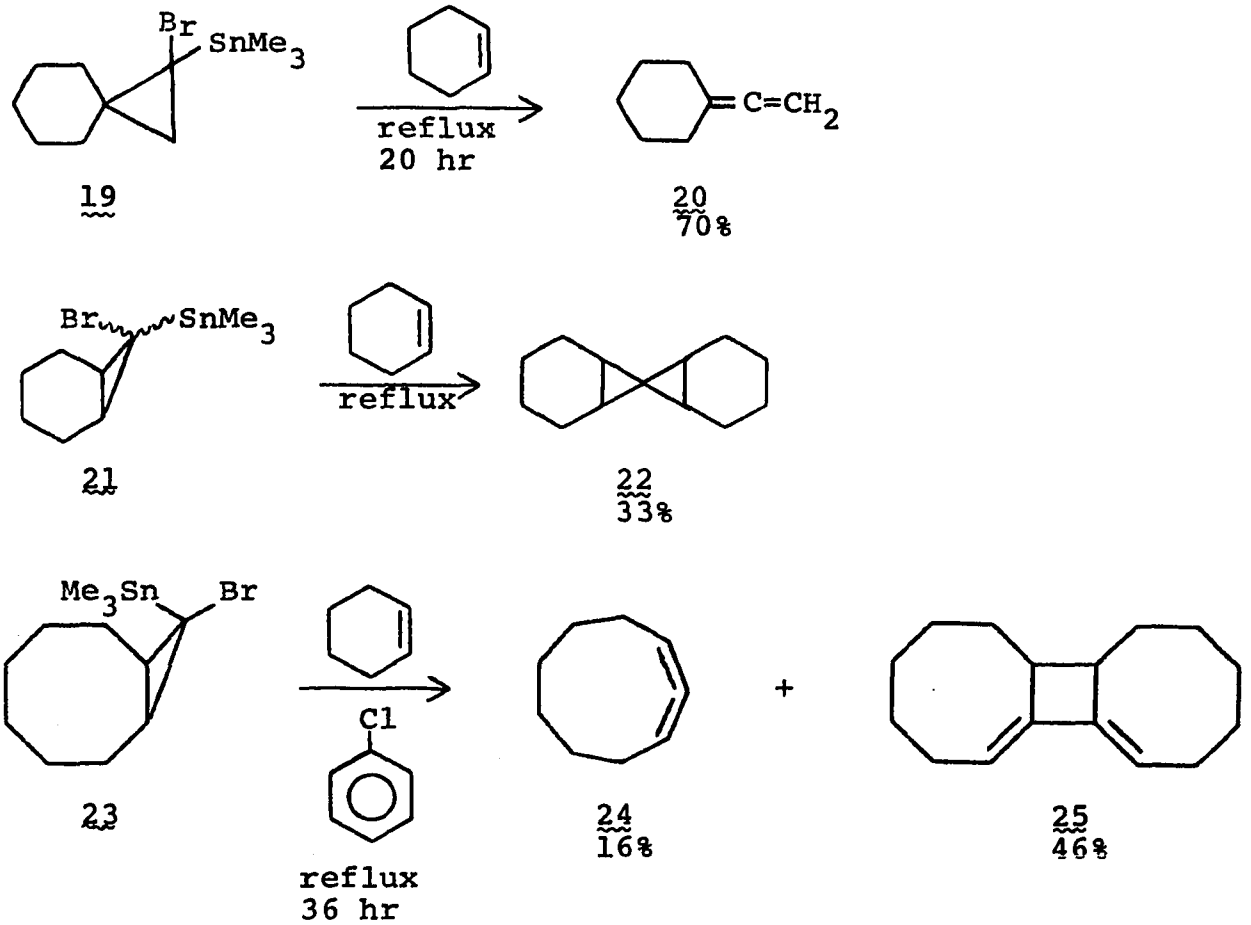
found it was smoothly transformed in 80% yield into a single bicyclo[1.1.0]butane derivative. Through Ag^+-promoted isomerization, the cyclization product was isomerized to ring-expanded diene 16. It was suggested that small differences in internuclear distances, as well as C-H bond nucleophilicity, affects the regiochemistry of intramolecular carbenoid capture.

An alternative method for generating cyclopropylidenes is via pyrolysis of α-bromocyclopropyl derivatives of tin.[12] The thermolysis of 1-bromo-1-trimethyltin-cis-



17 18

52%



2,3-dimethylcyclopropane (17), 1-bromo-1-trimethyltinspiro-[2.5]octane (19) and 9-bromo-9-trimethyltinbicyclo[6.1.0]-nonane (23) in refluxing cyclohexene or a mixture of cyclohexene and chlorobenzene afford only the allenic type products 18, 20, 24 and 25. However, in the case of 7-bromo-7-trimethyltinnorcarane (21). An intermolecular divalent carbon transfer reaction occurs to give spiro compound 22.

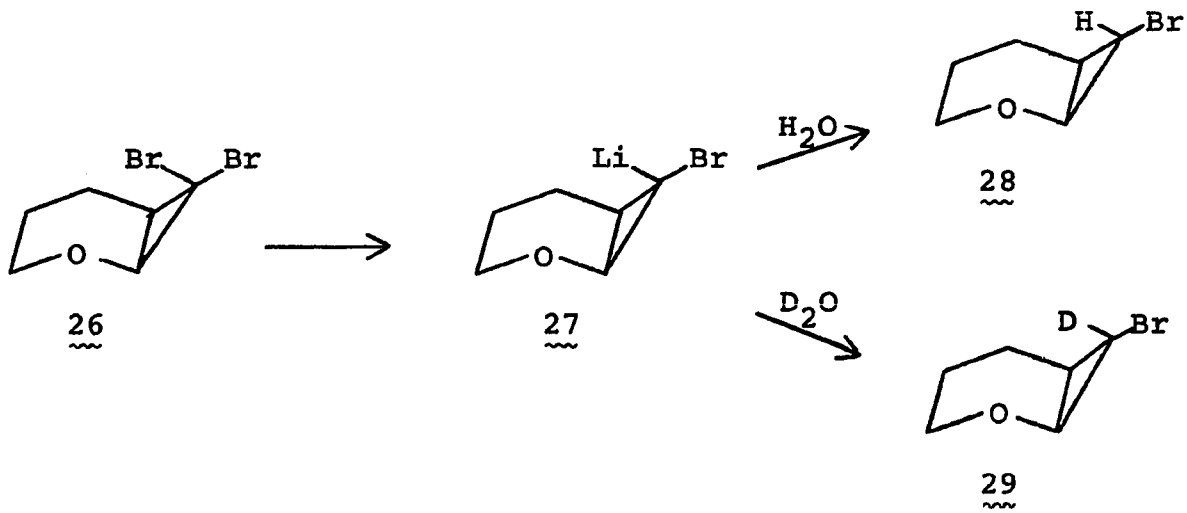
Carbenoids With Neighboring Heteroatoms

Miller and Whalen,[13] and Closs and Moss[14] obtained firm evidence implicating α-haloalkyllithium compounds, not free carbenes, as the intermediates directly involved in cyclopropane formation when aryldihalo- and polyhalomethanes were treated with alkyllithium reagents in the presence of olefins. In addition, Hoey, Lusk and Crumbliss[15] reported their discovery, made almost simultaneously with that of Köbrich[16], that tetrahydrofuran solvent exhibited a marked stabilizing effect on α-haloalkyllithium compounds. The direct intermediacy of lithium carbenoids in an intramolecular C-H insertion reaction has been indicated by the results of Goldstein and Dolbier[17] who showed that the formation of hexadeuterated 1,1-dimethylcyclopropanes from 1-halo-2,2-di(methyl-d_3)-propyllithium was accompanied by a halogen-dependent (I, Br, Cl) deuterium isotope effect. Thus, the reactions of a number of the "carbenes" produced by α elimination are now attributable to organometallic compounds, and the study of such compounds has revealed that carbenoids can exhibit both nucleophilic and electrophilic reactivity.

Recently, Taylor et al.[18,19] and Taylor and Chaney[20,21] investigated the effect of neighboring n electron donors on the reactivity of carbenoid species and reports on a stereo-

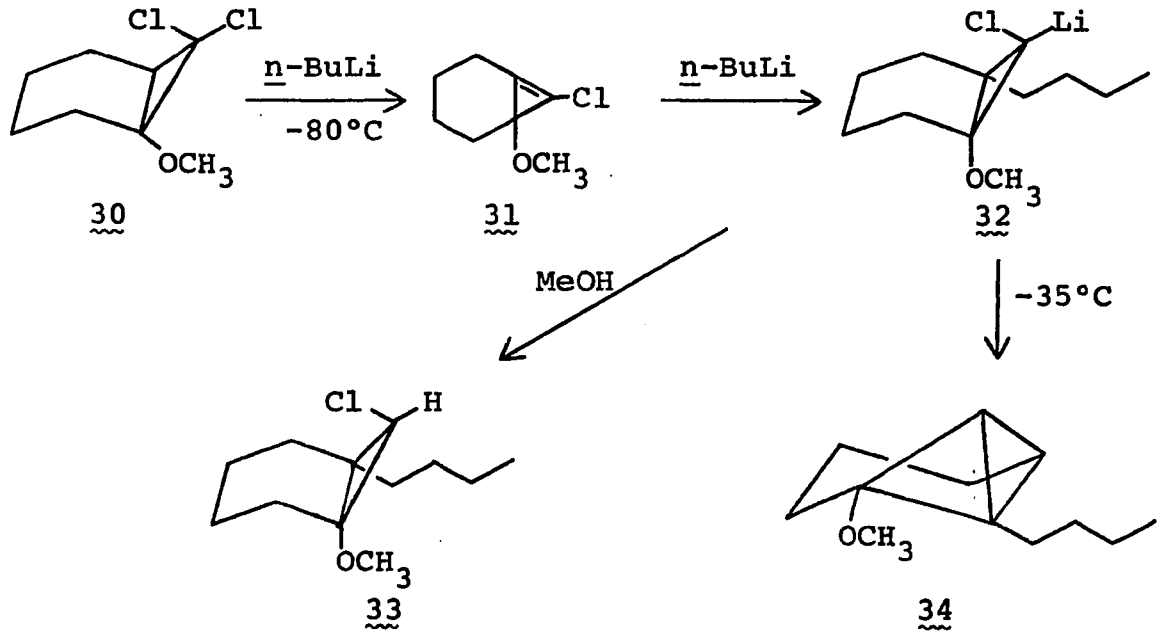
of intramolecularly stabilized lithium carbenoids and some of their nucleophilic, thermal and electrophilic reactions.

The reaction of 26[18] with ethereal methyllithium at -80 or -20°C resulted in stereospecific formation of 28 or 29 upon water or deuterium oxide quench, respectively. This result was rationalized in terms of intramolecular coordination of lithium to the oxygen atom (27), a complexation feature which is not possible in the epimer.



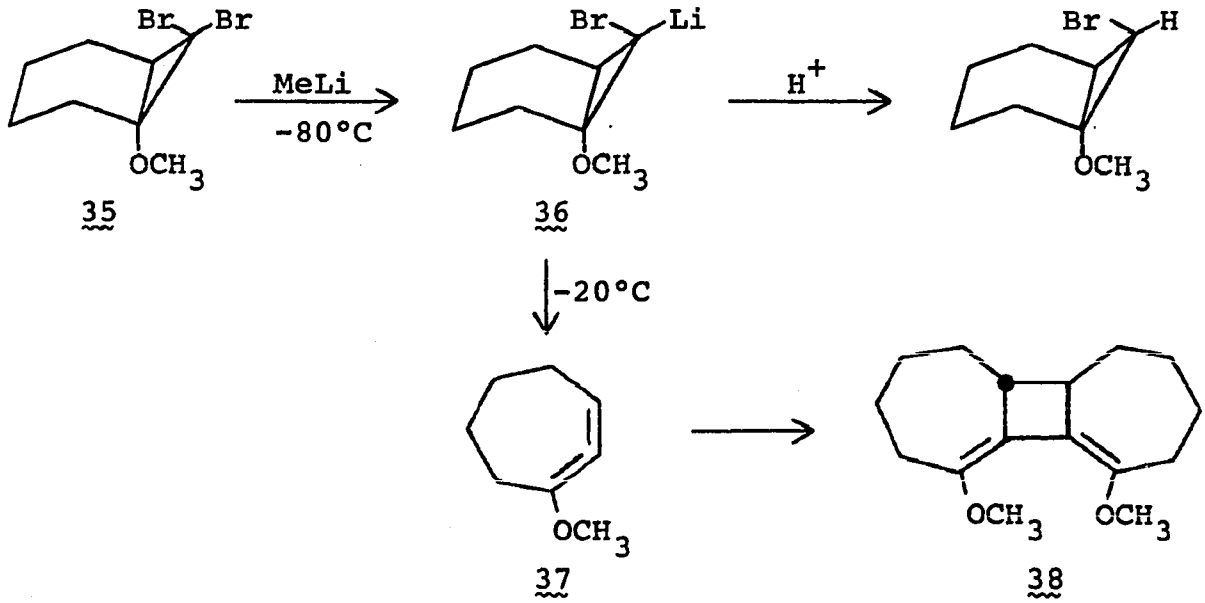
26 27 28 29

Solutions of carbenoids 32 and 36[19] were prepared by the reaction of alkyllithiums with dihalocyclopropanes 30 and 35 respectively. Bicyclobutane 34 was the major product of thermal decomposition (-35°C) of 32. The formation of carbenoid 32 from 30 can be envisioned as occurring by way of the strained olefin 31, by addition of n-BuLi. The formation of 34 is an example of an electrophilic reaction which



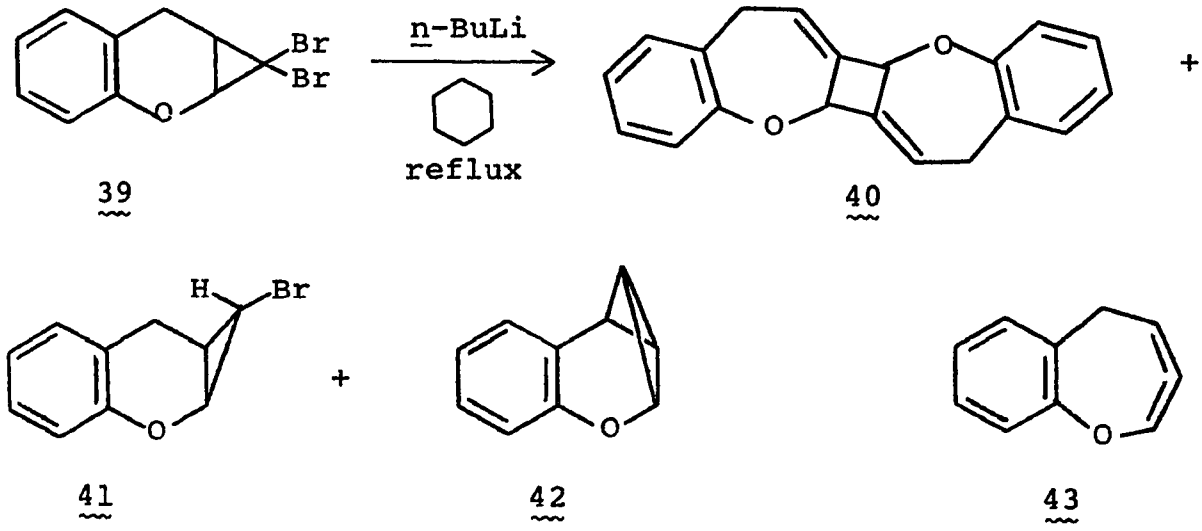
30 31 32 33 34

proceeded via an intramolecularly stabilized carbenoid. When the reaction was quenched at -80°C, compound 33 was obtained. Thermal decomposition of carbenoid 36 at -20°C gave diene 38, presumably via dimerization of 1-methoxyclclohepta-1,2-diene (37).



35 36 37 38

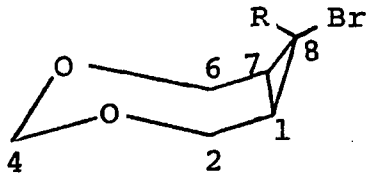
Uyegaki et al.[22] also reported obtaining an allenic type product when oxygen was contained in the ring. Treatment



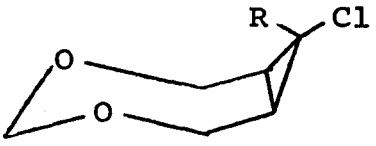
39 40 41 42 43

of 39 with excess n-butyllithium in refluxing hexane for 30 min gave 40 in 33% yield, along with 41 and a minor amount of 42. The formation of 40 was presumed to occur via dimerization of the cyclic allene 43.

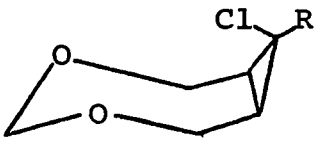
The reactions of molecules with two oxygens in the ring,[21] e.g. 44a, 45a and 46a, with MeLi at -78°C have also been reported. Carbenoids derived therefrom containing an exo halogen (44b, 45b) gave high yields of intramolecular insertion, 47, while that carbenoid with an endo halogen gave almost exclusively products of intermolecular reactions (48 and 49). Carbenoids 44b and 45b were stable in ether



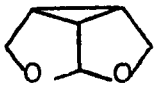
44a, R=Br
b, R=Li
c, R=CH_3



45a, R=Cl
b, R=Li



46a, R=Br
b, R=Li



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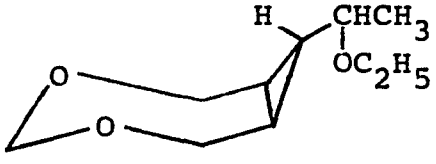

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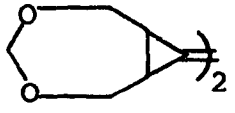


49, syn,anti

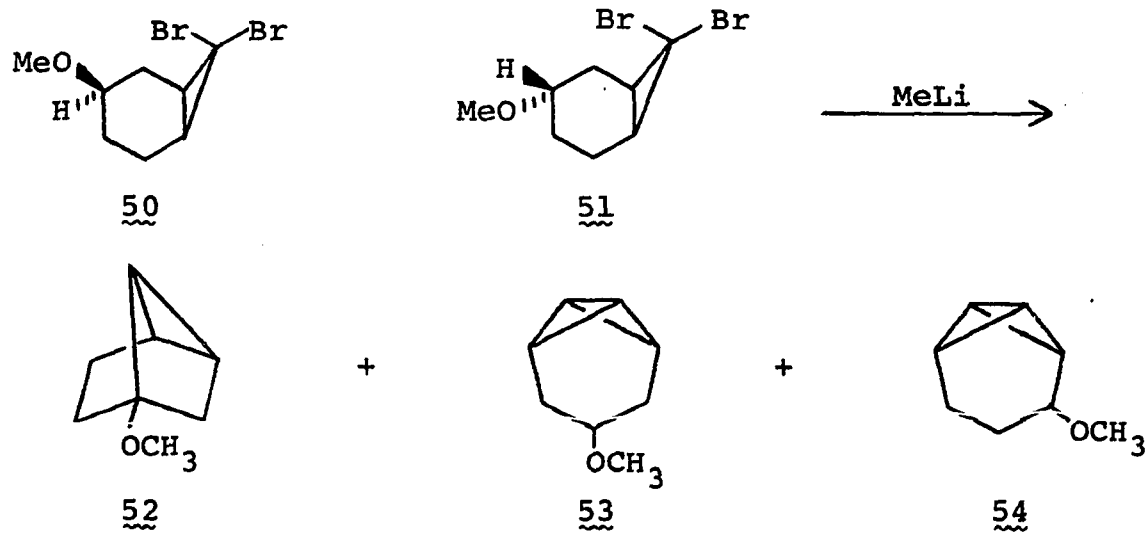
below -20°C, while, in contrast, carbenoid 46b yielded products of electrophilic reaction slowly even at -78°C. Under more dilute conditions and at higher formation temperatures, carbenoid 46b, when prepared in the absence of LiBr, gave reduced yields of dimer 49 and higher yields of 48 but never more than 3% of 47.

The above results indicate that in the transition state for α elimination, LiX is bound to carbon tightly enough to influence the stereochemical outcome of these electrophilic reactions. Epimers 45b and 46b differ in thermal stability and perhaps in state of aggregation as well. The stereochemistry at C-8, dictates the product distribution.

Carbenoid 44b failed to react with MeI or MeBr[22] at -78°C when the solvent was ether. The addition of THF to the reaction, however, dissolved 44b and permitted methyla-

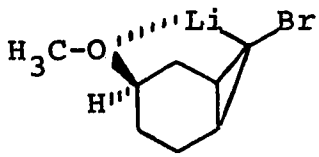
tion to proceed, yielding 44c in 75% yield. The effect of THF is, presumably, to "loosen" the binding of the Li atom of 44b with the ring oxygen atoms, a process which must occur in order for methylation to proceed. However, Paquette et al.[23] have reported that the carbenoid derived from 50 does not give intramolecular insertion products.

Reaction of 50[23] with MeLi led to consumption of the dibromide without formation of volatile products isomeric



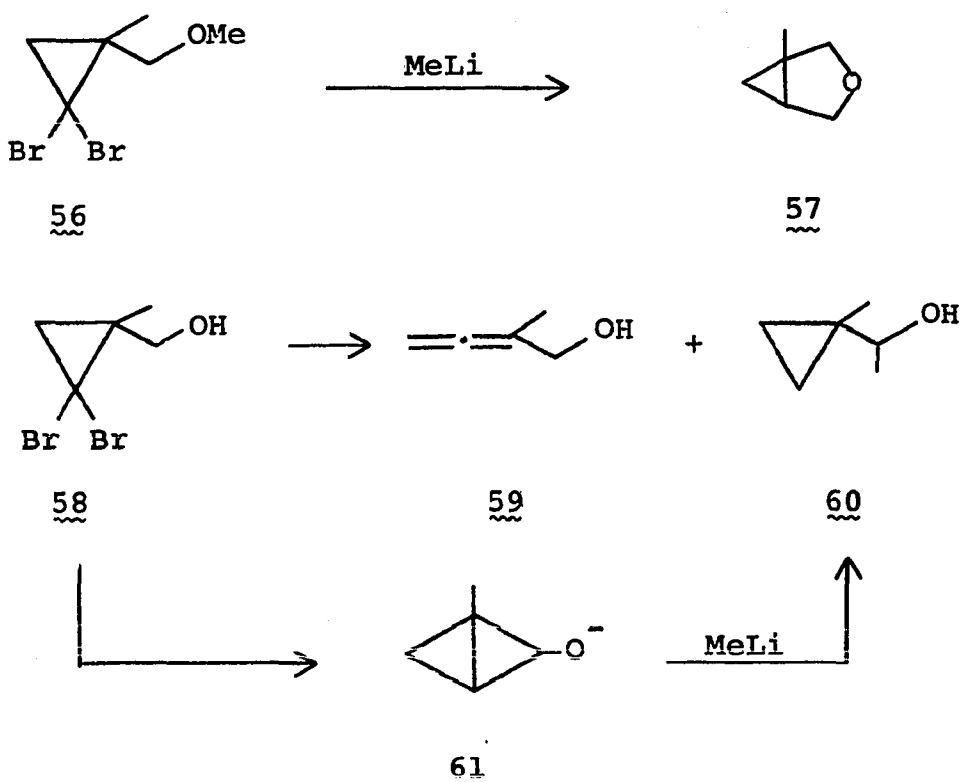
50 51 52 53 54

with the carbenoid formulation. Under identical conditions, 51 was transformed into a mixture of 52 (71%), 53 (22%), and 54 (7%). It was rationalized on this basis that the cis-oriented methoxyl oxygen in 50 directs the course of the exchange reaction to provide 55, which because of intra-



55

molecular solvation of lithium by neighboring oxygen, is deterred from further reaction of the customary type. For monocycle 56, an intramolecular C-H insertion was observed. Treatment of 56[24] with MeLi afforded 57 while 58 gave one product (60) which was presumed to arise from the corre-

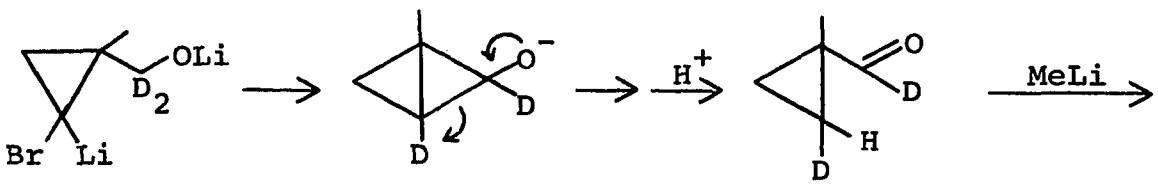


56 57

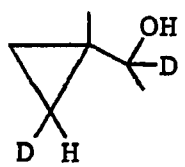
58 59 60

61

sponding bicyclo[1.1.0]butan-2-olate (61), as well as the allenyl alcohol 59.[25] Labelling experiments provided



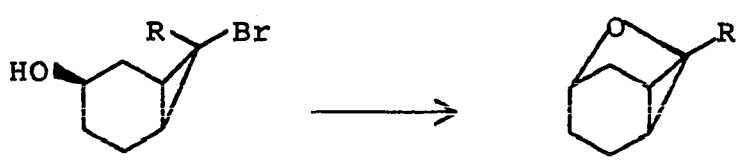
62 63 64



65

conclusive evidence for the intramolecular insertion of the carbenoid 62 into the C-H bond adjacent to the oxygen function, which leads to the bicyclo[1.1.0]butanolate 63. Ring opening of 63 could yield an aldehyde 64 which then further reacts with MeLi to afford alcohol 65.

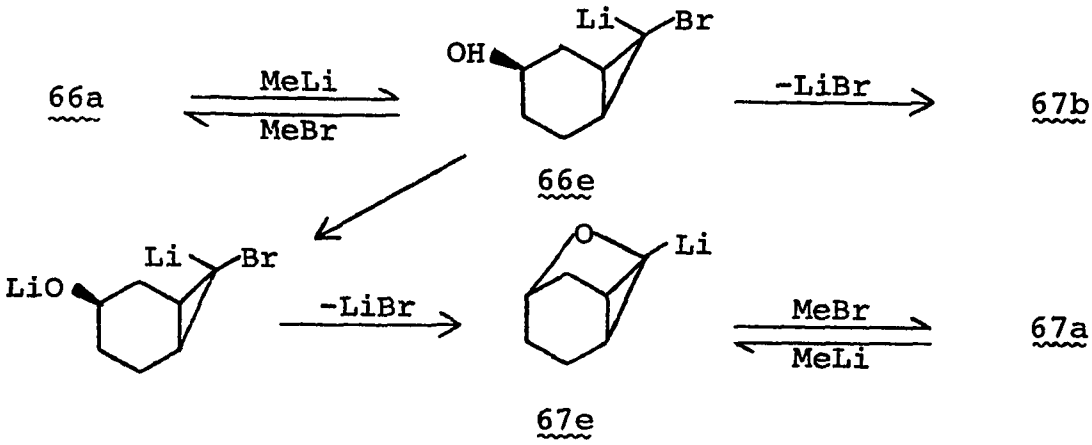
The reaction 66a → 67a,[24] involving substitution at a cyclopropane carbon atom, can be observed only with alkyl-



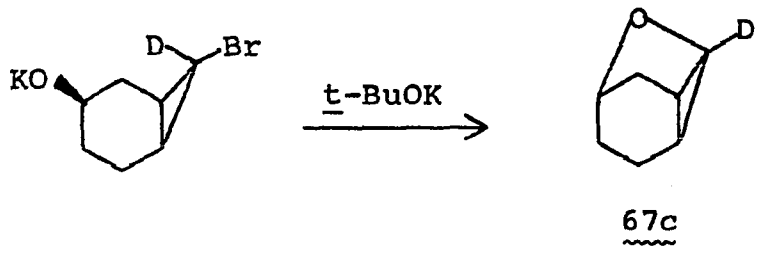
66 67

a, R=Br d, R=CH_3
b, R=H e, R=Li
c, R=D

lithium reagents but not with (i-Pr)$_2$NLi or t-BuOK. This suggests an insertion mechanism.



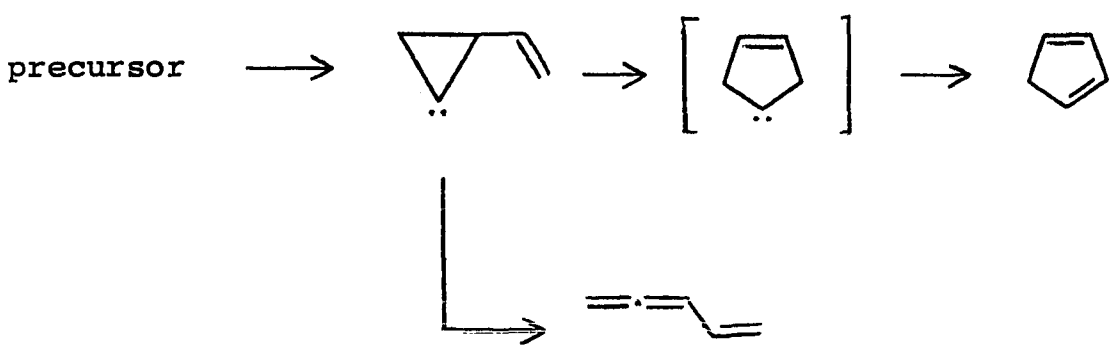
In contrast, t-BuOK effects substitution in high yield with no loss (from 66c) or incorporation of deuterium at the cyclopropane center; this process is an S_N2-type reaction:



Rearrangement of Vinylcyclopropylidenes to Cyclopentenylidenes

Carbene-carbene rearrangements are defined as reactions in which an initially formed carbene rearranges to a new carbene prior to product formation. Jones[26] has subdivided these rearrangements into two broad categories: (1) type I rearrangements, in which the divalent carbon of the unrearranged and rearranged carbene are different; and (2) type II rearrangements, which involve the generation of a carbene with a different structure but one in which the divalent carbon has retained its identity.

For example, Skattebol[5] discovered that a vinylcyclopropylidene precursor would undergo rearrangement to afford cyclopentadiene; this rearrangement may be of the type II variety. Since the original discovery, a number of



examples of reactions of vinylcyclopropylidenes that may undergo this type of rearrangement have been reported.

These include cyclopropylidenes (or their carbenoids) generated from both dehalogenation of gem-dihalocyclopropanes[5,28,29] (Table I) and reaction of N-nitrosourethanes[5d,30,31] with base (presumably giving diazocyclopropanes).

In the instance of 2-vinyl-3-methyl-1,1-dibromocyclopropane[30,31], only the cyclopentadiene product was formed. This was attributed to steric hindrance between the two alkyl substituents, which kept the cyclopropylidene from opening. On the other hand, in the cases of 2-(2-methylpropen-1-yl)-1,1-dibromocyclopropane and 1-vinyl-2,2-dimethyl-1,1-dibromocyclopropane, allene formation was the sole reaction mode. This was thought to be due to substituent effects.[30,31] However, 1,1-dibromo-4-methylenespiro[2.5]octane[5c] reacted with MeLi affording bicyclo[4.3.0]nona-1(6), 7-diene as the exclusive product, while its fixed s-trans analog, (1,1-dibromospiro[2.5]oct-2-ene) afforded only ring-opened products. It was concluded that the s-trans nature of the carbene (or carbenoid) derived from 1,1-dibromospiro[2,5]oct-2-ene prevents interaction of the cyclopropylidene with the double bond and subsequent cyclopentadiene formation. These results indicate that the product distribution is influenced by the conformation of the precursor.

Table I. Reaction of 2-(1-alkenyl)-1,1,-dibromocyclopropanes with MeLi at -78°C

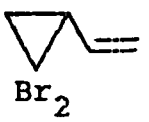
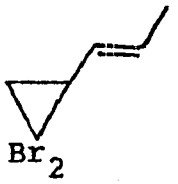
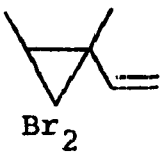
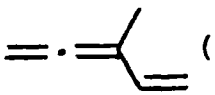
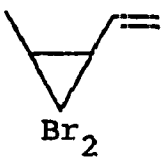
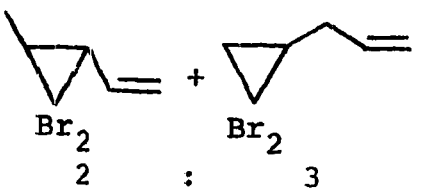
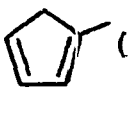
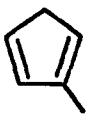
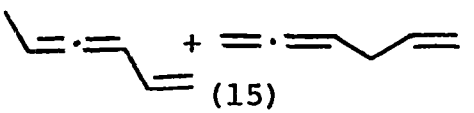
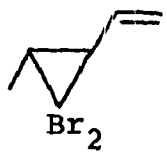
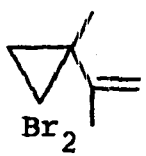
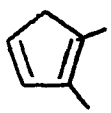
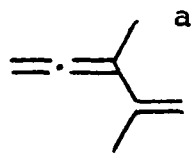
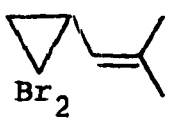
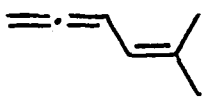
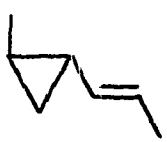
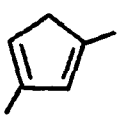
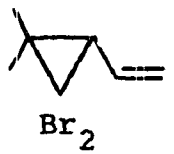
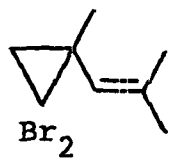
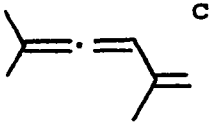
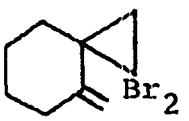
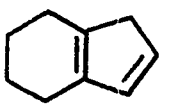
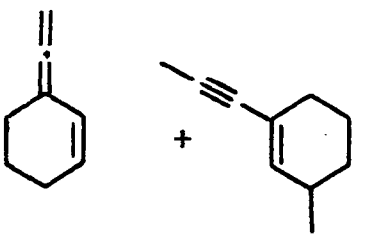
Dibromides	Products (% of mixture)		Ref.
	Cyclopentadienes	Allenes	
	 (86)	 (14)	5b
	 (86)	 (14)	32
	 (83)	 (17)	5b
	 (100)	—	32
 2 : 3	 (14) +  (71)	 (15)	5b

Table I. (Continued)

Dibromides	Products (% of mixture)		Ref.
	Cyclopentadienes	Allenes	
	 (74)	 (26)	3
	 (98)	 (2)[a]	5b
	—	 (100)	32
	 (20) +  (48)	 (32)	

[a]The product distribution between cyclopentadiene and allene is 94:6 if generated from the diazo compound.

Table I. (Continue)

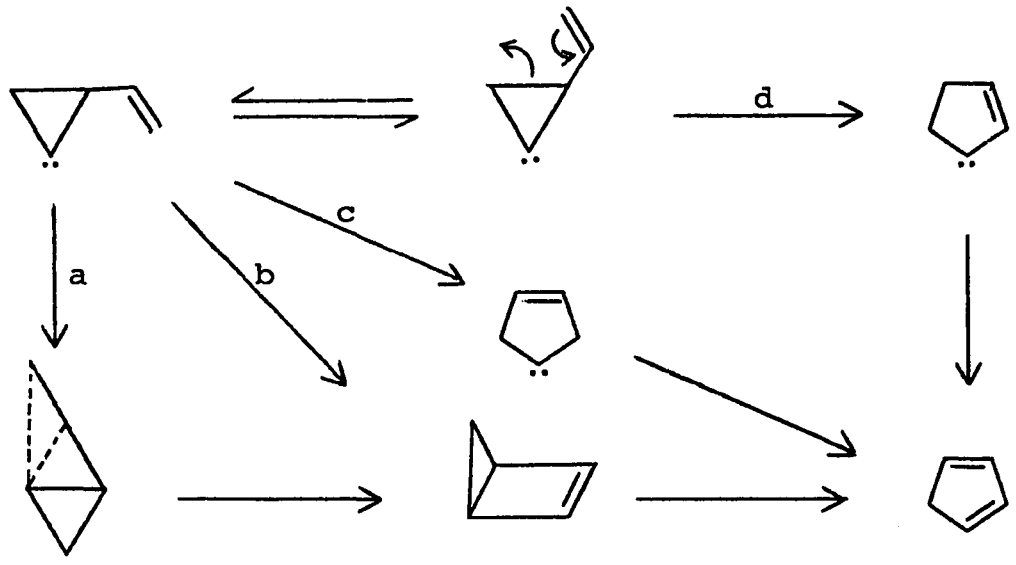
Dibromides	Products (% of mixture)		Ref.
	Cyclopentadienes	Allenes	
	—	 (100)	5b
 [b]	 (70)	 [c] (7)	5b
	 (100)	—	5c
	—		5c

[b] Some (<10%) of the isomer 1,1-dibromo-2,2-dimethyl-3-isopropenyl propane was present.

[c] 2,4-Dimethyl-1,3,5-hexatriene was also isolated from this mixture.

At least four different paths (a, b, c and d, Scheme I - carbene rather than carbenoid assumed for simplicity) have been considered for this reaction.[5a,5b]

Scheme I



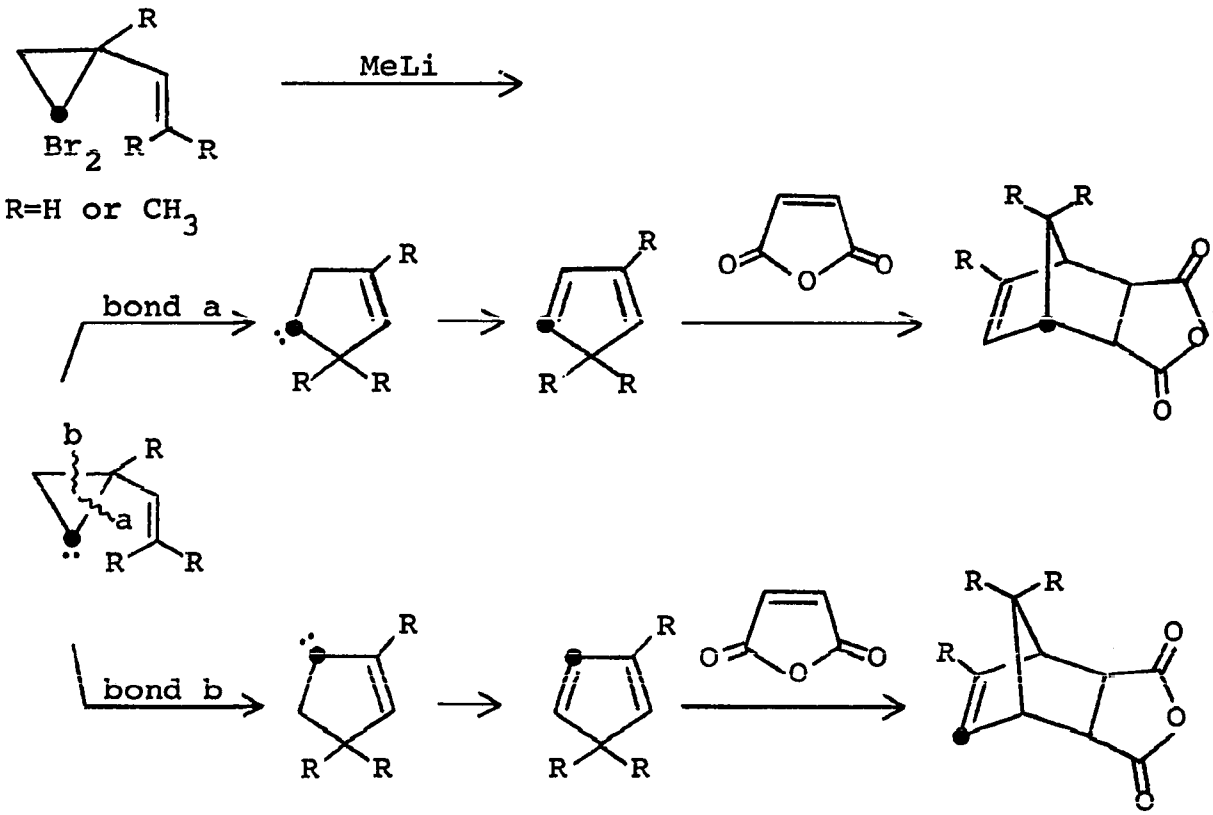
68 69

Path "b" represents an intramolecular C-H insertion. It may be excluded because it does not explain the rearrangement of vinylcyclopropylidenes which have no terminal vinyl hydrogens (Table I). The absence of tricyclo[2.1.0.$0^{2,4}$]-pentanes, as well as the substitution patterns in the products, supports the exclusion of path "a". Addition to the double bond, according to path "a", would give the unprecedented tricyclopentane derivative 68. A crude estimate of the strain energy[33] in this molecule is about 90

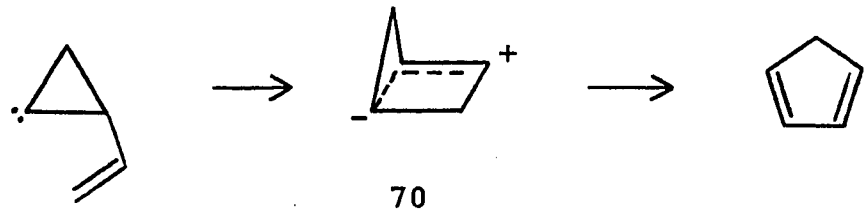
kcal/mole indicating that the formation of 68 is rather unlikely.

Path "d" which corresponds to a vinylcyclopropane-vinylcyclopentene interconversion (not involving the carbene) is ruled out because it is inconsistent with the substitution patterns in the products (Table I). A labelling experiment (^{12}C label indicated by heavy dots in Scheme II)[5d] also excludes the path "d" but supports the path "c" (cleavage of bond a) mechanism in Scheme I.

Scheme II



Bond formation between the double bond and the electron deficient carbon, resulting in a dipolar intermediate 70, has been suggested[5b] by Skattebol as the initial process of the mechanism "c".



70

A MINDO/3 investigation[34] of the singlet state suggests that the reaction of vinylcyclopropylidene to cyclopentenylidene is initiated by a π-complex formation between the double bond and the empty p atomic orbital at the carbene

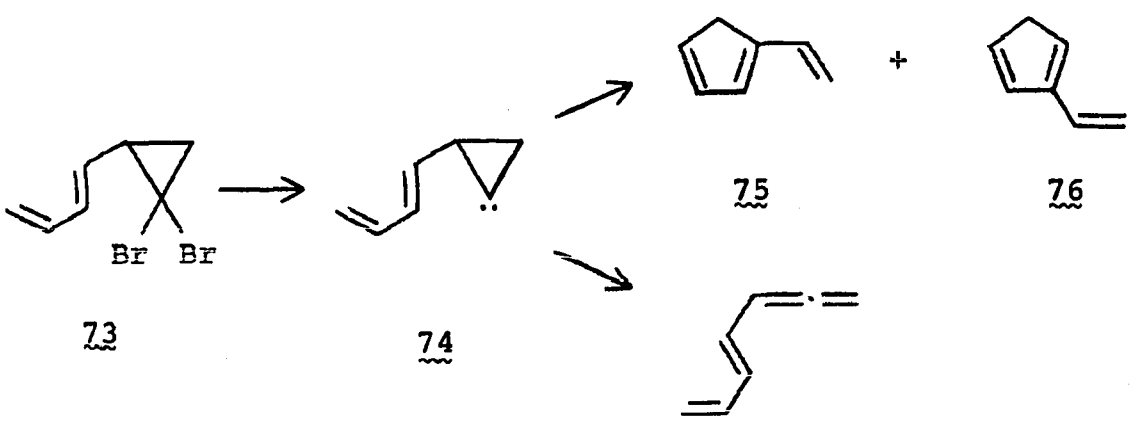
site. The two electrons occupying the σ orbital do not participate in this interaction. A nonclassical carbene 71 is formed in an intermediate stage, the π electrons are delocalized over three carbon centers. The nonclassical carbene 71 is isoelectronic with the nonclassical carbonium ion 72.

71

72

In other words, in 71 electron density is shifted from the initial double bond toward the carbene site. The energy needed for the reaction, which has an early transition state, is calculated to be 13.8 kcal/mole.[34] This is close to the theoretically estimated activation energy of 13.7 kcal/mole for the competing ring opening to allene.[35]

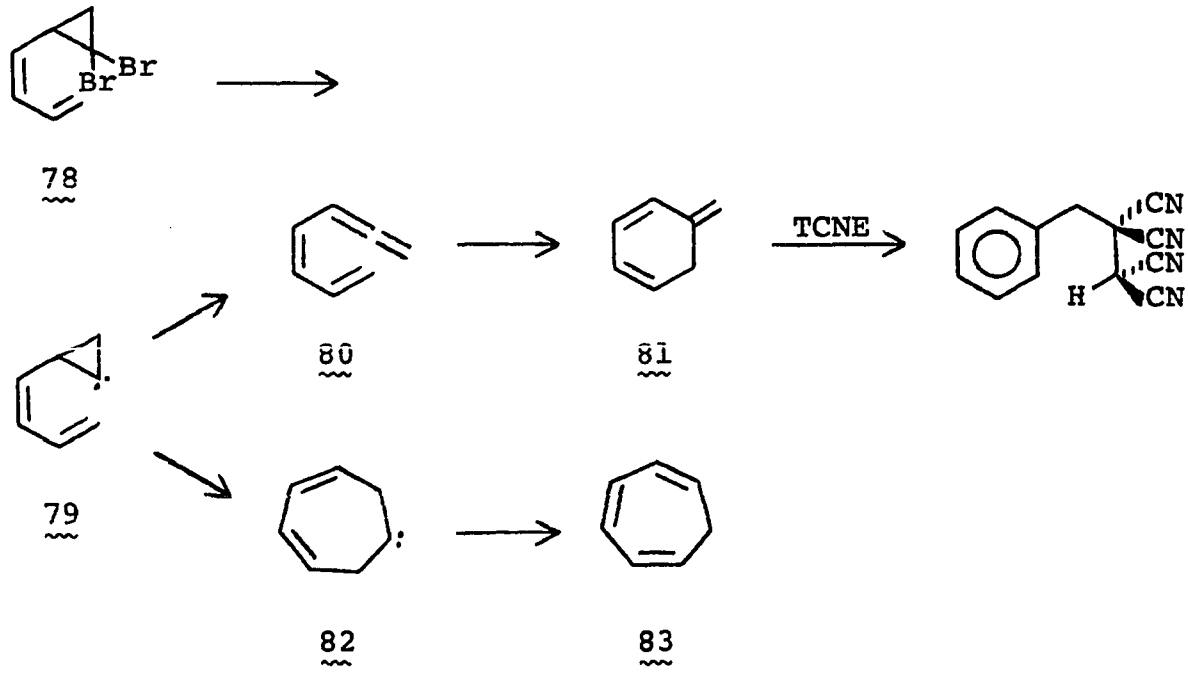
Replacement of the vinyl group in vinylcyclopropylidene by a 1,3-butadiene unit affords configurational isomers 74 and 79.[5e] Brinker and Fleischhauer[5e] reported the treatment of 73 with MeLi in ether at 0°C, whereupon the isomeric vinylcyclopentadienes 75 and 76 (52% yield) and the previously unknown 1,2,4,6-heptatetraene 77 (48% yield) were



73 74 75 76 77

observed. Consequently, in the trans-isomer, the competing processes--carbene-carbene rearrangment with 1,3 carbon shift and cyclopropylidene-allene rearrangement[27]--take place to a comparable extent.

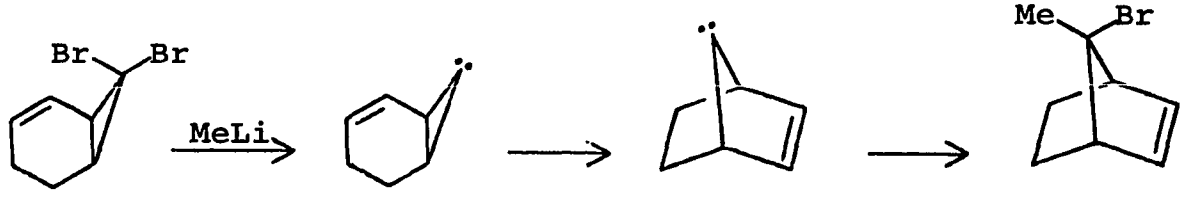
Perhaps surprisingly, no 1,3-shift, which should again afford the isomers 75 and 76, was observed on reaction of the cis-isomer 78 under the same conditions. However, 1,3,5-cycloheptatriene (83) (17%) was formed as a major product, along with 81 (14%) and products derived from



81.[5c,36] The formation of 81 can be initiated by cyclopropylidene-allene rearrangement 79 → 80. Thus while 77 is

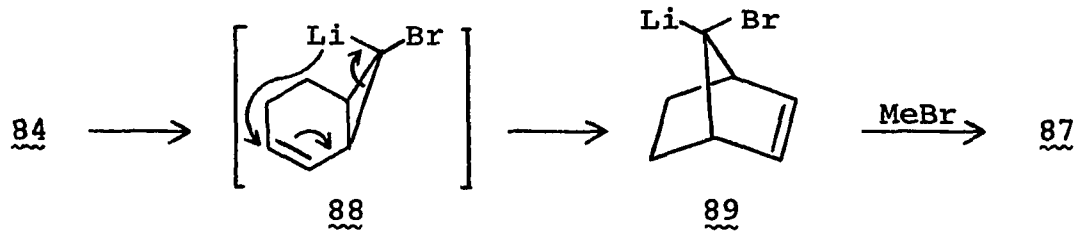
stable under the reaction conditions, the cis allene 80 can readily cyclize to 81. In the presence of tetracyanoethylene, 81 is trapped to give the known ene adduct.[37]

A plausible explanation for the formation of 83 was suggested to be the novel carbene-carbene rearrangement involving a 1,5-carbon shift (79 to 82), followed by a 1,2-hydrogen shift. Carbenes 74 and 79 constitute the first pair of configurational isomers which behave regiospecifically in carbene-carbene rearrangements. In bicyclic systems, reaction of 7,7-dibromobicyclo[4.1.0]hept-2-ene (84)[5b] with MeLi afforded rearranged product 87. Skattebol



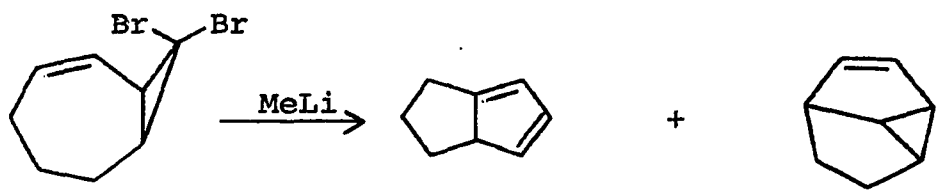
84 85 86 87

proposed that the first formed carbene, 85, rearranged to give norbornenylidene (86), which was added the elements of MeBr to give 87. However, the stereoselectivity seen in the product 87 remains unexplained. Paquette and Taylor[38] have proposed that the rearrangement involves carbenoids 88 and 89, where 89 would yield 87 via nucleophilic reaction with MeBr.



84 88 89 87

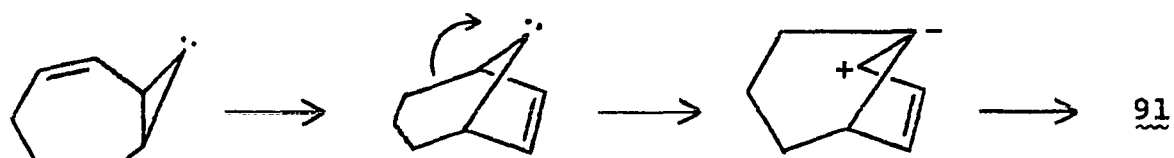
Reaction of 8,8-dibromobicyclo[5.1.0]oct-2-ene (90)[39] with MeLi at -30 to -40°C, followed by quenching with H_2O or D_2O at below -20°C, led to major product 91 (65%) and a minor



90 91 (65%) 92 (5%)

insertion product 92 (ca. 5%). Baird and Reese[39a] proposed that the formation of 91 from 90 can be explained (Scheme III)

Scheme III

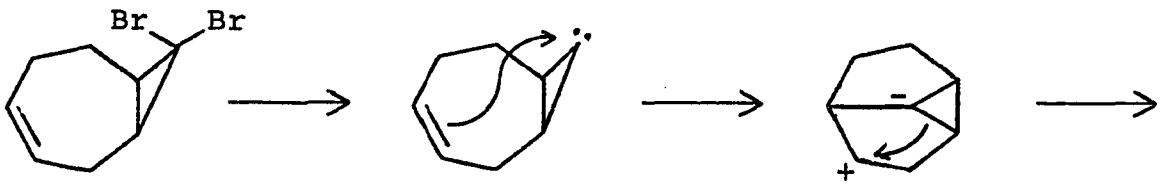


93 94

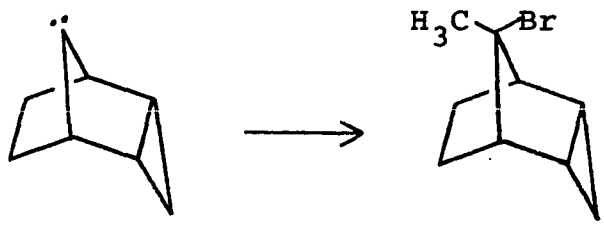
in terms of an initial carbene-carbene rearrangement to 93, followed by a second rearrangement via a zwitterionic inter-

mediate 94 to give 91. Such rearrangements have been described for a variety of bridged systems.[40]

As a very important extension of this general type of rearrangement, they also reported[41] 93% of 97 from treatment of the dibromocyclopropane 95 with MeLi. The dipolar intermediate 96 was postulated to rationalize the product.

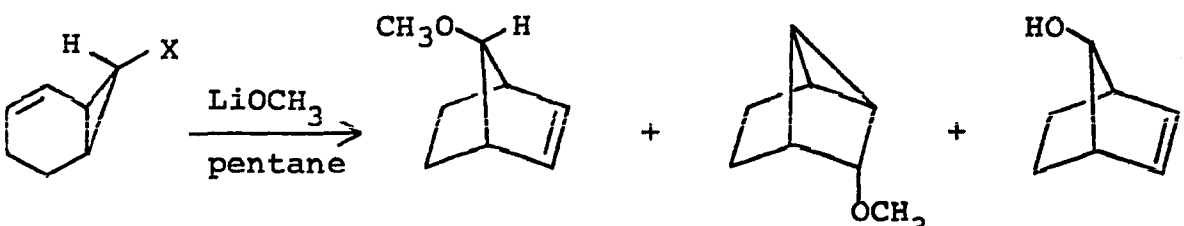


95 96



97

Treatment of N-nitrosourea 98a with $LiOCH_3$ in pentane[30,31] produced mainly a liquid (75%) which consisted

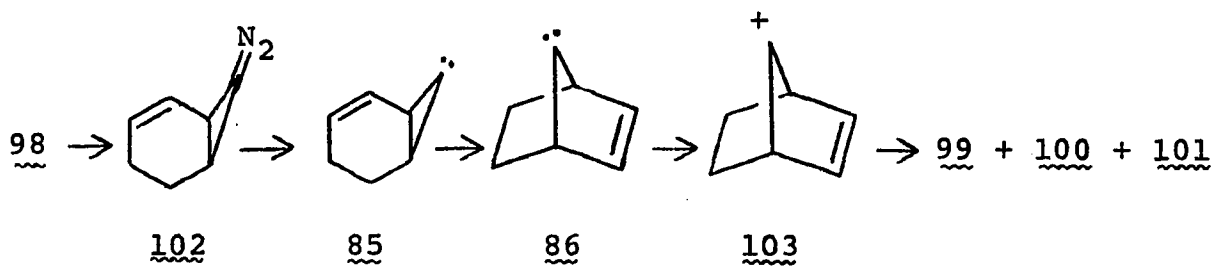


98 99 100 101

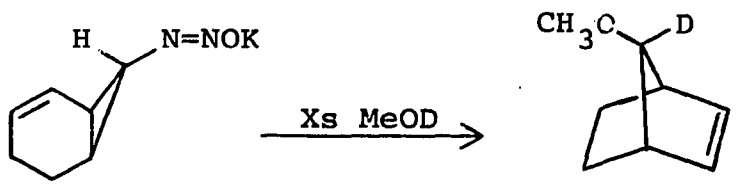
a, X=N(NO)CONH$_2$

b, X=N=NOK

of the ethers 99 and 100 (in a 4:1 ratio) and a small amount of 101.[42] The same products were isolated when pentane was replaced by cis-2-butene; no addition to the double bond of the alkene was observed. It was proposed that the reaction involved formation of the diazo compound, 102, followed by the carbene 85, which rearranged to 7-norborneneylidene 86 which



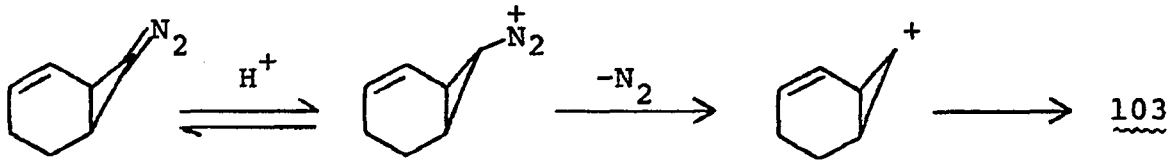
should be nucleophilic rather than electrophilic, due to interaction of the double bond with the electron-deficient carbon.[43] Such interaction was also supported by experimental data[44], although protonation of 86 had not been observed. Under these conditions, however, protonation of 86 by methanol would afford the carbonium ion 103, from which the observed products 99 and 100 can be derived. Decomposition of 98b in excess methanol-d_1 resulted in better than 97% incorporation of deuterium at C-7 of the ether 99, which lends support to the proposed protonation step.



98b 99-d_1

The chemistry of 98 contrasts with that reported[45] for the decomposition of the homologue, N itroso-N-antibicyclo-[3.1.0]hex-2-en-6-ylurea, which rearranged via diazonium ions.

There are alternative mechanisms to account for the formation of 99 and 100 which cannot be excluded by Skattebol's results. For example, the diazo compound formed from 98 may equilibrate with the corresponding diazonium ion.



104

Subsequent loss of nitrogen from the latter gives the cation 104[46] which may rearrange to 103.

Twisted Olefins

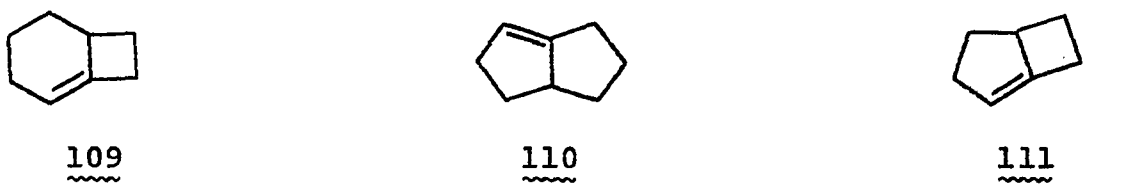
Of the four modes of distortion[47] of olefinic linkages, (105-108), this thesis will mainly deal with torsinally[48]

105 106 107 108

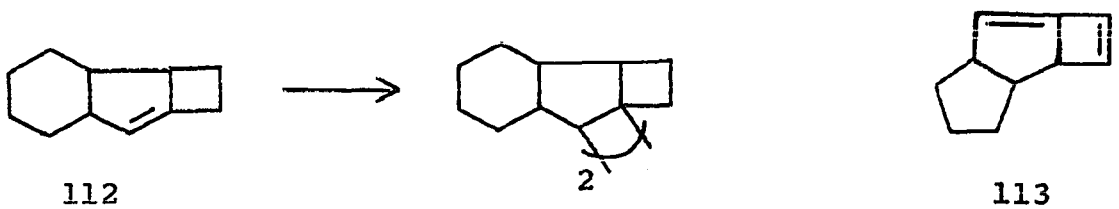
strained olefins (105), which include bridgehead olefins, tricyclic allenes (i.e., double bridgehead olefins), and sterically crowded olefins.

Bridgehead monoenes

In order to study the reactivity and chemistry of twisted olefins, molecules containing bridgehead double bonds have been synthesized. Bridgehead olefinic linkages in suitably small bicyclo[m.n.o]alkenes possess considerable torsional character. While $\Delta^{1,2}$-bicyclo-[4.2.0]octene (109),[49] bicyclo[3.3.0]oct-1-ene (110),[50] and $\Delta^{1,2}$-bicyclo[3.2.0]heptene (111)[40a,40b] are isolable at room temperature, 112 gives cyclobutane

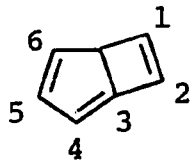


109 110 111

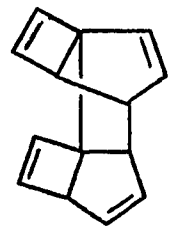


112 113

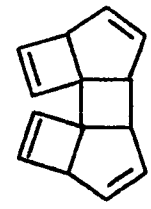
type dimers[51], and diene 113[52] polymerizes in a matter of minutes in air at room temperature, or over several hours under nitrogen. Bicyclo[3.2.0]hepta-1,3,5-triene (114)[53,54] is not isolable at room temperature (half-life at 25°C for 3 hr in dilute solution); it dimerizes fairly rapidly. On



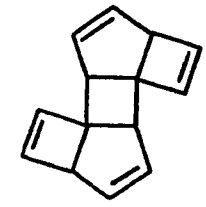
114



115

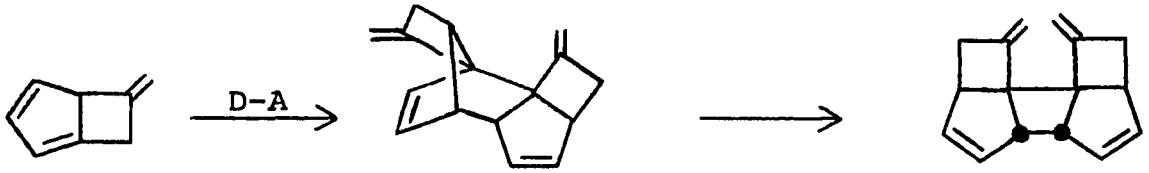


116
(syn-anti pair)



117

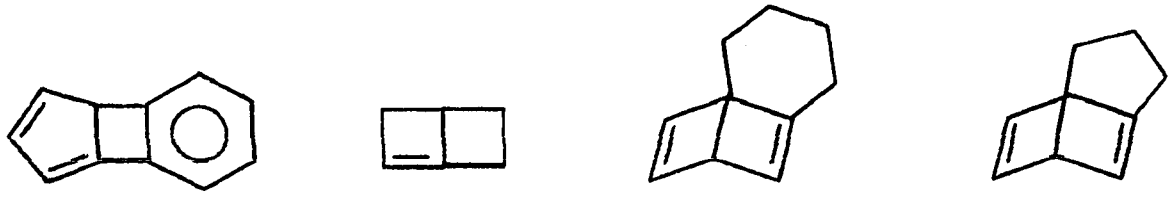
the basis of ^{1}H NMR data, Breslow et al.[53] suggested a structure (115) arising from 1,4 addition of the cyclopentadiene in 114 to the strained trisubstituted double bond of a second molecule of 114. However, Bauld et al.[54] observed two isomeric dimers (ca. 50-50 mixture) 116 by ^{1}H NMR and UV studies. Triene 114 has also been trapped as its DPIBF and cyclopentadiene adducts both of which have structures analogous to 116. Compound 116 is preferred over 117 on the basis of the two-step mechanism of olefin [2 + 2] cycloaddition and the expectation that more strain would be relieved if the two bridgehead (C_3) positions couple initially. In the case of exo-methylenebicyclic triene (118),[55] it was proposed that



118 119 120

dimerization initially occurred in Diels-Alder fashion to produce the highly strained and thermally labile kinetic dimer 119, which then rearranged upon attempted GLC purification or in refluxing benzene ($t_{\frac{1}{2}}$ 80°C=8h) to produce a new, highly symmetrical dimer. Spectral data suggested that the rearranged dimer was a formal [2 + 2] cycloaddition product of the bicyclic triene 118. Structure 120 was confirmed by X-ray analysis.

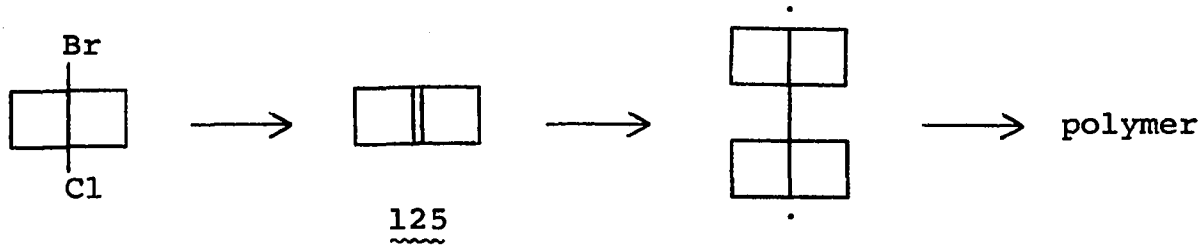
The benzologue of 114, 121,[56] is not isolable. Indications are that bicyclo[2.2.0]hex-1-ene 122 is probably not



121 122 123 124

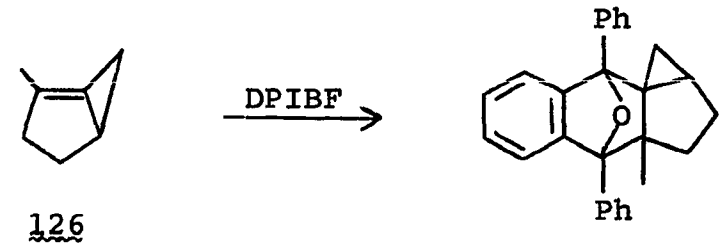
isolable[57]. The novel Dewar benzene 123 has a half-life of 58 min in solution at room temperature[58], while 124 was generated but could not be detected.[59,60a] Bicyclo[2.2.0]-

hex-1(4)-ene[57], (125) generated via electrolysis of 1-bromo-4-chlorobicyclo[2.2.0]hexane, led to a polymeric material, probably through a diradical species. The more strained



125

2-methylbicyclo[3.1.0]hex-1-ene (126)[60b] could be trapped with DPIBF or else allowed to dimerize to three different dimers.



126

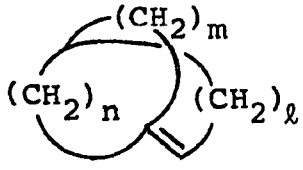
↓

dimers

Bredt[61] postulated that compounds of the camphane and pinane series, and related bicyclo[2.2.1]heptanes and bicyclo[3.1.1]heptanes, could not accommodate bridgehead double bonds. This idea is known as Bredt's rule.

In 1950, a modification of Bredt's rule was proposed by Fawcett.[62] From Prelog's[63] results, he concluded that

Bredt's rule is only valid when $S \geq 9$, where S, the strain number, is $S=m+n+\ell$ (m, n and $\ell \neq 0$) in a bicyclic[m.n.ℓ]alk-1-ene 127. More recently, Wiseman and Pletcher[64] further modified "Bredt's Rule" when he recognized that 128 should be structurally related to trans-cycloolefin 129. In other words, the strain of olefin 128 is comparable to the strain of the corresponding trans-cycloalkene 129.



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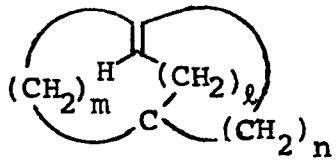

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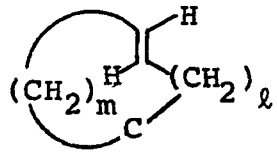
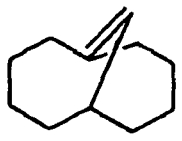


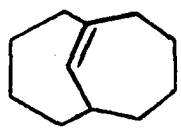
129



130

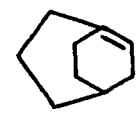
A strong interest primarily in the synthetic aspects of bridgehead olefin chemistry has been developed recently and reviewed several times.[57,65,66] However, questions still remain regarding the ultimate limits of bridgehead olefin synthesis, while some of the details of the effects of bridge size on strain can not be explained by Köbrich's treatment.[57] In 1973, Köbrich[57a] formulated a rule ("Rule A") according to which increasing the number of carbon atoms in the bridge should decrease the strain of the Bredt olefins. However, according to force-field calculations[67], relative strain energies of bridged trans-cycloheptenes do not follow a regular pattern, since subtle conformational differences not

related to the number of carbon atoms, may be controlling.[68] Recent work on the synthesis of 131 has shown that the trans-



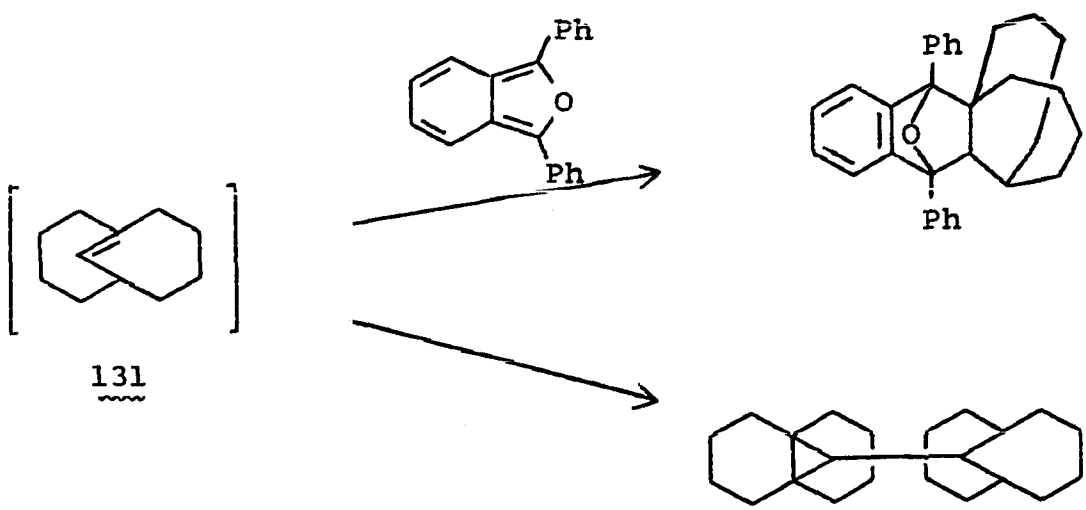
131

132



133

cycloheptene moiety of 131 is more strained than that in 132 or 133. In fact, 131 was not isolable, but could be trapped with DPIBF or else allowed to dimerize to "ene" dimer:



131

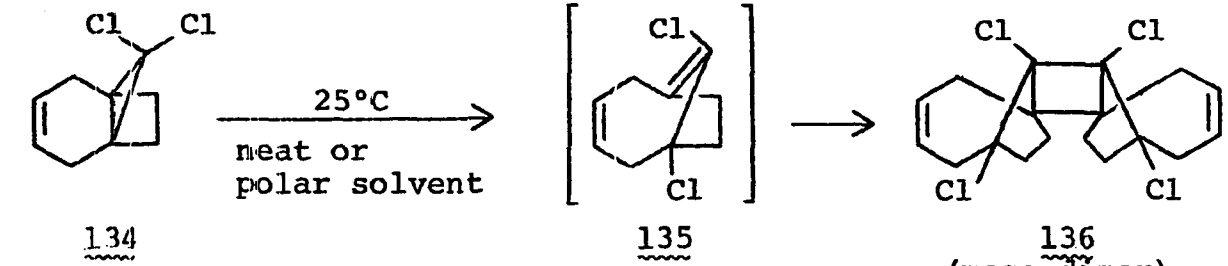
This result belies Köbrich's statement[57a] that, within a series of homologous bridgehead olefins, increasing the total number of carbon atoms should lead to less strained compounds.

Warner and his coworkers have used a cationic approach to some bridgehead olefins where the strained double bond is specifically in a one carbon bridge (128, ℓ=0). Aspects of their findings are summarized in Table II. They have demonstrated the generation of trans-cycloheptenoids 135,[69] 137,[70] and 140[71] and trans-cyclohexenoid 143.[72] Their study of 144, 146 and 148[73] has shown the configurational stability of the derived olefins 145, 147 and 149, all of which are halo-substituted bridgehead olefins. However, 150,[74] which affords the "unsubstituted" 151[75], also leads stereospecifically to product (152); the epimer of 150 gives the epimer of 152. These latter studies are complimentary to those of Lindner et al.[76] These configurational studies indicate that distortion of a potentially 90° twisted, symmetrical olefin is a facile and desirable process; rehybridization[77] is implicated.

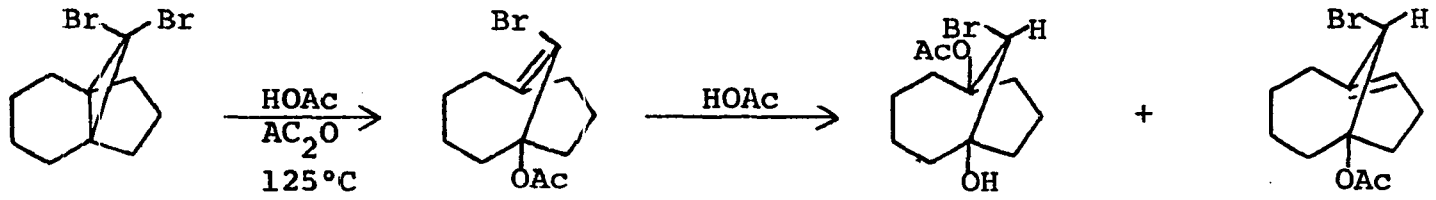
Bridgehead dienes

More recently, investigators have begun to explore the possibility of constructing bicyclic molecules with two bridgehead double bonds, where both π bonds are trans-cyclononenoid or more strained. Examples of isolated species include 153[78], 154[79] and 155[80], while 156[81] has been proposed as an intermediate. Whereas the bridgehead double bonds of 153 and 154 are trans-cyclononenoid in character, those of 155 and 156 are trans-cyclooctenoid.

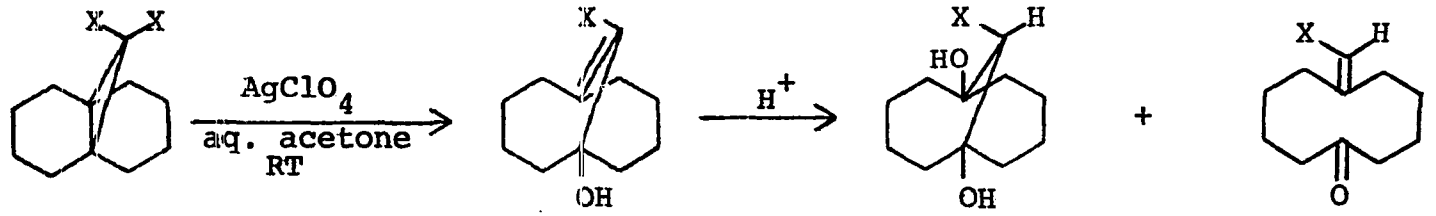
Table II. Summary of some findings by Warner group



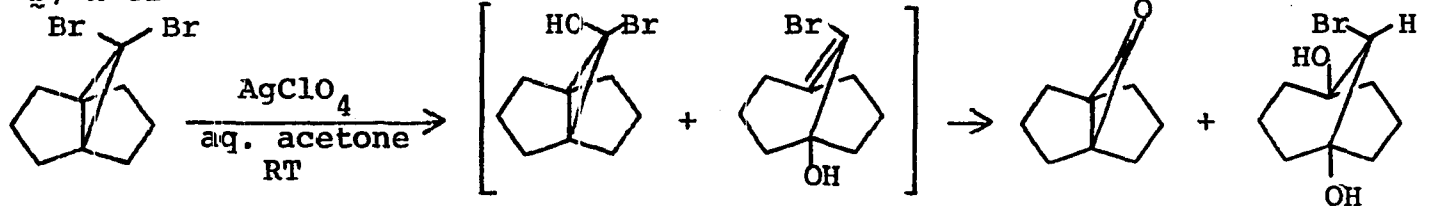
134 135 136 (meso dimer) — Ref. 69



14 137 138 — Ref. 70

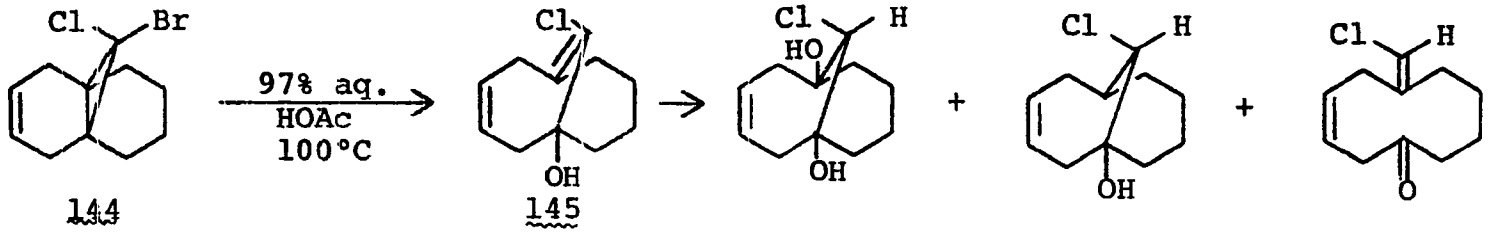
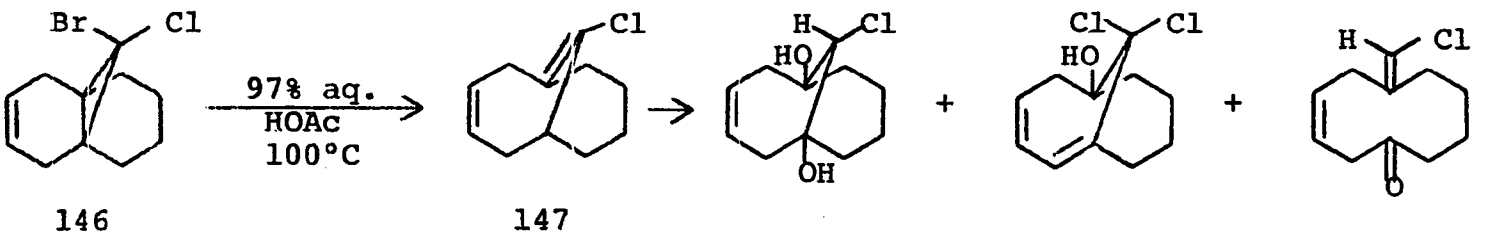
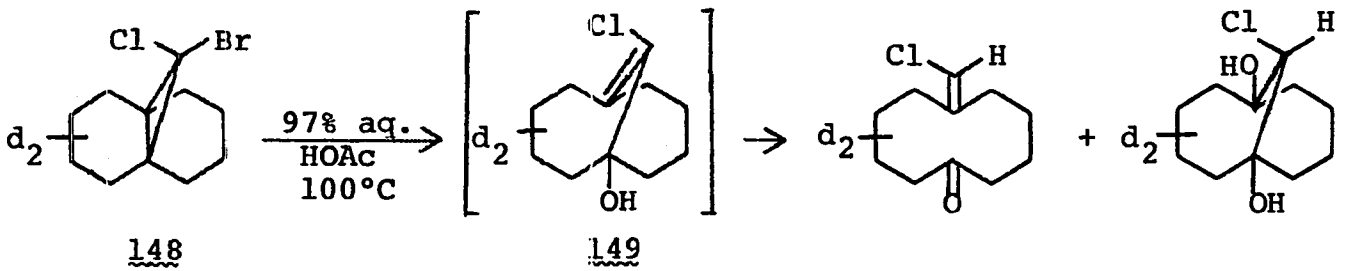
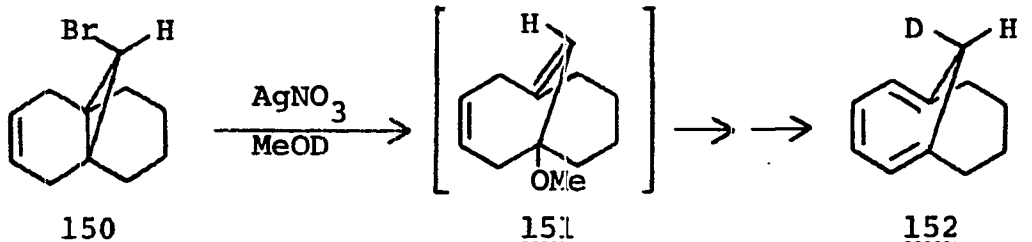


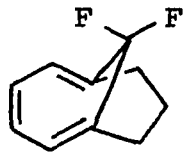
139a, X=Br
b, X=Cl
140 — Ref. 71



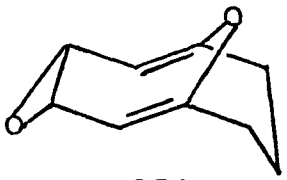
141 142 143 — Ref. 72

Table II. (Continued)

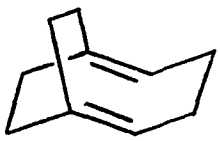
	Ref.
 144 → 145	73
 146 → 147	73
 148 → 149	73
 150 → 151 → 152	74



153



154



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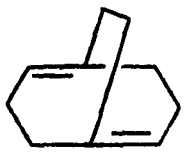
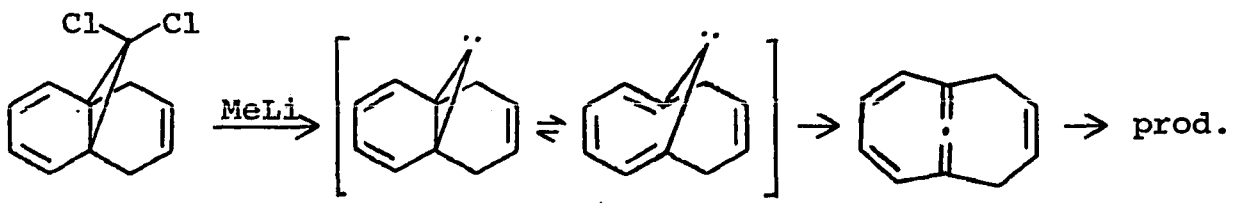
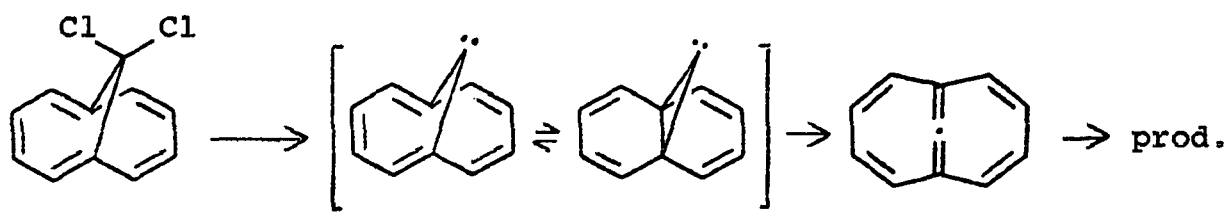


156

A second way of placing two bridgehead double bonds in a bicyclic system is to have them both in a one carbon bridge, i.e., to cumulate them. In this category, allenes[82] 157 and 158[83] have been proposed as intermediates arising from the corresponding carbene or carbenoid; they (157, 158) could



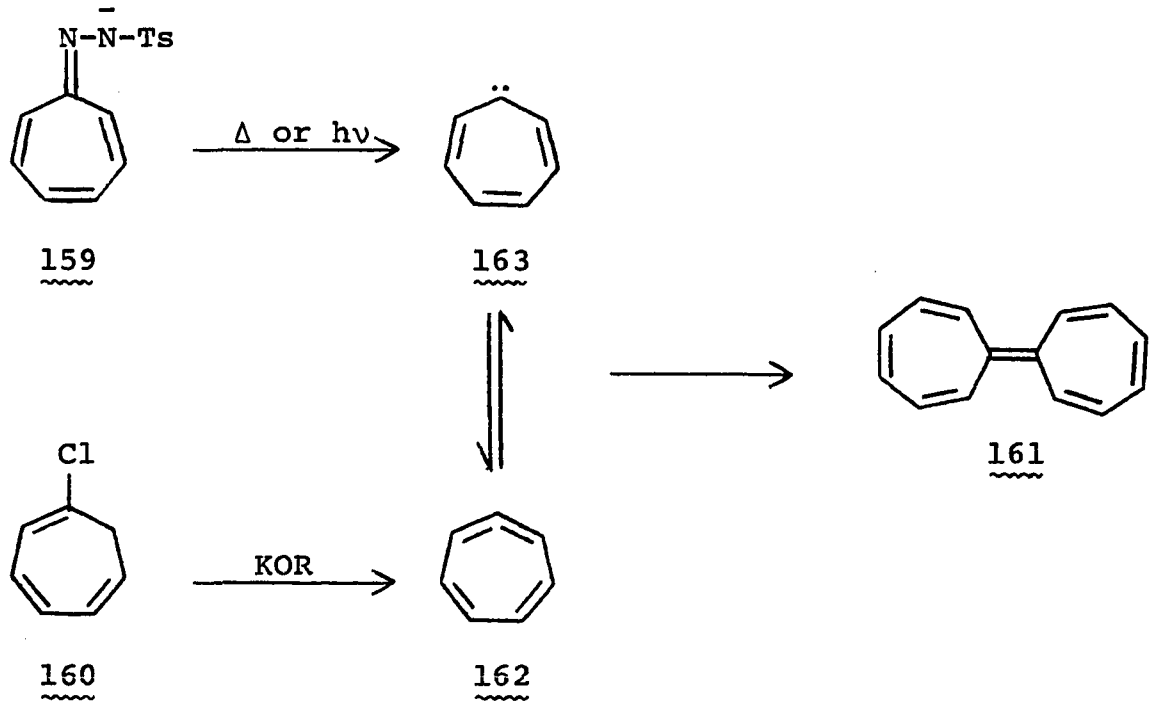
157



158

arise as a manifestation of the cycloheptatrienylidene-cycloheptatetraene equilibrium[84], or as an example of the cyclopropropylidene-allene interconversion.[4,6b,85]

Jones[84] has demonstrated that photolysis or thermolysis of 159 affords dimer 161, which was also generated by dehydro-

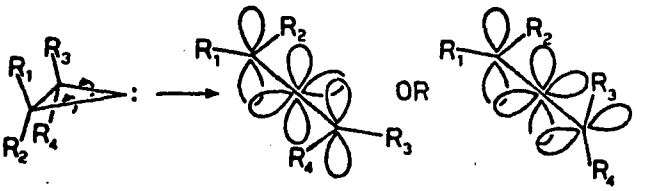


halogenation of 160 (via allene 162). Allene 162 is in equilibrium with cycloheptatrienylidene (163), wherefrom emanates 161.

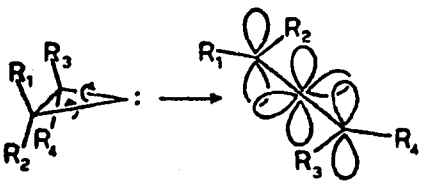
The preparation of allenes by the ring opening of cyclopropylidenes (or the corresponding carbenoids) has been used widely in the synthesis of both cyclic[29,86] and acyclic[86] allenes since the reaction was first reported by Doering in 1958.[87]

In principle there are four basic modes for ring opening in this reaction:

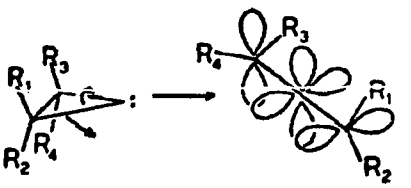
(1) A conrotatory opening leading either to an orthogonal or a planar[88] allene.



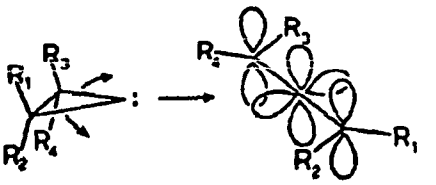
(2) A disrotatory opening to give a planar allene.



