1978

Part I: An investigation of the rehybridization of bridgehead olefins, solvolytic formation of bridgehead olefins. Part II: The effect of silver(I) ion upon the solvolysis products in the dibromo-and monobromobicyclo[6.1.0]nonane systems

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7813240

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by

Richard Francis Palmer

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1978

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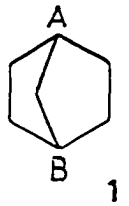
PART I: AN INVESTIGATION OF THE REHYBRIDIZATION OF BRIDGEHEAD OLEFINS, SOLVOLYTIC FORMATION OF BRIDGEHEAD OLEFINS.

INTRODUCTION

New chemical reactivity can result from the incorporation of specific structural features into a carbocyclic molecule which already contains structural elements restricting the geometrical skeleton. This reactivity is a consequence of the lower bond energy resulting from the bonds not being in their optimal geometry due to restricting structural elements. Chemists have long been intrigued by these types of molecules, which contain excess or "strain" energy (1).

Bridgehead Olefins

From studies of compounds in the camphane and pinane series and the related bicyclo[2.2.1]heptane (1) and bicyclo[3.1.1]heptane (2), Bredt postulated that the branching points A and B of the carbon bridges (the bridgeheads) cannot be involved in carbon double bonds (2). This idea, known as Bredt's rule, initiated research into higher homologs of bicyclic compounds. With a sufficiently large number of atoms in the ring, it is possible to construct completely strain free molecular models of bridgehead



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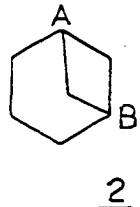

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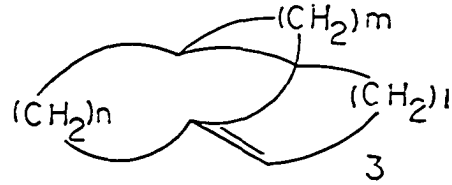

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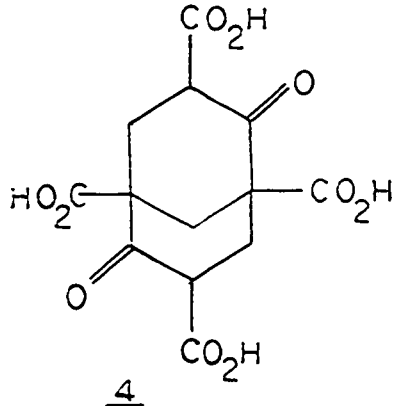
olefins (3). Many workers, mainly since 1950, have attempted to establish a boundary to Bredt's hypothesis or, in other words, to determine the ring size beyond which Bredt's rule is no longer valid. Fawcett (3) proposed a convenient numerical formula to define the limits of Bredt's rule. From Prelog's results (4), Fawcett concluded that Bredt's rule ceased to be valid when $S \geq 9$, where the strain number (S) in a bicyclo[m.n.1]alk-1-ene is $S=m+n+1$ (m,n and $1 \neq 0$). But he did recognize that for transient intermediates, the limit might be as low as S=6, since keto acid (4) could be decarboxylated (5) via a process proposed to involve an enol intermediate such as 5 (6).



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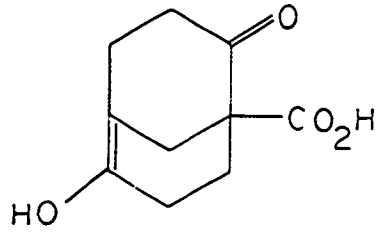

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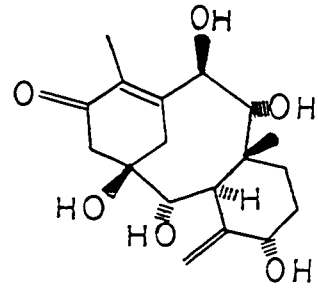

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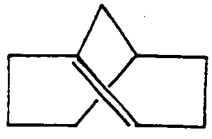

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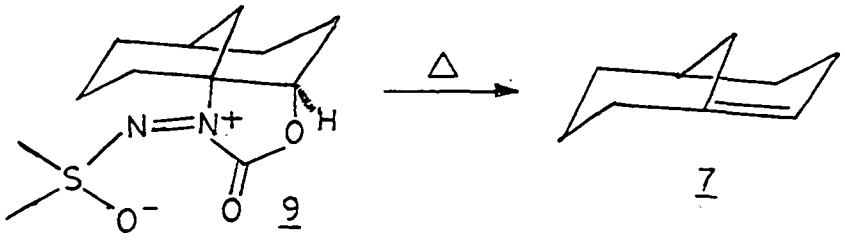
8

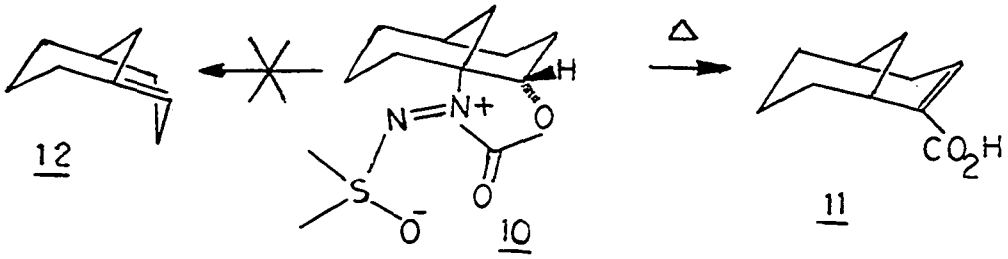
Today many bridgehead olefins are known, including some that occur naturally (e.g., the diterpene taxicin, 6,

(7a) and some alkaloid derivatives (7b)). Several recent reviews on anti-Bredt compounds have appeared and a number of large ring anti-Bredt olefins have been prepared (8). Marshall and Faubl (9a) and Wiseman (9b), independently in 1967, succeeded in preparing the stable bicyclo[3.3.1]-non-1-ene (7), which at present marks the lower limit for stable bridgehead olefins and which has an S number of 7. Wiseman and coworkers (9b, 9c, 10a, 10b) also postulated a means of defining the limits of Bredt's rule by comparison of the corresponding trans-cycloalkene to the bridgehead olefin. Thus, the number of atoms in the larger of two rings with the endocyclic double bond provides information about the relative stability of the bicycloalkene. Comparison of trans-cyclooctene (8), an isolable compound (11), to bicyclo[3.3.1]non-1-ene (7) shows that the bridgehead olefin may be regarded as a bridged trans-cyclooctene. Compound 7 can be constructed from 8 using models without the introduction of much additional strain while, according to thermochemical data, 7 has a ring strain of 12 kcal/mole, as compared with 9.2 kcal/mole for trans-cyclooctene (8) (12).

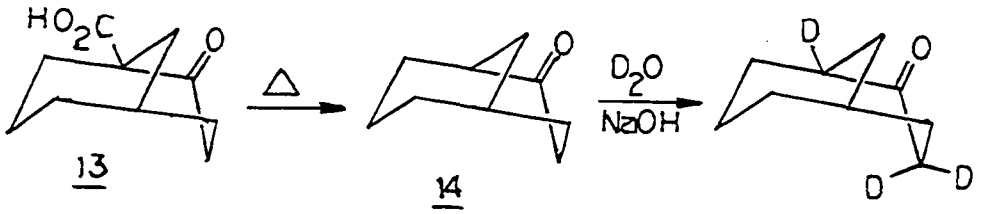
Wiseman's postulate is supported by the decomposition of exo-sulfoximine (9) to 7; the corresponding endo-sulfoximine (10) resisted decomposition and only gave bicyclo-[3.3.1]non-2-ene-2-carboxylic acid (11) rather than the E

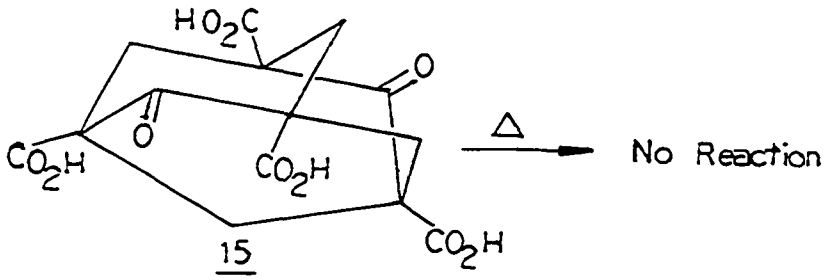
conformer of bicyclo[3.3.1]non-1-ene (12), which should be equivalent to trans-cyclohexene (13). The importance of the



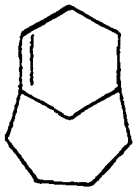


conformation of the molecule is also shown in the ready decarboxyation of 13 (14) (the ketone (14) undergoes H/D exchange at the bridgehead (15)) while the adamantane





derivative (15) resists decarboxyation (16) since a structure analogous to trans-cyclohexene would have to be formed. By use of the strain number, S, 16, 17 and 18 are not differentiated, but even Wiseman's rule for stability of bridgehead



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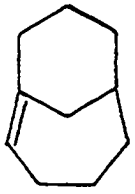

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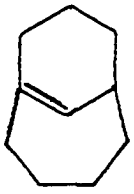

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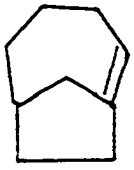

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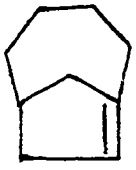


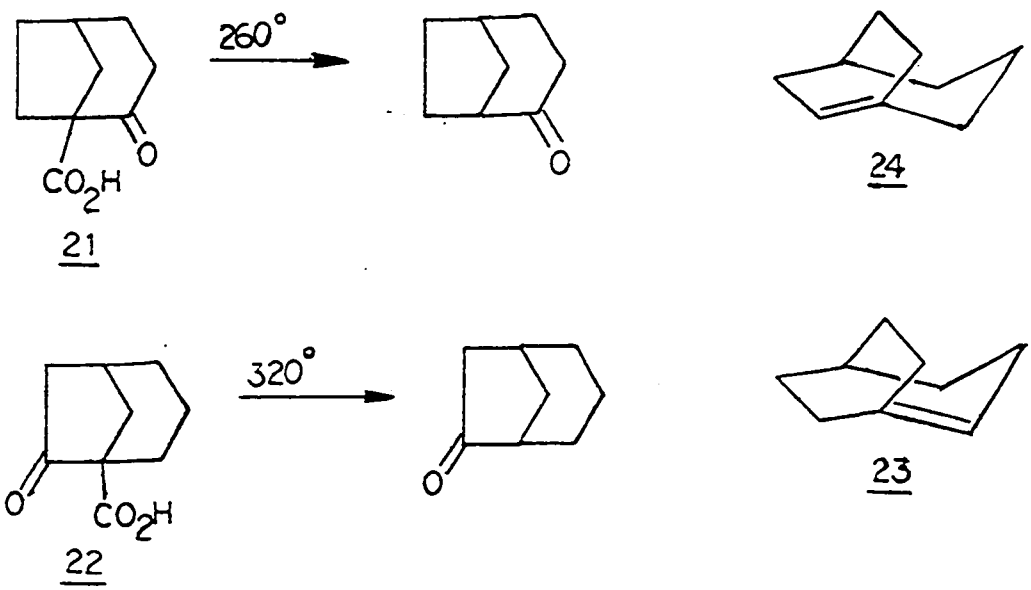
20

olefins fails to distinguish between 16 and 17. Köbrick (8b) attempted to modify Fawcett's contribution by including secondary rules in order to differentiate structures like 16, 17 and 18. But Köbrick's statements are rather cumbersome in practice and recent molecular mechanics calculations have questioned the use of an empirical rule for determining the stability of 16 and 17 (17).

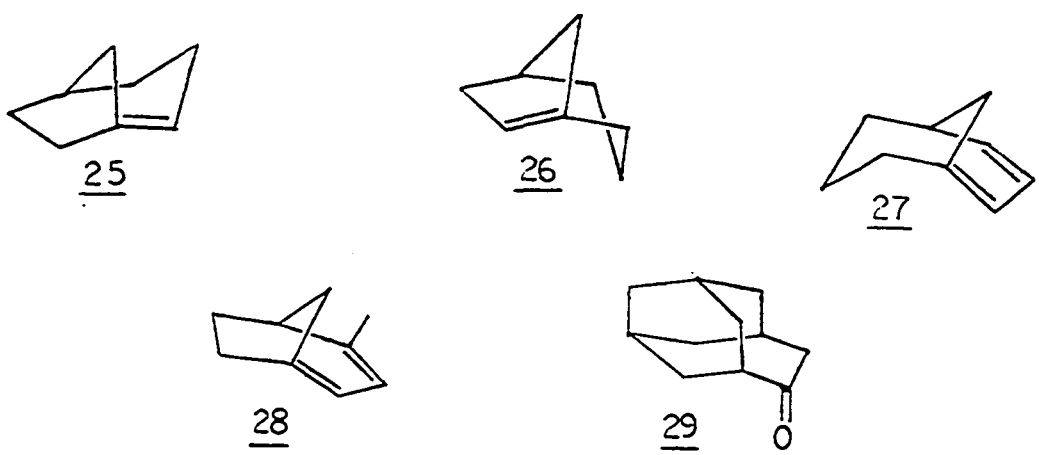
Recently, Becker (17a) has shown that it is difficult to order the stability of bridgehead olefins; for example, from electrophilic additions, he concluded that 19 has a strain energy of 9 kcal/mole, while 20 has a strain energy of 8 kcal/mole. These isomeric bridged trans-cyclooctenes were first synthesized by Wiseman et al. (10a) who proposed the

opposite order of stability, although 20 was obtained as the major product. Bicyclo[3.3.1]non-1-ene (7) has the greatest amount of strain energy (12 kcal/mole), according to Becker, of the three studied transoid olefins in eight-membered rings. Thus, Wiseman's hypothesis about stability of the bridged-head olefin compared to trans-cycloolefins is maintained, but no empirical rule can be used to deduce the stability of isomeric compounds like 16 and 17 or 19 and 20 (17b).

Even though trans-cycloheptene has been trapped as a reactive transient species (18a), it can isomerize with relief of strain to cis-cycloheptene, a pathway not open to a bridged trans-cycloheptene. Recently the existence of trans-1-phenylcycloheptene and trans-2-cycloheptenone have been observed (18b, 18c). Ferris and Miller (14b) reported the decarboxylations of two isomeric β-keto acids (21 and 22), which seems to indicate that the corresponding bridgehead alkenes, each incorporating a trans-cycloheptene, might be isolable or detectable as transient intermediates. Vogt reported a similar decarboxylation of a homoadamantane derivative (19). Bicyclo[3.2.2]non-1-ene (23) and bicyclo-[3.2.2]non-1(7)ene (24) were synthesized by Wiseman and Chong, using a Hofmann elimination to generate the double bond, as they had for the synthesis of 7 (10b). Wiseman and Chong were later able to demonstrate the presence of

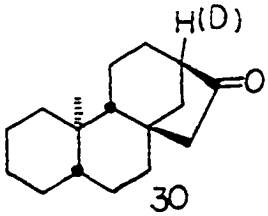


two isomeric bicyclo[3.2.1]oct-1-enes (25 and 26) but contrary to 23 and 24, these compounds could not be observed by pmr at -80°; rather, they were trapped as Diels-Alder adducts (19c). Dauben and coworkers (20) have developed an elegant high yield synthesis of bridgehead olefins from cycloalkenones by intramolecular Wittig reactions. They have prepared some isolable large ring bridgehead olefins, as well



as 27 and 28, which dimerized or could be trapped as Diels-Alder adducts with suitable dienes. An intramolecular Wittig reaction was used by Becker (21) to synthesis 7, 19 and 20 and later Dauben and Robbins used the identical method to synthesize 26 (20b).

In contrast to the report by Schleyer and coworkers (22) that homoadmantanone (29) does not undergo base-catalyzed H/D exchange at the bridgehead, two other groups



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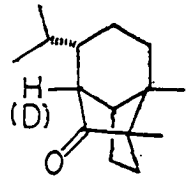

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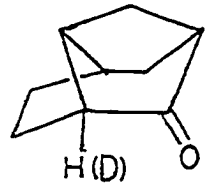

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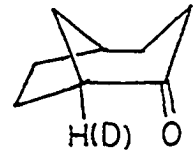
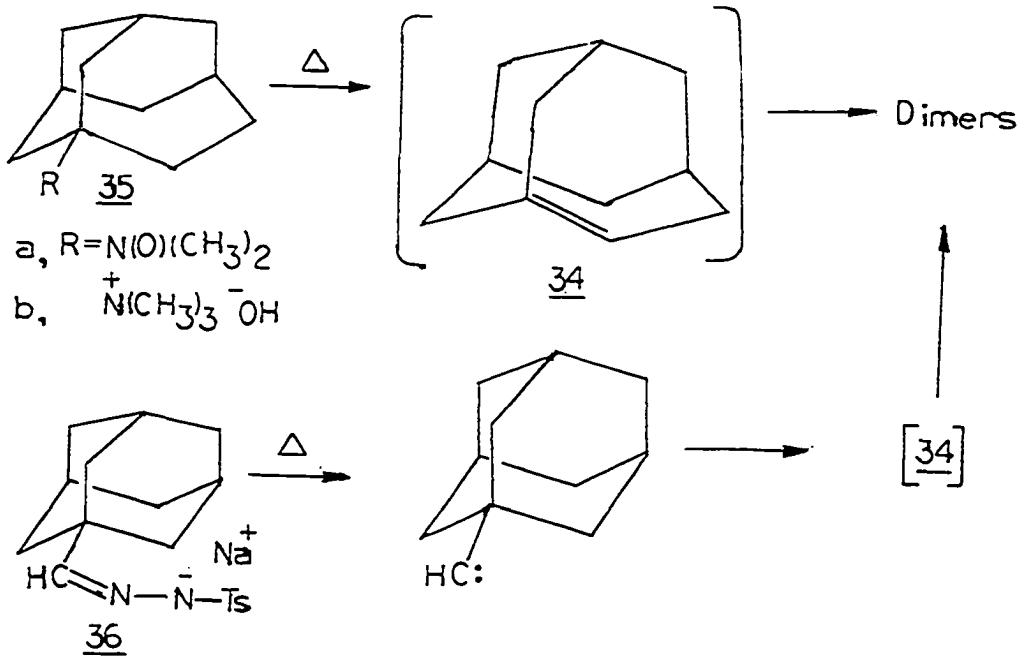


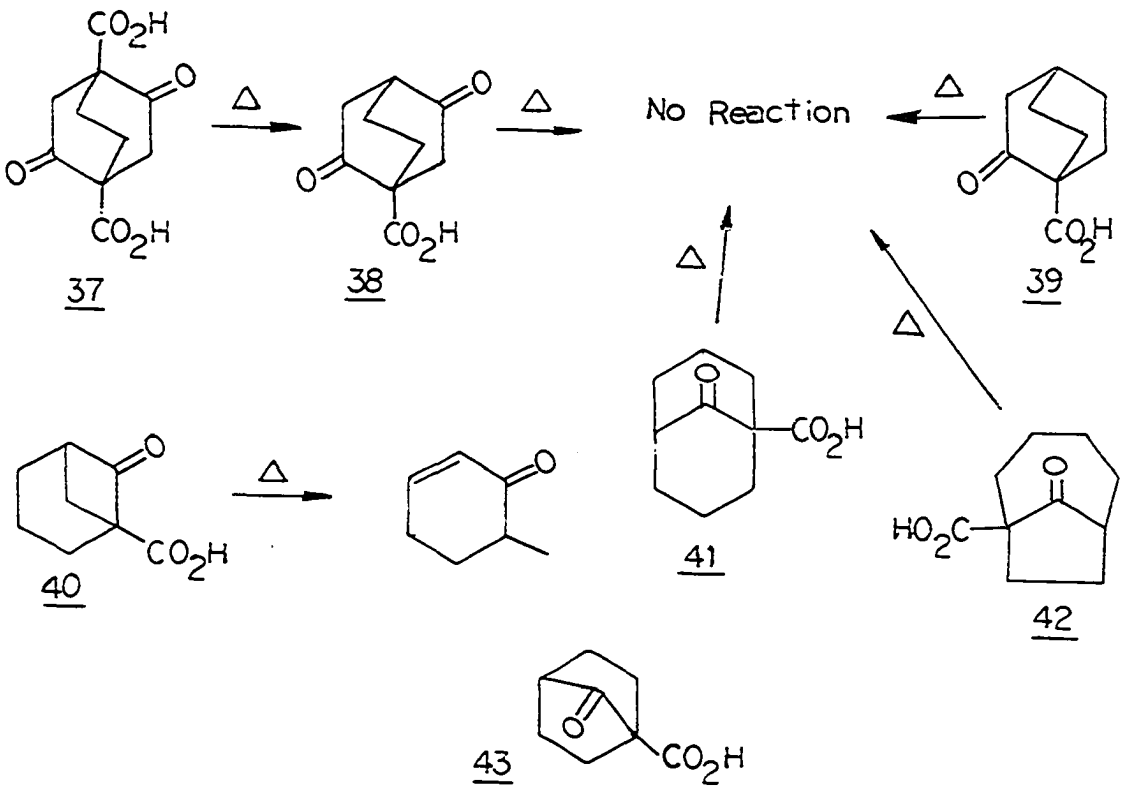
33

reported H/D exchange at the bridgehead in two natural products (30 (23) and 31 (24)). Nickon and coworkers (25) reported a facile base-catalyzed exchange at room temperature for the locked boat cyclohexanone of brendan-2-one (32) while temperatures >170° are needed for H/D exchange to proceed in 30 and 31. The anti-Bredt enolates of 30 and 31 also contain transoid olefins in seven-membered rings. Exchange at the bridgehead in the bicyclic analog (33) of brendan-2-one, which is conformationly more flexible, required conditions similar to that of 30 and 31 to effect exchange (25, 26).