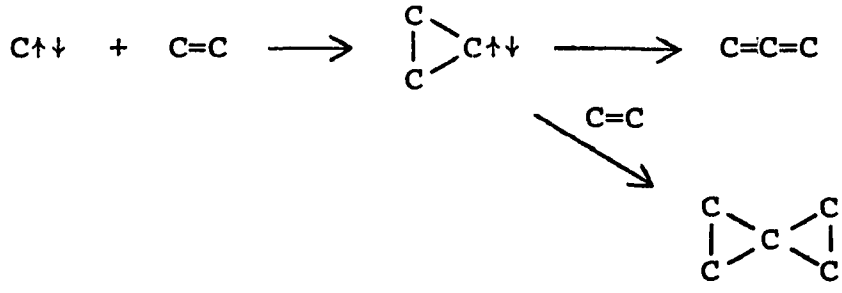
(3) A "monorotatory" opening to give an orthogonal allene.



(4) A "nonrotatory" opening to give a planar allene.



In 1967 Borden[89] using correlation diagrams, suggested that singlet cyclopropylidene opened by the "monorotatory" mode described above and the triplet did not open at all. This suggestion appeared to be supported by the reports[90-93] that olefins reacted with singlet carbon atoms to form allenes and spiropentanes. Here, cyclopropylidene was proposed as an intermediate:



Boder et al.[35] and Dewar et al.[94] have theoretically studied the reaction of a singlet carbon atom with ethylene using MINDO/2. These calculations indicate that the initial reaction produces singlet cyclopropylidene, which opens in a nonrotatory manner[94] to give a linear planar allene, which substquently undergoes internal rotation to yield the final product, orthogonal allene. These calculations suggest an energy of activation for the ring opening of 50 kcal/mol.[94] More recent calculations[35] have lowered this to 14 kcal/mole (Figure 1).

Pasto et al.[95] used ab initio SCF calculations, employing the STO-3G and 4-31G basis sets with full geometry

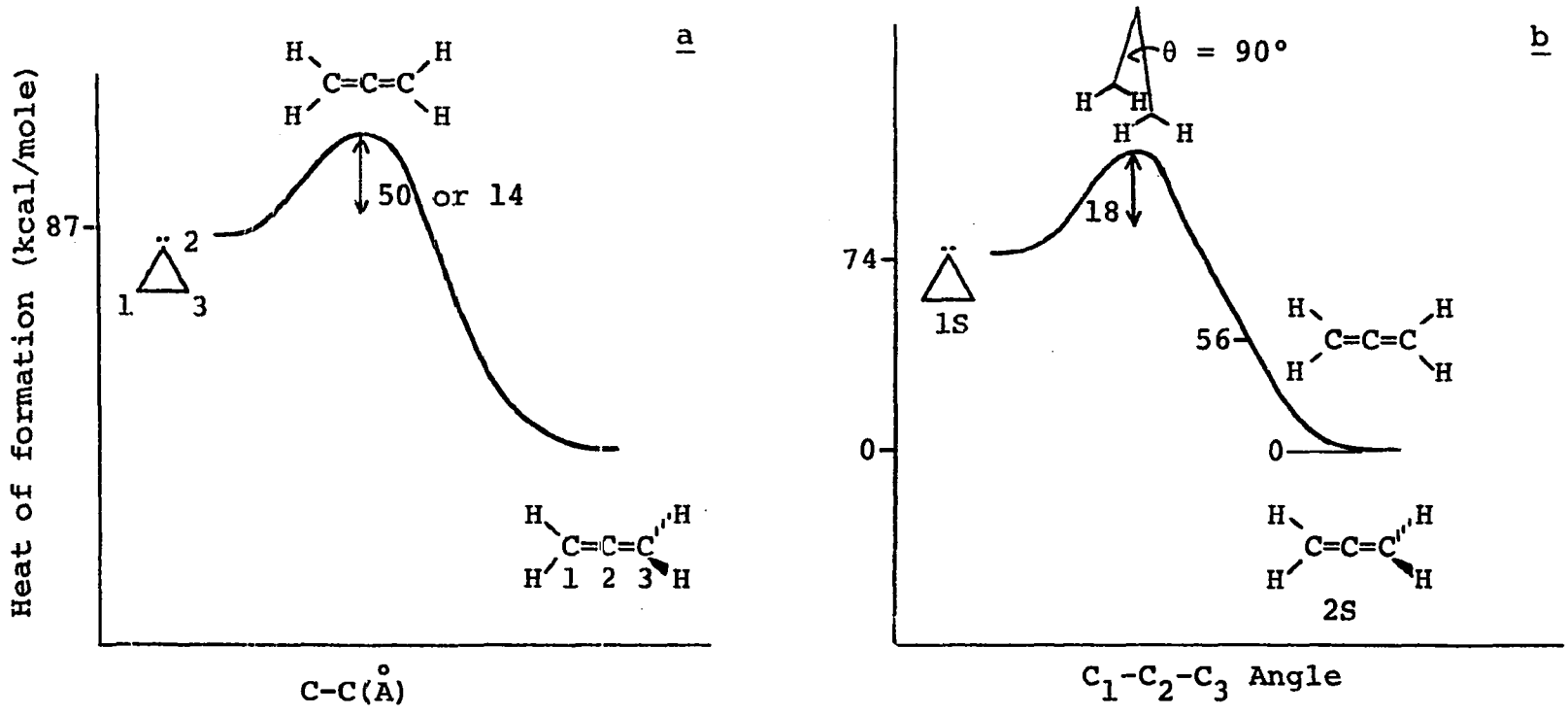


Figure 1. Reaction path for singlet cyclopropylidene-allene conversion based on (a) MINDO-2 calculations (b) Ab inito SCF calculations

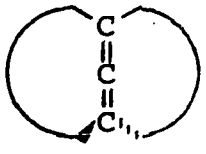
optimization to study the singlet and triplet cyclopropylidene-allene energy surfaces. They calculated that triplet cyclopropylidene (1T) has lower energy than singlet cyclopropylidene (1S) by 8.4 kcal/mol. Triplet allene is calculated to be a bent, planar species, being 8.0 kcal/mol lower in energy than the linear, planar form. Both 1S and 1T undergo disrotatory ring opening, although the intimate details of the two processes differ greatly. In both cases substantial shortening of the C-C bond lengths are observed as the ring opens. Barrier heights for the ring opening of 1S and 1T are calculated to be 18 and 19 kcal/mole, respectively (4-31G level).

The conversion of 1S to allene 2S was suggested to involve three distinct processes: (a) initial disrotatory opening proceeding almost to the transition state; (b) a rapid transformation from the disrotatory mode to a distorted monorotatory (from 1s) mode between C_1-C_2-C_3 bond angles of 90 and 100°; and (c) nonrotatory conversion of the 100° structure to allene by opening of the C_1-C_2-C_3 bond angle with flattening of the out of plane methylene group.

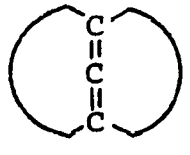
INDO-MO calculations[96] indicate that singlet 1,2-cyclooctadiene and 1,2-cycloheptadiene are probably bent at C-2 and also twisted somewhat from the orthogonal geometries. These distortions also bring about a moderate increase in charge separation, as compared with linear allenes. The

singlet states of the smaller cyclic allenes are probably planar and bent. In these cases there is considerable charge delocalization and the allene moiety may be best considered as an allyl cation with an anion located at C-2 in the in plane sp^x orbital. For the triplet state the allene moiety is probably planar in all cases and is bent if the ring contains six or fewer atoms. These systems have little charge separation and may best be visualized as an allyl radical with a second unpaired electron in the in plane p (or sp^x) orbital at C-2. The calculations also indicate that while 1,2-cycloheptadiene and larger cyclic allenes would have singlet ground states, 1,2-cyclohexadiene and smaller cyclic allenes may have triplet ground states.

Summarizing the above mentioned theoretical findings, one can assume that in a bicyclic system, if the rings are big



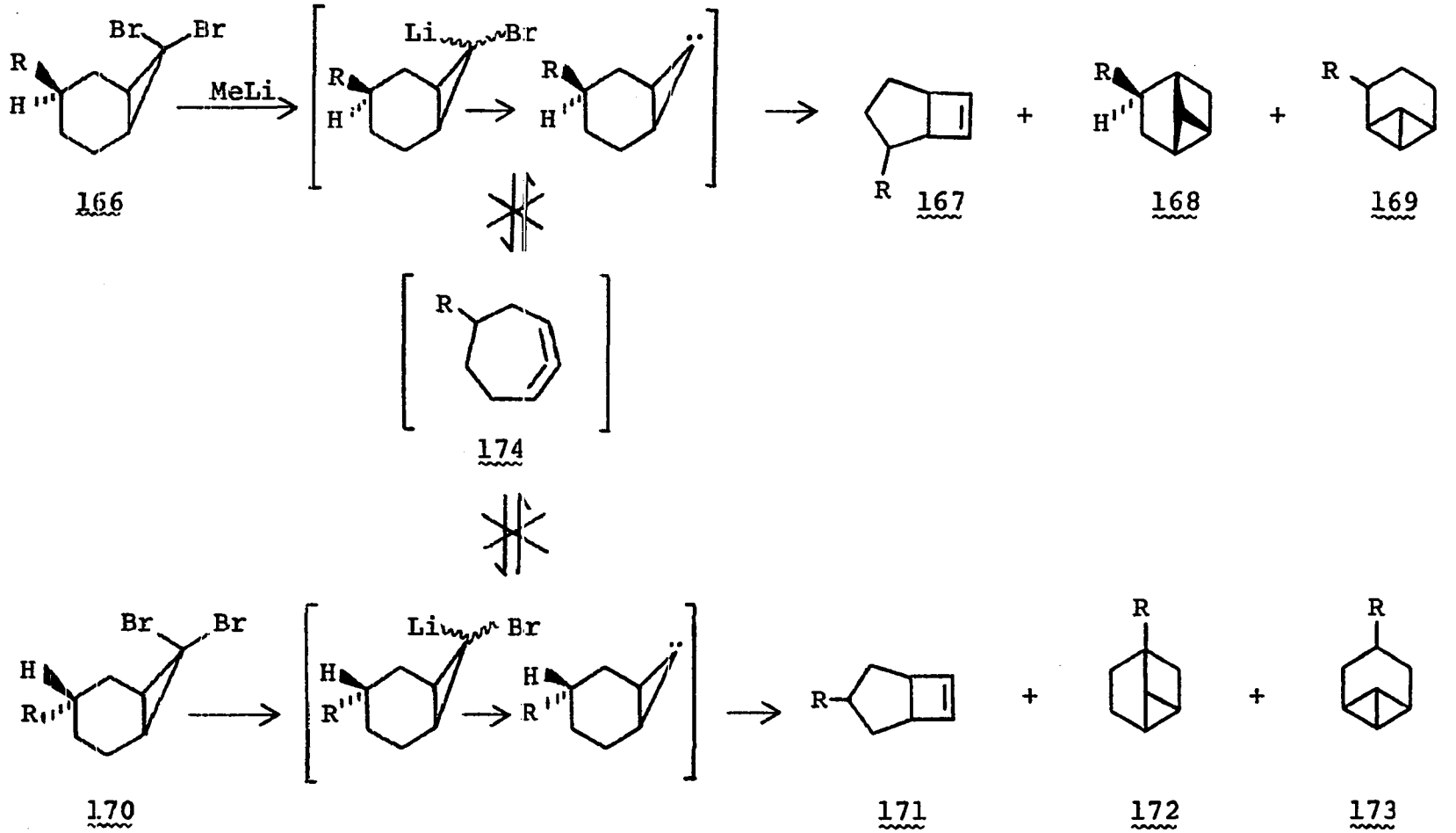
164



165

enough; a normal orthogonal allene (164) could be a reaction intermediate, while in small rings, one would expect to have a (linear or bent) planar allene (165) as a reaction intermediate.

Scheme III[a]

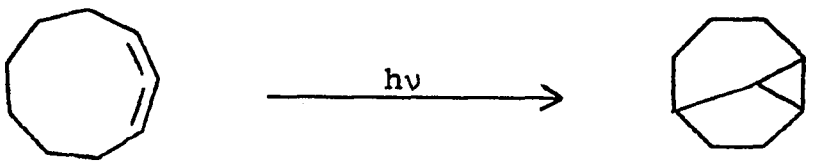


R = t-Butyl

[a]All species are dl, only one enantiomer is shown.

On the experimental side, Moore and King[6b] treated 166 with MeLi, which lead, via intramolecular carbenoid insertion (Scheme III), to products (167, 168, 169) which are different from the products (171, 172, 173) obtained from the epimer 170. This result establishes that the stereoisomeric cyclopropylidene intermediates derived from 166 and 170 do not interconvert and precludes the possibility of reversible opening of the cyclopropylidenes to 5-tert-butyl-1,2-cycloheptadiene (174).

Photolysis of 1,2-cyclononadiene in vapor phase (benzene-sensitized) at 2537Å yields one major product, tricyclo-[4.3.0.$0^{2,9}$]nonane 175. It was postulated that the triplet

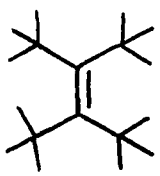


175

allene is either formed in its planar configuration[97] or is quickly deactivated to that state by collision. This molecular arrangement is then suitable for closure to the cyclopropylidene followed by insertion into a C-H bond to give 175.

Sterically Crowded Olefins

In recent years there has been considerable interest in the synthesis and properties of highly crowded olefins. Several excellent reviews have been published in this area.[98] The highly crowded olefin 176 has not yet been synthesized



176

despite a lot of effort.[99] Nevertheless, some analogs of 176 have been obtained.

Synthesis of crowded olefins has been a challenging task, as the bulky groups often preclude the use of methods that are successful for less strained analogs, and the branched structures themselves are often prone to rearrangements.

The McMurry procedure[100], using a reduced titanium reagent has been successfully applied to the preparation of tetraisopropyl, 177[101], tetrabenzyl, 178[102], and tetraneopentylethylene, 179[99c], but unsuccessfully to the synthesis of 176[99d] and a number of other crowded alkenes.[99d]

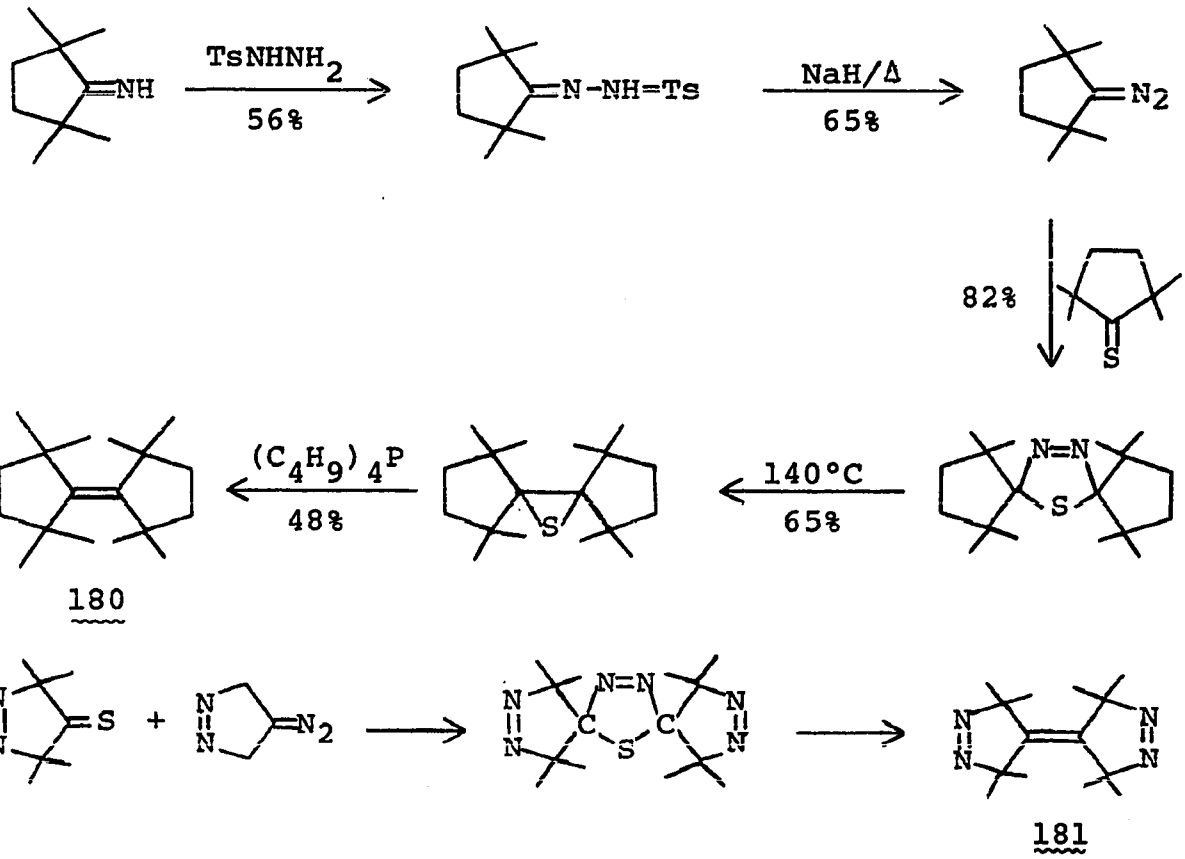
$$R_2C{=}O \xrightarrow[\substack{TiCl_3 \\ \text{or } K\text{-}TiCl_3}]{LiAlH_4} R_2C{=}CR_2$$

177, R=i-Pr

178, R=$PhCH_2$

179, R=neopentyl

Another successful route to crowded olefin structures has been a double extrusion method. The reactions of thioketones[99a,103] and selenoketones[104] have led to a number of crowded tetrasubstituted olefins (e.g., 180, 181, 182).



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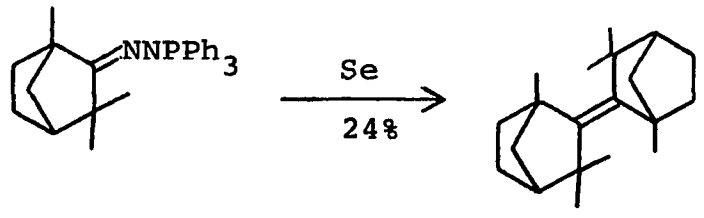
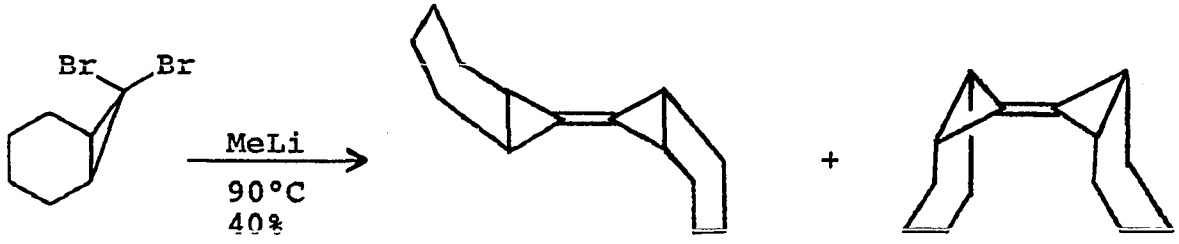


182

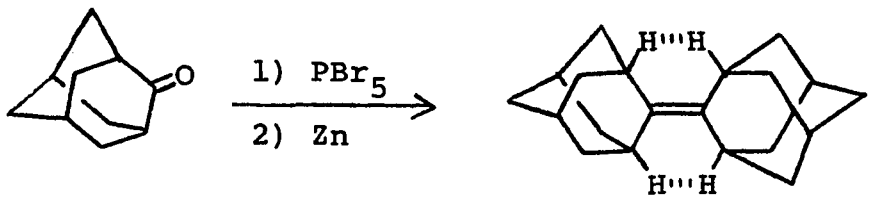
Simple carbene or carbenoid dimerization is also a route for preparing hindered olefins.[105,106]

$$Mes_2CN_2 \xrightarrow{h\nu} MesC: \longrightarrow Mes_2C{=}CMes_2$$

Mes = 2,4,6-trimethylphenyl

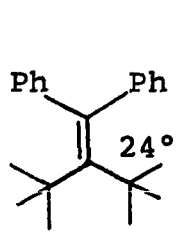


Cyclic analogs of tetraisopropylethylene such as adamantylideneadamantane (183)[107] and 7,7'-norbornylidene-norbornane[108] are readily available by the reaction of geminal dibromides and metals.



183

X-ray crystallographic studies have determined the molecular structure of some hindered olefins. In the case of diphenyl-di-tert-butylethylene, 184,[108] X-ray analysis



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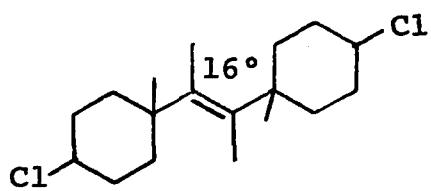

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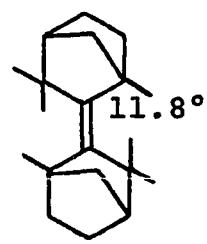
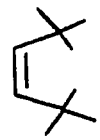


182

revealed a 24° twisting of the π bond whereas the corresponding twist in 185[109] is 16° and in 182[110] is only 11.8°. The C-C double bond lengths in 184, 185 and 182 are 1.360Å, 1.349Å, and 1.353 respectively, indicating that the central bond-lengthening due to steric hindrance is not very significant in those cases.

Force field calculations on hindered olefins[111] suggest that steric crowding is often relieved by twisting about the

double bond. For trans-1,2-di-tert-butylethylene, (187)[111], this twist is calculated to be ca. 22°; for tri-tert-butylethylene, (189)[111], it is 16°; for tetra-tert-butylethylene, (176), it is 75°[111] (however, Allinger's[112] force field



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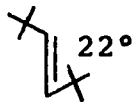

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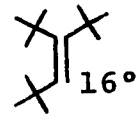
188



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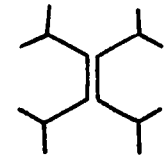
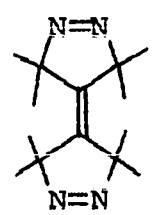


177

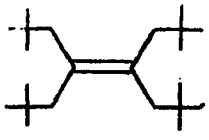
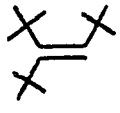
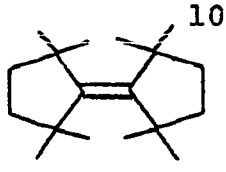
predicts the π bond in 176 to be twisted by only 43.3°). The strain energies of various crowded hydrocarbons, as calculated by molecular mechanics are: cis-1,2-di-tert-butylethylene (186): 11.1 kcal/mol[111a] (experimental = 10.7 kcal/mol), 1,1-di-tert-butylethylene (188): 12.05 kcal/mol[111a]; tri-tert-butylethylene (189): 32 kcal/mol[111a]; tetraisopropylene (177): 18 kcal/mol.[111a] It was concluded that the strain energy of the unknown 176 could not be reasonably estimated from this procedure. Biadamantylidene (183)[113] maintains an untwisted double bond in spite of the presence of significant nonbonded hydrogen repulsions, as does permethyl-4,4'-bis-$\Delta^{1,2}$-pyrazolinylidene (181).[103e]



181

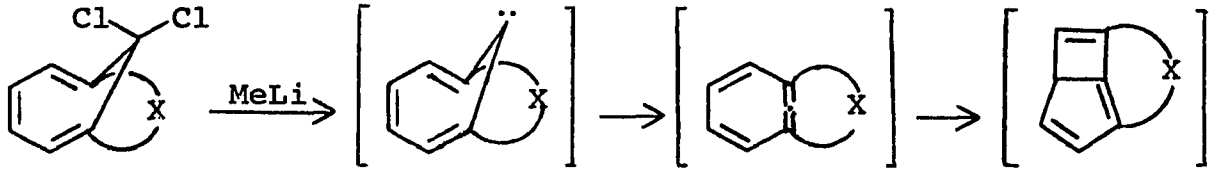
Spectral properties of crowded olefins often show distinct differences from those of less hindered ones. Table III shows some Raman and some UV absorption data:

Table III. Raman and ultraviolet absorption spectra of olefins

	Raman	UV (Cyclohexane)
	π C=C (cm^{-1})	λ max (nm)
 99c	1607	
 114	1610	
 115	1583	194.5 (ε13300)
 103	1540	203.0 (ε15100)

RESULTS AND DISCUSSION

Our interest in bridgehead olefins generated from cyclopropanes drew our attention to the purported formation of allenes 157 and 158 from their corresponding dichlorides.



157, X=CH_2-CH=CH-CH_2

158, X=CH=CH-CH=CH

190

dimers or trapping products

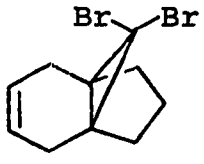
We wondered whether the ultimate formation of 190 was a manifestation of cycloheptatrienylidene-cycloheptatetraene chemistry[26], or related to the transformations of vinyldibromocyclopropanes and 10 (Eq. 4 and Eq. 6), or something else. Therefore, compounds 191, 192a-192d, and 206 were synthesized.

Prior to this work, the reactions of unsaturated tricyclic[4.3.1]dibromides 15, 192, tricyclic[3.3.1]dibromide 17, and the more strained tricyclic[4.2.1]dichloride 134 with MeLi had not been reported. We investigated these systems in order to test for allene formation in small ring tricyclic systems. An alternative method of generating carbenes--

pyrolysis of α-bromotin compounds--was utilized also to examine the possible formation of linear planar allenes from tricycliccyclopropylidenes.

Synthesis

Compound 15 was synthesized in good yield[116] by adding dibromocarbene to 4,7-dihydroindane. Hydrogenation of 15 afforded 14 quantitatively. Oxidation of 15 with DDQ[117] (1,2-dichloro-4,5-dicyanoquinone) in CH_2Cl_2 at 70°C for 4 days gave diene 191 (Fig. 3) in 53%.



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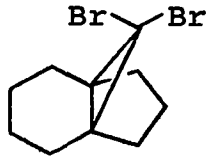

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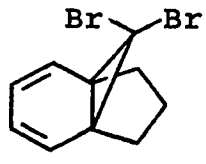

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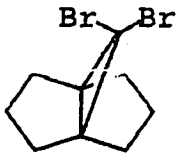

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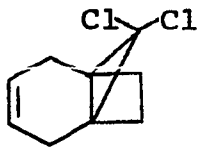
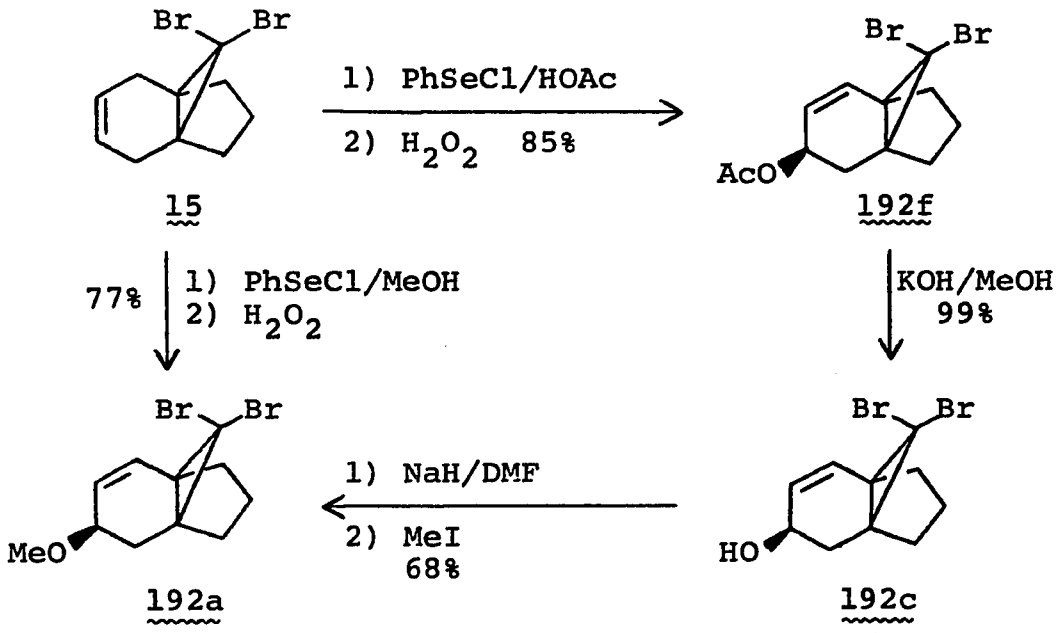


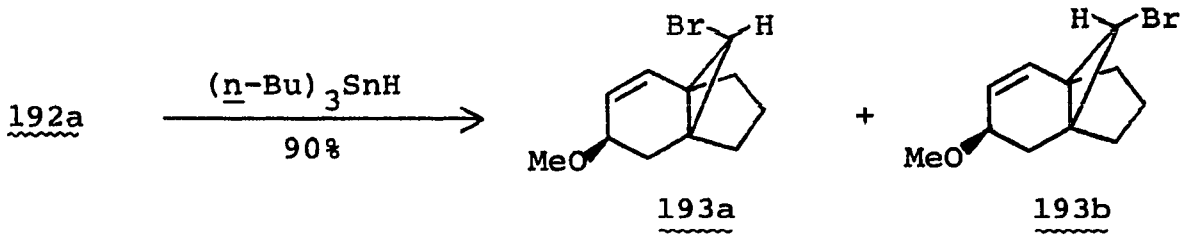
134

9,9-Dibromotricyclo[3.3.1.$0^{1,5}$]nonane (141) was synthesized according to the published procedure.[118] Compound 134 was synthesized by the addition of dichlorocarbene to dihydrobenzocyclobutene.[119] Propellane 192a (Fig. 6, 7) was synthesized by first reacting 15 with PhSeCl[120] in MeOH,

followed by oxidation (77% overall). Compound 192f was formed in an analogous manner; hydrolysis of 192f afforded



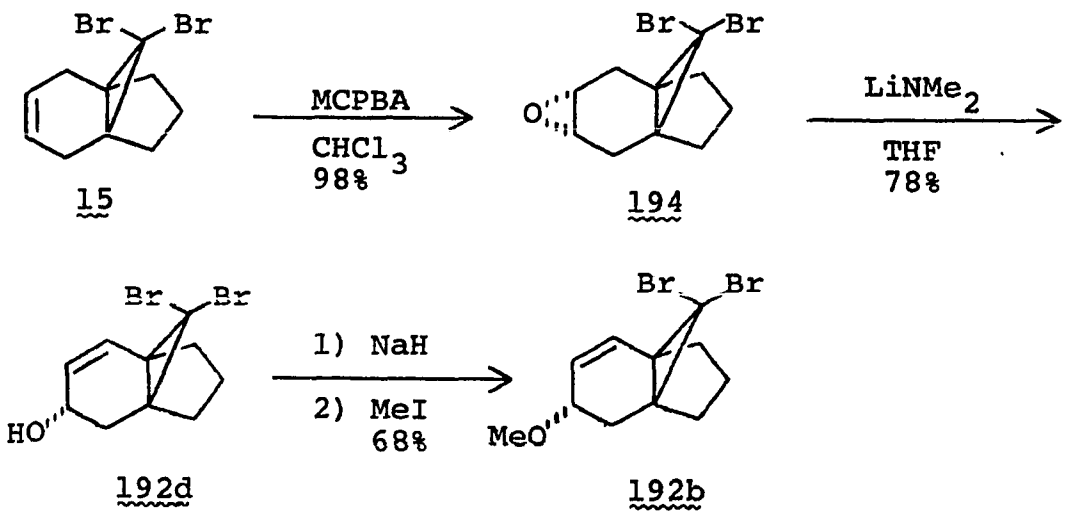
the corresponding alcohol 192c (Fig. 4, 5) quantitatively. Treatment of 192c with NaH in DMF at room temperature, followed by addition of MeI, also gave 192a. Tin hydride[121]



reduction of 192a gave a mixture of two epimers 193a (Fig. 8) and 193b (90% yield) in a ratio of 12:1. The mixture was

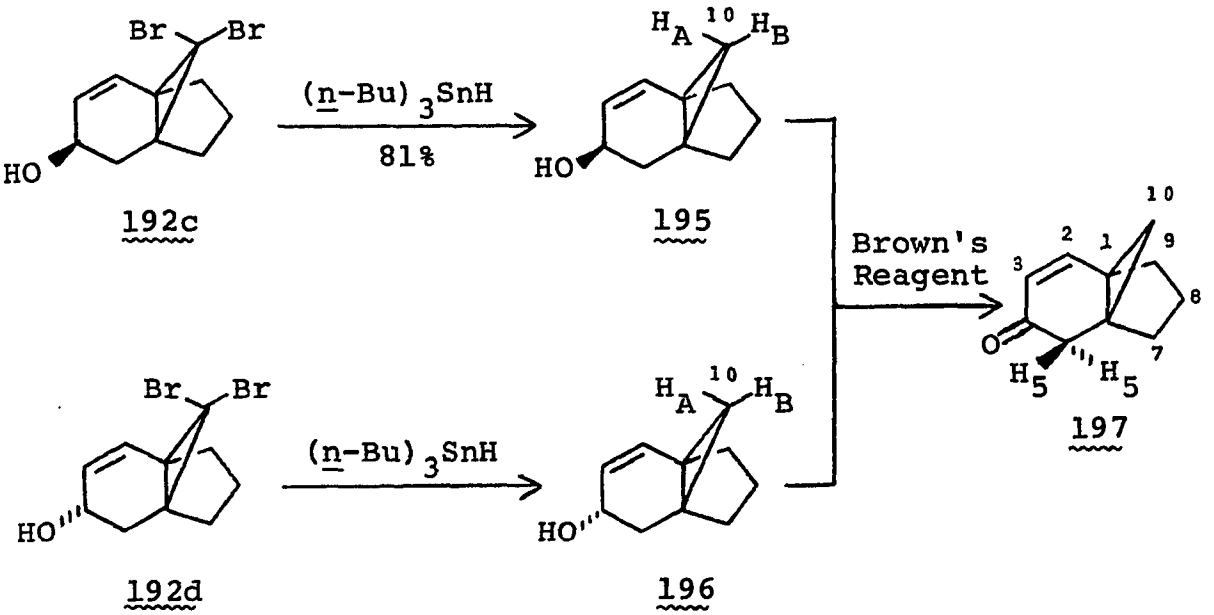
chromatographed on silica gel to afford pure 193a (4% ethereal hexane). The structural assignments were based on the chemical shift of the C_{10}-methine protons, where that of 193b (δ3.25) should appear downfield from that of 193a (δ3.15).

Formation of 192d[122] was achieved by a 2-step process. First, oxidation of 15 with MCPBA (m-chloroperbenzoic acid) produced a single epoxide 194[123] (Fig. 9) quantitatively. Next, ring opening with $LiNMe_2$ gave 192d (78%), which was then reacted with NaH and quenched with MeI to give the



endo-methoxide 192b in 52% overall yield. Compounds 195 (Fig. 10) and 196 were obtained by tin hydride reduction of 192c and 192d. Oxidation[124] of both 195 and 196 gave the same product 197 (Fig. 11). The mass spectrum of 197 showed an

exact mass at m/e 147.0810 (P-1). The infrared spectrum showed a strong C=O absorption at 1680 cm^{-1}.



192c 195 197

192d 196

The stereochemistry[125] of 192c and 192d was confirmed by comparing the Eu(DPM)$_3$-shifted ^{1}H NMR spectra of 195 and 196 (See Table IV).

Table IV shows that H_A in 195 was shifted more down field than H_A in 196. This indicates that the -OH group, which complexes with shift reagent, is closer to H_A in 195 than the one in 196; i.e., in 195 the stereochemistry of the -OH group is exo while in 196 it is endo. It is thus concluded that initial attack on 15 occurred from the less hindered side away from the bromine atom. In the case of selenenylation, acetate subsequently attacks from the side syn to the bromine atom. This suggests that the reactive

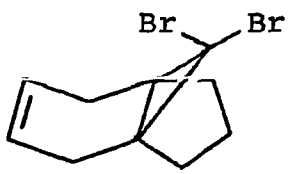
Table IV. $Eu(DPM)_3$ Induced ^1H NMR shifts (LIS) for 195 (in ppm)

			[Shift Reagent]/[Cpd.]		
			0.1	0.2	0.3
Cpd.	195[a]	(H_A)	1.32	4.11	7.28
		(H_B)	1.05	-	3.33
	196[b]	(H_A)	0.28	0.73	1.23
		(H_B)	0.44	0.82	1.09

[a]Measured in CCl_4 solution.

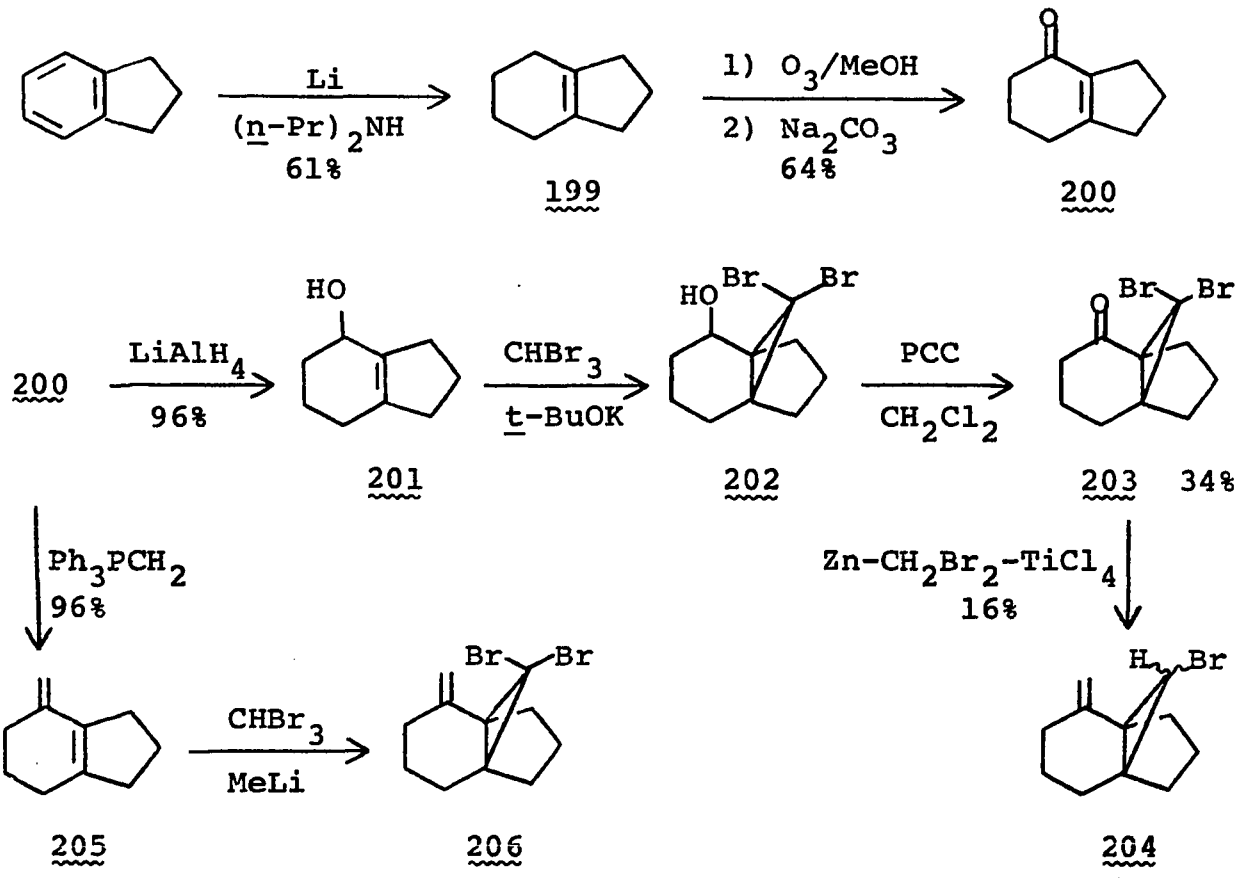
[b]Measured in $CDCl_3$ solution; the assignments of H_A and H_B may be reversed.

conformation of 15 must be the seemingly uncomfortable atomic arrangement shown in 198. Synthesis of compound 206



198

was first attempted by using Takai et al.'s[126] reagent to try to convert 203 to the desired compound. However, the monobromide 204 (Fig. 16) resulted (18%); 204 turned out to be rather useful. Compound 203 was synthesized by first

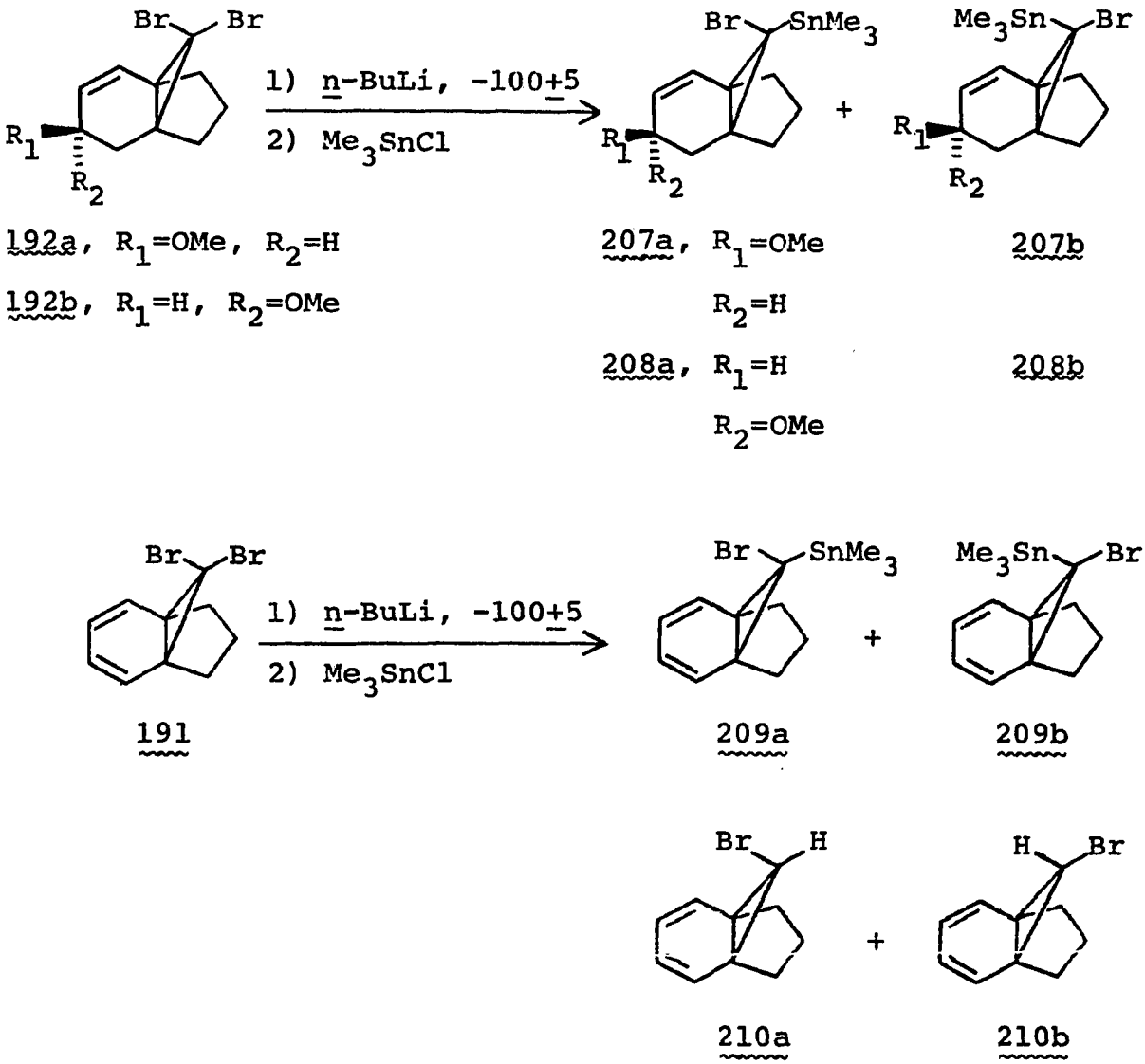


reducing indane with Li in $(n\text{-Pr})_2NH$ to afford 199 in 61% yield; 199 was ozonized and then treated with Na_2CO_3 in refluxing methanol to give 200 in 64% yield. Reduction of 200 gave 201 (Fig. 13) quantitatively. Subsequent dibromocarbene addition gave a mixture of 202 (Fig. 14) and 203 (Fig. 15). Compound 202 was purified by recrystallization from CCl_4 to afford white crystals (mp 87-88.5°C). Oxidation of the mixture of 202 and 203 with pyridinum chlorochromate in CH_2Cl_2 gave a two phase reaction mixture, with a black

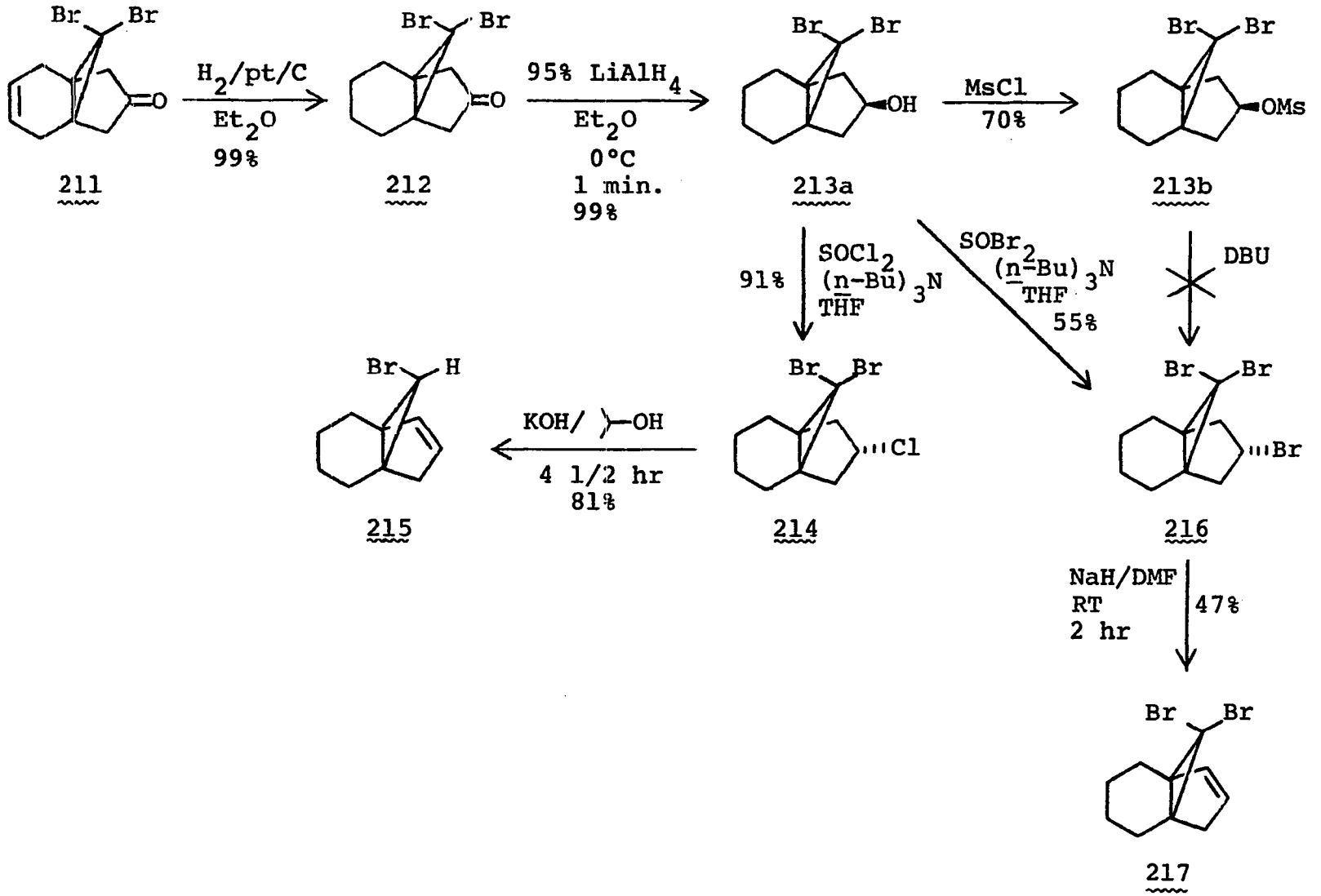
gum at the bottom of the flask. The crude product mixture was filtered through a florisil short column. After concentration, compound 203 was obtained in 34% yield (based on 201). Another approach to 206 was moderately successful: Wittig reaction of 200 gave 205 (Fig. 12) in 96% yield. Dibromocarbene addition then afforded a mixture of 206 (Fig. 17) and a highly brominated uncharacterized material. Further purification of 206 was unsuccessful.

Synthesis of tin compounds 207a (Fig. 18, 19), 207b (Fig. 18, 19), 208a (Fig. 20, 21) and 208b (Fig. 20, 21) was achieved according to Seyferth and Lambert's[12] method; the isomers were separated by thin layer chromatography. However, 209a (Fig. 22) and 209b (Fig. 22) could not be purified. Both 209a and 209b were isolated along with reduction products 210a (Fig. 3) and 210b (thin layer chromatography). Structural assignment of epimers 209a and 209b was based upon the ^{1}H NMR olefinic splitting pattern. Both 191 and 209a have the bromine atom over the 6-membered ring and thus showed the same splitting pattern. The structural assignment of epimers 207a, 207b and 208a, 208b was based on comparison with the ^{1}H NMR olefinic splitting pattern of 192a and 192b, respectively.

Compound 211 was prepared by a known[127] procedure in good yield. Hydrogenation of compound 211 gave 212 (Fig. 23) quantitatively. Reduction of 212 by $LiAlH_4$ in ether at



0°C for one minute followed by quenching with H_2O gave 213a (Fig. 24) quantitatively. Because of the steric hindrance of the bromine atom, the hydride attacked the bottom side of the ketone to give the exo alcohol, 213a. The stereochemistry of 213a at C_8 was supported by the fact that the corresponding mesylate (213b) (Fig. 25), although refluxed

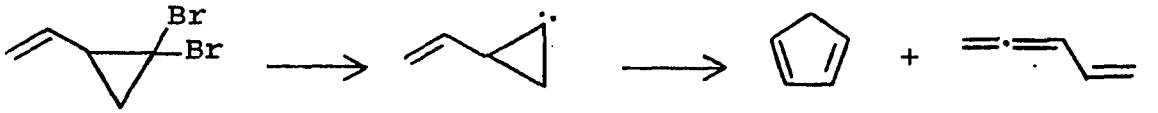

Br Br
O
211
H_2/pt/C
Et_2O
99%
212
95% $LiAlH_4$
Et_2O
0°C
1 min.
99%
OH
213a
MsCl
70%
OMs
213b
91%
$SOCl_2$
$(n\text{-}Bu)_3N$
THF
214
Cl
$SOBr_2$
$(n\text{-}Bu)_3N$
THF
55%
DBU
Br
216
NaH/DMF
RT
2 hr
47%
217
KOH/)—OH
4 1/2 hr
81%
H
215

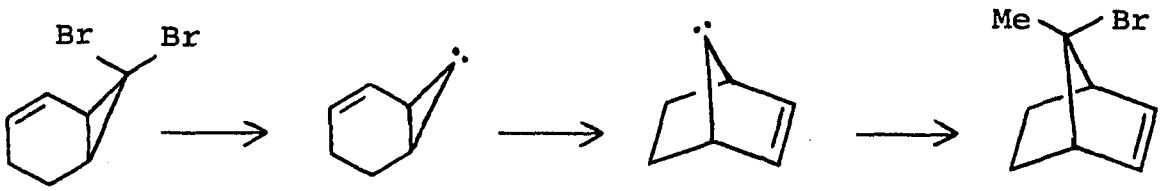
with DBU in benzene for 12 hr, afforded only starting material. This failure of an exo derivative to eliminate is in accord with similar observations with the 8-substituted [4.3.1]propellane parent system.[128] Treatment of 213a with 3 equiv. of $SOCl_2$ and 1 equiv. of $(n\text{-Bu})_3N$ in refluxing THF afforded endo-chloride 214 (Fig. 26) in 91% yield. Compound 214 was treated with a $KOH/(CH_3)_2CHOH$ solution at reflux for 4 1/2 hr, whereby a reduced product 215 (Fig. 28) resulted. The stereochemical assignment at C_{10} of 215 is based on the ^1H NMR olefinic splitting pattern of 215 which is different from that of 217.

In view of the above, a compound with a better leaving group was made (216) and a milder elimination reaction was undertaken. Reaction of 213 with $SOBr_2$ and $(n\text{-Bu})_3N$ in refluxing THF afforded 216 (Fig. 27) in 55% yield. Subsequent treatment with NaH in DMF at room temperature for 2hr gave 217 (Fig. 29) in 47% yield.

On the Rearrangement of Vinylcyclopropylidenes to Cyclopentenylidenes

A recent review[26] cites the vinylcyclopropylidene to cyclopentenylidene conversion[5] as one of two known types of carbene-carbene rearrangements. The additional formation of bona fide carbene product 1,2,4-pentatriene[5] lends credence to the intermediacy of vinylcyclopropylidene. More relevantly, 10 is converted uniquely to 11 by a process pro-

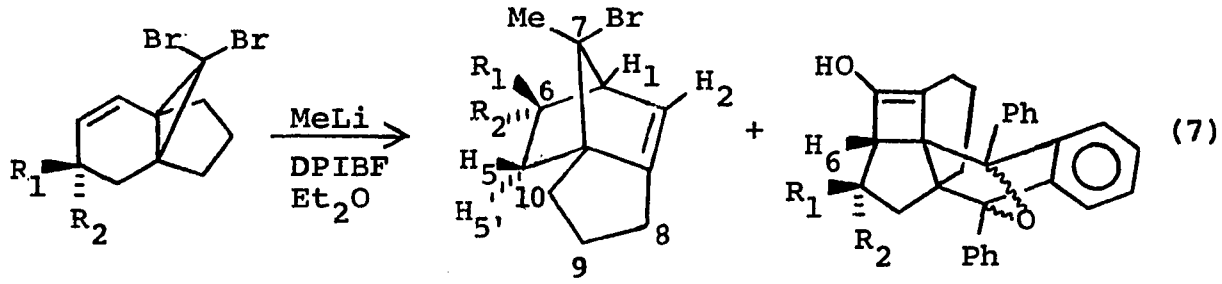




10 11

posed[5b] to involve norcarenylidene and norbornenylidene, although none of the bona fide products from norbornenylidene were detected; the stereoselectivity apparent in the formation of 11 remains unexplained. We now provide evidence which shows that these rearrangements do not involve carbenes[5,38b,41], but rather species in which bonding to lithium is necessary.[38]

Treatment of dibromide 192 with 10 equiv. of MeLi in ether at -78°C in the presence of 1.1 equiv. of DPIBF (diphenylisobenzofuran) resulted in primarily 218a (53% isolated yield) with a small amount of 219a visible in the ^{1}H NMR spectrum of the crude product. Reaction at room temperature provided the same products 218a and 219a in 34% and 62% yield, respectively (the yields were determined by ^{1}H NMR using benzaldehyde as an internal standard).



192a, R_1=OMe, R_2=H

b, R_1=H, R_2=OMe

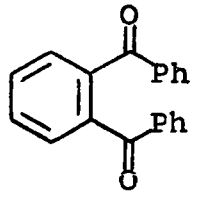
c, R_1=OH, R_2=H

d, R_1=H, R_2=OH

e, R_1=-O-C(=O)-C$_6$H$_4$-Br, R_2=H

218

219



220

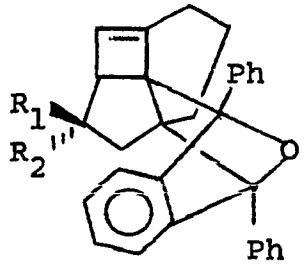
Compounds 218a and 219a were isolated by silica gel thin layer chromatography (5% ethereal hexane); the excess DPIBF was destroyed either by letting the crude product mixture sit at room temperature overnight or in the refrigerator for 4 days to give a colorless ethereal solution (DPIBF is bright yellow). It is essential to allow all the excess DPIBF to oxidize to colorless diketone 220, since DPIBF has a similar R_f value to 218a, while the highly polar 220 has

a very small R_f value, which makes it easily separable from the other products. A yellow band with R_f=0.75 proved to be 218a (Fig. 30). The structure was established on the basis of its spectral and analytical properties. The infrared spectrum showed olefinic absorption at 3070 and 1650 cm^{-1} and ether C-O stretching vibrations at 1100 cm^{-1}. The ^1H NMR spectrum showed the vinyl proton as a broad singlet at δ5.5, and the methine proton at C_6 as a doubled doublet ($J_{6,5}$=5 Hz, $J_{6,5'}$=3 Hz) centered at δ3.6; there was no apparent coupling between H_6 and H_1, in accord with expectations based on examination of models which indicate these two hydrogens have a dihedral angle of 90°. Also, the methine proton at C_1 appeared as a doublet ($J_{1,2}$=3 Hz) centered at δ3.11, the methoxy protons at C_6 as a singlet at δ3.26, the methyl protons at C_7 as a singlet at δ1.92, the two protons at C_8 as a multiplet at δ2.16, the four protons at C_9 and C-10 as a multiplet at δ1.92, the exo proton at C_5 as a doublet centered at δ1.70 ($J_{5,5'}$=6.0 Hz, $J_{5,6}$=5 Hz), and the endo proton as a doublet ($J_{5,6}$=3 Hz) centered at δ1.66. Irradiating the doublet at δ5.5 (H_2), collapsed the doublet at δ3.11 (H_1) to a singlet. Also, irradiating the multiplet at δ2.16 (H_8,H_8') caused the broad singlet at δ5.5 to collapse to a doublet (J_{12}=3 Hz). Furthermore, irradiation of the doublet doublet at δ3.6 (H_6) collapsed the two doublets at 1.62 and 1.70 to two singlets

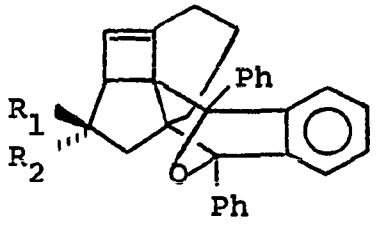
($J_{5,5'}$=6.0 Hz). Finally, irradiation of the doublet at δ 1.62 ($H_{5'}$) collapsed the doubled doublet at δ3.6 (H_6) to a doublet.

$Eu(fod)_3$ shift reagent ^1H NMR studies also supported the structure and stereochemistry at C_7 of 218a. The fact that the methyl and methoxy groups were shifted more downfield than the other protons indicated that the two groups are syn to each other. Further support for the stereochemistry at C_7 came from more thorough Eu shift reagent ^1H NMR studies of 218c and 221 (vide infra).

The mixture of the two isomeric products of structure 219a (Fig. 31,32) was isolated by thin layer chromatography and the structures assigned as 219-1-a and 219-2-a on the basis of spectral and analytical properties. Most importantly, the structures were verified by X-ray analyses of 219-1-e and 219-2-e (see Appendix). One of the isomers



219-1



219-2

(Fig. 31,32) was separated by recrystallization from MeOH (four times).

Reaction of 192b with MeLi in the presence of DIPBF in ether at room temperature afforded two products in the ratio ratio of 1:3.05. The minor product was purified by preparative TLC (10% ethereal hexane) and was assigned structure 218b (19%) (Fig. 33) on the basis of its spectral similarity to 218a and its analytical properties. The major product (R_f=0.2, 58%), isolated by thin layer chromatography, was a mixture of two isomeric adducts, 219-1-b and 219-2-b. The structures were assigned on the basis of their spectral similarities to 219a and 219e. One of the isomers (Fig. 32, 34) was isolated by recrystallization from ether to give white needles (mp 203-204°C).

Reaction of 192c with 10 equiv. of MeLi in the presence of 1.1 equiv. DPIBF in ether at room temperature afforded two products in a ratio of 1:1.88. The minor product was purified by preparative TLC (25% ethereal hexane) and was assigned structure 218c (33.6%) (Fig. 35, 36) on the basis of its spectral similarity to 218a and 218b and analytical properties. The infrared spectrum showed absorptions at 3600 (strong, free OH), 3570-3200 (broad, H-bonded OH) 3060 (C=C-H), and 1050 cm^{-1} (C-O). The ^1H NMR spectrum showed a broad vinyl proton singlet at δ5.6, a doubled doublet at δ4.1 ($J_{1,6}$=4 Hz and $J_{6,5}$=7 Hz) for the methine

proton at C_6, a doublet at δ2.9 (J=4 Hz) for an allylic proton, a methyl singlet at δ2.03 and a multiplet (δ2.5 to 1.16) for the remaining 9 protons. Lanthanide induced shifts (LIS) for Me-, H_1, H_2 and H_6 of 218c are shown in Table V.

Table V. $Eu(fod)_3$ induced ^1H NMR shifts (LIS) for 218c (in ppm)

$[Eu(fod)_3]/[218c]$[a]	LIS(Δδ)			
	H1	H2	H6	-Me
0.07	0.43	0.00	0.56	0.29
0.22	0.87	0.12	1.40	0.67
0.37	1.66	0.40	2.81	1.29
0.51	3.30	0.86	--	2.62

[a]Measured in $CDCl_3$ solution.

When $[Eu(fod)_3]/[218c]$ was ~0.5, the LIS for the methyl group was 2.62, while that for H_2 was only 0.86. This relatively large methyl shift established the syn relationship between the methyl and hydroxyl groups. ^{13}C NMR showed two olefinic carbons at δ162.7 and δ121.5.

The major product, isolated by preparative TLC (R_f= 0.25, 44%), was a mixture of two isomeric adducts 219c in a ratio of 1:2.3 (^1H NMR). Thin layer chromatographic purification (20% ethereal hexane) of 219c gave one pure isomer (Fig. 37) (R_f=0.22).

The p-bromobenzoate derivatives of the two isomeric adducts, 219-c, were synthesized by reaction of the mixture with p-bromobenzoylchloride in pyridine at room temperature overnight. The two isomers were then isolated by preparative TLC (15% ethereal hexane). The structure of compound 219-1-e (Fig. 44) (R_f=0.83) was established via a single X-ray analysis (see Appendix). A singlet crystal of 219-1-e was obtained by slow evaporation (in the refrigerator) of a CH_2Cl_2/MeOH solution of 219-1-e to afford colorless plates (mp 200-201°C). The structure of 219-2-e (Fig. 45) was also established as the result of a single crystal X-ray analysis (see Appendix). Slow evaporation of a solution of 219-2-e in CH_2Cl_2/MeOH in the refrigerator afforded a colorless needles (mp 193.5-195°C). A dimer (19%) (Fig. 38) was also isolated by thin layer chromatography (vide infra).

Reaction of 192d with 10 equiv. of MeLi in the presence of 1.1 equiv. of DPIBF in ether at room temperature afforded two products in a 1:47 ratio. The minor product was purified by preparative TLC (80% ethereal hexane, R_f=0.47) and was identified as 218d (2%) (Fig. 35, 36) on the basis of its spectral similarity to 218a, 218b and 218c and its analytical properties.

The major product, isolated by preparative TLC (80% ethereal hexane, R_f=0.34, 94%) was a mixture of two isomeric

products, identified as 219-1-d and 219-2-d on the basis of observed spectral and analytical properties. The ratio of 218 to 219 from 192 are summarized in Table VI.

Table VI. Ratios[a] of 218 and 219 from Eq. 7.[b]

192	218	219
192a	1	1.8
192b	1	3.1
192c	1	1.8[c]
192d	1	47.0

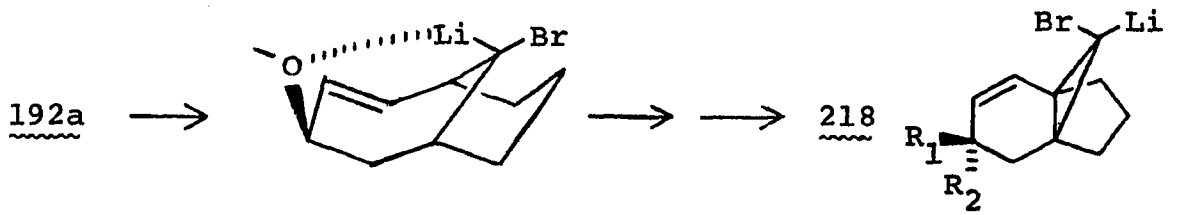
[a]For reactions run at room temperature to completion; ratios determined by ^{1}H NMR and/or GLC.

[b]10 Equiv. of MeLi and 1.1 equiv. of DPIBF were used, and less than 1% of 230 was observed by GLC for each reaction.

[c]Based on 219c + 2 x 303c.

The results in Table VI indicate that, in the initially formed carbenoid, the possibility of complexation of the Li^+ with the oxygen seems to facilitate formation of 218. This idea is illustrated by structure 221, which is an over-simplification of the aggregated Li species which really exists in solution. From the data in Table VI, it can be seen that complexation as in 221 is not an absolute necessity for formation of 218. The question is whether the epimeric

carbenoid, 222, can also yield 218, or is the reaction stereoselective. One might expect that due to the boat-like conformation of the right hand portion of 221 or 222, the bulky bromine atom would prefer to be on the left hand side (as in 222), in the absence of complexation. Thus 222 might pre-

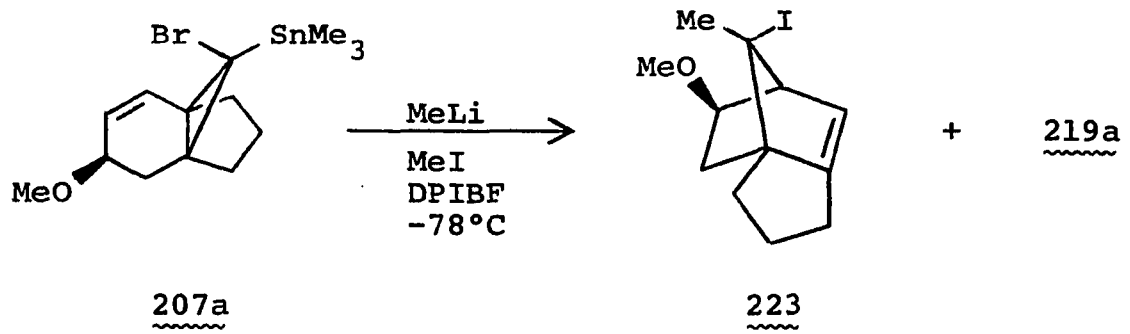


221 222

dominate at equilibrium (and these carbenoids equilibrate rapidly at even -78°C[127] for endo oxygen containing substituents). Then if 222 gave rise to 218, while 223 gave rise to 219, the predominance of 219 from 192b and 192d could be understood. In the case of 192d, 222d would be highly favored due to the negative charge on oxygen.

To gain some further insight into these questions, carbenoids 221 and 222 were generated stereospecifically.

Treatment of 207b with n-BuLi in THF and n-BuBr in the presence of DPIBF at -100°C afforded (an n-butyl containing) rearrangement product only (GC-mass spec and ^{1}H NMR). When 207b was treated with MeLi in MeI at -78°C products 223 (vide infra) and 219a resulted in a 3.8:1 ratio. When 207a was



207a 223

allowed to react in the same manner, the ratio of 223 to 219a was only 2.5:1. This indeed suggests that carbenoid 221 affords rearranged product, while carbenoid 222 gives the DPIBF adduct. At -78°C, however, equilibration of the carbenoids is competitive with further reaction.

Because either 218 or 219 could be formed via a process involving loss of Li^+ of Br^- or both, we decided to study the reaction under varying ionic conditions. To this end, 192a was treated with MeLi in ether in the presence of several different salts and 1.1 equiv. DPIBF. The results are shown in Table VII.

One sees that when the ionic strength of the medium is increased ($NaClO_4$, KI), the proportion of rearrangement (to 218) decreases at the expense of adduct (219). A decrease in solvent polarity, as when a large amount of MeI is added (*vide infra*), or when the temperature is lowered, has the expected opposite effect--more 218 is formed. Contrariwise, a specific, "common ion" effect is seen for Li^+ (LiI, $LiClO_4$),

Table VII. Yields[a] of 218a and 219a in the presence of various substances

Salt[b] or Crown Ether	% 218a	% 219a	Total Yield
None	34	62	96
LiI	48	56	104
$LiClO_4$	47	49	96
$NaClO_4$	29	62	91
KI	32	65	97
Et_4NBr	26	74	100
12-C-4 (10 equiv.)	3	72	75
12-C-4 (20 equiv.)	0	59	59

[a]For reactions run at room temperature to completion; yields determined by ^1H NMR and/or GLC.

[b]4 Equiv. salt were used each time, but dissolution was incomplete for the last 3 salts.

where addition of this ion to the medium results in more rearrangement to 218! However, Br^- (Et_4NBr) shows a normal salt effect. Thus the point of divergence in the formation of 218 vs. 219 involves loss of Li^+ (probably to at least a solvent separated ion pair stage) from carbon. Such loss then facilitates formation of adduct 219. If Li^+ is allowed

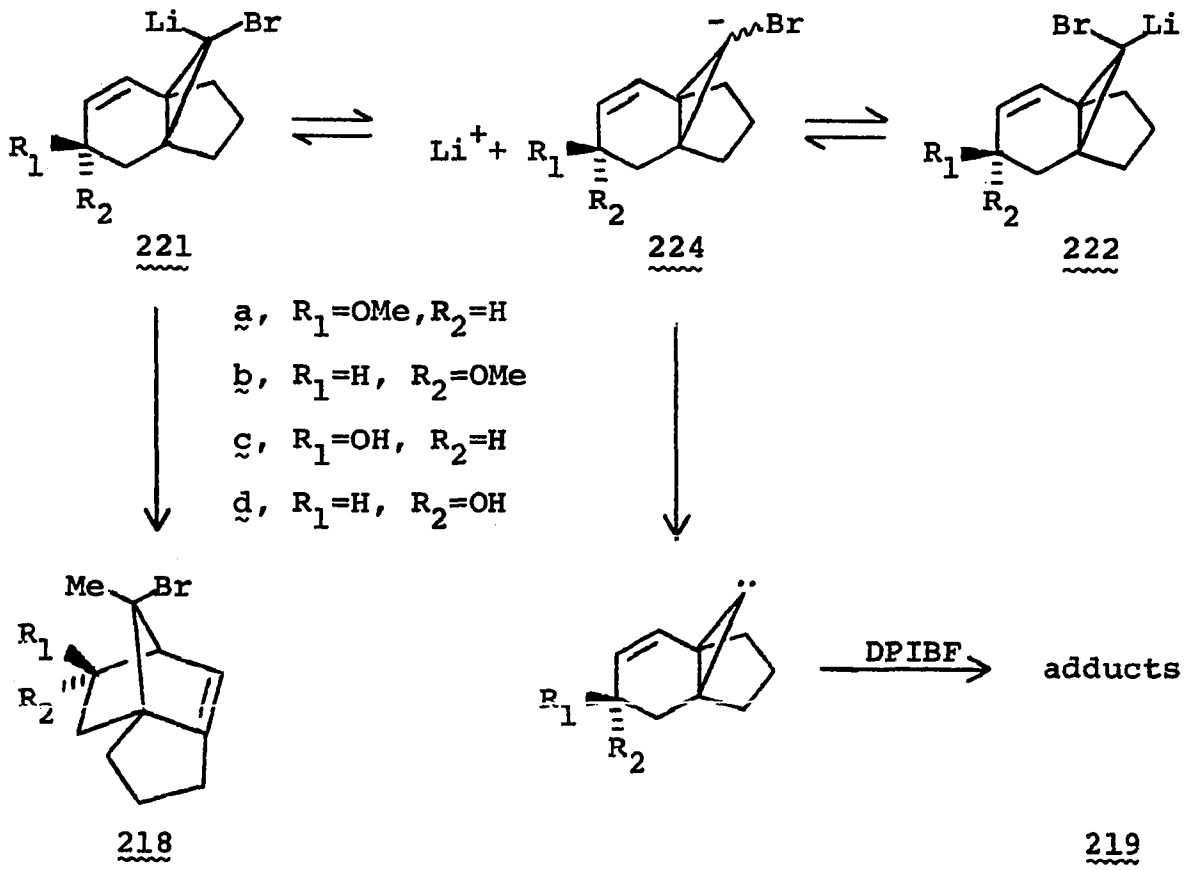
to remain attached to carbon, rearrangement product 218 results. Loss of Br^- must come either before or after the divergence point. (From studies of 9,9-dichloro[4.2.1]-propell-3-ene, we think the loss of Br^- occurs after the divergence point--vide infra).

The quantitative aspects of the Li^+ salt effect were studied for LiI (Table VIII, Figure 2). The leveling off of the [218a)/[219a] ratio is probably due to insolubility of the LiI. Interestingly, 192b also is subject to a Li^+ common ion effect, with the ratio of 218b to 219b increasing to 1:2 in the presence of 4 equiv. of LiI. All this suggests a mechanism such as shown in Scheme IV, where keeping the Li^+ on carbon (as in 221) leads to 218, while removing it (to 224), leads to 219. With respect to stereochemistry, 222, which doesn't give product directly, must pass through 224 (or something similar) to get to 221, whereby it has a better chance to go on to 219 (rather than 218).

Complete verification of the role of Li^+ was obtained through the use of 12-crown-4[129] (Aldrich). A large excess of 12-C-4 had to be used because 12-C-4 is competitively destroyed by MeLi. Nevertheless, in the presence of 12-C-4, rearrangement (to 218a) was completely suppressed, and adduct formation (219a) occurred exclusively. In a separate control experiment, 218a was treated with 8 equiv. of MeLi in the presence of 10 equiv. of 12-C-4 (with p-di-t-butyl-

benzene as an internal standard). Work up returned 218a quantitatively (^{1}H NMR), indicating the veracity of Scheme IV.

Scheme IV



With the role of the Li atom largely established, we turned to the question of whether or not both bromine atoms of of 192a were replaced during the formation of rearrangement product 218, since the Paquette mechanism[38a] suggested they

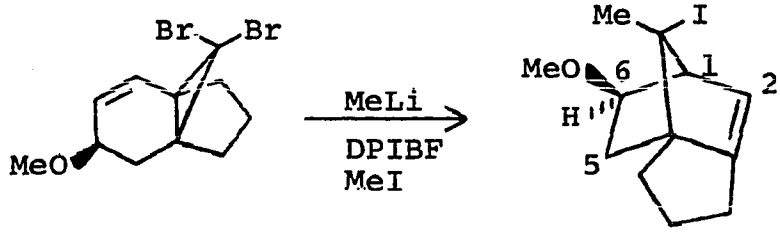
Table VIII. Yields[a] of 218a and 219a in the presence of various amounts of LiI

[LiI]/[192a]	218a	219a	218a/219a
none[b]	19.50	71.00	0.27
1.00	35.30	87.70	0.40
2.00	32.40	62.20	0.52
4.00	27.50	42.10	0.65
8.00	28.70	36.52	0.78
20.00	37.50	42.70	0.88

[a]Reactions were run at room temperature for 55 min simultaneously; 0.0016 M of 192a, 1 equiv. of DPIBF, 10 equiv. of MeLi (1.96 M) and 9 ml of ether were used; yields determined by GLC.

[b]Differences between these results and those reported in Table VII might be due to the use of a different bottle of MeLi, since the concentration of LiBr in MeLi (alfa) varies from bottle to bottle.

were not. Thus, the reaction was run in the presence of a huge excess of MeI (it was essentially the solvent). The products, from 16a, were 223 and 219a (in a 3:2 ratio), along with a minor amount of 218a. Thin layer chromatographic purification



192a 223

+ 219a + 218a (8)

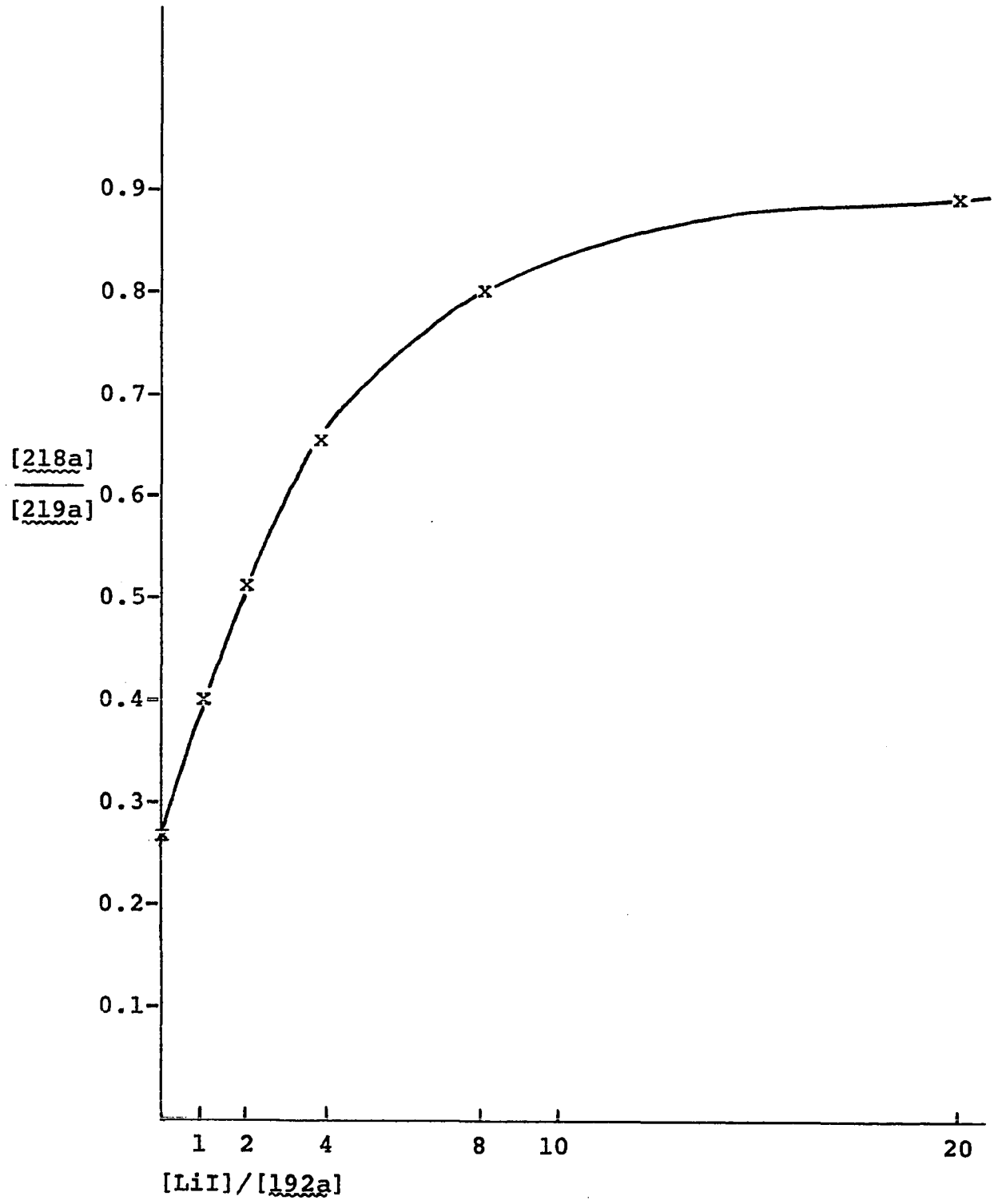


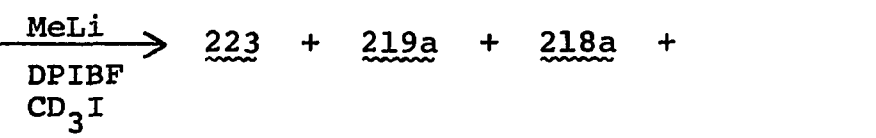
Figure 2. Plot of data in Table VIII

(3% ethereal hexane) gave 223 (Fig. 46) in 37% yield. The infrared spectrum showed C=C-H absorption at 3066 cm^{-1}, C=C absorption at 1650 cm^{-1}, and C-O-C absorption at 1110 cm^{-1}. The ^1H NMR spectrum showed a broad hump at δ5.5 for an olefinic proton, H_2, a doublet of doublets at δ3.66 (J=5 Hz, 6 Hz) for methine proton H_6, a methoxy singlet at δ3.30, a doublet at δ3.20 for allylic proton H_1, a methyl singlet at δ2.2, a doublet at δ1.61 for H_5, $H_{5'}$, and a multiplet (δ2.25-1.75) for the remaining 6 protons. Decoupling the doublet at δ1.61 (H_5, $H_{5'}$) collapsed the doublet of doublets at δ3.66 (H_6) to a singlet. Irradiating the doublet at δ3.20 (H_1) collapsed the broad hump at δ5.5 to a broad singlet. Lanthanide induced shift (LIS) studies for Me, and H_2 of 221 demonstrated the stereochemistry of the Me group (Table IX).

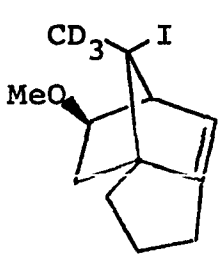
Table IX. $Eu(fod)_3$ Induced ^1H NMR shifts (LIS) for 221 (in ppm)

$[Eu(fod)_3]/[221]$	LIS(Δδ)				
	H_1	H_2	H_6	MeO-	Me-
0.10	0.13	0.04	0.20	0.16	0.09
0.20	0.20	0.05	0.30	0.23	0.15
0.30	0.26	0.10	0.42	0.33	0.20
0.40	0.31	0.10	0.45	0.38	0.23
0.50	0.35	0.11	0.56	0.44	0.27

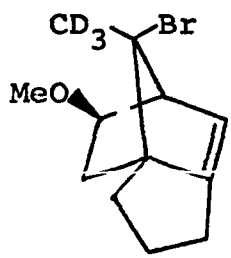
The fact that treatment of 218a with MeLi in the presence of excess MeI led to no 223, but rather quantitative recovery of 218a, confirms that indeed both bromines are lost during the conversion of 192 to 218, thereby invalidating the Paquette mechanism.[38a] Clearly the source of halide in 218 or 223 is an organic halide (since no 223 was formed when 192a was reacted in the presence of LiI). But what is the source of the methyl group in 218 and 223? In order to probe this question, CD_3I was used in place of CH_3I as cosolvent. The products were still primarily 223 and 219a. A detailed



(9)



223-d_3



218a-d_3

analysis of the mass spectral data for 218a and 223 (Table X) obtained from this reaction showed only 6.2% incorporation of CD_3 in 218a, and 7.7% in 223. Therefore, the source of the Me- group in compound 223 must be MeLi! The few percent of deuterated products probably arose from metal halogen exchange of CD_3I and MeLi to give CD_3Li:

$$CD_3I + CH_3Li \underset{}{\overset{\text{slow}}{\rightleftharpoons}} CH_3I + CD_3Li$$

$$\downarrow \text{ fast}$$

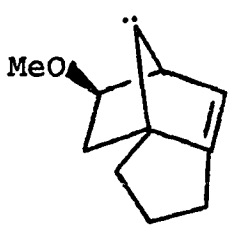
$$CD_3CH_3 + LiI$$

Table X. Mass spectral intensities for 221 and 218a derived from Eq. 9 at 70 eV (GLC-mass)

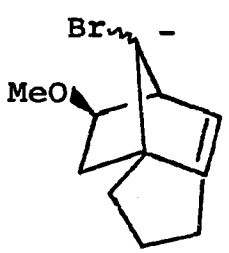
m/e	peak intensity		Formula of ions of interest
	221	218a	
180[a]	1434	126	$C_{12}H_{14}D_3O$
177	17088	1922	$C_{12}H_{17}O$

[a]This mass was not observed in the case of Eq. 8.

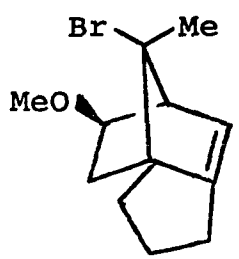
These results indicate that insertion of a rearranged norbornenylidene, 225, into MeX is eliminated since the Me



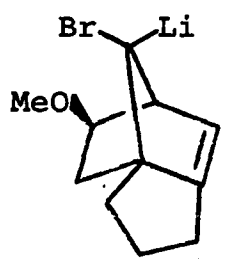
225



226



227

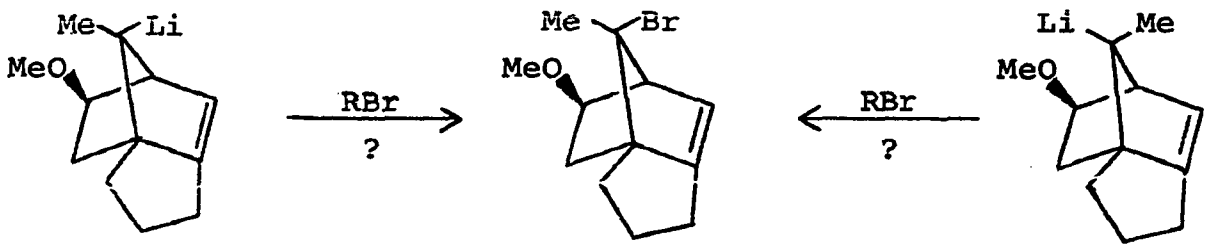


228

group doesn't come from MeX. Similarly excluded is an S_N2 displacement by 226 on MeX (the Paquette mechanism). Also,

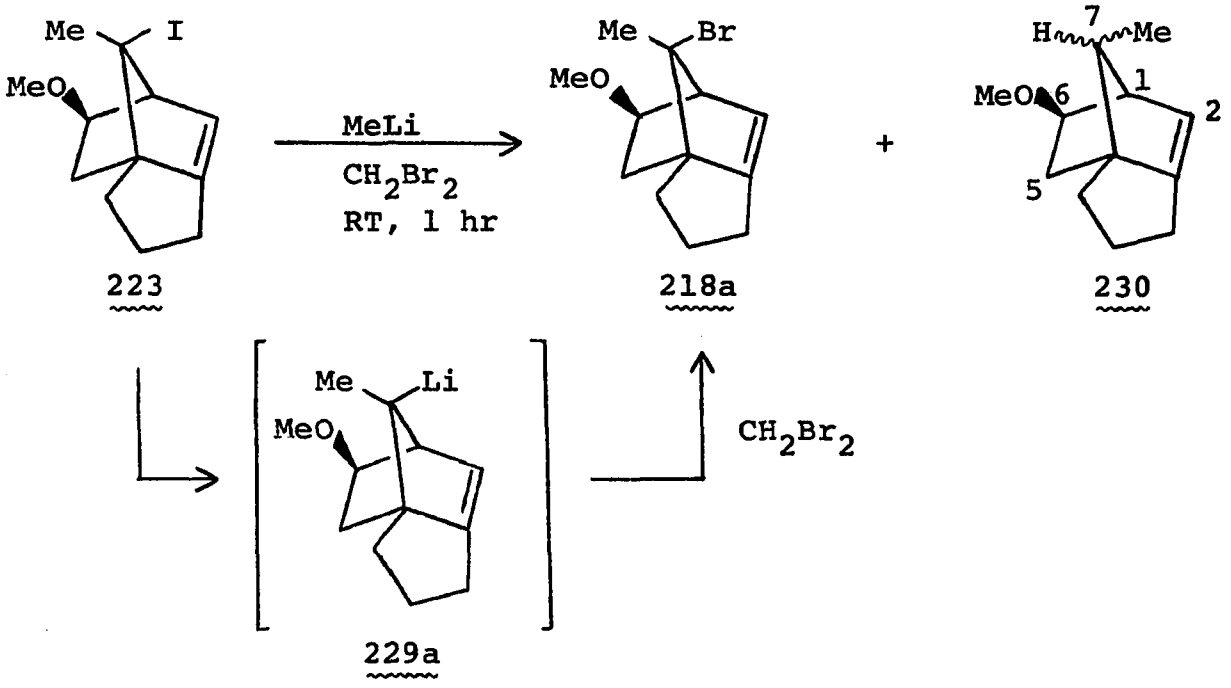
if carbenoids such as 221a or 228 undergo halogen exchange, it is meaningless in terms of product formation, since no 223 is formed in the presence of I^- (e.g., LiI).

From the previous results, it is apparent that 218a must be formed from either 229a or 229b (or both). Since retention of stereochemistry is the generally observed pattern for metal-halogen interchanges, 229a must be considered the more likely source of 218a. We found that reaction of 223 with MeLi in CH_2Br_2 at room temperature gave 218a, together with reduced product 230. Thus 223 is converted to 218a with overall retention, most likely via 229a.