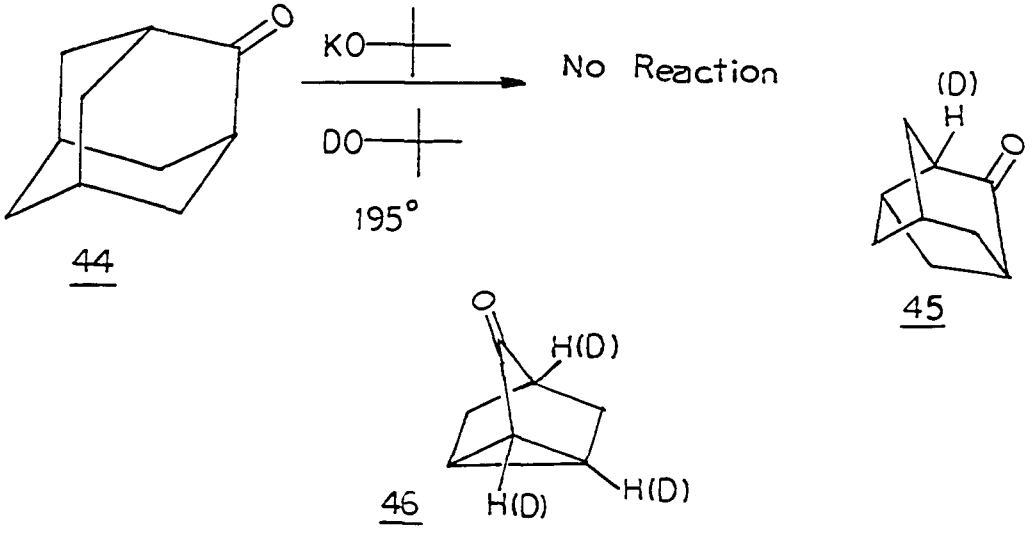


Two groups have reported the preparation of bridgehead homoadamantene (34). Adams and Kovacic pyrolyzed the amine oxide (35a) (27) and the quaternary ammonium hydroxide (35b) to give ∿10% of 34 while Farcasiu and coworkers (28) pyrolyzed the tosylhydrazone salt (36) which proceeded via the carbene to 34, and then to an identical set of dimers isolated by Adams and Kovacic.

The existence of trans-cyclohexene has been postulated as an intermediate in the photosensitized ionic additions to cyclohexene (29a) and recently the existence of trans-1-phenylcyclohexene has been claimed (29b). Presently there is no report of a decarboxylation which embodies a bridged trans-cyclohexene in the enol intermediate. The long standing report by Guha (30) that 37 undergoes a



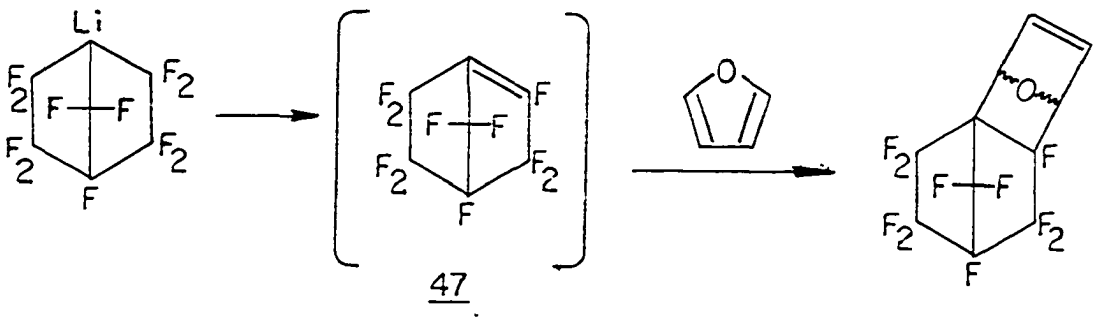
monodecarboxylation has been shown to proceed via a ring-opened intermediate, in that loss of optical activity occurs in the product (31). Buchanan and coworkers also showed that 38 and 39 did not decarboxylate. Bicyclo-[3.1.1]heptan-6-one-1-carboxylic acid (40) was shown to decarboxylate but with a concurrent ring opening (32). The two isomeric keto acids (41 and 42) (33) are unchanged after heating in contrast to 13 which readily decarboxylates. Allen et al. recovered 43 unchanged after heating to 500° but the enol intermediate in the decarboxylation would have had a transoid olefin in a five-membered ring (34).



44 45 46

Nordlander and coworkers (35) investigated the possibility of base-catalyzed H/D exchange in adamantanone 44, but even at 195° with potassium t-butoxide no exchange was observed. But noradamantan-2-one (45) does undergo exchange under vigorous alkaline treatment (25) although this case seems similar to that reported for nortricyclanone (46) (36). Gassman and Zalar attribute the exchange to a combination of inductive effects (37), homoenolization (38), and enhanced acidity from the increase in s character of the carbon-hydrogen bond in strained rings (39). From this data it is obvious that decarboxylation is a better test of the possible intermediacy of bridgehead olefins than is enolization.

Campbell et al. (40) were the first to demonstrate the presence of a transoid olefin in a six-membered ring by the



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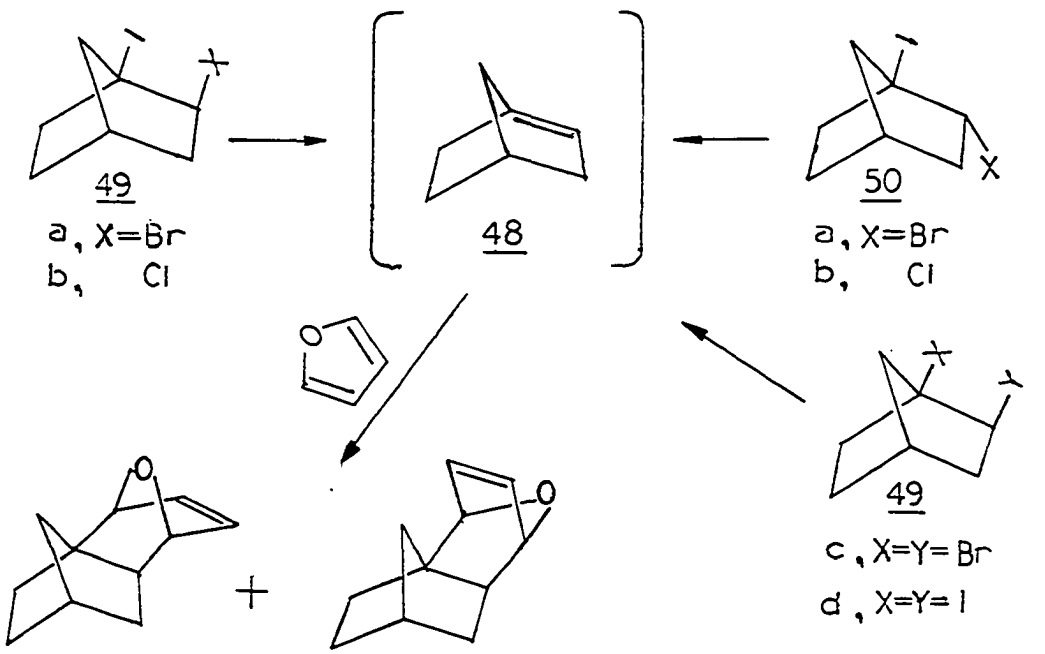
furan trapping of decafluorobicyclo[2.2.1]hept-1-ene (47). The presence of 1-norbornene (48) as a discrete intermediate in the bisdehalogenation of the diastereoisomeric pairs of



49
a, X=Br
b, Cl

48

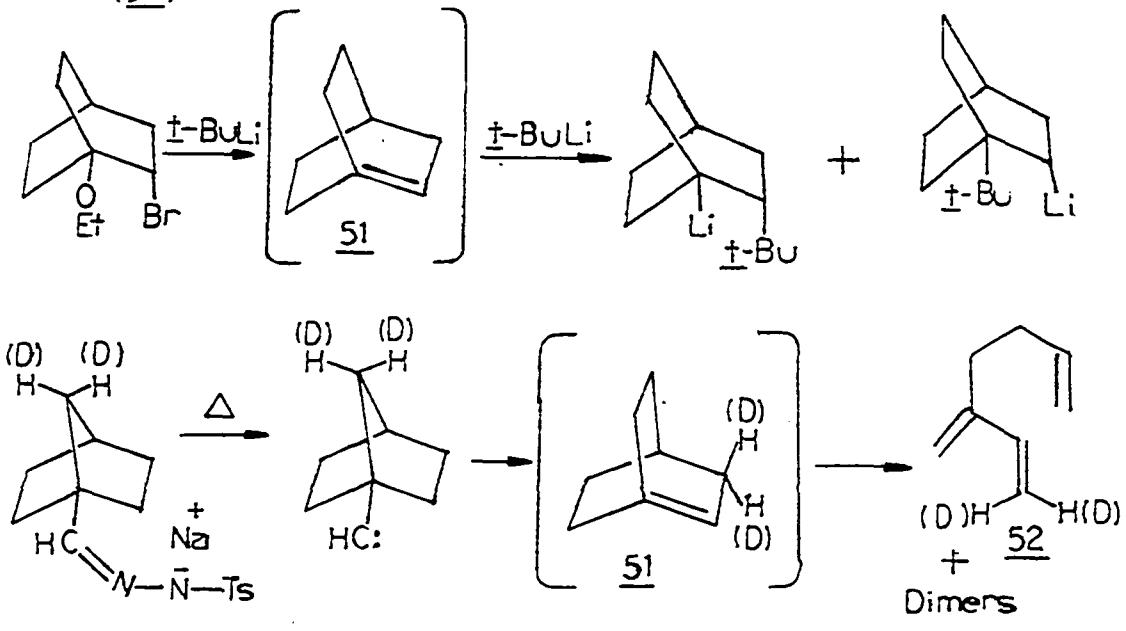
50
a, X=Br
b, Cl

49
c, X=Y=Br
d, X=Y=I

1,2-dihalonorbornanes under varying conditions was demonstrated by Keese and Krebs (41). Treatment of diastereoisomeric dihalides 49a/50b and 49b/50b with butyl lithium (n-butyl, tert-butyl or sec-butyl) or sodium amalgam gave

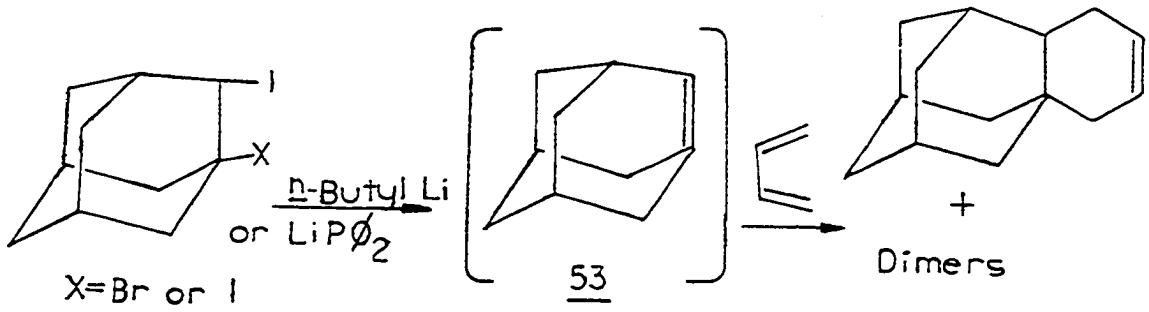
the same ratio of diastereoisomeric trapping products, which indicated a common intermediate.

In a similar reaction bicyclo[2.2.2.]oct-1-ene (51) was proposed as a transient intermediate which reacted with t-butyl lithium to give the observed products (42). Wolf and Jones (43) have prepared 51 by the flash pyrolysis of a tosylhydrazone salt which gave the carbene and then the bridged trans-cyclohexene (51) by a ring expansion. A labeling experiment indicated the intermediacy of 51 and not 25, as shown by analysis of the retro-Diels-Alder product (52).



Several groups have postulated the fleeting presence of adamantene (53) by the treatment of 1,2-dihalo adamantane with n-butyl lithium (44, 45) or lithium diphenylphosphide (46), but only dimers were isolated (45a, 44). Later, Burns and McKervey, using butadiene as trapping

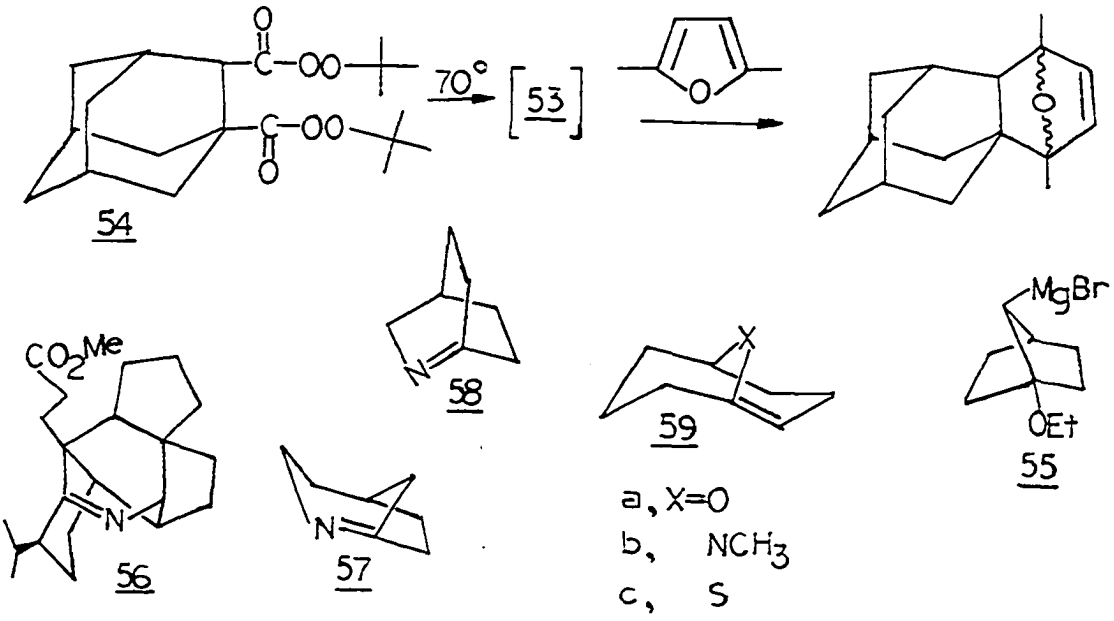
agent, were able to capture adamantene (53) generated from 1,2-diiodoadamantane with n-butyl lithium, while Alberts et al. (47) were able to trap 53, generated by the pyrolysis of the bis-t-butyl perester (54), with dimethyl



furan. Although an initial attempt to generate adamantene photochemically failed (48), Gano and Eizenberg (49) were apparently able to demonstrate its presence by the photolysis of 1-adamantyl and 2-adamantyl phenylacetate.

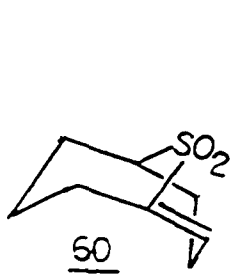
A report (50) relating to the attempted generation of a transoid olefin in a five-membered ring describes the alleged stability of 55 which only undergoes radical reactions at C_7.

A number of heterocyclic bridgehead olefins have been prepared including an alkaloid derivative (56) (51). Compounds 57 and 58 are possible intermediates in a nitrene rearrangement analogous to that used by Wolf and Jones to generate 51 although the authors (52) concluded that the products could be explained by an alternative mechanism. Other workers (53) were able to synthesize a number of bicyclo[3.3.1]non-1-enes (59) with the bridging carbon

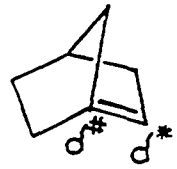


atom replaced by different heteroatoms. These compounds showed some interesting properties; when the bridging atom was a third row element, the effect of the d-orbitals became important (54, 55). This group was also able to show the presence of E isomer (60) and the Z isomer (61) in the 9-thiabicyclo[3.3.1]non-1-ene-9,9-dioxide system by trapping with 1,3-diphenylisobenzofuran (56). The E isomer (60) has a trans double bond in a six-membered ring which is perhaps stabilized by the sulfonyl group (61). Keese and Krebs (41) have suggested an ylid structure (62a) for bridgehead olefins and the sulfonyl group is in the correct geometry (57, 58) for stabilization of such a structure. But their conclusion from calculations is questioned by the work on hydration and other reactions of bridgehead olefins (9, 17, 59). However, a highly twisted olefin in a polar

solvent might exist in a double-well potential as zwitterionic structures (62a or 62b) as shown by other calculations (60). Thus, a qualitative statement about the structure of



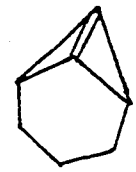
60



62

a,# = − * = +

b, + −



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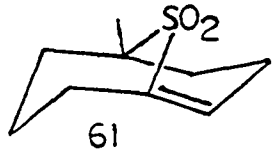

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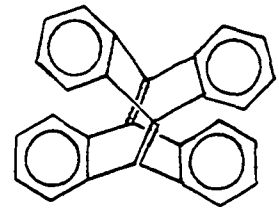

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60 is difficult to make without more evidence on the perturbing influence of the sulfonyl group.