229a 218a 229b

Thin layer chromagraphic purification (4% ethereal hexane, developed twice, R_f=0.29) gave pure 230 (Fig. 47), identified on the basis of its spectral and analytical properties. The infrared spectrum showed C=C-H absorption at 3070 cm^{-1}, C=C absorption at 1650 cm^{-1} and C-O absorption



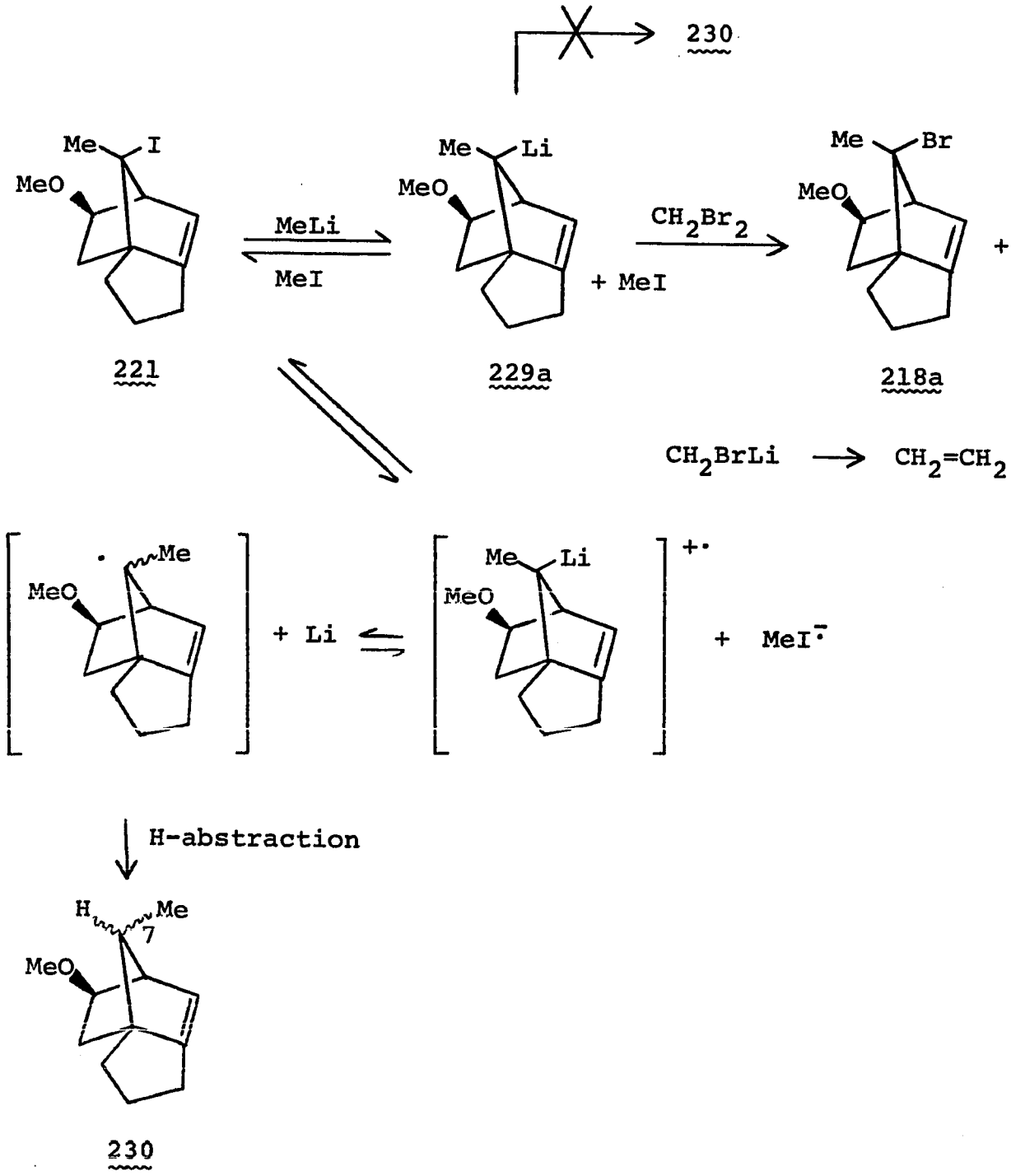
223 218a 230

229a

at 1105 cm^{-1}. The ^1H NMR spectrum showed a multiplet (δ5.25 to 5.08) for the olefinic proton, a broad doublet at δ3.39 for the methine proton at C_6, a methoxy singlet at δ3.23, a multiplet (δ2.75 to 2.6) in the allylic proton, a doublet at δ0.8 for the methyl group at C_7 (J=7 Hz), and a multiplet (δ2.4 to 0.9) for the remaining 9 protons. Reduction product 230 presumably arises via deomposition of 229a, most likely via electron transfer (Scheme V). Certainly 230 does not result from protonation of 229a work up.

The stereochemistry of 230 at C_7 is not clear, but Lanthanide induced shift (LIS) studies for Me, and H_2 of

Scheme V


230
Me
I
MeO
MeLi
MeI
Me
Li
MeO
+ MeI
CH_2Br_2
Me
Br
MeO
+
221
229a
218a
CH_2BrLi
$CH_2=CH_2$
Me
MeO
+ Li
Me
Li
MeO
+·
+ $MeI^{-\cdot}$
H-abstraction
H
Me
7
MeO
230

230 seem to support the idea that the methyl group at C_7 is syn to the double bond (Table X).

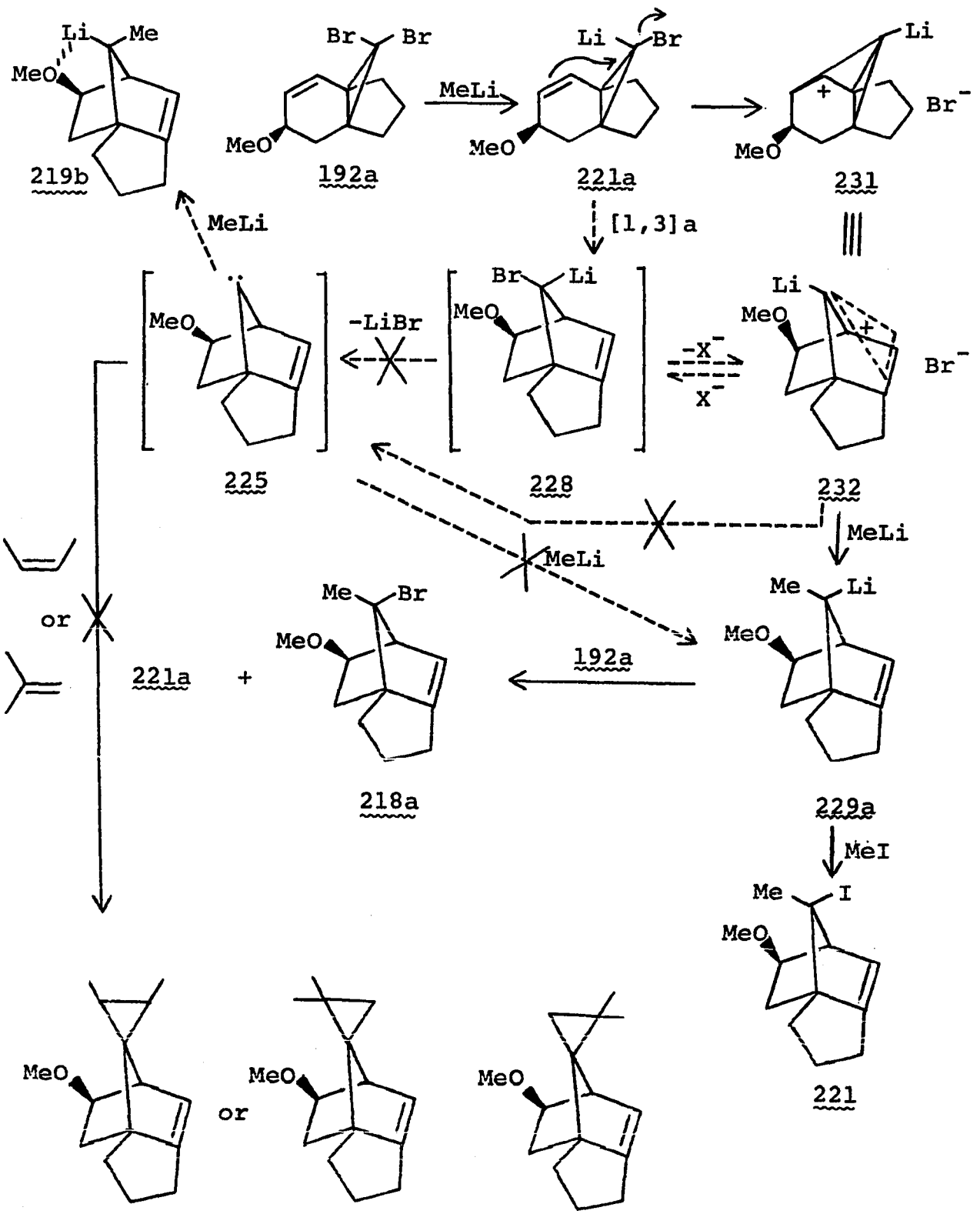
Table XI. $Eu(fod)_3$ Induced ^1H NMR shifts (LIS) for 230 (in ppm).

$[Eu(fod)_3]/[230]$	LIS ($\Delta\delta$)				
	H_1	H_2	H_6	MeO-	Me-
0.1	0.64	0.20	0.77	0.76	0.13
0.2	1.17	0.37	1.37	1.33	0.22
0.3	1.49	0.47	1.82	1.77	0.30
0.4	1.84	0.52	2.19	2.13	0.37
0.5	2.08	0.67	2.45	2.46	0.45

A mechanism[130] which accounts for the stereochemistry of 218a and 223, as well as the other facts, is illustrated in Scheme VI.

Thus, 192a exchanges with MeLi to give, in part, carbenoid 221a. A [1,3] antarafacial sigmatropic shift to directly yield 228 would seem to have no driving force, whereas nucleophilic attack at the backside of the "Li-loosened" C-Br bond of 221a seems reasonable and is a precedented[46] type of reaction. This would provide 231, which can be written as a nonclassical ion, 232. Such a

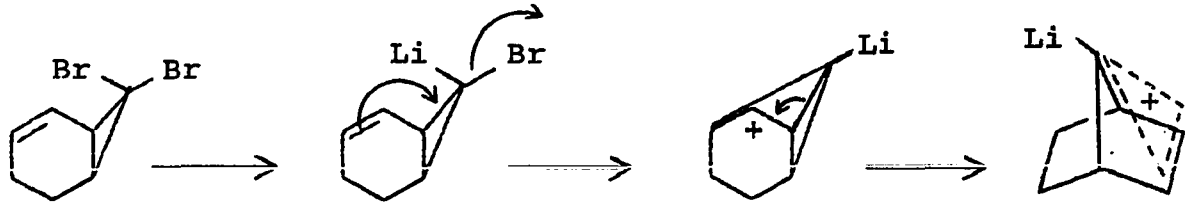
Scheme VI


Li
Me
MeO
219b
Br
Br
MeO
192a
MeLi
Li
Br
MeO
221a
Li
+
Br⁻
MeO
231
MeLi
[1,3]a
MeO
-LiBr
Br
Li
MeO
-X⁻
X⁻
Li
MeO
+
Br⁻
225
228
232
MeLi
MeLi
or
221a
+
Me
Br
MeO
218a
192a
Me
Li
MeO
229a
MeI
Me
I
MeO
221
MeO
or
MeO
MeO

norbornenyl cation should be attacked[131] by the nucleophile, MeLi, from the anti side to give 229a. Reaction of 229a with a good halogen source (e.g., 192a[12]), gives the product.

We consider the intervention of 225 unlikely. In the first place, we could not trap 225 when the reaction was carried out in 2-butene or isobutylene, in contrast to similar successful trapping of 7-norbornenylidene.[40] Additionally, we would expect 225 to insert into MeLi to give primarily 229b (oxygen complexation), which we feel (vide supra) is not involved in the reaction pathway.

Therefore, in the bicyclic case, the Skattebol rearrangement can be reinterpreted as follows:

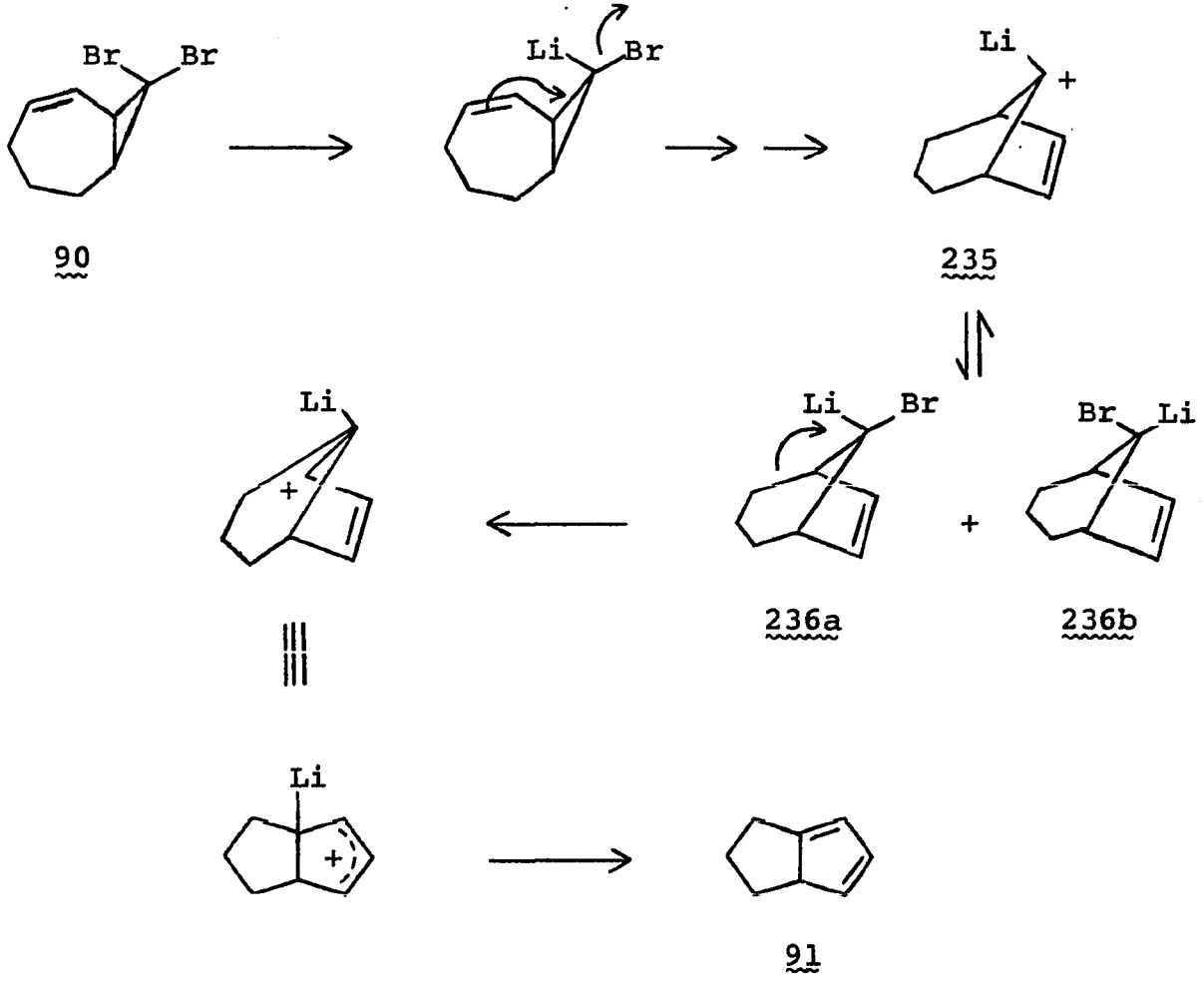


10 233 234

234 → 10 → 11

It can be seen that carbenoid 233 should be preferred over its epimer for steric grounds, thereby facilitating the rearrangement.

In the case of 8,8-dibromobicyclo[5.1.0]oct-2-ene (90)[39], carbonium ion 235 has less nonclassicity than norbornenyl cation 234. This allows internal return to the epimeric carbenoid 236a[40], which can undergo ionization-rearrangement to lead to diene 91.

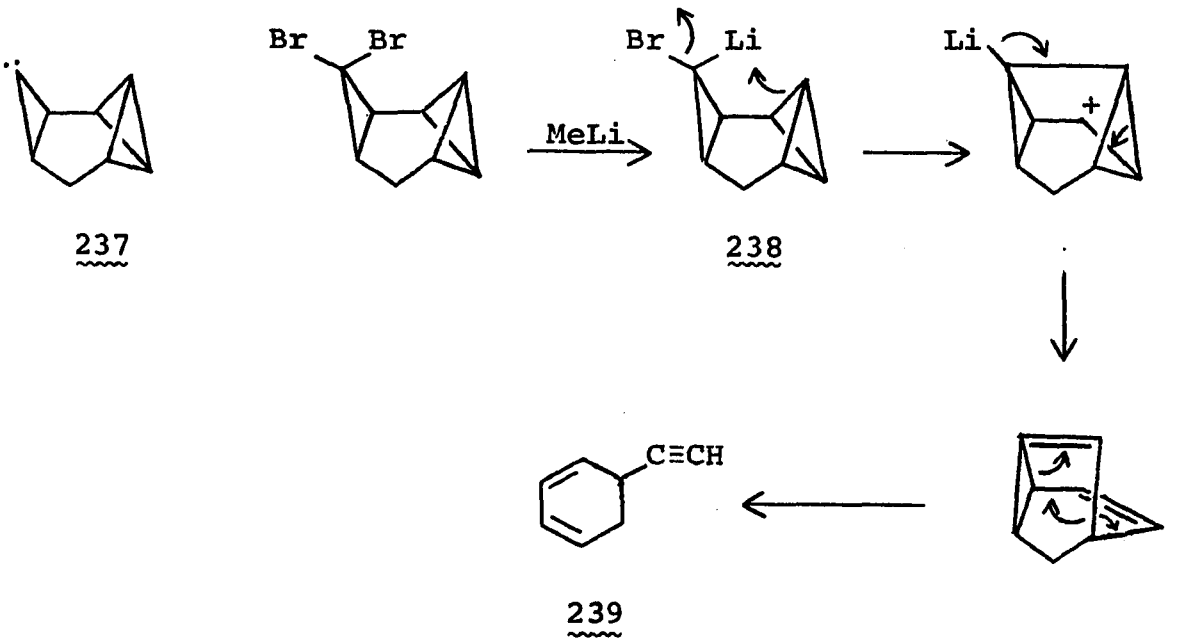


90 235 236a 236b

91

Paquette[38b] envisioned the formation of 239 via the free carbene 237. Our results indicate that a carbenoid 238 is

involved, where Li^+ is syn to the bicyclobutane ring (sterically favored); rearrangement as shown would afford 239.

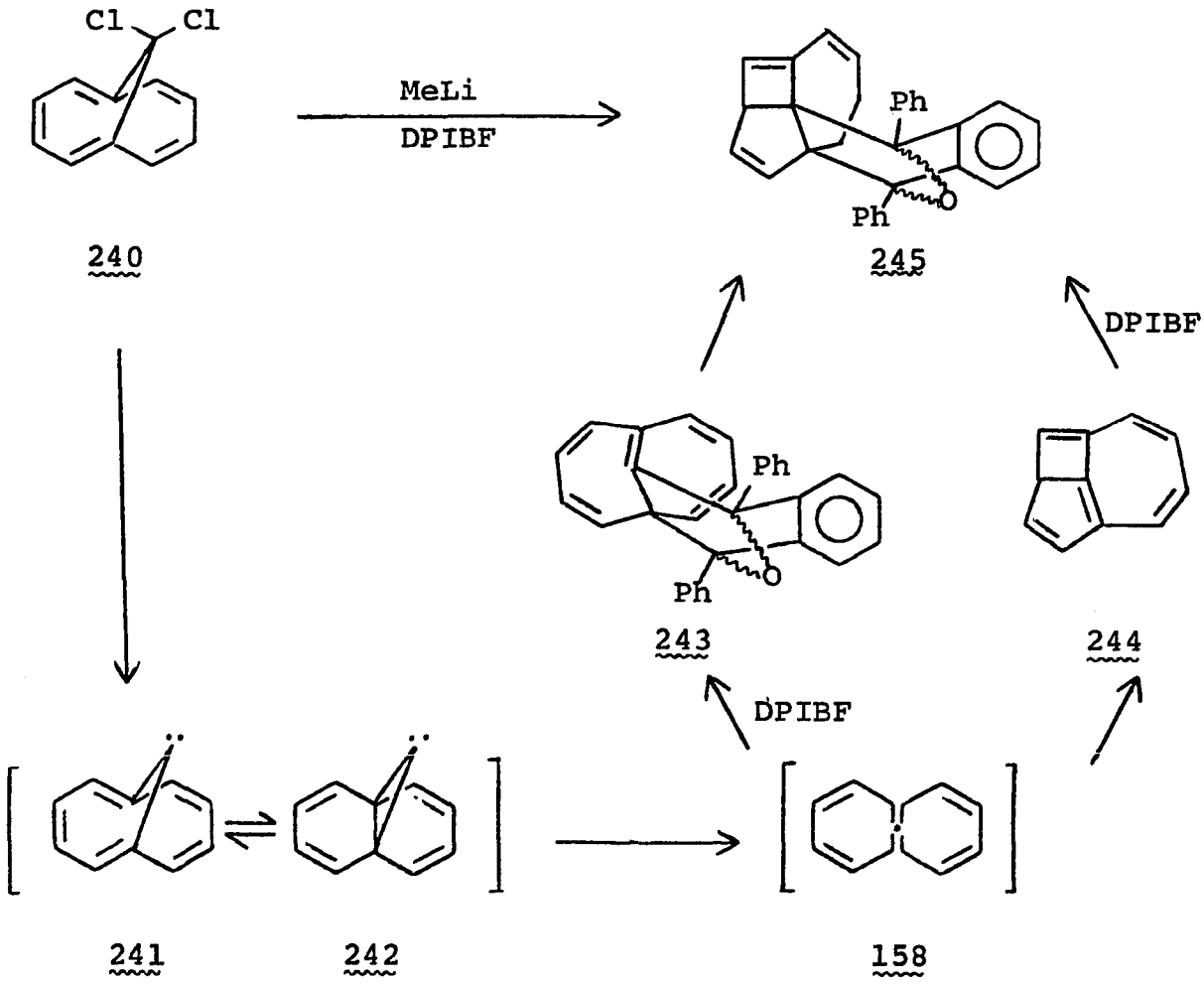


237 238 239

On the Question of Allene Formation
from Tricyclic Cyclopropylidenes

Carlton, et al.,[82] reported that reaction of 240 with MeLi affords dimer(s) of unknown structure(s); in the presence of DPIBF, two Diels-Alder adducts 245 were obtained. The authors suggested that this reaction involved allene intermediate 158. The mechanism (Scheme VII) they proposed involves conversion of 240 to a carbene or carbenoid which they drew as 241 ⇄ 242. Either of these species could be envisioned to transform to the allene 158. In the former

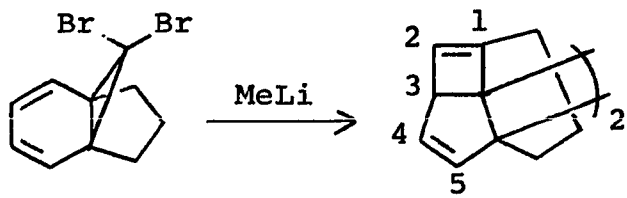
Scheme VII



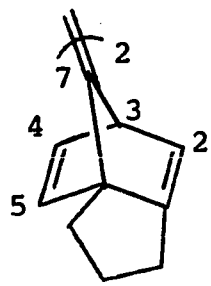
case, it would require a reorganization of the cyclohepta-trienylidene-cycloheptatetraene type, while in the latter case (242), it would be of the cyclopropylidene-allene type. That the former is not viable is shown by our results for 191. Once 158 is formed, two reaction pathways were suggested. The first (less likely) involved Diels-Alder trapping with DPIBF to give 243 followed by (disallowed

disrotatory) ring closure to give the product 245. The kinetically more likely route involved (allowed) electrocyclization of 158 to give 244, followed by DPIBF trapping to afford the product, 245.

We wondered whether the two extra double bonds of 240 were necessary for the observed reaction. To this end, we decided to investigate possible allene formation from 191, with the added incentive of generating a more strained allene than from 240 (i.e., 191 has one less carbon atom than 240). Treatment of 191 with MeLi in ether at -78°C or



191 246a

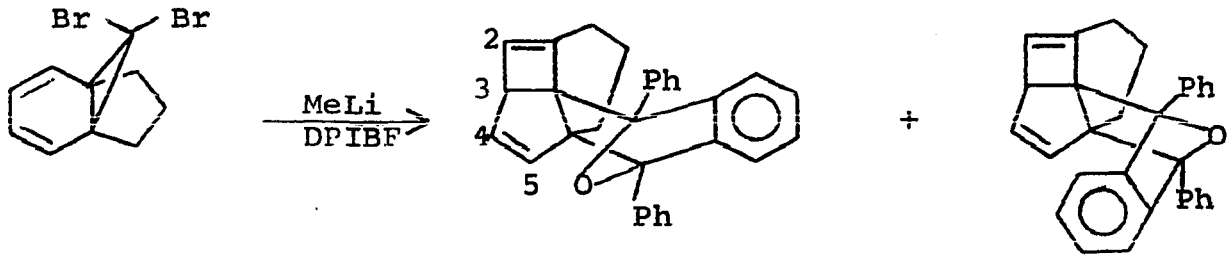


246b

room temperature gave one isolable dimer, 246 (Fig. 50), which was purified by GLC (column A, 22%) to give an air sensitive white solid (stable in ether in a degassed sealed tube for 2 months at -10°C, but decomposed when opened to air within 2 hr at room temperature) with a mp 155-157°C. The structure of 246 is unknown, but it is thought to be either a [2 + 2]-type dimer (246a) due to the observation of 4

olefinic peaks in the ^{13}C NMR spectrum or a norbornadiene type dimer (246b) due to the observation of only 9 peaks in the ^{13}C NMR spectrum where the missing peak is in the olefinic region presumably. The high resolution mass spectrum of 246 gave an exact mass at m/e 259.1485 for a molecular formula of $C_{20}H_{19}$ (P-1, parent ion was unmeasureable because the P-1 peak intensity was 10% stronger than the parent peak; calcd. for $C_{20}H_{19}$: m/e 259.1485. The ^{1}H NMR spectrum revealed a doublet of doublets at δ6.13 ($J_{4,5}$=5 Hz, $J_{4,3}$=2 Hz) for the proton at C_4, a broad singlet at δ5.86 for the proton at C_2, a doublet at δ5.32 ($J_{5,4}$=5 Hz) for the proton at C_5, a multiplet at δ3.55 for the proton at C_3, and a multiplet (δ2.45 to 1.08) for the remaining 12 protons. Decoupling the doublet of doublets at δ6.13 (H_4) collapsed the doublet at δ5.32 (H_5) to a singlet, while decoupling the doublet at δ5.32 (H_5) expectedly collapsed the doublet of doublets at δ6.13 (H_3) to a doublet (J=5 Hz).

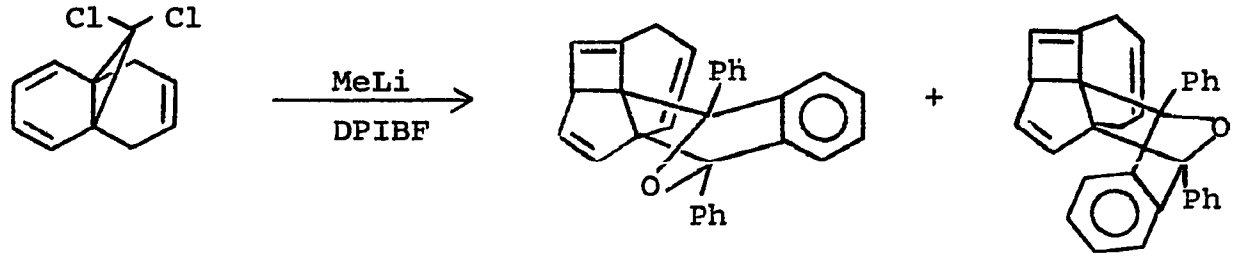
Reaction of 191 with MeLi/Et_2O in the presence of DPIBF provided two adducts in a 2:1 ratio (24%). The structures



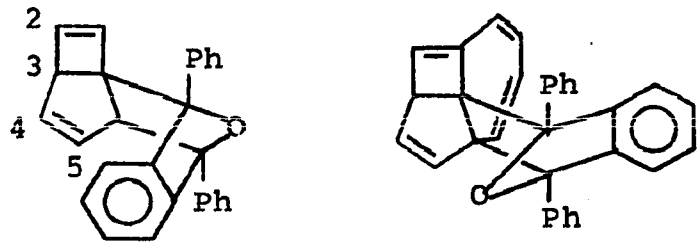
191 247-1 (247-2) 247-2 (247-1)

of 247 were assigned based on their close spectral resemblance to 245, 249 and 250 (Table XI). Thin layer chromatographic purification (15:85 CH_2Cl_2/hexane) gave 247-1 (Fig. 48, R_f=0.52) in 8% yield (by GLC), mp 155-157°C. The second isomer, 247-2 (Fig. 49), was also isolated by TLC (R_f=0.44, 16% by GC), mp 207-209°C (d).

The similar reactions of 240 and 191 indicate that only one diene moiety (viz., in 242 or 158) is necessary to effect the observed molecular reorganizations. This is also demonstrated by Carlton and Levin's[83] study of the reaction of 248 with MeLi, from which compounds 249-1 and 249-2 were isolated (Table XII).



248 249-1 249-2



250 245-1

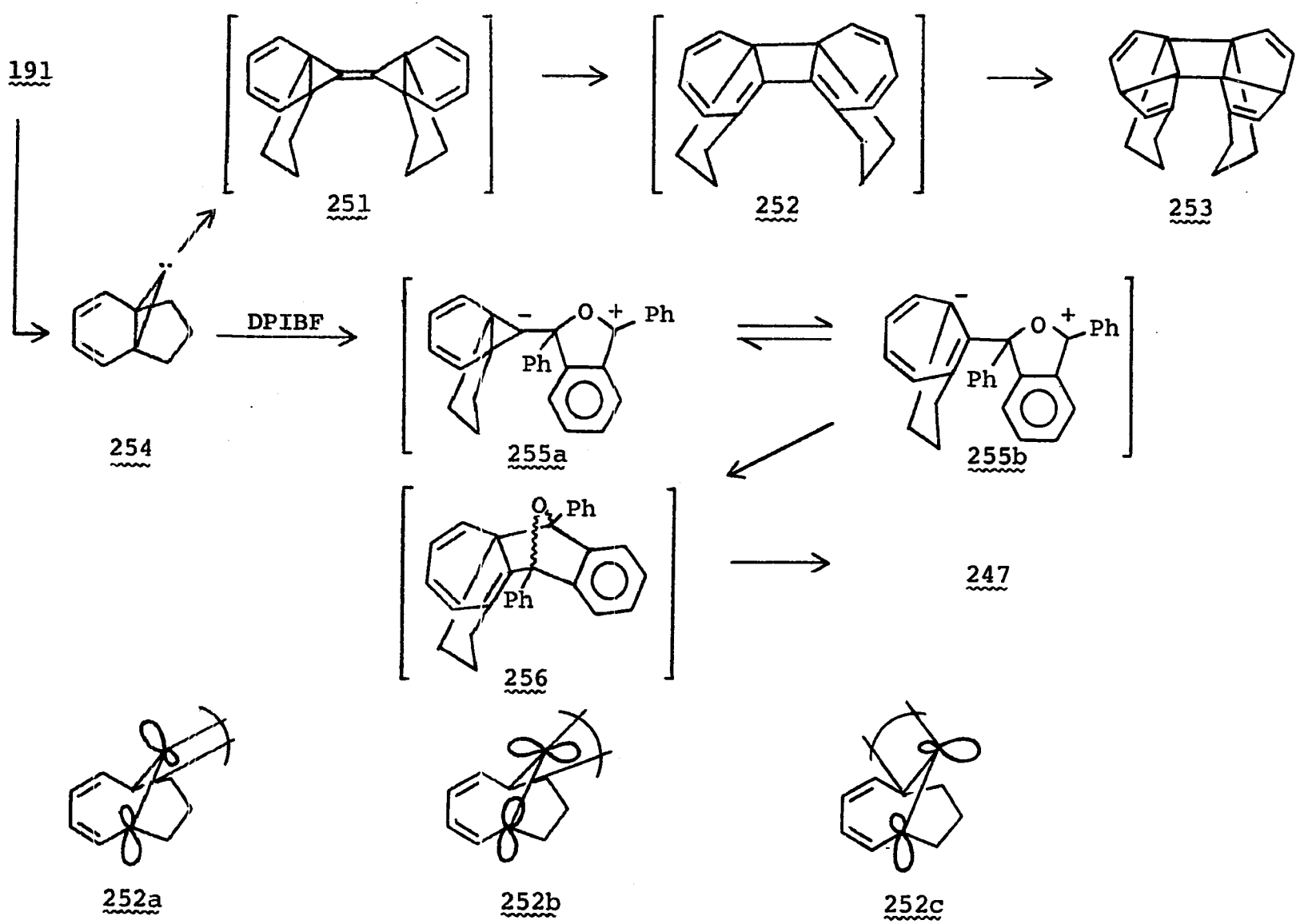
Table XII. ^{1}H NMR Data for DPIBF adducts[a]

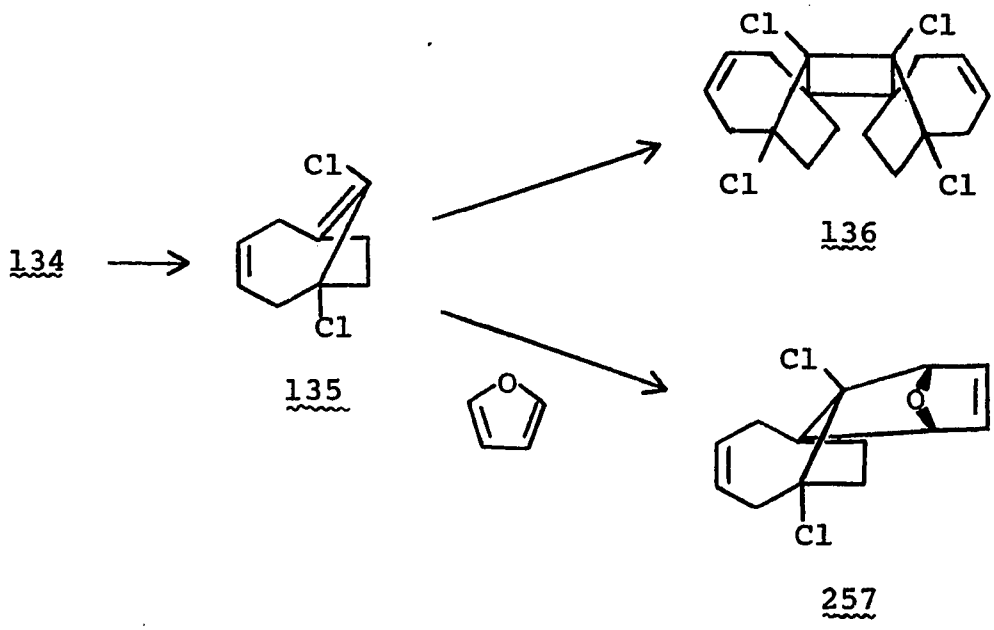
	245-1[82]	249-1[83]	249-2[83]	250[133]	247-1[134] (247-2)	247-2[134] (247-1)
H_2	6.38(br,s)	5.87(br,s)	5.72(d, J=3.0 Hz)	6.24,6.05 (ABq-2H)	5.84(br,s)	5.90(s)
H_3	J=2.4 Hz, 2.4 Hz)	3.07(br,s)	3.14(dd, J=3.0 Hz, 3.0 Hz)	3.27 (quintet)	2.97(br,s)	3.00(br,s)
H_4	6.04 (dd, J=2.4,5.9 Hz)	5.56(dd, J=2.5,5.9 Hz)	5.31(dd, J=3.0, 6.0 Hz)	5.53(dd)	5.64(br,s, H-4,H-5)	5.65(dd, J=3.0 Hz)
H_5	5.32(d, J=5.9 Hz)	5.18(d, J= 5.9 Hz)	5.65(d, J=6.0 Hz)	5.76(dt)	5.64(br,s)	5.05(d, J=3.0 Hz)

[a] CCl_4 was used as solvent for 247-1 and 247-2, the othes using $CDCl_3$ as solvent.

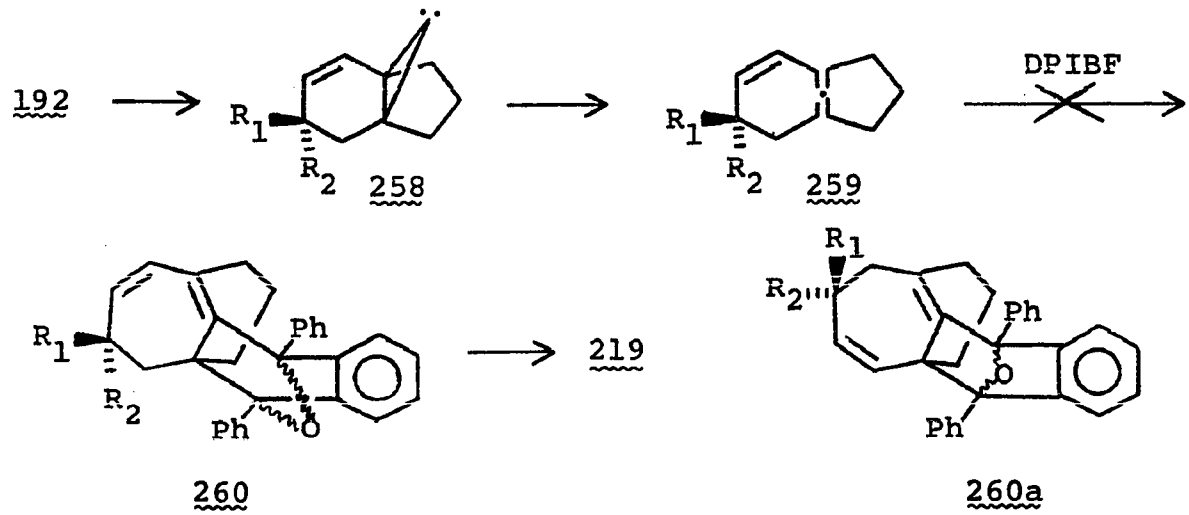
Some new mechanistic deductions can now be made. First of all, the possibility that dimer formation occurs via a carbene dimer must be considered (e.g., 251 → 252 → 253), because in a related case[135] such a possibility was not readily excludable. However, after a detailed look at the structure of the bridgehead double bonds of 252 and 256 (derived from closure of 255b), the possibility that dimer formation occurs via a carbene dimer and that trapping proceeds by way of zwitterion 255 (Scheme VIII) can be ruled out. The three possible orbital orientations of the bridgehead double bond of 252 depicted by 252a-c are as follows: 252b represents the unrehybridized[136], nearly perpendicular olefin structure, not found in any bridgehead olefins[65b]; 252b is particularly poor due to the extra bond angle strain imposed by the cyclobutane ring. Contrariwise, 252a represents the rehybridized form which contains a trans-cyclohexene moiety.[64,135] Compound 252c depicts the more stable trans-cycloheptenoid isomer. However, 252c is incapable of internal cyclization without substantial atomic movement and overlap loss in the transition state (i.e., it must pass through something like 252a); were it to be formed, it would probably dimerize or be trapped[68] (as, for example, is 135, Scheme IX). Obviously, the same arguments mitigate against the pathway involving 243, since the analogous intermediate 256 has apparently been excluded.

Scheme VIII



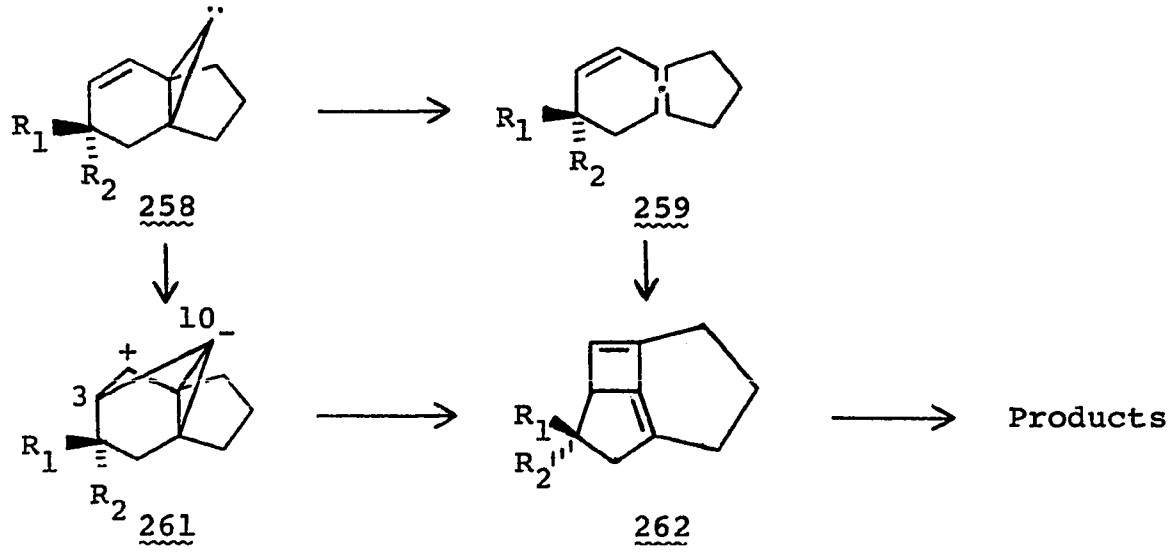


Even with one more double bond removed (192), the same reaction mode was observed (Eq. 7). Thus in order to obtain the "Levin-type" products, only one double bond next to the cyclopropane ring is necessary. Now, a stronger argument exists against any mechanism yielding 260, for it would be necessary to form 260 while excluding 260a:

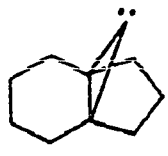


What likely pathways are left for the formation of 247 and 219? Most viable are the allene mechanism, and the zwitterionic mechanism, in which C_3, C_{10} bond formation is initiated first via electrophilic attack by the carbene on the π bond (Scheme X).

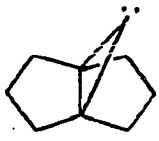
Scheme X



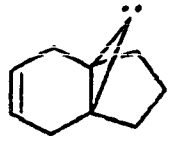
In order to check for allene formation from simple, unconjugated tricyclic cyclopropylidenes, we reinvestigated 263 and 265, as well as the previously uninvestigated 264.



263



264

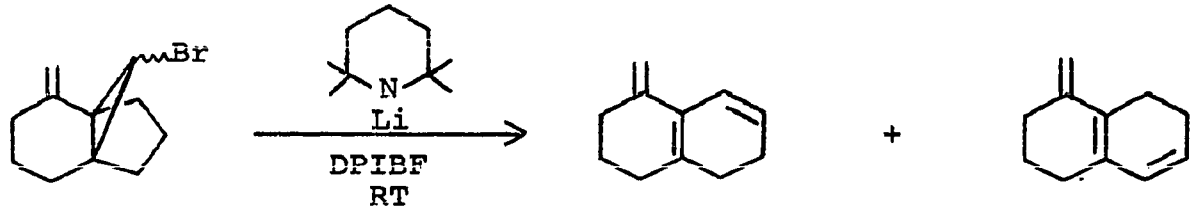


265

The dibromo precursor of these carbenes, 137, 14, and 15 were treated with MeLi in the presence of DPIBF. None of them gave any evidence for the formation of allene-type products, in as much as no DPIBF trapping products were observed. The mainly intramolecular C-H insertion products will be described later.

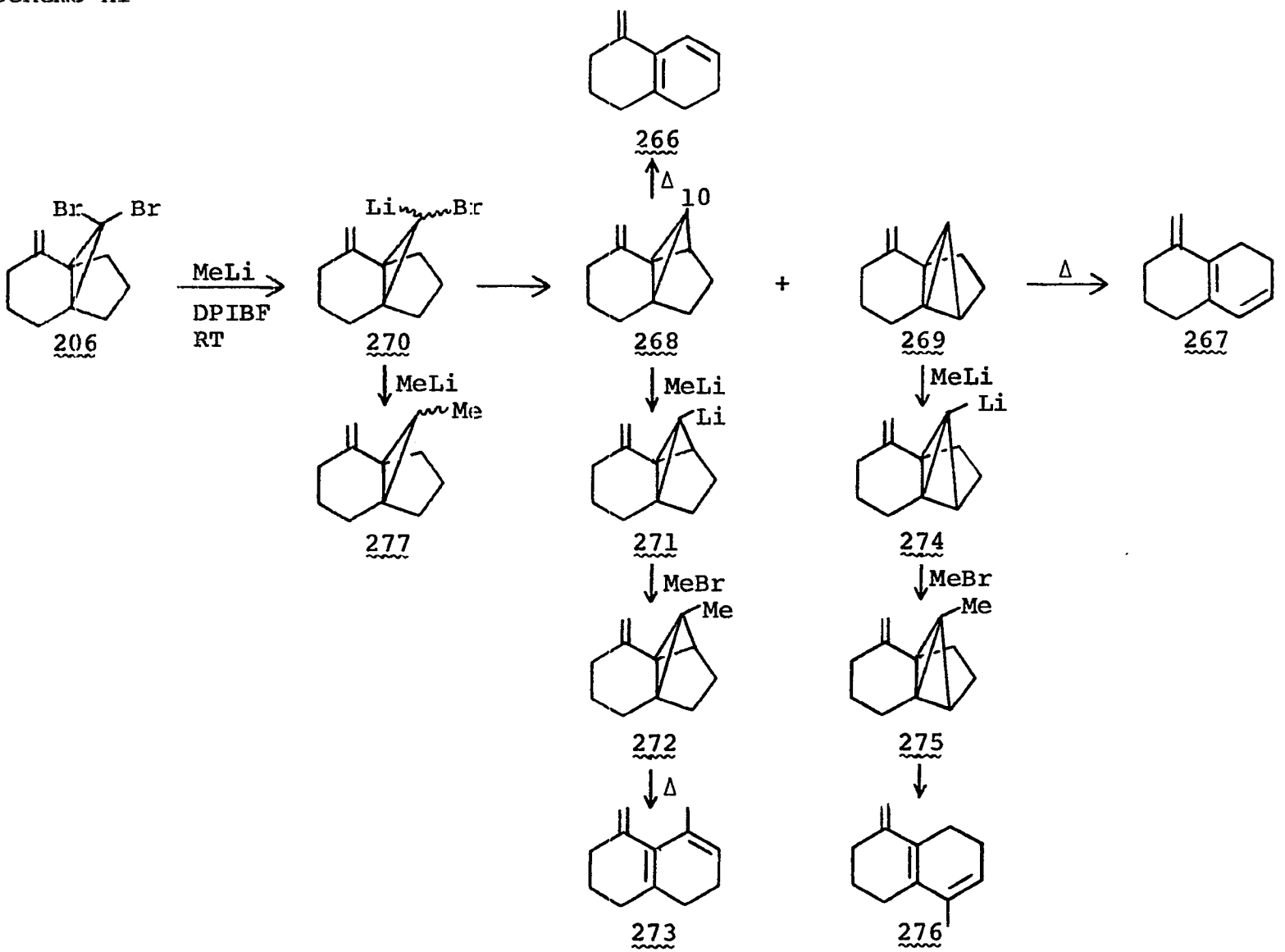
The lack of allenic products is not surprising, since no carbocyclic 7-norcaranylidene has ever been found to afford allenic products. Therefore, Levin's claim that allenes are involved in the chemistry of 240 was quite daring. If an allene were involved in the rearrangements, its formation would require the special conjugative effect of a double bond next to the cyclopropane ring. As a test of this hypothesis, we investigated the chemistry of the exocyclic methylene compounds, 204 and 206.

When the monobromide 204 was treated with harpoon base[137] (lithium tetramethylpiperidide) in the presence of DPIBF, no trapping product was observed, but rather only products derived from intramolecular C-H insertion were found by GLC-mass analysis (column C).



204 266 267

Scheme XI


Br
Br
206
MeLi
DPIBF
RT
Li
Br
270
MeLi
Me
277
266
Δ
10
268
MeLi
Li
271
MeBr
Me
272
Δ
273
+
269
MeLi
Li
274
MeBr
Me
275
276
Δ
267

Treatment of 206 with MeLi in the presence of DPIBF at room temperature gave intramolecular and intermolecular insertion products, but no trapping products, as revealed by GLC-mass studies. Since none of the products from either 204 or 206 were isolated, the structural assignments were based on precedent[11a] and can only be said to be reasonable. The proposed reaction pathways are shown in Scheme XI.

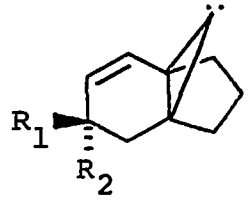
Molecular models suggest that insertion occurs in the 5-membered ring because the interatomic distance is the shortest (cf. Paquette's paper[11c]). Thus, the two insertion products 268 and 269 might be expected to rearrange to 266 and 267, respectively, in the GLC column.

Since the bicyclobutane proton at C_{10} is rather acidic, it can react further with another mole of MeLi to give 271 and 274, which can in turn attack MeBr to give 272 and 275, each of which can undergo ring cleavage to afford 273 and 276, respectively.

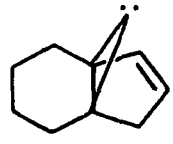
The reduced product, 277, may be formed by several different pathways, but no attempt has been made to elucidate the correct one.

We thus conclude that allene formation does not result from the conjugative aid of a neighboring double bond. Rather, a direct (through space) interaction of the carbenic center with the olefinic center is apparently required to

ultimately effect ring opening. Before returning to the question of allene formation from 258, we ask whether a double bond oriented as in 278 would be effective in promoting ring opening.

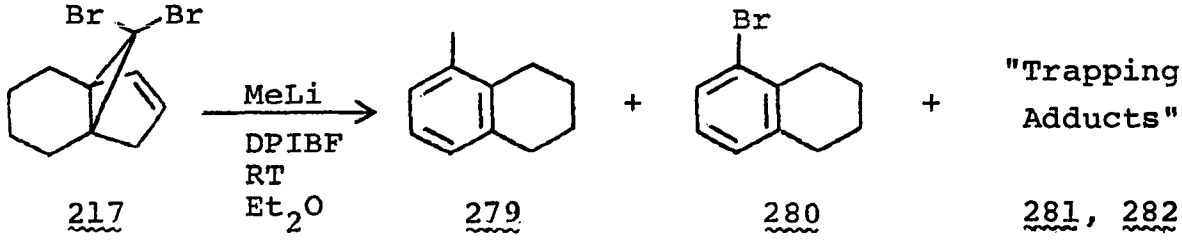


258



278

Treatment of compound 217 with ethereal MeLi in the presence of DPIBF at room temperature afforded upon workup,



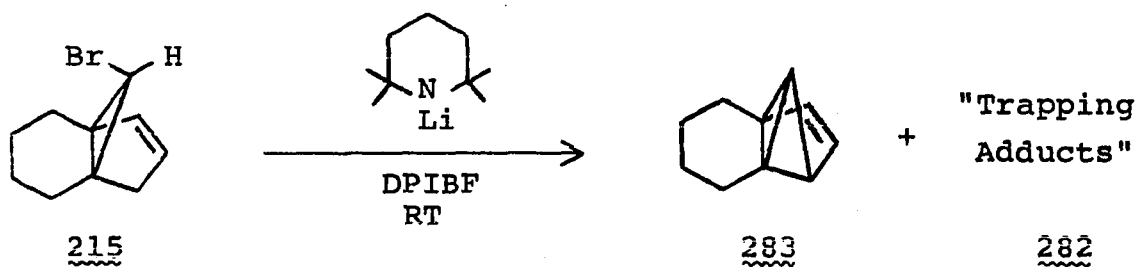
217 279 280 281, 282

a yellow ethereal solution which turned dark after concentration. GLC-mass studies of the black residue gave results consistent with the presence of 279 and 280 in a ratio of ca. 3:1 (uncorrected ratio). A very small amount of DPIBF adduct, 281 (parent ion at m/e 402) was also present; this corresponds to 278 plus DPIBF. There were also two isomeric products with

base peaks at m/e 384 (283). Since these two products have longer retention times that the adduct with mass at m/e 402, the parent ions have probably not been observed (column C, where the separation is based on bp, was used). So far no structures have been elucidated for these products.

When the same reaction was carried out in the absence of DPIBF, a black residue was also obtained after work up (solution turned dark after concentration). Thin layer chromatographic purification (hexane) afforded compound 279 (Fig. 51), as deduced from infrared ^{1}H NMR and GLC-mass studies. The infrared spectrum showed a C=C-H absorption at 3050 and 3000 cm^{-1}; ^{1}H NMR showed a broad singlet at δ6.76, a multiplet from δ2.9 to 2.5 with a maximum at 2.67, a singlet at δ2.22 and a multiplet from δ2.12 to 1.1 with two maxima at δ1.76 and 1.25.

When compound 215 was treated with harpoon base[137] in the presence of DPIBF at room temperature, an insertion



215 283 282

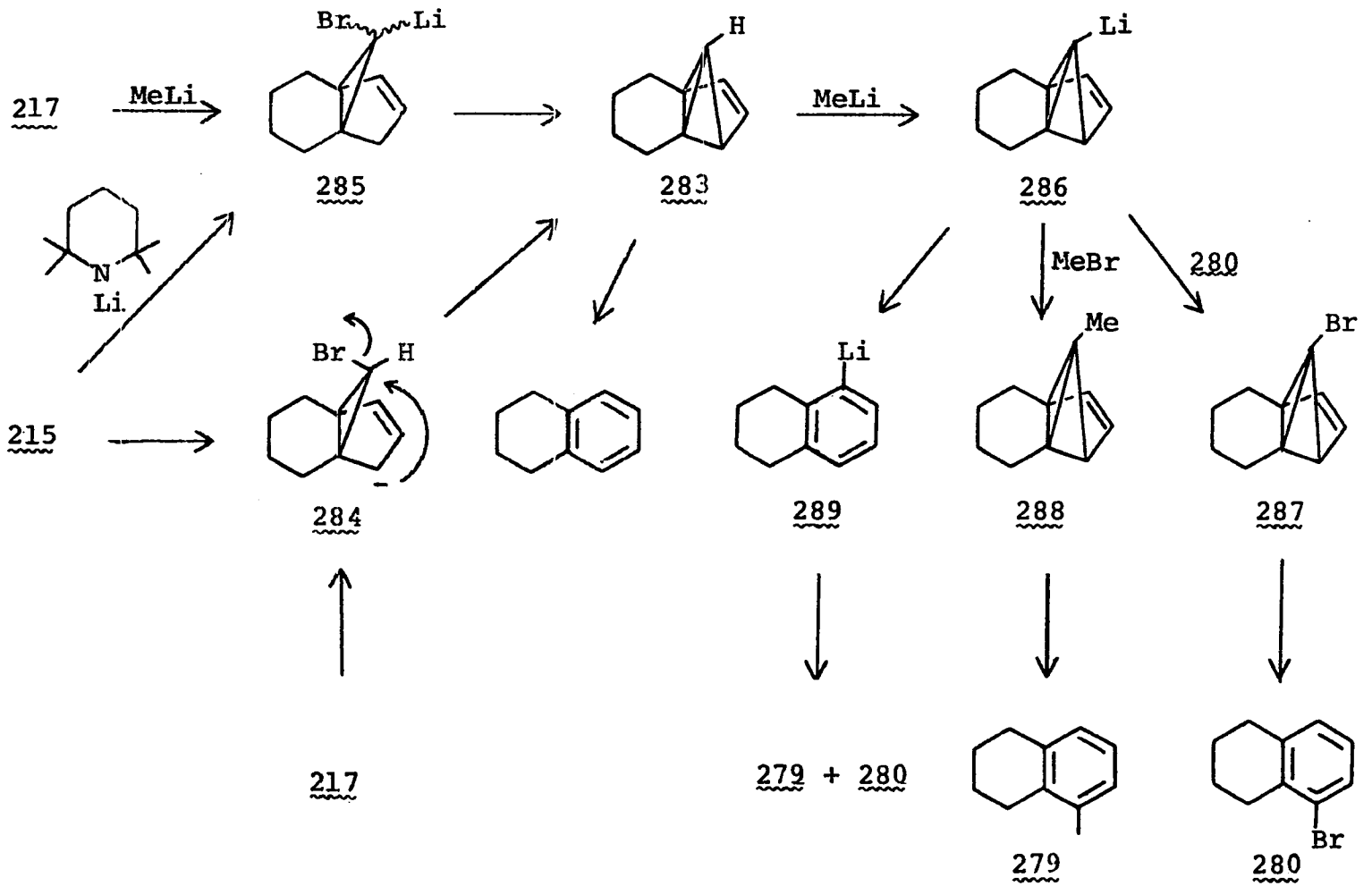
product, possibly 283, and 282 were observed by GLC-mass studies. Thin layer chromatography (7% ethereal hexane) gave

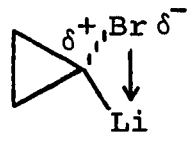
compound 282 (R_f=0.7). The ^1H NMR showed a multiplet from δ7.44 to 7.07 with two maxima at δ7.5 and 7.45, a singlet at δ6.95, a multiplet from δ3.08 to 2.58, a multiplet from δ2.08 to 1.56, a multiplet from δ1.4 to 1.05, and another multiplet from δ1.05 to 0.7. Compound 283 was not isolated; it could have decomposed on the TLC plate. Possible mechanisms for the formation of 279, 280, and 283 are illustrated in Scheme XII. The nature of 282 remains unknown.

Compound 217 might react with MeLi to give a carbenoid 285 which would then suffer intramolecular C-H insertion to afford 283 (insertion into the most proximal bond). Compound 283 could rearrange on a GLC column to give tetralin. If the acidic proton at C_{10} reacted with another mole of MeLi to give the alkyllithium 286, subsequent reaction could involve halogen-metal exchange to give 287, nucleophilic substitution to afford 288, or ring opening to 289. Both 287 and 288 would undergo rearrangement to lead to products 280 and 279 respectively, while 289 could lead to 279 and 280. In the case of the harpoon base initiated reaction of 215, the absence of a reactive dibromide (e.g., 217) or MeBr mitigated against the formation of exchange product 280 or methylated product 279.

Recently, Siegel et al.[138] has reported the ^{13}C NMR spectra of two CBr_3Li species in solution. Both species show

Scheme XII

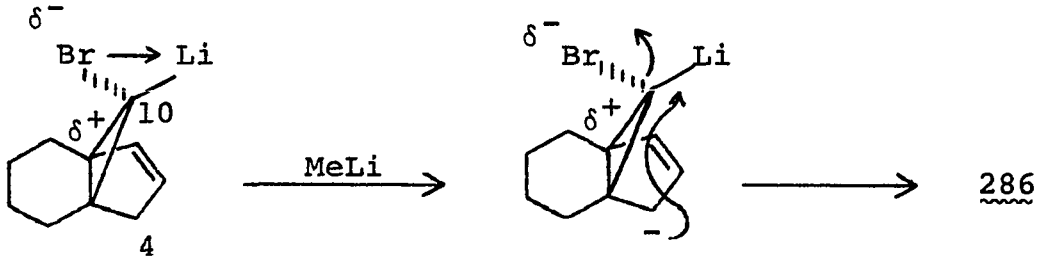

217
MeLi
Br
Li
285
H
283
MeLi
Li
286
MeBr
280
N
Li
215
Br
H
284
Li
289
Me
288
Br
287
217
279 + 280
279
Br
280



290

very large ^{7}Li-^{13}C coupling constants, which supports structure 290. Extrapolation from Schleyer's calculated (4-31G) results results on CF_3Li[139] and CCl_3Li[140] suggests that a species corresponding to 290 might be the most stable form of CBr_3Li.

Scheme XIII

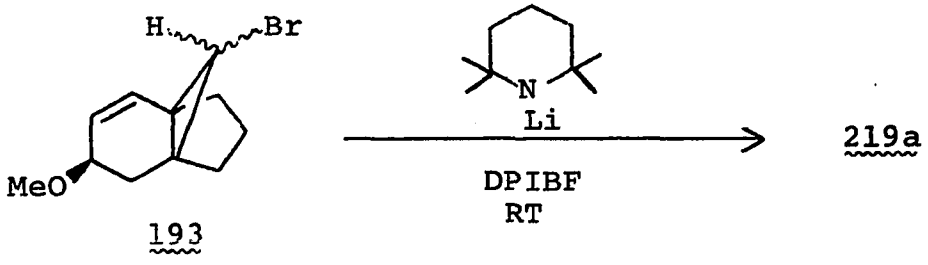


285 291

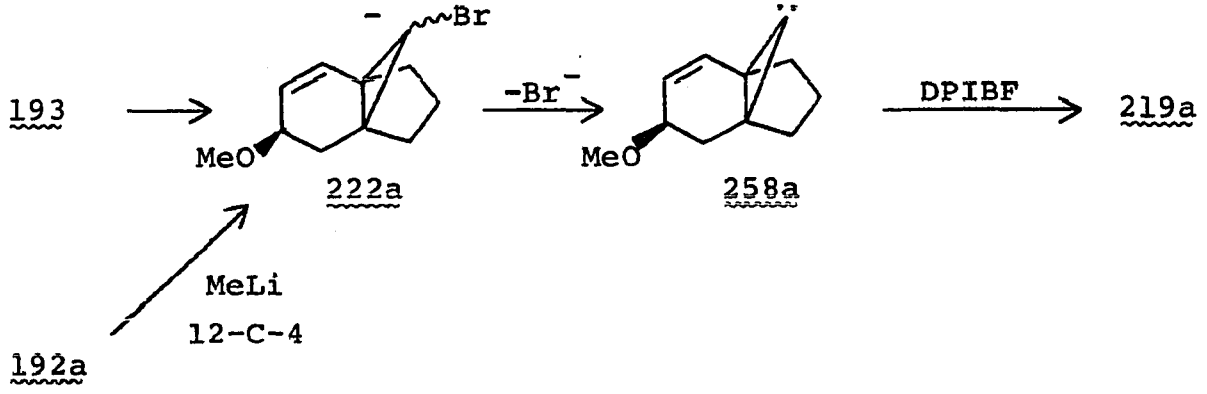
Therefore, an alternative mechanism for the formation of 286 is illustrated in Scheme XIII. The cyclopentene moiety in 285 can be considered as a homocyclopentadiene, where the protons at C_4 are rather acidic. Reaction of 285 with another mole of MeLi would afford anion 291, which could intramolecularly give 286.

No conclusions can be drawn regarding allene formation from tricyclic cyclopropylidene 278, since the structure(s) of adducts 283 are unknown. Further investigation of 283 and 282 needs to be pursued.

We thus return to the question of allene formation from 258. In addition to the aforementioned results, treatment of 193 with harpoon base in the presence of DPIBF at room temperature only the DPIBF adducts, 219a, were identified. This parallels the chemistry observed when MeLi was

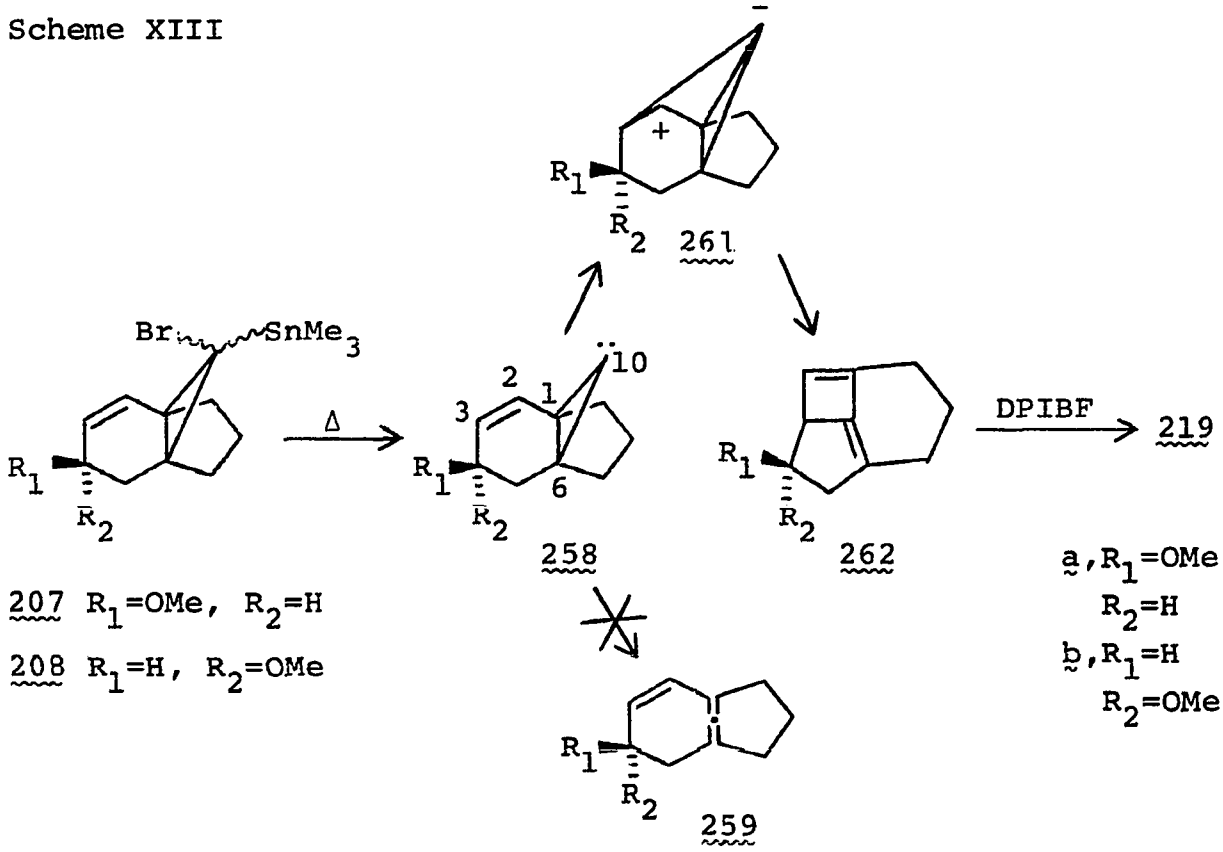


reacted with 192. The results with 12-C-4 require that 219a be formed via at least an α-bromoanion, 222a, but whether or not 258a subsequently intervenes is unknown. To further



investigate this point, we sought an alternate route to 219a, where 258a would be a logical intermediate, but where 222a would be excluded. To this end, the pyrolytic decomposition[141] of 207 and 208, which would supposedly generate carbene 258, was studied. Both 207 and 208 were pyrolyzed in sealed tubes in Ph_2O at 250°C for 1 min in the presence of 1.1 equiv. DPIBF (ca. 0.1M). The products were 219a and

Scheme XIII



207 R_1=OMe, R_2=H

208 R_1=H, R_2=OMe

a, R_1=OMe, R_2=H

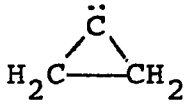
b, R_1=H, R_2=OMe

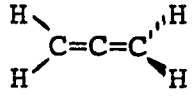
219b, respectively, without any detectable crossover (GLC, column D, and ^1H NMR analysis).

Similar reaction of 207 in benzene (150°C, $t_{1/2}$=100') also produced only 219, even under high dilution conditions where the [207] and [DPIBF] were 0.002M, and the rate of loss of 207 remained constant. Assuming we could have observed 219b only if it constituted as much as 5-10% of the product mixture, the minimum energy difference between that required for DPIBF trapping and epimerization at C_4 is ca. 8 kcal/mole. This stereospecificity precludes the intermediacy of a standard[6b] linear planar allene (259) in the formation of 219 (or, presumably, 245 or 247). If an "allene" were formed, it would have to be puckered, out of the rough plane of the 9-membered ring, whereby two diastereotopically distinct products could result. However, reaction via the zwitterionic intermediate 261, which is favored theoretically[34], seems consistent with the results (Scheme XIII), although there may be some 1,6-bond breaking in 258 on the way to 261 (or 262). This mechanism seems all the more compelling when one realizes that tetrasubstituted cyclopropylidenes generally insert into neighboring C-H bonds, rather than ring open to allenes. Here we are proposing precedence of a process ca. an order of magnitude more rapid than C-H insertion, namely C=C addition.

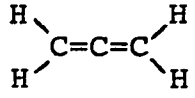
While a linear planar allene (259) has been excluded as an intermediate, partial C_1-C_6 bond breaking prior to C_3-C_{10}

bonding has not. If this actually occurs, one has a partial "allene", which leads us to inquire as to the structural requirements for the appelation "allene". Boder et al.[35] used MINDO/2 calculations to study the rearrangement of cyclopropylidene to allene. According to his calculations, the normal twisted form 292 is the more stable form only when

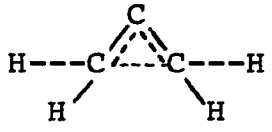




292

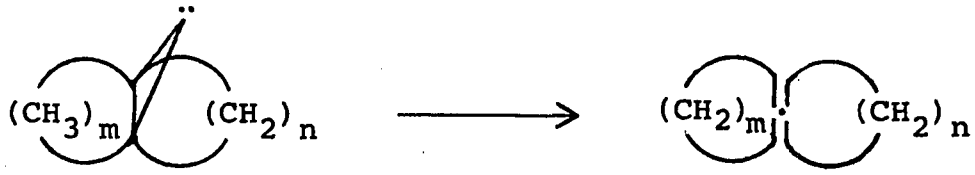


293



294

the C-C-C bond angle is greater than that in 294; ring opening in 294, therefore, leads in effect to untwisted linear planar allene 293. Rotation to form the normal twisted allene takes place only after the transition state is passed, i.e., when the ring opening is effectively complete. More recent calculations[95] also suggest the ring opening of cyclopropylidene to orthogonal allene involves a linear planar allene (Fig. 1). However, a carbene such as 258 cannot form a standard orthogonal allene due to the ring constraint. If the ring opening of 258 must be nonrotatory, then the calculations[95] predict a very high energy barrier.

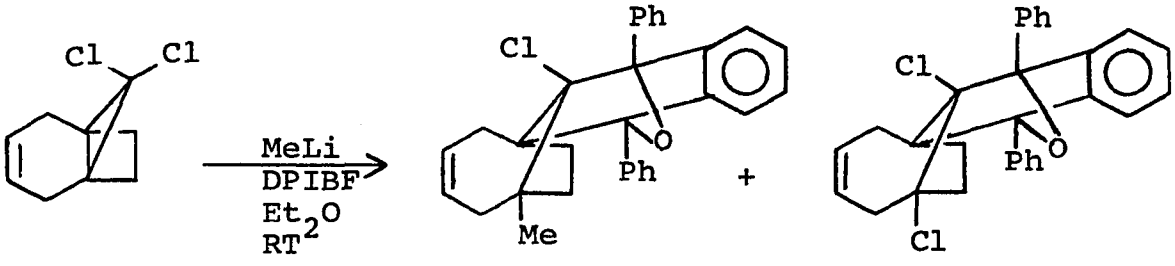


295 296

Thus, in order to generate an allene via the 295 → 296 route, one must either have large m and/or n or small enough m and/or n to make strain relief in the ring opening a significant driving force. Therefore, it would be appropriate to study the carbene generated from 134, as this should be an excellent system for small ring allene generation because of the maximal strain release obtained from the ring opening of a bicyclopentane moiety.

265 297 298 299

Treatment of compound 134 with MeLi in the presence of DPIBF at room temperature afforded compound 300 and 301 (Et_2O, 16 hr; when reaction was run in pentane for 1 hr at RT ca. 90% of starting material was recovered). Thin layer chromatographic purification (20% ethereal hexane) gave 300



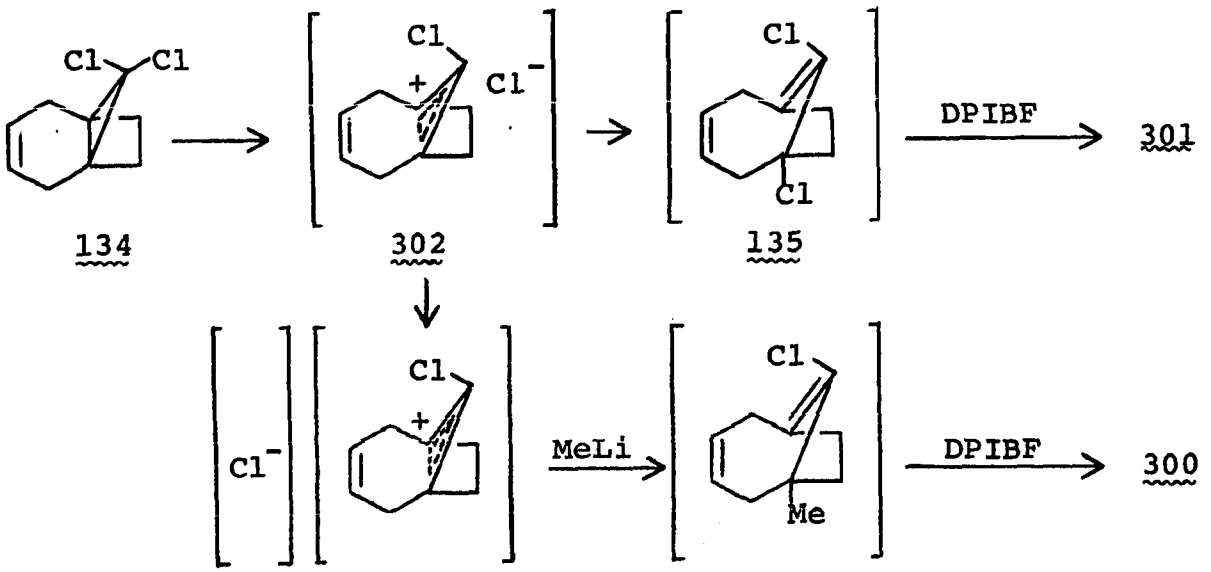
134 300 301

13% 11%

(R_f=0.93, 13%). Recrystallization of 300 (Fig. 52) from CH_2Cl_2/MeOH afforded colorless crystals (mp 195-196°C). The structure of 300 was confirmed by X-ray analysis (see Appendix). Compound 301 (Fig. 53, R_f=0.85, 11%) was isolated and recrystallization of 301 from CH_2Cl_2/MeOH also afforded colorless crystals (mp 183-184.5°C). The structure of 301 was also confirmed by X-ray analysis (see Appendix). Unfortunately, neither 300 nor 301 appear to result from carbenes or carbenoids. Rather, both are readily seen as solvolysis products (Scheme XIV), where an intimate ion pair (302) may collapse with chloride to give 135 (which is trapped), or dissociate to (at least) a solvent-separated ion pair which can be trapped by the nucleophilic MeLi and then by DPIBF. This pathway is supported by the relatively slow reaction at room temperature, and is consistent with the previously observed solvolytic chemistry of 134.[68,142] Since

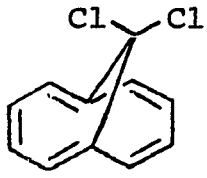
the dibromide corresponding to 134 is unavailable, carbenoid chemistry might be obtainable via reaction of 134 with a more reactive alkyl lithium. In fact, 134 reacts rapidly with n-BuLi at -78°C (after 3 hr, only trace of 134 was observed by GLC analysis), which is indicative of a carbenoid, rather than a solvolytic, process. This latter reaction will be pursued in the future, in the hope that evidence for 299 may be obtained.

Scheme XIV

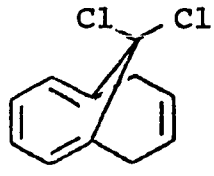


On the Dimerization of Bridgehead Olefins From Tricyclic Cyclopropylidenes

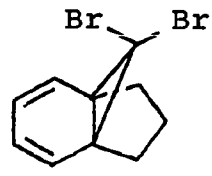
Recently, Carlton et al.[82] and Carlton and Levin[83] have reported the formation of dimer(s) from the treatment of 240 and 248 with MeLi, but he was not able to isolate and characterize them. Interestingly, treatment of 191 with MeLi affords only one dimer[134], which ^{13}C NMR indicates to be either a [2 + 2]type dimer (246a) or a norbornadiene type dimer (246b) (vide supra). However, no detailed structural information regarding any of these dimers has been obtained. A study of dimerization from the related system 192 was therefore undertaken.



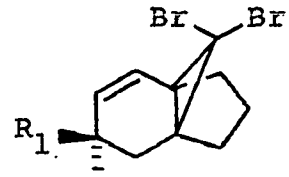
240



248



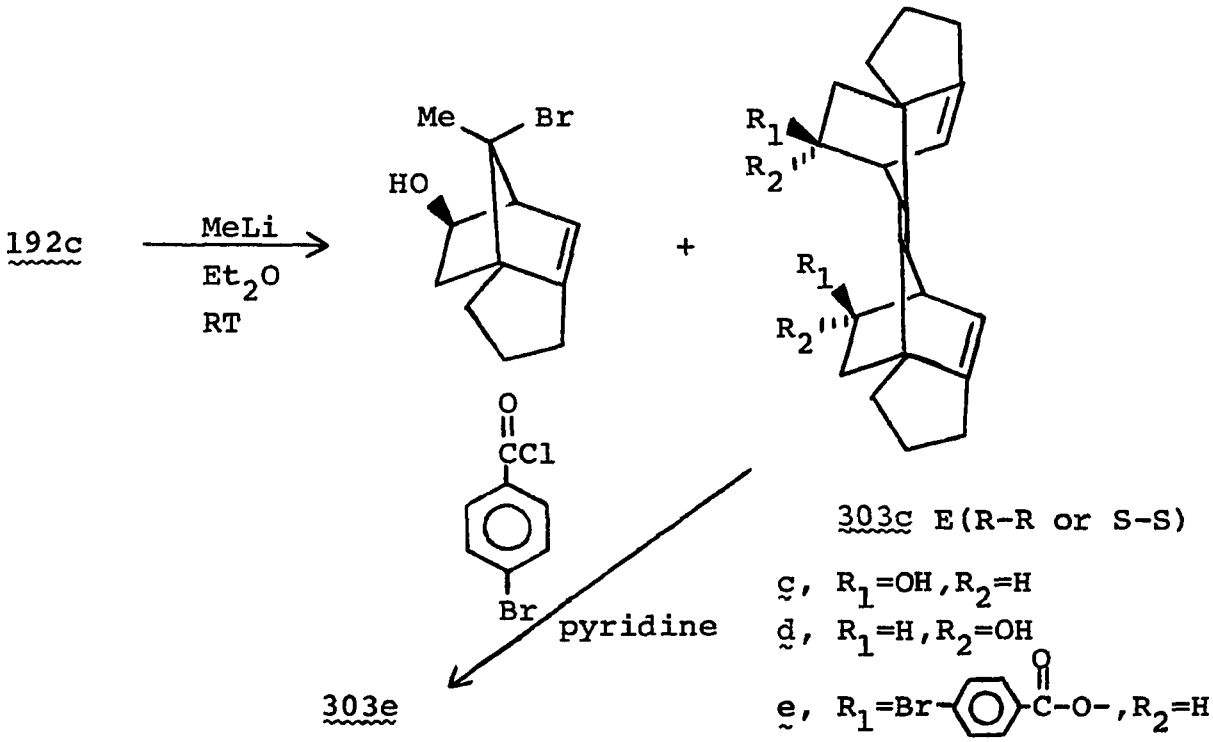
191



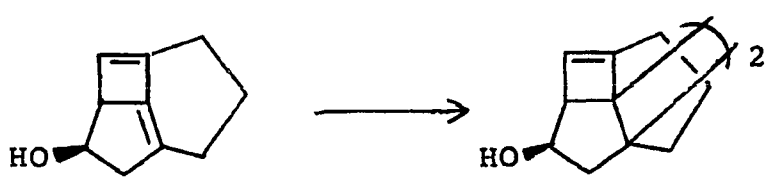
192

a, R_1=OMe, R_2=H
b, R_1=H, R_2=OMe
c, R_1=OH, R_2=H
d, R_1=H, R_2=OH

Treatment of 192c[125] with MeLi at either -78°C or room temperature afforded, in addition to rearranged product[131], only one dimer (42%, at RT). Surprisingly, the ^{13}C NMR



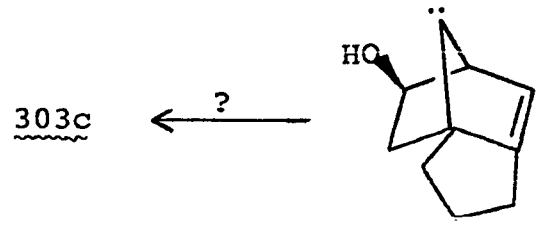
showed 3 olefinic peaks. If the bridgehead olefin 262c had dimerized in a [2 + 2] fashion to give 304c, one would



262c 304c

expect to see only 2 olefinic peaks in the ^{13}C NMR. Single crystal X-ray analysis (see Appendix) of the derived bis-p-bromobenzoate 303e (Fig. 39) revelated the structure of the dimer to be 303c (Fig. 38). In 303e, the two carbonyl groups point away from each other, suggesting a nonbonding interaction between these two groups in the solid state.

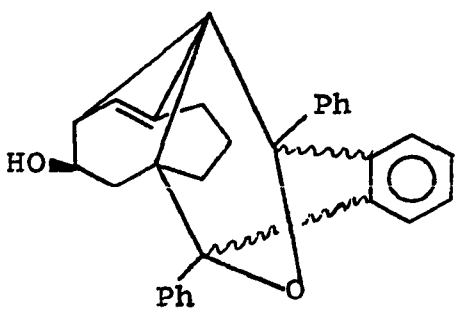
Compound 303c is a chiral dimer resulting from the formal dimerization of two R (or S) monomers to give an E olefin. At first glance, it might appear that this dimer arose from the dimerization of a norbornenylidene 225c,



225c

derived from 262c. If so, this would lend support to the Skattebol carbene-carbene rearrangement. However, were 225c to be formed, we would expect a rapid rearrangement of 225c to the relatively less strained 307,[44] rather than 262c (Scheme XV), where the strained double bonds can be trapped by DPIBF to give 308 or 309. It thus became critical to be

sure of the structure of the trapping products from 192c. In fact, the only previous really solid structural work in this whole area is the X-ray structural analysis of but one of the two DPIBF adducts obtained from 240.[82] Reaction of 192c with MeLi in the presence of DPIBF (1.1 equiv.) led to 2 adducts (24% and 21%). The single crystal X-ray analysis of the desired p-bromobenzoate of each (see Appendix) showed both have structure 219c, differing only in whether the bridging oxygen points toward the hydroxyl group or away from it.

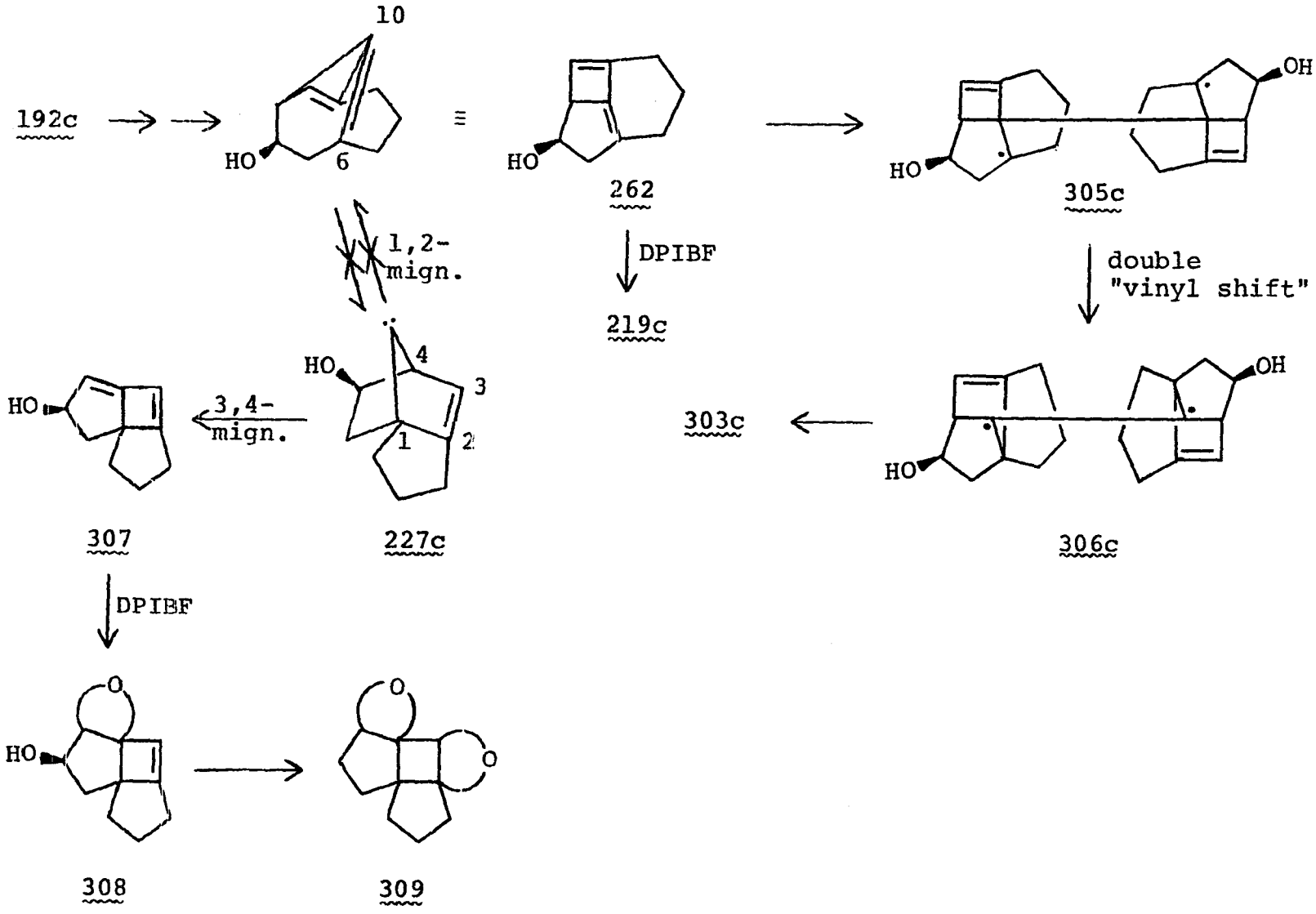


219c

Since some dimerization does occur (19%) in the presence of DPIBF, one would expect that this carbene 225c would have been trapped, if it had been formed. Thus we feel 227c is not an intermediate in these reactions.

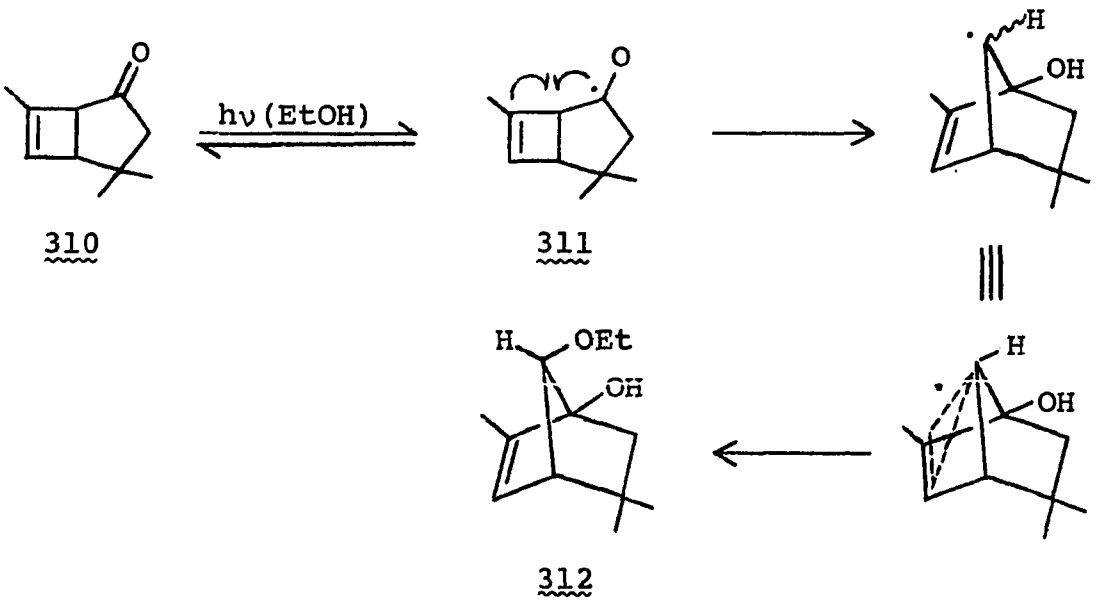
To account for the R-R (S-S) dimer, we propose that (Scheme XV) the strained double bond C_6-C_{10} of one monomer

Scheme XV


192c
10
HO
6
≡
HO
262
DPIBF
219c
1,2-
mign.
305c
OH
HO
double
"vinyl shift"
306c
OH
HO
303c
HO
4
3
2
1
3,4-
mign.
307
227c
DPIBF
O
HO
O
O
308
309

reacts with another monomer to give a diradical 305c. A double 1,2 vinyl migration gives a new tertiary diradical 306c, where the two adjacent radical centers then interact to form the central double bond.