Rehybridization of Strained Olefins

By constructing a double bond at the bridgehead of a bicyclic compound, a twisting of the normally planar double bond occurs (except where pains are taken to otherwise fix the geometry, as in 63 and 64) with a concurrent loss of overlap of the p-orbitals (61). As discussed by Köbrick (8b) three types of distortions occur, with the most important being the twisting of the two p-orbitals out of the same plane (Figure 1). Planar (62a) (Figure 2) and nonplanar (62b) (Figure 3) deformations of the σ bonds emerging from the unsaturated centers also occur due to the restricting

carbocyclic skeleton. N. S. Zefirov and V. I. Sokolov (63) compiled an excellent review on strained double bonds in which they discussed different distortions of double bonds.

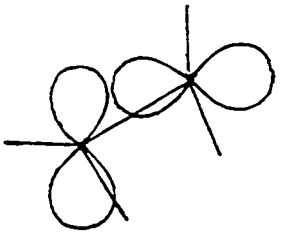


Figure 1. Twisting distortion

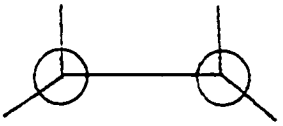


Figure 2. Planar deformation

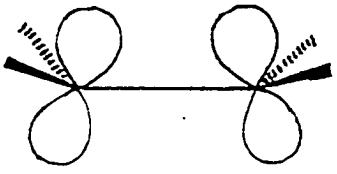


Figure 3. Nonplanar deformation

Many workers have calculated the energy of the lowest lying states of ethylene as a function of the twist angle (64) (Figure 4). Chemists have used these diagrams as an aid in describing photochemical reactions where excitation to these other states occur (65). Much theoretical (64) and experimental (66) work has been done on ethylene which shows that the planarity of the molecule is lost on electronic excitation. It is noticed that the curves of the N (ground

state) and T (triplet state) states intersect each other, so that if the perturbation mixes both states, radiationless

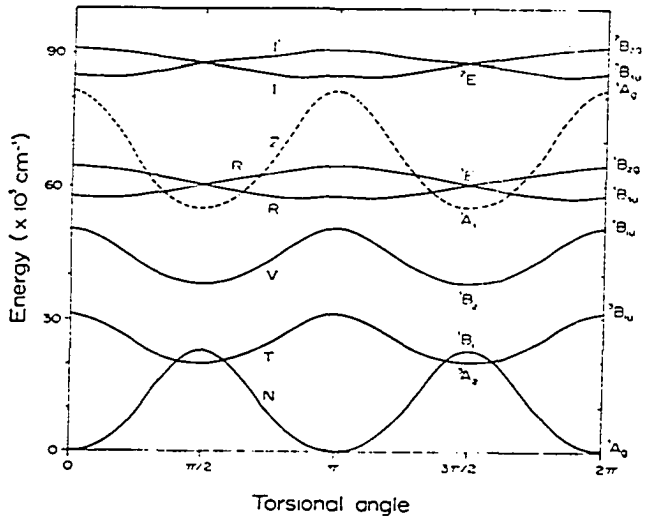
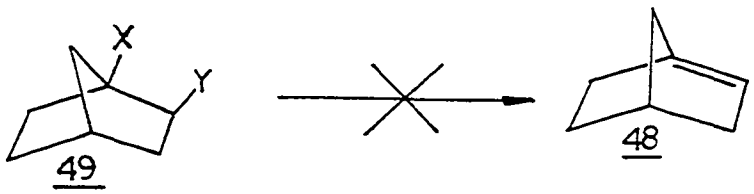


Figure 4. Potential energy curves as a function of the angle of rotation about the double bond in ethylene (64d)

transition is allowed though the states involved are of different multiplicities (67, 64c). As the twist angle is increased to $\pi/2$ or $3\pi/2$, the two molecular orbitals (ψ and ψ') approach each other in energy and the system approaches a diradical ground state which would be a triplet but could be a singlet in some cases (68). Salem concludes that there is no quantitative way of defining when the system stops behaving as a diradical or olefin; 1-norbornene (48) may

exist in this doubtful region. Berson and Willcott (69) concluded that if intersystem crossing to a triplet state occurs in a twisted species, then the change in multiplicity



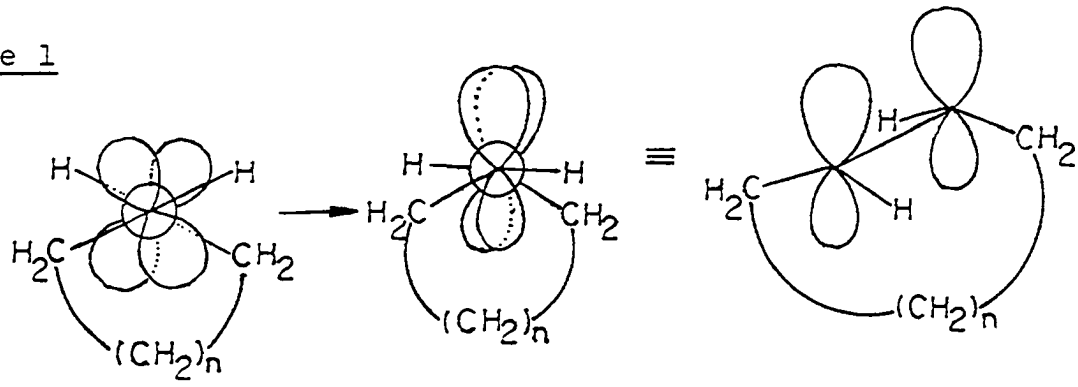
49 48

necessary for "olefin" formation would affect the rate by causing a drop in the pre-exponential term (70). Thus, they concluded anti-Bredt species (48) would be kinetically inaccessible by the way of vicinal elimination from a 1,2-disubstituted norbornane (49). This conclusion was reached before the results of Keese and Krebs (41) and others (40, 42, 44-47) were published. Another interesting phenomenon that might be observed for compounds with torsional strain is thermochromism (71) which has not been reported yet for anti-Bredt olefins.

There is the possibility of representing certain changes in valence angles as a result of rehybridization. Walsh has accounted for the structure of cyclopropane with this idea and it is now widely adopted (72). The overlap of the orbitals, and thus the bond energy, of a double bond twisted by restricting structural elements, can be increased by rehybridizing the orbitals (mixing in s character into the p-orbital) as proposed by a number of workers (73-75) (Scheme 1). Mock proposed that as a consequence of this

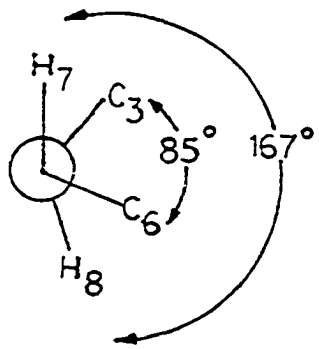
rehybridization, these systems would be more susceptible to cis addition rather than trans addition (73a). But in trans-cycloalkenes the carbocyclic ring blocks attack from

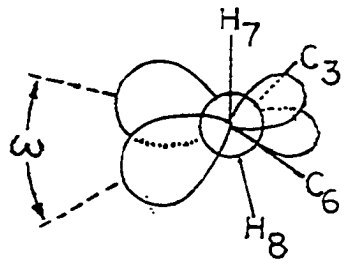
Scheme 1

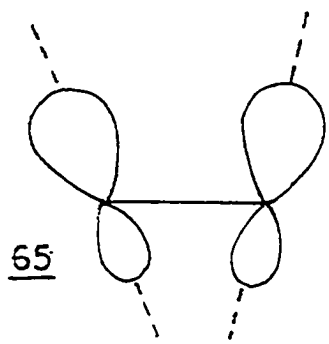


one side which could account for the observed cis additions (76). Radom et al. (73b) examined these twisting distortions by ab initio molecular orbital studies and concluded that there is significant pyramidalization of the bonds at the carbon atoms.

Scheme 2





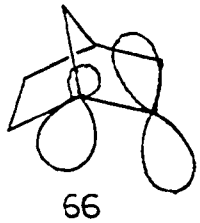


65

Allinger and Sprague (74b), using a force field method, have calculated that trans-cyclohexene is 42.4 kcal/mole less stable than cis-cyclohexene; considerable distortion of the π-bond is envisioned (Scheme 2). The π-bond is only half disrupted (30.9 kcal/mole torsional strain across $C_1=C_2$), and they attribute this to rehybridization and thus the increase in overlap. A limiting point is reached though when the increase in overlap due to smaller angle ω is offset by the decrease in overlap due to the orbitals being canted away from one another as in 65. Allinger has discussed the dipole moment, infrared spectrum and other physical and chemical properties of trans-cyclooctene as a consequence of rehybridization (74a). Rummens (75) and others (77) have examined infrared and ultraviolet frequency shifts which can be accounted for on the basis of rehybridization which alleviates the effects of ring strain and steric hindrance in olefins. Keese and Krebs (41b) have used the extended Hückel method to calculate the energies of 66 and 67 in the 1-norbornene system, with the conclusion that 66 is more stable than 67. As noted earlier, they find an excess of negative charge develops on the sp^3 hybridized carbon atom (at the bridgehead) in 66 independent of the torsion angle.

A photoelectron spectroscopic approach to the question of rehybridization of deformed π-bonds by Batich et al. (78)

gave no definite answer. The authors concluded that the energy difference was 0.1 to 0.2 ev which coincided within experimental error to values expected for substituted and fully planar π-bonds (78). But recently an x-ray study of trans-2-cyclooctenyl 3',5'-dinitrobenzoate (68) showed that the double bond in this molecule is rehybridized (79). Also 9,9',10,10'-tetradehydrodianthracene (64), which was synthesized by Viavattene and coworkers (80), has bond angles approaching sp^3 hybridization, as shown by x-ray diffraction studies. This double bridgehead olefin has the substituents on the alkene bent 19.7° out of the plane of the double bond (Figure 5). Vogel et al. (81) were able to synthesize a number of 1,6-methano-cyclodecapentaene



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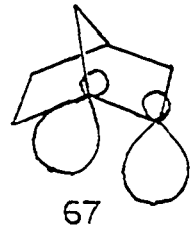

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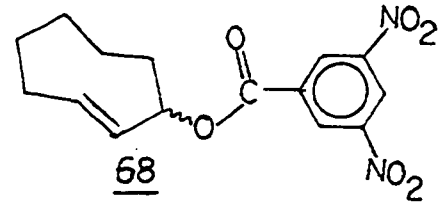

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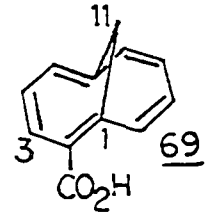

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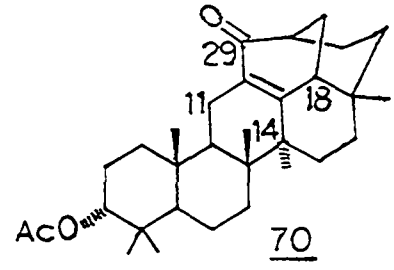

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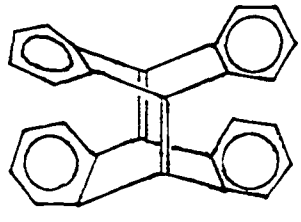

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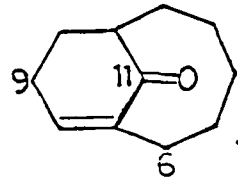


71

systems and a crystal structure of 1,6-methano-cyclodecapentaen-2-carboxylic acid (69) shows some pyramidalization of the orbitals (82) (Figure 6). A similar situation is observed in the ketone (70) obtained from the triterpene, katonic acid (83) (Figure 7) and in the substituted enone (71) which also has a transoid alkene in a 10-membered ring (84) (Figure 8). Thus, the question of whether a symmetrical bridgehead olefin can exist in a triplet ground state or is rehybridized (with interesting stereochemical consequences), remains open.

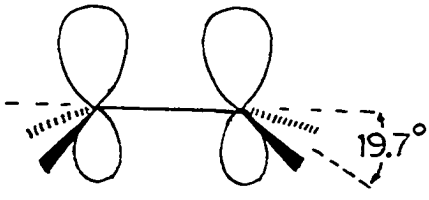


Figure 5. Distortion of π-bond in 64

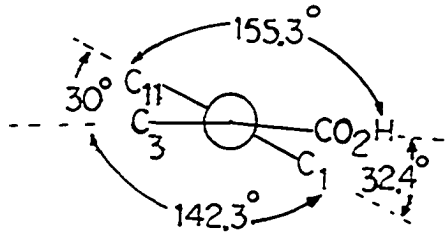


Figure 6. Distortion of π-bond in 69

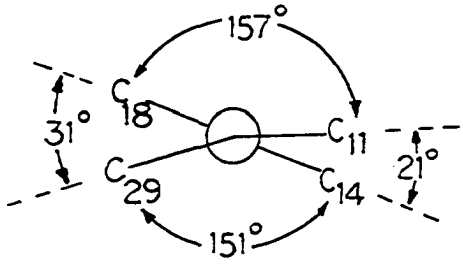


Figure 7. Distortion of π-bond in 70

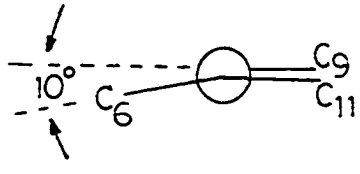
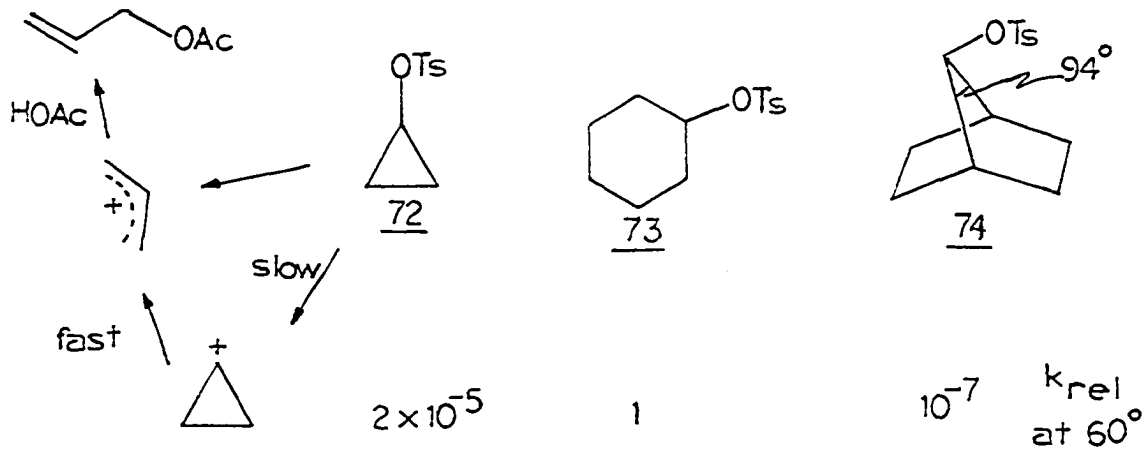


Figure 8. Distortion of π-bond in 71

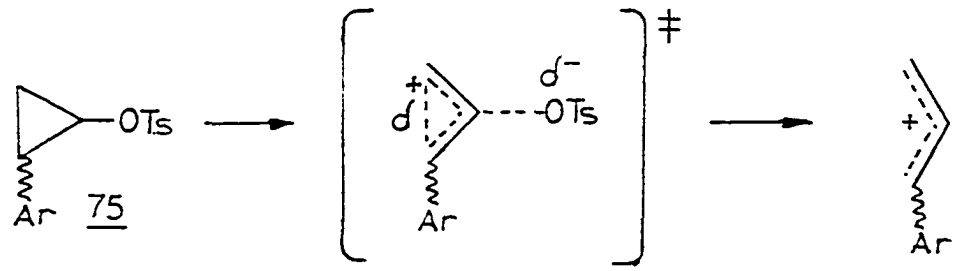
Cyclopropyl Cation

Roberts and Chambers were the first workers to study the extremely inert cyclopropyl tosylate (72) under solvolytic conditions (85). Based on the slow rate of acetolysis when compared to cyclohexyl tosylate (73), they proposed a



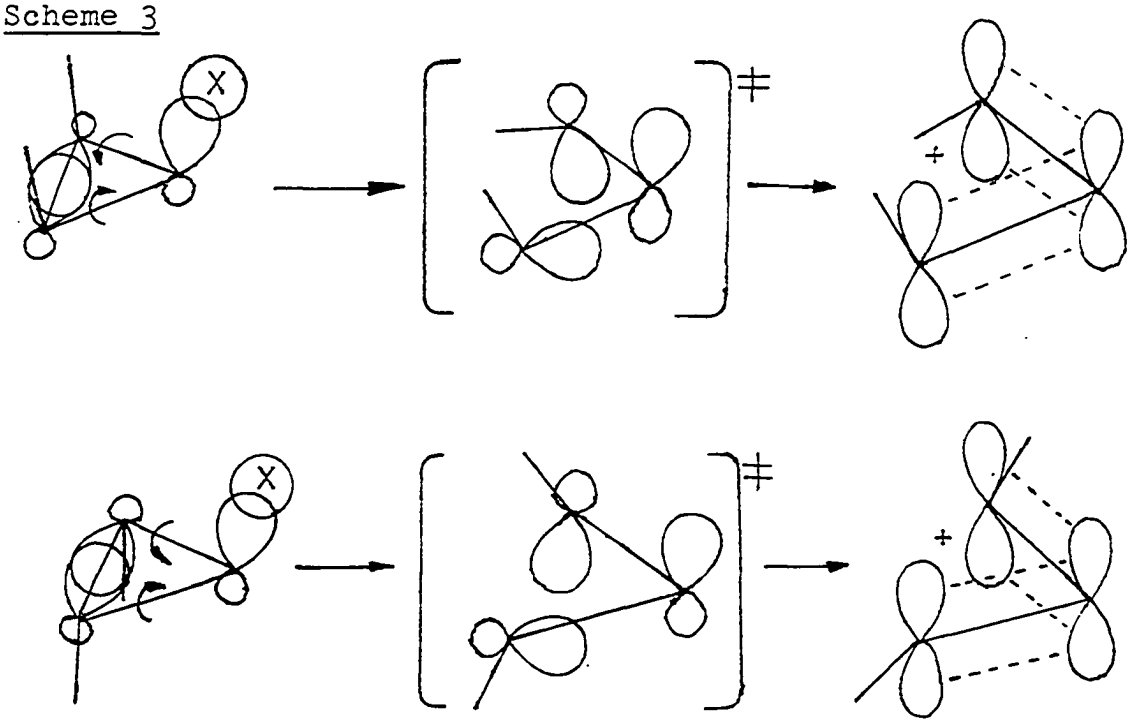
slow ionization to a cyclopropyl cation, followed by fast opening to an allyl cation which was trapped to give the observed product, allyl acetate. Schleyer and Nicholas questioned this interpretation based on the slower solvolysis of 7-norbornyl tosylate (74) despite the large angle at the reaction center (86). More quantitative examinations by Foote (87a) and Schleyer (87b) showed that the rate of solvolysis of 72 was actually enhanced, and the ionization and ring opening occurred simultaneously. Investigations by DePuy and coworkers (88) on cis and trans 2-arylcyclopropyl

tosylates (75) indicated that the solvolysis and ring opening were concerted. The phenyl group should retard the reaction because of its inductive effect but the rate for solvolysis of 75 was accelerated (89).