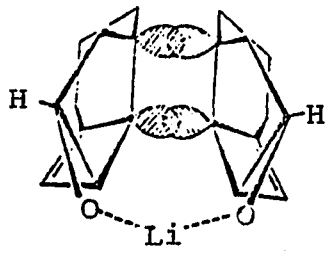
Precedent for this sort of vinyl radical migration exists. Thus, in order to account for the formation of the norbornene type product 312 from photolysis of 310 in EtOH, Boyle et al.[143] proposed that the intermediate 311 undergoes a 1,2 vinyl shift.



310 311 312

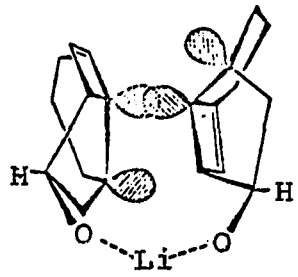
However, this mechanism still does not explain why the exo-OH compound 192c affords only one dimer 303c. We believe the reason is that 2 molecules of monomer 262c are held together by lithium bridging prior to the onset of

dimerization. If so, an R-S pair can only dimerize in a strongly disallowed [2 + 2] fashion (313), in which the



313

(R,S Dimerization Mode; only front lobes of p orbitals shown)

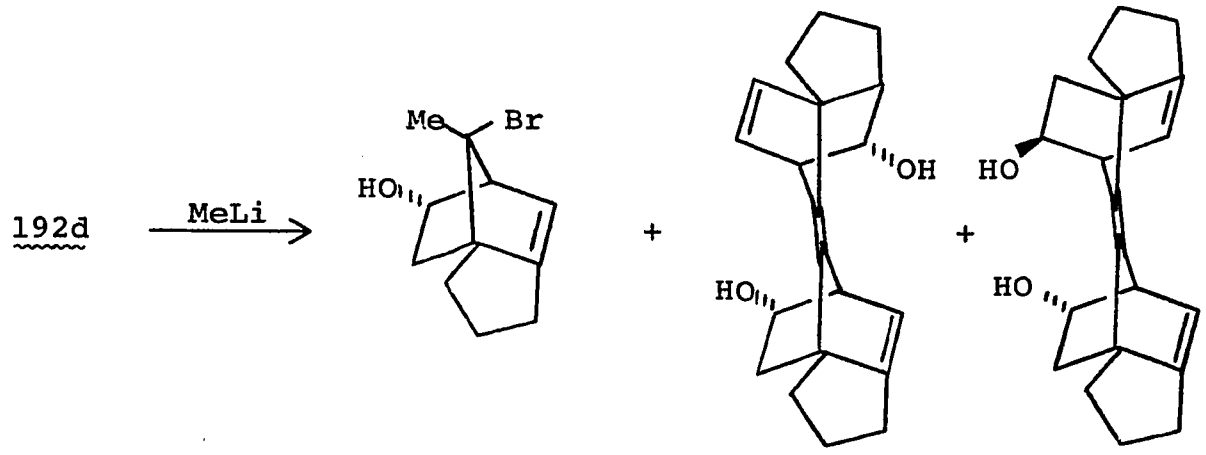


314

(R,S Dimerization Mode; only front lobes of p orbitals shown)

transition state is crowded, bringing the two oxygens close to or within van der Waals radii of each other. Contrariwise, an R-R (S-S) pair can give only a trans-1,4-diradical (314). Due to the bridging, 312 cannot rotate around and close to a cyclobutane dimer; rather, rearrangement ensues. In support of the above explanation, it has been found that 192d gives 4 dimers; ^{13}C NMR spectra indicate that 2 of these are of the cyclobutane type, and 2 of the norbornenyl type. In the case of 192d, dimers were also observed.

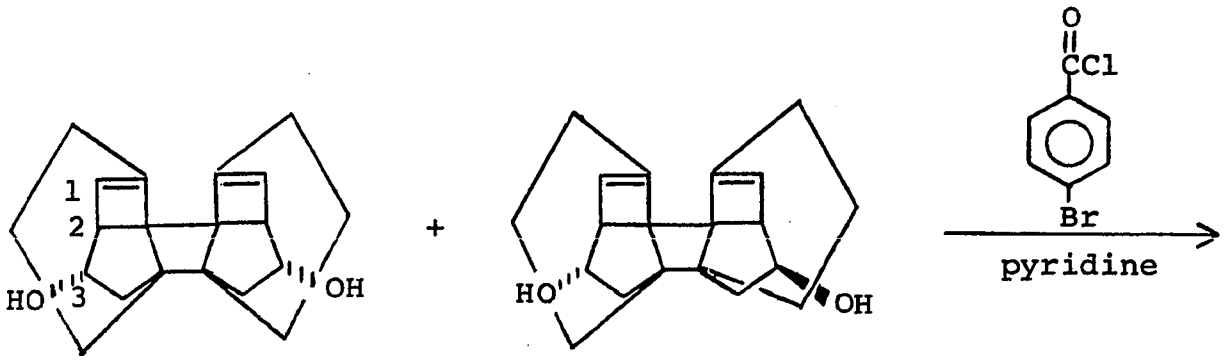
Treatment of 192d with MeLi at -78°C or room temperature gave 218d, 315, 316, 317 and 318.



218d

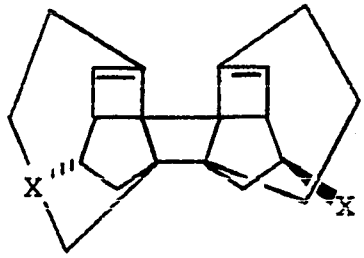
315
E(R-S)

316
E(R-R/S-S)

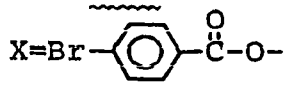


317
(R-S)

318
R-R(S-S)



318a



Thin layer chromatographic purification (80% ethereal hexane, developed twice) gave a mixture of dimers (R_f=0.31) in 61% yield. GLC-mass showed two broad peaks (column C) with a mass at m/e 296. Thin layer chromatographic purification (Et_2O) of the dimer mixture gave an R-R (S-S) [2 + 2] type dimer 318 (R_f=0.25, 16%) (Fig. 42), the structure of which was confirmed by X-ray analysis (see Appendix) of the p-bromobenzoate derivative 318a (Fig. 43). The isomer of 318 was also isolated (317, R_f=0.31, 10%) (Fig. 41). The ^1H NMR spectrum ($CDCl_3$ + CD_3OD) of 317 showed a singlet at δ5.8 for the olefinic protons, a multiplet from δ4.7 to 4.2 for the methine protons at C_3, a multiplet from δ3.75 to 3.15 for the methine protons at C_2, and a myltiplet from δ3.0 to 1.1 for the remaining protons. The ^{13}C NMR showed 2 olefinic peaks: δ156.43 and 124.08, and 8 aliphatic peaks at δ72.40, 62.76, 55.01, 48.29, 45.64, 29.55, 26.73 and 26.57. The infrared spectrum showed -OH absorption at 3605 cm^{-1}, and a broad band ranging from 3540 to 3200 cm^{-1}, a C=C-H absorption at 3045 cm^{-1}, and C=C absorption at 1610 cm^{-1}.

A mixture of the two isomeric dimers 315 and 316 was isolated (R_f=0.39, 35%). The ^1H NMR showed a multiplet from 5.9 to 5.55, a multiplet from δ4.5 to 2.75, and another multiplet from 2.75 to 1.1. The ^{13}C NMR showed 6 olefinic

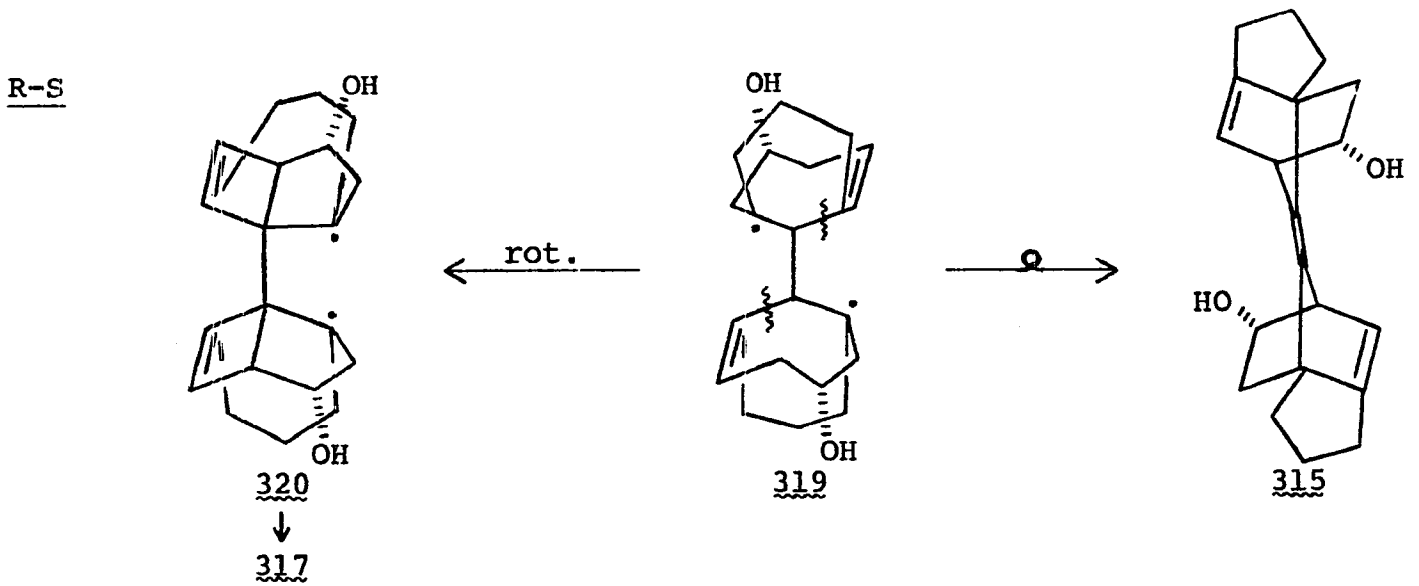
peaks: δ161.20, 154.00, 146.60, 126.40, 124.10 and 122.60 and 14 aliphatic peaks: 71.80, 68.80, 59.20, 58.00, 51.70, 51.10, 50.00, 34.10, 33.70, 27.60, 24.70, 24.00, 23.70 and 23.40.

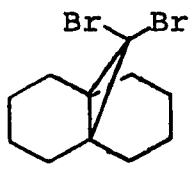
Thus, in the absence of Li bridging, dimerization does not favor the R-R (or S-S) combination over the R-S pairing. These results again[142] indicate the strong preference for trans-1,4-biradical formation in [2 + 2] dimerization. As shown in Scheme XVI, an R and S monomer first dimerize to give a transoid 1,4-biradical 319. Since there is no Li bridging in this case, the diradical 319 can either rotate and close to the cyclobutane dimer 317, or rearrange to give an E olefin, norbornenyl-type dimer 315. For an R-R (S-S) pair of monomers, the transoid-1,4-diradical 321 can behave in a similar fashion to give an E olefin 316 and a cyclobutane dimer 318.

Reactions of Some Tricyclic Cyclopropylidenes or Tricyclic Cyclopropylidenoids

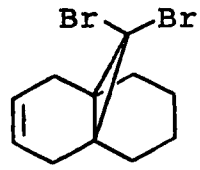
When Moore and Broadway[11a] treated compounds 139a, 12, 13 and 14 with MeLi at -15°C, they observed mainly intramolecular C-H insertion products in various yields (Table XIII) and concluded that both electronic and geometrical differences must be taken into account to explain the results. Table XIII shows that the yield of intramolecular

Scheme XVI

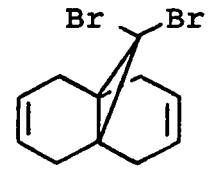

R-S
OH
OH
320
317
rot.
OH
OH
319
OH
HO
315
R-R or S-S
OH
OH
322
318
rot.
OH
OH
321
316



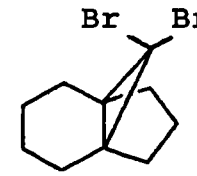
139a



12



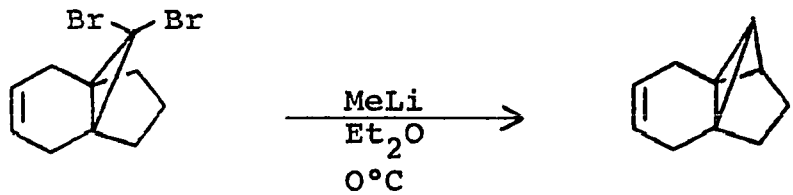
13



14

insertion products is dramatically reduced when only allylic positions are available. It also indicates that the carbenoid species show an apparent preference for the non allylic protons over the allylic protons where such a choice is available, even though the allylic position might appear to be a more attractive site for attack by the electrophilic intermediate.

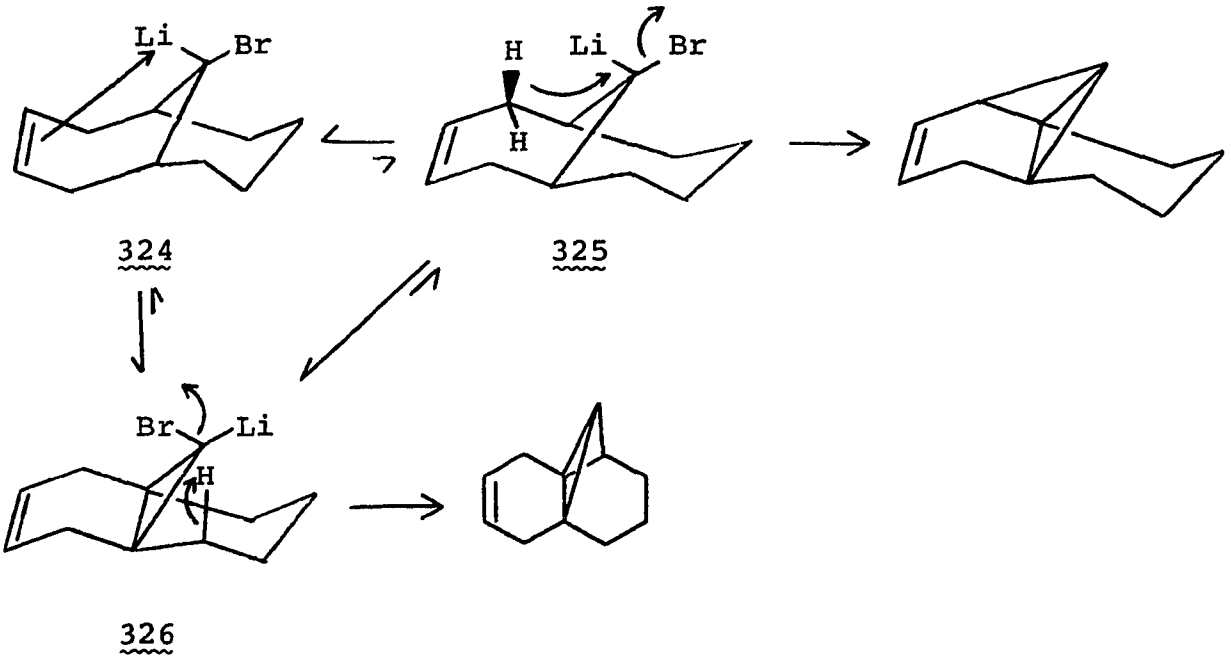
Further evidence to support this comes from Paquette et al.'s[11c] recent finding of 323. When 15 was treated with MeLi in ether at 0°C, 15 was smoothly transformed in 80% yield into a single bicyclo[1.1.0]butane derivative, 323.



15 323

The carbenoid intermediate derived from dibromide 12 would have two configurations 324 and 325 (Scheme XVII),

Scheme XVII

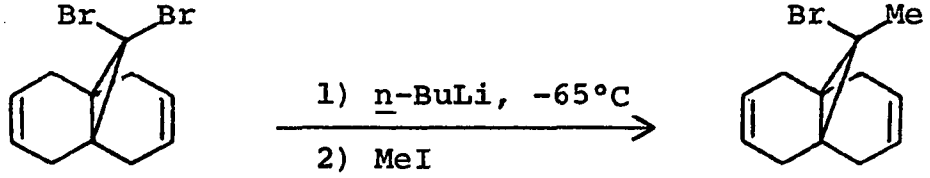


where the saturated 6-membered rings are in twisted chair forms and the unsaturated rings are in boat forms.

Allylic insertion is relatively slow because 324 predominates over 325, whereby the allylic H's are not in position to insert (i.e., 325 is required). This also explains the lesser amount of intramolecular insertion when only allylics are available. Additionally, 326 predominates over 325, because the Br over the π bond is less sterically a problem than when it is over the saturated ring. Therefore, 325 can undergo insertion as shown in Scheme XVII. This fits in with Taylor and Chaney's[20] work on dihalo bicyclic compounds, where carbenoids derived therefrom

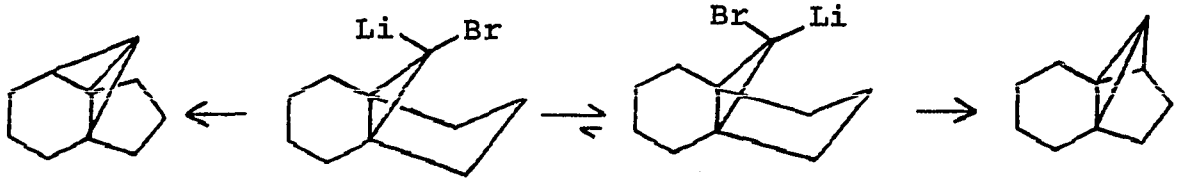
containing an exo halogen (44b, 45b) gave high yields of intramolecular insertion, 47, while that carbenoid with an endo halogen (46b) gave almost exclusively, products of intermolecular reactions (48 and 49).

Straube[144a] also investigated the reaction of 13 with n-BuLi at low temperature, followed by quenching with MeLi. This led to the methylated product in 78% yield.



13 78%

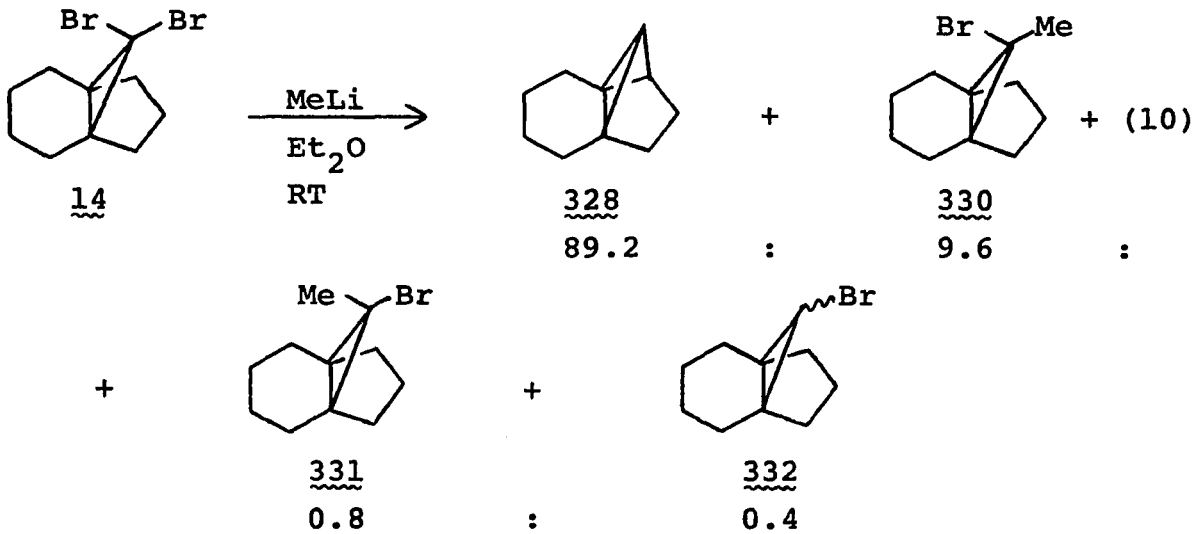
In the case of compound 14, the carbenoid derived therefrom shows an extremely high preference for insertion into the 5-membered ring over the 6-membered ring, even though the strain energy of the tricyclo[3.1.0.$0^{4,6}$] system in 328 is apparently higher than that of the tricyclo-



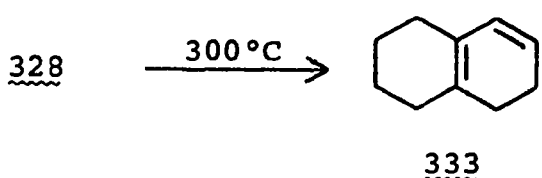
329 327a 327b 328

[4.1.0.$0^{5,7}$] system in 329. Carbenoid 327b should predominate over 327a sterically. However, the normally preferred boat configuration on the right side is not particularly good for insertion, but 327a is also bad. Thus 327b might do some configurational wiggling prior to insertion. This explains the exclusive formation of 328 over 329. The stereochemistry of the carbenoid center is a more important factor in insertion reactions than the strain energy of the product. Table XIII shows that only the intramolecular insertion products from 139a, 12, 13 and 14 (at 15°C) were observed. Does compound 44 give only the intramolecular C-H insertion product? Would intermolecular reaction also take place and what would the products be? Does strain energy really have no effect on the intramolecular insertion mode? In order to answer these questions, we have reinvestigated carbenoid formation from 14, the unsaturated 15; the relatively more strained molecule, 17, has also been investigated.

Treatment of 14 with MeLi at room temperature gave compounds 310, 312, 313 and 314 by GLC-mass studies and the product distributions (without correction factors) are 89.2, 9.6, 0.8 and 0.4 respectively. GLC-mass spectra showed five different peaks with parent ions at m/e 134. These might correspond to rearranged products from 328, either via acid

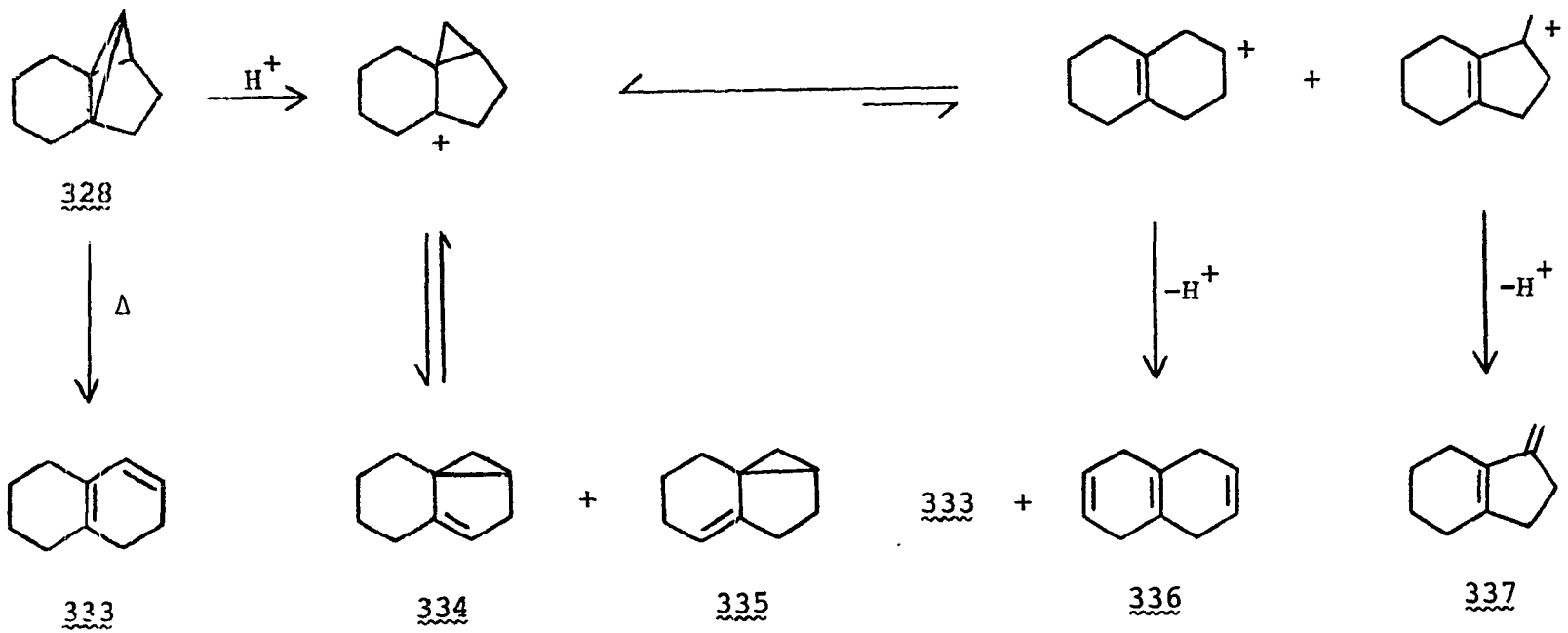


catalysis by the nonbase-washed column (column C) or thermal processes in the injector (250°C) and detector (300°C) of the GLC. This is a reasonable presumption, since it is known[11a] that 328 isomerizes to 328 at 300°C. Also acid-



catalyzed bicyclobutane rearrangements have been well documented.[145,146] Thus the compound of mass 134 are most likely 333-337 (Scheme XVIII).

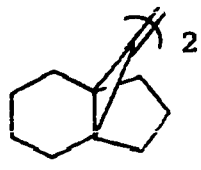
Scheme XVIII



Thin layer chromatographic purification (hexane) gave compound 330 (R_f=0.59, developed twice) (Fig. 54) in 5% isolated yield. The mass spectrum of 330 showed an exact mass at m/e 228.0512 for $C_{11}H_{17}Br$. The ^1H NMR spectrum revealed a multiplet ranging from δ2.15 to 1.0, with a singlet at δ1.73, and two other maxima at 1.92 and 1.33. The infrared spectrum showed a strong C-H stretching at 2930 cm^{-1}, and C-H bending at 1460 and 1446 cm^{-1}. The stereochemistry at C_{10} was confirmed by hydrogenation of analogous unsaturated compound, 10-bromo-10-methyltricyclo[4.3.1.$0^{1,6}$]-deca-3-ene (vide infra).

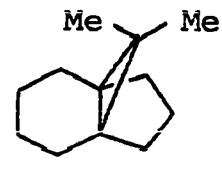
When compound 14 was treated with MeLi in the presence of 12-crown-4 at room temperature, the insertion product (328) decreased, but 331 and 332 increased, while dimer 338 and dimethylated compound 339 appeared as new products. The product distributions shown in Eq. 11 were determined by GLC-mass studies (without correction factors).

$$\underset{14}{} \xrightarrow[12\text{-C-4}]{\text{MeLi}} \underset{69.7}{328} + \underset{10.3}{330} + \underset{6.5}{331} + \underset{8.3}{332} + \quad : \quad : \quad : \quad :$$



338
2.0

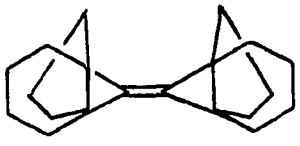
+ :



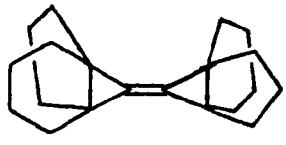
339
3.2

(11)

Thin layer chromatographic purification (hexane) gave a white solid (R_f=0.94, 2%) with an exact mass at m/e 268.2194 for $C_{20}H_{28}$. The possible structures for the two dimers are 338a and 338b (Figure 55). The infrared spectrum



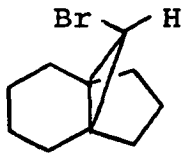
338a



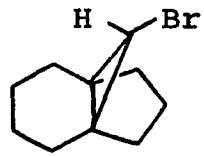
338b

showed a strong C-H stretching at 2940 and 2860 cm^{-1}, and a C-H bending at 1452 cm^{-1}. The ^1H NMR showed a multiplet from δ2.2 to 1.0 with two maxima at δ1.7 and δ1.25.

A mixture of 330 and 331 was also isolated (R_f=0.59). The mass spectrum showed a parent ion at m/e 228. The ^1H NMR showed a multiplet from δ2.5 to 1.0 with two singlets at δ1.73 and δ1.82. The singlet at δ1.73 was tentatively assigned to the methyl protons of 330 while the singlet at δ1.82 was assigned to the methyl protons of 331. This assignment was based on the ^1H NMR spectra[147] of 332a and 332b, where the methine proton at C_{10} in 332a is more upfield (δ2.9) than in 332b (δ3.1).

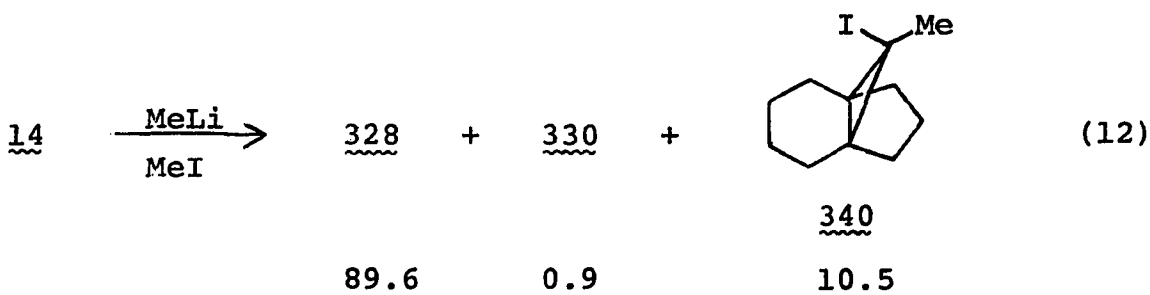


332a



332b

Treatment of 14 with MeLi in MeI at room temperature afforded compounds 328, 330 and 340, as determined by GLC-mass studies (column C). Thin layer chromatographic purifi-



(12)

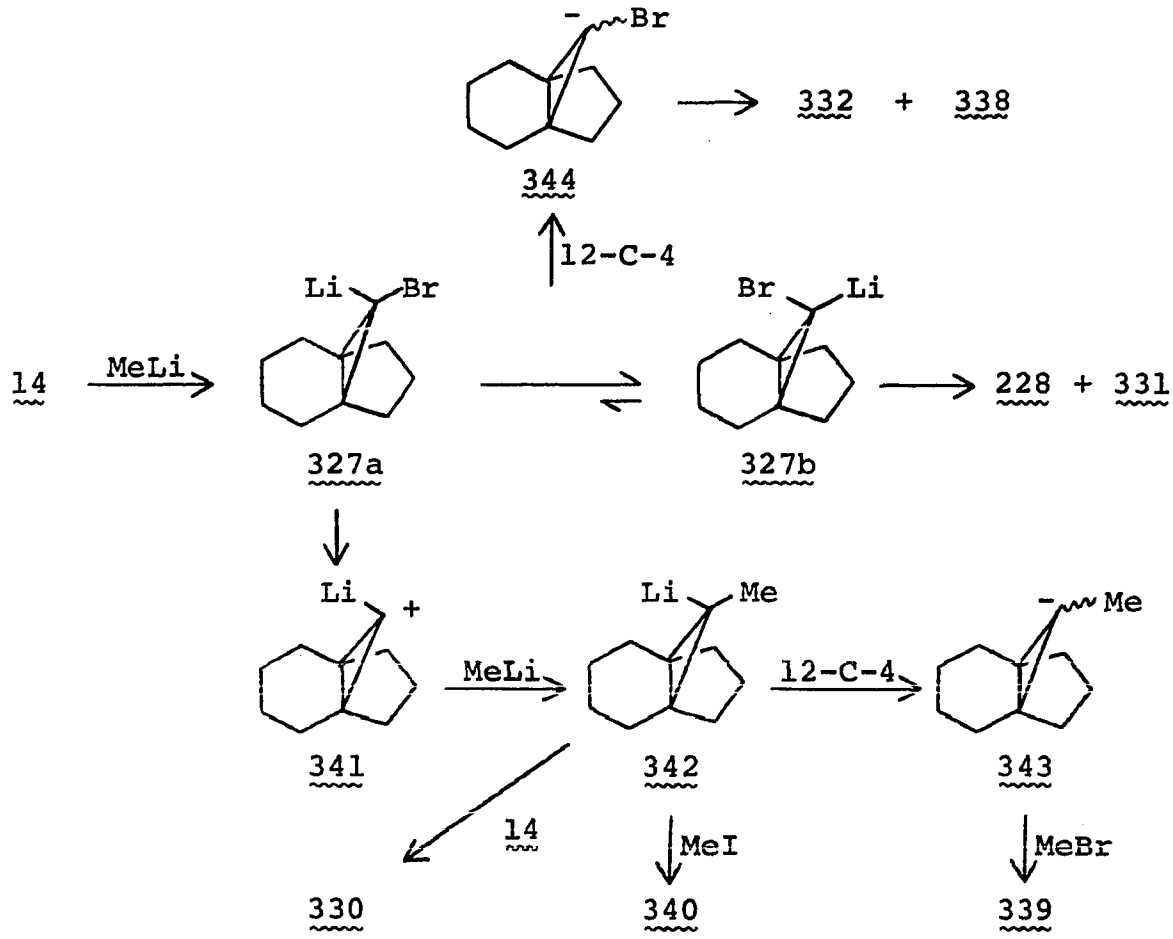
cation (hexane) gave compound 340 (R_f=0.74, Fig 56) in 7% yield. The mass spectrum showed an exact mass at m/e 276.0370 for $C_{11}H_{17}I$. The infrared spectrum showed exactly the same absorption pattern as for compound 330. The ^1H NMR spectrum showed a multiplet ranging from δ2.46 to 1.1 with a singlet at δ2.04 and a maximum at δ1.92.

The fact that treatment of 330 with MeLi in the presence of excess MeI led to no 340, but rather quantitative recovery of 330, confirms that indeed both bromines are lost during

the conversion of 14 to 330. Clearly the source of halide in 330 and 340 is an organic halide (since no 340 was formed when 14 was reacted in the presence of LiI). But what is the source of the methyl group in 330 and 340? In order to probe this question, CD_3I was used in place of CH_3I as solvent. The products were still primarily 330 and 340. Therefore, the source of the Me-group in compound 330 must be MeLi!

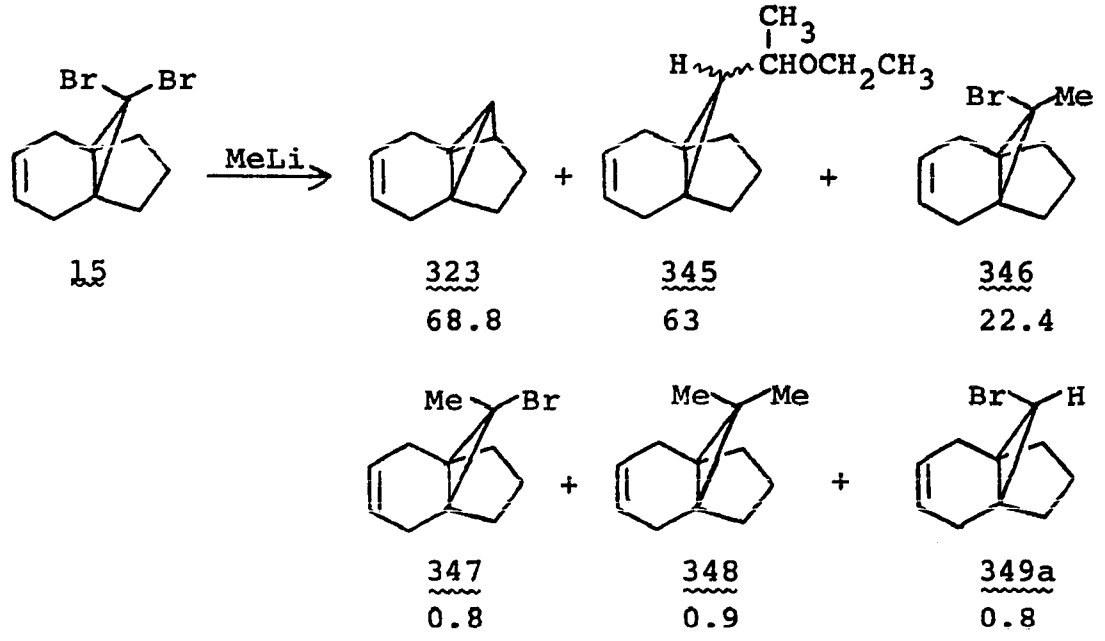
A proposed mechanism for the formation of the products shown in Eq. 10, 11 and 12 is illustrated in Scheme XIX.

Scheme XIX



In the presence of 12-crown-4, a lithiated reaction intermediate 342 would give anion 343 which is less crowded than an ordinary tertiary anion, because two of the three substituents are tied back by a 3-membered ring. Since 339 was observed only in the presence of 12-crown-4, it seems likely that 343 reacts via an S_N2 reaction with MeBr to give 339. The dimers 338 were also observed when 12-crown-4 was present in the system. Both 327a and 327b would give the bromoanion 344 which may then dimerize via attack on 327.

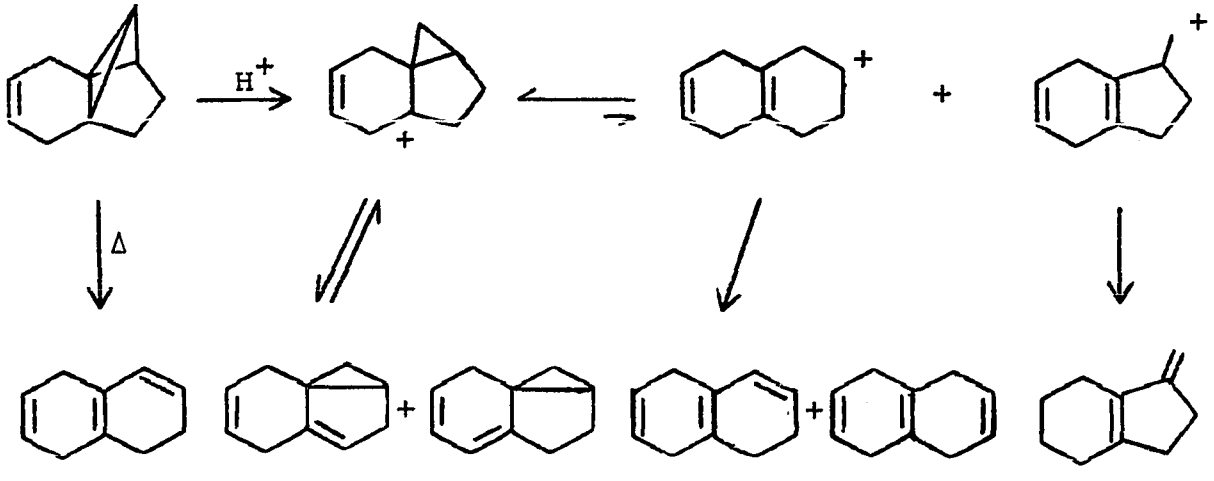
Treatment of compound 15 with MeLi in ether at room temperature gave two C-H insertion products (323[11c] and 345);



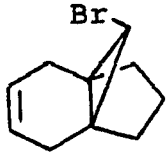
15 → 323 (68.8) + 345 (63) + 346 (22.4) + 347 (0.8) + 348 (0.9) + 349a (0.8) (13)

methylated products 346, 347 and 348, and the reduced product, 349a, (GLC-mass studies, column C). The product distributions were 68.8:6.3:22.4:0.8:0.9:0,8, respectively (GLC, uncorrected). GLC-mass spectrum showed 5 different peaks with parent ions at m/e 132; they are presumably the rearranged products from 323. We assigned the structure of intramolecular C-H insertion product 323 in accord with the previously reported work[11c]; we have no independent evidence for the structure of 323. The most likely rearranged products from 331 are analogous to the ones from 328 (Scheme XX).

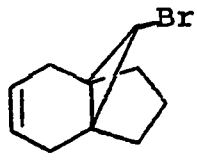
Scheme XX



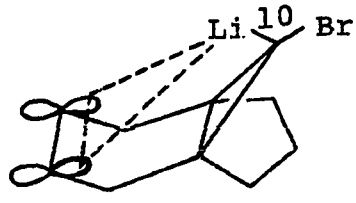
Thin layer chromatographic purification (20% ethereal hexane) gave 346 (R_f=0.8, Fig 57) in 12% yield. The mass spectrum showed an exact mass at m/e 226.0357 for $C_{11}H_{15}Br$. The infrared revealed a C=C-H absorption at 3015 cm^{-1}. The ^1H NMR showed a broad singlet at δ5.5 with shoulders at δ5.52 and 5.48 for the olefinic protons, a singlet at δ2.3 for the 4 allylic protons, a multiplet (δ2.16 to 1.83 with a maximum at δ1.98) for the 6 protons in the 5-membered ring, and a sharp singlet at δ1.73 for the methyl protons. The ^{13}C NMR ($CDCl_3$) showed 7 peaks: δ124.18 (rel. int. 6.14), 51.65(1), 36.25(7.51), 32.25(1.32), 30.19(7.82), 26.66(4.68), 22.55(2.00). The stereochemistry of 346 at C_{10} was assigned on the basis of comparison with the ^1H NMR spectra of 349a and 349b[147], where both 346 and 349a exhibit a singlet for the allylic protons, while 349b shows a multiplet for those protons.



349a



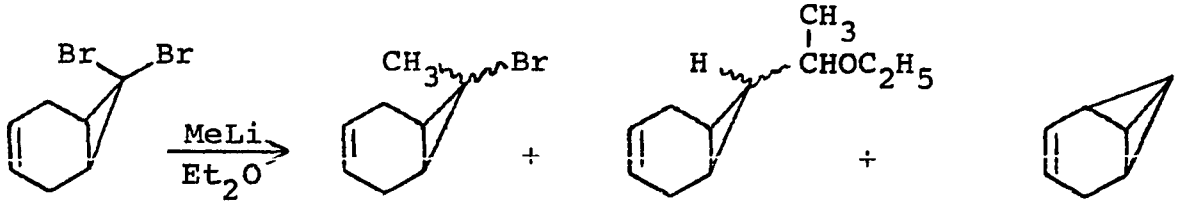
349b



350

Compound 345 was also isolated (R_f=0.6, Fig. 58) in 4% yield. The mass spectrum showed a mass at m/e 206. The ^1H NMR revealed a singlet at δ5.43 for the olefinic protons, a

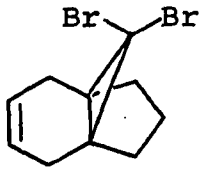
quintet at δ3.52. A multiplet from δ3.2 to 1.3 with a maximum at δ2.23, and an overlapping doublet and triplet at δ1.13. The infrared spectrum showed a C-O-C absorption at 1110 cm^{-1}. The appearance of intermolecular insertion product 345 can be accounted for if it is assumed that carbenoid 350 is stabilized by π interaction, giving it a reasonable lifetime relative to its epimer. Since 350 cannot undergo intramolecular insertion (whereas its epimer can), it lives long enough to insert into solvent. This type of process was first observed by Merrit[148] who noted mostly in insertion into the solvent, and methylated products, when 9 was reacted with MeLi in cold ether. Later, Klumpp and



9 1-4%

Vrielink[8] reported that only a 1-4% yield of intramolecular C-H insertion product was formed.

Upon treatment of 15 with MeLi in the presence of 12-crown-4 at room temperature, compound 323, 345-349a and 351 were observed. The product distributions were 46.2:2.5:18.5:

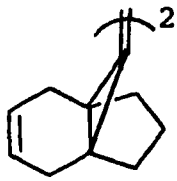


15

$$\xrightarrow[12\text{-}C\text{-}4]{MeLi}$$

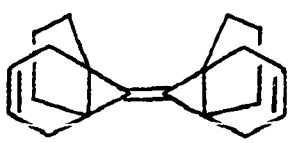
323 (46.2) + 345 (2.5) + 346 (18.5) + 347 (0.2) +

348 (8.3) + 349a (20.5) +

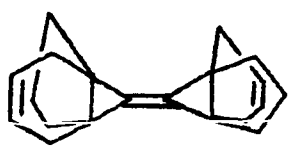


351 (3.8) (14)

0.2:8.3:20.5:3.8, respectively, (GLC-mass spec, uncorrected). The two possible dimers are 351a and 351b (Fig. 59). Thin layer chromatographic purification (hexane) gave a white



351a

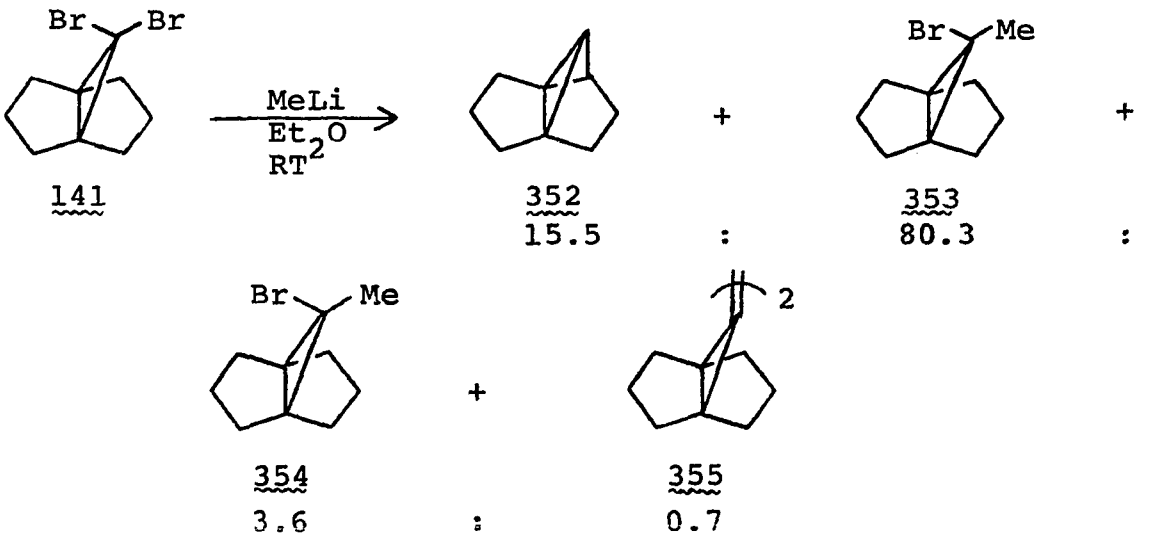


351b

solid (R_f=0.9) which was assigned as dimers 351a and 351b on the basis of spectral and analytical data. The mass spectrum showed a parent ion at m/e 264. The infrared spectrum showed a C=C-H absorption at 3030 cm^{-1} and C=C absorption at 1650 cm^{-1}. The ^1H NMR spectrum revealed two broad singlets at δ5.4 and δ5.25 for the olefinic protons (in a ca. 2.7:1 ratio) and a multiplet from δ2.72 to 0.5. The mechanisms

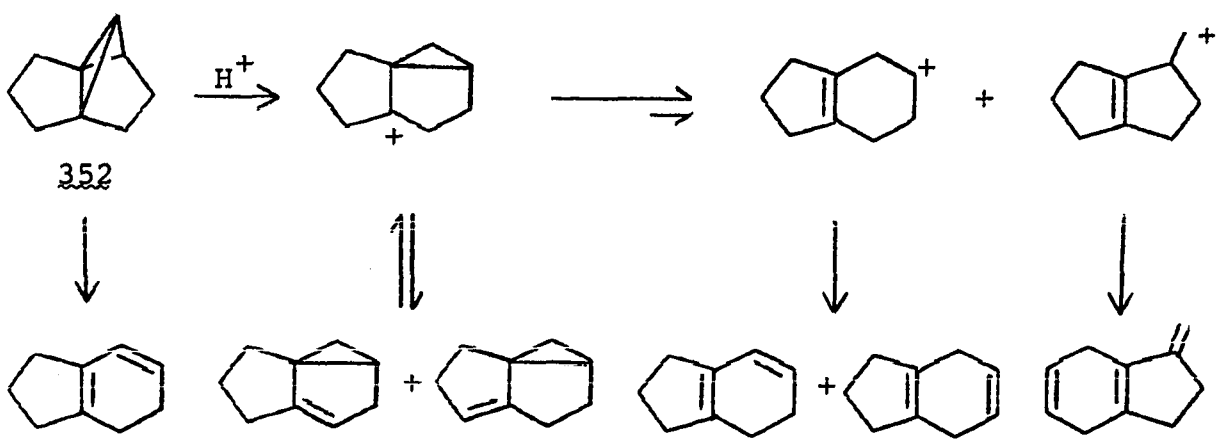
for the formation of the products in Eq. 13 and 14 must be similar to those for product formation from the reaction of 14 with MeLi.

Treatment of compound 141 with MeLi in ether at room temperature gave 352-355 (GLC-mass spec) in a ratio of 15.5:



141 → 352 15.5 : 353 80.3 : 354 3.6 : 355 0.7

80.3:3.6:0.7, respectively (uncorrected). There are 5 peaks with parent ions at m/e 120 which presumably correspond to rearranged products (in the GLC column) from 352:



352

Table XIII. Product yields or distributions of dibromotricyclopropellanes with MeLi

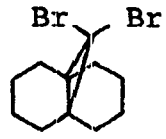
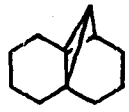
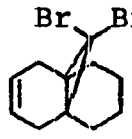
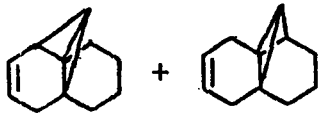
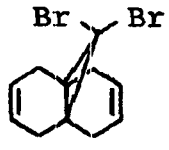
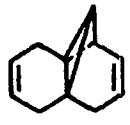
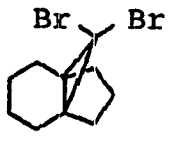
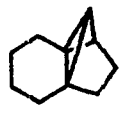
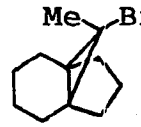
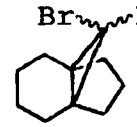
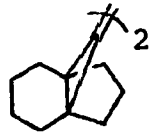
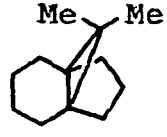
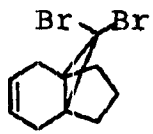
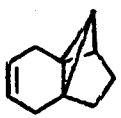
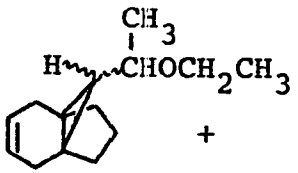
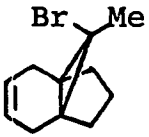
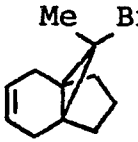
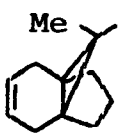
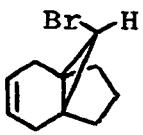
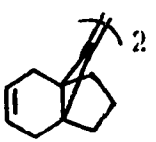
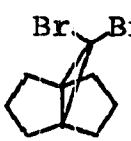
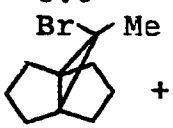
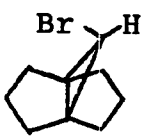
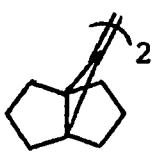
Compound	Product(s) ratio of distributions	Yield	Reaction Temp.
 139a		80%	-15°C
 12	 1 : 13	71%	-15°C
 13		45%	-15°C
 14	 328	66%	-15°C

Table XIII. (Continued)

Compound	Product(s) ratio or distributions	Yield	Reaction Temp.
14	328 +  +  +  89.2 330 9.6 + 331 0.8 + 332 0.4		RT[a]
14 + 12-C-4	328 + 330 + 331 + 332 +  +  69.7 10.3 6.5 8.3 338 2.0 + 339 2.2		RT[a,b]

[a]10 Equiv. of MeLi was used.
[b]10 Equiv. of 12-crown-4 was used.

Table XIII. (Continued)

Compound		Yield	Reaction Temp.
 15	 323 68.8 +  345 6.3 +  346 22.4 +  347 0.8 +  348 0.9 +  349a 0.8		RT^a
15 + 12-C-4	323 45.2 + 342 2.5 + 347 18.5 + 348 8.3 + 349a 20.5 +  351 3.8		$RT^{a,b}$
 141	 352 15.5 +  353 80.3 +  354 3.6 +  355 0.7		RT^a

Thin layer chromatographic purification (hexane) afforded compound 353 (R_f=0.65, Fig. 60) in 33% yield. The mass spectrum showed an exact mass at m/e 214.0356 for $C_{10}H_{15}Br$. The ^1H NMR showed a multiplet from δ2.75 to 1.2 with a singlet at δ1.83 and a maximum at δ2.06. The ^{13}C NMR ($CDCl_3$) gave 7 peaks at δ57.28 (rel. area 1.0), 51.69(2.08), 36.10(8.80), 34.12(6.34), 33.92(2.59), 32.10(9.30) and 23.52(1.59).

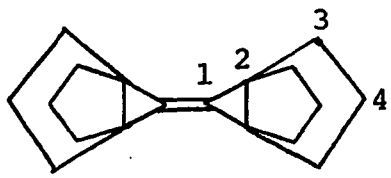
The product yields and/or distributions from the reactions of dibromotricyclo[4.4.1]-, [4.3.1]- and [3.3.1] propellanes with MeLi are summarized in Table XIII.

It is noteworthy that in the presence of 12-crown-4, both 14 and 15 gave a decreased yield of intramolecular C-H insertion products, while the yield of reduced products increased. This indicates that the α-bromolithium carbenoids are responsible for the intramolecular C-H insertion, while the α-bromo anions most likely remove a proton from solvent to afford the reduced products (332, 349a). Additionally, when the system becomes more strained (e.g., 141), the yields of intramolecular C-H insertion products decrease, while the intermolecular component of the reaction increases (at RT).

Sterically Crowded Olefins

Treatment of 141 with MeLi in ether at -78°C afforded a symmetrical dimer 355 (Fig. 61) in 6.4% yield (recrystallized

from Et_2O, mp 202-204°C). The mass spectrum showed an exact mass at m/e 240.1879 for $C_{18}H_{24}$. The ^1H NMR showed a multiplet between δ2.23 and 1.1. The ^{13}C NMR showed one peak within the olefinic region at δ127.98 for C_1; off

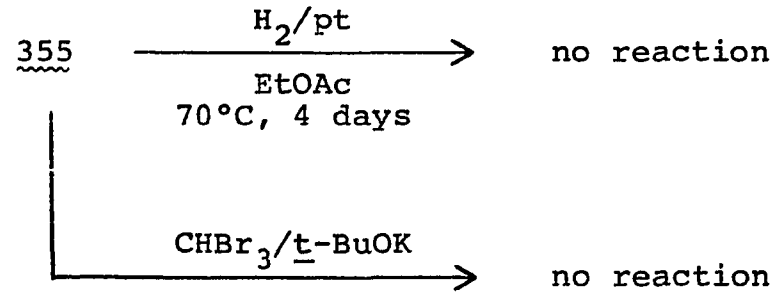


355

resonance decoupling confirmed the assignment of the peak at δ41.20 to C_2. Since C_3 should have twice as many protons as C_4, the peak at δ33.23 was assigned to C_3, and the peak at δ30.80, which was half the intensity of that at δ33.23, was assigned to C_4. In order to observe the olefinic carbon C_1, which has no NOE and a long relaxation time a 1μ sec pulse, which is equivalent to 7° pulse width, was used. X-ray analysis (see Appendix) of 355 confirmed the structure of 355 as a planar olefin with an inversion center at the center of the double bond. The infrared spectrum showed no typical C=C stretching around 1600 cm^{-1}, which was in accord with an inversion center at the midpoint of the carbon-carbon double bond. Strangely, however, the Raman spectrum (measured both in solution and the solid

state) showed no absorption around 1600 cm^{-1}, but rather showed a reasonably strong absorption band at 1450 cm^{-1}. The appearance of two bands in that general region of the infrared spectrum leaves us in doubt as to the precise meaning of these results. As shown in Table III, the more sterically crowded are groups attached to the olefinic carbons, the lower the frequency of C=C absorption in the Raman spectrum. However, no olefin has ever been observed to absorb as low as 1450 cm^{-1}!

Hydrogenation of 355 at 70°C in ethyl acetate on 5% pt/C for four days led to the recovery of starting material



quantitatively. Attempted addition of dibromocarbene to 355 also gave no reaction. These results suggest that 355 is a very sterically hindered olefin. While the crystallographically observed C=C distance for 355 (1.307Å) appears

to be shorter than a normal double bond, it may be that methylene cyclopropanes ordinarily have even shorter double bonds. If so, the double bond of 355 may be longer than "normal", whereby steric strain is relieved.

EXPERIMENTAL

General

Infrared spectra were recorded on Beckman IR-12, IR-18A and IR-4250 spectrophotometers. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The proton magnetic resonance spectra were obtained on Varian HA-100, Hitachi Perkin-Elmer R-20B and Varian EM360 spectrometers, using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard, unless otherwise specified. The carbon magnetic resonance spectra were recorded on a Bruker HX-90, equipped with a Nicolt Model 1089 data package, or a JEOL FX-90Q spectrometer. The mass spectral studies were conducted using High Resolution MS-9, MS-50 (in MCMS, Lincoln, Nebraska for organometallic compounds) and Finnegan 4023 GLC-mass spectrometers. GLC analyses were conducted on Varian Aerograph Model 9700 (for analytical runs) and Varian Aerograph Model 90-P (for preparative runs) gas chromatographs. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Spany Microanalytical Laboratory, Eagle Harbor, Michigan.

The following GLC columns were utilized. All the columns listed are glass columns except column B, which is stainless steel. The inlet part of the Varian Aerograph

Model 90-P contained a glass insert to insure no contact with a metal surface.

A. 6 ft x 1/4 in, 4% SE-30 on Chromosorb W A/W 80/100 mesh

B. 1 2/3 ft x 1/8 in, 5% OV101 on Chromosorb A, 100/120 mesh

C. 6 ft x 1/8 in, 3% OV1 on Chromosorb W, 100/120 mesh

D. 6 ft x 1/16 in, 3% OV17 on Chromosorb Q, 80/100 mesh

E. 16 ft x 1/4 in, 10% FFAP on Chromosorb W, A/W 60/80 mesh

F. 16 ft x 1/4 in, 14% Carbowax 20M on Chromosorb W, A/W 60/80 mesh

G. 16 ft x 1/4 in, 12% DC-550 (Dow Corning phenyl methyl silicone fluid) on chromosorb W A/W 60/80 mesh

All reactions involving organometallic reagents, active metals, metal hydrides and metal alkoxides were carried out in a nitrogen atmosphere.

Synthesis

10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene (191) (Fig. 3)[3]

A 20 ml methylene chloride solution containing 9.68 g (33.2 mmol) 15 and 16.72 g (73.7 mmol) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was placed in a 1 in x 7 in tube and sealed with a torch. The mixture turned a yellowish

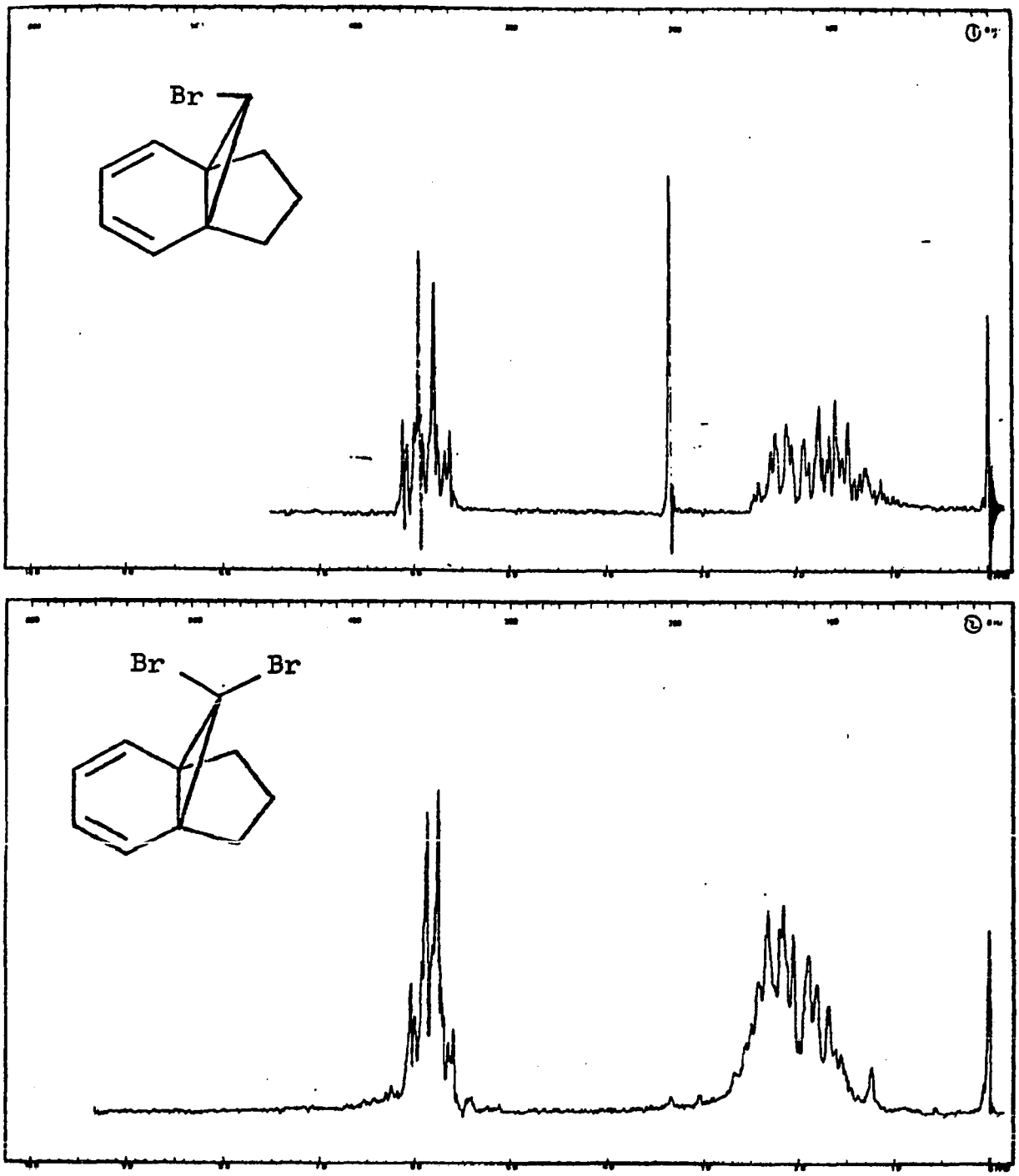


Figure 3. ^{1}H NMR spectra of 10α-bromotricyclo[4.3.1.0^{1,6}] deca-2,4-diene: 210a (top) and 10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2,4-diene: 191 (bottom)

green color after heating at 70°C for four days. After cooling, the tube was opened and the solid was filtered off and washed several times with hexane. Evaporation of solvent solvent afforded a green solid which was chromatographed (neutral alumina, hexane as eluent) to give 3.99 g (53.4% on the basis of 77.8% conversion) of white crystals (191), mp 73-74°C; ^{1}H NMR: δ6.3-5.5(AA'BB', 4H), 3.0-1.1(m, 6H); ^{13}C NMR($CDCl_3$): δ124.68(rel. area: 4.45), 123.98(4.48), 49.32(1.75), 48.08(1), 37.89(5.15), 25.59(2.87); UV(cyclohexane): λ_{max} 235 (ε=1600)nm; IR(CCl_4): 3040(C=C-H), 2970, 2940, 2870, 1445, 1170, 1155, 1040(cyclopropyl C-C), 635 (C-Br) cm^{-1}. Anal. Calc'd for $C_{10}H_{10}Br_2$: m/e 287.9150. Found: m/e 287.9149.

exo-10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-acetate (192f)

To a stirring solution of 2.92 g (10 mmol) 15[116] and 1.92 g (10 mmol) phenylselenenyl chloride in 10 ml HOAc, was added a solution of 1.96 g (20 mmol) KOAc in 15 ml HOAc under N_2 at room temperature.[120] The initially red solution turned yellow immediately. After stirring for 4 hr, the mixture was diluted with H_2O and extracted with ethyl acetate. The combined extracts were washed with H_2O, saturated K_2CO_3 solution, dried and concentrated to yield a yellow oil which was dissolved in 40 ml dry THF and cooled in ice; 10 ml of

30% H_2O_2 was then added dropwise at 0-4°C. Stirring was continued for 17 hr. The resulting mixture was diluted with H_2O, and extracted with ethyl acetate. The combined extracts were washed with saturated NaCl solution, dried, and the solvent removed to afford 3.26 g solid material. This was recrystallized from ether/hexane to give 2.96 g (85%) of 192f, mp 79-82°C; ^{1}H NMR: δ5.7(br s, 2H), 5.35-4.95 (m, H_4); 2.8-1.5(m, 11H, including an acetate s at 2.0); ^{13}C NMR($CDCl_3$): δ136.32(rel. area 6.55), 127.81(5.85), 64.88 (426), 57.77(1.00), 40.06(1.84), 39.54(1.85), 38.73(3.54), 38.14(5.36), 34.83(3.67), 25.83(3.46); IR(CCl_4): 3045, 1745, 1630, 1235 cm^{-1}. Anal. Calc'd for $C_{12}H_{14}O_2Br_2$: m/e 347.9374. Found: m/e 347.9361.

exo-10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (192c) (Fig. 4,5)

To a solution of 2.04 g of acetate 192f in 10 ml MeOH was added 68 ml of a 1.0 M KOH/95% MeOH solution. The resulting reaction mixture was stirred for several hours (or overnight), whereafter H_2O was added, the MeOH evaporated, and 100 ml $CHCl_3$ added. The $CHCl_3$ layer was washed with H_2O (until neutral) and then dried over K_2CO_3. Filtration and solvent evaporation afforded 1.78 g (99%) 192c, mp 102.5-103°C; ^{1}H NMR($CDCl_3$): δ5.84(br s, 2H), 4.25(apparent quartet, H_4), 2.8-1.4(m, 9H); IR($CDCl_3$): 3613(free OH), 3050,

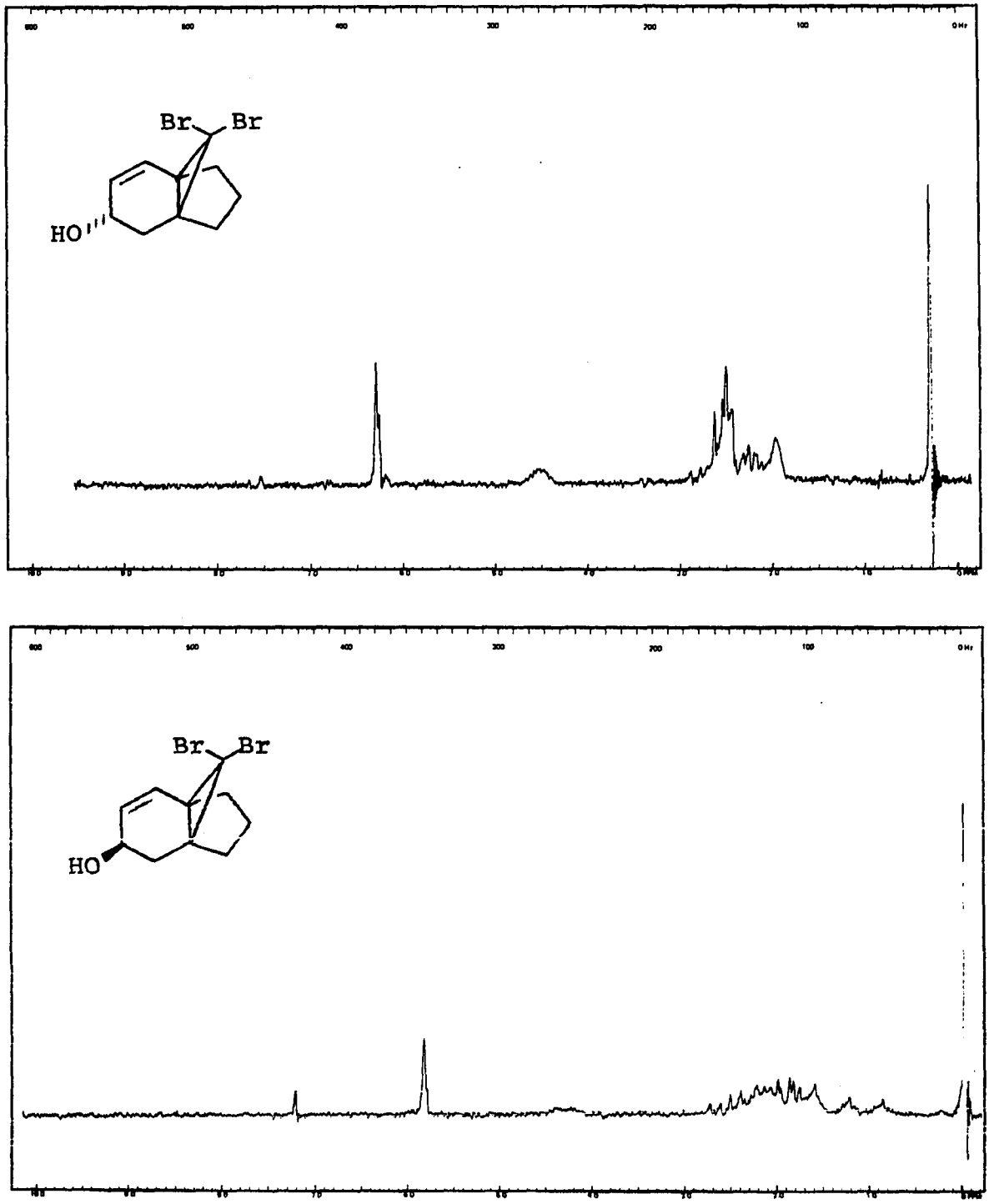


Figure 4. ^{1}H NMR spectra of endo-10,10-dibromotricyclo-[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (192d, top) and exo-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (192c, bottom)

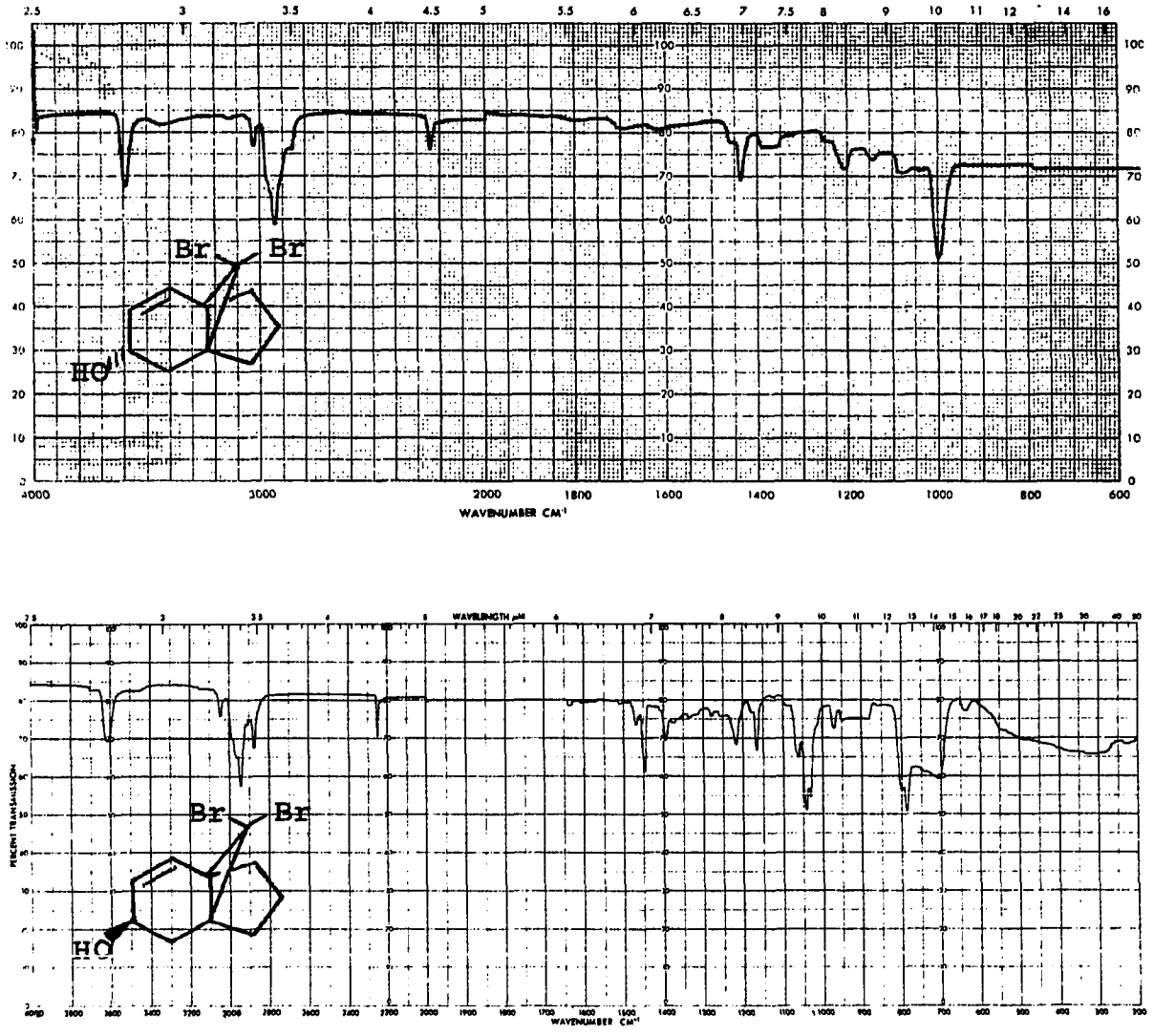


Figure 5. IR Spectra of endo-10,10-dibromotricyclo-[4.3.1.0^{1,6}]deca-2-ene-4-ol (192d, top) and exo-10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2-ene-4-ol (192c, bottom)

1635, 1088 cm^{-1}. Anal. Calc'd for $C_{10}H_{12}Br_2O$: C, 38.99; H, 3.93. Found: C, 38.87; H, 3.87.

exo-4-Methoxy-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene (192a) (Fig. 6,7)

(a) In a 25 ml three-necked round bottom flask, equipped with an addition funnel, a gas inlet and a gas outlet, was placed a suspension of 10 mg NaH[149] (0.42 mmol, obtained from Metal Hydrides as a 50% suspension in mineral oil) in 0.5 ml DMF (freshly distilled over 4A molecular sieves). A magnetic stirrer was used to stir the suspension. A solution of alcohol 192c (100 mg, 0.32 mmol) in 5 ml DMF was added dropwise. Excess MeI was then added (100 mg), and the resulting reaction mixture was stirred overnight, whereafter H_2O was added, the DMF evaporated, and 20 ml Et_2O added. The Et_2O layer was washed with H_2O (until neutral) and then dried over $MgSO_4$. Filtration and solvent evaporation afforded 150 mg of crude product which was chromatographed (silica gel, hexane as eluent) to give 65 mg(62.2%) of colorless oil. ^1H NMR: δ6.10-5.62(m, 2H), 3.82(apparent quartet, H_4), 3.31(s, 3H), 2.22-1.56(m, 8H); ^{13}C NMR ($CDCl_3$): δ134.24(rel. area: 8.99), 127.87(8.73), 73.52(8.25), 57.67 (1.27), 56.01(5.41), 39.64(5.06), 38.96(1), 38.08(9.69), 35.22(6.88), 34.83(6.47), 25.83(7.18); IR(CCl_4): 3044 (C=C-H), 1635(C=C), 1115(C-O)cm^{-1}. Anal. Calc'd for

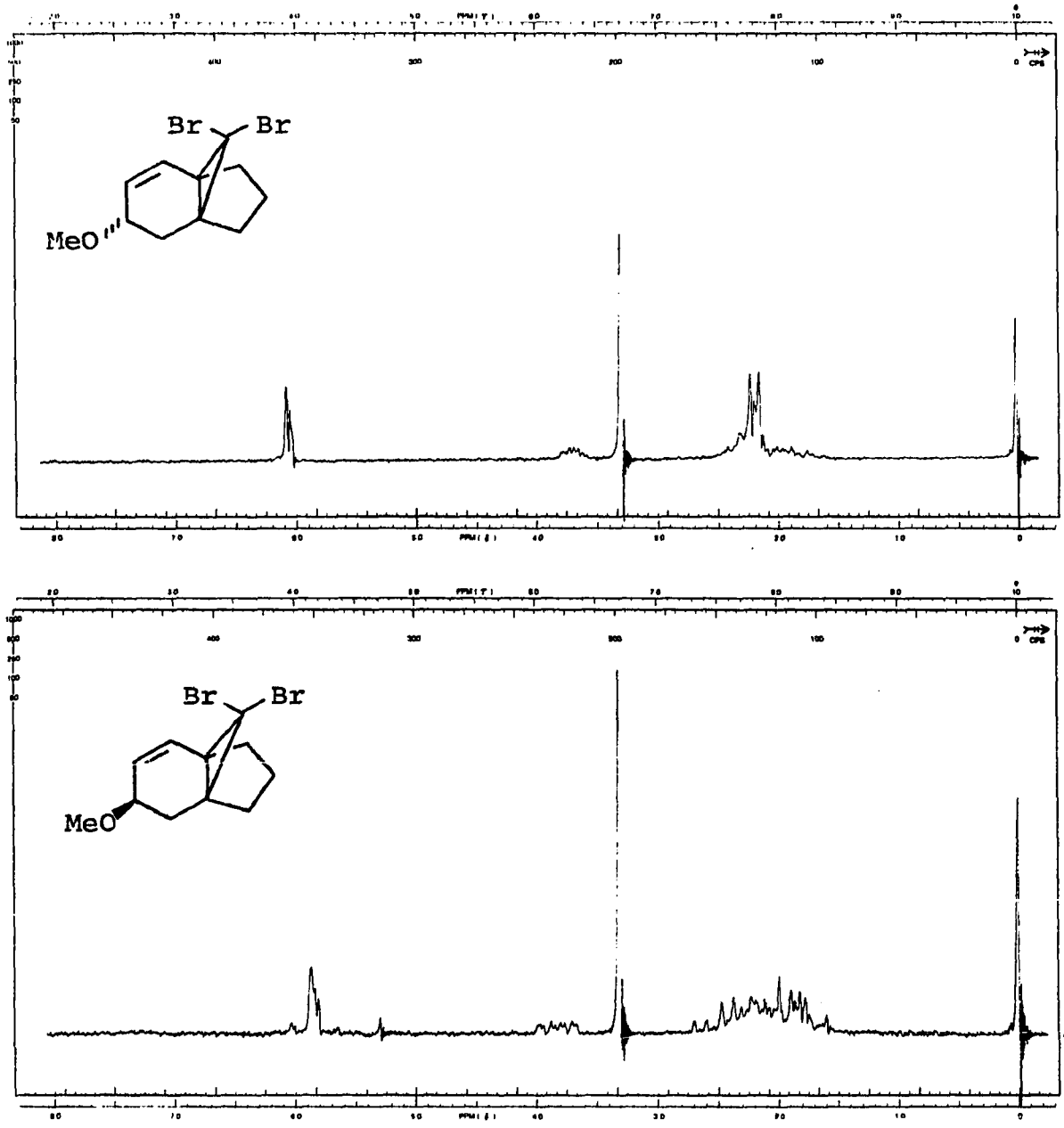


Figure 6. ^{1}H NMR spectra of endo-4-methoxy-10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2-ene (192b, top) and exo-4-methoxy-10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2-ene (192a, bottom)

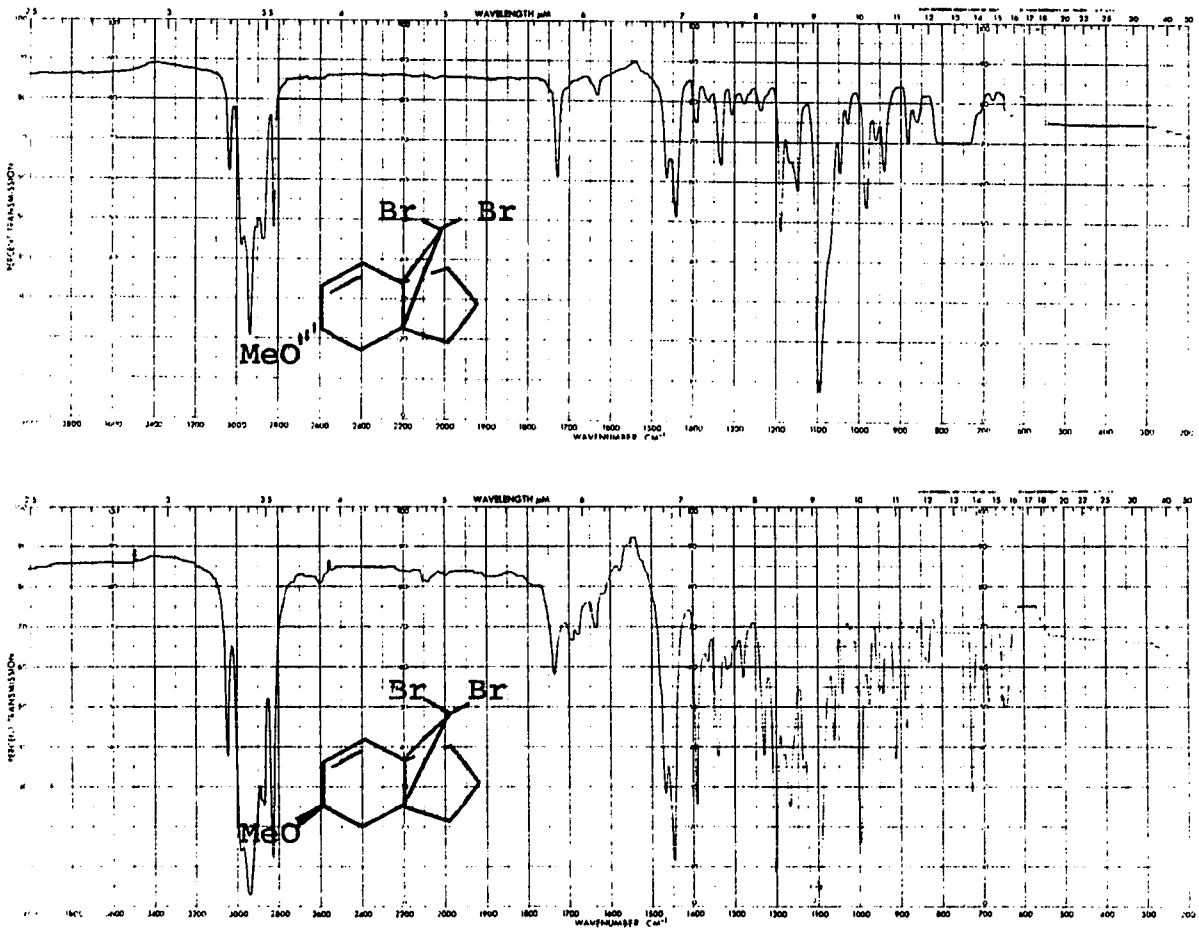


Figure 7. IR Spectra of endo-4-methoxy-10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2-ene (192b, top) and exo-4-methoxy 10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2-ene (192a, bottom)

$C_{11}H_{14}Br_2O$: C, 41.02; H, 4.38; Br, 49.63. Found: C, 41.02, H, 4.22; Br, 49.67.