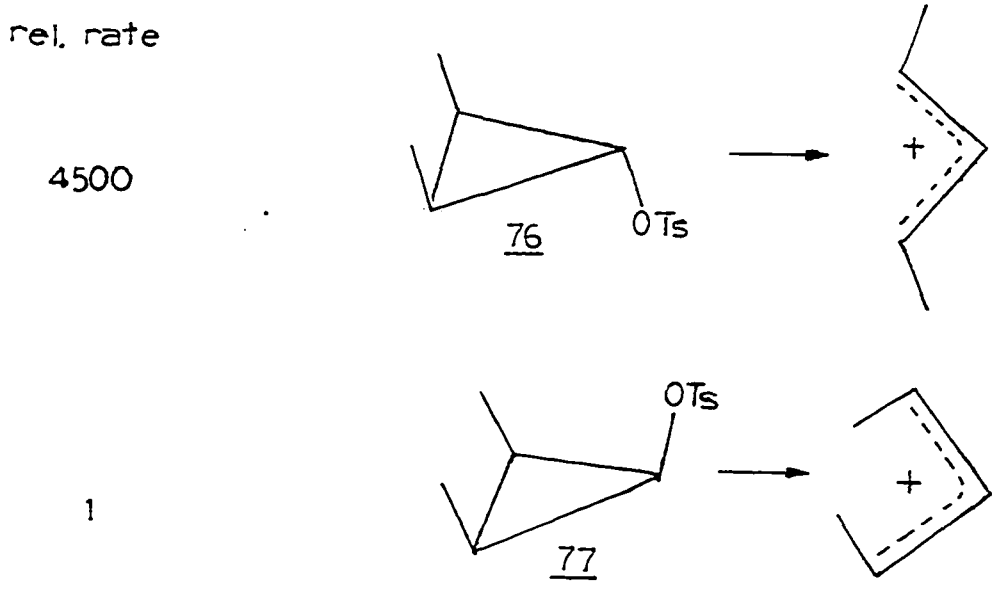


Woodward and Hoffmann treated the rearrangement of cyclopropyl cation to allyl cation as an electrocyclic reaction and predicted the ring opening to be stereospecific

Scheme 3

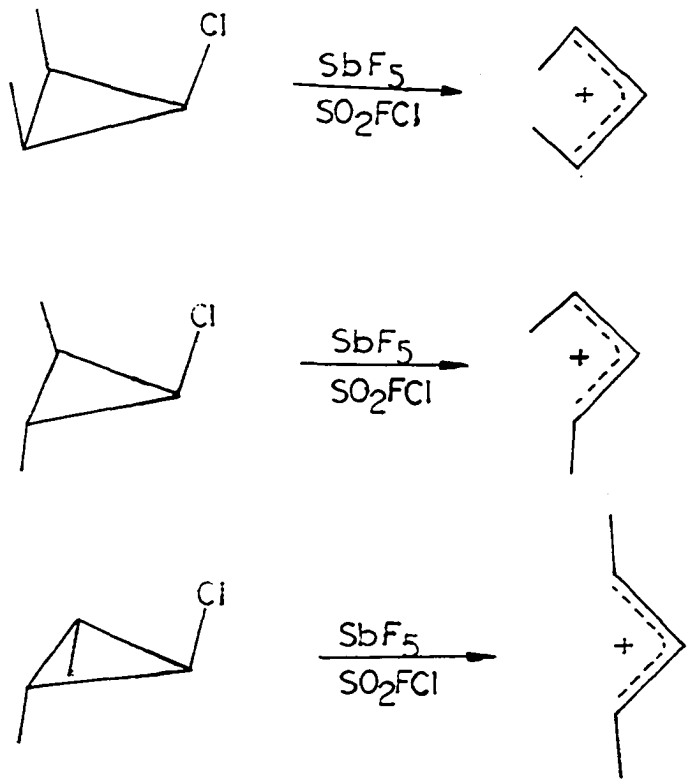


and disrotatory (90a). Speculation by DePuy that the mode of rotation is dependent upon the stereochemistry of the leaving group was later verified by experimental results (91) and predicted by calculations (90). Thus, substituents cis to the leaving group rotate inwardly while trans substituents rotate outwardly and the orbitals of the cyclopropyl C_2-C_3 bond maintain good overlap with the developing p-orbital on C_1 (Scheme 3). These predictions have received much support from theoretical calculations (92) including an ab initio calculation with CI (93) and from experimental evidence (94). The most extensive investigations are those of Schleyer et al. (95) who showed that 2-trans-3-trans-dimethylcyclopropyl tosylate (76) undergoes acetolysis 4,500 times faster than its C_1 epimer (77), which can be explained on the basis of the stability of the resulting allyl cations.



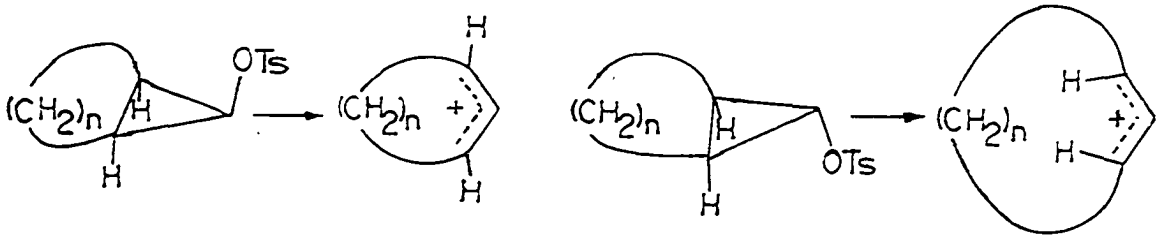
These conclusions about the opening of the cyclopropane ring in solvolysis reactions were later verified by the direct observation of the allyl cations, arising from cyclopropyl halides, in strong acid media at low temperatures (96) (Scheme 4).

Scheme 4



If the two alkyl substituents are joined in a ring, then a trans,trans-allyl cation (78) cannot be accommodated if the ring is small; thus, the order of solvolytic reactivity would be reversed from the monocyclic cases. These kinetic effects dependent upon ring size have been studied by other workers (97) and are shown in Table 1. The stereospecificity of these ring openings in bicyclic systems has

Table 1. Relative acetolysis constants of endo and exo-bicyclo[n.1.0]alkyl-p-toluenesulfonates

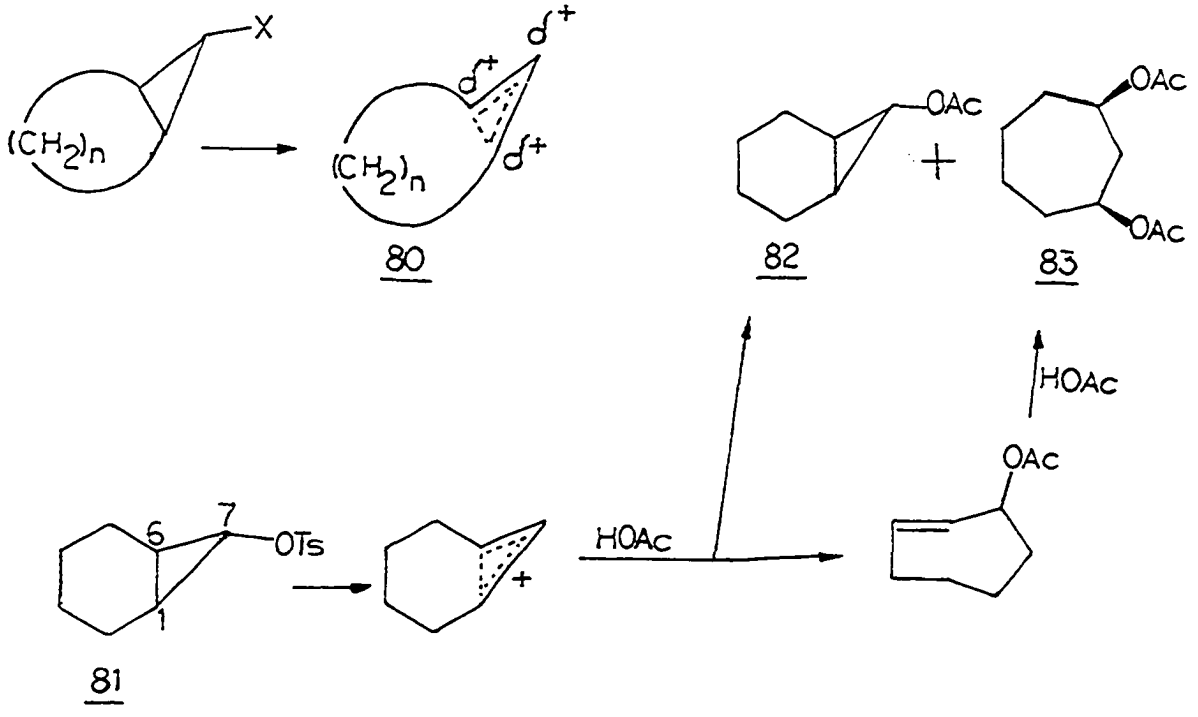


endo 79 exo 78

n	K_{rel} at 100°	n	K_{rel} at 100°
3	25,000	3	0.01
4	62	4	1.7
5	3.1	5	2,500
6	3.5	6	10,000

been verified by experimental results (98). The rate decrease observed in the endo-series was attributed to torsional and transannular strain in the large ring cis,-cis-allyl cation (79) which has been supported by Wiberg and Nakahira's results (99). Although strain free Dreiding models can only be constructed for trans,trans-allyl

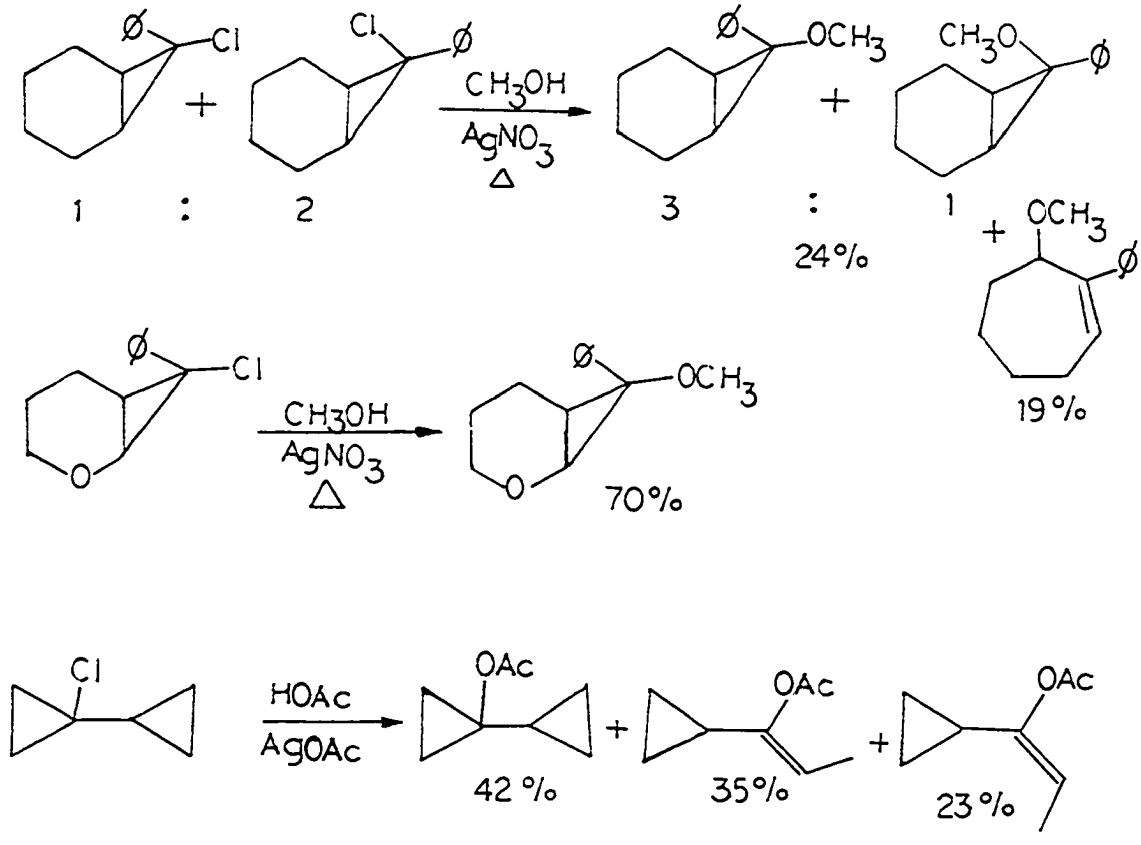
cations (78) in 12 or 13-membered rings, the opposite order of reactivity is observed in the exo-series. Schöllkopf et al. (97) proposed a semi-opened cyclopropyl cation (80) to account for these results. The products of the solvolysis of 7-norcaryl p-toluenesulfonate (81) are readily explained by a partially-opened cyclopropyl cation which can react at C_7 to give 82 or at $C_1(C_6)$ to give the trans-2-cyclo-hepten-1-yl acetate, which adds acetic acid to form 83.



Many workers have presented evidence consistent with the formation of a classical cyclopropyl cation in the solvolysis of cyclopropyl derivatives with cyclopropyl (100, 101) and phenyl groups (102, 103) (Scheme 5). But these results are consistent with a partially-opened cyclopropyl

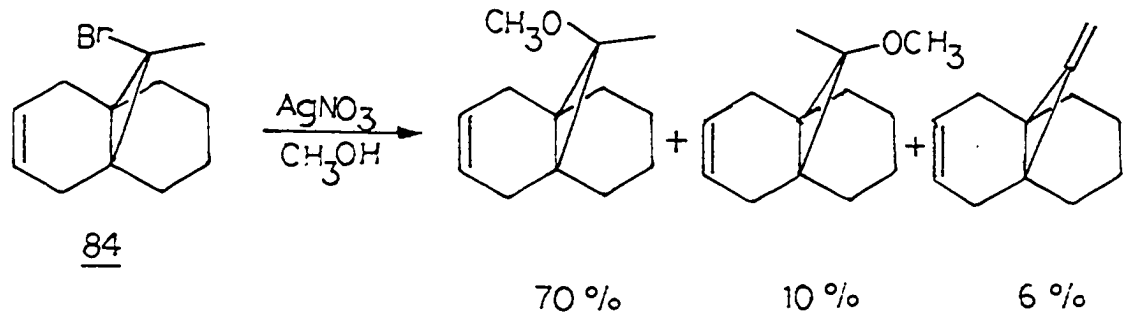
cation, especially the high stereoselectivity observed for retention products, which suggests some pyramidalization at C_7 in these cases (92a).

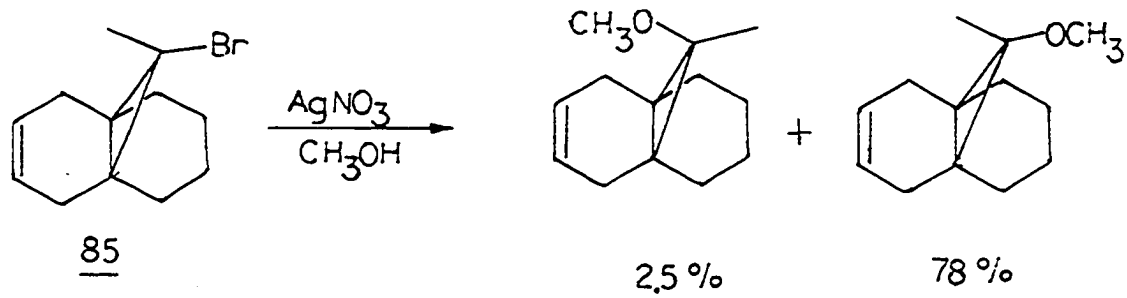
Scheme 5



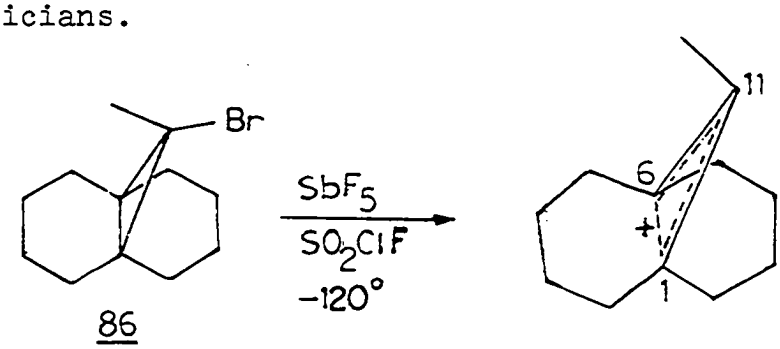
Recently Ledlie et al. (104) reported similar results in the solvolysis of the two epimers 84 and 85, where retention products again predominated. Olah and coworkers (105) were able to demonstrate the presence of a partially-opened cyclopropyl cation (86) from the treatment of 11-methyl-11-bromotricyclo[4.4.1.$0^{1,6}$]undecane (86) in sulfuryl chloride fluoride with antimony pentafluoride. There seems to be

significant pyramidalization at C_{11}, with the methyl group bent out of the plane of the cyclopropane ring. The substantial deshielding at C_1, C_6 and C_{11} in the ^{13}C NMR spectrum shows that the positive charge has been delocalized to these positions (Equation 1). Thus, it seems unsubstituted





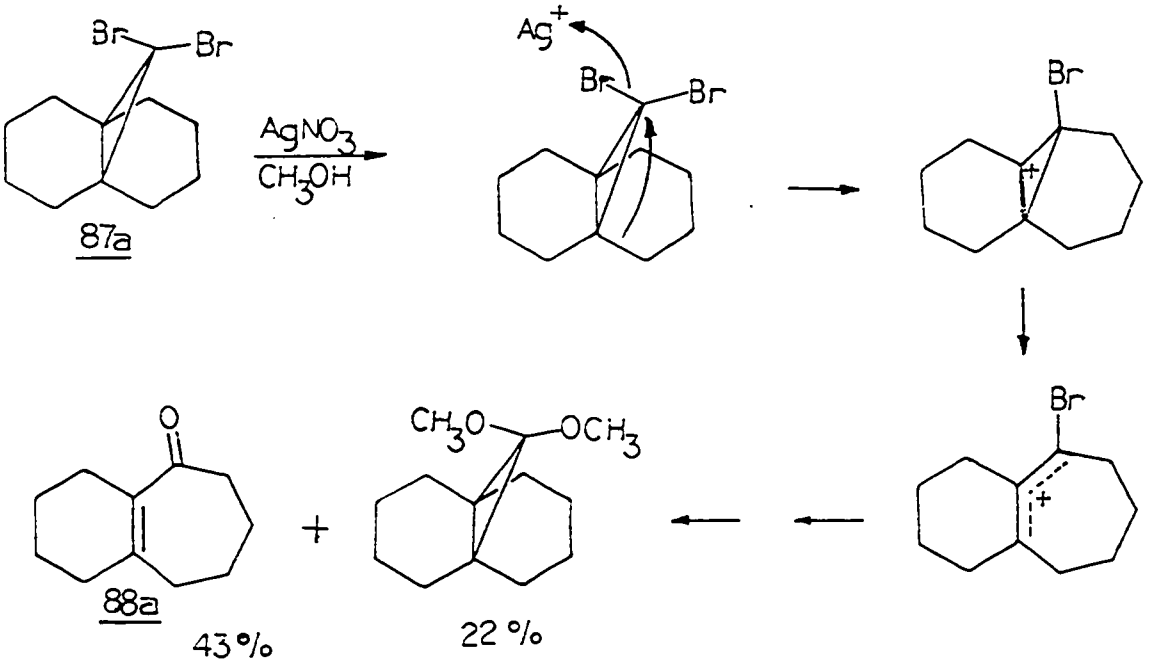
cyclopropyl cations exist only in the calculations of theoreticians.



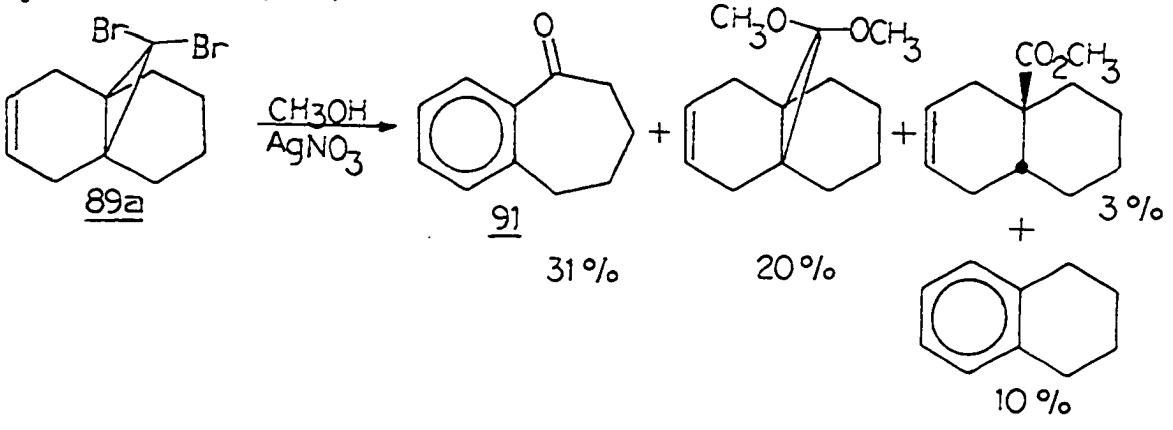
(1)

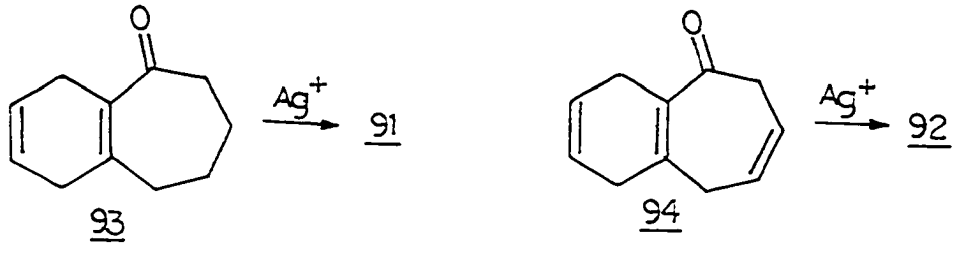
Propellanic Cyclopropyl Cations

Many workers have been interested in the transformations of gem-dihalocyclopropanes (106). Through studies of gem-dihalocyclopropyl propellanes, which upon solvolysis would generate constrained cyclopropyl cations, access to bridgehead olefins was realized. When the gem-dihalocyclopropyl unit is constrained in a propellane structure, solvolysis with disrotatory ring opening to a fully-opened allyl cation is impossible. Thus, Ledlie (107) and Reese and Stebles (108) independently rationalized the major product (88a) in the silver-assisted solvolysis of 87a as having arisen via a Wagner-Meerwein rearrangement of the initially formed cationic species. Ledlie and Knetzer (109) isolated similar



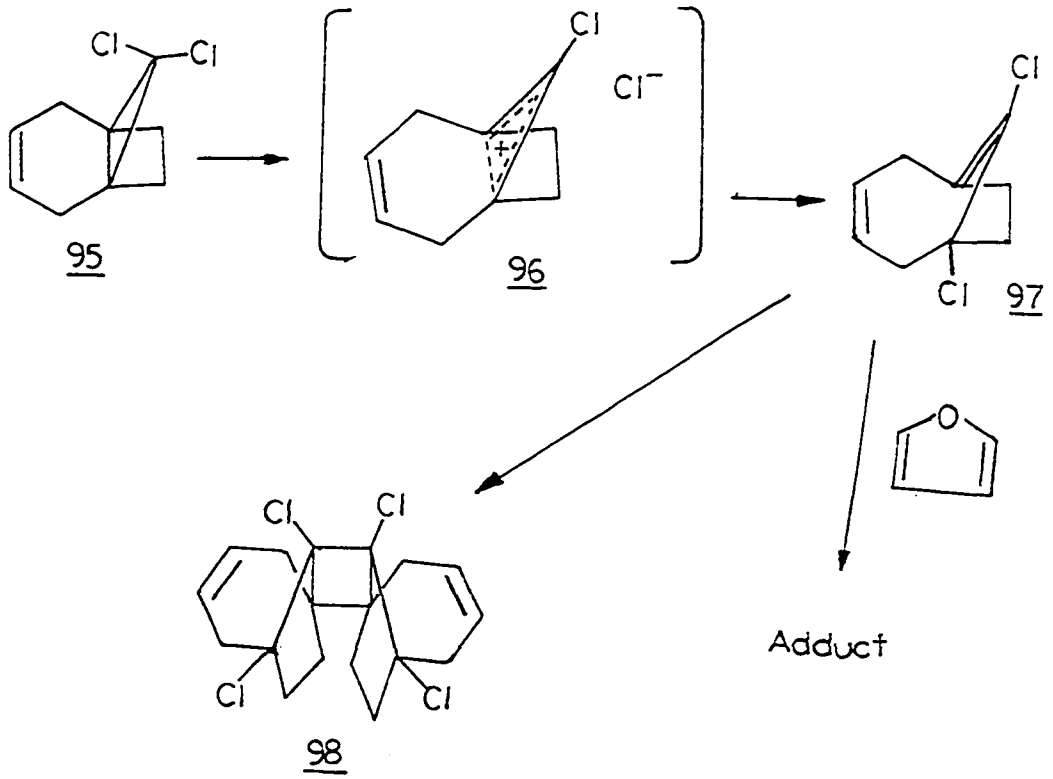
products in the solvolysis of the unsaturated systems 89a and 90 and postulated a similar mechanism for their formation. Products 91 and 92 were rationalized as coming from the corresponding dienes 93 and 94 by oxidation with silver ion (109b); these proposed oxidations were deemed reasonable on the basis of calculations utilizing available thermodynamic data (110).





Warner et al. (111) found that 9,9-dichlorotricyclo-[4.2.1.$0^{1,6}$]non-3-ene (95) underwent spontaneous generation of a bridgehead olefin (comparable to trans-cycloheptene)

which subsequently dimerized. The bridgehead olefin (97) can be trapped with furan and the dimerization showed a rough dependence on solvent polarity. These observations support a mechanism where 95 solvolyzed with release of strain to partially-opened cyclopropyl cation 96, which subsequently collapsed to give bridgehead olefin 97 and finally the RS dimer 98 (one of the 11 possible stereoisomeric structures), as shown by an x-ray analysis.

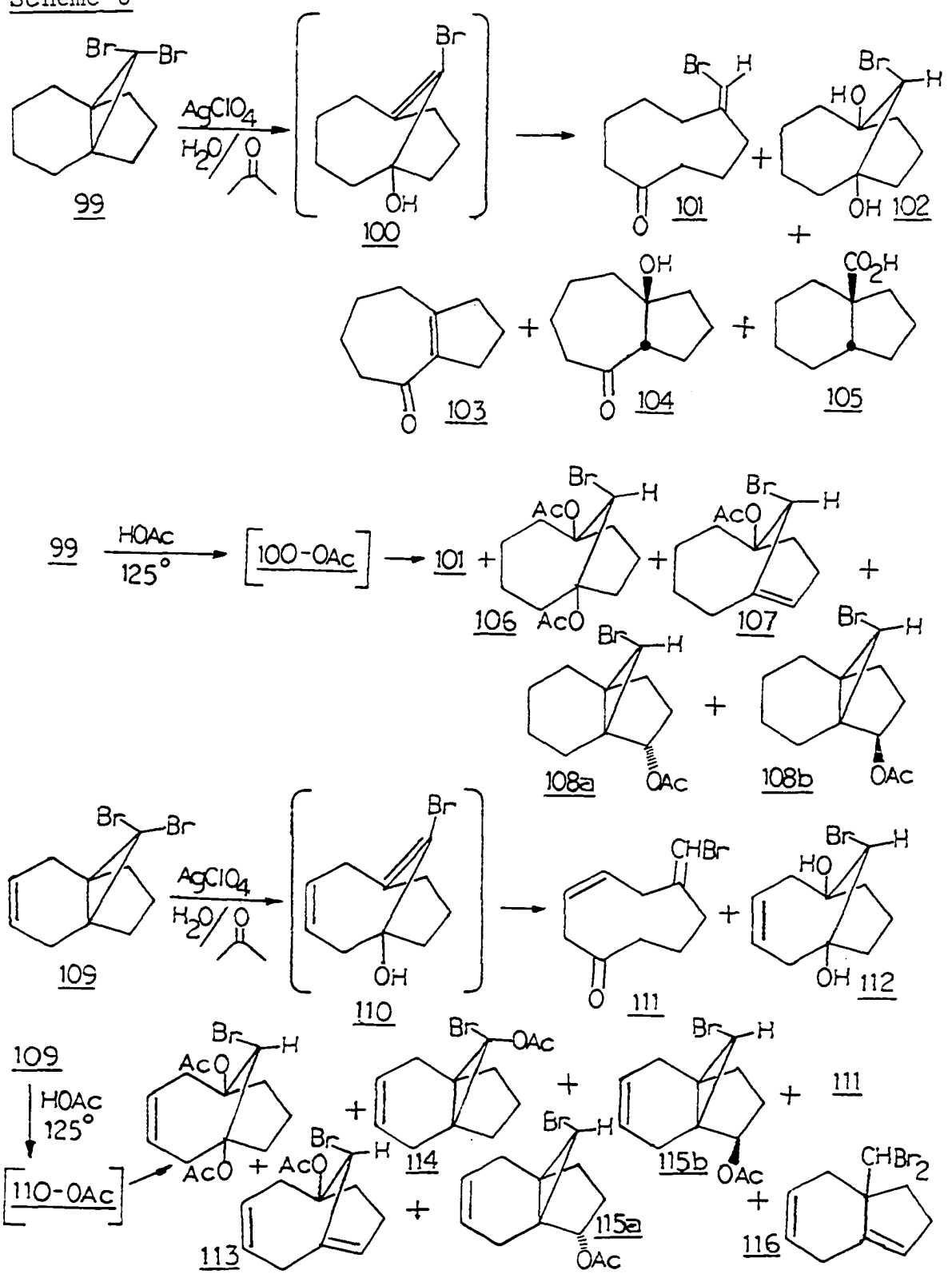


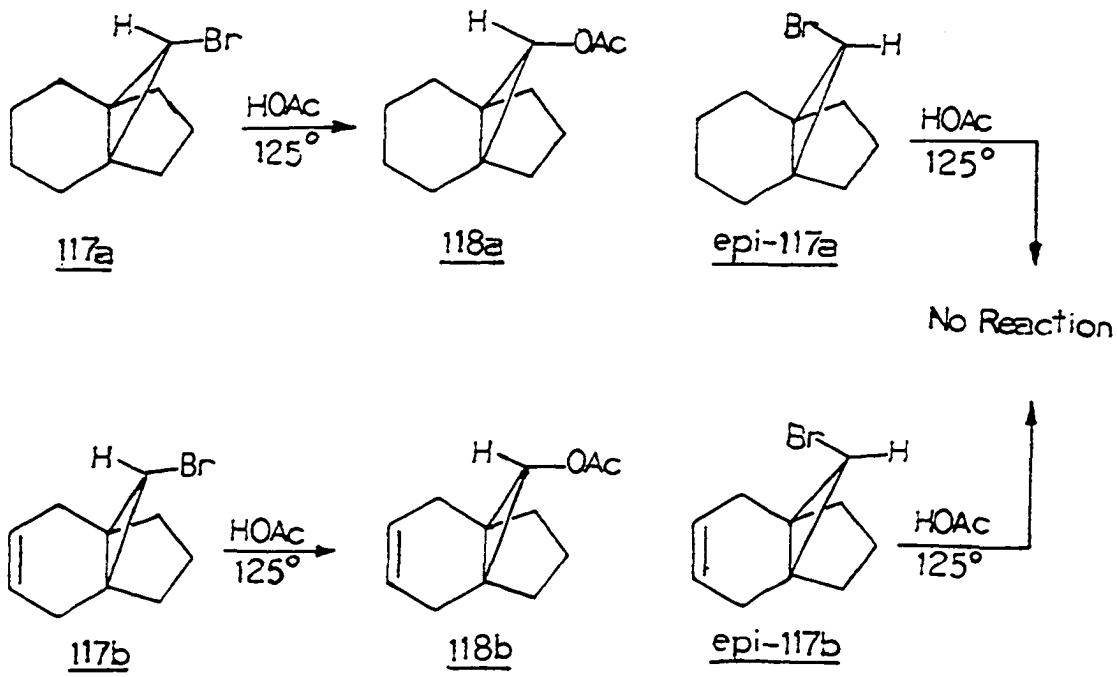
Other dimerizations in strained olefin systems (112) occurred contrary to Woodward-Hoffmann rules of orbital symmetry (90c), while some may have given the expected $\pi^2s+\pi^2a$ dimers (113). Although in the dimerization of adamantene

(53) the head to tail dimers predominate by 2 to 1 (44b), none of these other structures were proven by an x-ray structure but rather by physical properties.

Warner and coworkers (114) then investigated the more stable [4.3.1]propellane system, and the reactions and products that they and Reese and Stebles (115) independently found are illustrated in Scheme 6. Reese concluded that product (101) arose from protonation of a bridgehead olefin intermediate (100), but postulated that 103 arose from a Wagner-Meerwein rearrangement either concerted with the loss of bromide or very soon after the loss of bromide (similar to his proposal for 87a). Warner et al. (114b) were able to isolate diol 102, which is the product of addition of water to the bridgehead olefin intermediate 100. The structure of isomerically pure 101 was proven by an x-ray analysis of the 2,4-DNP derivative. This structure, together with the crystal structure of 112 (112 could be hydrogenated to 102), indicated ring opening followed the Woodward-Hoffmann-DePuy rules to give a partially-opened cyclopropyl cation (97), which reacts with solvent to give bridgehead olefin products (101 and 102; 111 and 112) or the complete retention cyclopropyl product (114). A study of the monobromides 117a and 117b, together with their epimers (epi-117a and epi-117b), reinforced the existence of a partially-opened cyclopropyl cation and the operation of

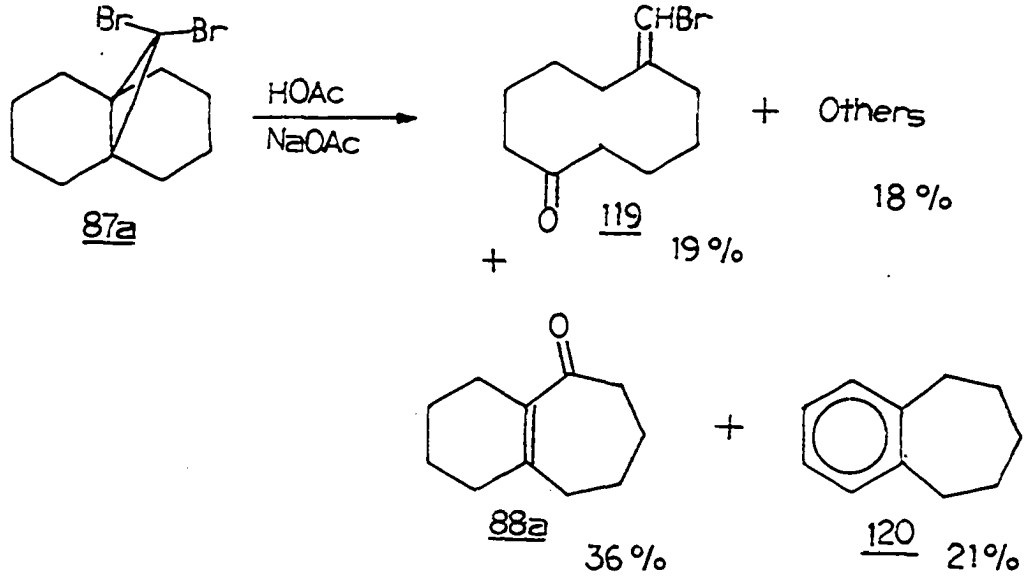
Scheme 6


Br
Br
99
AgClO4
H2O/ O
OH
100
Br
H
HO
101
102
103
104
CO2H
105
99
HOAc
125°
100-OAc
AcO
106
107
108a
108b
OAc
109
110
CHBr
111
112
HOAc
125°
110-OAc
113
114
115a
115b
116
CHBr2



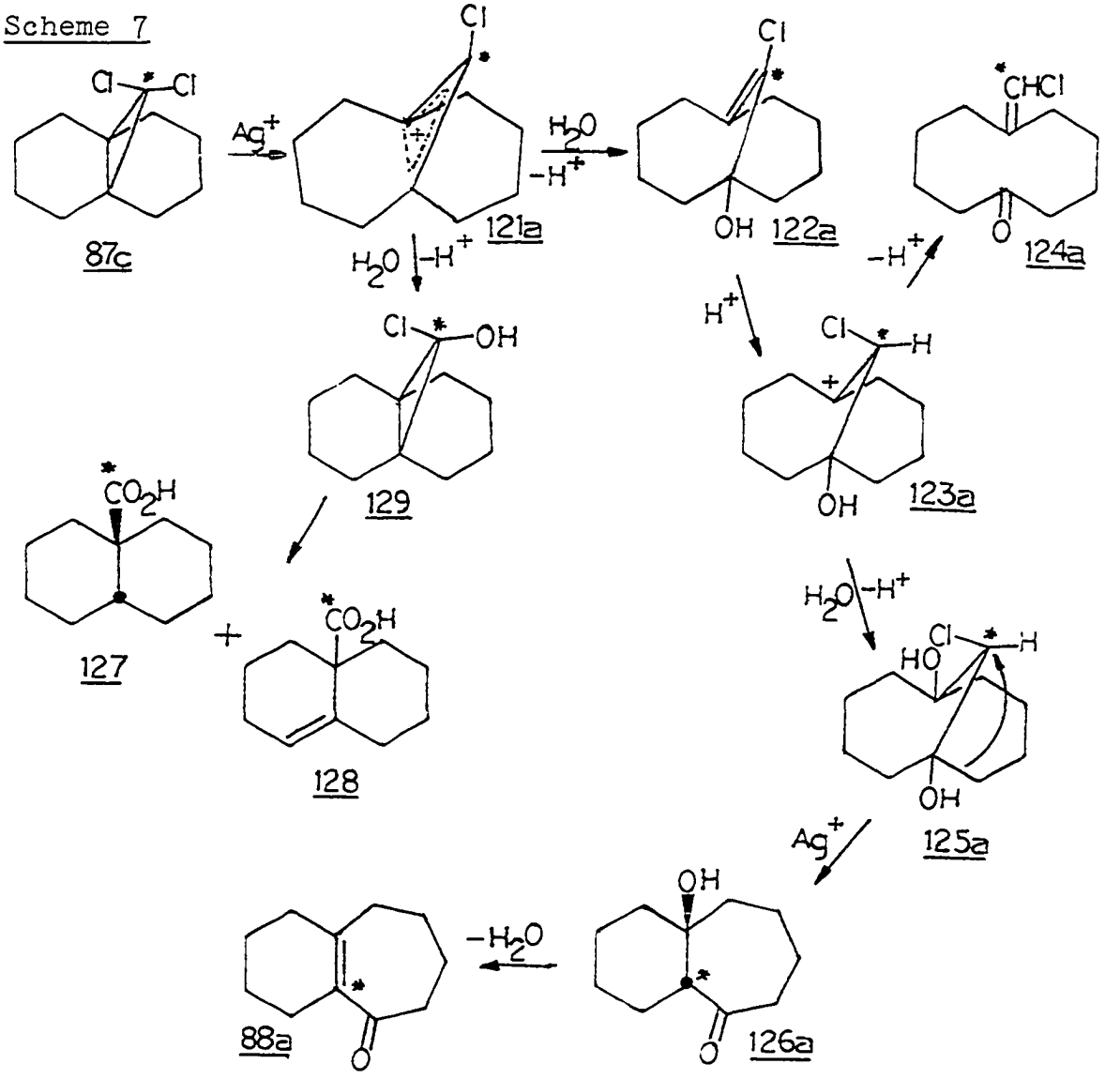
Woodward-Hoffmann-DePuy rules. The formation of 103 did not apparently fit the mechanistic scheme, since the 4 carbon bridge must have shifted exclusively if Reese and Stebles' mechanism was operative (115). They also proposed, in a related case, that a hydride migration accounted for the observed products (108). However in a related gem-dihalocyclopropyl propellane, Parham et al. (116) showed by a ^{13}C labeling experiment that an analogous phenyl shift did not occur. The authors (116a) had originally suggested a phenyl shift which was similar to the mechanistic pathway used by Reese and Stebles (115), and Ledlie et al. (109) to account

for 88a, 91, 92 and 103. Warner and Lu (117a) were able to isolate hydroxyketone 104 and convert it to 103 under the solvolytic conditions. Similarly 102 gave hydroxyketone 104 and enone 103 in a ratio of 14:1 under the solvolytic conditions. This showed that 103 in fact arose via a bridgehead olefin intermediate.