(b) To a stirring solution of 3.50 g (12 mmol) of 15 in 90 ml of anhydrous MeOH (dried over 4A molecular sieves overnight), was added 2.45 g (12.8 mmol) phenylselenenyl chloride[120] under N_2 at room temperature. The initially red solution turned light green immediately and white solids gradually precipitated. After stirring for 3 hr, MeOH was stripped off and the residue was diluted with ethyl acetate and washed subsequently with water and saturated NaCl solution, dried and concentrated to yield a white solid which was dissolved in 55 ml freshly distilled THF (over $LiAlH_4$) and cooled in ice; 12.5 ml of 30% H_2O_2 was then added dropwise at 0-4°C. Stirring was continued for 5 hr. The resulting mixture was diluted with H_2O and extracted with ethyl acetate. The combined extracts were washed with H_2O, saturated NaCl solution and then dried over $MgSO_4$. Concentration gave a light green oil which was chromatographed (silica gel, hexane as eluent) to give 2.95 g (77%) of 192a.

exo-4-Methoxy 10-bromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene (193) (Fig. 8)

To 714 mg (2.22 mmol) of dibromide 192a was added 810 mg (2.22 mmol) of (n-Bu)$_3$SnH and the resulting mixture stirred for 11 hr at room temperature. The reaction mixture

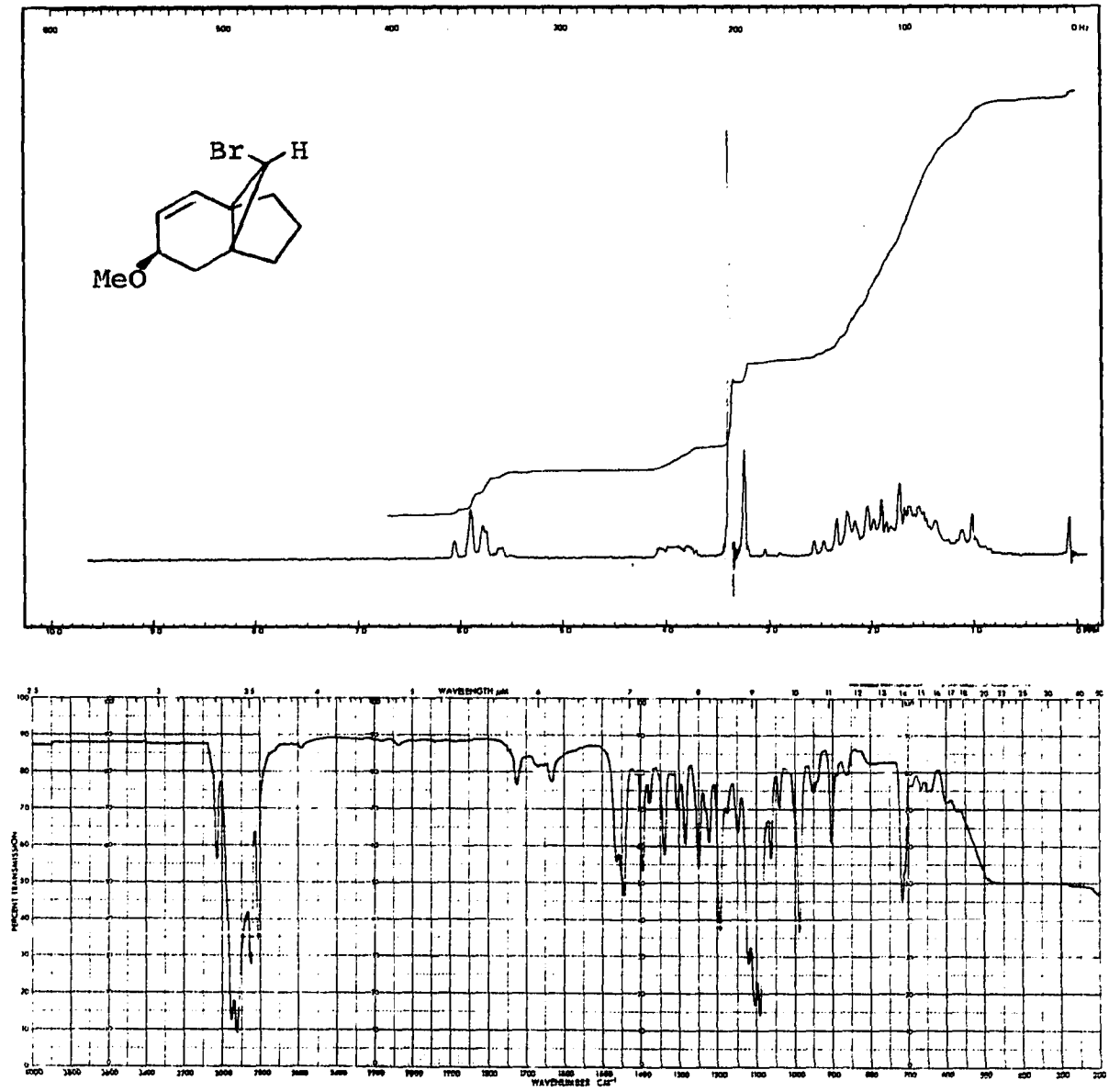


Figure 8. ^{1}H NMR and IR spectra of exo-4-methoxy 10α-bromo-tricyclo[4.3.1.$0^{1,6}$]deca-2-ene (193a)

was then chromatographed on a silica gel column (hexane as eluent) to give 485 mg (90%) of a mixture of two isomeric monobromide 193. ^{L}H NMR: δ6.35-5.5(m), 3.85~3.35(m), 3.50 (s), 3,32(s), 3.25(s), 3.15(s), 2.40~0.9(m). A pure sample of 193a was obtained via silica gel column chromatography (4% ethereal hexane). ^{1}H NMR: δ6.0-5.5(m, 2H), 4.05~3.62 (m, H_4), 3.32(s, 3H), 3.15(s, H_{10}), 2.5~0.8(m, 6H); ^{13}C NMR ($CDCl_3$): δ134.81 (rel. int.: 2.34), 127.01(2.47), 74.23 (2.97), 55.72(2.33), 41.36(1.59), 34.48(2.62), 32.58(2.13), 32.04(2.33), 30.74(1.05), 29.60(1), 20.94(2.28); IR(CCl_4): 3025(C=C-H), 1630(C-C), 1120, 1105, 1090, 715 cm^{-1}. Anal. Calc'd for $C_{11}H_{14}BrO$: m/e 242.0307. Found: m/e 242.0318.

endo-3,4-Epoxy-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (194) (Fig. 9)

To a solution of 7.0 g (23.5 mmol) of 15 in 20 ml $CHCl_3$ was added, at 0°C, a solution of 5.0 g (24.5 mmol) of m-chloroperbenzoic acid (m-CPBA) in 60 ml $CHCl_3$. After stirring the reaction mixture for 4 hr at room temperature, a dilute $NaHSO_3$ solution was added to destroy any excess m-CPBA. After dilution with ether, the organic phase was washed with a 5% NaOH solution, a saturated NaCl solution, and dried over K_2CO_3. Filtration and evaporation of solvent afforded a white solid identified as 194 (7.2 g, 98%), mp 102-104°C; ^{1}H NMR: δ2.9(br s, 2H), 2.6-1.4(m, 10H), IR

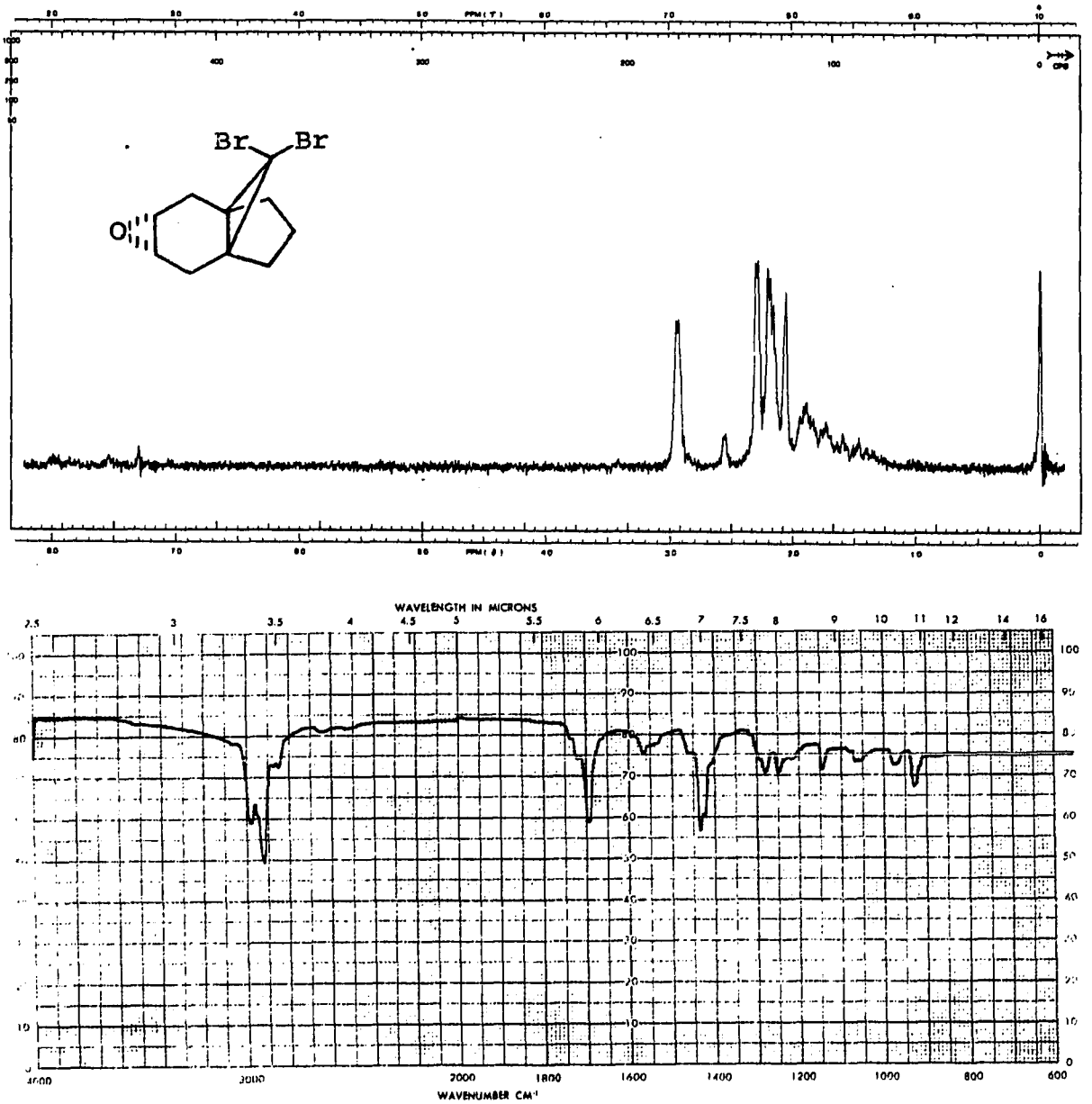


Figure 9. ^{1}H NMR and IR spectra of endo-3,4-epoxy-10,10-dibromotricyclo[4.3.1.0^{1,6}]decane (194)

(CCl_4): 1190 cm^{-1}(C-O-C). Anal. Calc'd for $C_{10}H_{12}Br_2O$: m/e 305.9255. Found: m/e 305.9256.

endo-10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (192d) (Fig. 4, 5)

A solution of 0.24 ml (3.6 mmol) of Me_2NH in 5 ml THF was cooled to 0°C in a flame-dried flask. To this was added 2.7 ml (3.6 mmol) of 1.33 M n-BuLi (previously titrated with diphenylacetic acid). After stirring the resulting mixture for 15 min, a solution of 0.74 g (2.4 mmol) of the above-synthesized epoxide in 10 ml THF was added dropwise via syringe. After completion of the addition, stirring was continued for 5 min, after which the mixture was diluted with ether, washed with 1N HCl and then a saturated NaCl solution, dried over Na_2CO_3, filtered, and stripped of solvent. The residue was chromatographed on a silica gel column. Elution with 40% ethereal hexane afforded 0.16 g starting epoxide; further elution with 67% ethereal hexane provided 0.45 g (78%) of 192d, mp 88.5-89-5°C; ^1H NMR: δ5.98(center of apparent d with 2 Hz splitting, 2H), 4.15 (m, H_4), 2.5-1.5(m, 9H); ^{13}C NMR($CDCl_3$): δ131.34(rel. area: 2.00), 130.26(2.78), 74.78(1.09), 63.25(1.96), 56.53(1.13), 40.17(1.37), 39.90(2.25), 35.35(3.86), 32.69(1), 26.68(2.50); IR(KBr): 3500-3100 (-OH), 3020, 2920, 1630, 1430, 1010 cm^{-1}. Anal. Calc'd for $C_{10}H_{12}Br_2O$: C, 39.00; H, 3.95; Br, 51.88. Found: C, 39.17; H, 3.93; Br, 51.83.

endo-4-Methoxy-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene (192b) (Fig. 6,7)

To a suspension of 23.5 mg NaH (50% in oil, 2 equiv.) 192d in 1 ml DMF, was added a solution of 150 mg (0.49 ml) in 192d in 7 ml DMF under N_2 at room temperature. The solution turned brownish grey. Excess MeI (2 ml) was then added, whereupon an exothermic reaction occurred. The resulting mixture was stirred overnight, whereafter H_2O was added. Work up afforded 155 mg of light yellow oil which was purified by thin layer chromatography (5% ethereal hexane). The first band (R_f=0.8) was mineral oil from NaH, while the 2nd band (R_f=0.2, 107.5 mg) was 192b (68%), mp 29-30°C. ^{1}H NMR: δ5.98(AB quartet, J=21 Hz, 2H), 3.8-3.52(m, H_4), 3.26(s, 3H), 2.62-1.43(m, 6H); ^{13}C NMR ($CDCl_3$): δ130.64 (rel. int.: 3.18), 129.18(3.51), 71.70(3.67), 57.07(1.27), 56.20(1.99), 40.22(1.50), 39.63(2.77), 38.81(1.00), 35.18 (3.12), 31.93(2.40), 26.57(3.11); IR(CCl_4): 3035(C=C-H), 2932, 2870, 1632(C=C), 1190, 1150, 1095(C-O), 640 cm^{-1}. Anal. Calc'd for $C_{11}H_{14}Br_2O$: m/e 319.9411. Found: m/e 319.9411.

exo-Tricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (195) (Fig. 10)

A mixture of 50 mg (0.16 mmol) 192a and 118 mg (0.41 mmol) n-Bu_3SnH[121] was heated in an 80°C oil bath for ca. 7 hr. After cooling, the resulting material was chromatog-

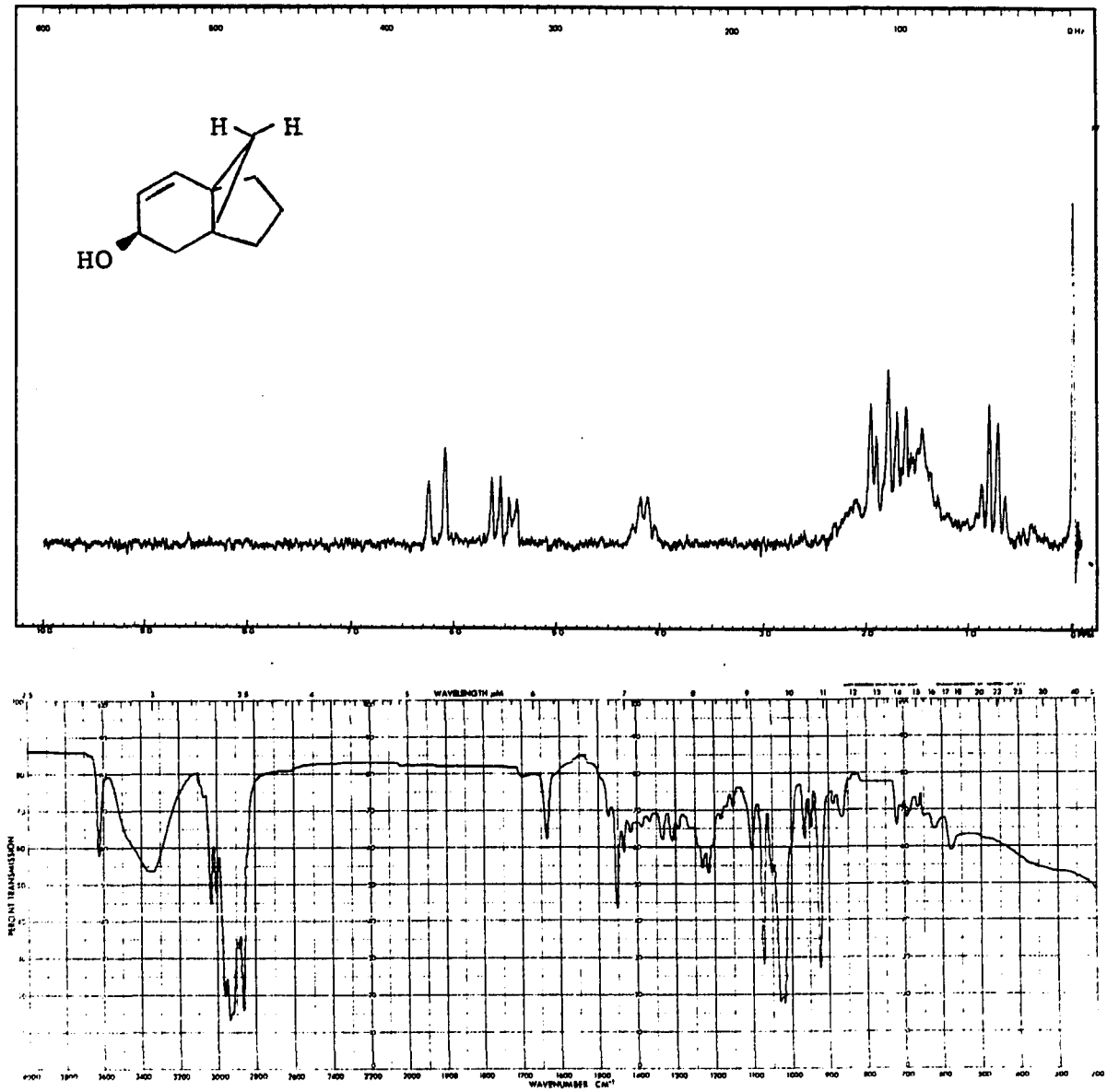


Figure 10. ^{1}H NMR and IR spectra of exo-tricyclo-[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (195)

raphed on a preparative thin layer plate, utilizing 95% ethereal hexane as the developing solvent. Obtained were 19 mg (81%) of 195; ^{1}H NMR: δ6.60(d, H_2, J=10 Hz), 5.48 (dd, H_3, J=5, 10 Hz), 4.15(q, H_4, J=5 Hz), 2.3-1.1(m, 9H), 0.76(center of AB quartet, $2H_{10}$, J=5 Hz); IR(CCl_4): 3630 (s, free -OH), 3595-3170(br, -OH), 3040(C=C-H), 3010 (C=C-H), 1640(C=C), 1030(C-O) cm^{-1}. Anal. Calc'd for $C_{10}H_{14}O$: m/e 150.1045. Found: m/e 150.1042. Lanthanide-induced shifts (LIS) for H_A demonstrated the exo stereochemistry of -OH (Table IV).

Tricyclo[4.3.1.0^{2,6}]deca-2-ene-4-one (197) (Fig. 11)

To a stirring solution of 38.5 mg (0.26 mmol) of 195 in 1 ml Et_2O at 0°C, was added 0.17 ml of chromic acid solution (prepared according to Brown[124]). The reaction mixture was stirred for 10 min at 0°C, following which the cooling bath was removed and the solution allowed to stir for an additional 2 hr. The now green solution was diluted with ether, washed with saturated $NaHCO_3$, then saturated NaCl, and dried over $MgSO_4$. Filtration and evaporation gave 25 mg crude yellow oil. Thin layer chromatographic purification (90% ethereal hexane) gave 20.5 mg (54%) 197. ^{1}H NMR (CCl_4): δ7.10(d, H_2, $J_{2,3}$=10 Hz), 5.56(d, H_3), 2.82(d, H_{5endo}, $J_{5exo,5endo}$=18 Hz), 2.32(d, H_{5exo}), 2.1-1.3(m, 6H), 1.17(d, H_{10A}, $J_{10A,10B}$=5 Hz), 0.37(d, H_{10B}); IR(CCl_4):

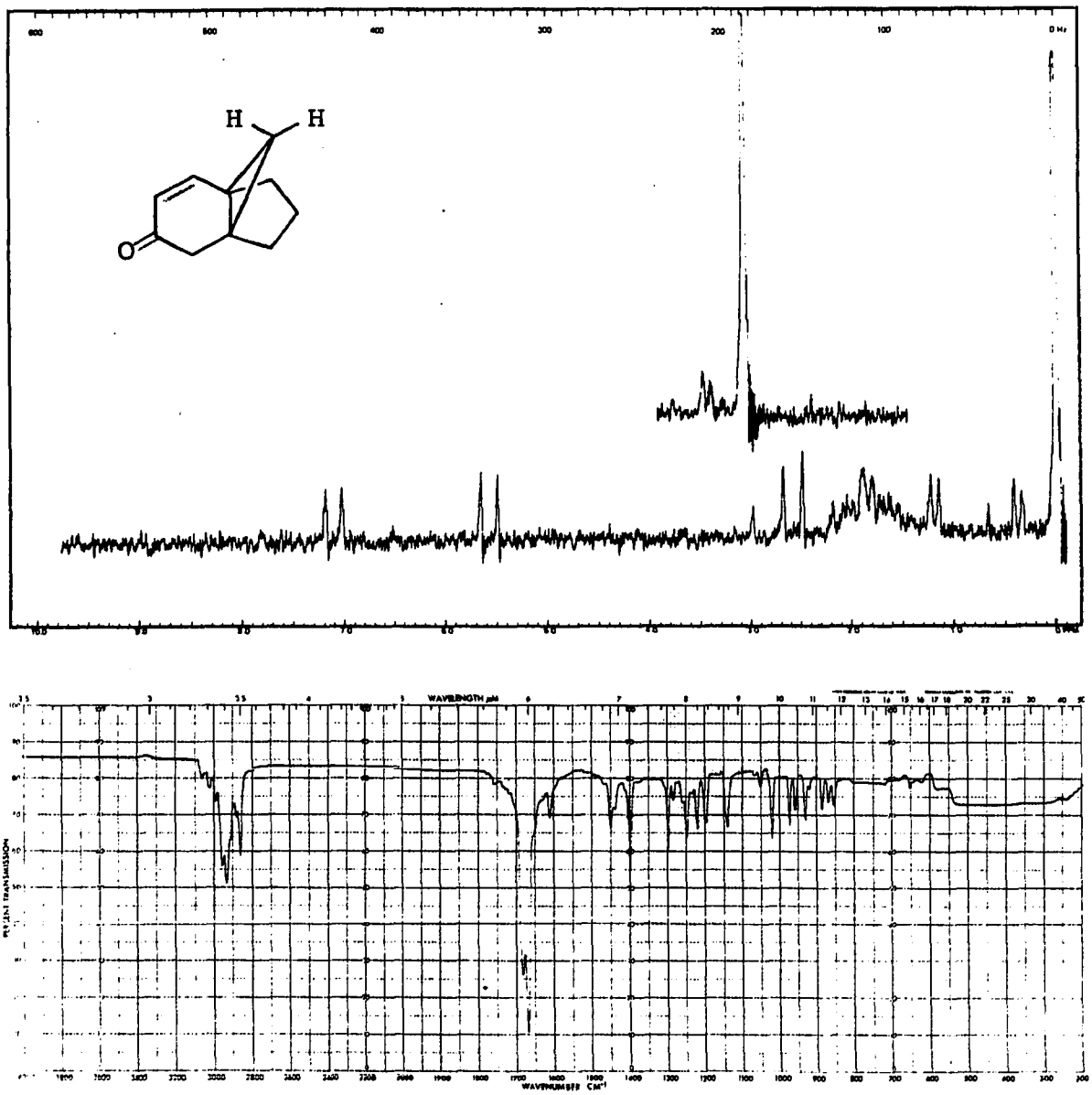


Figure 11. ^{1}H NMR and IR spectra of tricyclo[4.3.1.$0^{1,6}$]-deca-2-ene-4-one (197)

3070, 3030(C=C-H), 1680, 1660, 1610, 1400 cm^{-1}. Anal. Calc'd for $C_{10}H_{11}O$ (P-1, P not strong enough for exact mass): m/e 147.0810. Found: m/e 147.0804.

4,5,6,7-Tetrahydroindane (199)[150]

Reduction of indane with Li in n-$BrNH_2$ was achieved according to the published procedure[149] to give 61% yield; bp 24.5(2.0 mm); ^1H NMR: δ2.45-1.3(m).

Bicyclo[4.3.0]-1(6)-nonen-2-one (200)[151]

Ozonolysis of 199 in MeOH at -78°C followed by refluxing with Na_2CO_3 in MeOH according to the published procedure[151] gave 200 in 64% yield; bp 80.5-85°C(0.9 mm); ^1H NMR: δ2.92-1.5(m).

2-Methylenebicyclo[4.3.0]-1(6)-nonene (205) (Fig. 12)

To a suspension of 2.95 g (8.26 mmol) of methyltriphenylphosphonium bromide in 15 ml freshly distilled THF (over LAH) was added 5.1 ml of n-BuLi (8.26 mmol Aldrich) at room temperature. A clear red solution was obtained, to which after stirring for 20 min, was added 100 mg methyltriphenylphosphonium bromide to ensure no excess n-BuLi was present in the reaction mixture. The resulting mixture was cooled to 0°C followed by addition of 1 g (7.40 mmol) of 200 in 5 ml THF; a white precipitate was immediately formed. The reaction mixture was then gradually warmed up to room temperature and allowed to stir overnight. Solvent evaporation gave a residue which was diluted with hexane and

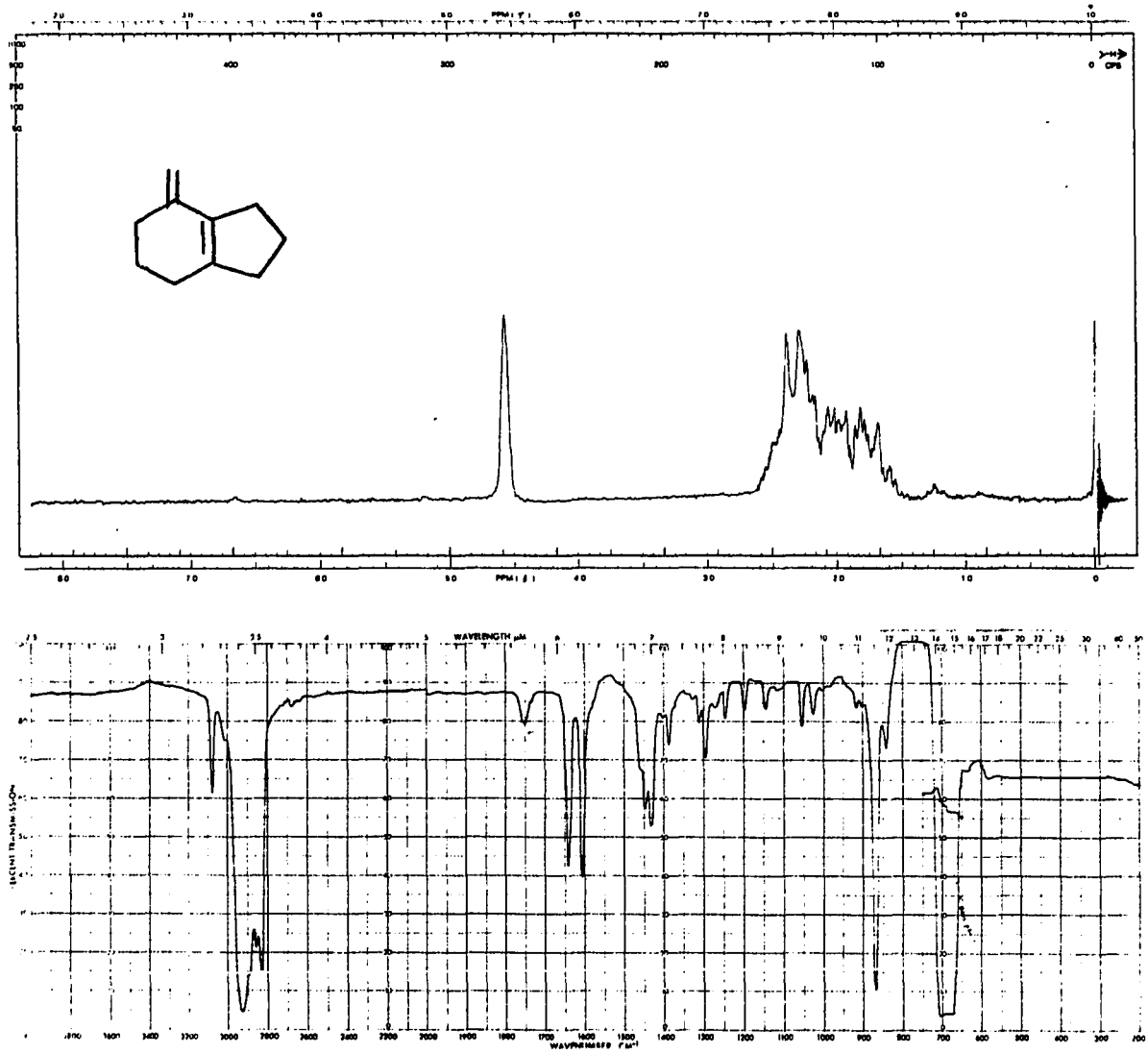


Figure 12. ^{1}H NMR and IR spectra of 2-methylene-bicyclo-[4.3.0]-1(6)-nonene (205)

filtered through a short column (silica gel). Concentration gave 951 mg (96%) of colorless oil (205); ^{1}H NMR: δ4.57 (unresolved s, 2H), 2.65-1.4(m, 12H); IR(CCl_4): 3080, 2930, 2860, 2830, 1640, 1604 cm^{-1}. Anal. Calc'd for $C_{10}H_{14}$: m/e 134.1096. Found: m/e 134.1092.

Bicyclo[4.3.0]-1(6)-nonen-2-ol (201) (Fig. 13)

To a suspension of 430 g (1.10 mmol) of $LiAlH_4$ in 30 ml ether was added 3 g (2.21 mmol) of 200 in 35 ml of ether at 0°C. The resulting mixture was stirred for 15 min at 0°C and then quenched with 3 ml of distilled water and dried over $MgSO_4$. Filtration and solvent evaporation gave 2.92 g (96%) of colorless oil (201); ^{1}H NMR: δ4.02(br s, 1H), 3.02-1.23(m, 7H); IR(CCl_4): 3610(s, free -OH), 3580-3100 (br, -OH), 2940, 2840, 1443, 1090, 1053, 1015 cm^{-1}. Anal. Calc'd for $C_9H_{14}O$: m/e 138.1045. Found: m/e 138.1040.

10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]decan-2-ol (202) (Fig. 14)

To a suspension of 1.23 g (10.96 mmol) of t-BuOK in 25 ml hexane (MCB, pesticide quality) was added a solution of 756.5 mg (5.48 mmol) 201 and 0.48 ml (5.48 mmol) bromoform in 25 ml hexane at -78°C. The solution turned light brown. The resulting reaction mixture was gradually warmed up to room temperature and stirred overnight, after which the mixture was diluted with ether, washed with H_2O (until neutral), saturated NaCl solution, and dried over $MgSO_4$.

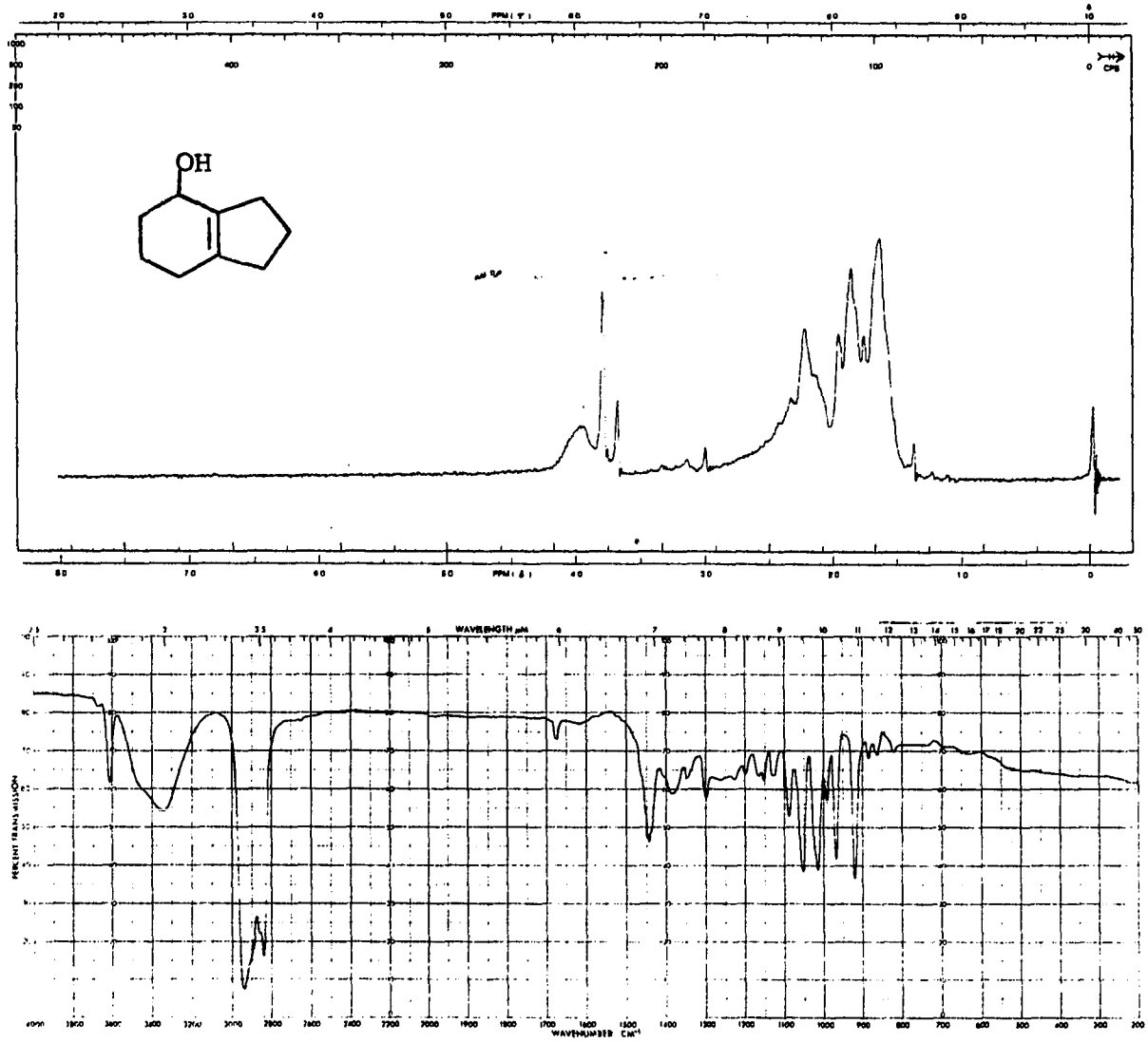


Figure 13. ^{1}H NMR and IR spectra of bicyclo[4.3.0]-1(6)-nonen-2-ol (201)

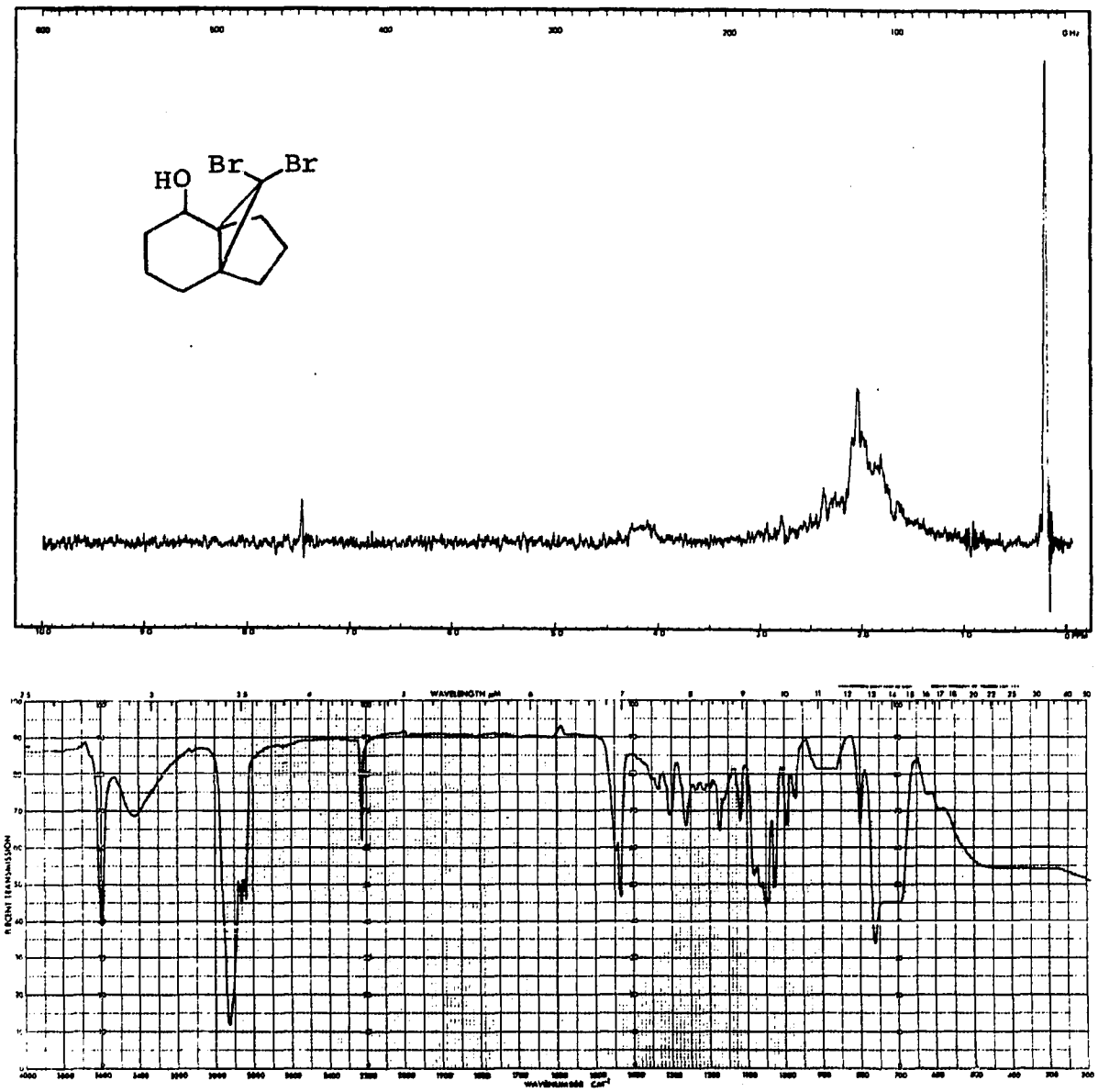


Figure 14. ^{1}H NMR and IR spectra of 10,10-dibromotricyclo-[4.3.1.$0^{1,6}$]deca-2-ol (202)

Filtration and concentration gave 1.07 g of brown oil which was chromatographed on a dry column (54 x 4 cm, ICN Silica Gel Woelm Activity III/30 mm containing 0.5% inorganic fluorescent indicator for 254 nm UV light. Elution with 20% ethereal hexane provided 276 mg (R_f=0.28, brown oil) of a mixture of 202 and 203 which was recrystalized from CCl_4 to afford white crystals of 202 in 16% yield, mp 87-88.5°C; ^1H NMR($CDCl_3$): δ4.1-3.8(m), 2.9-0.8(m, with a maximum at 1.85); IR(CCl_4): 3600(s, free -OH), 3540-3140(br, -OH), 2930, 2860, 2840, 1170, 1120, 1050, 1025, 760 cm^{-1}. Anal. Calc'd for $C_{10}H_{12}Br_2O$: m/e 305.9255. Found: m/e 305.9276.

10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-one (203) (Fig. 15)

(a) In a 100 ml round bottom flask fitted with a reflux condenser was suspended 138.2 mg (0.64 mmol) of pyridinum chlorochromate[152] and 10.6 mg of NaOAc (as a buffer due to the slightly acidic character of the reagent) in 3 ml CH_2Cl_2. Compound 202 (132.5 mg, 0.43 mmol) in 3 ml of CH_2Cl_2 was added in one portion to the stirring solution. After 2 hr, 15 ml of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly 3 times with 15 ml portions of anhydrous ether, whereupon it became a black granular solid. The combined organic solution was passed through a short florisil column, after which concentration gave 42.5 mg (32%) of a white solid, 203, mp 69-71.5°C; ^1H NMR: δ2.65-1.03(m);

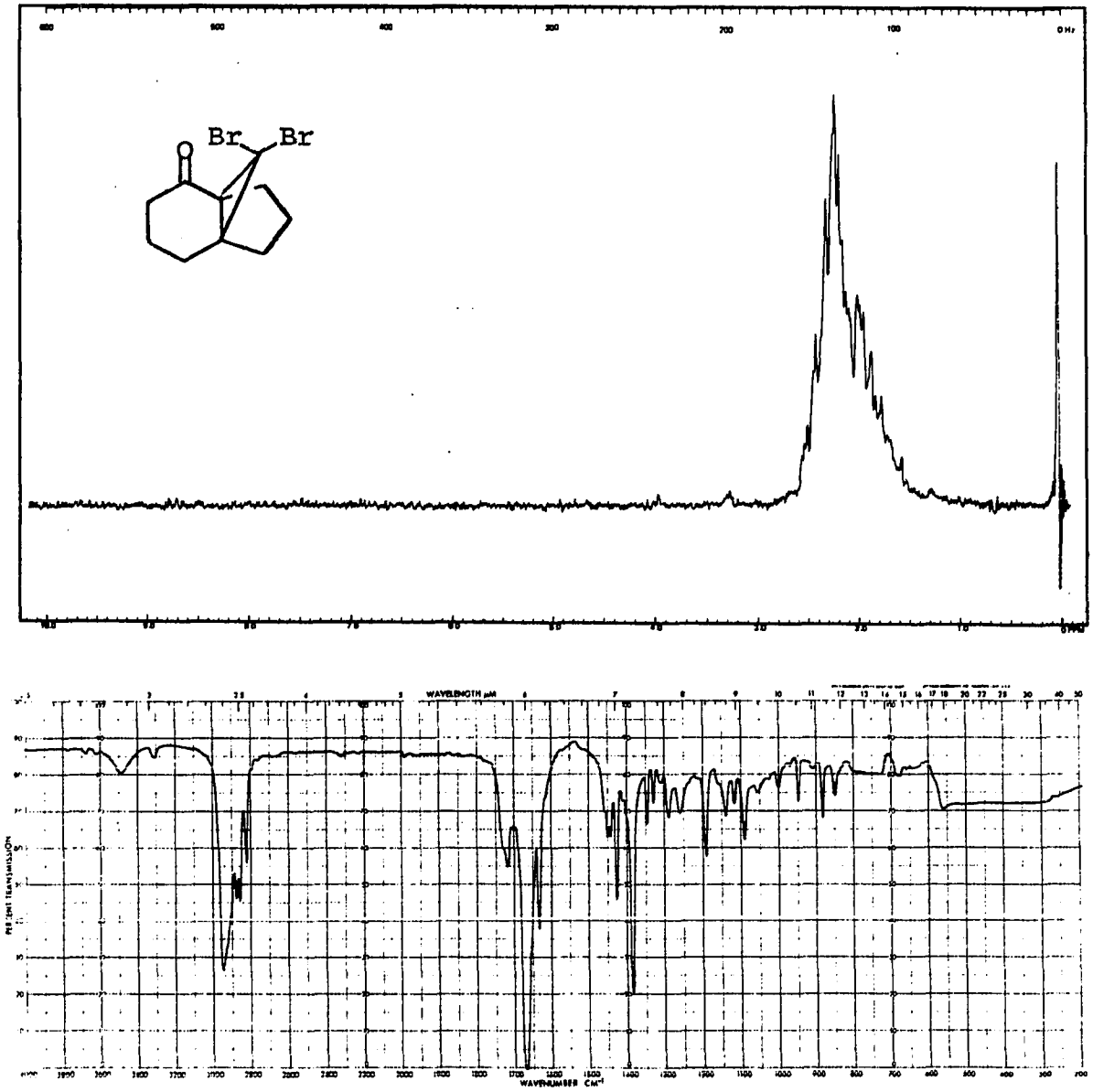


Figure 15. ^{1}H NMR and IR spectra of 10,10-dibromotricyclo-[4.3.1.$0^{1,6}$]deca-2-one (203)

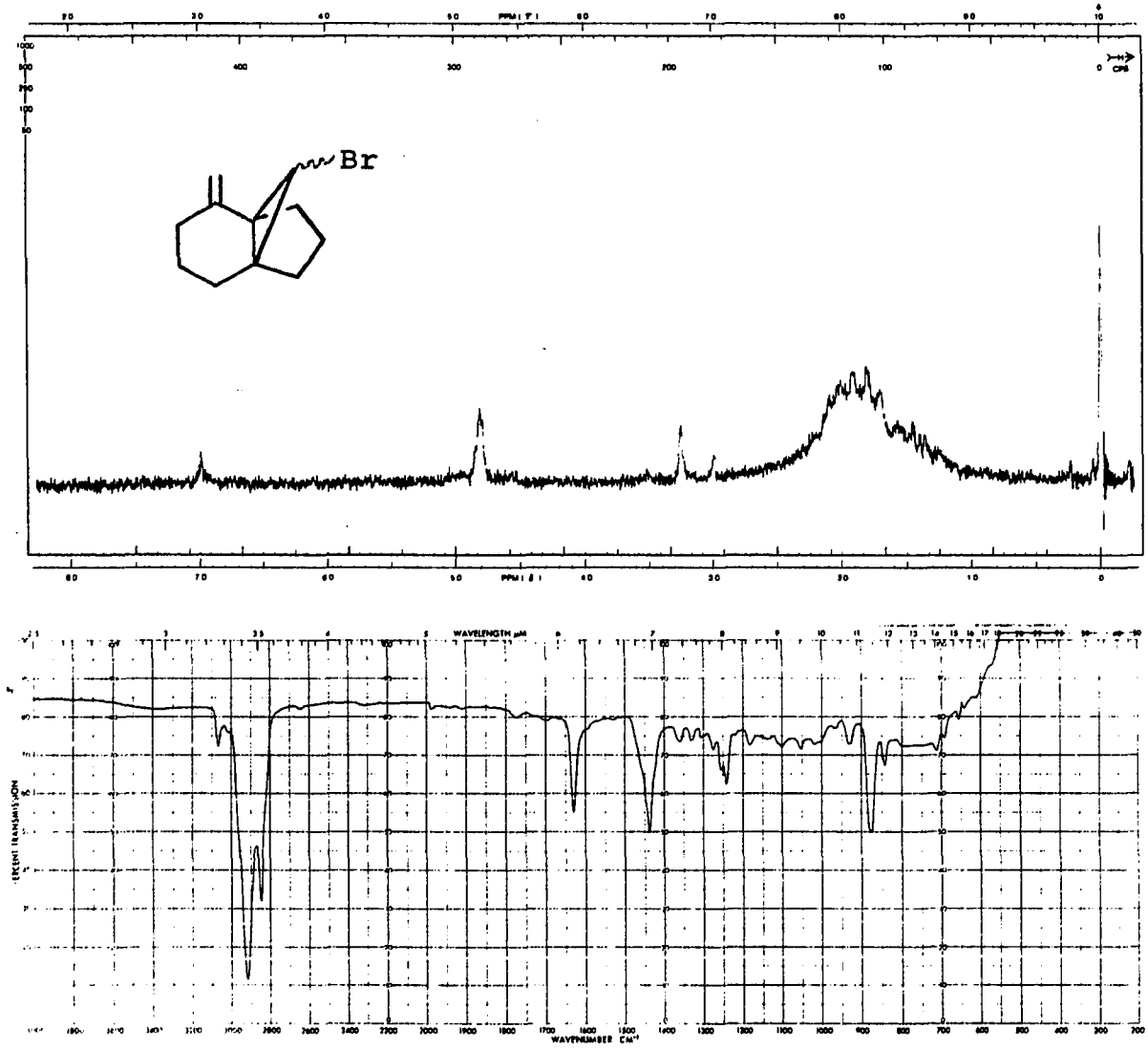


Figure 16. ^{1}H NMR and IR spectra of 2-methylene-10-bromotricyclo[4.3.1.$0^{1,6}$]decane (204)

IR(CCl_4): 2950, 1710, 1030, 730 cm^{-1}. Anal. Calc'd for $C_{10}H_{12}Br_2O$: m/e 305.9255. Found: m/e 305.9253.

(b) To a suspension of 4.74 g (40 mmol) of t-BuOK in 90 ml hexane was added a solution of 2.92 g (20 mmol) of 201 and 1.85 ml (20 mmol) of bromoform at -78°C. The usual work up afforded 4.5 g of brown oil which was oxidized with 4.7 g (30 mmol) of pyridinium chlorochromate in 100 ml CH_2Cl_2 according to the method described above. The usual work up gave 3.07 g of yellow oil which was chromatographed on a silical gel dry column to afford 1.70 g of 203 (34% overall yield), and 0.7 g of 201 (76% conversion in the first step).

2-Methylene-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (206) (Fig. 17)

(a) Attempted synthesis of 206 with Oshima's reagent.[126] A suspension of zinc dust[126] (0.59 g, 9.0 mmol) and 0.52 g (3.0 mmol) of CH_2Br_2 in 10 ml of freshly distilled THF (from $LiAlH_4$) was treated with $TiCl_4$ (0.24 ml, 2.2 mmol, Fisher) at room temperature. Instantaneous reaction occurred with evolution of heat and rapid color change to dark brown. After 15 min, 203 (616 mg, 2.0 mmol) in 20 ml of THF was added dropwise and the resulting mixture was stirred at room temperature for 24 hr. The solution was then diluted with water, extracted with ether

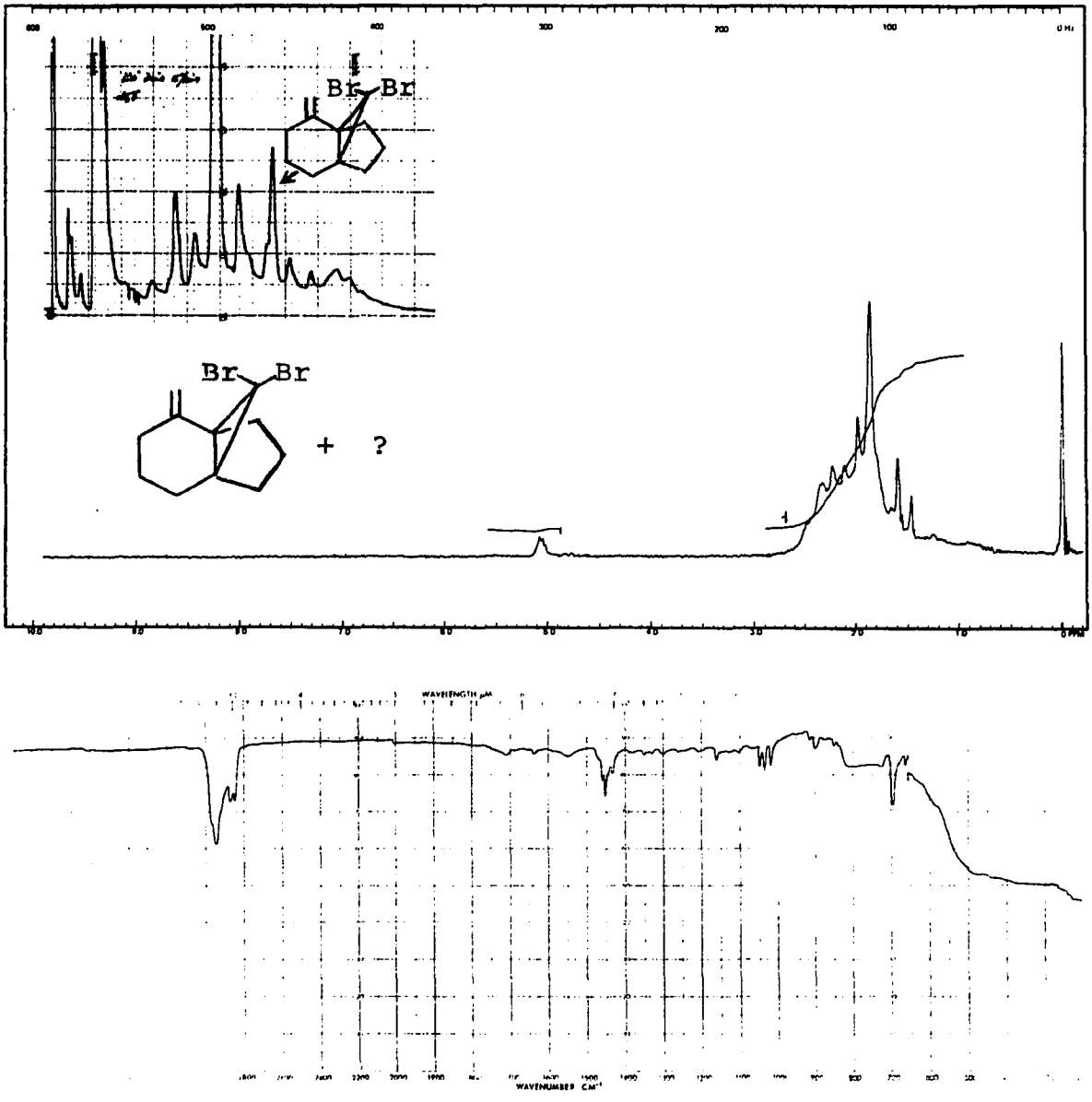


Figure 17. ^{1}H NMR and IR spectra of a mixture of 2-methylene-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (206) and its impurities

and the combined ethereal solution washed with H_2O, saturated NaCl solution, and dried over $MgSO_4$. Concentration afforded 1.2 g of yellow oil which was diluted with hexane and filtered through a short silica gel column. Concentration gave 81 mg of light yellow oil which was identified as 2-methylene-10-bromotricyclo[4.3.1.$0^{1,6}$]decane 204 (18%). (Fig. 16); ^{1}H NMR: δ4.8(br s), 3.25(s), 3.0(s), 2.7-1.1(m); IR(CCl_4): 3070(C=C-H), 2910, 2850, 1630(C=C), 1440, 1240, 875, 840 cm^{-1}. Anal. Calc'd for $C_{11}H_{15}Br$: m/e 226.0358. Found: m/e 226.0355.

(b) Dibromocarbene addition to 205 To a solution of 222 mg (1.66 mmol) 205 and 1.45 ml bromoform (16.6 mmol) in 15 ml hexane was added 6.37 ml (16.6 mmol) MeLi at -78°C. The reaction flask was wrapped with aluminum foil to avoid any light-induced radical reaction.[152] The resulting mixture was gradually warmed up to room temperature and stirred overnight (17 hr). After the usual work up, filtration and concentration afforded 235 mg of yellow oil. Thin layer chromatographic purification gave a mixture of (206) and a highly brominated uncharacterized material (R_f=0.71, 186.5 mg) which has a shorter retention time than 206 on the GLC-mass spectrometer (column B). Further purification of 206 was not successful. The following spectral data were obtained from the above mixture: ^{1}H NMR

δ5.05(m), 2.81-1.1(m, with three maxima at 1.85, 1.6, 1.46). GLC-mass: m/e 308.10(P+4, % rel. area: 0.96), 306.10 (P+2, 2.18), 304.14(P, 0.91), 227.04(P+2-Br, 31.15), 225.10(P-Br, 28.83), 146.14(P-2Br, 41.89), 116.94 (P-187, 72.46), 104.96 (P-199, 32.31), 90.90(P-213, 100), 76.94(P-227, 47.15).

exo-4-Methoxy-10-bromo-10-trimethyltintricyclo[4.3.1.$0^{1,6}$]-deca-2-ene (207a, 207b) (Fig. 18, 19)

A flame dried 50 ml three-necked round bottom flask was charged with 2.05 g (6.35 mmol) 192a and 100 ml freshly distilled THF (from $LiAlH_4$) under nitrogen. After the mixture had been cooled to -100±5°C (liq. N_2-Et_2O slurry), 4.37 ml (1.1 equiv.) of 1.6 M n-BuLi was added dropwise along the edge of the flask. After the mixture had stirred for 25 min at -100±5°C, there was added a solution of 1.39 g (1.1 equiv.) of Me_3SnCl dissolved in 50 ml THF. The mixture was stirred for an additional hour, and then allowed to warm to room temperature (which took another hour). The solvent was removed under reduced pressure and the residue was diluted with 60 ml of hexane and washed sequentially with water, 0.5 N HCl, water and saturated NaCl, and then dried over $MgSO_4$. Filtration and evaporation gave 2.35 g of light yellow oil which was chromatographed on a silica gel column (45 x 2 cm) using a mixture of ether and hexane as the eluting solvent (50 ml fractions). Fraction 8 contained 1.22 g of 207a and 207b (8% ethereal hexane),

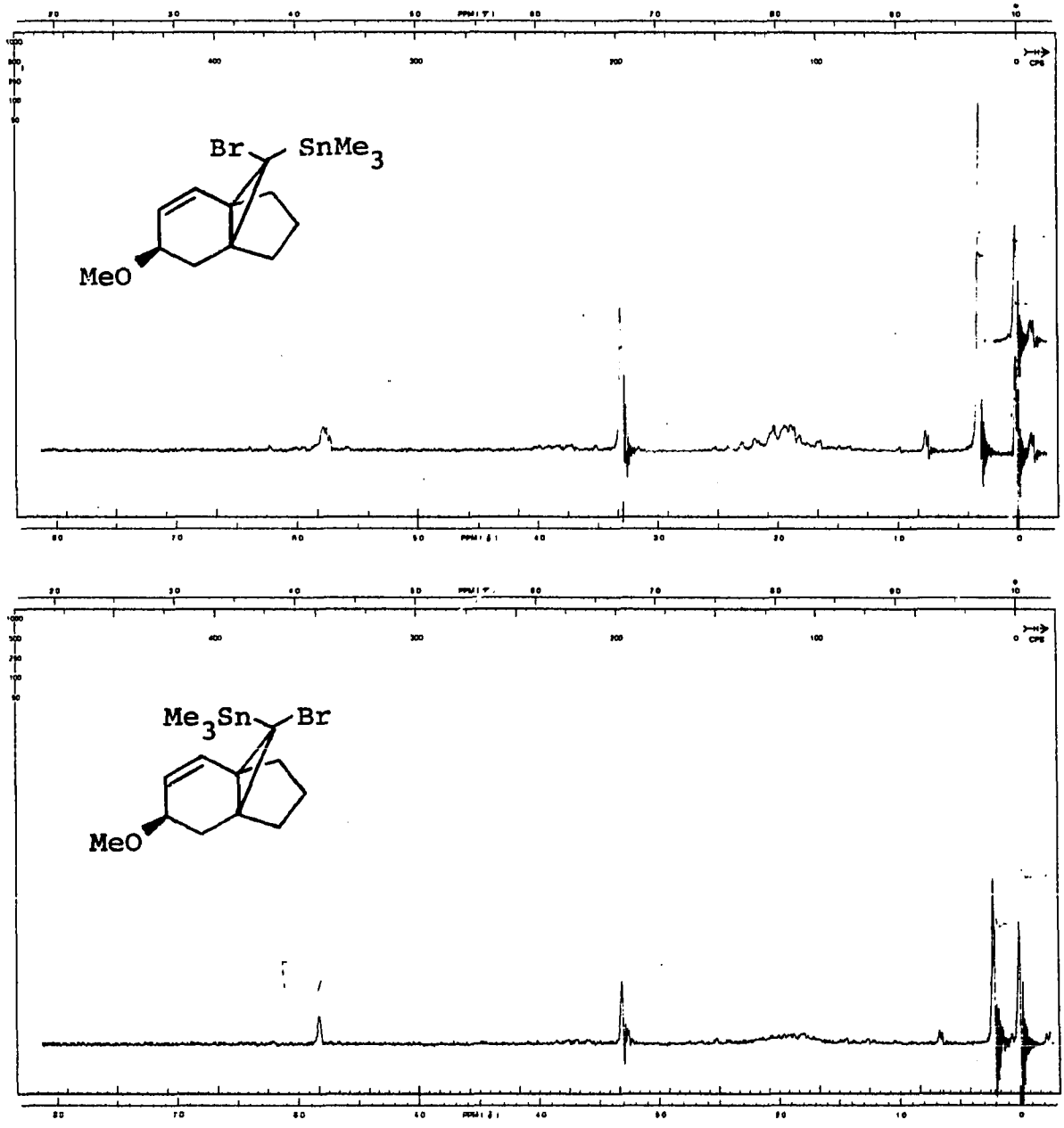


Figure 18. ^{1}H NMR spectra of exo-4-methoxy-10α-bromo-10-trimethyltintricyclo[4.3.1.0^{1,6}]deca-2-ene (207a, top) and its epimer 207b (bottom)

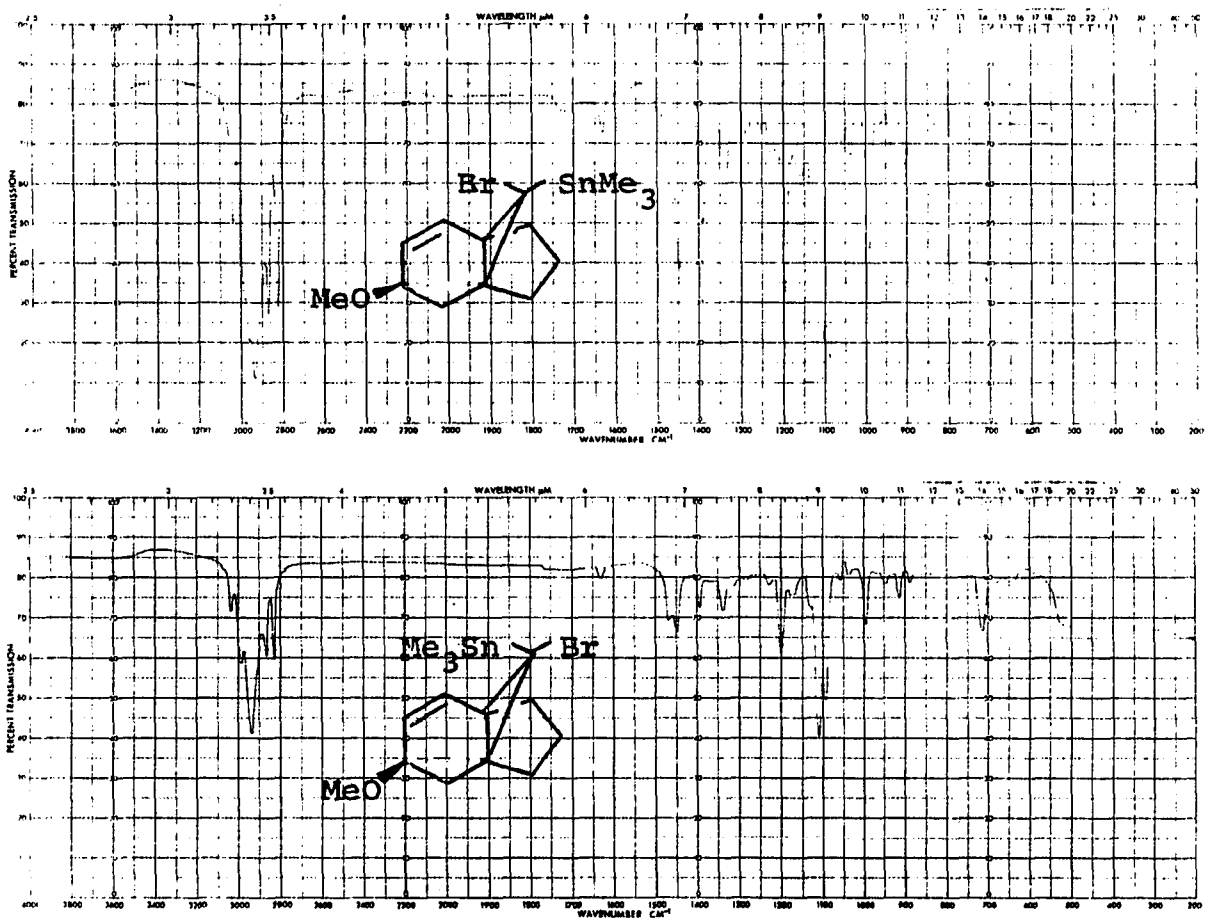


Figure 19. IR spectra of exo-4-methoxy-10α-bromo-10-trimethyltintricyclo[4.3.1.0^{1,6}]deca-2-ene (207a, top) and its epimer 207b (bottom)

while fractions 9 and 10 contained 0.9 g of 207a (16% ethereal hexane). The ratio of 207a to 207b (82.5%) was 1.2:1.0 (NMR). The mixture of 207a and 207b was separated by thin layer (silica gel) chromatography (15% ethereal hexane). The first band with R_f=0.68 was identified as 207b; ^{1}H NMR: δ5.81 (br s, 2H), 3.88-3.45(m, 1H), 3.3(s, 3H), 2.9-1.0(m, 6H), 0.21(s, 9H, Me_3Sn, J(^{117,119}Sn-H 52.55 Hz); IR(CCl_4): 3033(C=C-H), 1630(C=C), 1110, 1092 (C-O) cm^{-1}. Anal. Calc'd for $C_{14}H_{23}BrOSn$; C, 41.41; H, 5.67; Br, 19.72. Found: C, 41.65; H, 5.40; Br, 19.84. The 2nd band with R_f=0.58 was identified as 207a; ^{1}H NMR: δ6.4-5.53(m, 2H, with a maximum at 5.76; this band has the same splitting pattern as does 192a), 403-3.45(m, 1H), 3.29(s, 3H), 2.4-1.06(m, 6H), 0.3(s, 9H, J(^{117,119}Sn-H) 51, 54 Hz); IR(CCl_4): 3038(C=C-H), 1632(C=C), 1110, 1090 (C-O) cm^{-1}. Anal. Calc'd for $C_{14}H_{23}BrOSn$: C, 41.41; H, 5.67; Br, 19.72. Found: C, 41.69; H, 5.35; Br, 19.89.

endo-4-Methoxy-10-bromo-10-trimethyltintricyclo[4.3.1.$0^{1,6}$]-deca-2-ene (208a, 208b) (Fig. 20, 21)

In the manner described for the synthesis of 207a, b, 735 mg (2.28 mmol) 192b in 50 ml THF was allowed to react with 1.1 equiv. n-BuLi (exchange time 30 min at -100°C), followed by addition of 500.7 mg (1.1 equiv.) Me_3SnCl in 35 ml THF. The expected products were obtained in 31% yield, with a syn-Br/anti-Br isomer ratio of 6.8/1 (NMR).

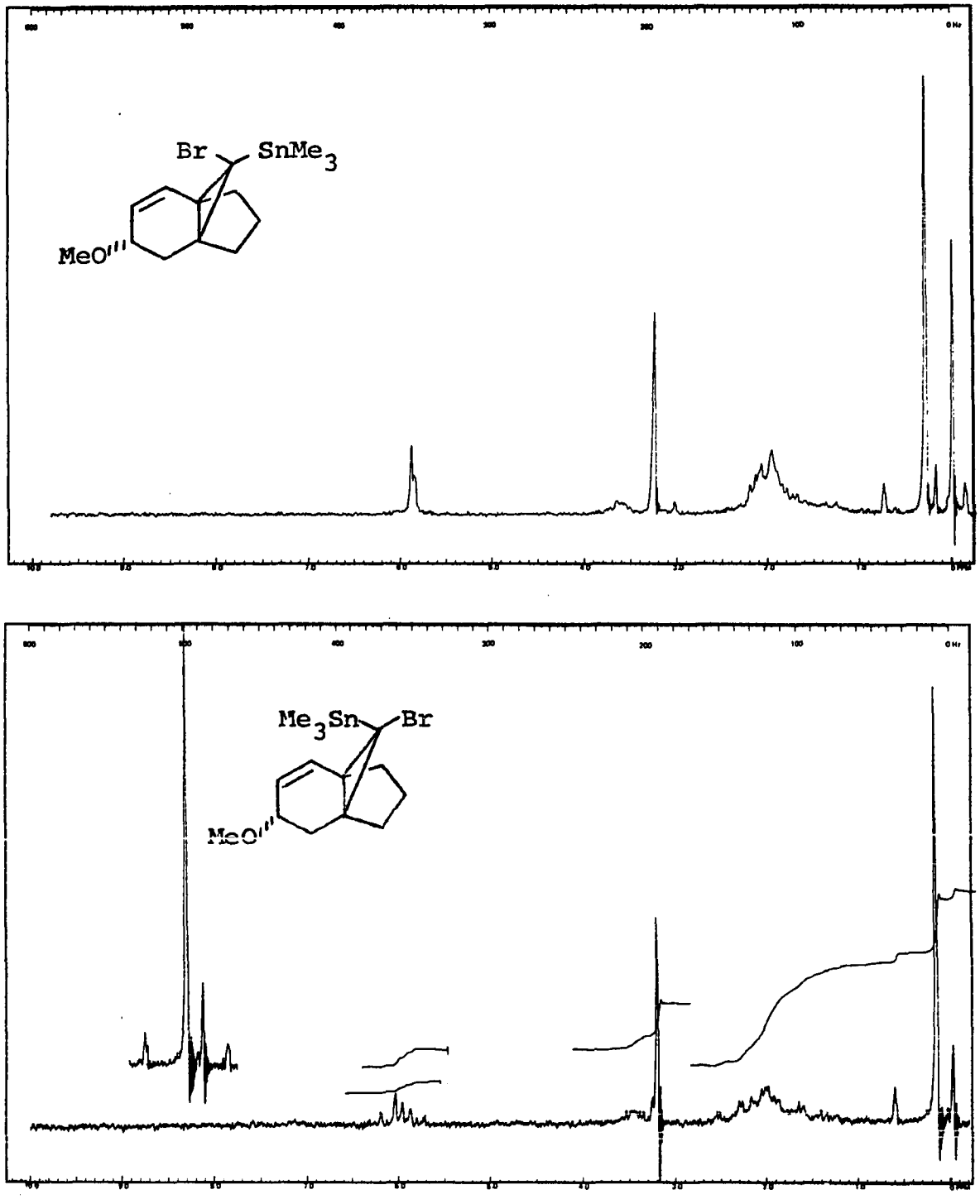


Figure 20. ^{1}H NMR spectra of endo-4-methoxy-10α-bromo-10-trimethyltintricyclo[4.3.1.0^{1,6}]deca-2-ene (208a, top) and its epimer (208b, bottom)

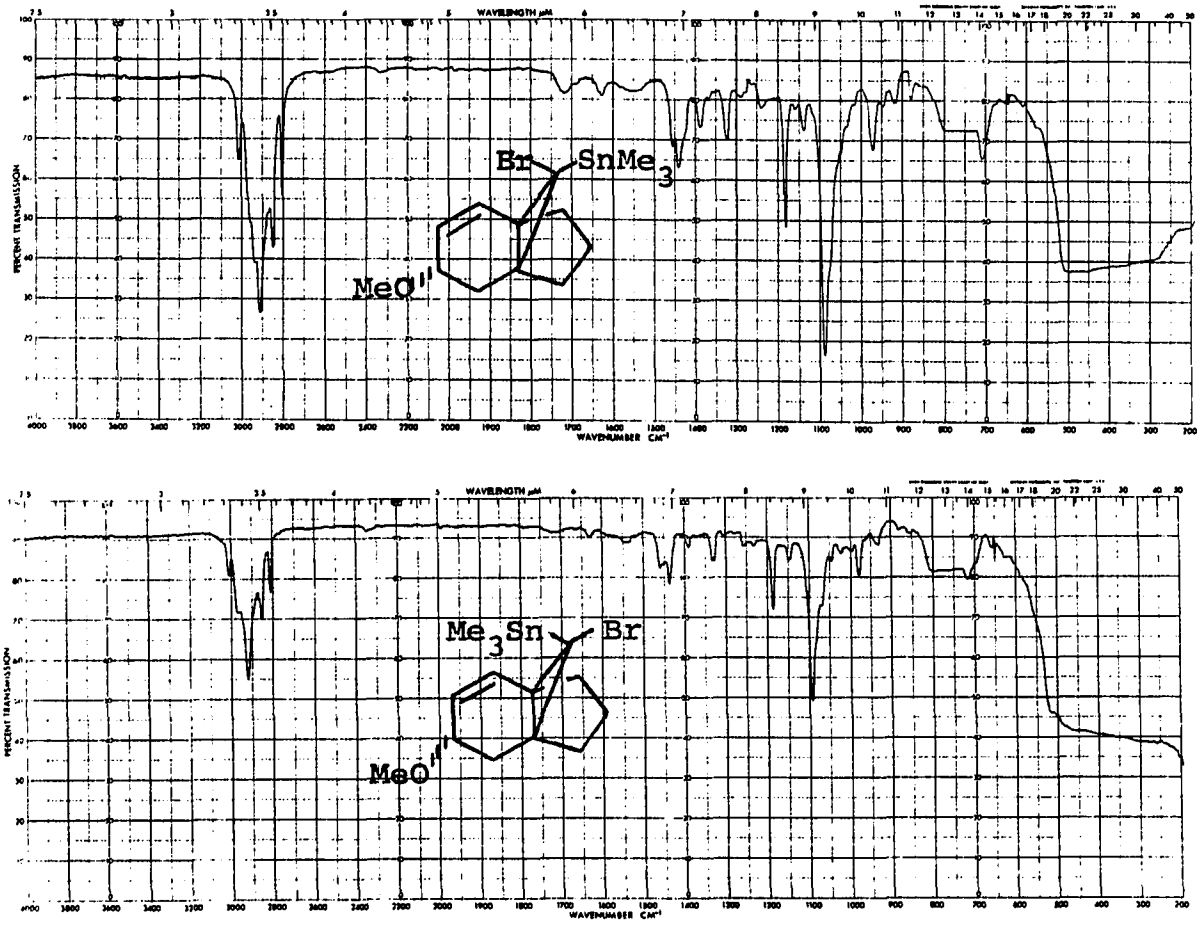


Figure 21. IR Spectra of endo-4-methoxy-10α-bromo-10-trimethyltintricyclo[4.3.1.0^{1,5}]deca-2-ene (208a, top) and its epimer (208b, bottom)

Thin layer chormatographic purification (20% ethereal hexane) gave 250.2 mg (R_f=0.62, 27%) 208a; ^{1}H NMR: δ5.95-5.8(m, with a maxima at 5.88), 3.9-3.4(m, 1H), 3.22(s, 3H), 2.5-1.1(m, 6H), 0.3(s, 9H, J(^{117,119}Sn-H) 51, 54 Hz); IR(CCl_4): 3020(C=C-H), 2810, 1630(C=C), 1090(C-O) cm^{-1}. Anal. Calc'd for $C_{13}H_{20}BrOSn$ (P-15, P not strong enough for exact mass): m/e 386.9720. Found: m/e 386.9717. Compound 208b was isolated in 47% yield (34.5 mg, R_f=0.26); ^{1}H NMR: δ6.25-5.70(m, 2H), 3.65-3.22(m, 1H), 3.22(s, 3H), 2.65-1.1 (m, 6H), 0.2(s, 9H, J(^{117,119}Sn-H) 52,55 Hz); IR(CCl_4): 3010 (C=C-H), 2810, 1630(C=C), 1095(C-O) cm^{-1}. Anal. Calc'd for $C_{13}H_{20}BrOSn$ (P-15, P not strong enough for exact mass): m/e 386.9720. Found: m/e 386.9717.

10-Bromo-10-trimethyltintricyclo[4.3.1.0^{1,6}]deca-2,4-diene (209a, 209b) (Fig. 22)

In the manner described for the synthesis of 207a, b, 543 mg (1.87 mmol) 3 in 40 ml THF was allowed to react with 1.1 equiv. of n-BuLi (exchange time 30 min at -100°C), followed by addition of 410.4 mg (2.06 mmol) Me_3SnCl in 40 ml THF. The expected products were obtained with a syn-Br/anti-Br isomer ratio of 6.6/1 (NMR). Thin layer chromatographic purification (hexane) gave 34.5 mg (R_f= 0.86, 209b; 4.4%, 210b; 2.7%) of a mixture of 209b and 210b which were not separated (the yields of 209b and 210b were calculated by measuring the peak area of the Me_3Sn-

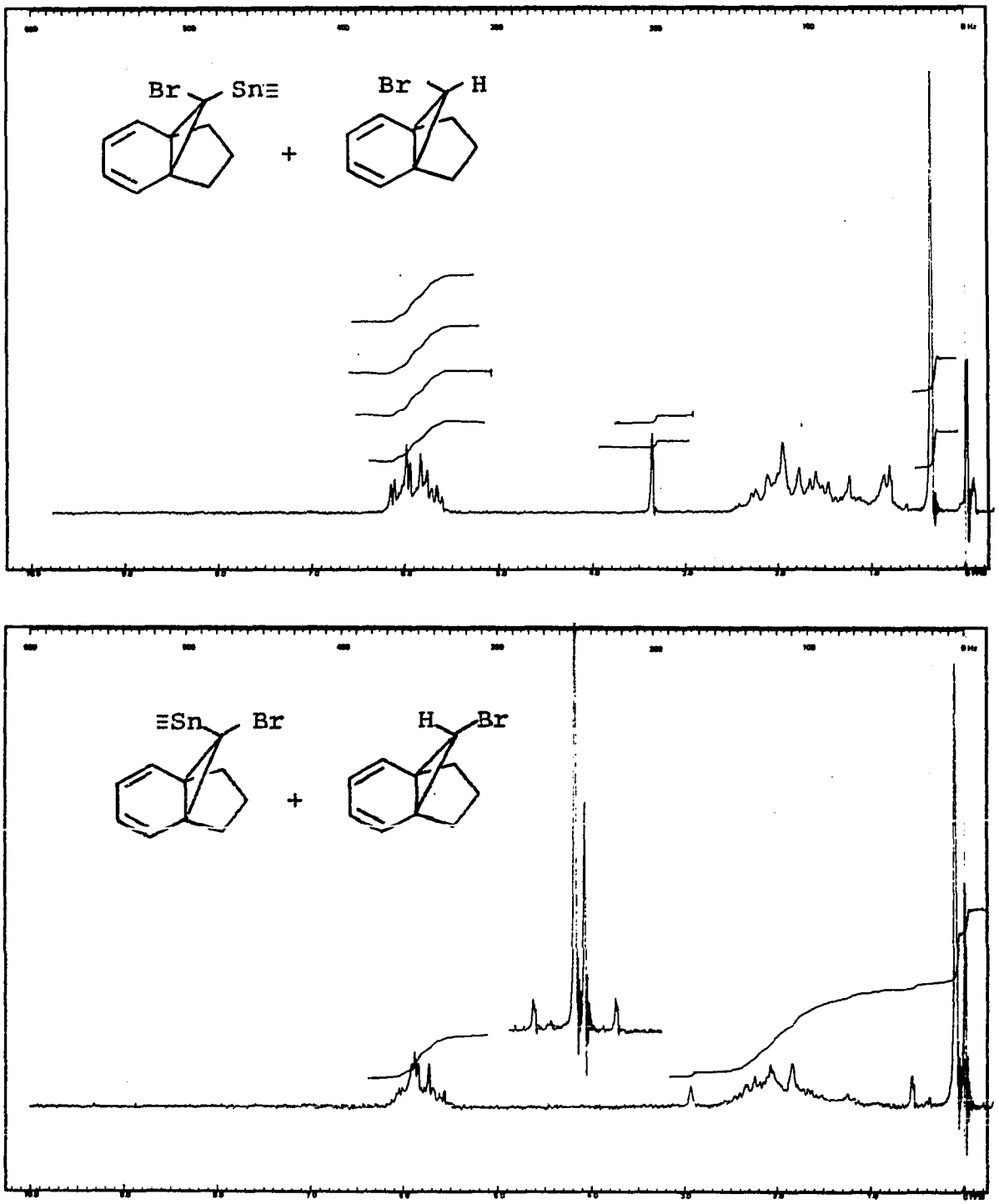


Figure 22. ^{1}H NMR spectra of a mixture of 10α-bromo-10-trimethyltintricyclo[4.3.1.0^{1,6}]deca-2,4-diene (209a, top) and its corresponding monobromide (210a, top) and their epimers (209b, 210b; bottom)

and cyclopropyl hydrogens at δ2.94 and 1.0, respectively). ^{1}H NMR (209b + 210b): δ6.2-5.5(m), 2.94(s), 2.7~1.1(m), 0.1(s, J(^{117,119}Sn-H) 51, 54 Hz). Anal. Calc'd for $C_{12}H_{16}BrSn$ (P-15): m/e 358.9431. Found: m/e 358.9440. A mixture of 209a and 210a (Fig. 3) (R_f=0.57, 345 mg, 209a, 29%; 210a, 56%) was isolated, ^{1}H NMR (209a + 210a): δ6.25-5.5(m), 3.36(s), 2.5-0.7(m), 0.38(s, J(^{117,119}Sn-H) 52, 55 Hz). Anal. Calc'd for $C_{12}H_{16}BrSn$ (P-15): m/e 358.9431. Found: m/e 358.9440.

10,10-Dibromotricyclo[4.3.1.0^{1,6}]deca-8-one (212) (Fig. 23)

A solution of 2.8 g (9.20 mmol) 211 in 20 ml of anhydrous ether was placed in a Parr shaker bottle with 0.28 g 5% Pt/C and hydrogenated (50 psi H_2) for 2 hr. Filtration and concentration gave 2.8 g (9.0 mmol, 98.6%) 212, mp 124.5-125.5; ^{1}H NMR: δ2.76(d, J=20 Hz), 2.34(d, J=20 Hz), 2.13-1.83(m, 4H), 1.75-1.16(m, 4H); IR(CCl_4): 2940, 1750(C=O), 1147 cm^{-1}. Anal. Calc'd for $C_{10}H_{12}Br_2O$: C, 38.96; H, 3.70; Br, 51.95. Found: C, 39.03; H, 3.86; Br, 51.94.

exo-10,10-Dibromotricyclo[4.3.1.0^{1,6}]decan-8-ol (213a) (Fig. 24)

To a suspension of 0.13 g $LiAlH_4$ (95%, Alfa, 3.25 mmol) in 10 ml anhydrous ether, was rapidly added 2 g (6.5 mmol) 212 in 40 ml ether at 0°C; there resulted an exothermic reaction; stirring was continued, for 1 min. followed by

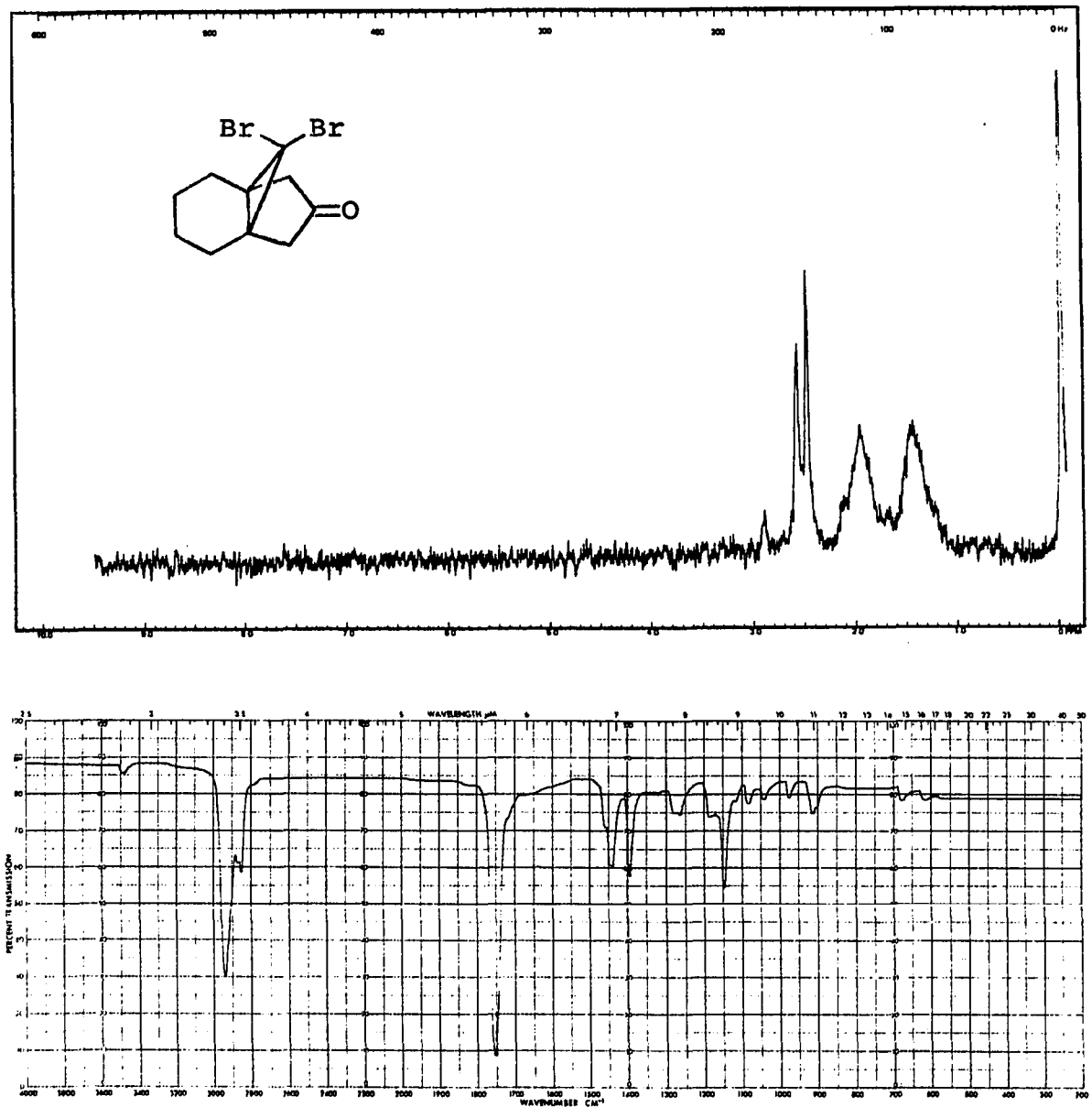


Figure 23. ^{1}H NMR and IR spectra of 10,10-dibromotricyclo-[4.3.1.$0^{1,6}$]deca-8-one (212)

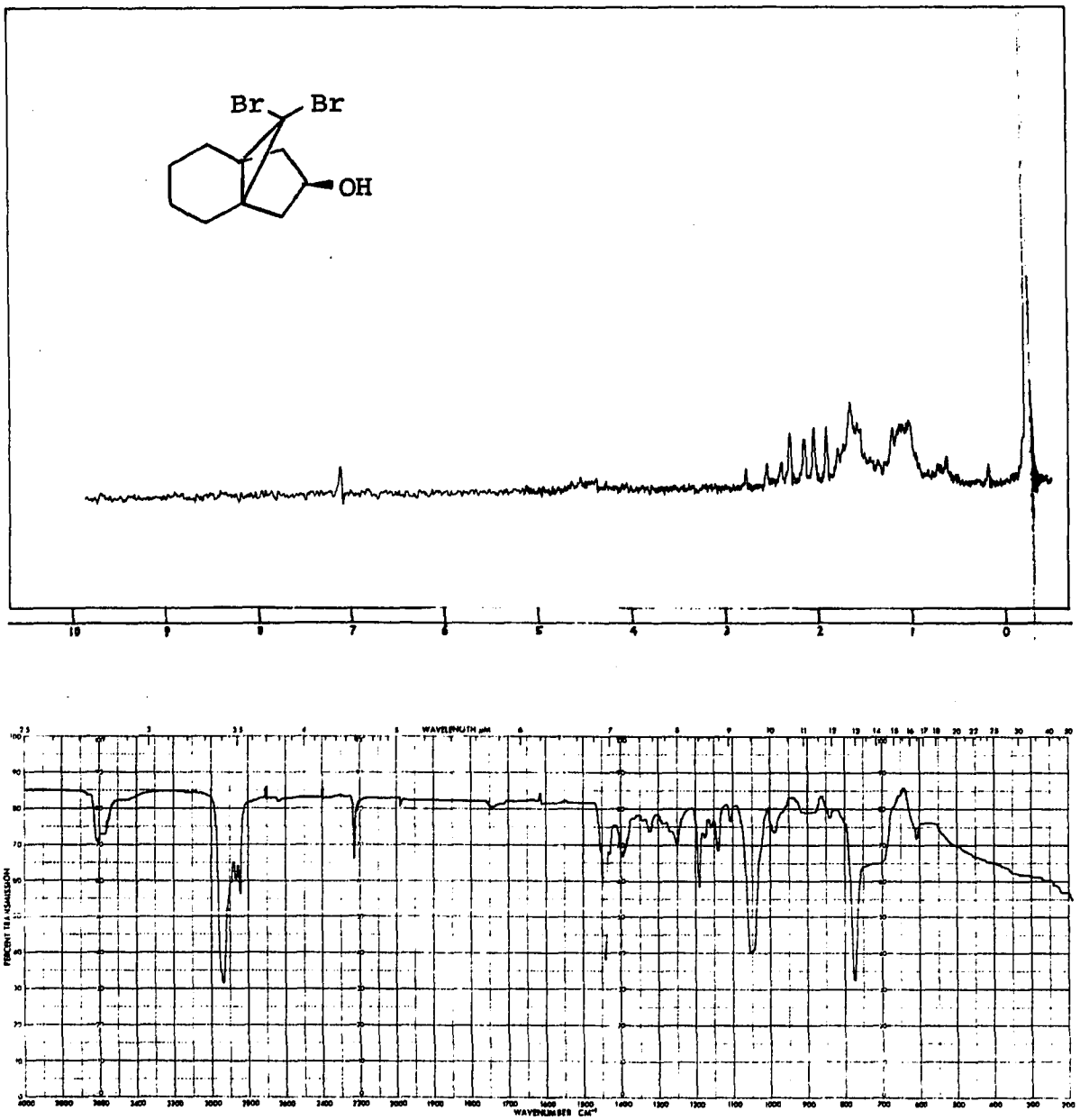


Figure 24. ^{1}H NMR and IR spectra of exo-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-8-ol (213a)

quenching with 1 ml H_2O and drying over $MgSO_4$. Concentration gave 1.99 g (98.6%) 213, mp 130-131°C (d); ^1H MMR: δ4.95-4.40(m, 1H), 2.6(d, J=9 Hz), 2.35(d, J=9 Hz), 2.02(d, J=9 Hz), 1.60-1.10(m). IR($CDCl_3$): 3610(-OH), 1050(C-O) cm^{-1}. Anal. Calc'd for $C_{10}H_{14}Br_2O$: m/e 307.9411. Found: m/e 307.9438.

exo-9-Mesyl-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (213b) (Fig. 25)

To a solution of 100 mg (0.32 mmol) of 213a in 7 ml ether and 2 ml (8 equiv.) pyridine, 0.5 ml (8 equiv.) methylsulfonyl chloride was added at 0°C, the resulting mixture was then gradually warmed up to room temperature and stirred overnight. After work up, the crude product was filtered through a silica gel short column (ether) to give 88 mg of light brown oil, 213b (70%). ^1H NMR: δ5.30 (quintet, J=9 Hz), 3.0(s); 2.60(dd, J=9 Hz, 5 Hz), 2.15(d, J= 5 Hz), 2.22-1.76(m), 1.76-1.16(m). Anal. Calc'd for $C_{11}H_{16}Br_2O_3S$: m/e 385.9188. Found: m/e 385.9183.

endo-8-Chloro-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (214) (Fig. 26)

To a magnetically stirred solution of 200 mg (0.65 mmol) 213 and 0.15 ml (0.65 mmol) $(n\text{-Bu})_3N$ (Aldrich) in 10 ml THF, was slowly added 0.15 ml (3 equiv.) $SOCl_2$ (Fisher) at 0°C. After addition the mixture was refluxed for 1 hr (solution turned dark green) and then extracted with pentane

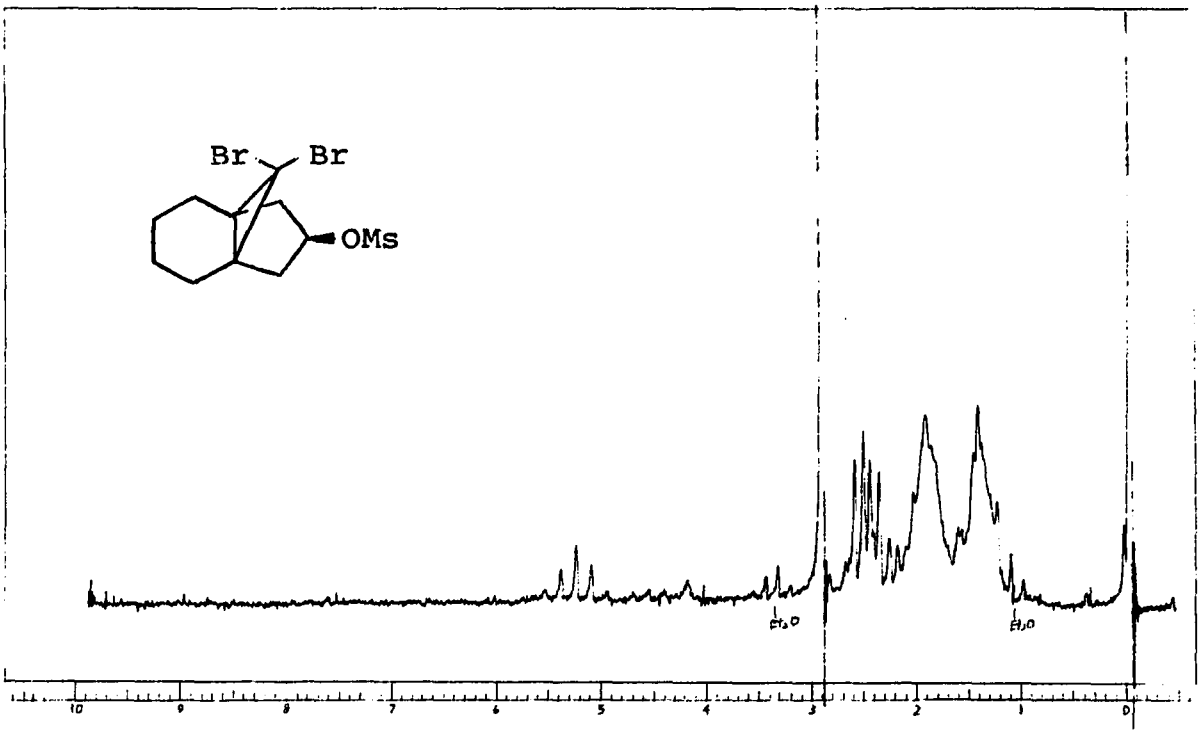


Figure 25. ^{1}H NMR spectrum of exo-8-mesyl-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (213b)

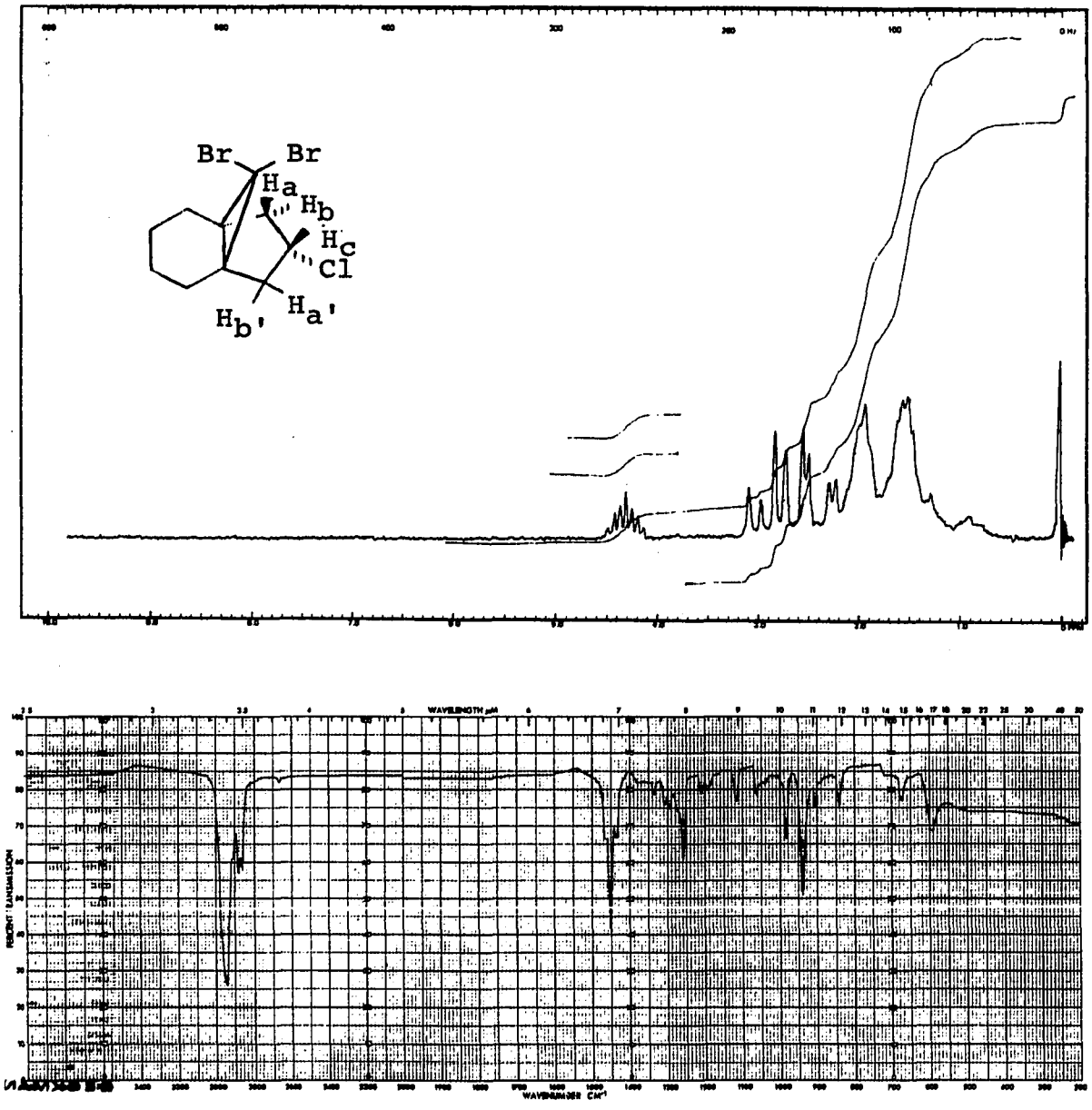


Figure 26. ^{1}H NMR and IR spectra of endo-8-chloro-10,10-dibromotricyclo[4.3.1.0^{1,6}]decane (214)

three times. The combined organic layer was washed sequentially with H_2O, saturated NH_4Cl solution, saturated $NaHCO_3$ solution, H_2O, and saturated NaCl solution. Drying and solvent evaporation gave 240 mg of a mixture of brown solid and oil. Thin layer chromatographic purification (10% ethereal hexane) afforded a light brown oil identified as 214 in 91% yield (R_f=0.82); ^{1}H NMR: δ4.26(heptet, H_2, J=3.75 Hz), 2.99(dd, 2 H_a, $J_{a,c}$=6.75 Hz, $J_{a,b}$=15.75 Hz), 2.36(dd, 2 H_b, $J_{b,c}$=3.75 Hz, $J_{a,b}$=15.75 Hz), 2.6-1.8(m), 1.8~0.7(m); IR(CCl_4): 2942, 2880, 2860, 1450, 1260. Anal. Calc'd for $C_{10}H_{13}Br_2Cl$: m/e 325.9072. Found: m/e 325.9024.

endo-8-Bromo-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (216) (Fig. 27)

To a solution of 1.5 g (4.84 mmol) 213 in 15 ml THF, was added 1.27 ml (1.1 equiv.) (n-Bu)$_3$N followed by 0.42 ml $SOBr_2$ (Pfaltz and Bauer). The resulting mixture was refluxed for 12 hr, and then extracted with three 15 ml portions of hexane. The combined organic solution was washed with H_2O (until neutral), saturated NaCl solution, dried over $MgSO_4$, filtered and the solvent removed, leaving a dark brown oil which was purified on a silica gel column (20 x 50 cm, hexane) to afford compound 216 as a white solid (55%), mp 33-34°C; ^{1}H NMR: δ4.46-4.02(m, H_8, with a maximum at 4.22), 2.98(dd, 2 H_7, $J_{7,8}$=7 Hz, $J_{7,7'}$=16 Hz), 2.43(dd, 2 $H_{7'}$, $J_{7',8}$=4.5 Hz, $J_{7,7'}$=16 Hz), 2.2-1.8(m,

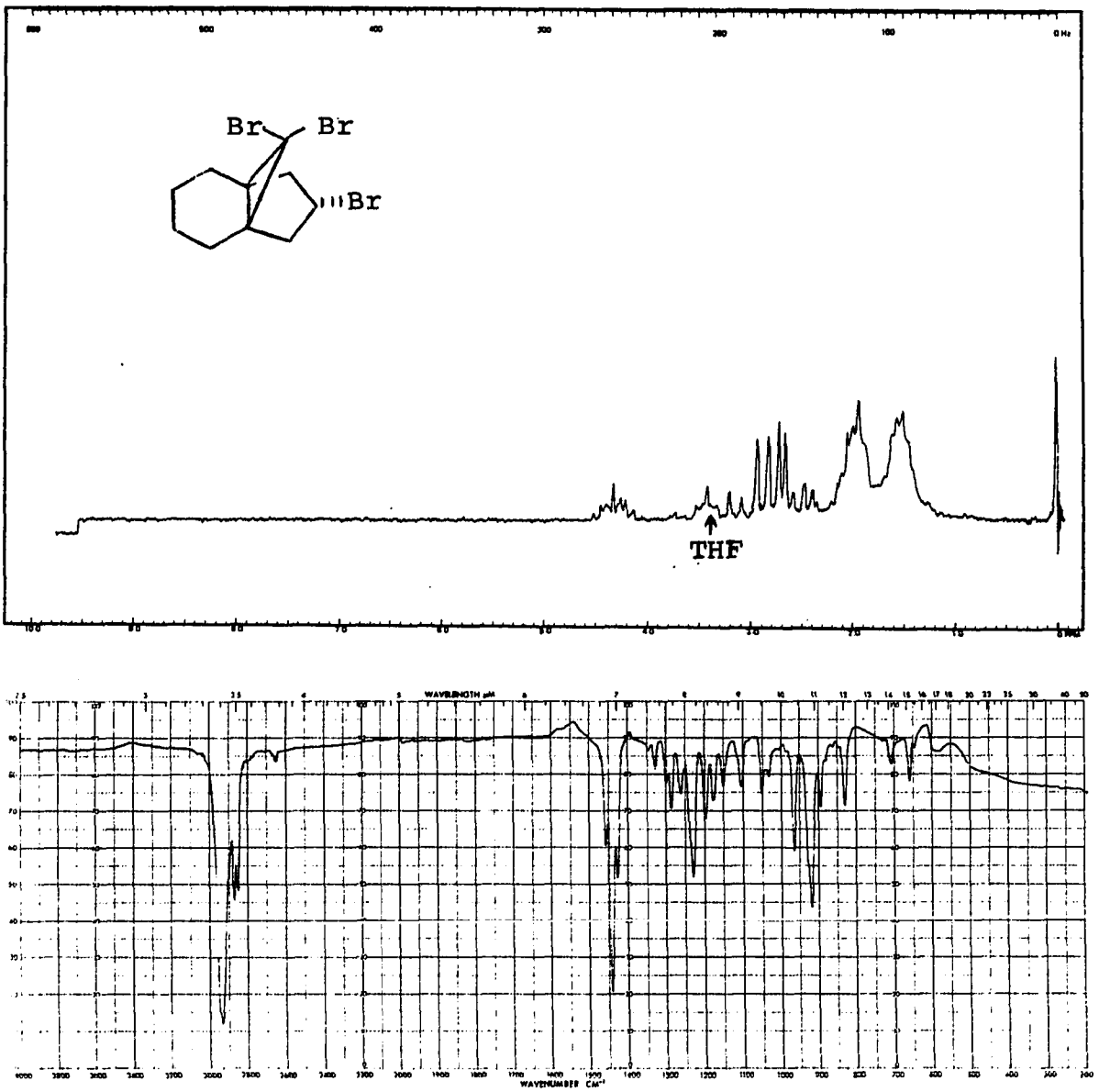


Figure 27. ^{1}H NMR and IR spectra of endo-8-bromo-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (216)

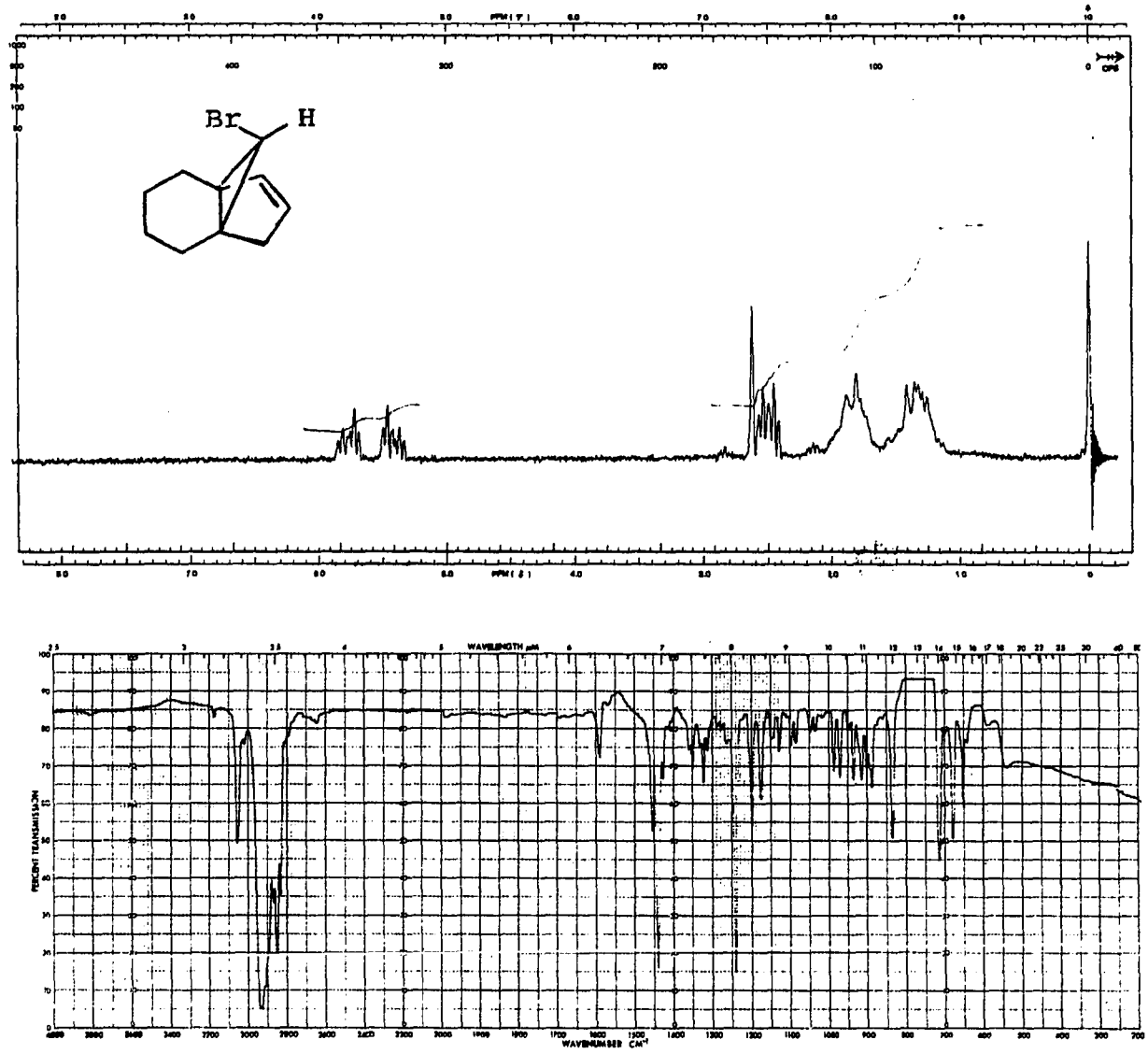


Figure 28. ^{1}H NMR and IR spectra of 10α-bromotricyclo-[4.3.1.0^{1,6}]deca-7-ene (215)

4H, with a maximum at 1.9), 1.8-1.22(m, 4H, with a maximum at 1.48); IR(CCl_4): 2938, 2870, 1440, 1230, 920, 830, 710, 660 cm^{-1}. Anal. Calc'd for $C_{10}H_{13}Br_3$: m/e 369.8567. Found: m/e 369.8574.

10,10-Dibromotricyclo[4.3.1.$0^{1,6}$]deca-7-ene (217) (Fig. 29)

(a) To a solution of 57 mg (0.15 mmol) 213b in 5 ml anhydrous benzene was added 0.025 ml (1.1 equiv.) DBU, the resulting solution mixture was refluxed overnight. After work up (DBU is soluble in water), concentration gave 54.5 mg (96% recovery) of starting material (^{1}H NMR).

(b) To a stirring, refluxing mixture of 3 g KOH in 12 ml $(CH_3)_2CHOH$ was added 284.5 mg (0.87 mmol) 214. The mixture was refluxed for 4 1/2 hr and then poured into 10 ml H_2O. This aqueous mixture was extracted with two 10 ml portions of hexane. The combined organic layer was washed with H_2O and saturated NaCl solution, and then dried over $MgSO_4$. Filtration and solvent evaporation afforded a brown liquid (200 mg) which was chromatographed on preparative silica gel plates (2% ethereal hexane, each plate developed twice). Compound 215 (Fig. 28) was isolated (R_f=0.92, yellow oil, 81%) and no 217 was observed; ^{1}H NMR: δ5.87-5.66(m, 1H), 5.54-5.32(m, 1H), 2.63(s, 1H), 2.6-2.38(m, 2H), 2.06-1.08(m, 4H, with a maximum at 1.82), 1.63-1.08(m, 4H, with a maximum at 1.36); IR(CCl_4): 3051(C=C-H), 2930, 1580(C=C),

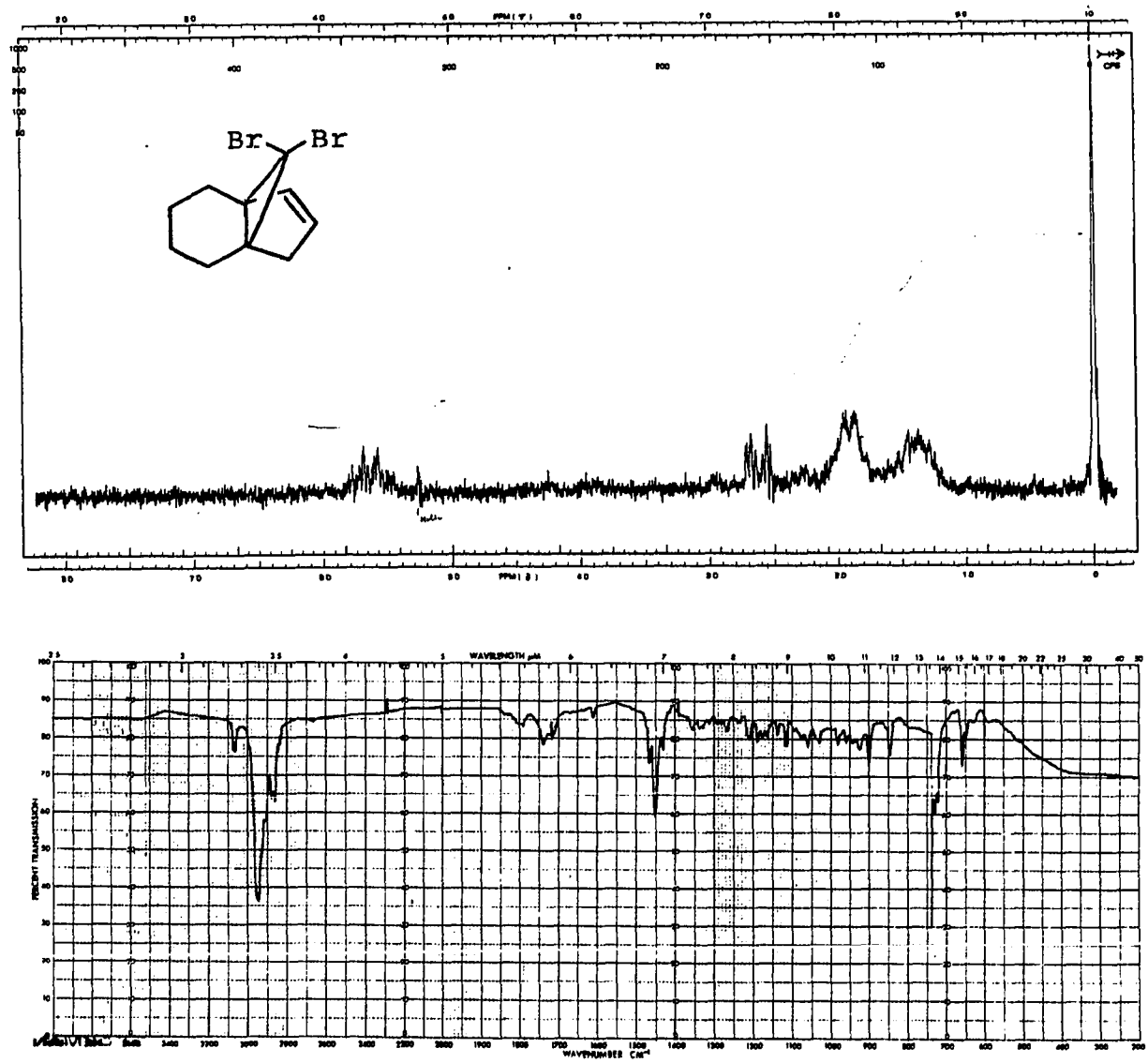


Figure 29. ^{1}H NMR and IR spectra of 10,10-dibromotricyclo-[4.3.1.$0^{1,6}$]deca-7-ene (217)

1454, 1240, 835, 715, 678, 650 cm^{-1}. Anal. Calc'd for $C_{10}H_{13}Br$: m/e 212.0201. Found: m/e 212.0189.

(c) To a solution of 20 mg (0.40 mmol, 50% in oil) NaH in 2 ml DMF, was added 76 mg 216 (0.20 mmol) in 3 ml DMF, at room temperature. The solution turned brown after 30 sec and the resulting mixture was stirred for an additional 20 hr. After extraction with hexane, the combined organic layers were washed with H_2O and saturated NaCl solution, and dried over $MgSO_4$. Filtration and solvent evaporation gave 69 mg of crude product which was chromatographed on a silica gel plate (hexane). Compound 217 was isolated (47%) as a colorless oil; ^1H NMR: δ5.83-5.43(m, 2H, with two maxima at 5.7 and 5.57), 2.66(t, H_B), 2.56(t, H_A), 2.15-1.66(m, 4H, with two maxima at 1.95 and 1.86), 1.66-1.06 (m, 4H, with a maximum at 1.36); IR(CCl_4): 3070 (C=C-H), 2942, 1610(c=C), 1450, 738, 660 cm^{-1}. Anal. Calc'd for $C_{10}H_{12}Br_2$: m/e 289.9306. Found: m/e 289.9324.

Reaction of exo-4-methoxy-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]-deca-2-ene (192a) with MeLi

(a) In the presence of DPIBF To a solution of 94 mg (0.30 mmol) 192a and 87.17 mg (0.32 mmol) DPIBF in 10 ml of freshly distilled ether (from $LiAlH_4$), was added 1.5 ml MeLi (3.0 mmol) at room temperature. An exothermic reaction occurred immediately. The resulting reaction mixture was

stirred for 20 min, followed by quenching with H_2O, dilution with ether, washing successively with H_2O (until neutral) and saturated NaCl solution, and drying over $MgSO_4$. After the ethereal solution was left in the hood overnight in order to let the excess DPIBF oxidize o-dibenzoylbenzene to (220), a colorless solution was obtained. Filtration and concentration gave a mixture of oil and yellow solid. The ratio of 218a to 219a was 1:1.82 (^{1}H NMR, benzalaldehyde internal standard). Thin layer chromatographic purification (5% ethereal hexane) gave 22 mg 218a (R_f=0.75, 29.3%, Fig. 30); ^{1}H NMR: δ5.5(br s, H_2, J_{12}=3 Hz), 3.6(dd, H_6, $J_{6,5}$= 5 Hz, $J_{6,5'}$=3 Hz), 3.26(s, -OMe), 3.11(H_1, $J_{1,2}$=3 Hz), 2.3=1.7(m, 6H), 1.92(s, -Me), 1.7(d, $J_{6,5}$=5 Hz), 1.62(d, $J_{6,5'}$=3 Hz). Decoupling the doublet at 85.5 (H_2) collapsed the doublet at 3.11 (H_1) to a singlet; decoupling the multiplet at δ2.16 (H_8, $H_{8'}$) caused the broad singlet at δ5.5 to collapse to a doublet ($J_{1,2}$=3 Hz); doubling the doublet of doublets at δ3.6 (H_6) collapsed the two doublets at δ1.62 and δ1.70 to two singlets ($J_{5,5'}$=6.0 Hz); doubling the doublet at δ1.62 ($H_{5'}$) collapses the doublet of doublets at 3.6 (H_6) to a doublet; ^{13}C NMR($CDCl_3$): δ162.87(rel. int.: 1.13), 121.32(2.92), 92.88(1.00), 81.94(2.52), 67.15(1.24), 61.84(2.85), 56.91(2.68), 32.80(2.85), 29.39(2.84), 26.19 (3.00), 25.54(2.96), 24.62(2.77); IR(CCl_4): 3070(C=C-H), 2960, 2814, 1100, 1070 cm^{-1}. Anal. Calc'd for $C_{12}H_{17}BrO$:

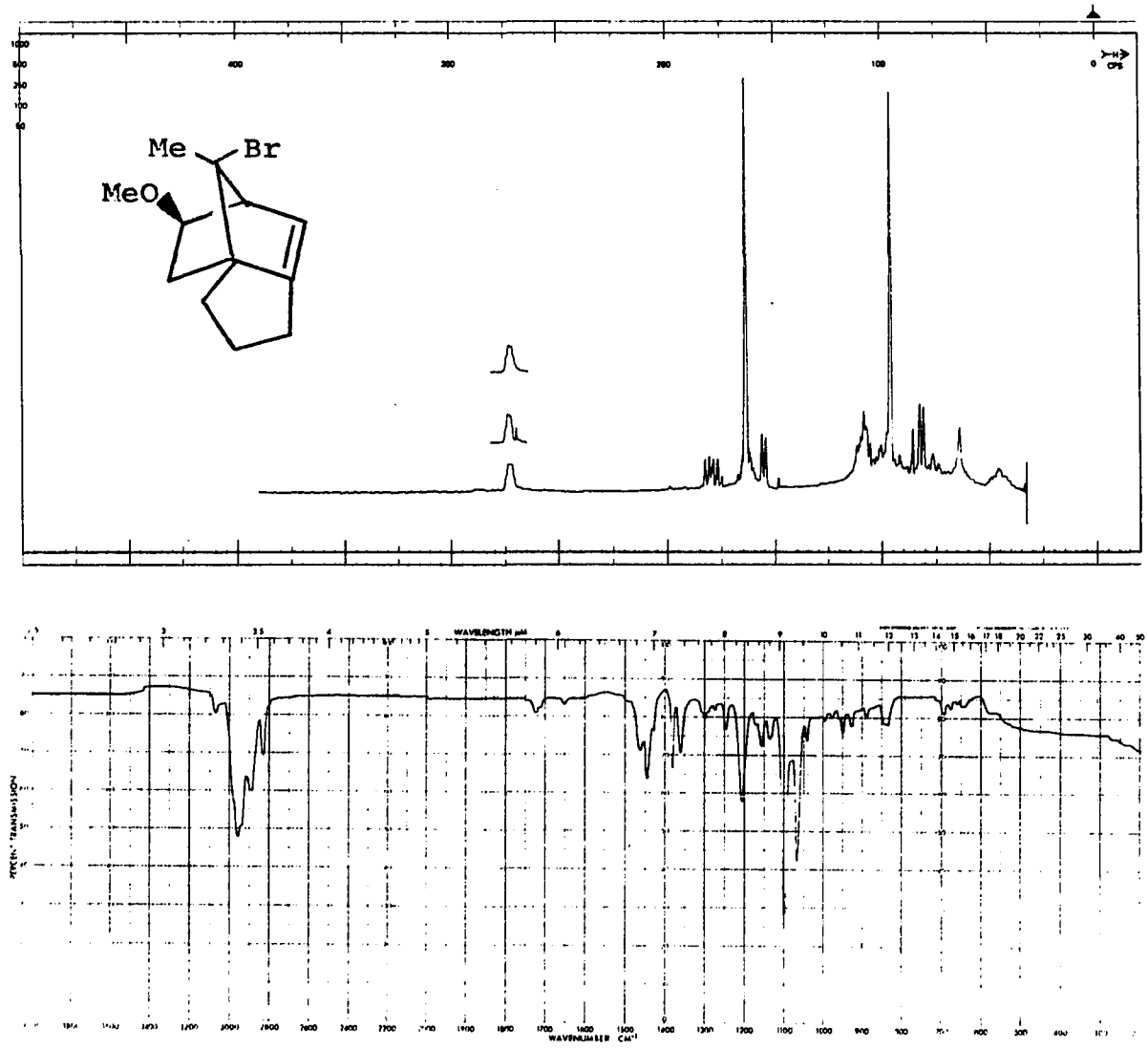


Figure 30. ^{1}H NMR and IR spectra of 1,2-trimethylene-exo-5-methoxy-syn-7-bromo-7-methylnorborna-2-ene (218a)

m/e 256.0467. Found: m/e 256.0462. The two isomers of structure 219a (in a ratio of 1:1.07, Fig. 31, 32) were isolated in 53.4% yield (R_f=0.2, 69.2 mg); ^{1}H NMR: δ7.8-6.6(m, with two singlets at 7.06 and 7.01), 5.82(br s), 5.58 (br s), 3.64~3.4(m), 3.02(s), 2.76(s), 2.7-2.4(m), 2.16(d), 2.25-1.1(m); IR(CCl_4): 3050, 3020, 2910, 2830, 2800, 1090, 900, 970, 690 cm^{-1}. GLC-mass psectrum (column C) of the two isomers: 219a-1 (-OMe at δ3.02, ret. time: 10.1 min), m/e (% R/C): 432.28(P, 0.04), 401.12(P-31, 0.41), 270.08 (P-162, 13.97); 219a-2 (-OMe at δ2.75, ret. time: 9.1 min), M^+(% R/C): 432.28(P, 0.03), 401.08(P-31, 0.17), 270.10 (P-162, 13.19). One of the isomers of 219a, 219a-2 (Fig. 31), was purified by recrystallization from MeOH (four times); ^{1}H NMR($CDCl_3$): δ7.8=6.8(m, with a singlet at 7.0, 14H), 5.58(AB quartet, H_a), 3.53(t, J=5 Hz, H_c), 2.81(m, H_b) 2.76 (s, 3H), 2.16(d, J=5 Hz, H_d), 2.0-1.0(m, 6H). Lanthanide-induced shifts (LIS) for H_a, H_b, R_1(=OMe), R_2(=H_c), H_d and H_d' support the structure proposed for 219a:

	LIS(Δδ)				
[Eu(fod)$_3$]/[219a]	H_a	H_b	R_1=OMe	R_2=HC	H_d,H_d'
0.1	0.04	0.14	0.19	0.27	0.14 Hd=0.44

0.3	0.07	0.39	0.50	0.65	Hd'=0.20 ($J_{dd'}$=15 Hz, J_{dc}= 5 Hz, $J_{dc'}$= 7 Hz)
0.6	0.11	0.65	0.76	1.13	H_d=0.72 $H_{d'}$=0.30

(b) In the absence of DPIBF To a solution of 448 mg (1.39 mmol) 192a in 20 ml ether was added 4.45 ml MeLi at room temperature. The resulting reaction mixture was stirred for 1 hr at room temperature. After the usual work up, thin layer chromatographic purification (20% ethereal hexane) gave 16.1% 218a (R_f=0.66). A mixture of two isomeric norbornenyl type dimers was also isolated (R_f=0.36, 5.9%). ^{1}H NMR($CDCl_3$): δ5.63(s), 5.5(s), 3.6-3.3(m, with a maximum at 3.4), 3.25(br s, might be two -OMe overlaps), 3.1~2.7(with two maxima at 2.9 and 3.0), 2.7~1.1(m); ^{13}C NMR ($CDCl_3$): δ159.2(rel. int. 0.19), 153.9(0.18), 147.5(0.17), 129.9(0.51), 124.5(0.66), 123.2(0.66), 81.5(0.73), 81.4 (0.69), 59.0(0.21), 57.0(0.49), 55.5(0.50), 52.9(0.64), 52.0(0.58), 48.1(0.71), 35.3(0.54), 33.3(0.72), 27.4(0.71), 25.2(0.55), 24.1(1, suggestive of two overlapping peaks), 22.7(0.64), 21.9(0.10). Anal. Calc'd for $C_{22}H_{28}O_2$: m/e 324.2089. Found: m/e 324.2083. A mixture of cyclobutane-type dimers was also obtained (R_f=0.23, 2.3%). ^{1}H NMR ($CDCl_3$): δ5.65-5.3(m), 3.55-2.7(m, with two singlets at

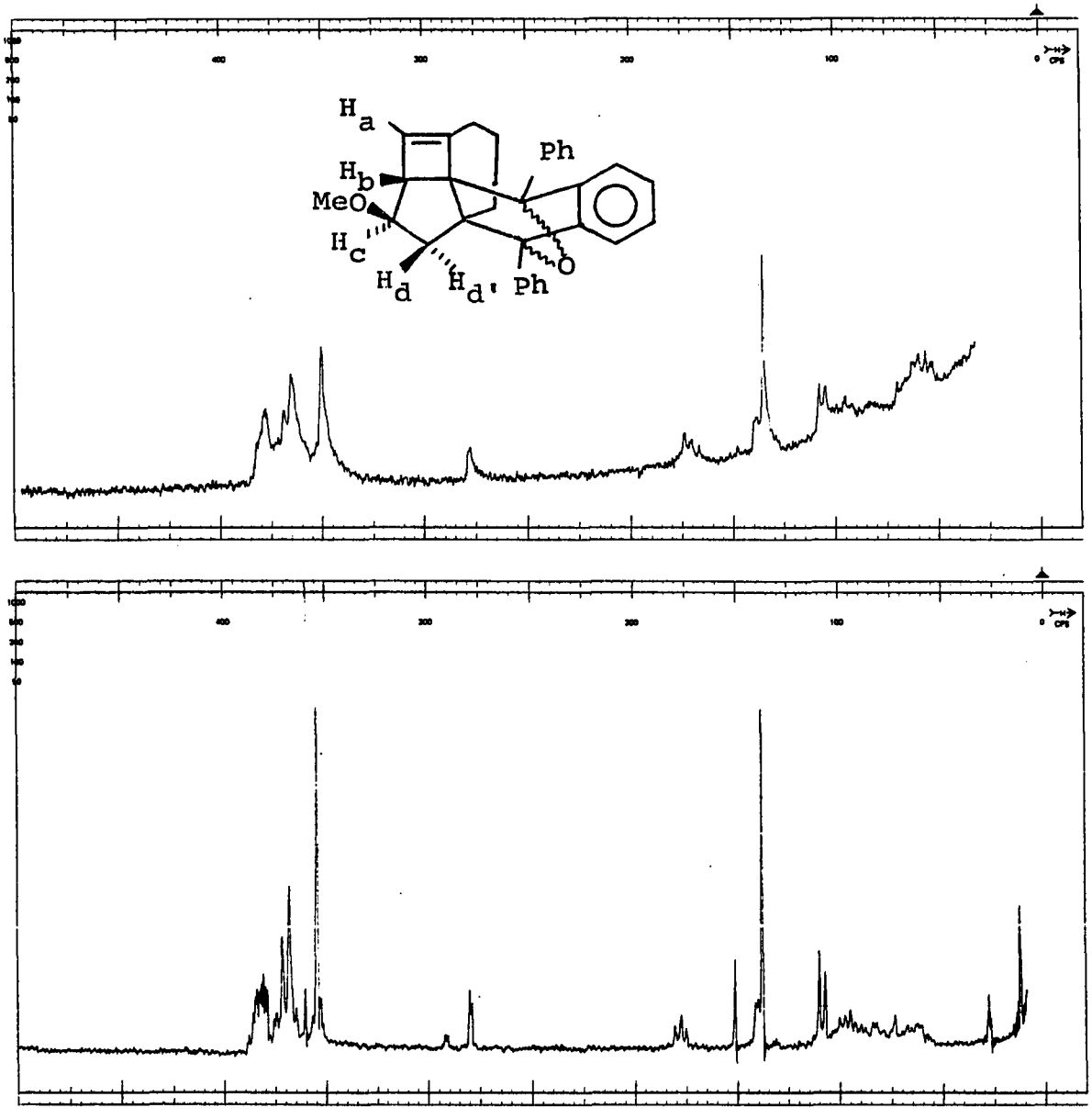
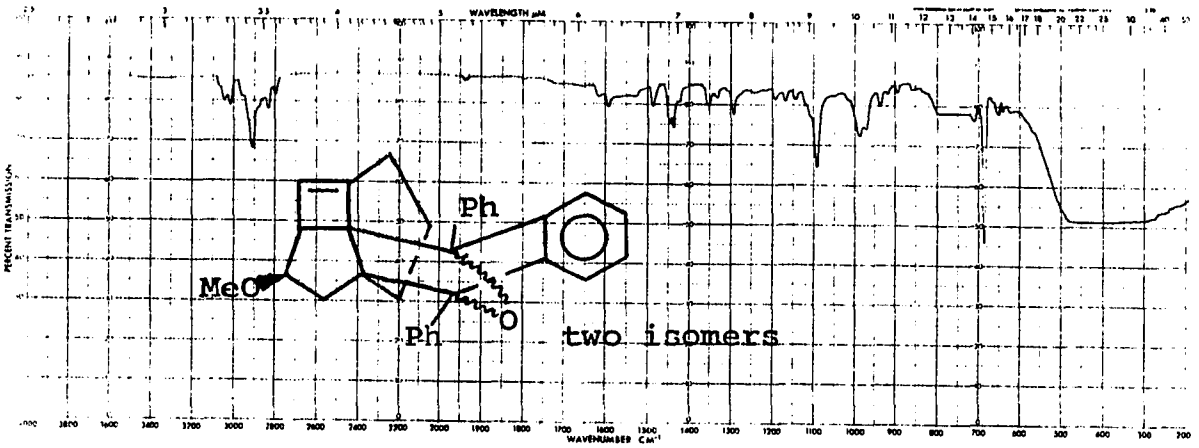


Figure 31. ^{1}H NMR spectra of one isomer of 219a, 219a-2 (top) and a mixture of two isomers of 219a (bottom)



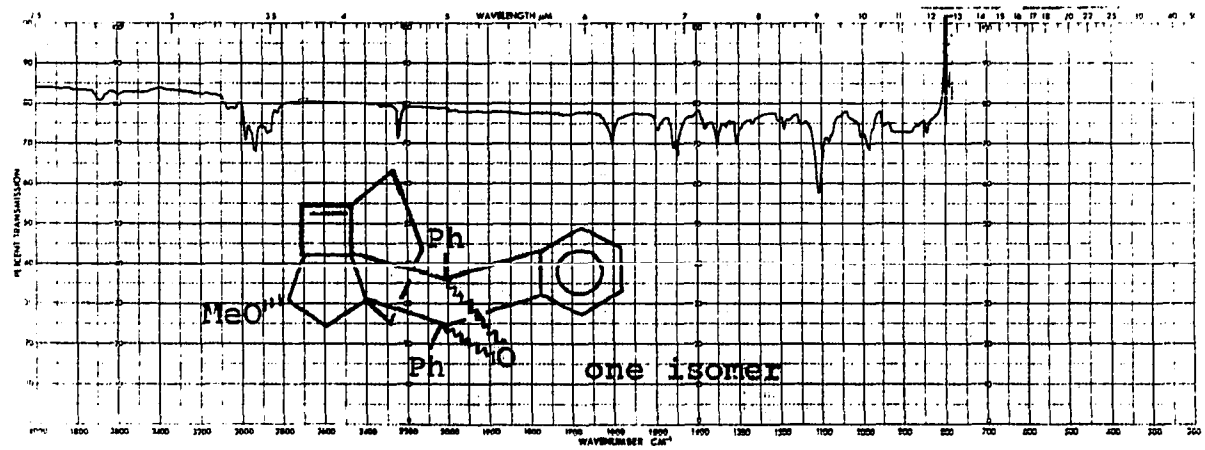


Figure 32. IR Spectra of 219a (two isomers, top) and 219b (one isomer, bottom)

3.27 and 3.24), 2.55-1.4(m). Thin layer chromatographic purification (20% ethereal hexane plate developed three times) afforded one cyclobutane dimer (6 mg) (one peak on GLC); ^{1}H NMR: δ5.4(s), 3.5~2.5(m, with a singlet at 3.23), 2.5-1.0(m).

Reaction of endo-4-methoxy-10,10-dibromotricyclo[4.3.1.0^{1,6}]-deca-2-ene (192b) with MeLi in the presence of DPIBF

To a solution of 118 mg (0.36 mmol) 192b and 1.1 equiv. DPIBF in 20 ml ether was added 1.74 ml (3.6 mmol), MeLi at room temperature. After 20 min, H_2O was added to quench the reaction. Upon work up, a mixture consisting of 218b and 219b in a 1:3.05 ratio (calculated by measuring the peak areas of the -OMe peaks in the ^{1}H NMR) was obtained. Thin layer chromatographic purification (10% ethereal hexane) gave 18 mg 218b (R_f=0.5, 19%, Fig. 33); ^{1}H NMR: δ5.35(br s, 1H), 3.95(m, 1H), 3.2(d, J=3 Hz, 1H), 3.11(s, 3H), 1.61(s, 3H), 2.35-0.88(m, 8H); IR(CCl_4): 3070(C=C-H), 2930, 2880, 1650(C=C), 1115(C-O), 1097 cm^{-1}. Anal. Calc'd for $C_{12}H_{17}BrO$: m/e 256.0467. Found: m/e 256.0463; H, 6.64. Two isomeric products (219b) (Fig. 32, 34) (in a ratio of 1:1.36) were isolated in 58% yield (R_f=0.2); ^{1}H NMR: δ7.91~6.91(m), 5.81(br s), 5.66(br s), 3.02(s), 2.94(s), 2.9~1.1(m). One isomer (Fig. 32, 34), was recrystallized from ether to give white needles, mp 203-204°C; ^{1}H NMR($CDCl_3$): δ8.0-

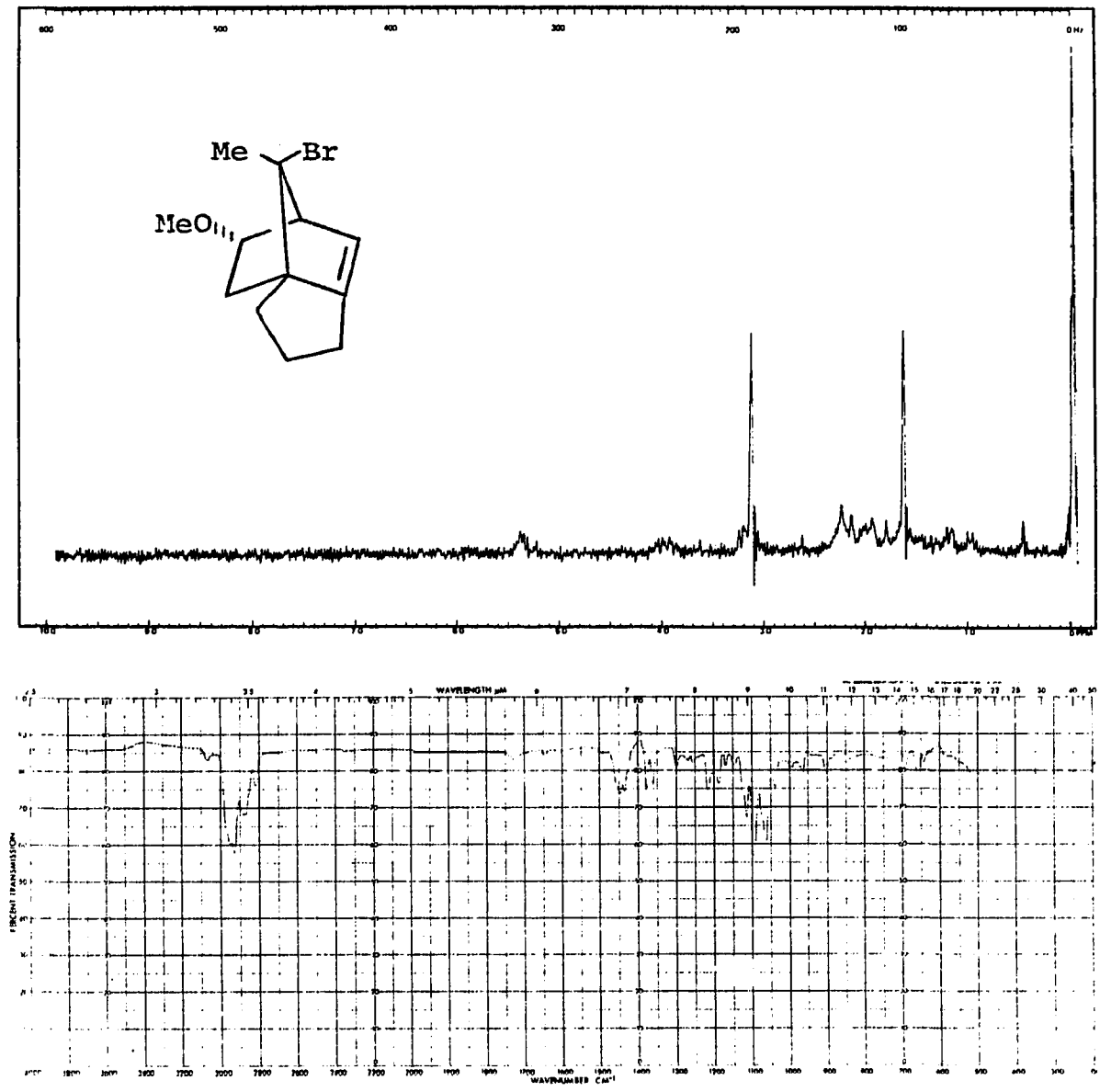


Figure 33. ^{1}H NMR and IR spectra of 1,2-trimethylene-endo-5-methoxy-syn-7-bromo-7-methylnorborna-2-ene (218b)

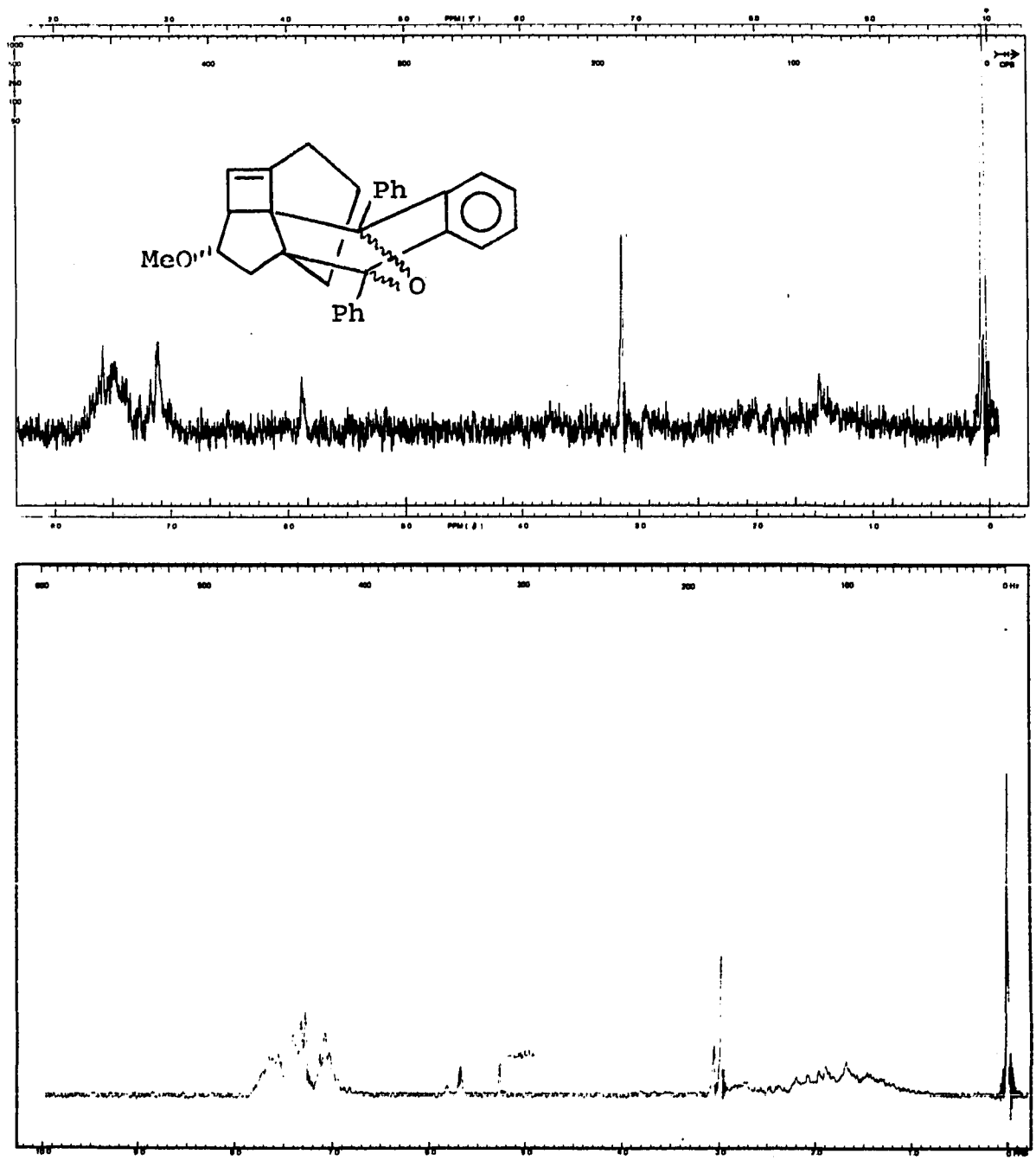


Figure 34. ^{1}H NMR spectra of one isomer (top) and a mixture of two isomers (bottom) of 219b

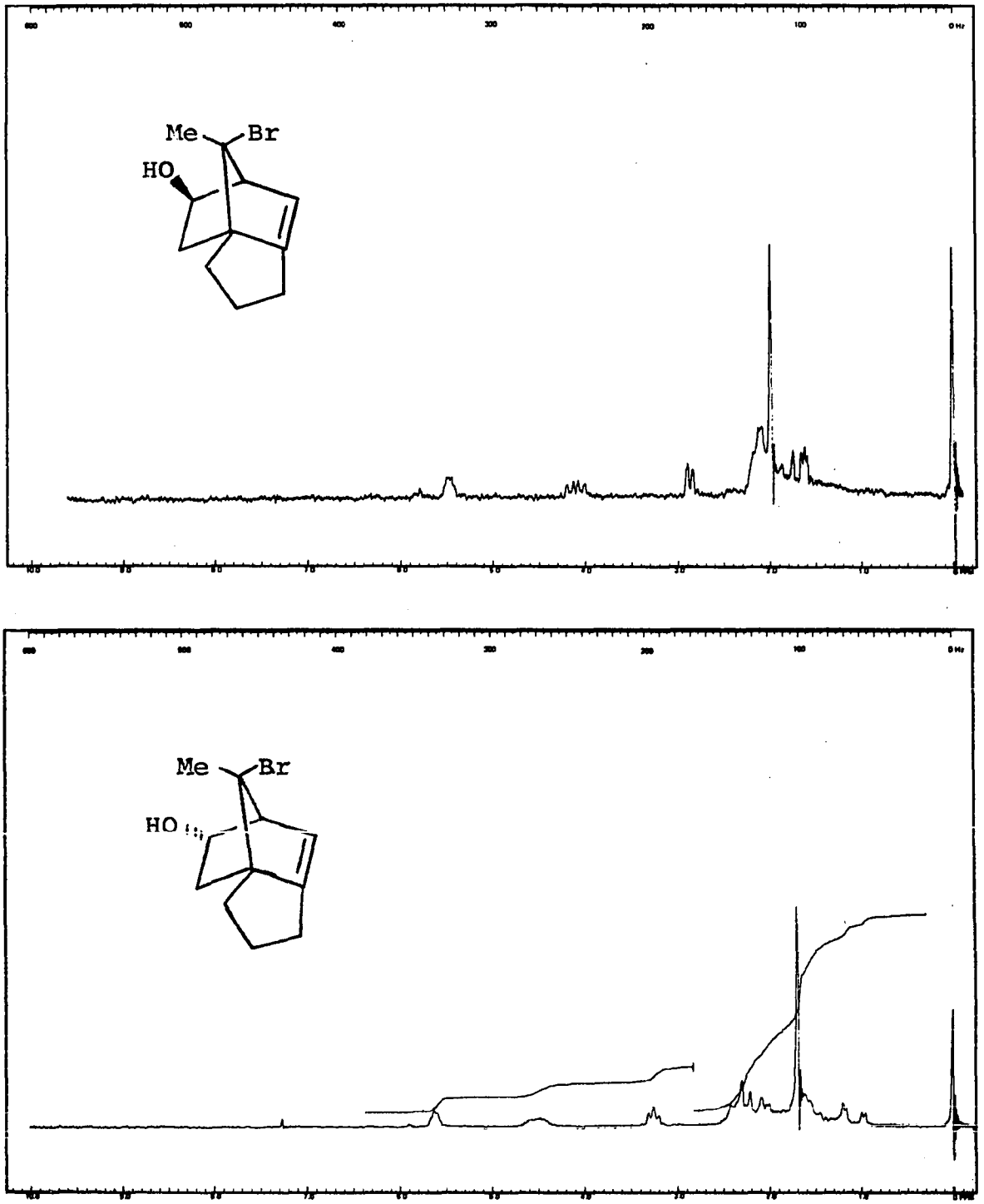


Figure 35. ^{1}H NMR spectra of exo-1,2-trimethylene-exo-5-hydroxy-syn-7-bromo-7-methylnorborna-2-ene-4-ol (218c, top) and the epimer (218d, bottom)

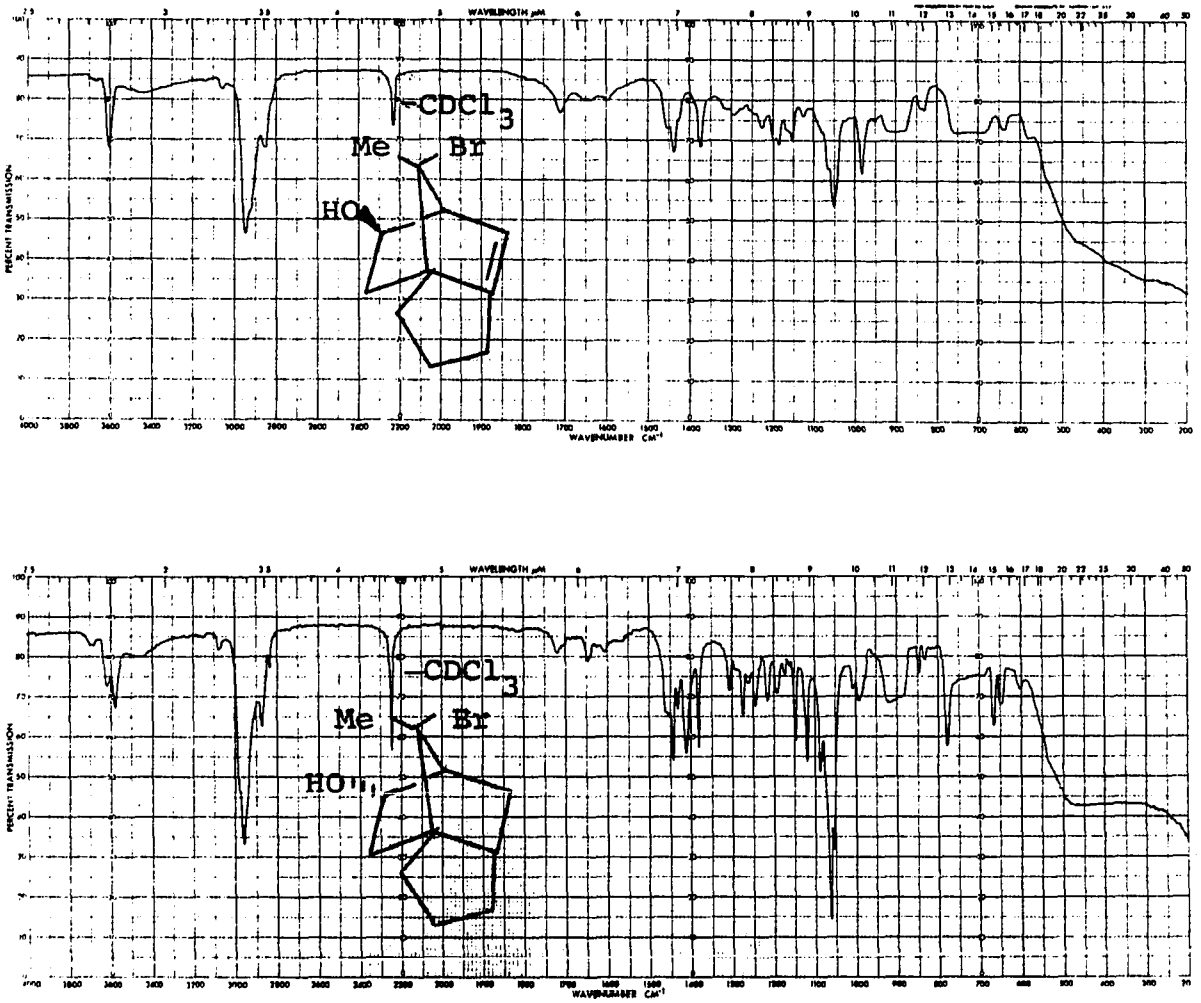


Figure 36. IR Spectra of exo-1,2-trimethylene-exo-5-hydroxy-syn-7-bromo-7-methylnorborna-2-ene-4-ol (218c, top) and the epimer (218d, bottom)

7.1(m, 14H), 5.9(6s, 1H), 3.10(s), 2.9~0.83(m, 9H); IR ($CDCl_3$): 3070, 3030, 2940, 2870, 2840, 1610, 1500, 1445, 1310, 1185, 1110, 1090, 900, 850 cm^{-1}. Anal. Calc'd for $C_{31}H_{28}O_2$: m/e 432.2089. Found: m/e 432.2083.

Reaction of exo-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (192c) with MeLi

(a) In the presence of DPIBF To a solution of 0.5 g 192c (1.6 mmol) and 1.1 equiv. DPIBF in 25 ml ether, was added 3.0 ml MeLi (10 equiv.) at room temperature. After 30 min, water was added, and the usual work up gave a yellow residue which was put on a preparative silica gel plate and developed with 25% ethereal hexane. Compound 218c (R_f=0.45) (Fig. 35, 36) was isolated in 33.6% yield; ^1H NMR($CDCl_3$): δ5.6(br s, 1H), 4.2(dd, J=4 Hz, 7 Hz, 1H), 2.87(d, J=3 Hz, 1H), 2.03(s, 3H), 2.5-1.16(m, 8H); ^{13}C NMR($CDCl_3$): δ162.71(rel. area 1.00), 121.54(2.242), 76.73(1.21), 75.92(1.21), 72.73 (1.66), 66.50(2.29), 34.91(1.79), 29.44(2.49), 26.68(2.15), 25.59(1.92), 25.67(2.55). Lanthanide induced shifts (LIS) H_1, H_2 and k_2=H_6 of 218c demonstrated the stereochemistry at C_7 (Table V). IR($CDCl_3$): 3600(s, free -OH), 3570-3200(br, -OH), 3060(C=C-H), 2940, 1440, 1375, 1050(C-O), 980 cm^{-1}. Anal. Calc'd for $C_{11}H_{15}BrO$: C, 56.02; H, 6.66; Br, 31.09. Found: C, 56.13; H, 6.69; Br, 31.30.

Two isomeric adducts, 219c (R_f=0.24, 297 mg) (Fig. 37) were obtained in 44.4% yield; ^1H NMR($CDCl_3$): δ8.0~7.0(m, with

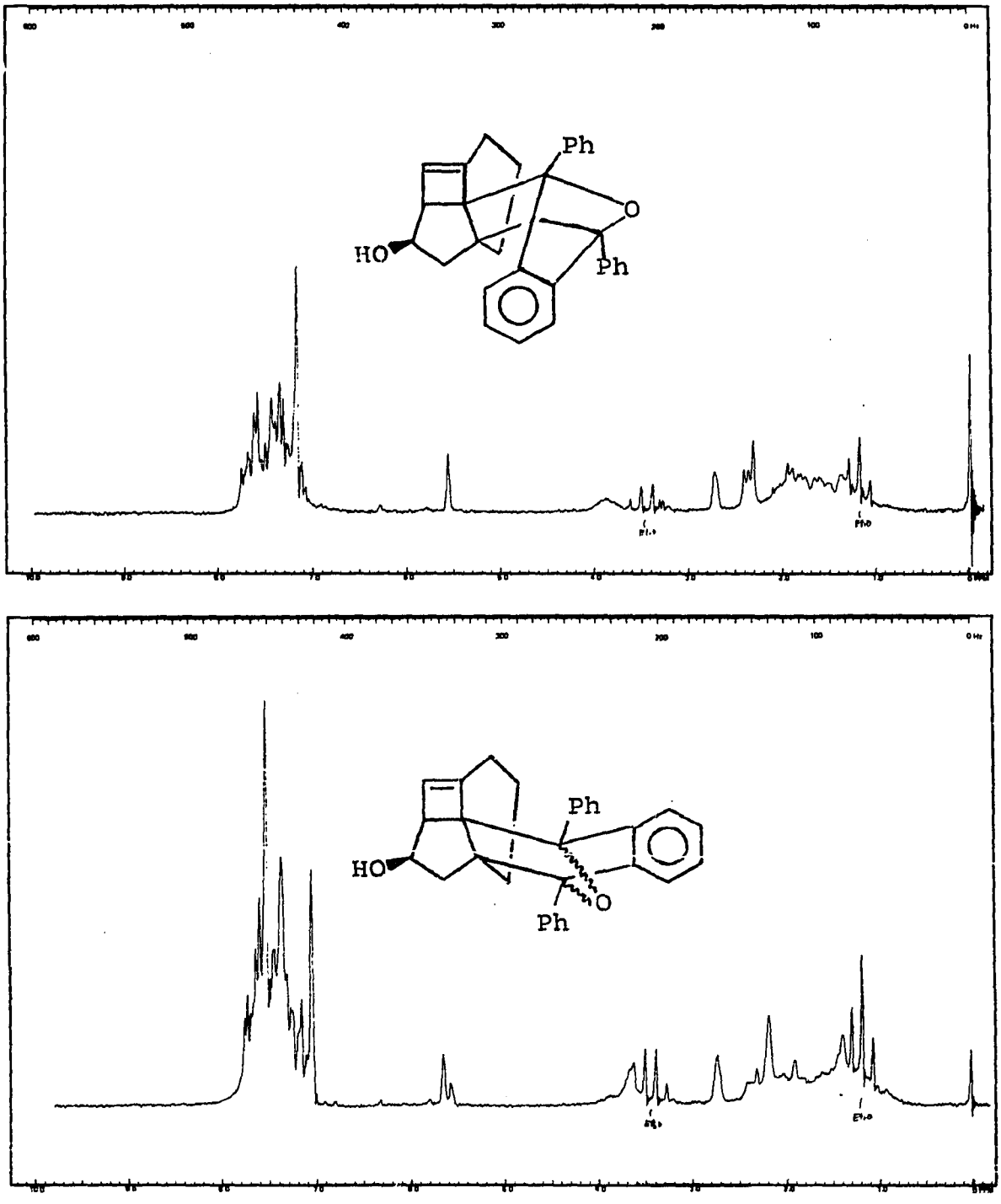


Figure 37. ^{1}H NMR spectra of one isomer (top) and a mixture of two isomers (bottom) of 219c

two sharp singlets at 7.51 and 7.18), 5.63(s), 5.56(s), 4.1-3.4(m), 2.72(bs), 2.5-0.8(m). Thin layer chromatographic purification (20% ethereal hexane) of 219c gave one pure isomer (R_f=0.22) (Fig. 37), ^{1}H NMR($CDCl_3$): δ7.85-7.0(m, with a sharp singlet at 7.18, 14H), 5.56(s, 1H), 4.1-3.7(m, 1H), 2.72(bs, 1H), 2.5-0.8(m, with three maxima at 2.4, 2.35, 2.3, 8H). GLC-mass spectrometry (column B) of 219c showed two peaks (with some overlap, ret. time: 15 min), each of which had parent ions at m/e 418, as appropriate for $C_{30}H_{26}O_2$. The material left at the base line of the TLC plate was collected and chromatographed again on a preparative silica gel plate (ether) to give 33 mg dimer 303c (Fig. 38) (14%). Recrystallization of 303c from MeOH gave colorless crystals, mp 198-205°C (d). Further atttmpted GLC purification of 303c on columns D, E, F, or G or by high pressure liquid chromatography was unsuccessful. ^{1}H NMR($CDCl_3$): δ5.5(m, 2H), 4.0(m, with two maxima at 4.05, 3.95, 2H), 3.25(br s, 2H), 2.4-0.8(m, 18H); ^{13}C NMR($CDCl_3$): δ163.69 (rel. int. 1.00), 136.00(1.06), 117.85(1.62), 73.70(2.35), 60.70(1.06), 55.12(2.83), 42.66(2.19), 29.30(2.13), 27.54(1.84), 24.40 (2.21); IR($CDCl_3$): 3610(s, free -OH), 3580-3120(br -OH), 3060(C=C-H), 2960, 2870, 1450, 1430, 1390, 1200, 1065, 1055, 1040, 1010, 985 cm^{-1}.

(b) In the absence of DPIBF To a solution of 300 mg (0.97 mmol) 192c in 15 ml ether was added 4.33 ml (10 equiv.) MeLi at room temperature. After the usual work up, 185 mg of

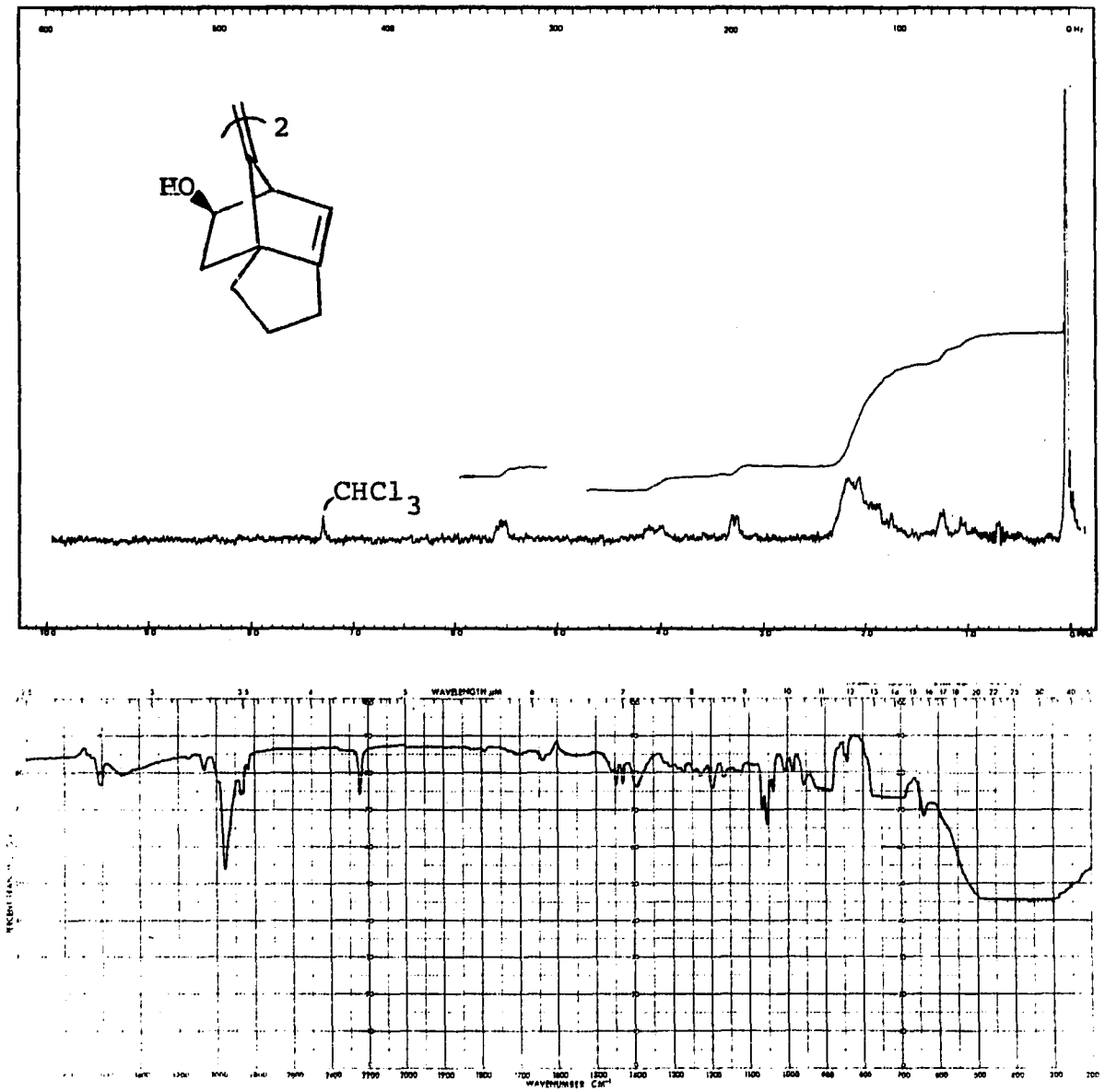


Figure 38. ^{1}H NMR and IR spectra of an R-R(S-S) dimer 303c

white solids were obtained. Thin layer chromatographic purification (ether) afforded only one dimer 303c (R_f=0.4) (Fig. 38) in 42% yield. The structure of 303c was established via a single crystal X-ray analysis of the p-bromobenzoate derivative 303e (see Appendix) (Fig. 39).

Reaction of endo-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene-4-ol (192d) with MeLi

(a) In the presence of DPIBF To a solution of 139.5 mg (0.45 mmol) 192d and 134.5 mg (1.1 equiv.) DPIBF in 15 ml ether, was added 3.24 ml (10 equiv.) MeLi at room temperature. After stirring for 25 min, the usual work up gave 211.5 mg of solids. Thin layer chromatographic purification (80% ethereal hexane) gave 177 mg (R_f=0.34, 94%) of two isomeric adducts 219d (Fig. 40). ^{1}H NMR($CDCl_3$): δ7.9-6.8(m, with three maxima at 7.52, 7.42, 7.12), 5.83(s), 5.7(s), 4.33-3.9(m), 2.8-0.96(m); IR($CDCl_3$): 3610(s, free -OH), 3540-3120(br, -OH), 3540-3120(br, -OH), 3060, 3030, 2920, 2850, 1595(C=C), 1490, 1445, 1440, 1295, 1110, 1040, 1000, 690 cm^{-1}; GLC-mass spectrum (70ev): 219-1-d (or 219-2-d, column C, ret. time, 24 min), m/e(% RA): 418(P, 11.27), 374(P-44, 26.54), 270(P-148,100), 241(P-177, 18.14), 193(P-225, 8.43), 165(P-253, 15.73), 105(P-313, 34.34), 91(P-327, 13.68), 77(P-341, 27.07); 219-2-d (or 219-1-d, ret. time, 25.5 min), m/e(% RA): 418(P, 12.99), 374(P-44, 19.81), 270(P-148, 100), 241(P-177, 18.33), 193(P-225, 8.92),

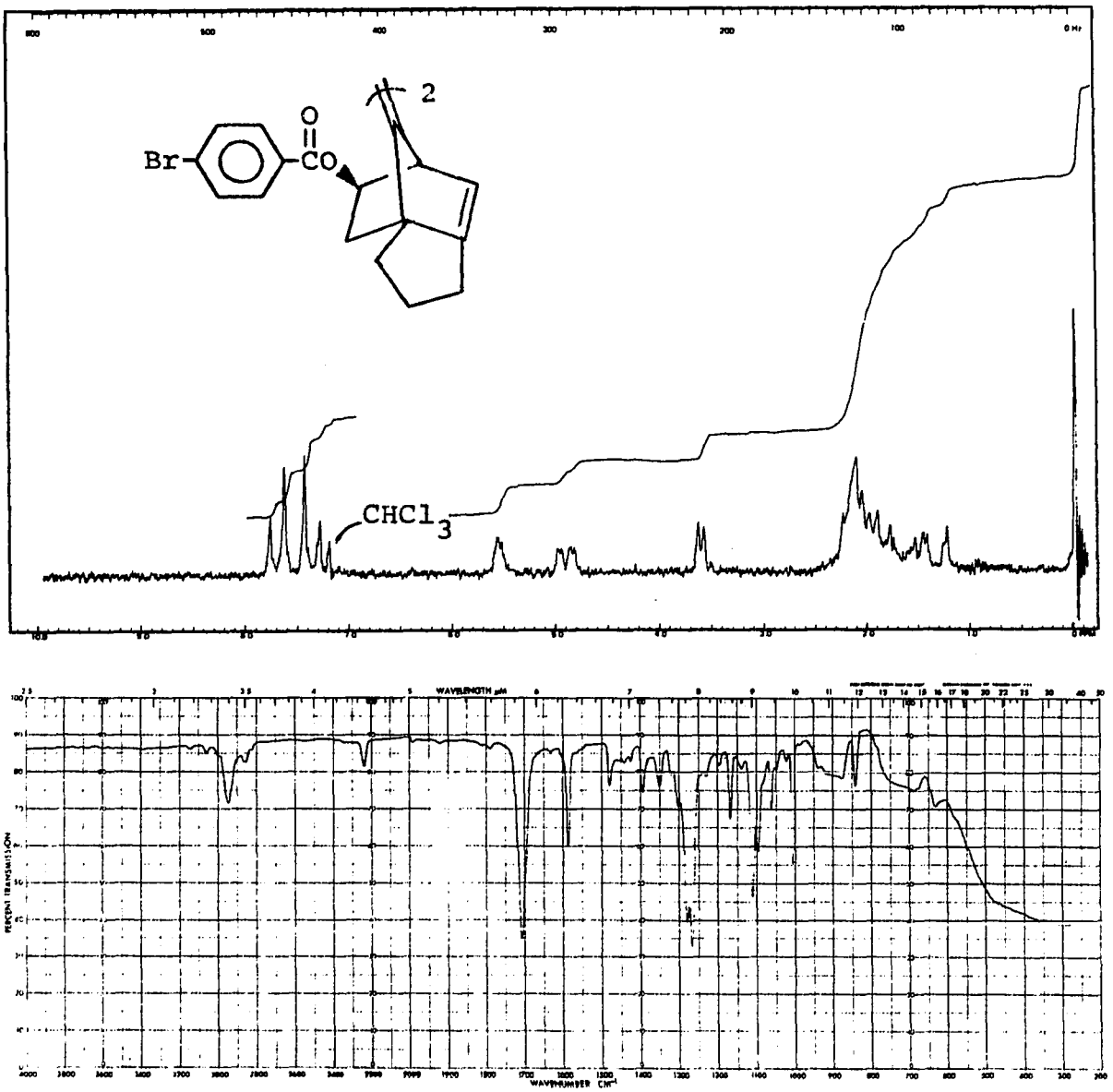


Figure 39. ^{1}H NMR and IR spectra of an R-R(S-S) dimer 343e

165(P-253, 16.44), 105(P-313, 36.93), 91(P-327, 14.72), 77(P-341, 31.77). Anal. Calc'd for $C_{30}H_{26}O_2$: m/e 418.1933. Found: m/e 418.1930. A small amount (ca. 2%) of the rearranged product 218d was also observed in the GLC-mass spectrum.

(b) In the absence of DPIBF To a solution of 327.5 mg (1.06 mmol) 192d in 15 ml ether was added 5.04 ml MeLi at -78°C, and the resulting mixture stirred for 40 min, followed by quenching with H_2O at -78°C. After the usual work up, 191.5 mg of white solids were obtained. Thin layer chromatographic purification (80% ethereal hexane, developed twice) gave 40 mg 218d (R_f=0.47, 17%) (Fig. 35, 36); ^1H NMR($CDCl_3$): δ5.7-5.5(m, 1H), 4.7~4.3(m, 1H), 3.25 (apparent t, 1H, J=3 Hz), 2.6-0.9(m, with a singlet at 1.7, 12H); ^{13}C NMR($CDCl_3$): δ164.17(rel. int.: 1.91), 117.91 (8.30), 89.85(2.19), 69.80(11.39), 69.58(1.00), 68.56(2.44), 64.76(7.7), 38.49(12.54), 29.39(12.80), 25.65(13.38), 25.32(25.63); IR($CDCl_3$): 3620, 3580(s, free -OH), 3540-3300(br, -OH), 3080(C=C-H), 2960, 1605, 1442, 1410, 1380, 1147, 1120, 1086, 1062, 780, 665, 650 cm^{-1}. Anal. Calc'd for $C_{11}H_{15}BrO$: 242.0306. Found: 242.0299.

A mixture of dimers (R_f=0.31, 96 mg) was also obtained in 61% yield. Thin layer chromatographic purification (ether, developed four times) gave 55 mg of a mixture of two isomeric norbornenyl-type dimers, 315, 316 (35% R_f=0.39);

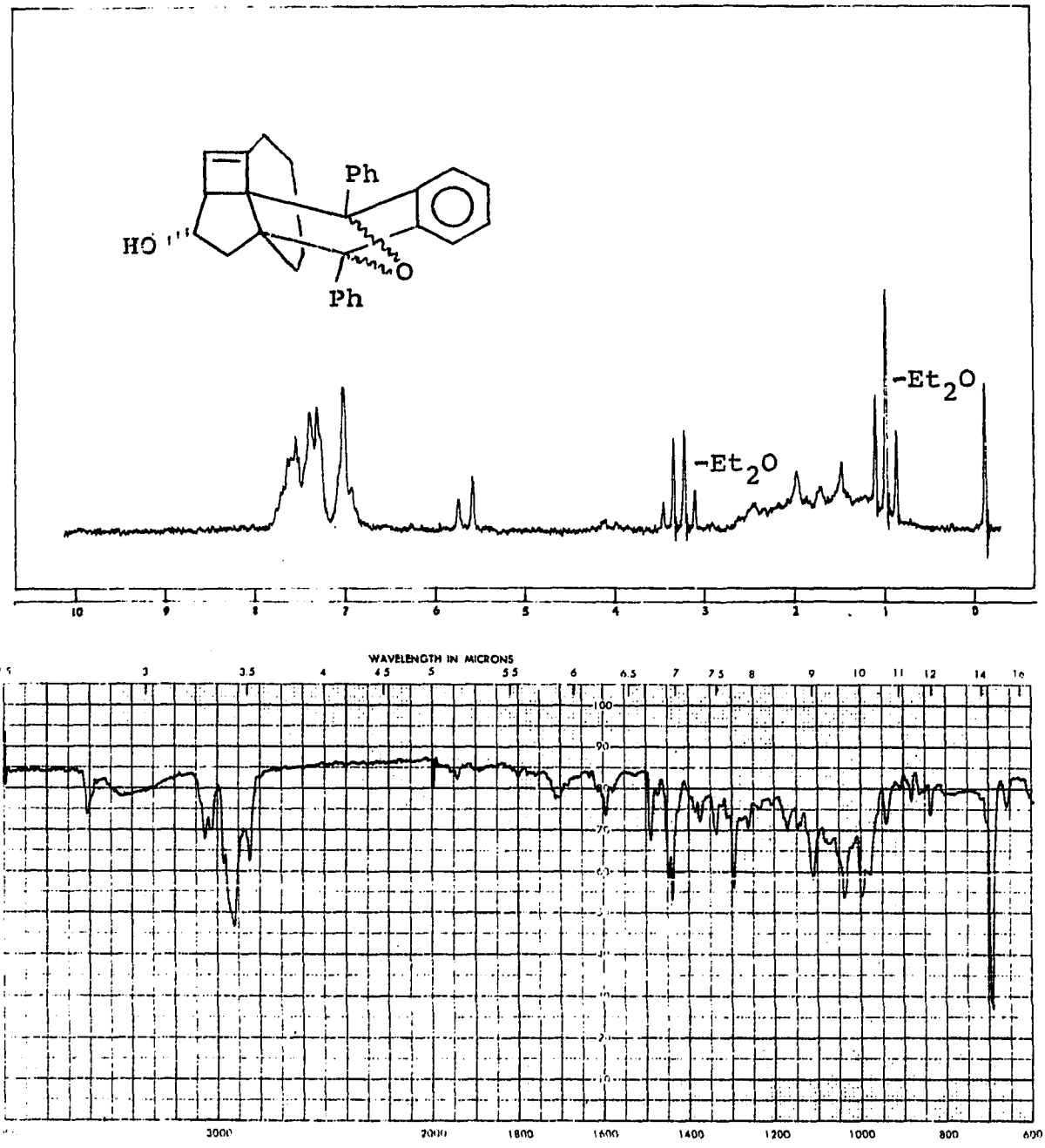


Figure 40. ^{1}H NMR and IR spectra of 219d (two isomers)

GLC (column D) gave one peak (ret. time: 29.2 min); ^{1}H NMR ($CDCl_3$); δ5.9-5.55(m), 4.5~2.75(m), 2.75-1.1(m); ^{13}C NMR ($CDCl_3$): δ161.2(rel. int.: 1.27), 154.00(1.26), 146.6 (1.48), 126.4(1.71), 124.1(1.68), 122.6(1.36), 71.8(1.48), 68.8(1.75), 59.2(1.05), 58.0(1.00), 51.7(1.30), 51.1(1.21), 50.0(1.66), 34.1(1.56), 33.7(1.44), 27.6(1.62), 24.7(1.71), 24.0(1.85), 23.7(1.57), 23.4(1.35); GLC-mass spectrometry gave a parent ion at m/e 296 for $C_{20}H_{24}O_2$. Anal. Calc'd for $C_{20}H_{24}O_2$: m/e 296.1776. Found: m/e 296.1774. A band with R_f=0.31(uv active, yellow band) consisted of a mixture of norbornenyl-type dimers and one cyclobutane dimer 317 (Fig. 41); this mixture was purified further by thin layer chromatography (ether, developed three times), whereby a cyclobutane-type dimer 317 (Fig. 41) (R_f=0.5, uv active, 10%) was isolated. ^{1}H NMR($CDCl_3$ + CD_3OD): δ5.8(s, 2H), 4.704.2(m, 2H), 3.75-3.15(m, 4H, with a singlet at 3.5 probably due to R-OH and CD_3OD H=D exchange), 3.0-1.1(m, 12H); ^{13}C NMR($CDCl_3$): δ156.41(rel. int.: 1.16), 124.08(1.77), 72.40(1.77), 62.76(1.00), 55.01(1.74), 48.29(1.58), 45.64(1.26), 29.55(1.42), 26.73(1.71), 26.47(2.09); IR ($CDCl_3$): 3605(s, free -OH), 3540-3200(br, -OH), 3045 (C=C-H), 2940, 1610(C=C), 1265, 1030 cm^{-1}. The GLC-mass spectrum showed one peak (column D, ret. time: 33.5 min) Anal. Calc'd for $C_{20}H_{24}O_2$: m/e 296.1776. Found: m/e 296.1775. Additionally, an isomer of 317, namely 318 (Fig. 42) (R_f=0.25, uv active), was also isolated in 16% yield.