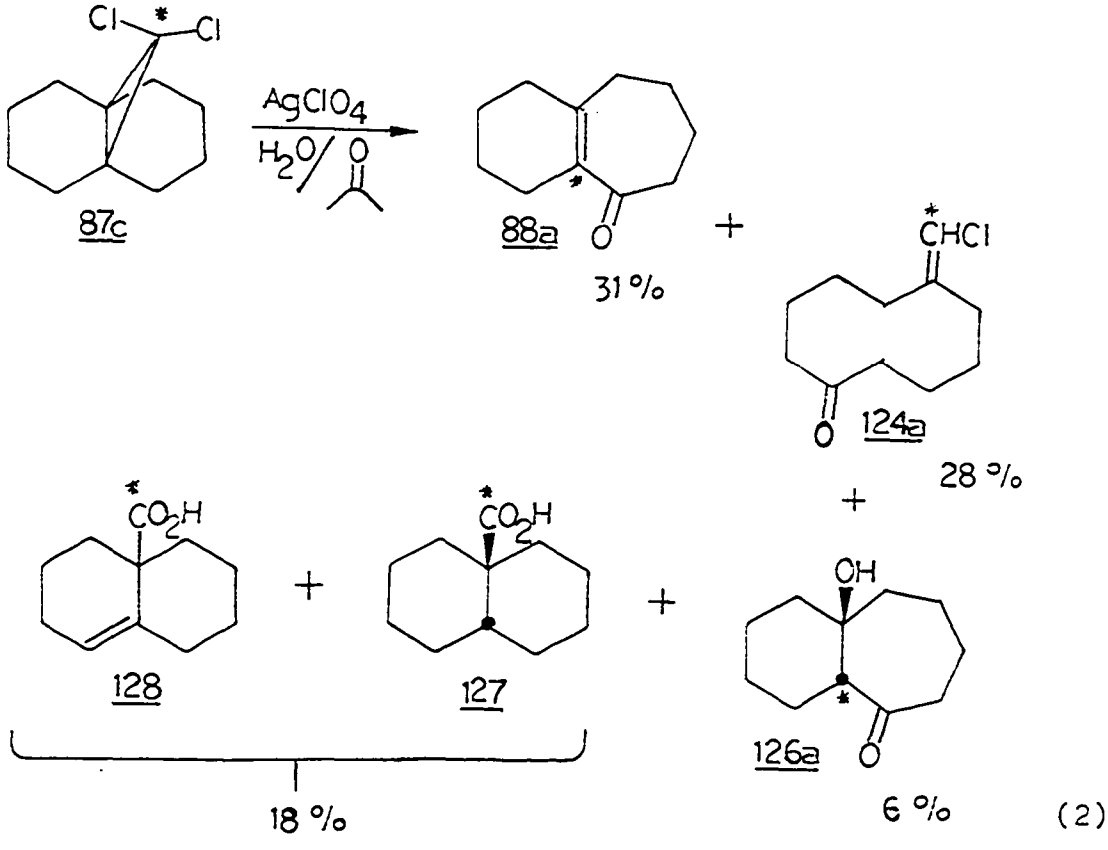


Warner and Lu (117a) repeated the solvolysis of 11, 11-dibromotricyclo[4.4.1.$0^{1,6}$]undecane (87a) in buffered acetic acid and were able to isolate the monocyclic ketone 119 which implied a bridgehead olefin intermediate. The same group then labeled 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]-undecane (87c) with $^{13}C(*)$ at C_{11} and performed the solvolysis (Equation 2). The mechanism which accounts

Scheme 7



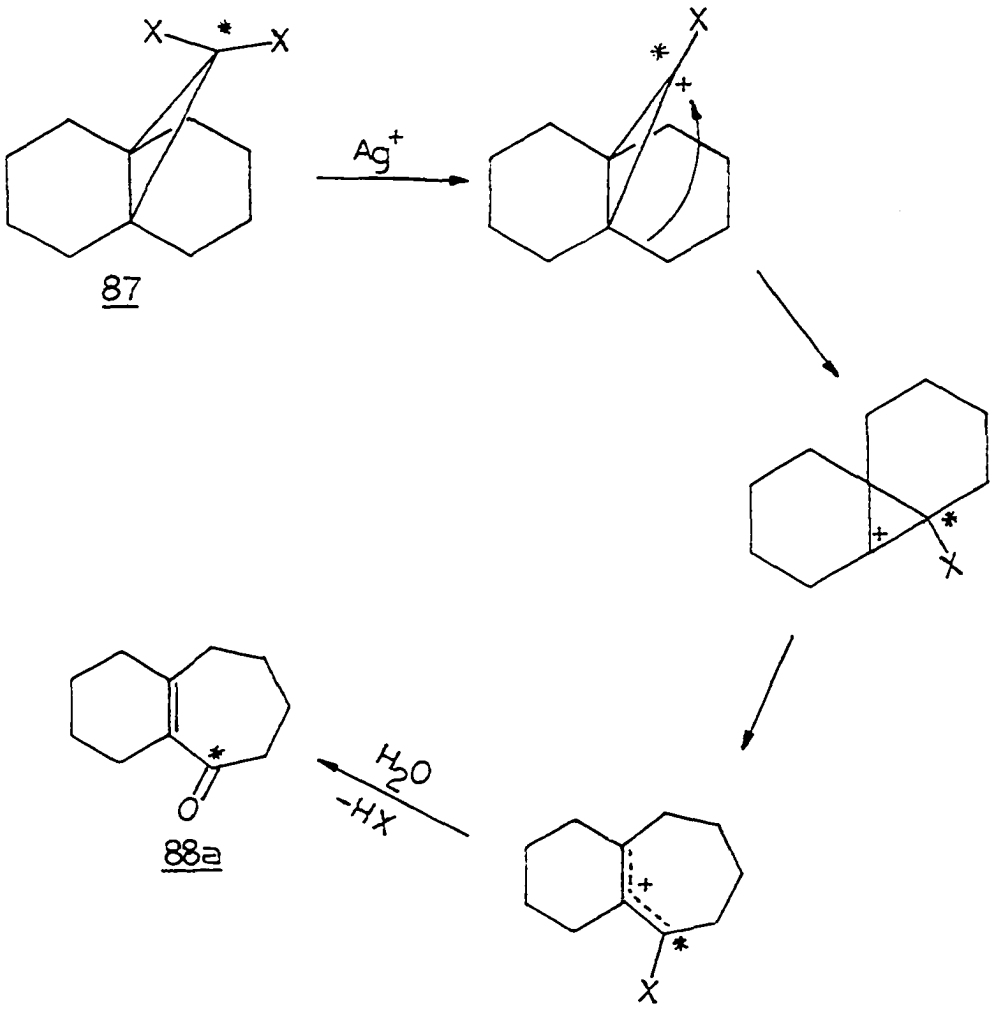
for the labeling experiment and is favored by the authors is shown in Scheme 7. Although other mechanisms can be proposed (117b), this one is the only one which accounts for all the experimental observations and products. From 87c the partially-opened cyclopropyl cation 121a is formed, which can be attacked by water at C_{11} or $C_{1(6)}$. Attack at C_{11} results in the formation of 129 and then acids 127 and



(2)

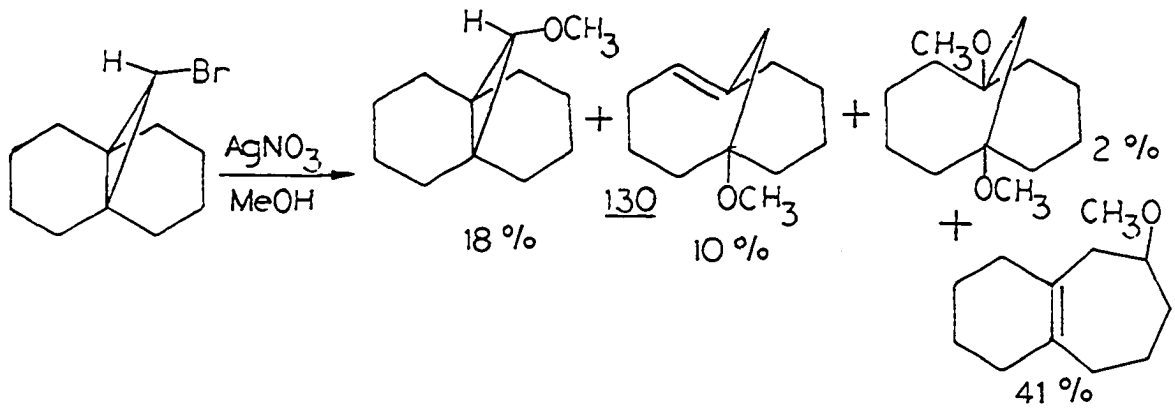
128 as precedented by the work of Groves and Ma (118a). Attack at $C_{1(6)}$ gives bridgehead olefin 122a which, after protonation to 123a, leads to fragmentation (to 124a) and addition of water (to 125a) as the major reaction channels. The isolation of hydroxyketone 126a, which could be converted to 88a under the acidic solvolysis conditions (118b), indicated that these products arose from the silver-assisted solvolysis of 125a. The alternative alkyl-shift mechanism (115, 109) required that the label be found in the carbonyl carbon, but none was (Scheme 8).

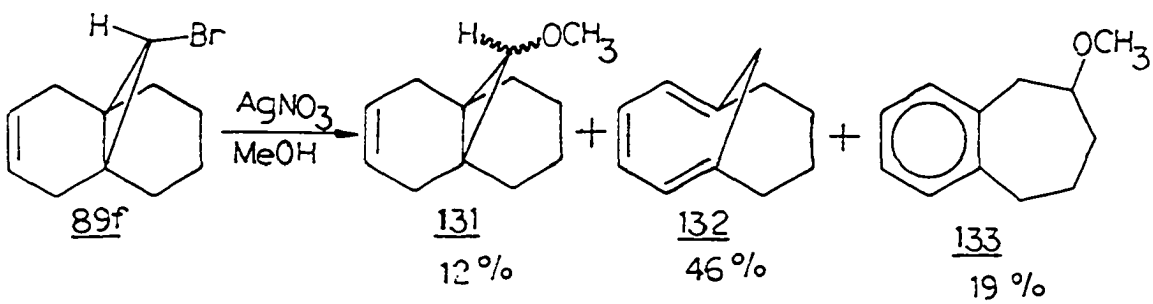
Scheme 8

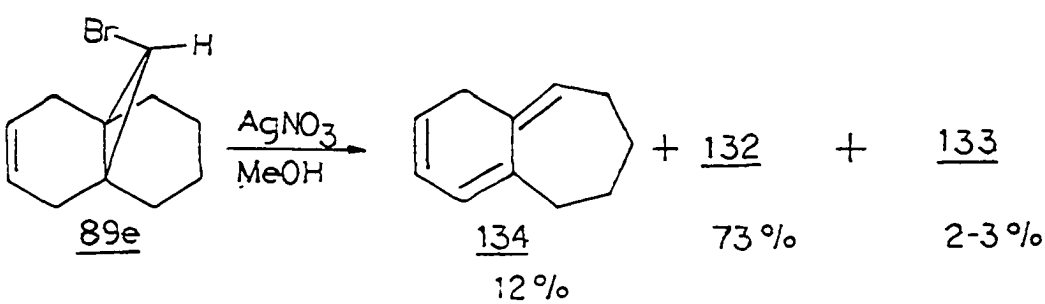


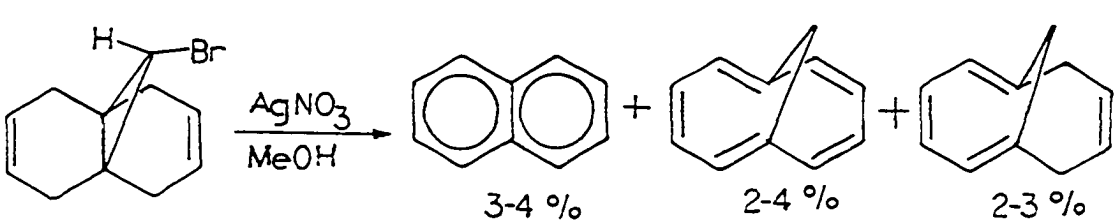
Ledlie et al. (119) have examined the solvolysis of a number of monobromotricyclo[4.4.1.$0^{1,6}$]undecane systems with varying degrees of unsaturation with $AgNO_3$ in refluxing methanol (Scheme 9). The volatile products that were isolated can be explained by a bridgehead olefin intermediate as noted by the authors. They acknowledge that an alkyl-shift mechanism is not operative and present evidence for a partially-opened cyclopropyl cation.

Scheme 9

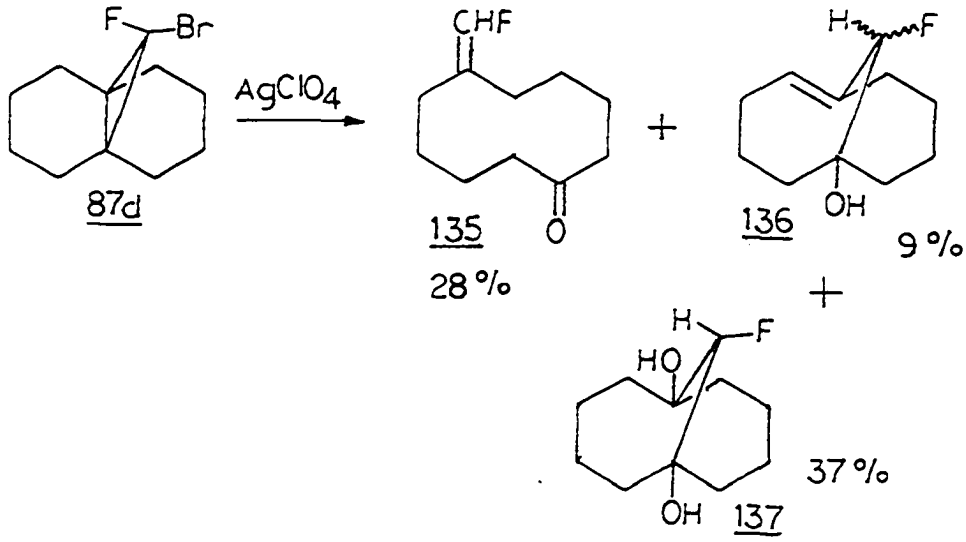

H
Br
AgNO3
MeOH
H
OCH3
18 %
130
OCH3
10 %
CH3O
OCH3
2 %
CH3O
41 %


H
Br
89f
AgNO3
MeOH
H
OCH3
131
12 %
132
46 %
OCH3
133
19 %


Br
H
89e
AgNO3
MeOH
134
12 %
132
73 %
133
2-3 %


H
Br
AgNO3
MeOH
3-4 %
2-4 %
2-3 %

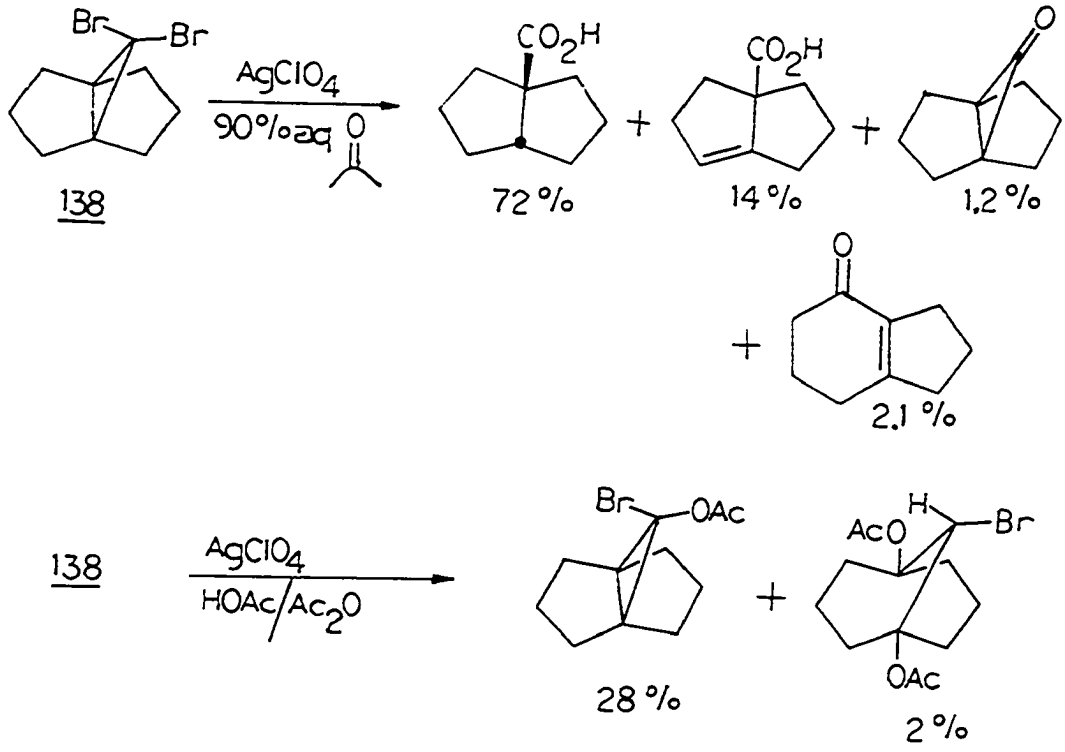
The silver-assisted solvolysis of 11-bromo-11-fluorotricyclo[4.4.1.$0^{1,6}$]undecane (87d) resulted in the formation of diol 137, which is analogous to the postulated intermediate (125a) in Warner's mechanism (Equation 3). Reese and Risius (120) also concluded that the alkyl-shift mechanism does not account for the products, but the intermediacy of a bridgehead olefin does.



(3)

Warner and Lu (121) reported the solvolysis of 9,9-dibromotricyclo[3.3.1.$0^{1,5}$]nonane (138) with silver perchlorate in 90% aqueous acetone or in acetic acid, which in both cases led to the formation of a bridgehead olefin transoid in a six-membered ring. The major products are those derived from solvent attack at C_9 in the partially-opened cyclopropyl cation, rather than the bridgehead carbons ($C_{1(5)}$) to give the bridgehead olefin. From a

comparison of 99 and 138, the authors concluded there is a difference of ca. 6 kcal/mole between a double bond transoid in a six-membered ring and one transoid in a seven-membered ring (where both double bonds bear a bromine substituent).