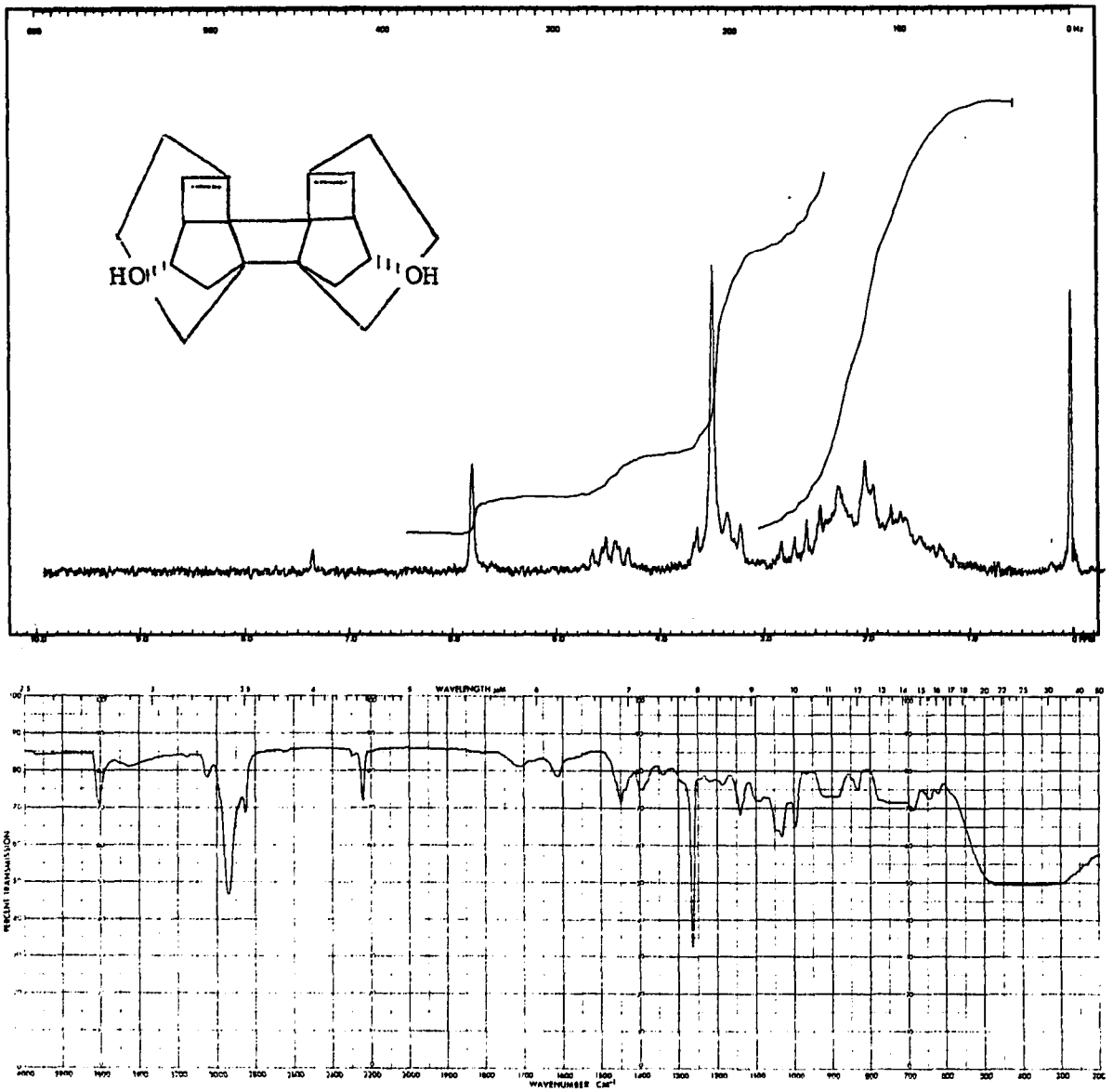


Figure 41. ^{1}H NMR and IR spectra of an R-S dimer 317

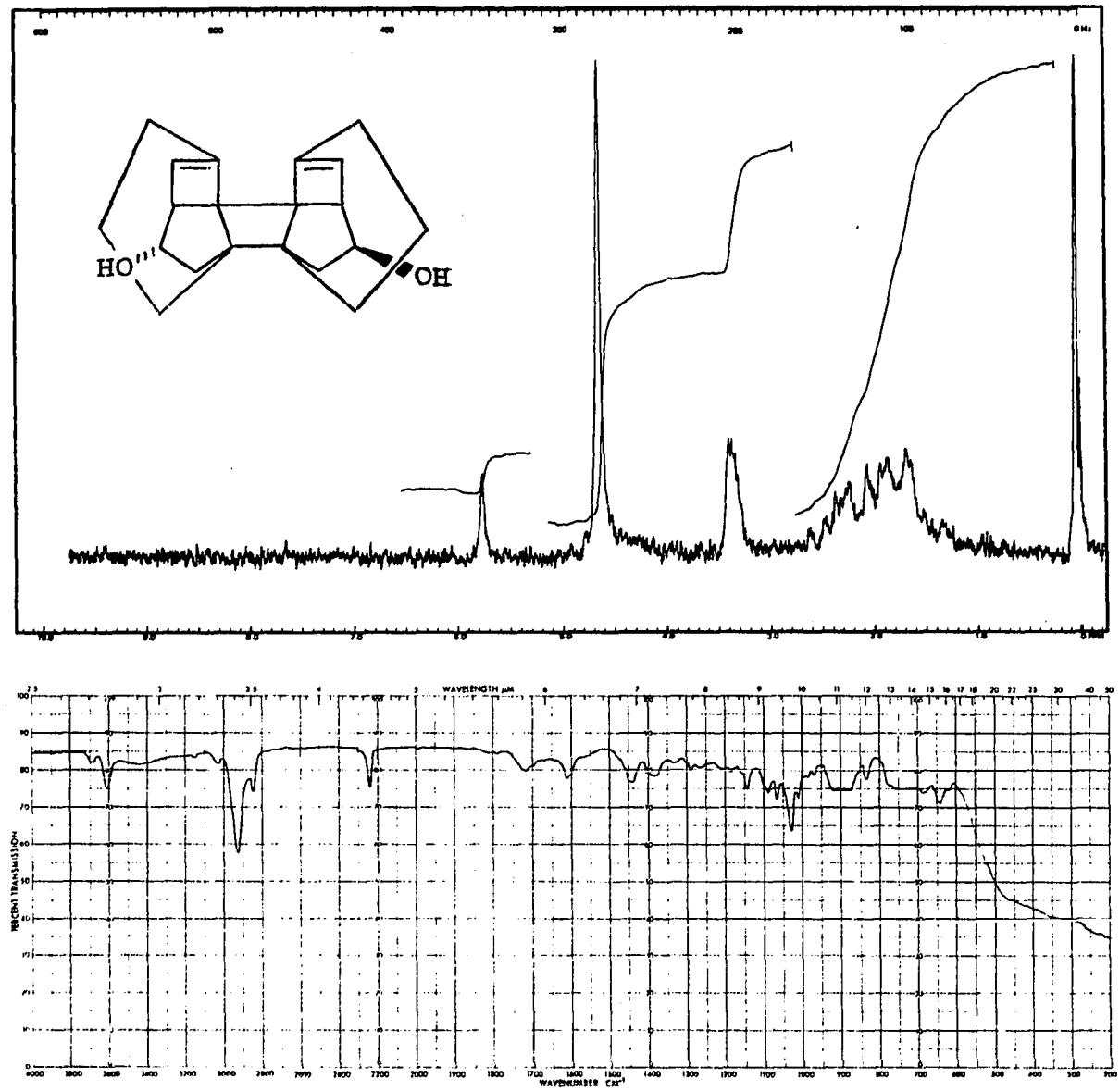


Figure 42. ^{1}H NMR and IR spectra of an R-R(S-S) dimer 318

^{1}H NMR($CDCl_3$, CD_3OD): δ5.75(s, 2H), 4.8-4.1(m, 2H, with a singlet at 4.61 probably due to H-D exchange with the solvent), 3.35(br s, 2H), 2.7-1.2(m); ^{13}C NMR($CDCl_3$): δ156.97(rel. int.: 1.47), 123.16(2.11), 73.76(2.10), 61.19 (1.00), 53.93(1.89), 46.72(1.72), 43.09(1.71), 28.95(1.82), 28.68(2.03), 28.41(2.09); IR($CDCl_3$): 3606(s, free -OH), 3560-3180(br, -OH), 3015(C=C-H), 2920, 1610(C=O), 1060(C-O) cm^{-1}. GLC-mass spectrometry showed (column D, ret. time: 33.5 min) one peak with a parent ion at m/e 296. Anal. Calc'd for $C_{20}H_{24}O_2$: m/e 296.1776. Found: m/e 296.1776.

p-Bromobenzoate derivative of 318 (318a) (Fig. 43)

To a solution of 21.5 mg 318 (0.07 mmol) in 5 ml pyridine was added 80 mg (5 equiv.) p-bromobenzoyl chloride under N_2 at room temperature. The resulting mixture was stirred overnight at room temperature to give a clear light reddish-brown solution. Solvent evaporation gave a residue that was diluted with 15 ml ether, and then washed with H_2O, saturated NaCl solution, and dried over $MgSO_4$. Filtration through a short neutral alumina column, and solvent evaporation gave 48.7 mg (70%) 318a. ^{1}H NMR($CDCl_3$): δ7.7 (AB quartet, J=9, 4 Hz, 8H), 5.9~5.4(m, with a maximum at 5.7, 2H), 3.9(s), 3.8-3.15(m), 2.95-0.6(m). The structure of 318a was established via a single crystal X-ray analysis (see Appendix).

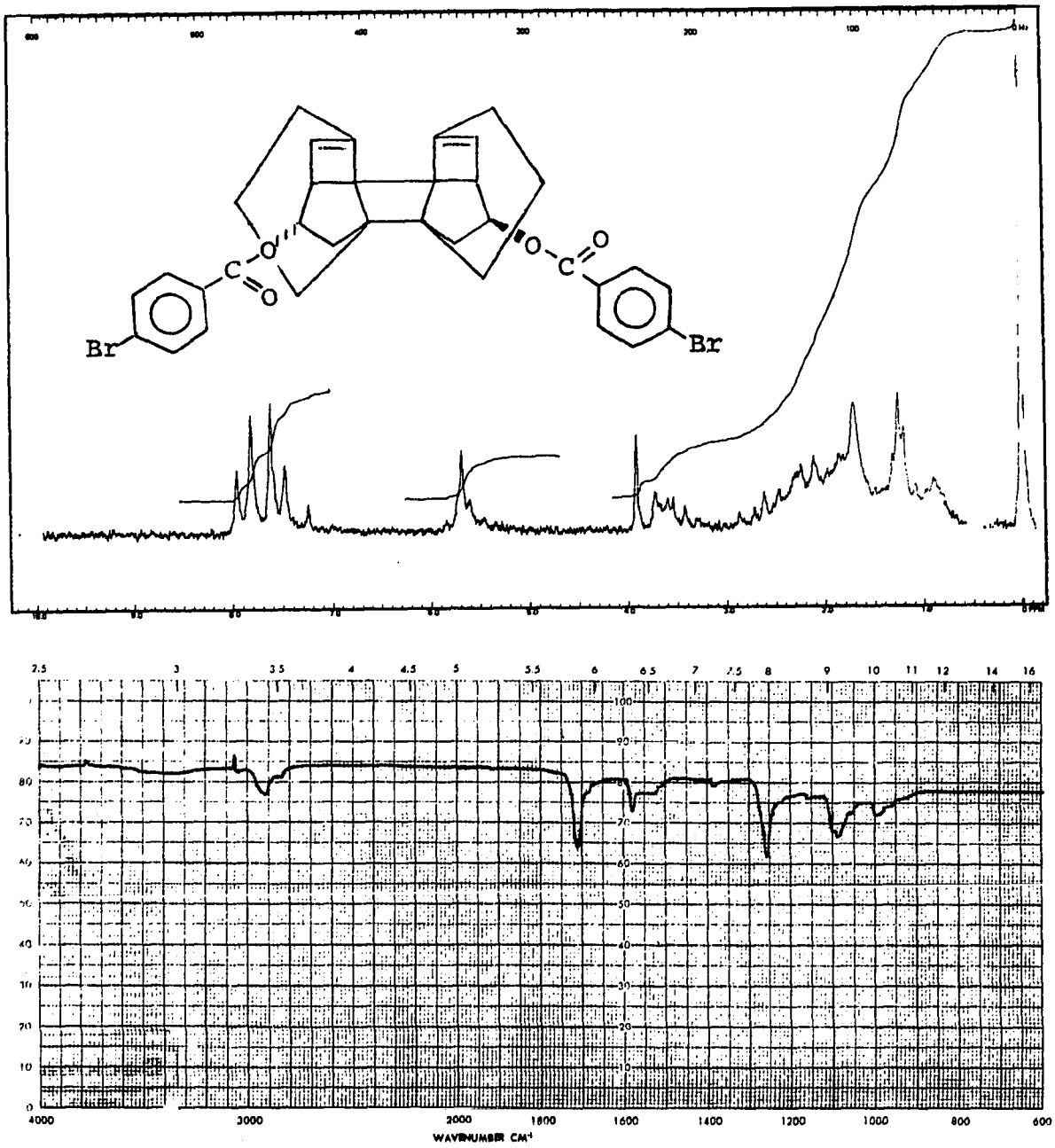


Figure 43. ^{1}H NMR and IR spectra of an R-R(S-S) dimer 318a

p-Bromobenzoate derivative of 219c (219-1-e, 219-2-e) (Fig. 44, 45)

To a solution of a mixture of the two isomeric adducts 219-1-c and 219-2-c (215.5 mg, 0.52 mmol) in 15 ml pyridine (dried over 4A molecular sieves) was added 5 equiv. p-bromobenzoyl chloride (566 mg) under N_2 at room temperature. The resulting mixture was stirred overnight at room temperature followed by solvent evaporation to give a residue which was diluted with ether and filtered through a neutral alumina short column. Concentration of the filtrate gave 91 mg of light brown solid. Thin layer chromatographic purification (15% ethereal hexane) gave 40 mg 219-1-e (R_f=0.83) (Fig. 44); ^{1}H NMR($CDCl_3$): δ7.3-6.8(m, with a singlet at 7.46, 18H), 5.72(br s, 1H), 5.05(br t, 1H), 3.0(br s, 1H), 2.6-2.3(m, with two maxima at 2.43 and 2.54, 2H), 2.3-0.9(m, 6H); IR ($CDCl_3$): 3060, 3030, 2925, 2842, 1710(C=O), 1630(C=C), 1590(C=C), 1280(-C(=O)-O), 1270(O=C=C assym. stretch), 1110 (C-O-C) cm^{-1}. Recrystallization of 219-1-e from CH_2Cl_2/MeOH afforded colorless plates, mp 200-201°C. For details of the X-ray single crystal analysis of 219-1-e, see the Appendix.

Compound 219-2-e (Fig. 45) was also isolated (R_f=0.69); ^{1}H NMR($CDCl_3$): δ8.0-7.0(m, with a singlet at 7.1, 18H), 5.2-4.8(m, 2H), 2.8(br s, 1H), 2.5-2.2(m, with three maxima at 2.42, 2.34 and 2.3, 2H), 2.2-1.0(m, 6H); IR($CDCl_3$): 3070,

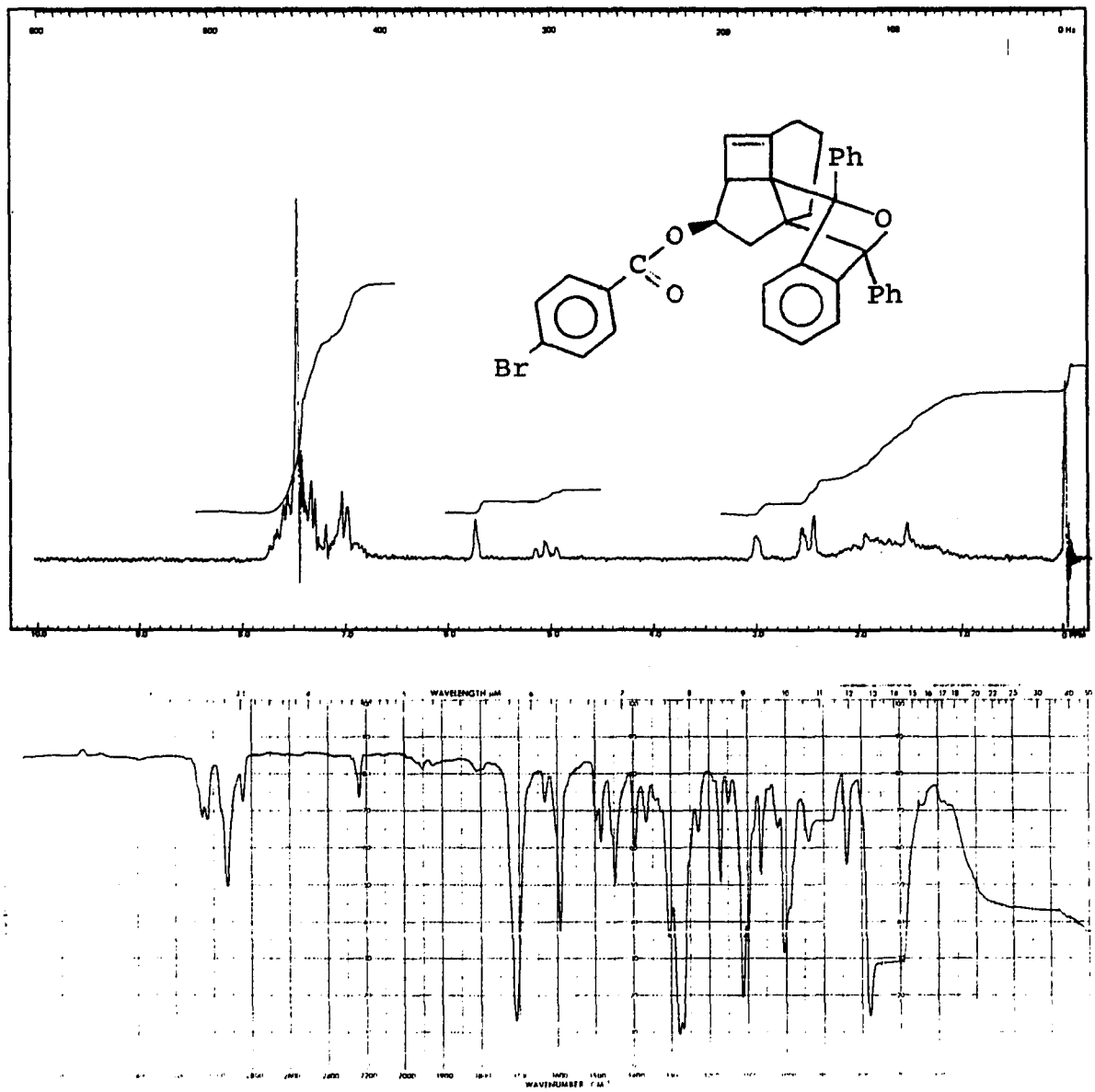


Figure 44. ^{1}H NMR and IR spectra of 219-1-e

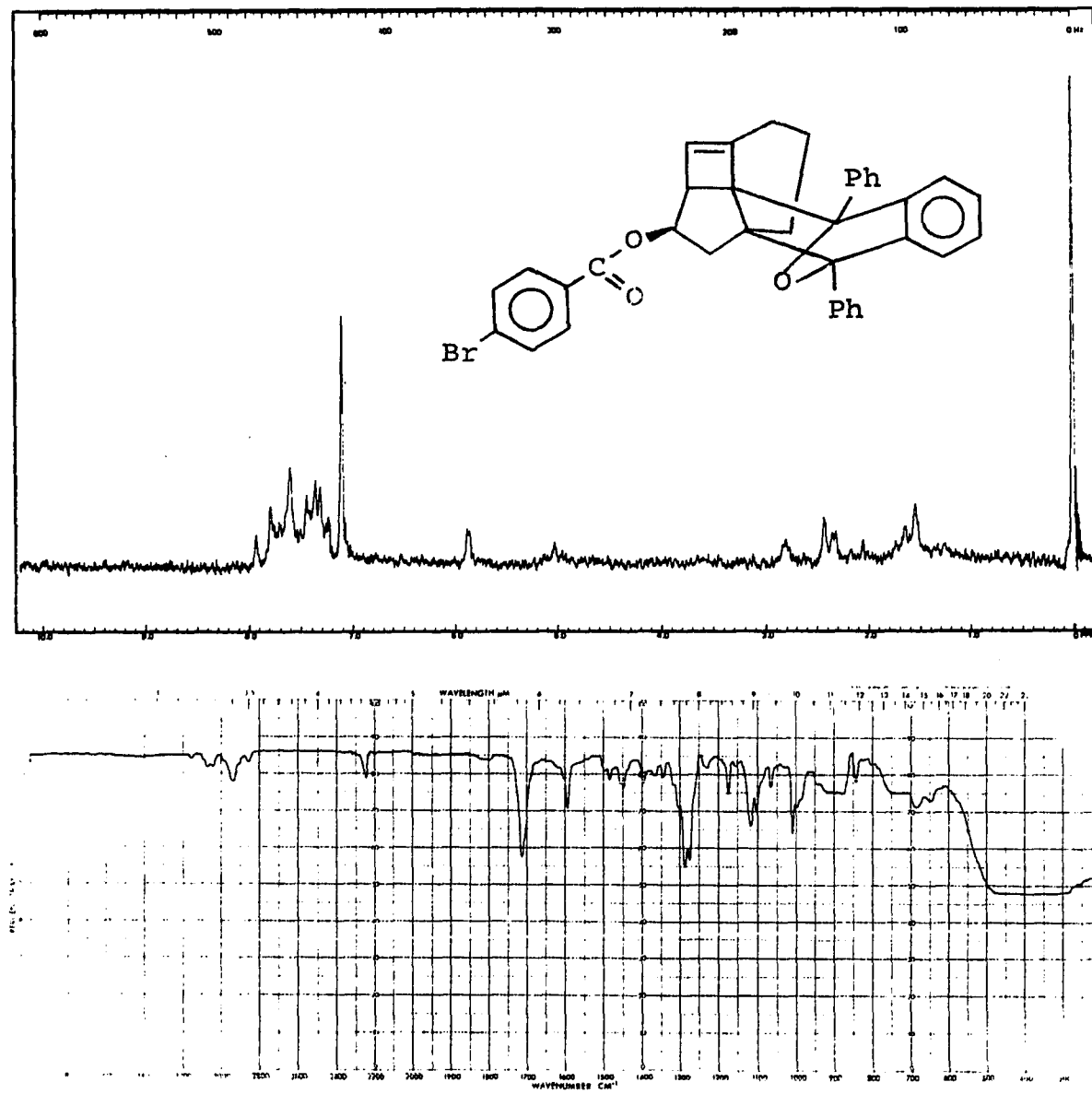


Figure 45. ^{1}H NMR and IR spectra of 219-2-e

3040, 2940, 2860, 1720(C=O), 1590(C=C), 1280(-C(=O)-O), 1270 (O=C=C assym. stretch), 1120(C-O-C) cm^{-1}. Recrystallization of 219-2-e from CH_2Cl_2/MeOH gave colorless needles, mp 193.5-195°C. For details of the X-ray single crystal analysis of 219-2-e, see the Appendix.

The overall yield of 219-e was 46%. Anal. Calc'd for $C_{37}H_{29}BrO_3$: 600.1300. Found: 600.1307.

p-Bromobenzoate derivative of 303c (303e) (Fig. 39)

To a solution of 39.5 mg (0.13 mmol) dimer 303c in 5 ml pyridine was added 175.8 mg (5 equiv.) p-bromobenzoyl chloride at room temperature. The reaction mixture was stirred overnight (20 hr), after which the pyridine was stripped off and the residue was diluted with ether (in this manner, the ether-insoluble solid, p-bromobenzoic acid was removed) and washed successively with H_2O and saturated NaCl, and then dried over $MgSO_4$. The ethereal solution was then filtered through a neutral alumina column; concentration gave 62.5 mg (71%) 303e, which was recrystallized from CH_2Cl/MeOH to afford a colorless solid, mp 189-193°C (d); ^1H NMR($CDCl_3$): δ7.7(d, 4H, J=9 Hz), 7.38(d, 4H, J=9 Hz), 5.55(m, 2H), 4.88(m, with two maxima at 4.92 4.80, 2H), 3.58 (with splitting on the top, 2H), 2.5-1.1(m, 16H); ^{13}C NMR ($CDCl_3$): δ165.74(rel. int.: 1.04), 164.01(1.45), 133.62 131.67(3.27), 130.75(3.24), 129.37(1.40), 128.04(1), 117.75

(1.65), 77.33(1.97), 60.81(1.40), 51.27(1.57), 38.49(1.35), 29.60(1.54), 27.38(1.42), 24.62(1.39); IR($CDCl_3$): 3140, 3060, 2940, 2860, 1708(C=O), 1586(C=C), 1280(-$\overset{O}{\overset{\|}{C}}$-O), 1268 (O=C=C), 1110(C-O-C) cm^{-1}. For details of the X-ray single crystal analysis of 303e, see the Appendix.

Reaction of 192a with MeLi in the presence of DPIBF and various other substances

(a) 4 Equiv. LiI To a solution of 56.5 mg (0.18 mmol) 192a, 94.05 mg LiI, and 50.9 mg (0.19 mmol) DPIBF in 15 ml ether was added 0.86 ml (10 equiv.) MeLi at room temperature, and the reaction mixture stirred for 40 min. After the usual work up, 218a and 219a were obtained in 32.4% and 62.2% yield, respectively. The yields were determined by ^1H NMR with benzaldehyde as an internal standard.

(b) 4 Equiv. $LiClO_4$ To a solution of 53.9 mg (0.17 mmol) 192a 58.8 mg $LiClO_4$, and 50 mg (1.1 equiv.) DPIBF in 15 ml ether was added 0.86 ml (10 equiv.) MeLi at room temperature, and the reaction mixture stirred for 40 min. After the usual work up, 218a and 219a were obtained in 47% and 49% yield, respectively. The yields were determined by ^1H NMR (benzaldehyde internal standard).

(c) 4 Equiv. $NaClO_4$ To a solution of 56.3 mg (0.17 mmol) 192a, 92.2 mg (4 equiv.) $NaClO_4$, and 52 mg DPIBF in

15 ml ether was added 0.85 ml MeLi at room temperature, and the reaction mixture stirred for 40 min. After the usual work up, 218a and 219a were obtained in 29% and 62% yield, respectively. The yields were determined by ^{1}H NMR (benzaldehyde internal standard) $NaClO_4$. However, it should be noted that the $NaClO_4$ was not completely dissolved.

(d) 4 Equiv. KI To a solution of 68.7 mg (0.21 mmol) 192a, 141.7 mg KI, and 63.4 mg DPIBF in 25 ml ether was added 1.04 ml (10 equiv.) MeLi at room temperature, and the reaction mixture stirred for 40 min. After the usual work up, 218a and 219a were obtained in 32% and 65% yield, respectively. The yields were determined by ^{1}H NMR (benzaldehyde internal standard). However, it should be noted that the KI was not completely dissolved.

(e) 4 Equiv. Et_4NBr To a solution of 67 mg (0.21 mmol) 192a, 174.0 mg Et_4NBr, and 62 mg (1.1 equiv.) DPIBF in 25 ml ether was added 1.01 ml (10 equiv.) MeLi at room temperature, and the reaction mixture stirred for 40 min. After the usual work up, 218a and 219a were obtained in 26% and 74% yield, respectively. The yields were determined by ^{1}H NMR (benzaldehyde internal standard). However, it should be noted that the Et_4NBr was not completely dissolved.

The ratio between two isomers 219-1-a (MeO downfield) and 219-2-a (MeO upfield) in the presence of various salts are:

Salt	219-1-a	219-2-a
None	1.1	1.0
LiI	1.0	1.0
$LiClO_4$	1.2	1.0
$NaClO_4$	1.1	1.0
KI	1.3	1.0
Et_4NBr	1.2	1.0

(f) 10 Equiv. 12-crown-4 To a solution of 54 mg (0.17 mmol) 192a, 50 mg DPIBF and 0.27 ml (1.7 mmol) 12-crown-4 in 15 ml ether was added 0.86 ml (0.17 mmol) MeLi at room temperature. An exothermic reaction occurred right away and a white precipitate was formed. The white solid is the product of the reaction of MeLi with 12-crown-4. The resulting mixture was stirred for 40 min at room temperature, followed by washing with H_2O, saturated NaCl solution and drying over $MgSO_4$. Filtration and concentration gave 218a and 219a in 2.8% and 71.7% yield, (GLC corrected yield) respectively. The yields were determined by GLC (column B, di-t-butyl-benzene standard). The GLC correction factor (Varian Aerograph Model 3700) for 218a is 1.969, and for 219a is 2.689.

(g) 20 Equiv. 12-crown-4 To a solution of 55 mg (0.17 mmol) 192a, 50 mg (0.18) DPIBF and 0.54 ml (3.4 mmol) 12-crown-4 in 15 ml ether was added 0.86 ml (1.7 mmol) MeLi at room temperature. An exothermic reaction occurred right away and a white precipitate formed after work up as above, 219a was obtained in 58.5% yield (corrected yield), while

218a was not observed. The yield was determined by GLC (column B, p-di-t-butylbenzene standard).

(h) Quantitative LiI salt effect In each of six different 50 ml three-necked round bottom flasks was placed a solution of 45 mg (0.0016 M) 192a and 1 equiv. (43.2 mg) DPIBF in 9 ml ether. Additionally, in the 2nd flask, 1 equiv. LiI was dissolved, in the 3rd flask, 2 equiv. LiI were dissolved, in the 4th flask, 4 equiv. LiI were dissolved, in the 5th flask, 8 equiv. LiI were dissolved, and in the 6th flask, 20 equiv. LiI (saturated solution) were dissolved. Subsequently, 10 equiv. MeLi were added to each flask within rapid succession (only a few seconds elapsed between additions to each flask) at room temperature. (All the MeLi was from the same bottle). The resulting reaction mixtures were stirred for 55 min at room temperature. After the usual work up, the yields (Table VIII) of 218a and 219a for each reaction were determined by GLC (column B, p-di-t-butylbenzene standard).

Reaction of 192b with MeLi in the presence of DPIBF and LiI

To 10 ml of a saturated solution of LiI in ether was added 66.5 mg (0.21 mmol) 192b, 61.4 mg (0.23 mmol) DPIBF and 1.15 ml (2.1 mmol) MeLi at room temperature, and the resulting mixture stirred for 40 min. After the usual work up, 218b and 219b were observed in a ratio of 1:2 by ^{1}H NMR.

(218b: 27% yield, 219a: 47% yield; benzaldehyde internal satndard).

Reaction of 218a with MeLi in the presence of 12-crown-4

To a solution of 21 mg (0.08 mmol) 218a, 0.13 ml (0.8 mmol) 12-crown-4 and 0.07 mmol p-di-t-butylbenzene in 10 ml ether was added 0.37 ml (0.64 mmol) MeLi at room temperature. A violent exothermic reaction occurred right away and a white precipitate formed. The resulting reaction mixture was stirred for an additional 40 min. After the usual work up, the ratio of 218a to p-di-t-butylbenzene in the crude product remained 1:0.83, the same as prior to reaction (^{1}H NMR).

Reaction of 192a with MeLi in MeI in the presence of DPIBF

To a solution of 95.5 mg (0.30 mmol) 192a and 1.1 equiv. (81 mg) DPIBF in 15 ml MeI was added 1.44 ml ethereal MeLi (10 equiv.) at room temperature, and the resulting reaction mixture stirred for 50 min. This was followed by adding 5 ml H_2O (no exothermic reaction occurred, indicating that the excess MeLi reacted with the MeI) and 20 ml ether. The ethereal solution was washed with H_2O and saturated NaCl solution, filtered and the solvent evaporated to give 77 mg yellow oil. Thin layer chromatographic purification (3% ethereal hexane) gave 33 mg 221 (R_f=0.45, 37%) (Fig. 46); IR(CCl_4): 3066(C=C-H), 1715, 1660(C=C), 1110(C-O-C); ^{1}H NMR:

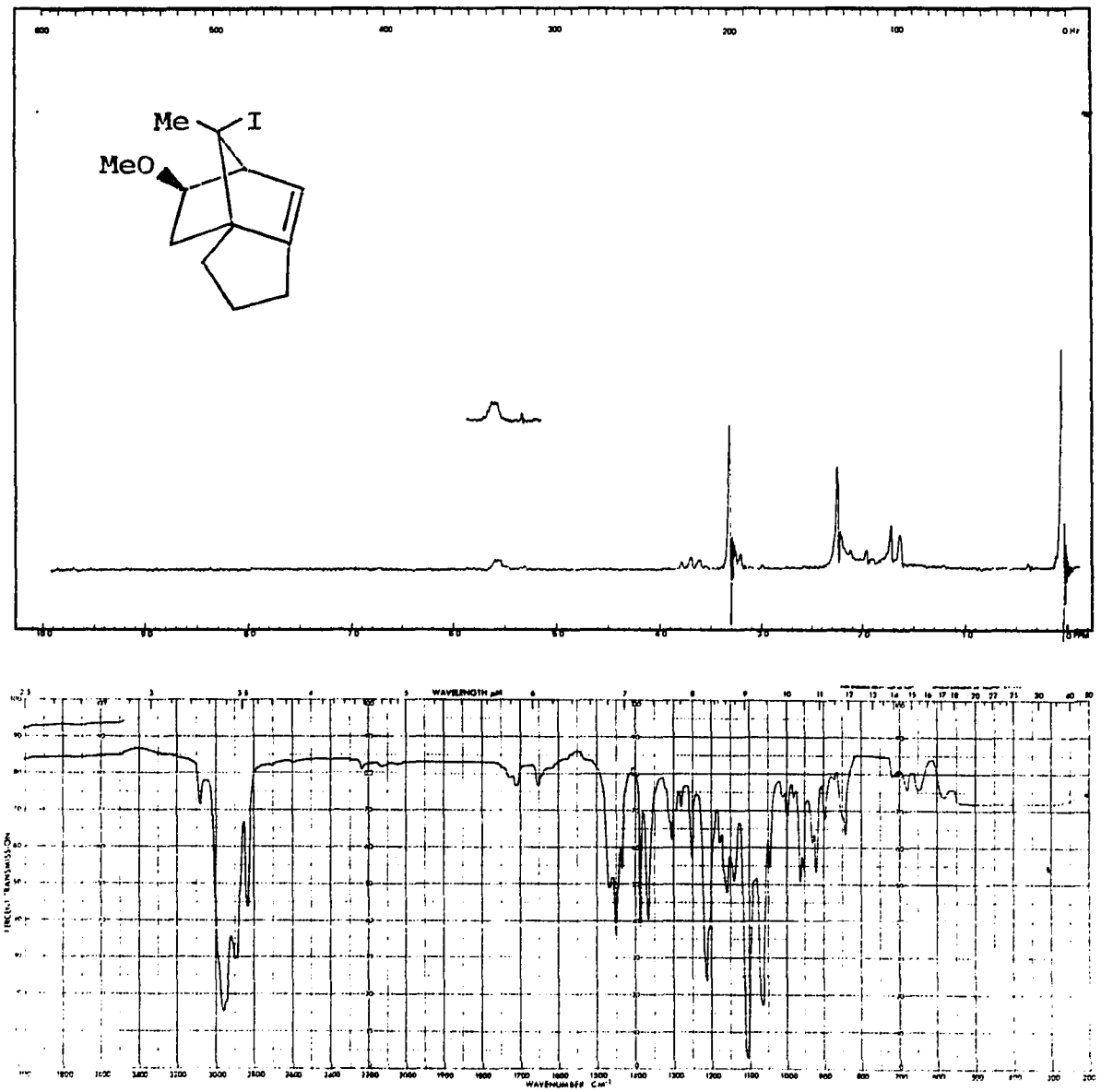


Figure 46. ^{1}H NMR and IR spectra of 1,2-trimethylene-exo-5-methoxy-syn-7-bromo-7-methylnorborna-2-ene (223)

δ5.50(br hump, 1H), 3.66(dd, J=5, 6 Hz, H_6), 3.30(s, 3H), 3.20(d, J=3 Hz, H_1), 2.22(s, 3H), 2.25-1.75(m, 6H), 1.61 (d, J=6 Hz, H_5, H_5,). Decoupling the doublet at δ1.61 (H_5, H_5,) collapsed the doublet of doublets at 3.66 (H_6) to a singlet. Decoupling the doublet at δ3.20 (H_1) collapsed the broad hump at 5.5 to a broad singlet. Lanthanide induced shifts (LIS) for Me-, MeO-, H_1, H_2 and R_2(=H_6) of 223 demonstrated the stereochemistry at C_7 (Table IX). Anal. Calc'd for $C_{12}H_{17}IO$: C, 47.53; H, 5.61. Found: C, 47.45; H, 5.67. Also, 219a was isolated in 24% yield, and a small amount of 218a was observed by GLC-mass spectrometry.

Reaction of 192a with MeLi in CD_3I in the presence of DPIBF

To a solution of 60.7 mg (0.19 mmol) 192a and 56.3 mg DPIBF in 2 ml CD_3I was added 2 ml MeLi (1.6 M) at -78°C, and the reaction mixture stirred for 40 min. After work up, layer purification (4% ethereal hexane) of the crude product gave 223 in 37% yield. The GC-mass spectrum (column C) of the crude product also showed the presence of 218a in low yield.

Determination of the amount of deuterium incorporated into 218a and 223

Comparison of the (P-I) and (P-Br) peaks in the mass spectra of the parent compounds 223 and 218a and the deuterated analogues (223-d_3, 218a-d_3) showed that only 7.7% (6.2% for 218a) of three deuteriums were incorporated

into 223 (comparison of the parent ions was impossible due to their weak intensities) (Table X). Since virtually all the peak intensity at m/e 180 was due to $C_{12}H_{14}D_3O$ (this ion was not observed in the mass spectrum of 221 obtained from the reaction in CH_3I) and that at m/e 177 was due to $C_{12}H_{17}O$, one could utilize their intensities to obtain the D_3 percentages shown below, assuming % D_3=I(m/e 180)·100/ [I(m/e 180) + I(m/e 177)] and the accuracy of the m/e 180 and m/e 177 (i.e., the background at m/e 177 could not be taken into account).

Reaction of 218a with MeLi in MeI

To a solution of 20 mg (0.07 mmol) 218a in 10 ml MeI was added 0.37 ml (0.64 mmol) MeLi at room temperature, whereupon an exothermic reaction occurred spontaneously (i.e., MeLi + MeI → EtH + LiI, a reaction which is slower than the reaction of MeLi with 192a). The resulting mixture was stirred for 40 min. After the usual work up, 19 mg 218a was recovered.

Reaction of 223 with MeLi in CH_2Br_2

To a solution of 21 mg (0.07 mmol) 223 (contaminated with 218a and 230) and p-di-t-butylbenzene (the ratio of 223: 218a:230:p-di-t-butylbenzene was 7.43:0.55:2.67:1, uncorrected) in 8 ml CH_2Br_2 (Eastman) was added 0.38 ml (0.7 mmol) MeLi at room temperature. The resulting reaction mixture was stirred for 1 hr at room temperature. After

work up, GLC (column B) of the crude product revealed the ratio of 223:218a:230:p-di-t-butylbenzene was 3.96:1.34:5.56:1 (uncorrected). These results show that both 230 and 218a increased while 223 decreased, indicating that 218a and 230 result from the reaction of 221 with MeLi in CH_2Br_2. (The starting materials and the product mixture were examined under the same GLC conditions.)

Thin layer chromatographic purification (4% ethereal hexane, developed twice) gave 230 (R_f=0.29) (Fig. 47); ^{1}H NMR: δ5.25~5.08(m, 1H), 3.39(d, H_6), 3.23(s, 3H), 2.75~2.6(m, H_1), 2.4-0.9(m, including a doublet at 0.8 for Me-, J=7 Hz); IR(CCl_4): 3070(C=C-H), 1650(C=C), 1105(C-O) cm^{-1}. Anal. Calc'd for $C_{12}H_{18}O$: m/e 178.1358. Found: m/e 178.1349. Lanthanide induced shifts (LIS) for H_2 and Me- suggest the Me- at C_7 is syn to the double bond (Table XI).

Reaction of 10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene (191) with MeLi

(a) In the presence of DPIBF To a solution of 200 mg (0.69 mmol) diene 191 and 202 mg (0.75 mmol) DPIBF in 10 ml ether was added 2.5 ml (3.5 mmol) MeLi at room temperature and the reaction mixture stirred for 30 min. After work up, solvent evaporation gave a yellow residue which was chromatographed on a silica gel column (fractions 1,2:hexane, fractions 3,4:2% ethereal hexane, fractions 5,6:4%.

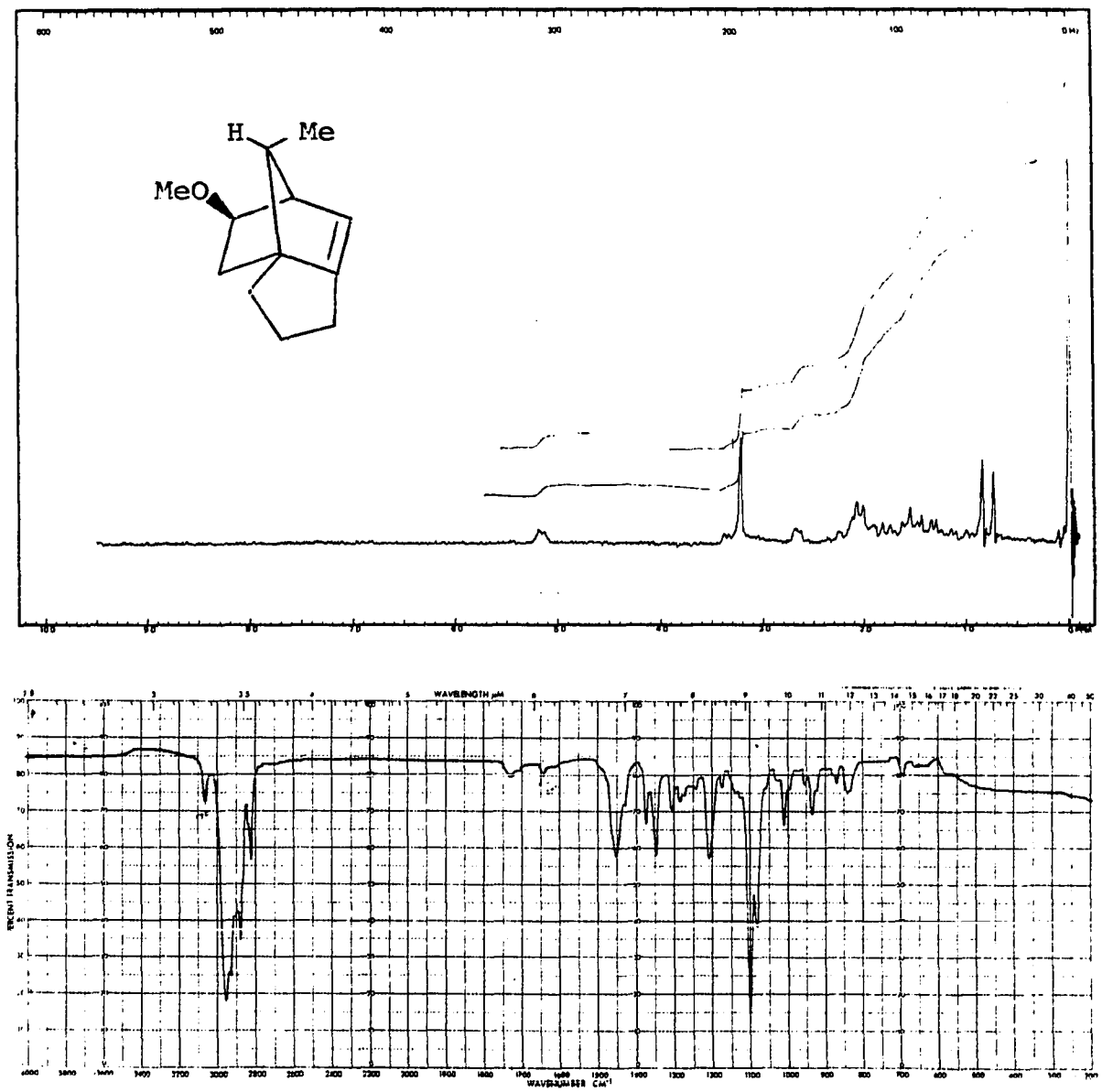


Figure 47. ^{1}H NMR and IR spectra of 1,2-trimethylene-exo-5-methoxy-7-methylnorborna-2-ene (230)

ethereal hexane). Thin layer chromatographic purification (15:85 mixture of CH_2Cl_2 and hexane) of fractions 4 and 5 (120 mg) afforded 247-1 (R_f=0.52, 8% GC yield) (Fig. 48), mp 155-157°C; ^1H NMR: δ7.9-6.9(m, 14H), 5.84(br s, 1H), 5.64(br s, 2H), 2.97(br s, 1H), 2.2-0.7(m, 6H); IR(CCl_4): 3040(C=C-H), 2920, 2860(C-H), 1625, 1610(C=C), 1505, 1460, 1453, 1310, 1270, 1180, 1155, 1010, 980, 910, 730, 700 cm^{-1}. Anal. Calc'd for $C_{30}H_{24}O$: m/e 400.1827. Found m/e 400.1846. Compound 247-2 was also isolated by TLC (R_f=0.44, 16% GC yield) (Fig. 49), mp 207-209°C (d); ^1H NMR: δ7.3-6.95(m, 14H), 5.9(s, 1H), 5.65(dd, 1H), 5.05(d, 1H), 3.0(br s, 1H), 2.0-1.0(m, 6H); IR(CCl_4): 3040(C=C-H), 2920, 2855(C-H), 1600(C=C), 1495, 1455, 1445, 1300, 1175, 1145, 1000, 970, 690 cm^{-1}. Anal. Calc'd for $C_{30}H_{24}O$: m/e 400.1827. Found: m/e 400.1817.

(b) In the absence of DPIBF To a solution of 200 mg (0.69 mmol) 191 in 15 ml ether was added 1.76 ml (3.5 mmol) MeLi at room temperature; after 2 min a few drops of H_2O were added to quench the excess MeLi, upon which a white solid (LiOH) was formed. The resulting mixture was diluted with ether and then dried over $MgSO_4$. Filtration and solvent evaporation gave 85 mg light brown oil mixed with some needle-shaped crystals. The residue was diluted with degassed (or freshly distilled from $LiAlH_4$) ether and

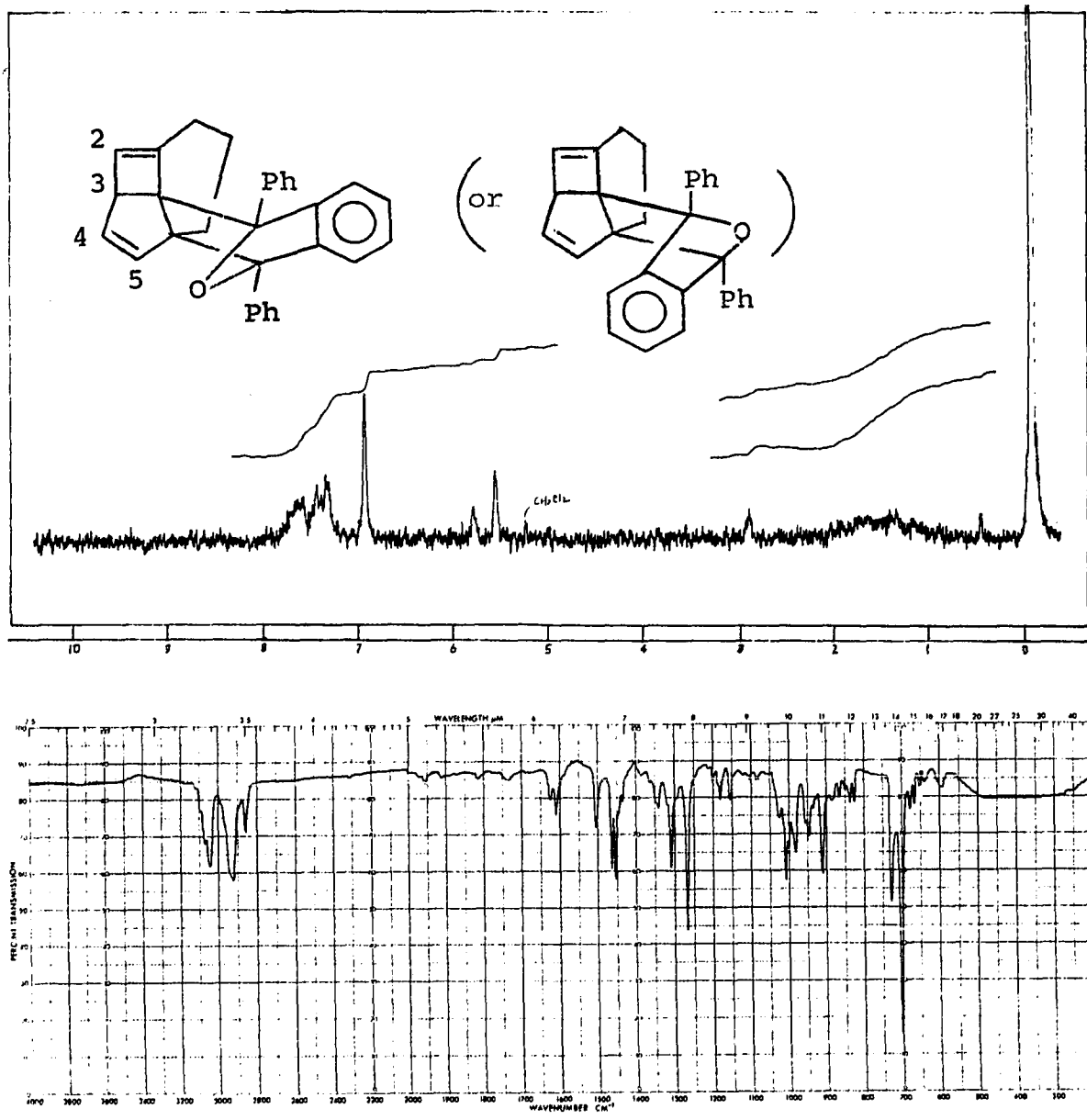


Figure 48. ^{1}H NMR and IR spectra of 247-1 (or 247-2)

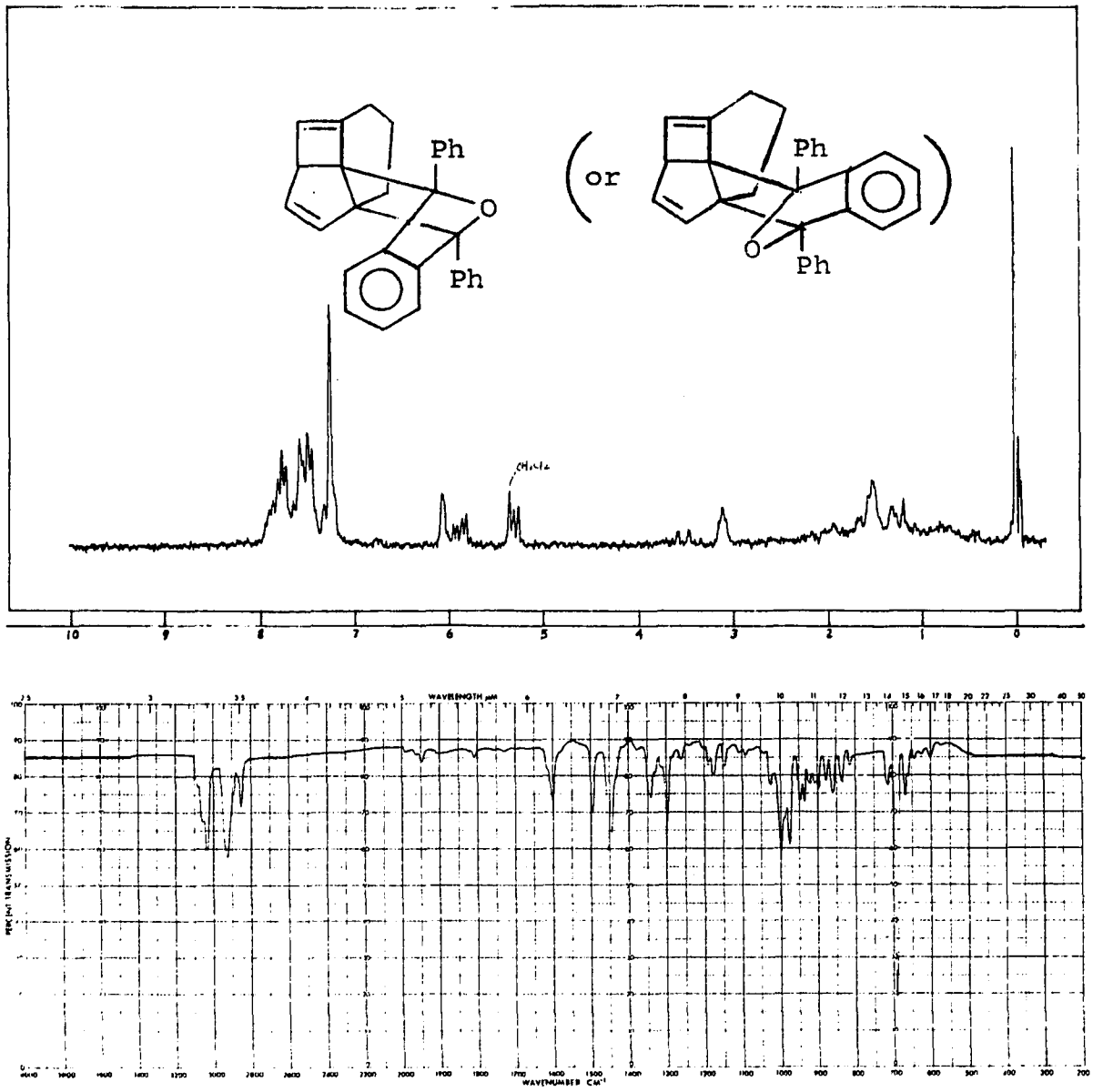


Figure 49. ^{1}H NMR and IR spectra of 247-2 (or 247-1)

purified by GLC (column A, column temperature: 120°C for 1 min, then programmed to 150°C), whereby dimer 246a (or 246b) was isolated (Fig. 50) (ret. time: 2 min, 22% GLC yield, white solid, air sensitive), mp 93-95°C; ^{1}H NMR: δ6.13(dd, $J_{4,5}$=5 Hz, $J_{4,3}$=2 Hz, $2H_4$), 5.86(br s, $2H_2$), 5.32(d, $J_{5,4}$=5 Hz, $2H_5$), 3.55(m, $2H_3$), 2.45-1.08(m, 12H). Decoupling the doublet of doublets at δ6.13 (H_4) collapsed the doublet at 5.32 (H_5) to a singlet; decoupling the doublet at 5.32 (H_5) collapsed the doublet of doublets at δ6.13 (H_3) to a doublet (J=5 Hz); ^{13}C NMR($CDCl_3$): 152.53(rel. area 1.31), 139.31(1.80), 136.11(2.38), 134.48(2.56), 59.18(1.00), 56.42(2.26), 28.63(2.36), 27.65(2.91), 27.49(2.71); IR(CCl_4): 3020(C=C-H), 2900, 2840, 1600(C=C), 1435, 1175, 1140, 1000, 940, 925, 825, 710 cm^{-1}. Anal. Calc'd for $C_{20}H_{19}$(P=1): m/e 259.1487. Found: m/e 259.1485.

Reaction of 2-methylene-10-bromotricyclo[4.3.1.$0^{1,6}$]decane (204) with Harpoon base in the presence of DPIBF

To a solution of 90.8 mg (0.40 mmol) 204 and 297 mg (1.1 equiv.) DPIBF in 10 ml ether was added 15 equiv. freshly prepared Harpoon base (made by mixing 1.02 ml 1,1,5,5-tetramethylpiperidene and 4.87 ml 1.24 M MeLi in 5 ml ether) at room temperature. The resulting solution turned dark brown, and the reaction mixture was then stirred for 2.5 hr at room temperature. After the usual work up,

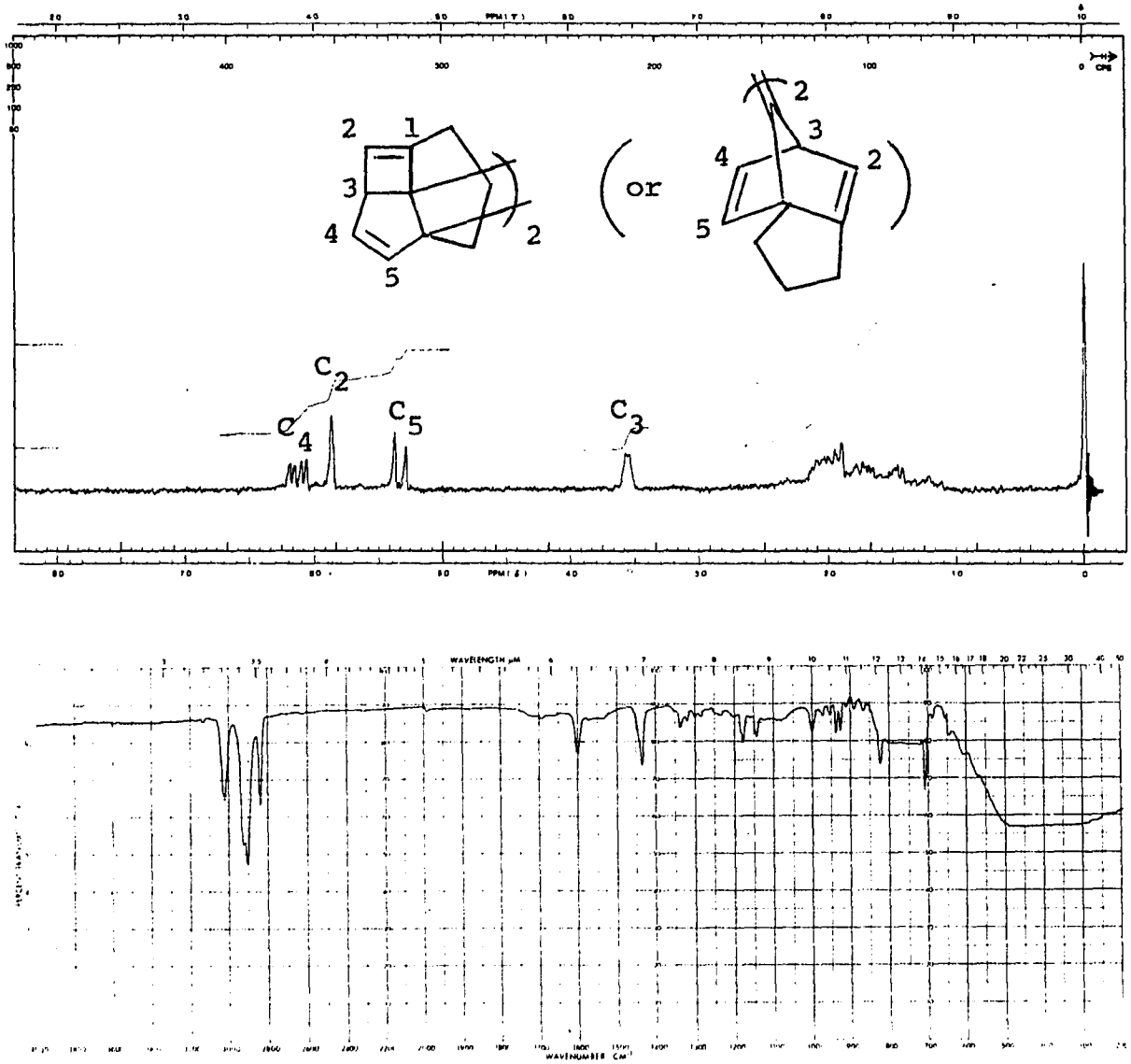


Figure 50. ^{1}H NMR and IR spectra of a diene dimer 246a (or 246b)

360.5 mg crude product was obtained. The crude product consisted mainly of intramolecular insertion products; no trapping products were observed by GLC-mass spectrometry. There were two peaks with parent ions at m/e 146 which might correspond to the rearranged products (266, 267) from 268 and 269 (column B, ret. time: 1.25 min, 1.7 min). Both peaks have exactly the same fragmentation pattern: m/e 146.02(P, rel. area: 66.46), 131.00(P-15, 81.80), 117.00 (P-29, 76.82), 105.98(P-40, 5.52), 90.92(P-55, 100.00), 76.94(P-69, 32.04), 64.84(P-81, 26.62).

Reaction of 2-methylene-10,10-dibromotricyclo[4.3.1.$0^{1,6}$]-decane (206) with MeLi in the presence of DPIBF

To a solution of 100 mg 206 (contaminated with highly brominated material) and 97 mg DPIBF in 10 ml ether was added 2.5 ml (10 equiv.) MeLi at room temperature. The resulting reaction mixture was stirred for 1 hr at room temperature. After the usual work up, 150 mg yellow residue was obtained. The GLC-mass spectrum showed two peaks with parent ions at m/e 146 which might correspond to the rearranged insertion products, 266 (column B, ret. time: 1.25 min, 1.7 min). Also observed were two peaks (ret. time: 2.2 min, 3.2 min) with parent ions at m/e 160, which might correspond to the rearranged products from 272 and 275 (273, 276). Both 273 and 276 showed the same fragmenta-

tion pattern: m/e 160.00(P, % RA: 19.29), 145(P-15, 100.00), 131.00(P-29, 13.14), 117.00(P-43, 47.08), 91.00 (P-69, 41.86), 79.00(P-81, 21.90), 77.00(P-83, 23.81), 51.00(P-109, 14.96). Lastly, 277 was also observed (ret. time: 4.2 min): m/e 162.00(P, % RA: 6.20), 158.00(P-4, 8.77), 135(P-27, 51.66), 128.00(P-27, 20.00), 115.00(P-47, 35.00), 108.00(P-54, 100.00), 91.00(P-71, 78.70), 79.00 (P-83, 70.00), 65.00(P-97, 29.60), 51.00(P-111, 46.50).

Reaction of 10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-7-ene (217) with MeLi

(a) In the presence of DPIBF To a solution of 128 mg (0.44 mmol) 217 and 130.3 mg DPIBF in 15 ml ether, was added 2.44 ml (10 equiv.) MeLi at room temperature. The resulting reaction mixture was stirred for 1 hr at room temperature followed by the usual work up to give a yellow residue which turned dark within 1 min. GLC-mass spectra of the black residue revealed the presence of 279 (Fig. 51) and 280 in an apparent ratio of ca. 3:1 (without correction factors). Compound 280 (ret. time: 1.7 min) exhibited the following fragmentation pattern: m/e 211.86(P+2, % RA: 15.30), 209.84(P, 16.47), 183.86(P+2-28, 6.39), 181.84 (P-28, 6.97), 130.98(P-79, 100.00), 114.98(P-95, 17.97), 102.96(P-107, 15.50), 90.98(P-119, 25.84), 76.94(P-133, 15.43), 63.94(P-146, 25.89). Also, a very small amount of DPIBF trapping adduct (281) was observed (ret. time: 14

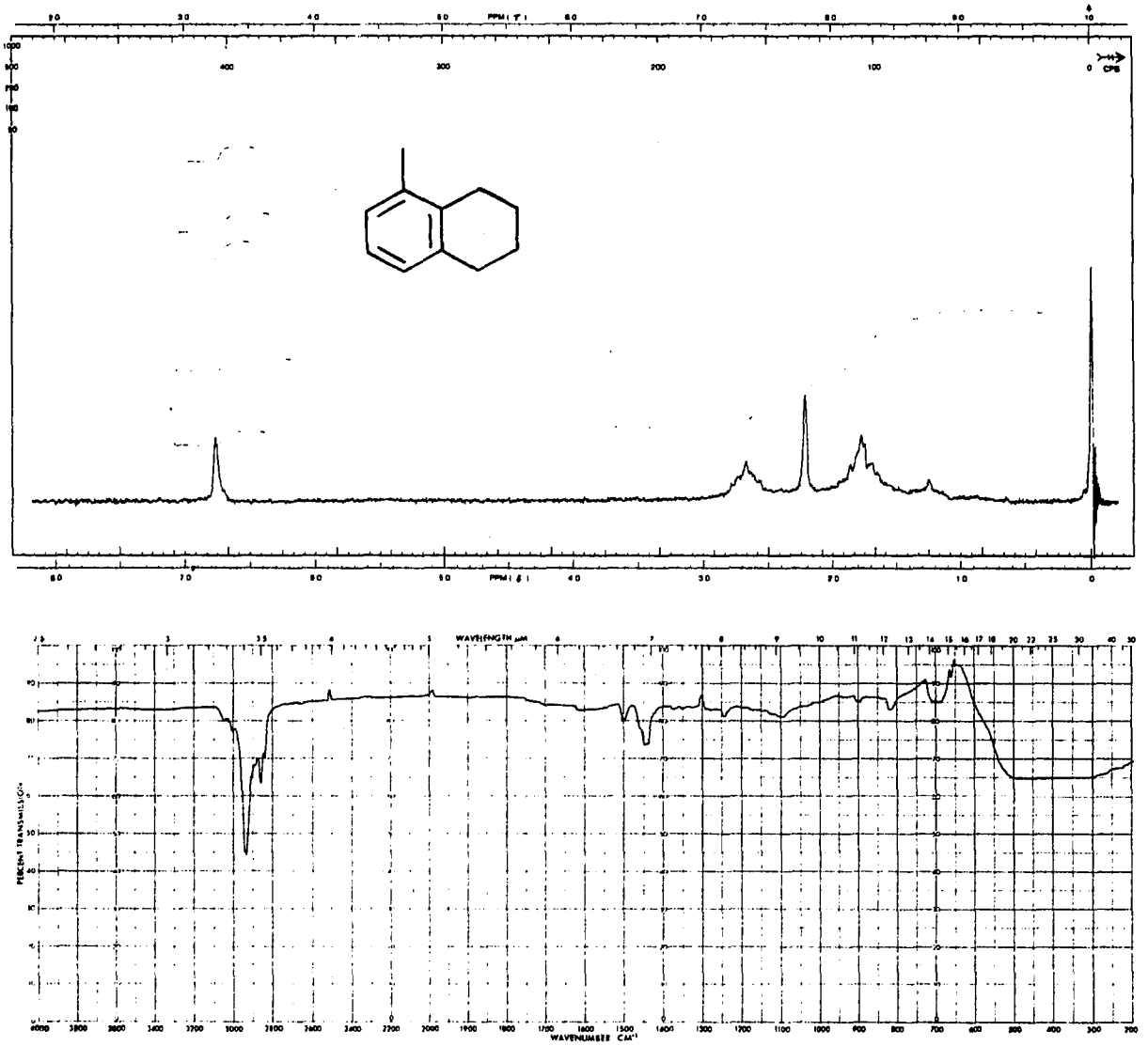


Figure 51. ^{1}H NMR and IR spectra of 279.

min): m/e 401.86(P, % RA: 3.21), 361.90(P-40, 7.16), 324.96(P-77, 7.91), 285.94(P-116, 14.42), 208.88(P-193, 58.12), 206.86(P-195, 47.22), 151.96(P-250, 38.78), 104.94 (P-297, 95.73), 76.96(P-325, 100.00), 72.96(P-329, 41.35), 68.96(P-333, 26.18), 57.00(P-345, 35.04), 54.98(P-347, 42.95). Lastly, there were two unidentified isomeric products (282a, 282b) with parent ions at m/e 384, both of which showed the same fragmentation pattern (ret. time: 31.3 min and 34.7 min): m/e 384.24(P, % RA: 100), 355.20 (P-29, 4.00), 341.20(P-43, 8.73), 252.12(P-132, 16.00), 207.02(P-177, 32.45), 171.14(P-213, 61.91), 163.10(P-221, 37.64), 156.74(P-227, 18.73), 73.00(P-311, 26.18), 55.02 (P-329, 18.55).

(b) In the absence of DPIBF To a solution of 72.5 mg (0.25 mmol) 217 in 10 ml ether was added 1.38 ml (10 equiv.) MeLi at -78°C, and the resulting reaction mixture stirred for 1 hr at -78°C. After the usual work up, filtration and concentration gave a black residue. Thin layer chromatographic purification afforded compound 279 (Fig. 51) in 30% yield; ^{1}H NMR: δ6.76(br s, 3H), 2.9-2.5(m, with a maximum at 2.67, 4H), 2.22(s, 3H), 2.12-1.1(m, with two maxima at 1.76 and 1.25); IR(CCl_4): 3050(C=C-H), 2930, 1500, 1450, 820 cm^{-1}. Anal. Calc'd for $C_{11}H_{14}Br$: m/e 146.1105. Found: m/e 146.1103.

The GLC-mass spectrometry fragmentation pattern of 279: m/e 147.02(P+1, % RA: 10.71), 146.00(P, 84.26), 145.00 (P-1, 16.31), 132.00(P-14, 13.36), 131.00(P-15, 100.00), 128.98 (P-17, 20.63), 127.98(P-18, 23.80), 118.02(P-28, 94.31), 117.00(P-29, 44.10), 114.98(P-31, 34.26), 104.98 (P-41, 51.09), 90.98(P-55, 33.09), 76.96(P-69, 18.26), 64.82(P-81, 17.57), 50.96(P-95, 16.98).

Reaction of 10-bromotricyclo[4.3.1.$0^{1,6}$]deca-7-ene (215) with Harpoon base in the presence of DPIBF

To a solution of 102 mg (0.35 mmol) 215 and 104 mg (1.1 equiv.) DPIBF in 10 ml ether was added a solution of 1.94 ml (1.8 M) MeLi in 1.18 ml 1,1,5,5-tetramethyl-piperidine at room temperature. The resulting reaction mixture turned brown and was then stirred for 16 hr at room temperature. The usual work up gave a yellow residue (175 mg) which contained 179 and the trapping adducts 282, as determined by GLC-mass spectral studies. Thin layer chromatographic purification (7% ethereal hexane) gave a mixture of two isomeric products (282a, 282b) with parent ions at m/e 384. ^{1}H NMR: δ7.44-7.04(m, with two maxima at 7.50 and 7.45), 6.95(s), 3.08-2.58(m), 2.08-1.56(m), 1.40-1.05(m), 1.05-0.70(m). The structure of compound 282 is not known.

Reaction of exo-4-methoxy-10-bromotricyclo[4.3.1.$0^{1,6}$]deca-2-ene (193) with Harpoon base in the presence of DPIBF

To a solution of 101 mg (0.42 mmol) 193 and 123.7 mg (1.1 equiv.) DPIBF in 20 ml ether was added a solution of 2.0 ml (10 equiv.) MeLi in 1.06 ml 1,1,5,5-tetramethylpiperidene at room temperature. The resulting reaction mixture was stirred for 3 hr at room temperature. After the usual work up, 203.8 mg yellow residue was obtained. The trapping products 219 was the only product identified by ^{1}H NMR and GLC studies.

Pyrolysis of endo-4-methoxy-10-bromo-10-trimethyltintricyclo[4.3.1.$0^{1,6}$]deca-2-ene (208) in the presence of DPIBF

A sealed NMR tube containing a solution of 9 mg (0.02 mmol) 208 and 6.6 mg (1.1 equiv.) DPIBF in 0.3 ml diphenyl ether was heated in an oven tube at 250°C for 1 min whereby the solution turned dark brown. GLC (column C) and ^{1}H NMR analysis showed the presence of 219b, whereas no 219a was observed. The two isomeric trapping adducts (219b) had retention times of 28.7 min and 29.8 min (column temperature: 120°C for 6 min programming 20°C/min up to 280°C; injector temperature: 250°C; detector temperature: 300°C).

Pyrolysis of exo-4-methoxy-10-bromo-10-trimethyltintricyclo-[4.3.1.$0^{1,6}$]deca-2-ene (207) in the presence of DPIBF

(a) In diphenyl ether A sealed NMR tube containing a solution of 21.5 mg (0.05 mmol) 207 and 15.8 mg (1.1 equiv.)

DPIBF in 0.6 ml diphenyl ether was heated in an oven tube at 250°C for 1 min, whereby the solution turned dark brown. The two isomeric DPIBF adducts, 219-1-a, and 219-2-a, were observed by GLC (column C) and ^{1}H NMR studies, whereas no 219b was observed. The retention time for 219-1-a and 219-2-a were 28 min and 31 min (column conditions were the same as above).

GLC (column C) trace of a mixture of 219-1-a, 219-2-a, 219-1-b and 219-2-b showed four different peaks with retention times: 28 min, 31 min, 28.7 and 29.8 min respectively (column conditions were the same as above).

(b) In 2.5 ml benzene A sealed 16 x 150 mm culture tube containing a solution of 14 mg (0.03 mmol) 207 and 10.3 mg (1.1 equiv.) DPIBF in 2.5 ml benzene was heated at 140-150°C for 80 min, 80% of the tube was submerged into the oil bath. Solvent evaporation gave a dark brown residue which contained 207 and 219-a in a ratio of 1.00:0.77 (^{1}H NMR analysis).

(c) In 25 ml benzene A sealed 16 x 150 mm culture tube containing a solution of 14 mg (0.03 mmol) 207 and 10.3 mg (1.1 equiv) DPIBF in 25 ml benzene was heated at 140-150°C for 80 min. Solvent evaporation gave a residue which contained 207 and 219-a in a ratio of 1.00:0.75 (^{1}H NMR analysis).

Reaction of 9,9-dichlorotricyclo[4.2.1.$0^{1,6}$]deca-3-ene (134) with MeLi in the presence of DPIBF

To a solution of ca. 100 mg 134 and 163 mg DPIBF in 10 ml pentane was added 4.22 ml MeLi (10 equiv.), and the reaction mixture stirred for 16 hr at room temperature. After the usual work up, 231 mg crude product was obtained. Thin layer chromatographic purification (20% ethereal hexane) gave 300 (R_f=0.93, 13%). Recrystallization of 300 (Fig. 52) from CH_2Cl_2/MeOH afforded colorless crystals, mp 195-196°C; ^{1}H NMR($CDCl_3$): δ8.4~7.0(m, 14H), 5.35(m, 2H), 3.0-1.0(m, 8H), 0.4(s, 3H); IR($CDCl_3$): 3090, 3060, 3020, 2990, 2950, 2870, 1600, 1455, 1295, 1260, 1010, 980, 670 cm^{-1}. For details of the X-ray single crystal analysis of 300, see the Appendix.

Compound 301 was also isolated (Fig. 53, R_f=0.85, 11%), and recrystallization of 301 from CH_2Cl_2/MeOH afforded colorless crystals, mp 183-184.5°C. ^{1}H NMR($CDCl_3$): δ8.3-7.0(m, 14H), 5.35(m, 2H), 3.2-1.6(m, 8H); IR($CDCl_3$): 3100, 3070, 3020, 2950, 2900, 1660, 1600, 1495, 1445, 1295, 1000, 670 cm^{-1}. For details of the X-ray single crystal analysis of 301, see the Appendix.

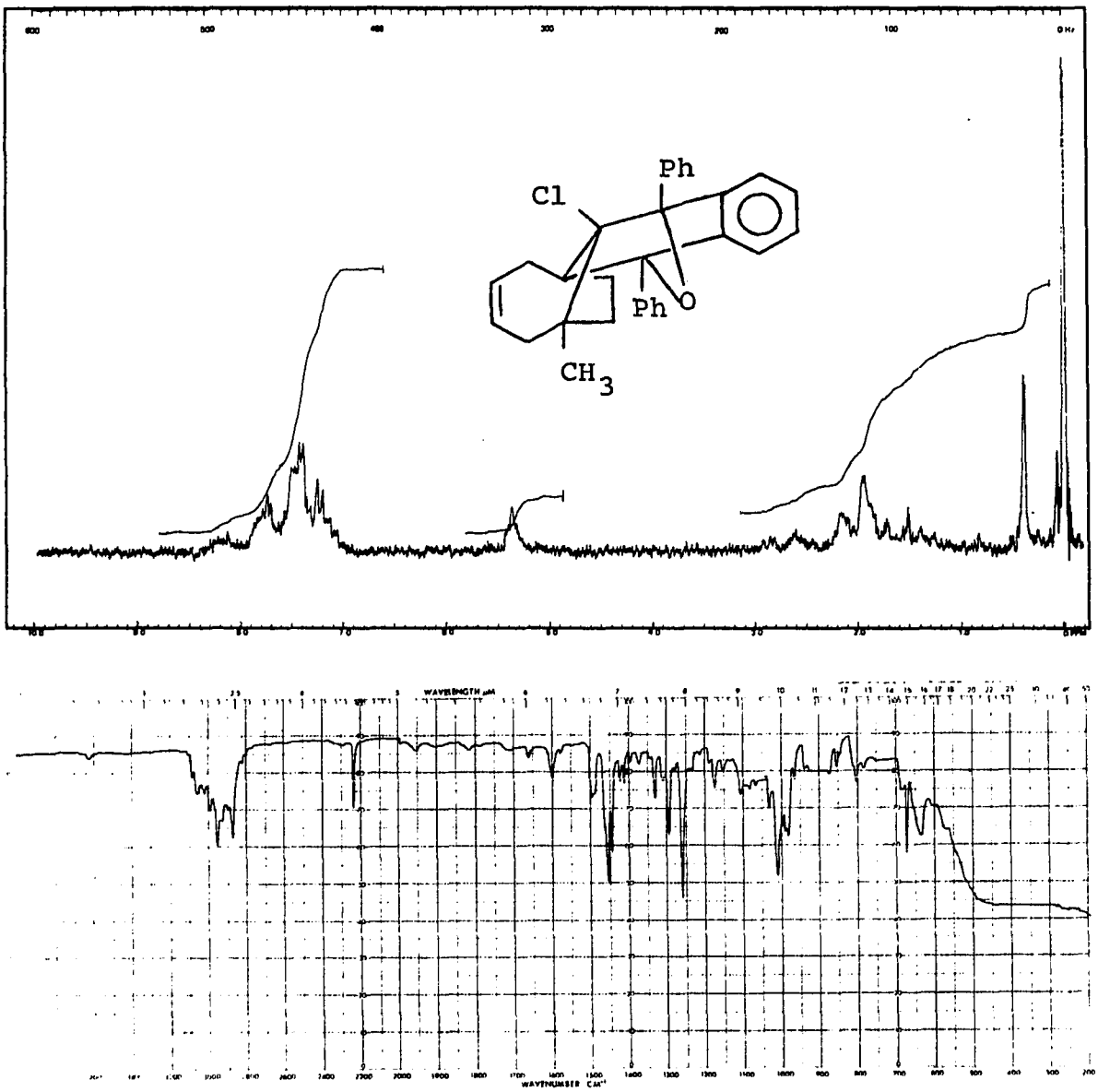


Figure 52. ^{1}H NMR and IR spectra of 300

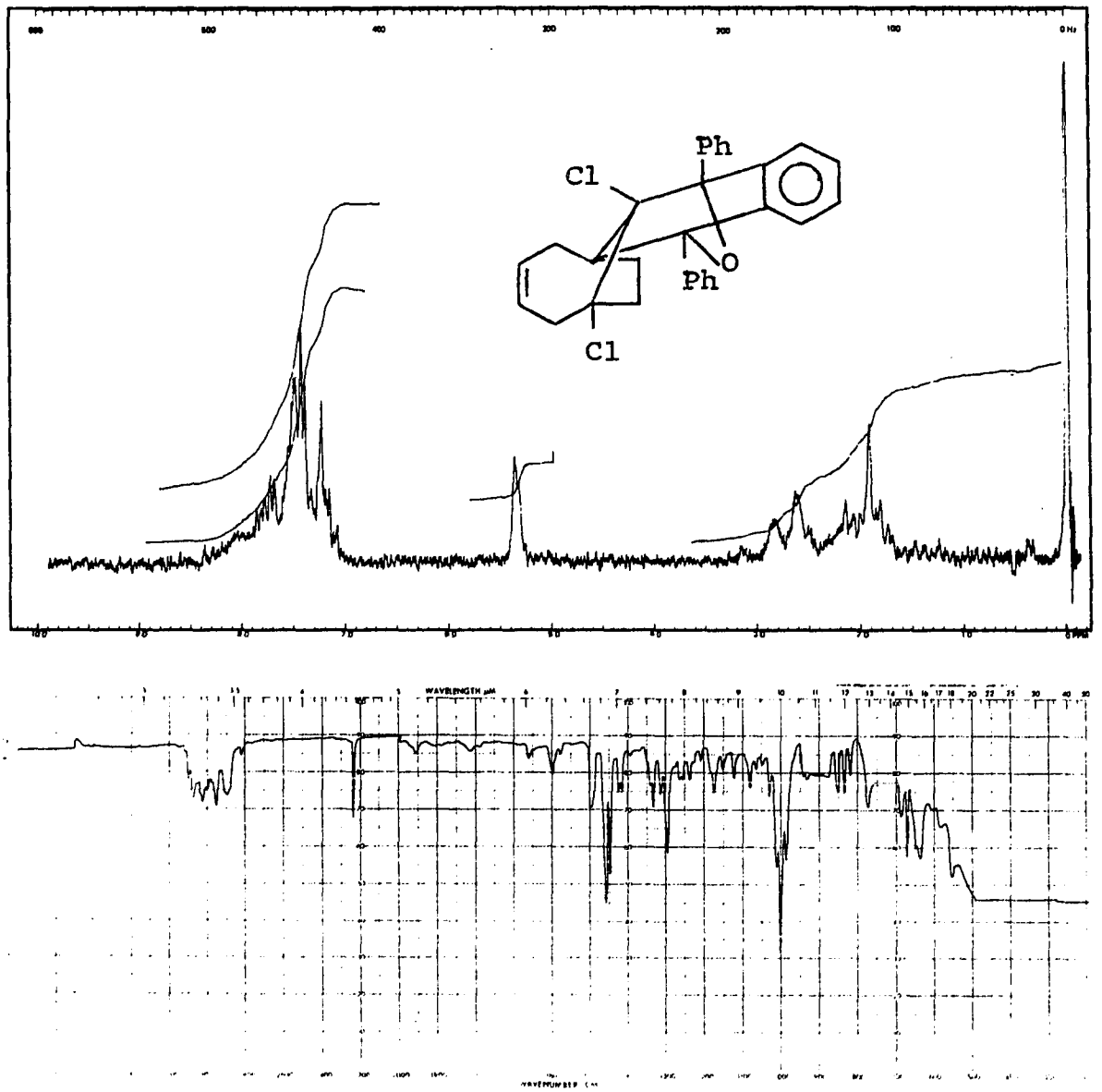


Figure 53. ^{1}H NMR and IR spectra of 301

Reaction of 10,10-dibromotricyclo[4.3.1.$0^{1,6}$]decane (14) with MeLi

(a) In the presence of DPIBF To a solution of 200 mg 14 (0.68 mmol) and 2.02 mg (0.75 mmol) DPIBF in 10 ml ether was added 1.73 ml (3.40 mmol MeLi at room temperature. The resulting reaction mixture was stirred for 1.5 hr, followed by the usual work up. GLC-mass spectral examination of the crude product mixture showed no indication of any trapping product, but rather the presence of insertion, methylation and reduction products.

(b) Without other additives To a solution of 200 mg 14 (0.68 mmol) in 10 ml ether was added 1.73 ml (3.40 mmol) MeLi at room temperature. The resulting reaction mixture was stirred for 1.5 hr. The usual work up gave 85 mg light yellow oil. GLC-mass spectroscopy showed the presence of 328, 330, 331 and 332 in an apparent ratio of 89.2:9.6:0.8:0.4, respectively (GLC-mass spectra, column C, without correction factors). There were 5 peaks (compounds derived from 328, and assumed to show identical GC detector responses) with parent ions at m/e 134: A (ret. time: 1.8 min): m/e 134.04 (P, % RA: 42.28), 119.06(P-15, 42.45), 106.02(P-28, 30.79), 105.00(P-29, 46.66), 91(P-43, 100), 77.02(P-57, 37.78), 65(P-69, 20.84), 51.00(P-83, 18.07); B (ret. time: 2 min), C (ret. time: 2.7 min), D (ret. time:

3.5 min), and E (ret. time: 4.2 min) all had the same fragmentation pattern as A (intensities were similar but not identical).

Monobromide 332 (ret. time: 6.3 min): m/e 216.00 (P+2, % RA: 3.45), 214.00(P, 3.81), 174.00(P+2-42, 10.16), 172.00(P-42, 10.04), 135.00(P-79, 100.00), 107.00(P-107, 29.44), 93(P-121, 72.78), 91(P-123, 29.40), 79.00(P-135, 66.75), 77(P-137, 27.22), 67.00(P-147, 51.51), 55.00(P-159, 14.40), 53(P-161, 12.30). Compound 330 (ret. time: 7.2 min) and 331 (ret. time: 7.4 min) both showed the same fragmentation patterns, but with different peak intensities; 330: m/e 229.90(P+2, 3.37), 227.9(P, 3.40), 187.84(P+2, 7.34), 185.86(P-42, 7.66), 172.86(P+2-58, 4.09), 170.88 (P-58, 3.38), 149.04(P-79, 100.00), 121.04(P-107, 20.48), 119.04(P-109, 11.74), 107.02(P-121, 90.76), 93.06(P-135, 68.07), 91.04(P-137, 51.07), 79.04(P-149, 60.56), 67.10 (P-161, 38.61), 54.96(P-173, 30.86); 331: m/e 230.00(P+2, 3.72), 228.00(P, 3.56), 188.00(P+2-42, 5.99), 186(P-42, 6.21), 173.00(P+2-58, 3.71), 171.00(P-58, 2.45), 149.00 (P-79, 100.00), 121.00(P-107, 21.27), 119.00(P-109, 30.72), 107.00(P-121, 90.06), 93.00(P-135, 72.05), 91.00(P-137, 90.34), 79.00(P-149, 97.94), 67.00(P-161, 43.34), 55.00 (P-173, 34.62). Thin layer chromatographic purification (hexane) of the crude product gave 330 (R_f=0.59, developed

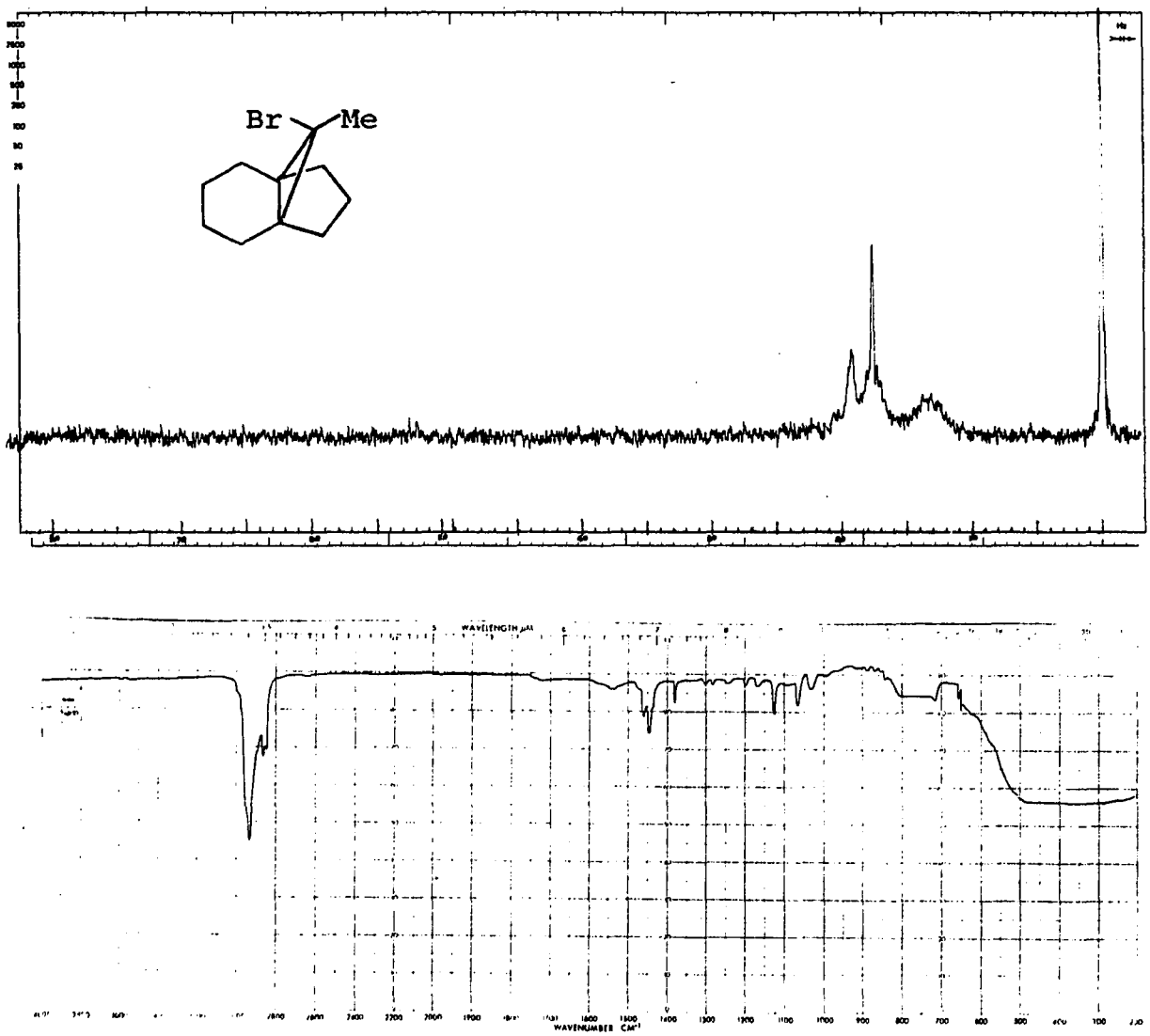


Figure 54. ^{1}H NMR and IR spectra of 10α-bromo-10-methyl-tricyclo[4.3.1.$0^{1,6}$]decane (330)

twice) (Fig. 54) in 5% isolated yield; ^{1}H NMR: δ2.15~1.0 (m, with a singlet at 1.73); IR(CCl_4): 2930, 1460, 1446 cm^{-1}. Anal. Calc'd for $C_{11}H_{17}Br$: m/e 228.0514. Found: m/e 228.0512.

(c) In the presence of 12-crown-4 To a solution of 400 mg (1.36 mmol) 14 and 0.66 ml (3 equiv.) 12-crown-4 in 15 ml freshly distilled ether was added 2.08 ml (3 equiv.) MeLi at room temperature. The reaction mixture was stirred for 2.5 hr followed by the usual work up. GLC-mass spectra of the crude product showed the presence of 328, 330, 331, 332, 338 and 339 in an apparent ratio of 69.7:10.3:6.5:8.3:2.0:3.2 (without correction factors). Thin layer chromatographic purification (hexane) gave dimer 338 (Fig. 55) (R_f=0.94) in 2% yield; ^{1}H NMR: δ2.2-1.0(m); IR(CCl_4): 2930, 2860, 1450 cm^{-1}. Anal. Calc'd for $C_{20}H_{28}$: m/e 268.2191. Found: m/e 268.2194. The fragmentation pattern of 339 in the GLC-mass spectrum was (ret. time: 8.3 min): m/e 164.00(P, rel. area: 3.82), 149.00(P-15, 100.00), 121.00(P-43, 15.42), 107.00(P-57, 46.05), 93.00 (P-71, 47.76), 79.00(P-85, 37.63), 67.00(P-97, 25.52), 55.00(P-109, 17.90).