Thus, in the solvolysis of gem-dihalocyclopropyl propellanes, the initially formed partially-opened cyclopropyl cation collapses with solvent to give a cyclopropyl derivative or a bridgehead olefin, both of which are then transformed into the products observed in these reactions. If 87a and 87b produced symmetrical, unrehybridized bridgehead olefin intermediates, then these olefins should have perpendicular (or nearly perpendicular) π orbitals, and their

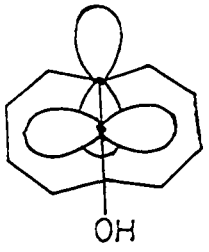


Figure 9. Unrehybridized bridgehead olefin

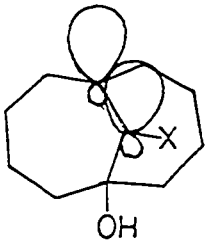
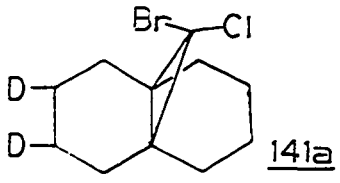
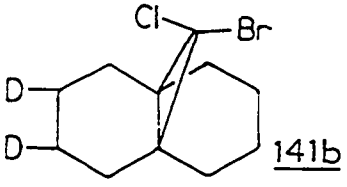


Figure 10. Rehybridized bridgehead olefin



141a



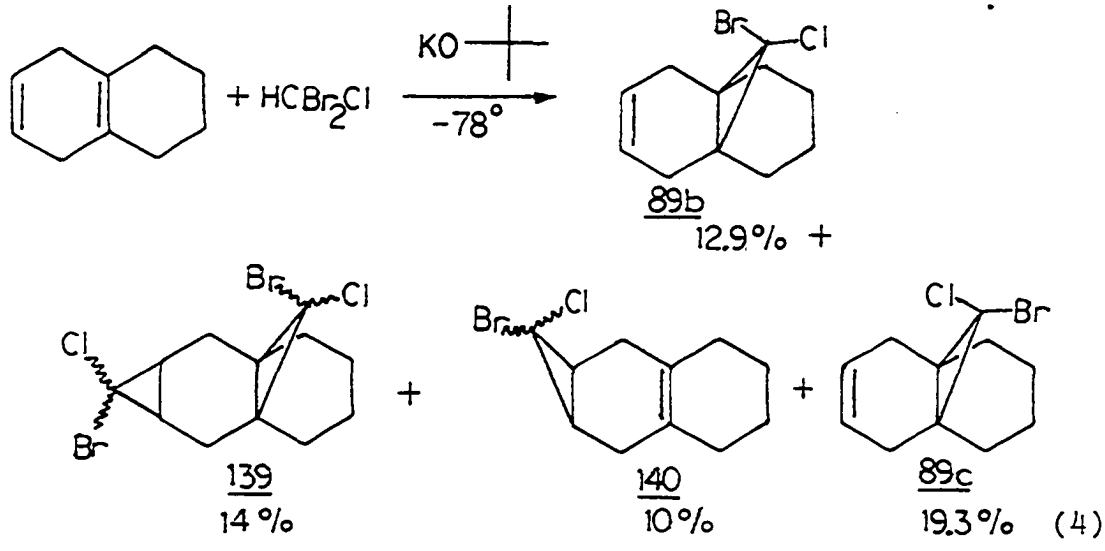
141b

ground states should be triplet (Figure 9). But if these bridgehead olefins are rehybridized (Figure 10), one of the seven-membered rings should contain a trans-olefin while the other contains a cis-olefin. As a result of this rehybridization, we would expect attack by an electrophilic reagent to occur from the cis-seven-membered ring onto the large lobe of the rehybridized orbital. By synthesizing compounds, 141a and 141b, we should be able to determine whether or not stereospecific attack on the intermediate bridgehead olefins occurs. If so, a symmetrical intermediate can be excluded.

RESULTS AND DISCUSSION

Synthesis

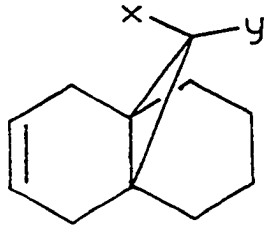
Compounds 89b and 89c were prepared by the addition of bromochlorocarbene to dihydrotetralin (122) (Equation 4). The isomeric bis-adducts (139) were separated from the reaction mixture via crystallization; the two end-adducts (140) were separated by recrystallization from ethyl acetate at low temperatures (123). The ratio of 89b to 89c was established by ^{13}C NMR after the end-adducts (140) had been removed by gas chromatography. After trying numerous glass



(4)

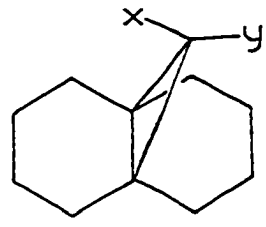
columns on the GLC, normal and reverse phase columns on the high pressure liquid chromatograph, normal pressure liquid column chromatography, thin layer chromatography, sublimation and zone refining, epimers 89b and 89c were separated by fractional recrystallization and partial solvolysis. Compound 89c (Figure 11) crystallized from absolute ethanol

preferentially and was obtained pure after 25-30 recrystallizations. Compound (89b) (Figure 12) was obtained pure after 4-5 partial solvolyses (1 eq. of $AgClO_4$ in 90% aqueous acetone) followed by column chromatography on $AgNO_3$-impregnated silica gel. Hydrogenation of 89b and/or 89c over Pt/C gave 87b (Figure 13) in quantitative yield.



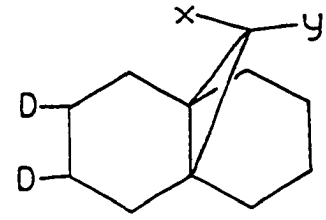
89

a, x=y=Br
b, x=Br y=Cl
c, x=Cl y=Br
d, x=y=Cl
e, x=Br y=H
f, x=H y=Br



87

a, x=y=Br
b, x=Br y=Cl
c, x=y=Cl
d, x=Br y=F



141

a, x=Br y=Cl
b, x=Cl y=Br

Compounds 89a (Figure 14) and 89d (Figure 15) had already been prepared by the analogous route (122, 123). The stereochemistry of 89b and 89c was assigned from comparison of the ^1H NMR spectra (notice allyl singlet for 89b and 89a and the symmetrical aliphatic peaks for 89b and 89d) and

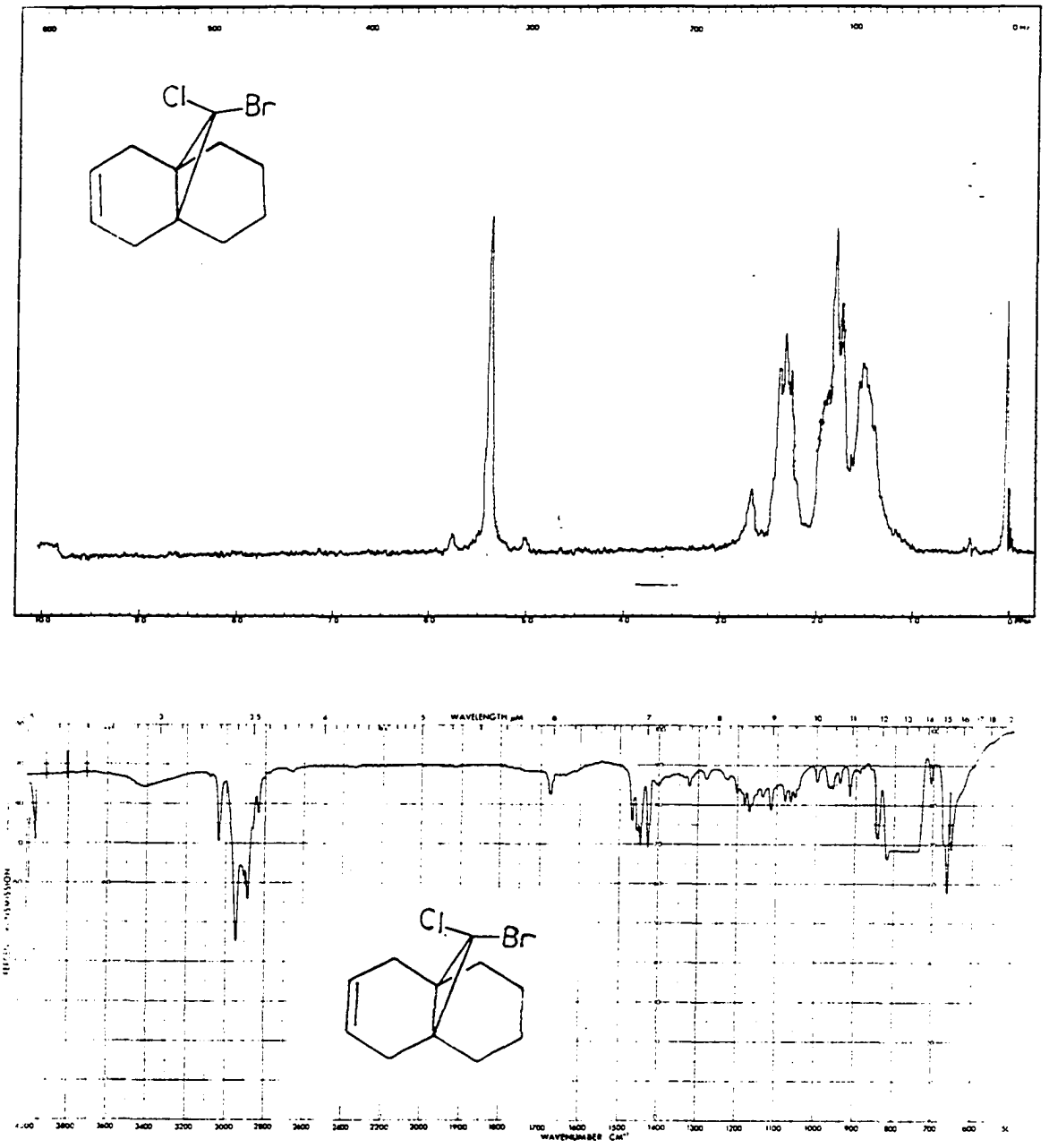


Figure 11. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of anti-11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89c)

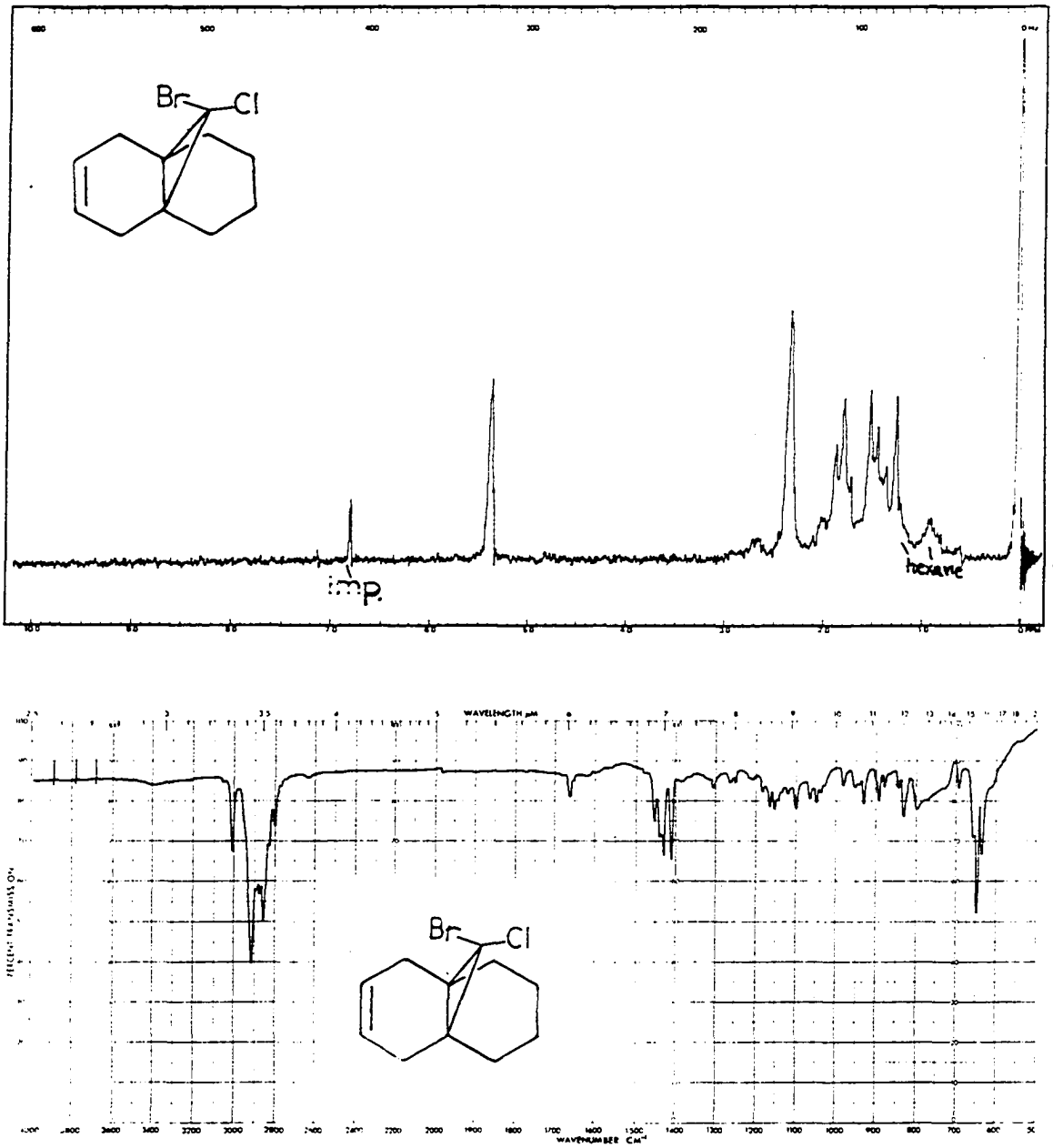


Figure 12. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of syn-11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89b)

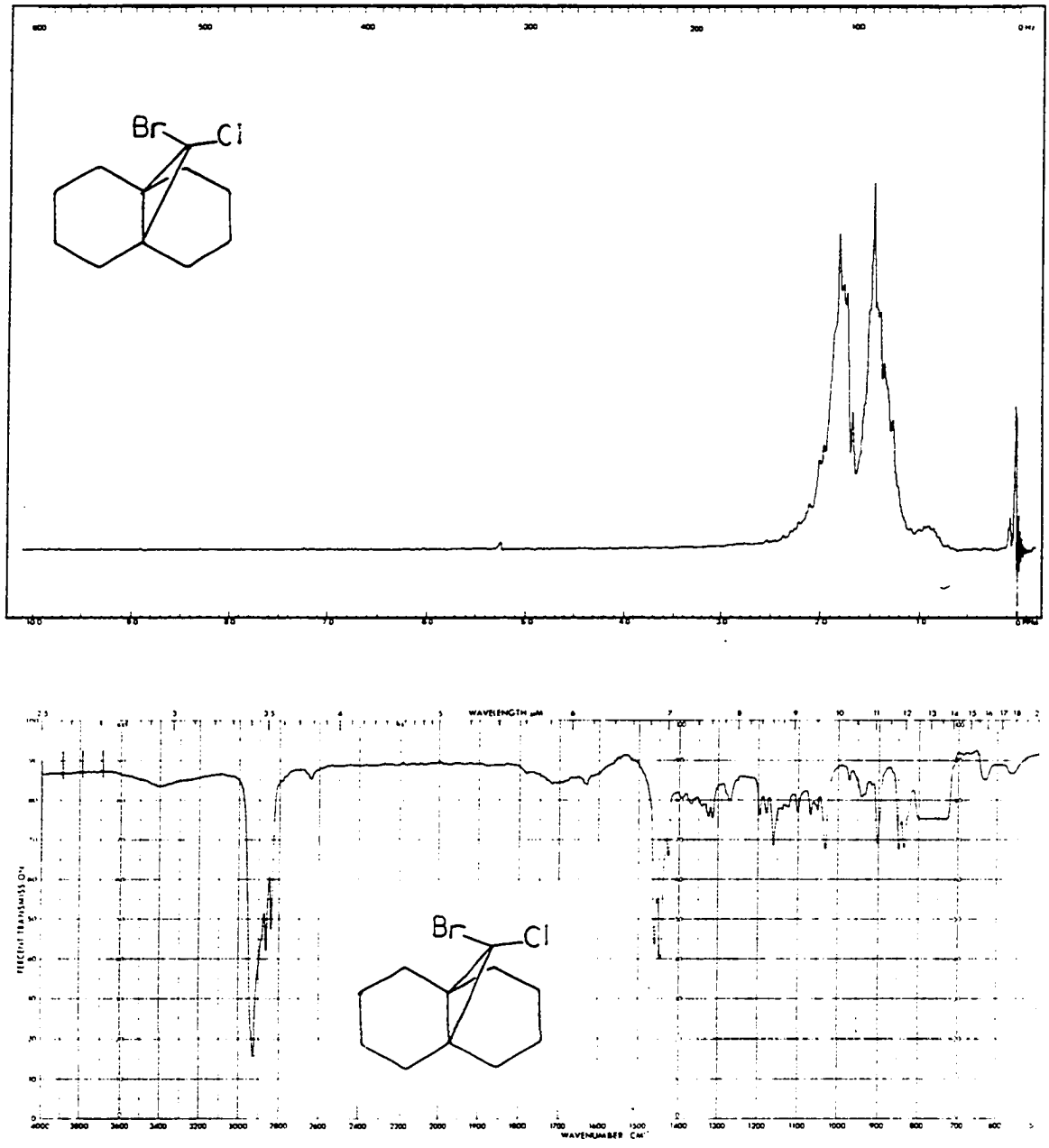


Figure 13. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of 11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undecane (87b)

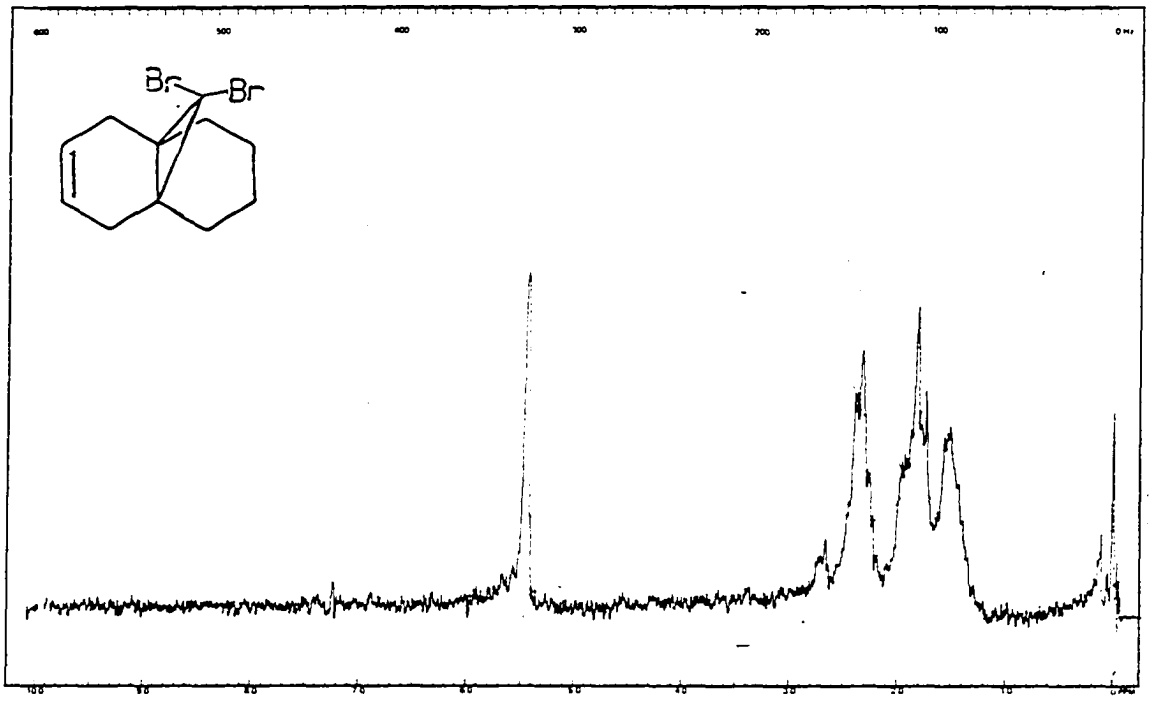


Figure 14. ^{1}H NMR spectrum (60 Mcps) of 11,11-dibromo-tricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89a)