(d) In MeI solvent To a solution of 150 mg (0.51 mmol) 14 in 15 ml MeI was added 1.30 ml (5 equiv.) ethereal MeLi at room temperature. The resulting reaction mixture was stirred for 1 hr. After the usual work up, 76 mg crude

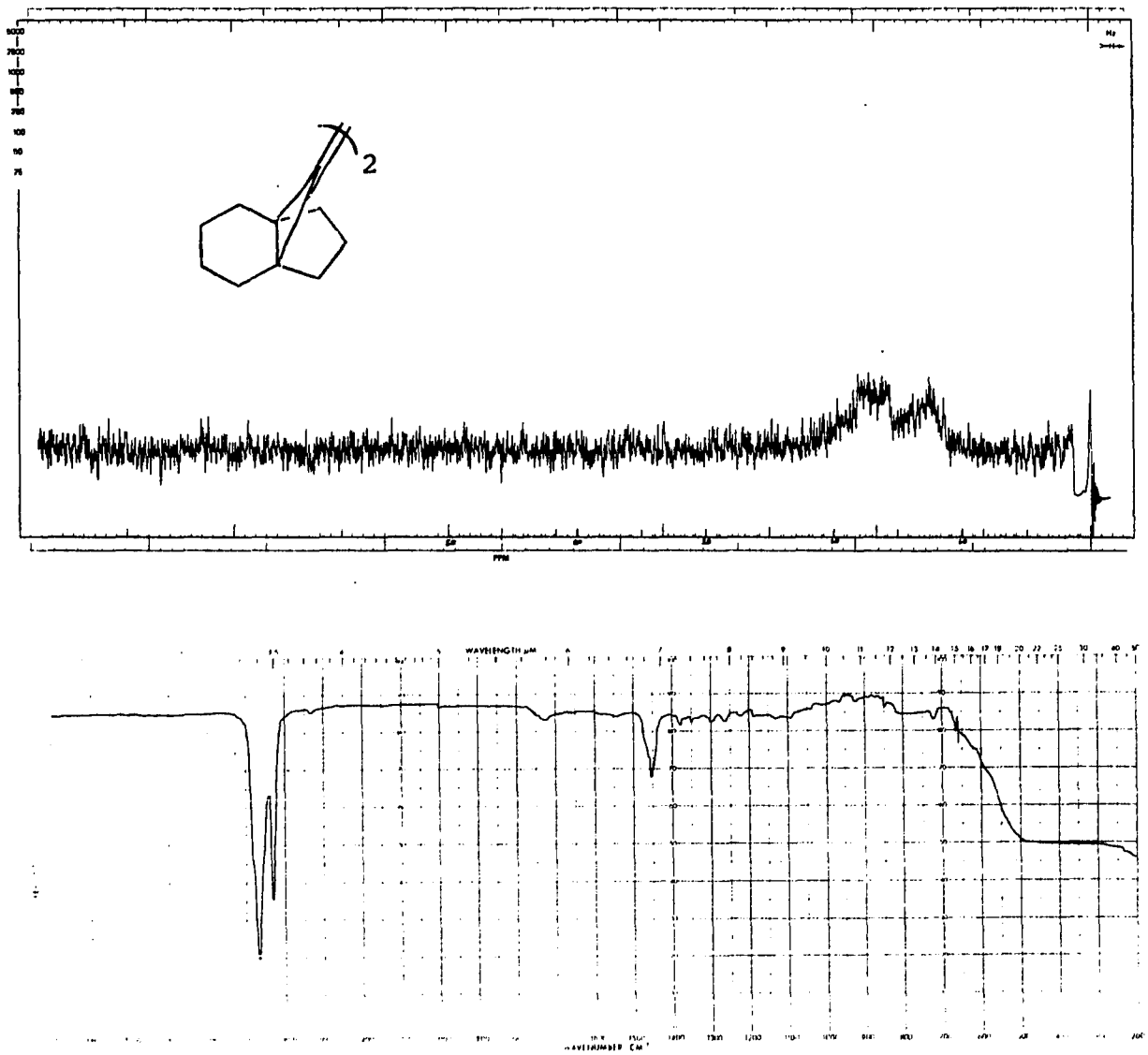


Figure 55. ^{1}H NMR and IR spectra of a mixture of dimers (338a and 338b)

product was obtained. GLC-mass spectra showed the presence of 328, 330, and 340 in an apparent ratio of 89.6:0.9:10.5 (without correction factors). Thin layer chromatographic purification (hexane) gave 340 (R_f=0.74, Fig. 56) in 7% yield; ^{1}H NMR: δ2.46-1.1(m, with a singlet at 2.04); IR(CCl_4): 2930, 1460, 1446 cm^{-1}. Anal. Calc'd for $C_{11}H_{17}I$: m/e 276.0377. Found: m/e 276.0370.

Reaction of 14 with MeLi in the presence of LiI

To a solution of 200 mg (0.68 mmol) 14, 364.6 mg (4 equiv.) LiI in 10 ml ether was added 2.13 ml (5 equiv.) MeLi (1.6 M) at room temperature. An exothermic reaction occurred spontaneously, the reaction mixture was stirred for 2 hr at room temperature. After the usual work up, 328, 330, 331 and 332 were observed, while 340 was not observed (GLC-mass).

Reaction of 330 with MeLi in MeI

To a solution of 14 mg (0.06 mmol) 330 in 10 ml MeI was added 0.38 ml (10 equiv.) MeLi at room temperature, whereupon an exothermic reaction occurred spontaneously. The resulting mixture was stirred for 1 hr at room temperature. After the usual work up, 13 mg of 330 was recovered.

Reaction of 14 with MeLi in CD_3I

To a solution of 186 mg (0.63 mmol) 14 in 2 ml CD_3I was added 3.95 ml (10 equiv.) MeLi at room temperature, and the reaction mixture was stirred for 1 hr at room temperature.

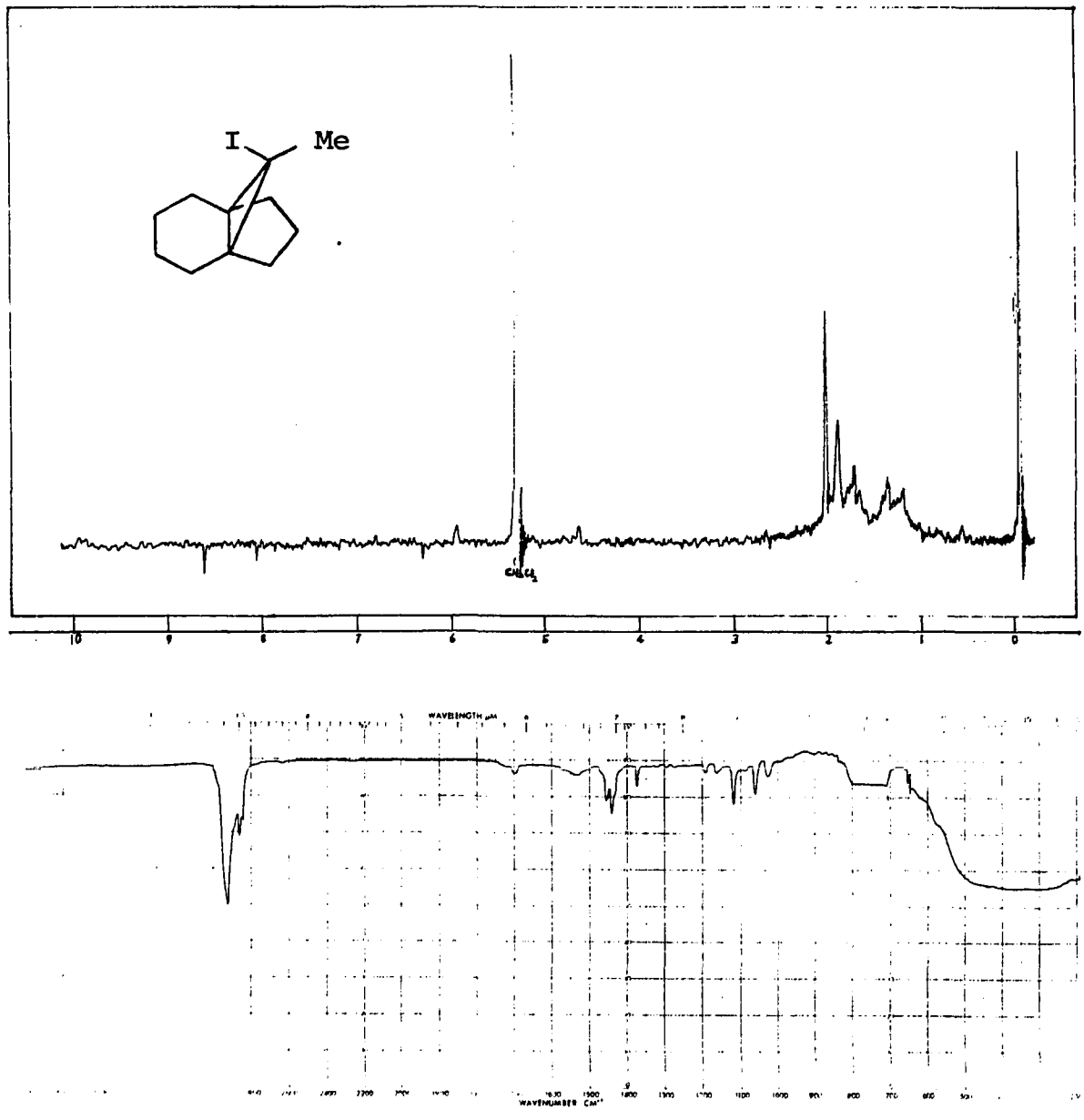


Figure 56. ^{1}H NMR and IR spectra of 10α-iodo-10-methyltricyclo[4.3.1.$0^{1,6}$]decane (340)

After work up, the GLC-mass spectrum (column C) of the crude product showed no incorporation of CD_3 in both 330 and 340.

Reaction of 10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-3-ene (15) with MeLi

(a) In the presence of DPIBF To a solution of 200 mg (0.68 mmol) 15 and 202 mg (0.75 mmol) DPIBF in 10 ml ether was added 1.73 ml (3.40 mmol) MeLi at room temperature. The reaction mixture was stirred for 1 hr, followed by the usual work up. GLC-mass spectra of the crude product showed no indication of any trapping product, but did reveal the presence of insertion, methylation and reduction products.

(b) Without other additives To a solution of 735 mg (2.52 mmol) 15 in 15 ml anhydrous ether was added 6.61 ml (5 equiv.) MeLi at room temperature. The resulting reaction mixture was stirred for 1 hr. After the usual work up 396.5 mg crude product was obtained. GLC-mass spectrometry showed the presence of 323, 345, 346, 347, 348 and 349a in an apparent ratio of 68.8:6.3:22.4:0.8:0.9:0.8 (without correction factors). There were 5 peaks (ret. times: 2.5, 3.0, 3.5, 4.4, 5.0 min presumed to come from rearrangement of 223 and to have identical GLC detected response factors) with parent ions at m/e 132 and the same fragmentation patterns (intensities were the same but not identical): m/e 132.06(P, % RA: 28.48), 131.06(P-1, 22.74), 117.02(P-15, 54.44), 115.00(P-17, 34.93), 104.02(P-28,

37.89), 91(P-41, 100.00), 78.04(P-54, 24.91), 77.02(P-55, 15.98), 65.02(P-67, 16.49), 64.06(P-68, 11.08), 51.00(P-77, 17.16). Monobromide 349a (ret. time: 6.7 min) was also observed: m/e 214.00(P+2, % RA: 0.60), 212.00(P, 0.54), 171.00(P+2-41, 0.20), 169.00(P-41, 0.16), 133.00(P-79, 56.00), 105.00(P-107, 29.74), 91.00(P-121.100), 79.00 (P-133, 17.71), 67.00(P-145, 11.37), 51.00(P-161, 9.84). Additionally, 346 (ret. time: 7.3 min) and 347 (ret. time: 7.7 min) showed the same fragmentation pattern but different peak intensities: 347: m/e 228.00(P+2, % RA: 10.39), 226.00(P, 12.56), 147.00(P-79, 77.30), 131.00(P-95, 12.38), 119.00(P-107, 66.63), 105.00(P-121, 96.77), 91.00(P-135, 100.00), 79.00(P-147, 28.41), 77.00(P-149, 27.05), 65.00 (P-161, 17.49), 67.00(P-159, 16.13), 55.00(P-171, 16.41), 53.00(P-173, 17.65); 346: m/e 228.00(P+2, % RA: 4.72), 226.00(P, 5.02), 147.00(P-79, 100%), 131.00(P-95, 15.97), 119.00(P-107, 62.60), 105.00(P-121, 93.54), 91.00(P-135, 98.22), 79.00(P-147, 32.23), 77(P-149, 32.67), 67.00 (P-159, 20.96), 65.00(P-161, 20.01), 55(P-171, 20.76), 53.00(P-161, 15.75). Lastly, 348 (ret. time: 5.2 min) was observed: m/e 162.02(P, % RA: 9.61), 147.02(P-15, 44.86), 133.04(P-29, 30.78), 117.02(P-45, 64.48), 105.00 (P-57, 51.64), 91.04(P-71, 100.00), 79.04(P-83, 30.71), 65.02(P-97, 17.30), 55.04(P-107, 17.53), 45.00(P-117, 6.01).

Thin layer chromatographic purification (20% ethereal hexane) of the crude product gave 346 (R_f=0.8, Fig. 57) in 12% yield; ^{1}H NMR: δ5.5(br s, 2H), 2.3(s, 4H), 2.16-1.83 (m, with a maximum at 1.98, 6H), 1.73(s, 3H), ^{13}C NMR ($CDCl_3$): δ124.18(rel. int. 6.14), 51.64(1.00), 36.25(7.50), 32.25(1.32), 30.19(7.82), 26.66(4.68), 22.55(2.00). IR (CCl_4): 3015(C=C-H), 2960, 2920, 2880, 1420, 1150 cm^{-1}; Anal. Calc'd for $C_{11}H_{15}Br$: m/e 226.0357. Found: m/e 226.0357; and 345 (R_f=0.6, Fig. 58) in 4% yield; ^{1}H NMR: δ5.43(s, 2H), 3.52(quintet), 3.2-1.3(m, with a maximum at 2.23, 1.13(quintet), 3.2-1.3(m, with a maximum at 2.23, 1.13 (quintet); IR(CCl_4): 2980, 2940, 2900, 2880, 2850, 1450, 1375, 1110 (C-O-C) cm^{-1}. Anal. Calc'd for $C_{14}H_{22}O$: m/e 206.1671. Found: m/e 206.1667. The fragmentation pattern for 345: m/e 206.00(P, % RA: 10.35), 205(P-1, 6.53), 191.00(P-15, 2.34), 177.00(P-29, 0.38), 161(P-45, 5.68), 160.00(P-46, 25.58), 159.00(P-47, 2.06), 151.00(P-55, 7.86), 146.00(P-60, 3.32), 145(P-61, 25.98), 143(P-63, 2.64), 138.00(P-68, 10.00), 132.00(P-74, 11.28), 131.00(P-75, 38.24), 120 (P-86, 25.88), 119.00(P-87, 28.49), 118.00(P-88, 27.19), 117(P-89, 36.63), 115(P-91, 10.70), 112.00(P-94, 47.79), 105(P-101, 27.69), 92.00(P-114, 33.62), 91.00(P-115, 89.45), 79.00(P-127, 27.69), 73.00(P-133, 72.76), 45.00(P-161, 100.00).

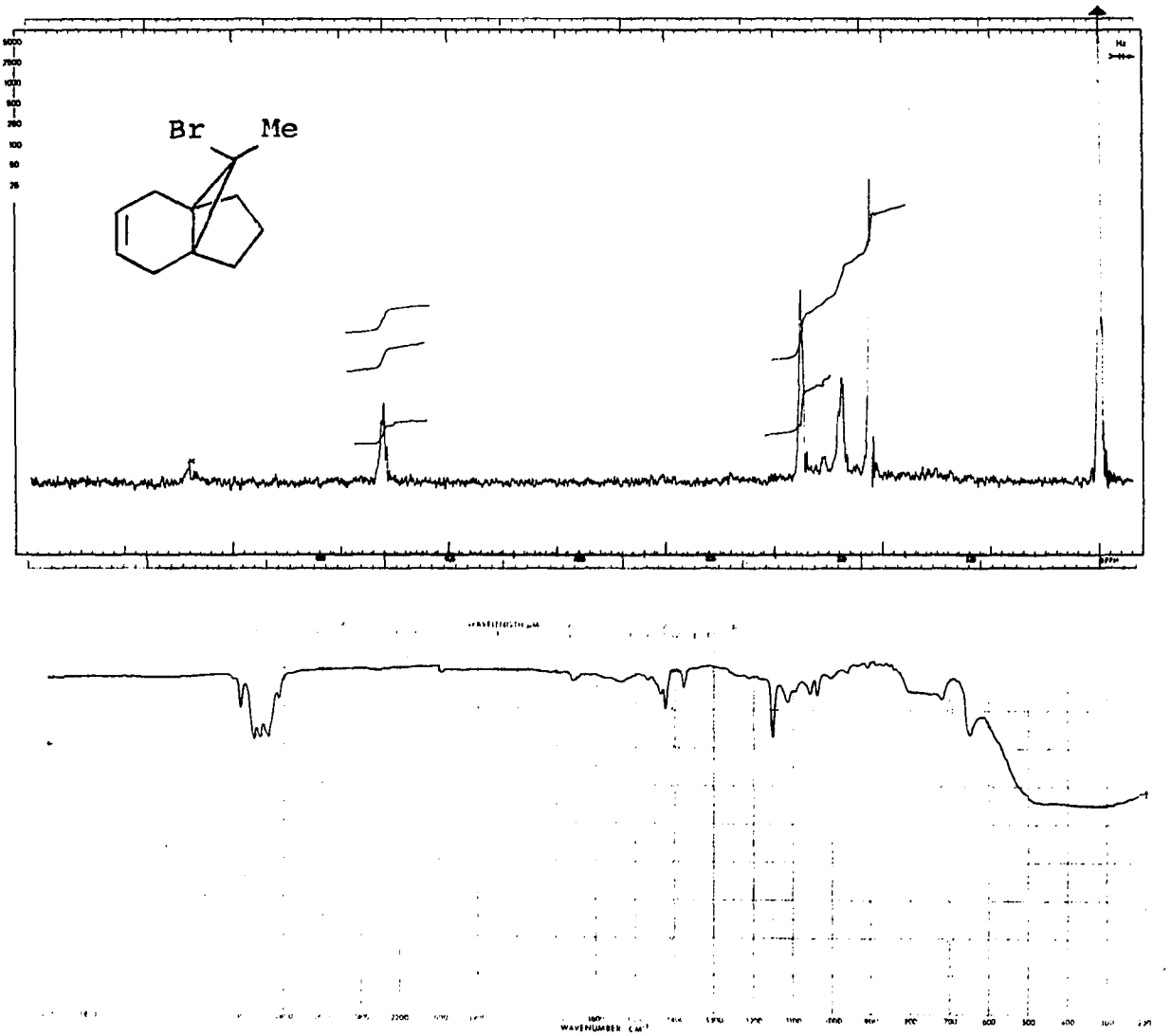


Figure 57. ^{1}H NMR and IR spectra of 10α-bromo-10-methyl-tricyclo[4.3.1.$0^{1,6}$]deca-3-ene (346)

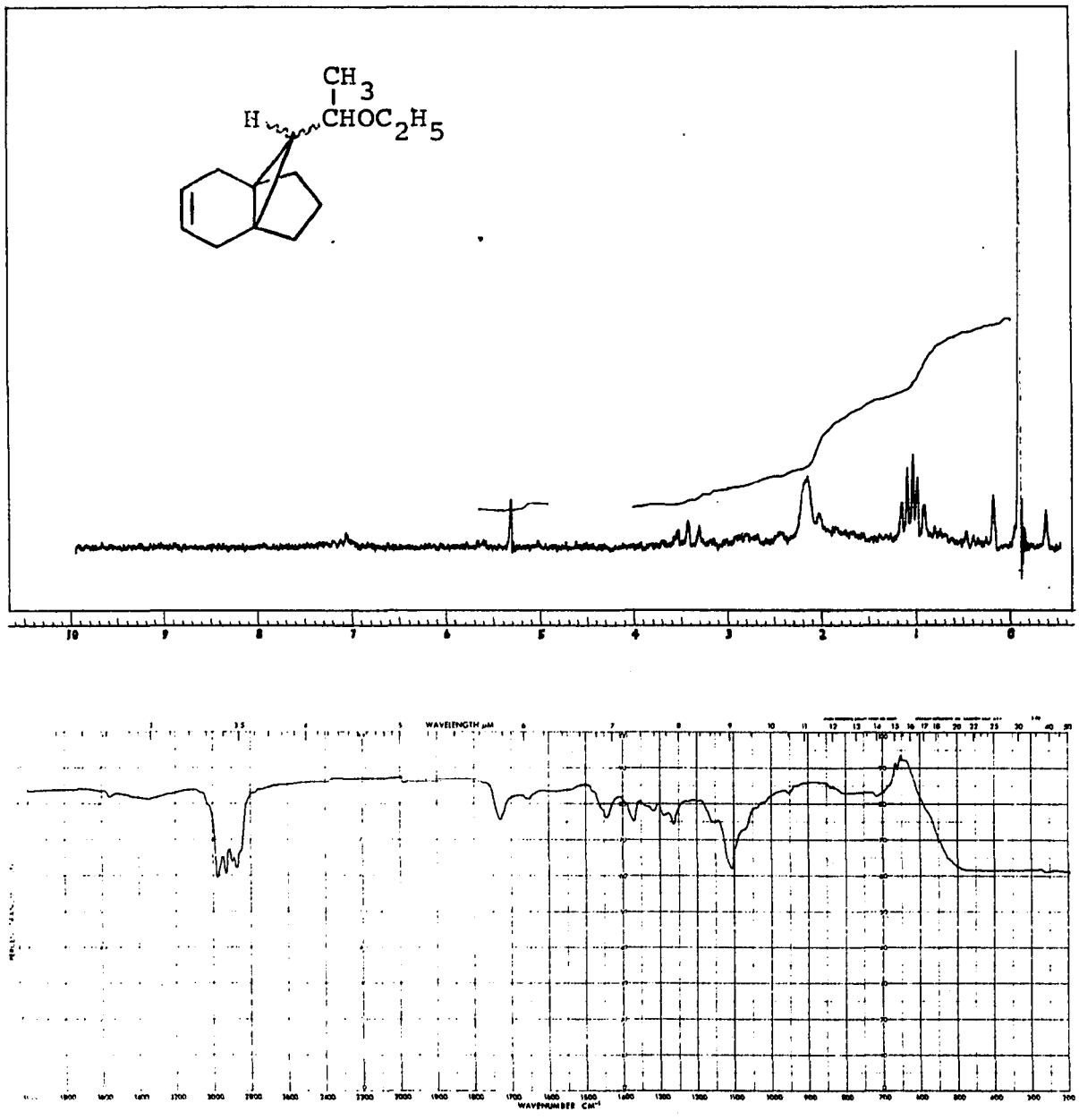


Figure 58. ^{1}H NMR and IR spectra of 345

(c) In the presence of 12-crown-4 To a solution of 205 mg (0.70 mmol) 15 and 1.14 ml (10 equiv.) 12-crown-4 in 15 ml anhydrous ether was added 1.79 ml MeLi (5 equiv.) at room temperature, and the resulting solution stirred for 2 hr at room temperature. After the usual work up, 100 mg crude product was obtained. GLC-mass spectrometry showed that the apparent ratio of 323:345:346:347:348:349a:351 was 46.2:2.5:18.5:0.2:8.3:20.5:3.8 (without correction factors). Thin layer chromatographic purification (hexane) gave dimer 351 (R_f=0.9; Fig. 59) in 2% yield; ^{1}H NMR: δ5.40 (br s), 5.25(br s), 2.72-0.50(m); IR(CCl_4): 3030, 1650, 1450, 1240, 665 cm^{-1}; Anal. Calc'd for $C_{20}H_{24}$: m/e 264.1878. Found: m/e 265.1872.

Hydrogenation of 346

To a solution of 7.5 mg (0.03 mmol) in 15 ml ether was added 6 mg of Pt/C. The resulting mixture was hydrogenated for 1 hr. After filtration, 7.6 mg of 330 was obtained (100% yield).

Reaction of 9,9-dibromotricyclo[3.3.1.$0^{1,5}$]nonane (141) with MeLi

(a) In the presence of DPIBF To a solution of 150 mg (0.54 mmol) 141 and 1.1 equiv. (160 mg) DPIBF in 15 ml ether was added 1.37 ml (4 equiv.) MeLi at room temperature. After stirring for 30 min at room temperature, the usual

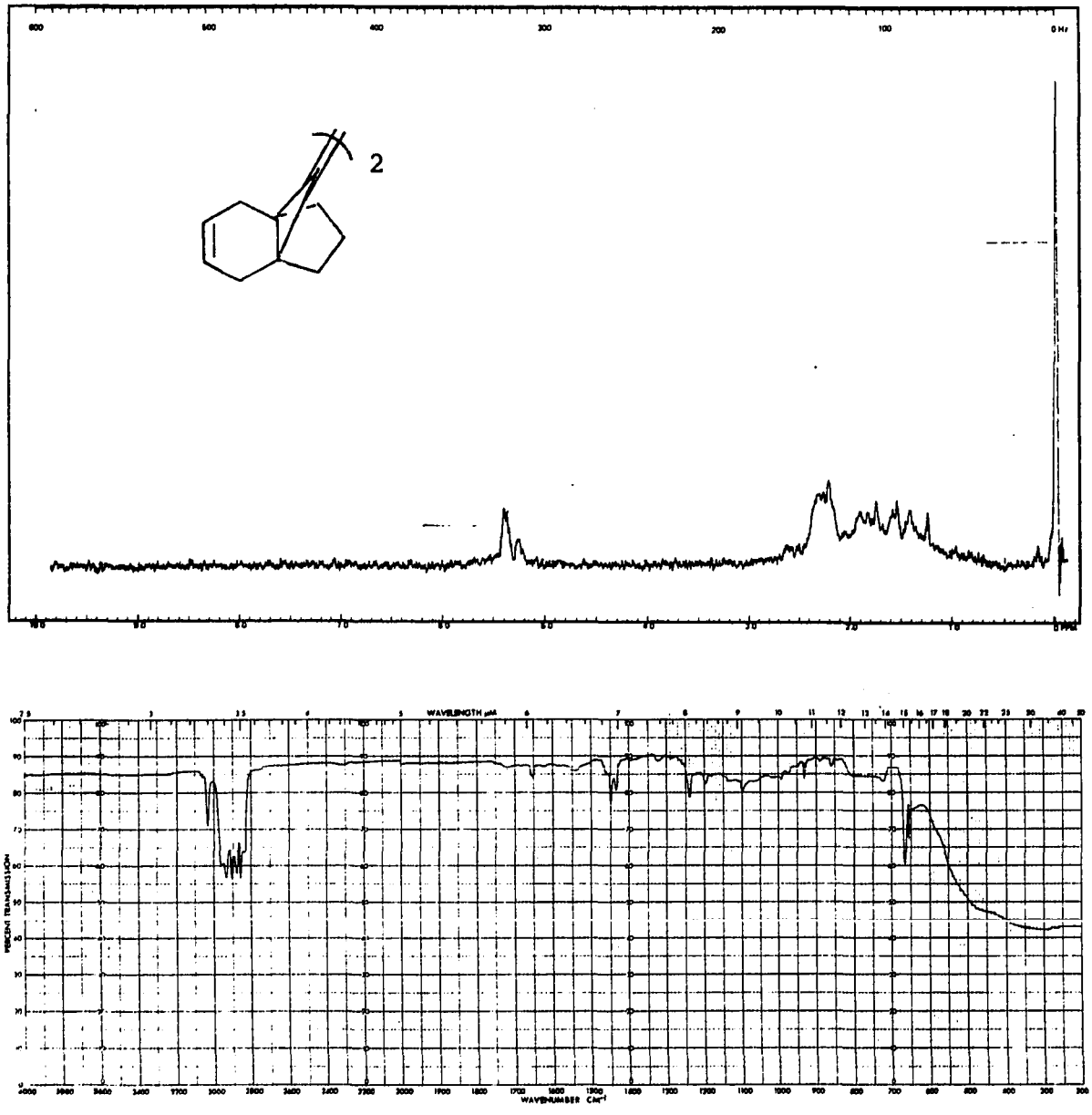


Figure 59. ^{1}H NMR and IR spectra of a mixture of dimers (351a, 351b)

work up afforded a yellow residue (220 mg), the GLC-mass spectra of which showed no indication of the presence of any DPIBF trapping products, but rather the formation of 352, 353, 354 and 355.

(b) In the absence of DPIBF To a solution of 140 mg (0.54 mmol) 141 in 15 ml ether was added 1.37 ml (4 equiv.) MeLi at room temperature, and the resulting reaction mixture stirred for 30 min at room temperature. After the usual work up, 69 mg crude product was obtained. The apparent ratio of 352:353:354:355 was 15.5:80.3:3.6:0.7 respectively (GLC-mass spectrometry, without correction factors). There were 5 peaks with parent ions at m/e 120 (ret. time: 1.2 min, 1.4 min, 1.7 min, 2.0 min, 2.7 min, all assumed to have the same GC detector response) which presumably arose from the rearrangement of 352. These 5 peaks all exhibit the same fragmentation pattern and similar but not identical intensities: m/e 120.00 (P, % RA: 48.06), 117(P-3, 11.86), 115.00(P-5, 9.59), 105.00(P-15, 24.48), 91.00(P-29, 100.00), 79.00(P-41, 20.36), 77.00(P-43, 13.94), 65.00(P-55, 9.92), 58.00(P-62, 11.57), 51.00(P-69, 9.00), 45.00(P-75, 3.69). Compound 354 showed the following fragmentation pattern: m/e 202.00(P+2, % RA: 7.04), 200.00(P, 7.18), 174.00(P+2-28, 65.76), 172.00(P-28, 66.89), 159.00(P-41, 3.09), 121.00(P-79, 100.00), 93.00

(P-107, 97.50), 91.00(P-109, 63.82), 79.00(P-121, 92.04), 67.00(P-133, 39.76), 51.00(P-149, 19.94).

Thin layer chromatographic purification (hexane) of the crude product afforded 353 (R_f=0.65, Fig 60) in 33% yield; ^1H NMR: δ2.75-1.2(m, with a singlet at 1.83); ^{13}C NMR ($CDCl_3$): δ57.28(rel. area 1.00), 51.69(2.08), 36.10(8.80), 34.12(6.34), 33.92(2.59), 32.10(9.30) and 23.52(1.59); IR(CCl_4): 2950, 2860, 1435, 1175, 1050 cm^{-1}. Anal. Calc'd for $C_{10}H_{15}Br$: m/e 214.0357. Found: m/e 214.0356. The fragmentation pattern of 353: m/e 216.90(P+3, % RA: 0.24), 215.90(P+2, 2.64), 214.94(P+1, 0.28), 213.88(P, 2.76), 188.82(P-51, 1.04), 187.82(P+2-18, 12.58), 185.82(P-18, 13.29), 172.86(P-31, 3.39), 170.86(P-33, 2.23), 136.02(P-68; 12.38), 135.06(P-69, 87.28), 107.12(P-97, 100.00), 105.00 (P-99, 23.28), 93.04(P+2-111, 61.21), 91.02(P-111, 64.87), 81.04(P-123, 23.20), 79.06(P-125, 71.87), 78.04(P-126, 13.42), 77.02(P-127, 41.97), 67.10(P-137, 37.61), 65.06 (P-139, 22.90), 55.04(P-149, 26.35), 53.02(P-150, 23.57), 52.02(P-151, 10.57), 51.00(P-152, 19.05).

When the above reaction was carried out at -78°C, a dimer 355 (Fig. 61) was isolated in 6.4% yield. Compound 355 was recrystallized from ether to afford transparent, highly symmetrical crystals, mp 202-204°C; ^1H NMR: δ2.23-1.1(m); ^{13}C NMR($CDCl_3$, with pulse width = 7°C): δ127.98 (C_1, rel. int. 1.00), 41.20(C_2, 2.28), 33.23(C_3, 6.46),

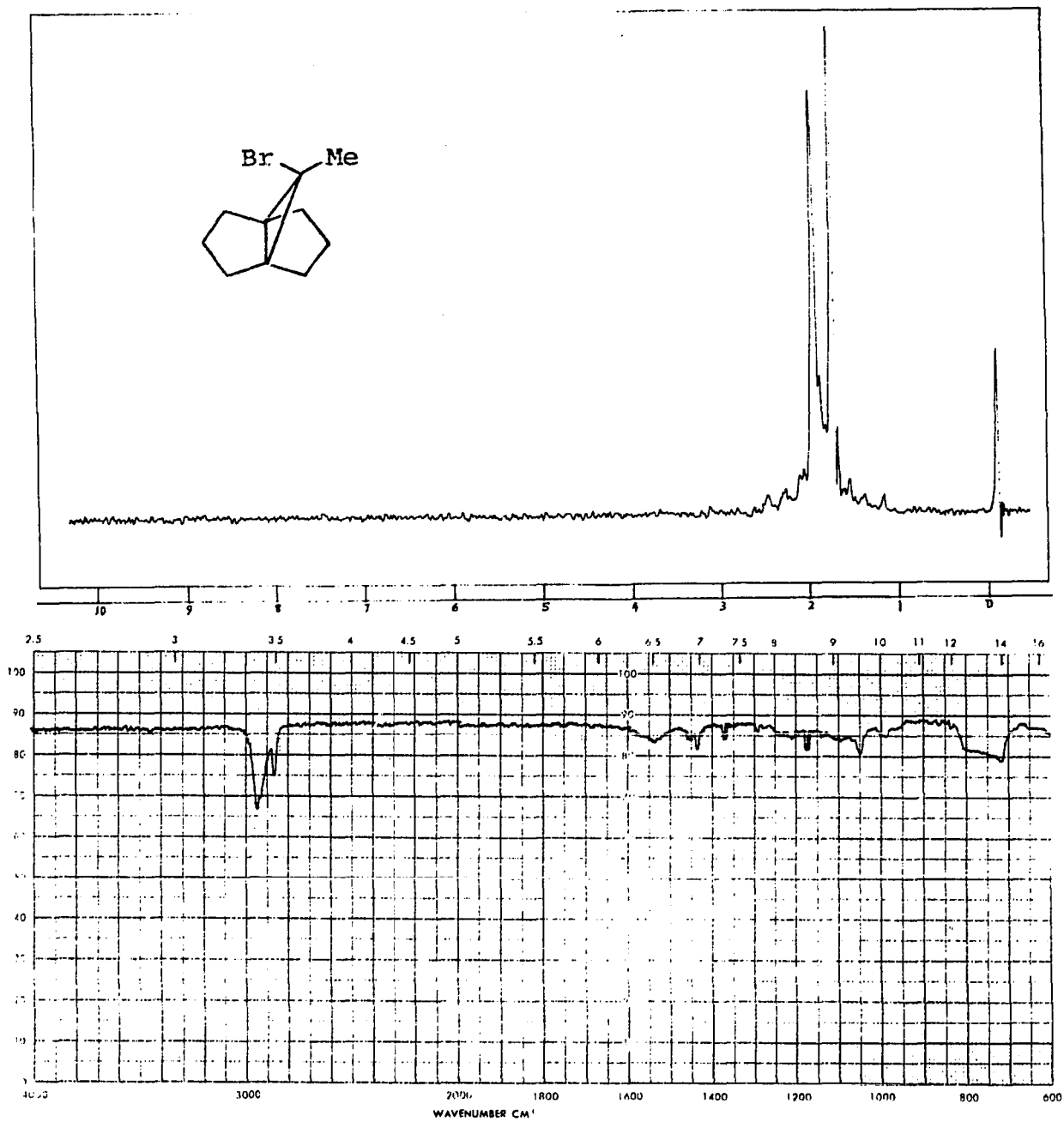


Figure 60. ^{1}H NMR and IR spectra of 9-bromo-9-methyltricyclo[3.3.1.$0^{1,5}$]nonane (353)

30.80(C_4, 3.25); off resonance decoupling gave singlets for the resonances identified as C_1 and C_2, and overlapping triplets for those C_1 and C_2, and overlapping triplets for those corresponding to C_3 and C_4; IR(CCl_4): 2948, 2860, 1460, 1445, 1385, 1319 (weak), 1290, 1244, 1210, 1175, 1070, 1055, 1021, 960, 895 cm^{-1}; Raman (as a single crystal or in CCl_4 solution): 2959, 2938, 2860, 1450 (strong), 1319, 1295, 1244, 1211, 1187, 1175, 1133, 1100, 1070, 1021, 971, 900, 845, 721, 673, 558, 476 cm^{-1}. Anal. Calc'd for $C_{17}H_{24}$: 240.1878. Found: 240.1879. The fragmentation pattern of 355: m/e 241.00(P+1, % RA: 0.42), 240.00(P, 26.01), 239.00(P-1, 0.14), 212(P-28, 16.41), 211.00(P-29, 27.40), 197(P-43, 50.49), 184.00(P-56, 39.36), 183(P-57, 33.24), 171.00(P-69, 18.22), 170.00(P-70, 13.77), 169.00 (P-71, 57.16), 167.00(P-73, 10.01), 157.00(P-83, 21.56), 156.00(P-84, 16.69), 155.00(P-85, 42.98), 143.00(P-97, 24.48), 141.00(P-99, 48.82), 131.00(P-109, 51.04), 129.00 (P-111, 53.96), 128.00(P-112, 46.87), 119.00(P-121, 29.62), 117.00(P-123, 54.80), 115.00(P-125, 53.41), 105.00(P-135, 29.35), 93.00(P-147, 22.95), 92.00(P-148, 19.75), 91.00 (P-149, 100.00), 81.00(P-159, 20.58), 80.00(P-160, 17.94), 79.00(P-161, 70.79), 77.00(P-173, 53.82), 67.00(P-183, 32.13). For details of the X-ray single crystal analysis of 355, see the Appendix.

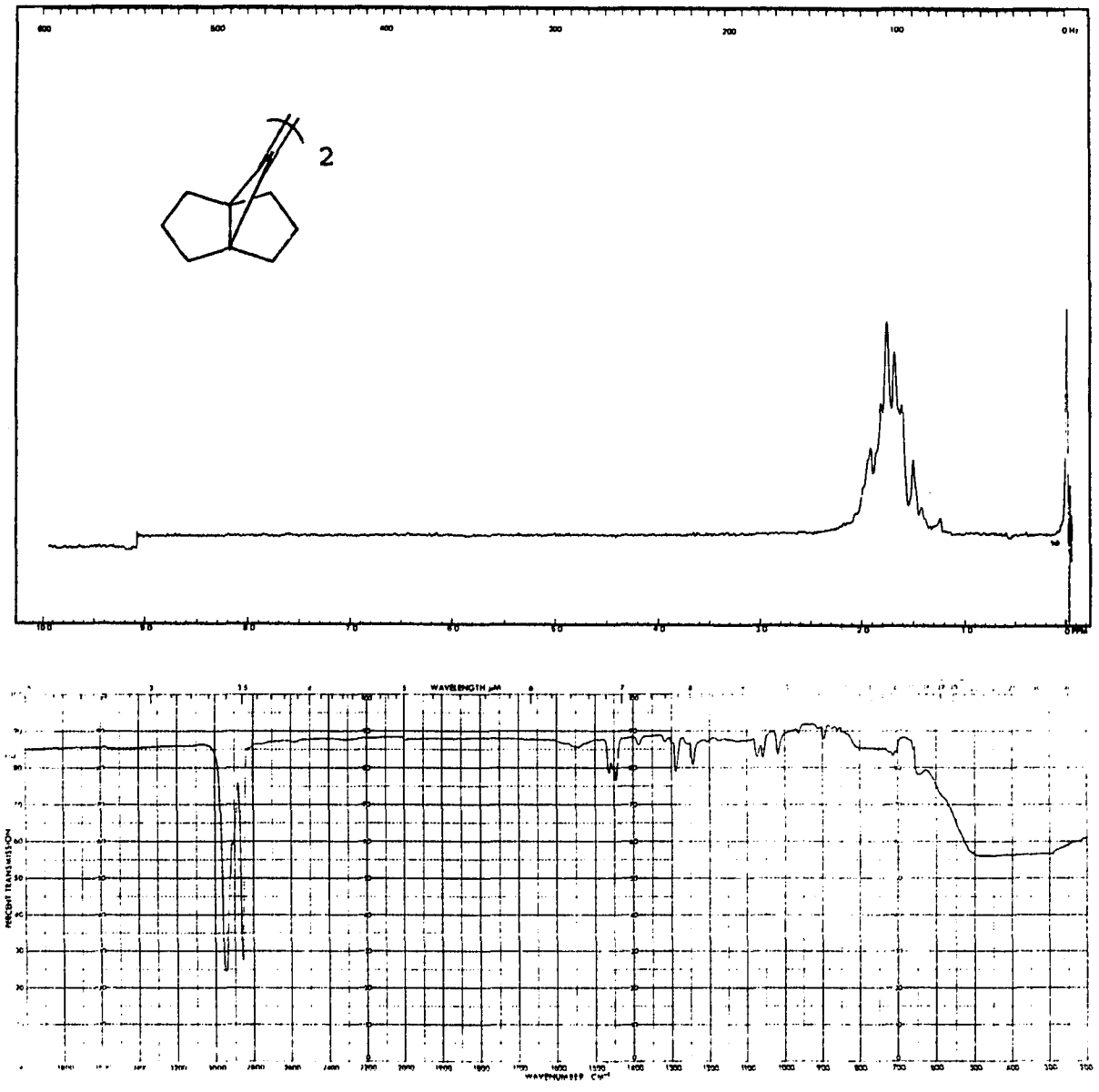


Figure 61. ^{1}H NMR and IR spectra of dimer 355

Attempted hydrogenation of 355

A solution of 8 mg 355 in 10 ml EtOAc over 4 mg 5% Pt/C was hydrogenated at 70°C and 50 psi H_2 for 4 days. A quantitative recovery of 355 was obtained after filtration and solvent evaporation.

Attempted addition of dibromocarbene to 355

To a mixture of 8 mg 355 and 3 equiv. KOtBu in 10 ml hexane was added 2.5 equiv. $CHBr_3$ dropwise at -78°C. The resulting reaction mixture was stirred for 1 hr at -78°C and then gradually allowed to warm to room temperature (5 hr). After the usual work up, starting material 355 was recovered quantitatively.

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Finally, I would like to express my appreciation for the love and support given to me by my parents.

APPENDIX

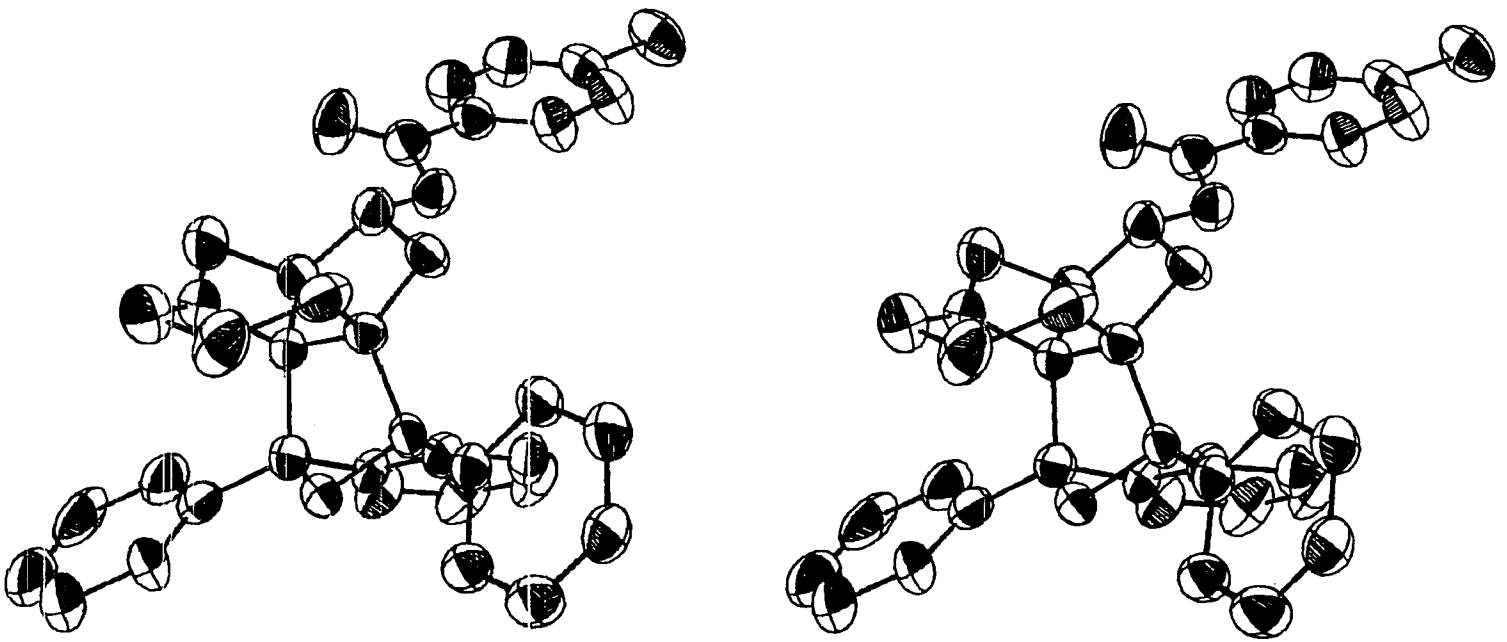

Figure A-1: ORTEP stereoview of 219-1-e

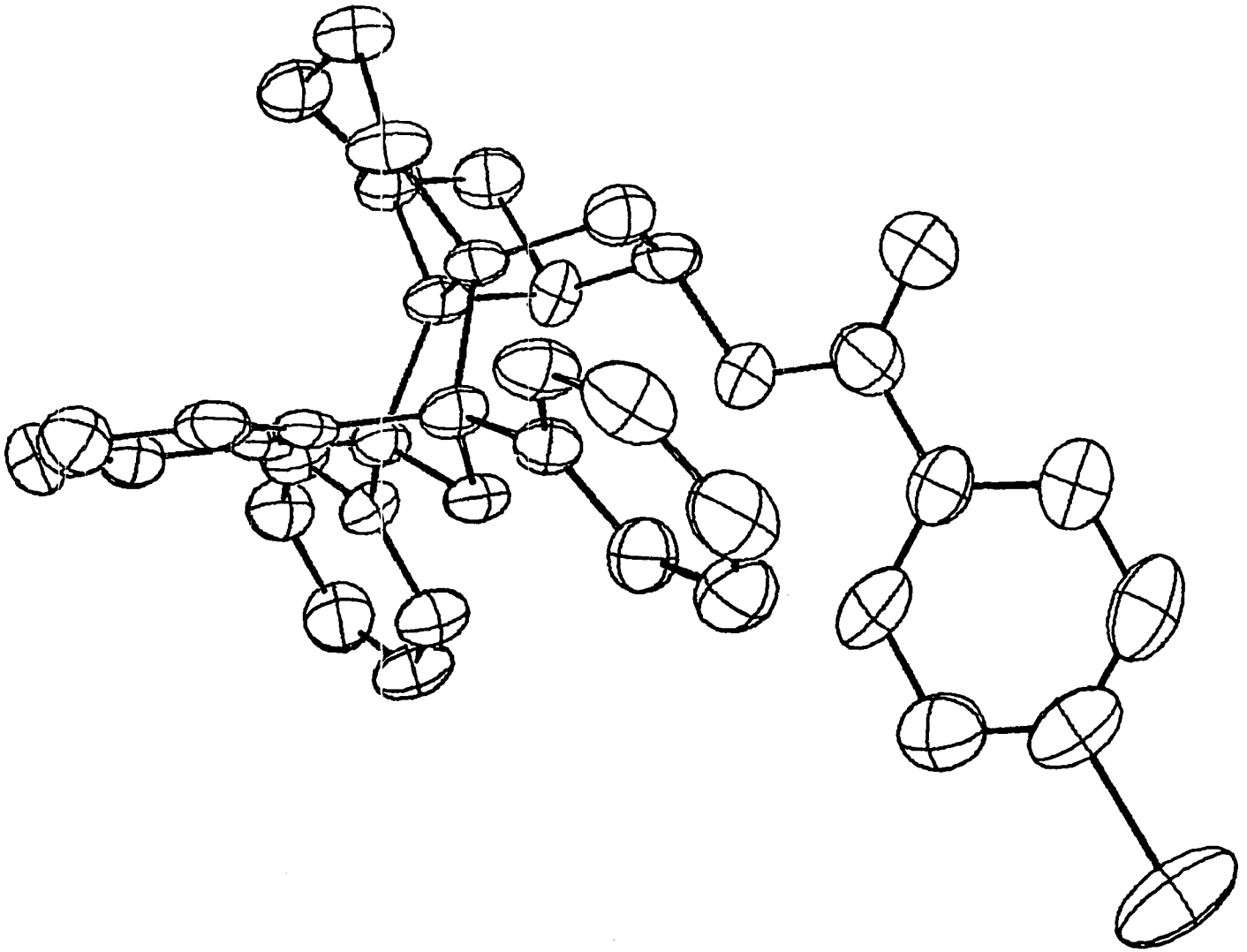

Figure A-2: An ORTEP drawing of 219-2-e

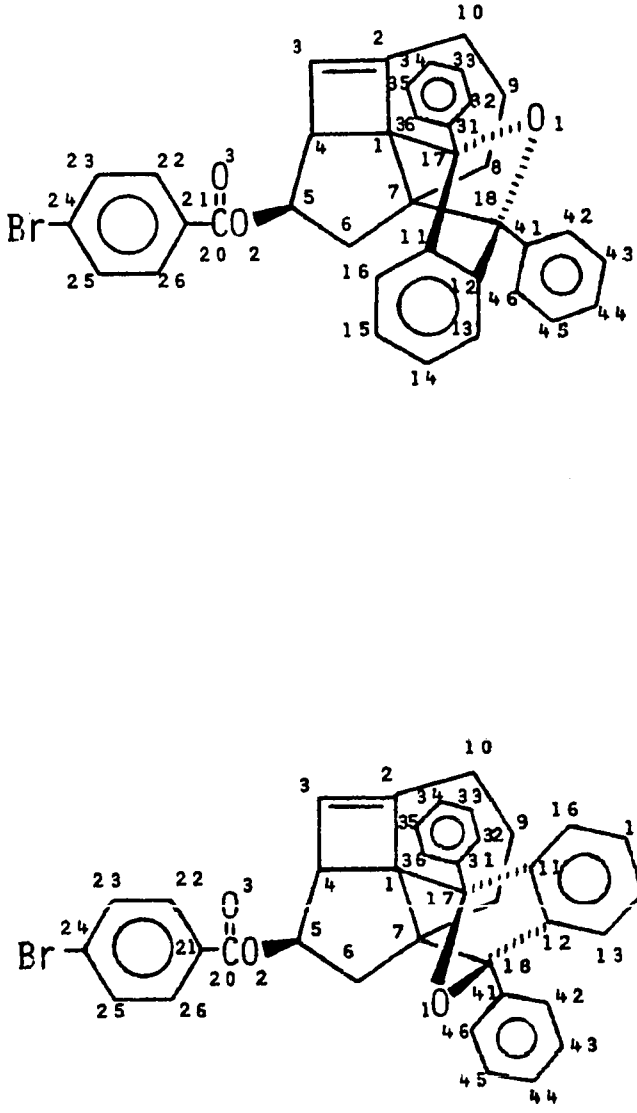

Figure A-3: Structure of 219-1-e (top) and 219-2-e (bottom), showing the atom numbering schemes

Table A-I. Selected bond distances[a] for adducts 219-1-e and 219-2-e

Atom	219-1-e	219-2-e
Br-C(24)	1.890(6)	1.921(8)
C(1)-C(2)	1.508(8)	1.523(9)
C(1)-C(4)	1.548(8)	1.557(10)
C(1)-C(7)	1.546(7)	1.543(10)
C(1)-C(17)	1.562(8)	1.577(9)
C(2)-C(3)	1.350(9)	1.334(11)
C(2)-C(10)	1.476(9)	1.474(11)
C(3)-C(4)	1.565(8)	1.530(10)
C(4)-C(5)	1.549(8)	1.508(8)
C(5)-C(6)	1.526(8)	1.535(12)
O(2)-C(5)	1.449(6)	1.461(8)
C(6)-C(7)	1.544(8)	1.534(8)
C(7)-C(8)	1.567(8)	1.552(11)
C(7)-C(18)	1.563(7)	1.622(9)
C(8)-C(9)	1.558(9)	1.542(9)
C(9)-C(10)	1.541(10)	1.544(10)
C(11)-C(12)	1.377(8)	1.397(9)
C(12)-C(13)	1.394(8)	1.375(11)
C(13)-C(14)	1.389(9)	1.379(8)
C(14)-C(15)	1.378(10)	1.387(11)
C(15)-C(16)	1.425(9)	1.398(11)
C(16)-C(11)	1.384(9)	1.363*8)
C(11)-C(17)	1.512(8)	1.527(10)
C(12)-C(18)	1.518(9)	1.501(8)
O(1)-C(17)	1.451(6)	1.456(7)
O(1)-C(18)	1.475(6)	1.463(9)
C(17)-C(31)	1.508(8)	1.489(11)
C(18)-C(41)	1.500(7)	1.490(8)
O(2)-C(20)	1.332(8)	1.320(7)
O(3)-C(20)	1.203(7)	1.225(10)
C(20)-C(21)	1.476(9)	1.491(11)
C(21)-C(22)	1.384(8)	1.388(11)
C(22)-C(23)	1.384(9)	1.396(12)
C(23)-C(24)	1.371(10)	1.358(10)
C(24)-C(25)	1.374(9)	1.358(12)
C(25)-C(26)	1.382(9)	1.405(12)
C(26)-C(21)	1.395(9)	1.387(8)
C(31)-C(32)	1.389(9)	1.390(11)
C(32)-C(33)	1.414(9)	1.384(12)

[a]The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure.

Table A-I. (Continued)

Atom	219-1-e	219-2-e
C(33)-C(34)	1.367(14)	1.370(10)
C(34)-C(35)	1.354(11)	1.392(12)
C(35)-C(36)	1.380(10)	1.396(12)
C(36)-C(31)	1.379(9)	1.384(9)
C(41)-C(42)	1.391(8)	1.393(12)
C(42)-C(43)	1.393(9)	1.399(10)
C(43)-C(44)	1.371(9)	1.388(12)
C(44)-C(45)	1.377(9)	1.375(14)
C(45)-C(46)	1.378(8)	1.400(10)
C(46)-C(41)	1.382(8)	1.383(10)

Table A-II. Selected bond angles[a] for adducts 219-1-e and 219-2-e

Atom	219-1-e	219-2-e
C(2)-C(1)-C(4)	88.6(4)	87.8(5)
C(2)-C(1)-C(7)	113.1(4)	111.3(6)
C(2)-C(1)-C(17)	119.6(4)	129.8(5)
C(4)-C(1)-C(7)	109.3(4)	108.4(4)
C(4)-C(1)-C(17)	122.8(5)	114.2(6)
C(7)-C(1)-C(17)	103.3(4)	103.7(5)
C(1)-C(2)-C(3)	93.4(5)	92.2(6)
C(1)-C(2)-C(10)	125.0(5)	123.3(7)
C(2)-C(3)-C(4)	93.9(5)	96.2(6)
C(2)-C(10)-C(9)	107.6(5)	103.8(5)
C(1)-C(4)-C(3)	84.0(4)	83.8(5)
C(10)-C(2)-C(3)	138.6(6)	137.3(6)
C(1)-C(4)-C(5)	105.1(4)	107.3(6)
C(3)-C(4)-C(5)	109.6(5)	113.8(6)
O(2)-C(5)-C(4)	113.9(4)	106.6(6)
C(4)-C(5)-C(6)	108.1(4)	107.6(5)
C(5)-C(6)-C(7)	107.1(4)	108.7(6)
O(2)-C(5)-C(6)	105.7(4)	110.7(6)
C(1)-C(7)-C(6)	106.1(4)	105.6(6)
C(1)-C(7)-C(8)	109.6(4)	113.5(5)
C(1)-C(7)-C(18)	100.7(4)	99.5(5)
C(6)-C(7)-C(8)	109.7(4)	110.2(6)
C(6)-C(7)-C(18)	115.6(4)	115.8(5)
C(8)-C(7)-C(18)	114.4(4)	111.7(6)
C(7)-C(8)-C(9)	114.8(5)	115.2(7)
C(7)-C(18)-O(1)	99.4(4)	100.6(5)
C(7)-C(18)-C(12)	108.8(4)	106.8(5)
C(7)-C(18)-C(41)	119.7(4)	115.2(5)
C(8)-C(9)-C(10)	112.4(5)	112.8(6)
C(1)-C(17)-O(1)	100.7(4)	96.6(4)
C(1)-C(17)-C(11)	106.5(4)	110.5(6)
C(1)-C(17)-C(31)	115.4(4)	114.6(6)
C(17)-O(1)-C(18)	97.5(4)	97.7(5)
O(1)-C(17)-C(11)	100.5(4)	101.0(5)
O(1)-C(17)-C(31)	110.0(4)	114.5(6)
C(11)-C(17)-C(31)	120.9(5)	117.0(5)
O(1)-C(18)-C(12)	99.3(4)	101.1(5)
O(1)-C(18)-C(41)	111.2(4)	112.1(5)

[a]Bond angles are in degrees. Estimated standard deviations are given in parentheses for the least significant figure.

Table A-II. (Continued)

Atom	219-1-e	219-2-e
C(12)-C(18)-C(41)	115.3(4)	118.6(6)
C(17)-C(11)-C(12)	104.5(5)	105.2(5)
C(17)-C(11)-C(16)	133.3(5)	132.9(6)
C(18)-C(12)-C(11)	107.0(4)	105.4(6)
C(18)-C(12)-C(13)	131.6(5)	134.5(6)
C(11)-C(12)-C(13)	121.4(5)	120.0(5)
C(12)-C(13)-C(14)	117.6(5)	118.4(7)
C(13)-C(14)-C(15)	121.0(6)	121.8(8)
C(14)-C(15)-C(16)	121.8(6)	119.7(6)
C(15)-C(16)-C(11)	116.0(6)	118.2(7)
C(16)-C(11)-C(12)	122.2(5)	121.9(7)
C(17)-C(31)-C(32)	118.8(6)	123.1(6)
C(17)-C(31)-C(36)	121.1(5)	118.2(6)
C(31)-C(32)-C(33)	118.7(7)	120.0(6)
C(32)-C(33)-C(34)	119.8(7)	121.0(8)
C(33)-C(34)-C(35)	120.8(7)	120.3(8)
C(34)-C(35)-C(36)	120.7(7)	118.4(6)
C(35)-C(36)-C(31)	120.0(6)	121.7(7)
C(36)-C(31)-C(32)	119.9(6)	118.7(7)
C(18)-C(41)-C(42)	120.4(5)	119.2(6)
C(18)-C(41)-C(46)	120.1(5)	121.4(7)
C(41)-C(42)-C(43)	118.9(6)	121.0(7)
C(42)-C(43)-C(44)	121.7(6)	118.5(8)
C(43)-C(44)-C(45)	118.7(6)	121.1(7)
C(44)-C(45)-C(46)	120.9(6)	120.0(8)
C(45)-C(46)-C(41)	120.5(5)	120.0(8)
C(46)-C(41)-C(42)	119.3(5)	119.3(6)
C(5)-O(2)-C(20)	116.8(4)	116.6(6)
O(2)-C(20)-O(3)	122.5(6)	124.6(7)
O(2)-C(20)-C(21)	112.7(5)	113.6(6)
O(3)-C(20)-C(21)	124.8(6)	121.5(6)
C(20)-C(21)-C(22)	118.5(6)	120.2(6)
C(20)-C(21)-C(26)	121.4(5)	119.4(7)
C(21)-C(22)-C(23)	119.8(6)	119.9(6)
C(22)-C(23)-C(24)	119.3(6)	118.1(8)
C(23)-C(24)-C(25)	121.9(6)	124.0(8)
C(24)-C(25)-C(26)	119.2(6)	118.2(6)
C(25)-C(26)-C(21)	119.7(6)	119.4(7)
C(26)-C(21)-C(22)	120.1(5)	120.3(7)
Br-C(24)-C(23)	119.7(5)	119.4(6)
Br-C(24)-C(25)	118.4(5)	116.6(5)

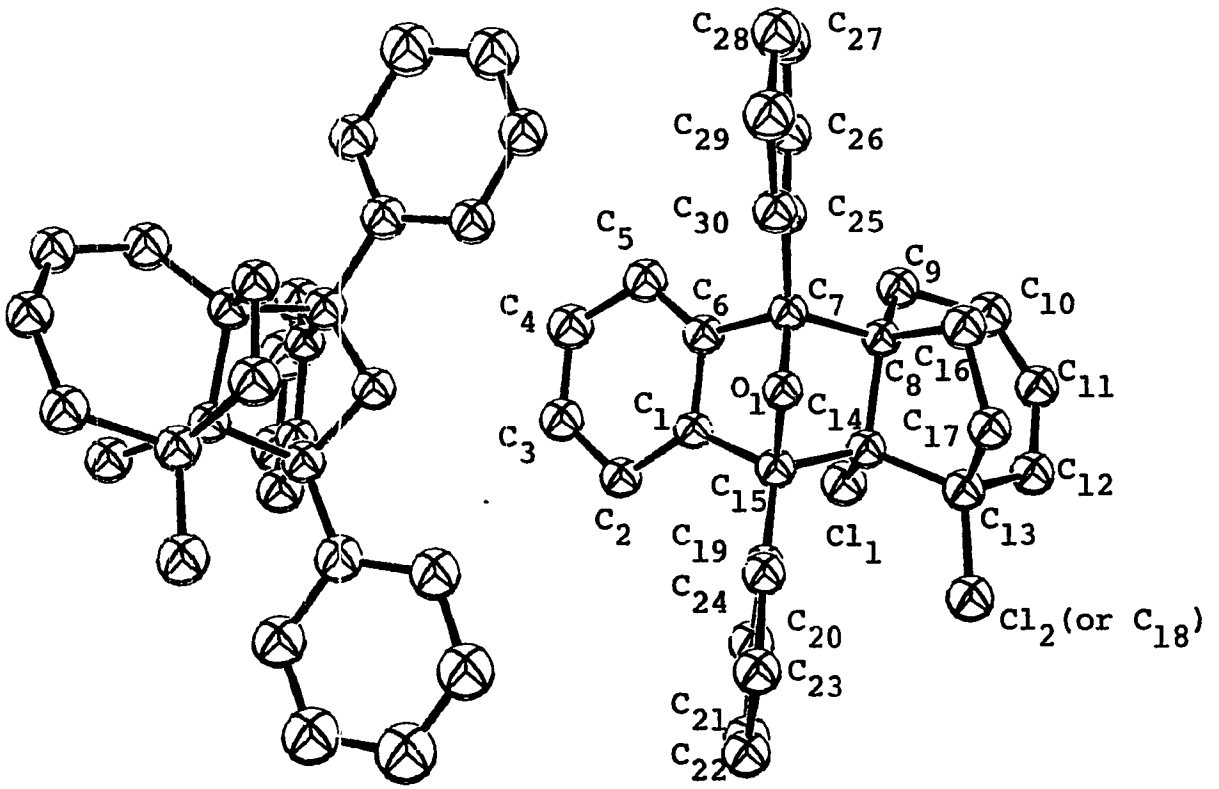

Figure A-4: Structure of 301 (or 300), showing the atom numbering scheme

Table A-III. Selected bond distances[a] for 301

Atom	301
Cl(1)-C(14)	1.783(2)
Cl(2)-C(13)	1.762(4)
O-C(7)	1.439(4)
O-C(15)	1.433(4)
C(1)-C(2)	1.395(9)
C(1)-C(6)	1.395(10)
C(1)-C(15)	1.533(12)
C(2)-C(3)	1.395(8)
C(3)-C(4)	1.395(10)
C(4)-C(5)	1.395(9)
C(5)-C(6)	1.395(8)
C(6)-C(7)	1.529(12)
C(7)-C(8)	1.593(18)
C(7)-C(25)	1.477(15)
C(8)-C(9)	1.496(19)
C(8)-C(14)	1.594(18)
C(8)-C(16)	1.590(16)
C(9)-C(10)	1.511(21)
C(10)-C(11)	1.329(22)
C(11)-C(12)	1.487(20)
C(12)-C(13)	1.543(19)
C(13)-C(14)	1.608(17)
C(13)-C(17)	1.516(18)
C(14)-C(15)	1.595(17)
C(15)-C(19)	1.471(14)
C(16)-C(17)	1.530(19)
C(19)-C(24)	1.395(9)
C(19)-C(20)	1.395(10)
C(20)-C(21)	1.395(11)
C(21)-C(22)	1.395(9)
C(22)-C(23)	1.395(10)
C(23)-C(24)	1.395(11)
C(25)-C(26)	1.395(12)
C(26)-C(27)	1.395(12)
C(25)-C(30)	1.395(11)
C(27)-C(28)	1.395(11)
C(28)-C(29)	1.395(12)
C(29)-C(30)	1.395(12)

[a]The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure.

Table A-IV. Selected bond angles[a] for 301

Atom	301
C(15)-O-C(7)	100.2(8)
C(6)-C(1)-C(2)	120.0(5)
C(15)-C(1)-C(2)	134.9(7)
C(15)-C(1)-C(6)	105.1(6)
C(3)-C(2)-C(1)	120.0(7)
C(4)-C(3)-C(2)	120.0(6)
C(5)-C(4)-C(3)	120.0(5)
C(6)-C(5)-C(4)	120.0(7)
C(5)-C(6)-C(1)	120.0(6)
C(7)-C(6)-C(1)	105.4(6)
C(7)-C(6)-C(5)	134.2(8)
C(6)-C(7)-O	100.3(7)
C(8)-C(7)-O	99.8(9)
C(8)-C(7)-C(6)	108.0(9)
C(25)-C(7)-O	112.2(9)
C(25)-C(7)-C(6)	116.6(9)
C(25)-C(7)-C(8)	117.4(8)
C(9)-C(8)-C(7)	118.2(11)
C(14)-C(8)-C(7)	99.8(9)
C(14)-C(8)-C(9)	116.2(11)
C(16)-C(8)-C(7)	105.1(10)
C(16)-C(8)-C(9)	111.8(10)
C(16)-C(8)-C(14)	104.0(10)
C(10)-C(9)-C(8)	113.9(12)
C(11)-C(10)-C(9)	129.3(14)
C(12)-C(11)-C(10)	134.8(14)
C(13)-C(12)-C(11)	125.5(13)
C(12)-C(13)-Cl(2)	105.5(10)
C(14)-C(13)-Cl(2)	115.5(8)
C(14)-C(13)-C(12)	109.3(10)
C(17)-C(13)-Cl(2)	111.2(9)
C(17)-C(13)-C(12)	114.6(10)
C(17)-C(13)-C(14)	101.1(10)
C(8)-C(14)-Cl(1)	114.8(8)
C(13)-C(14)-Cl(1)	108.3(9)
C(13)-C(14)-C(8)	101.8(8)
C(15)-C(14)-Cl(1)	110.5(7)
C(15)-C(14)-C(8)	101.7(10)

[a]The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure.

Table A-IV. (Continued)

Atom	301
C(15)-C(14)-C(13)	119.5(10)
C(1)-C(15)-O	99.0(8)
C(14)-C(15)-O	102.2(8)
C(14)-C(15)-C(1)	104.1(8)
C(19)-C(15)-O	112.5(8)
C(19)-C(15)-C(1)	115.9(7)
C(19)-C(15)-C(14)	120.3(10)
C(17)-C(16)-C(8)	106.5(10)
C(16)-C(17)-C(13)	103.9(10)
C(20)-C(19)-C(15)	119.9(7)
C(24)-C(19)-C(15)	120.0(7)
C(24)-C(19)-C(20)	120.0(7)
C(19)-C(20)-C(21)	120.0(6)
C(22)-C(21)-C(20)	120.0(6)
C(23)-C(22)-C(21)	120.0(7)
C(24)-C(23)-C(22)	120.0(6)
C(19)-C(24)-C(23)	120.0(6)
C(19)-C(24)-C(19)	120.0(8)
C(26)-C(25)-C(7)	119.5(8)
C(30)-C(25)-C(7)	120.5(8)
C(30)-C(25)-C(26)	120.0(8)
C(25)-C(26)-C(27)	120.0(7)
C(28)-C(27)-C(26)	120.0(8)
C(29)-C(28)-C(27)	120.0(8)
C(30)-C(29)-C(28)	120.0(7)
C(25)-C(30)-C(29)	120.0(8)

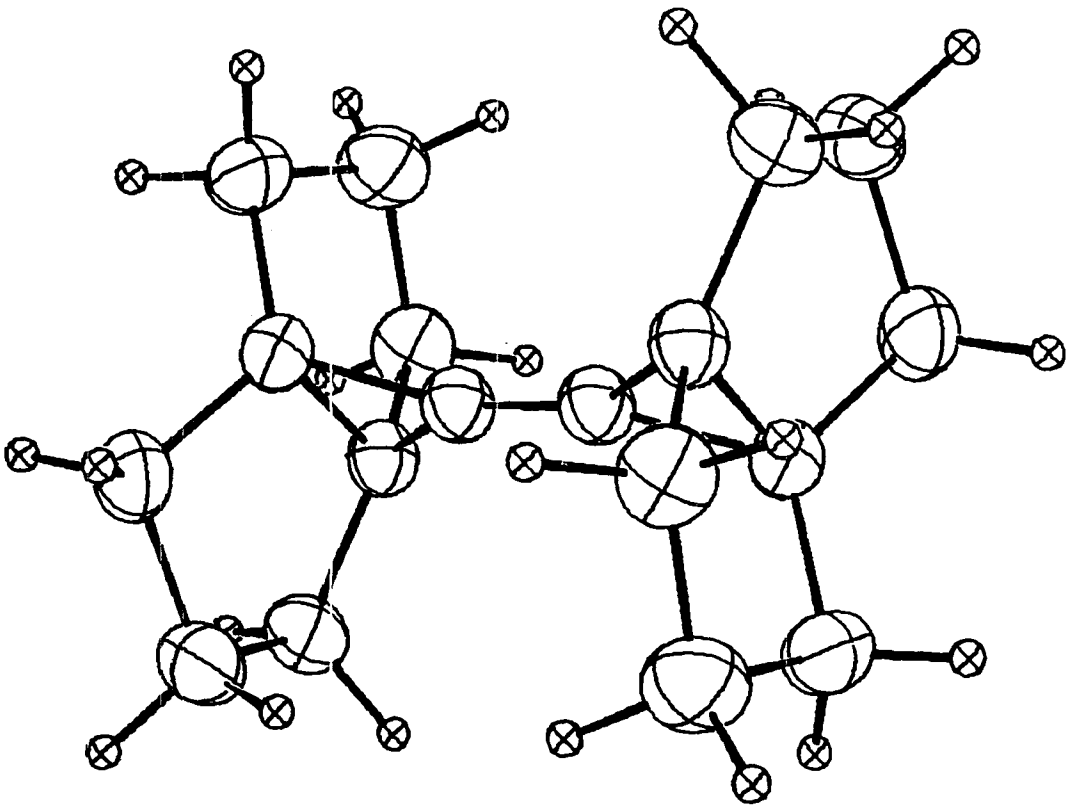

Figure A-5: Structure of 355, showing the atom numbering scheme

Table A-V. Selected bond distances[a] for 355

Atom		Atom	
C(1)-C(2)	1.513(4)	C(2)-H(2)	1.04(4)
C(2)-C(3)	1.538(4)	C(2)-H(2')	1.04(4)
C(3)-C(4)	1.546(4)	C(3)-H(3)	1.02(4)
C(4)-C(5)	1.515(3)	C(3)-H(3')	1.05(4)
C(1)-C(9)	1.470(3)	C(4)-H(4)	1.06(4)
C(9)-C(9')	1.307(3)	C(4)-H(4')	1.06(4)
C(5)-C(6)	1.515(3)	C(6)-H(6)	1.06(4)
C(6)-C(7)	1.531(4)	C(6)-H(6')	1.05(4)
C(7)-C(8)	1.543(4)	C(7)-H(7)	1.01(4)
C(8)-C(1)	1.518(4)	C(7)-H(7')	1.02(4)
C(5)-C(9)	1.470(3)	C(8)-H(8)	1.06(4)
C(1)-C(5)	1.549(3)	C(8)-H(8')	1.04(4)

[a]The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure.

Table A-VI. Selected bond angles[a] for 355

Atom	
C(1)-C(9)-C(9')	148.3(2)
C(1)-C(9)-C(5)	63.6(2)
C(9)-C(1)-C(5)	58.2(1)
C(9)-C(1)-C(2)	117.8(2)
C(9)-C(1)-C(8)	116.4(2)
C(2)-C(1)-C(8)	125.1(2)
C(1)-C(2)-C(3)	104.6(2)
C(2)-C(3)-C(4)	106.0(2)
C(3)-C(4)-C(5)	104.2(2)
C(5)-C(9)-C(9')	148.1(2)
C(9)-C(5)-C(1)	58.2(1)
C(9)-C(5)-C(4)	117.4(2)
C(9)-C(5)-C(6)	117.0(2)
C(4)-C(5)-C(6)	124.9(2)
C(5)-C(6)-C(7)	104.5(2)
C(6)-C(7)-C(8)	105.7(2)
C(7)-C(8)-C(1)	104.3(2)
Torsional angle: C(1)-C(9)-C(9')-C(5')	3.32°

[a]Bond angles are in degrees. Estimated standard deviations are given in parentheses for the least significant figure.

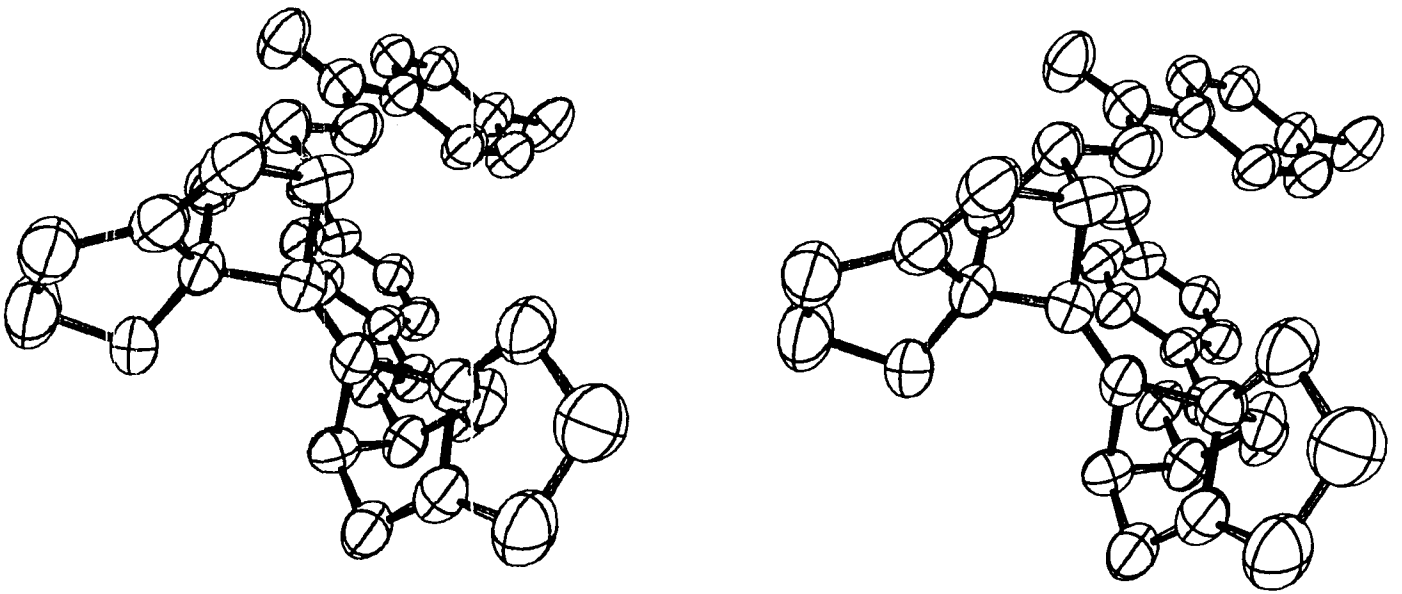

Figure A-6: ORTEP stereoview of 303e

Table A-VII. Selected bond distances[a] for dimer 303e

Atom	I	I'
Br-C(15)	1.891(7)	1.888(7)
O(1)-C(11)	1.222(8)	1.201(8)
O(2)-C(3)	1.446(8)	1.468(8)
O(2)-C(11)	1.333(8)	1.345(8)
C(1)-C(2)	1.555(9)	1.553(9)
C(1)-C(6)	1.533(10)	1.512(10)
C(1)-C(9)	1.542(12)	1.524(12)
C(1)-C(10)	1.520(9)	1.526(9)
C(2)-C(3)	1.539(11)	1.534(11)
C(3)-C(4)	1.538(9)	1.550(9)
C(4)-C(5)	1.526(9)	1.530(10)
C(4)-C(10)	1.537(10)	1.528(10)
C(5)-C(6)	1.318(11)	1.331(12)
C(6)-C(7)	1.501(11)	1.495(11)
C(7)-C(8)	1.495(15)	1.543(14)
C(8)-C(9)	1.594(12)	1.560(10)
C(10)-C(10')	1.302(8)	1.302(8)
C(11)-C(12)	1.474(9)	1.457(9)
C(12)-C(13)	1.396(9)	1.400(9)
C(12)-C(17)	1.364(10)	1.403(10)
C(13)-C(14)	1.377(10)	1.372(10)
C(14)-C(15)	1.354(10)	1.385(10)
C(15)-C(16)	1.369(10)	1.378(9)
C(16)-C(17)	1.389(10)	1.360(10)

[a]The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure. Column I gives the distances between the indicated atoms; column I' gives the distances between the corresponding primed atoms [C(10)-C(10') is common to both colums].

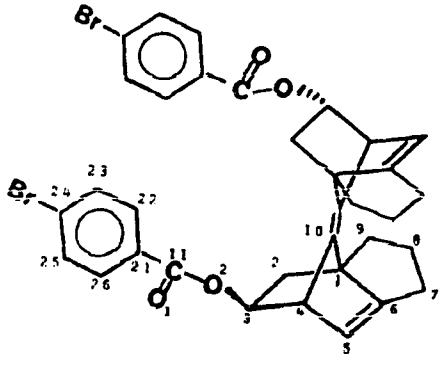

Figure A-7: Structure of 303e, showing the atom numbering scheme

Table A-VIII. Selected bond angles[a] for dimer 303e

Atom	I	I'
Br-C(15)-C(14)	119.5(5)	119.3(5)
Br-C(15)-C(16)	117.8(5)	118.8(5)
C(1)-C(2)-C(3)	102.1(5)	102.4(6)
C(1)-C(6)-C(5)	109.1(6)	108.3(6)
C(1)-C(6)-C(7)	110.2(7)	112.6(7)
C(1)-C(9)-C(8)	100.3(6)	102.8(6)
C(1)-C(10)-C(4)	95.0(5)	95.3(5)
C(1)-C(10)-C(10')	134.1(7)	132.2(7)
C(2)-C(1)-C(6)	104.5(5)	104.7(5)
C(2)-C(1)-C(9)	118.7(6)	118.8(6)
C(2)-C(1)-C(10)	99.8(5)	100.7(6)
C(6)-C(1)-C(9)	106.7(6)	104.0(6)
C(6)-C(1)-C(10)	99.7(6)	99.7(6)
C(9)-C(1)-C(10)	124.4(5)	125.8(6)
C(2)-C(3)-C(4)	104.6(5)	104.4(6)
C(2)-C(3)-O(2)	111.1(6)	110.2(5)
C(4)-C(3)-O(2)	106.4(5)	107.3(5)
C(3)-O(2)-C(11)	117.0(5)	115.0(5)
O(2)-C(11)-C(12)	113.8(5)	112.3(5)
O(1)-C(11)-O(2)	123.1(6)	122.6(6)
O(1)-C(11)-C(12)	123.0(6)	125.1(6)
C(3)-C(4)-C(5)	104.4(5)	102.9(5)
C(3)-C(4)-C(10)	98.8(5)	100.4(6)
C(5)-C(4)-C(10)	101.2(6)	99.7(6)
C(4)-C(5)-C(6)	106.5(6)	107.1(6)
C(5)-C(6)-C(7)	140.7(7)	139.1(7)
C(6)-C(7)-C(8)	104.7(7)	102.3(6)
C(7)-C(8)-C(9)	110.2(8)	106.7(7)
C(4)-C(10)-C(10')	130.8(7)	132.5(7)
C(12)-C(13)-C(14)	119.7(6)	121.5(6)
C(13)-C(14)-C(15)	119.1(6)	118.4(6)
C(14)-C(15)-C(16)	122.7(7)	121.9(6)
C(15)-C(16)-C(17)	118.2(6)	119.0(6)
C(16)-C(17)-C(12)	120.4(6)	121.6(6)
C(17)-C(12)-C(13)	119.9(6)	117.6(6)
C(11)-C(12)-C(13)	121.1(6)	123.6(6)
C(11)-C(12)-C(17)	119.0(6)	118.8(6)

[a]Bond angles are in degrees. Estimated standard deviations are given in parentheses for the least significant figure. Column I gives the bond angles for the indicated atoms; column I' gives the bond angles for the corresponding primed atoms.

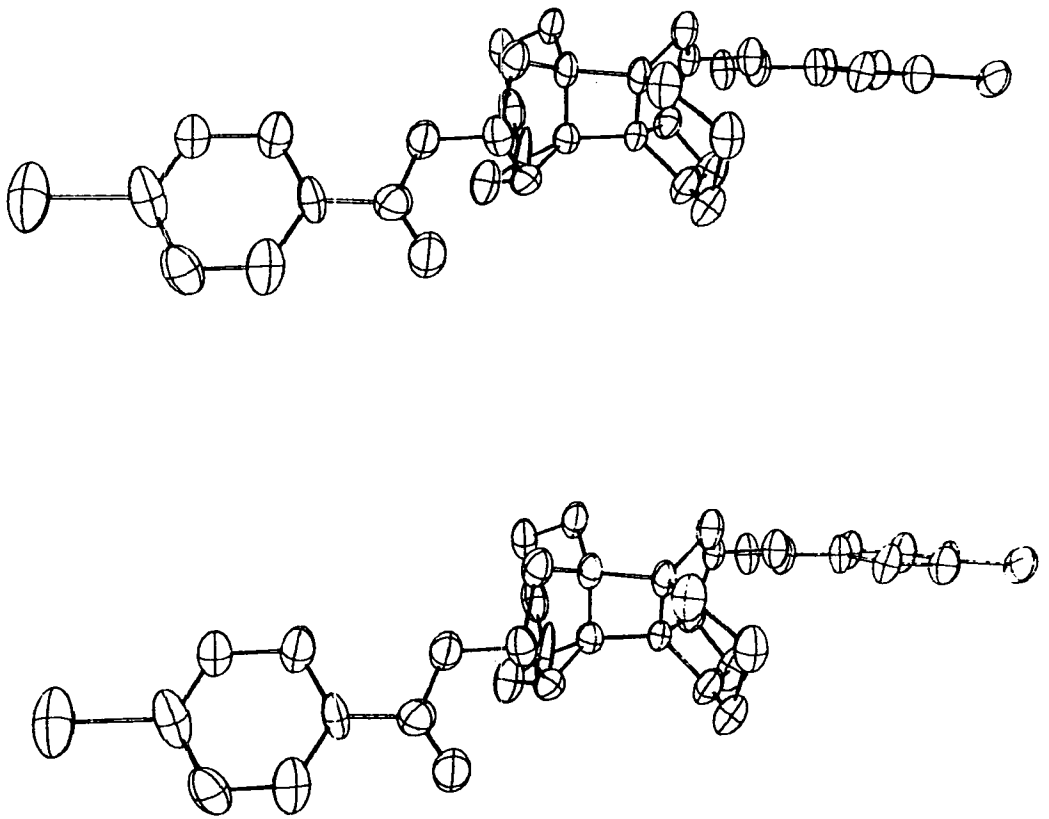

Figure A-8: ORTEP stereoview of 318a

Table A-IX. Selected bond distances[a] for dimer 318a

Atom	I	I'
C(1)-C(1')	1.52(2)	1.52(2)
C(7)-C(7')	1.58(2)	1.58(2)
C(1)-C(2)	1.58(2)	1.48(2)
C(1)-C(4)	1.55(2)	1.57(2)
C(1)-C(7)	1.53(2)	1.54(2)
C(2)-C(3)	1.22(2)	1.29(2)
C(2)-C(10)	1.56(3)	1.50(2)
C(3)-C(4)	1.52(2)	1.55(3)
C(4)-C(5)	1.53(2)	1.54(2)
C(5)-C(6)	1.49(2)	1.52(2)
C(6)-C(7)	1.54(2)	1.53(2)
C(7)-C(8)	1.58(2)	1.51(2)
C(8)-C(9)	1.52(2)	1.57(2)
C(9)-C(10)	1.58(3)	1.48(3)
Br-C(11)	1.89(2)	1.89(2)
O(1)-C(5)	1.47(2)	1.49(2)
O(1)-C(17)	1.29(2)	1.32(2)
O(2)-C(17)	1.23(2)	1.19(2)
C(11)-C(12)	1.31(3)	1.36(2)
C(11)-C(16)	1.40(3)	1.35(2)
C(12)-C(13)	1.41(2)	1.37(2)
C(13)-C(14)	1.40(2)	1.36(2)
C(14)-C(15)	1.36(3)	1.39(2)
C(14)-C(17)	1.48(2)	1.48(2)
C(15)-C(16)	1.38(2)	1.41(2)

[a]The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure. Column I gives the distances between the indicated atoms; column I' gives the distances between the corresponding primed atoms [C(1)-C(1') and C(7)-C(7') is common to both columns].

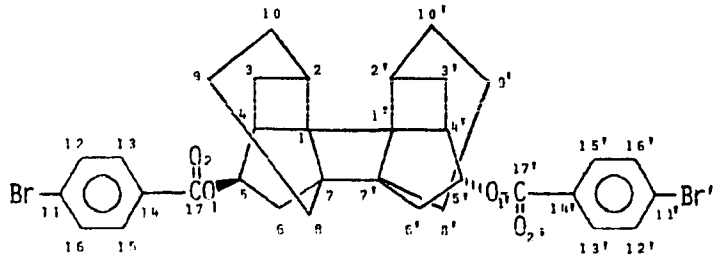

Figure A-9: Structure of 318a, showing the atom numbering scheme

Table A-X. Selected bond angles[a] for dimer 318a

Atom	I	I'
C(1')-C(1)-C(2)	132(1)	132(1)
C(1')-C(1)-C(4)	123(1)	122(1)
C(1')-C(1)-C(7)	90(1)	91(1)
C(7')-C(7)-C(1)	89(1)	87(1)
C(7')-C(7)-C(6)	121(1)	121(1)
C(7')-C(7)-C(8)	114(1)	115(1)
C(2)-C(1)-C(4)	84(1)	88(1)
C(2)-C(1)-C(7)	122(2)	116(1)
C(4)-C(1)-C(7)	106(1)	107(1)
C(1)-C(2)-C(3)	92(1)	95(2)
C(1)-C(2)-C(10)	109(2)	120(2)
C(1)-C(4)-C(3)	82(1)	81(1)
C(1)-C(4)-C(5)	107(1)	106(1)
C(1)-C(7)-C(6)	109(1)	108(1)
C(1)-C(7)-C(8)	112(1)	112(1)
C(3)-C(2)-C(10)	128(2)	134(2)
C(2)-C(3)-C(4)	99(1)	96(1)
C(2)-C(10)-C(9)	115(2)	108(2)
C(3)-C(4)-C(5)	114(1)	118(1)
C(4)-C(5)-C(6)	110(1)	109(1)
C(4)-C(5)-O(1)	113(1)	110(1)
O(1)-C(5)-C(6)	107(1)	106(1)
C(5)-C(6)-C(7)	106(1)	107(1)
C(5)-O(1)-C(17)	119(1)	116(1)
C(6)-C(7)-C(8)	110(1)	111(1)
C(7)-C(8)-C(9)	112(1)	114(1)
C(8)-C(9)-C(10)	113(1)	114(1)
O(1)-C(17)-O(2)	124(2)	124(1)
O(1)-C(17)-C(14)	114(1)	112(1)
O(2)-C(17)-C(14)	121(1)	124(2)
Br-C(11)-C(12)	119(1)	121(1)
Br-C(11)-C(16)	119(1)	118(1)
C(12)-C(11)-C(16)	122(2)	121(2)
C(11)-C(12)-C(13)	121(2)	118(2)
C(12)-C(13)-C(14)	118(2)	123(2)
C(13)-C(14)-C(15)	119(1)	119(1)
C(14)-C(15)-C(16)	122(2)	118(2)
C(15)-C(16)-C(11)	117(2)	122(2)
C(17)-C(14)-C(13)	120(2)	124(1)
C(17)-C(14)-C(15)	121(2)	117(1)

[a]Bond angles are in degrees. Estimated standard deviations are given in parentheses for the least significant figure.