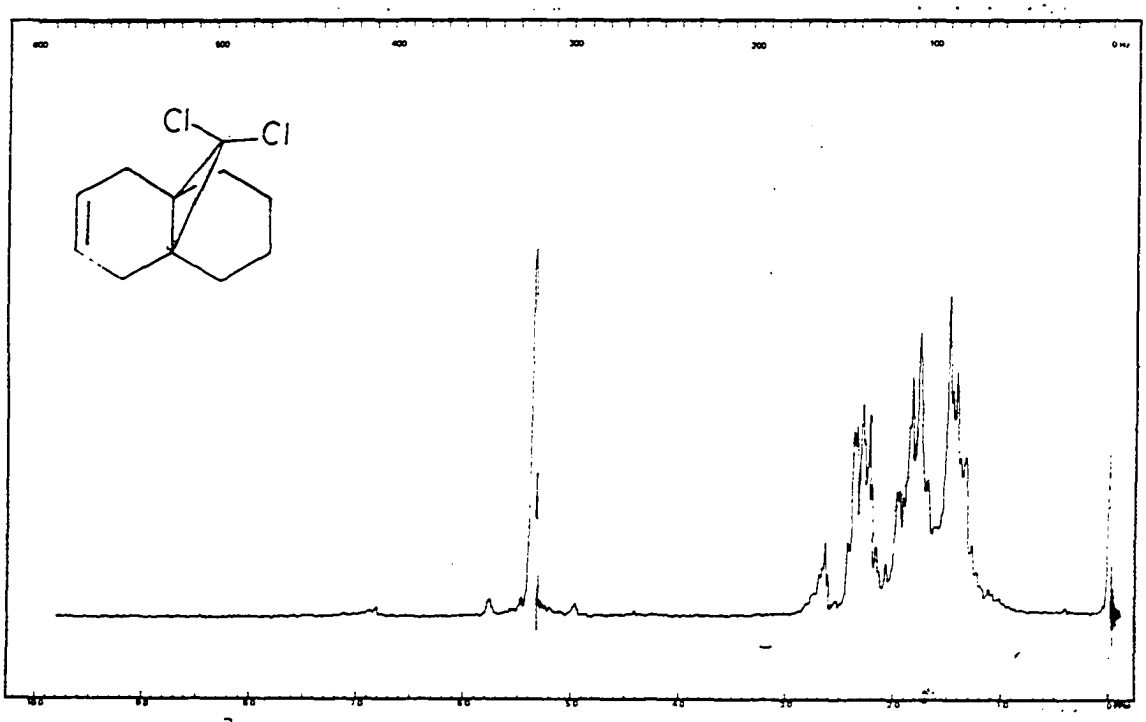
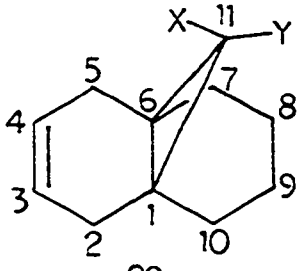


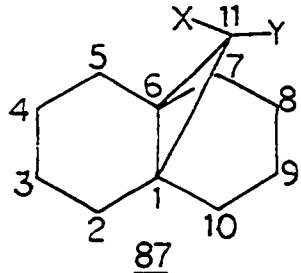
Figure 15. ^{1}H NMR spectrum (60 Mcps) of 11,11-dichloro-tricyclo[4.4.1.$0^{1,6}$]undec-3-ene

^{13}C NMR spectra. The ^{13}C assignments were from gated decoupling experiments (124) and deuteration of 89b and 89c to 141a and 141b, respectively (Table 2). Compounds 89e and 89f were synthesized by a known route (125) from 89a (tin hydride reduction) and were separated by chromatography on an alumina column.

Table 2. ^{13}C NMR data for compounds 87 and 89



89



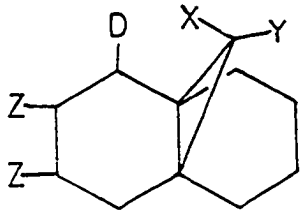
87

	89a	89b	89c	89d	89e	89f	87a	87b	87c
$C_{3,4}$	124.0	123.8	123.8	123.7	124.2	124.8	20.5	20.4	20.8
C_{11}	58.1	68.0	68.6	76.5	41.0	38.8	61.9	71.5	78.9
$C_{1,6}$	26.7	26.6	26.6	26.3	22.2	22.3	28.0	28.0	27.5
$C_{2,5}$	31.3	31.3	30.1	30.6	31.9	28.8	31.8	32.1	29.9
$C_{7,10}$	32.2	29.1	32.6	29.2	32.3	32.8	31.8	29.7	29.9
$C_{8,9}$	19.7	20.3	19.7	20.2	21.2	21.65	20.5	20.9	20.8

The incorporation of deuterium into 89b and 89c was initially tried using deuterated diimide (126), which gave only ∿5% reduction. Subsequent attempts with deuterated diborane, followed by protonolysis (127), proved undesirable since solvolysis of resulting products 141a and 141b occurred under the reaction conditions. Since both methods gave poor yields (∿40% with diborane and protonolysis), a catalytic homogeneous hydrogenation with tris(triphenylphosphine)chlororhodium (I), "Wilkinson's Catalyst" (128), was tried. An important concern was the possibility of deuterium scrambling, since heterogeneous catalytic reduction usually results in scrambling of the label. With "Wilkinson's Catalyst", 12% deuterium scrambling has been observed in the reduction of trans-1,4-dimethylcyclohexene (less in other trisubstituted olefins), while less scrambling has been observed in more reactive olefins (129). Cyclohexene, a model for 89, is reduced 15 to 100 times faster than the trisubstituted cyclohexenes. Forster (130) reported alkyl halide exchange upon treatment with "Wilkinson's Catalyst" but cyclopropyl halides (as in 89) are unreactive and no exchange was expected or observed.

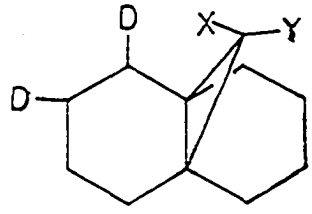
Treatment of a mixture of 89b and 89c with tris(triphenylphosphine)chlororhodium at room temperature in benzene with hydrogen or deuterium gas gave essentially a quantitative yield of 87b or 87b-D_2. Treatment of the

purified isomers 89b (twice) and 89c under similar conditions with deuterium gas gave 141a and 141b respectively. Table 3 gives the D_0, D_1, D_2 and D_3 content in 141, as determined from mass spectral data. The area of the peaks in the ^{13}C NMR of 141a and 141b are listed in Table 4. By comparing ratio of areas of $C_{2,5}$ and $C_{7,10}$ to $C_{1,6}$ in both deuterated and undeuterated (87b) samples, it was possible to establish how much deuterium was located at $C_{2,5}$ in 141a and $C_{7,10}$ in 141b (Table 5). It is impossible to determine the exact percentage or composition of the scrambled products, but 142 and 143 (particularly in the case of 141b) seem likely.



142

a, Z = H
b, Z = D



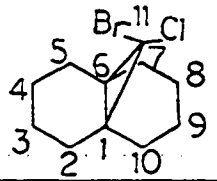
143

Table 3. Mass spectral results

	D_0	D_1		D_2		D_3		D_4
		A^a	B^a	A^a	B^a	A^a	B^a	
141a, 1st trial	0.1%	2.5%	2.4%	97.4%	93.9%	0	3.7%	0
141a, 2nd trial	0	2.9%	2.8%	95.9%	94.3%	1.2%	2.9%	0
141b	0	1.6%	1.6%	98.4%	98.4%	0	0	0

[a]Methods A and B. See Experimental Section for details.

Table 4. Areas from ^{13}C NMR



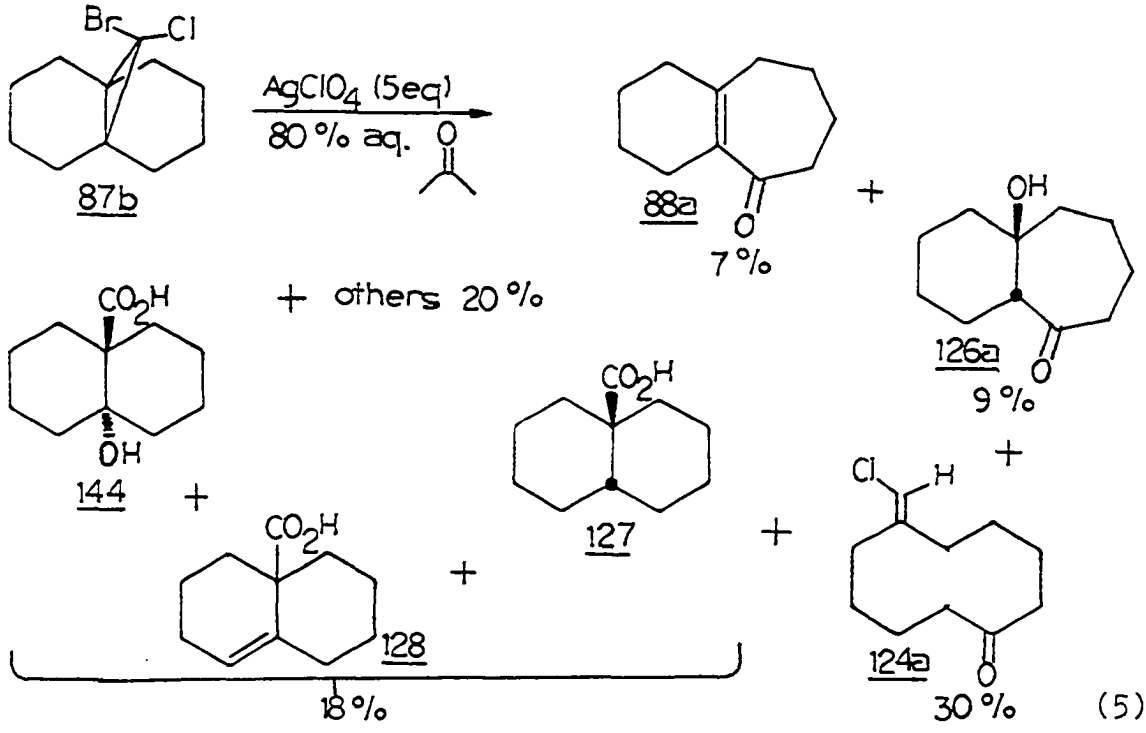
	$C_{3,4}$	C_{11}	$C_{1,6}$	$C_{2,5}$	$C_{7,10}$	$C_{8,9}$
141a, 1st trial	1628	233	647	1585	1705	----
141a, 2nd trial	141	117	359	1289	1390	----
141b	----	256	482	1735	1826	1706
87b	5372	842	2771	6356	6544	6331

Table 5. Per cent deuterium in $C_{2,5}$ of 141a and $C_{7,10}$ in 141b

	% D in $C_{2,5}$	% D in $C_{7,10}$
141a, 1st trial	4.4%	
141a, 2nd trial	4.4%	
141b		-2.2%

Solvolysis of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undecane

The silver-assisted solvolysis of 87a (107,108), 87c (117) and 87d (120) has been investigated by a number of workers. Initially the solvolysis of 87b was investigated under similar conditions (Equation 5). From the low yield of 88a and 126a it was assumed that part of the unidentified



(5)

material consisted of an intermediate(s) in the production of 88a and 126a. Thus, the reaction was repeated using only one equivalent of $AgClO_4$ and longer reaction time (Equation 6). The isolation of two new compounds [125a (Figure 16) and 145 (Figure 17)] reinforced the mechanistic Scheme 7, since 125a is the product from addition of water to bridge-head olefin 122a, while 145 is the elimination product from

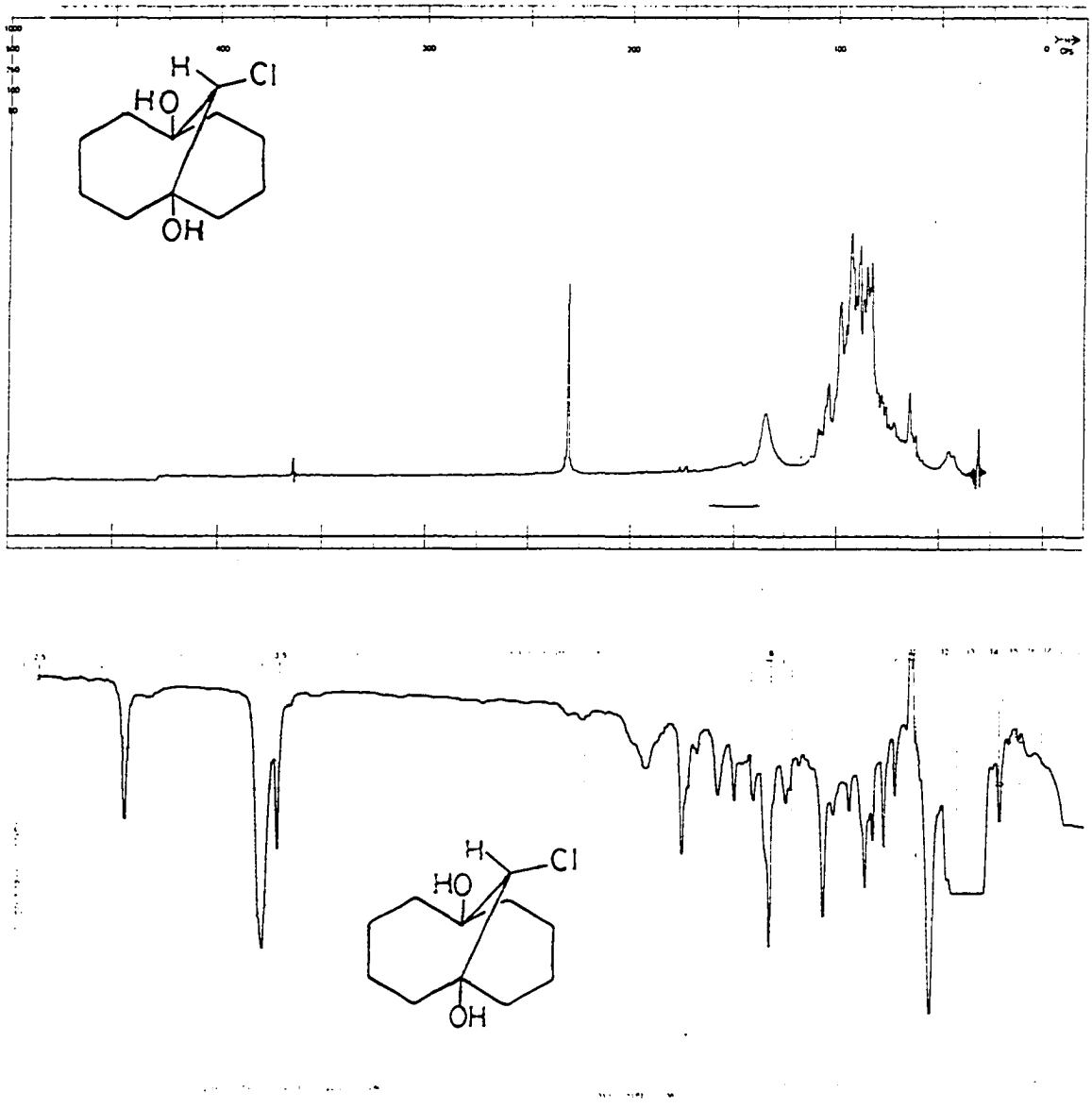


Figure 16. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of 11-chloro-1,6-dihydroxybicyclo-[4.4.1]undecane (125a)

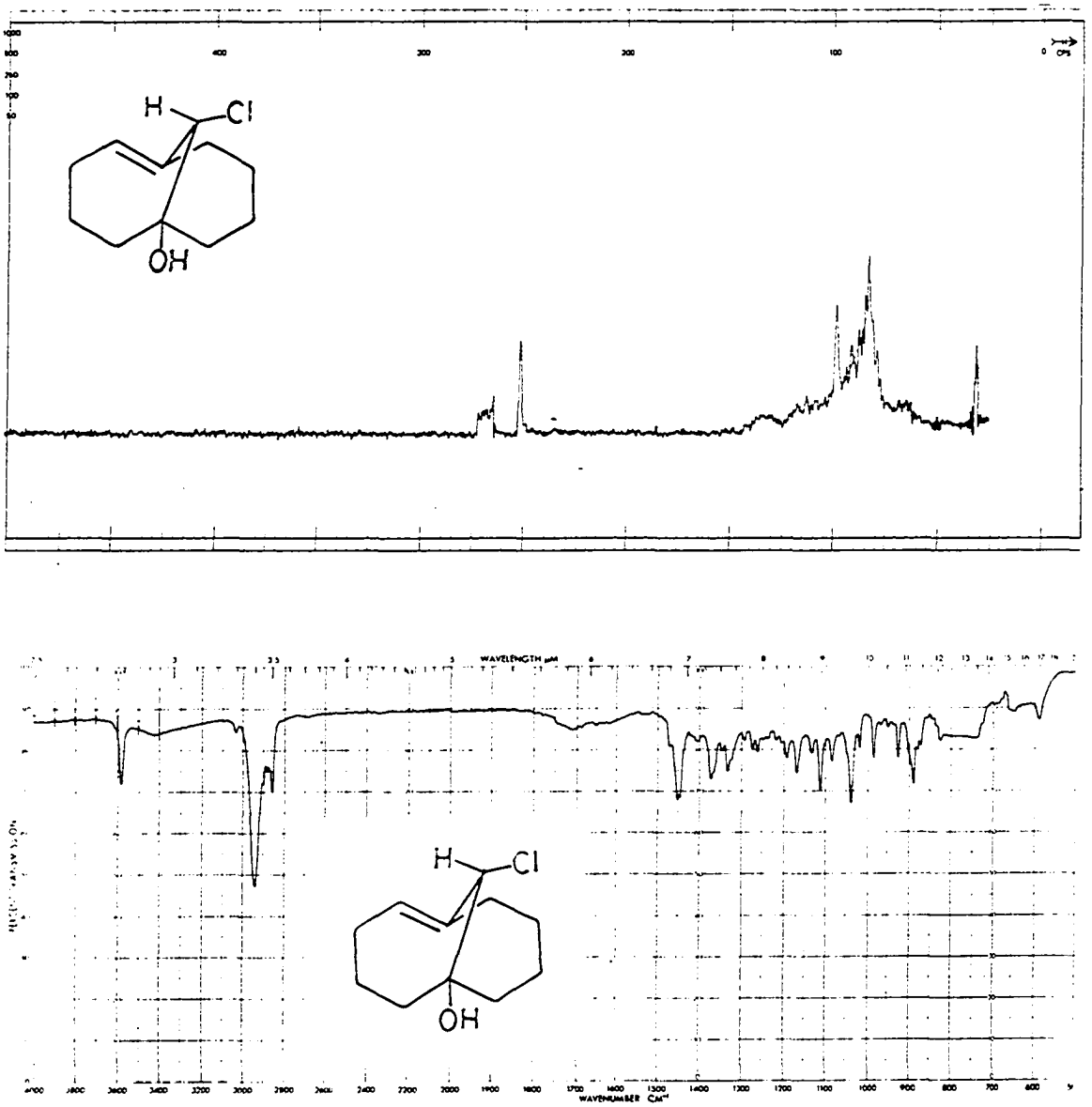
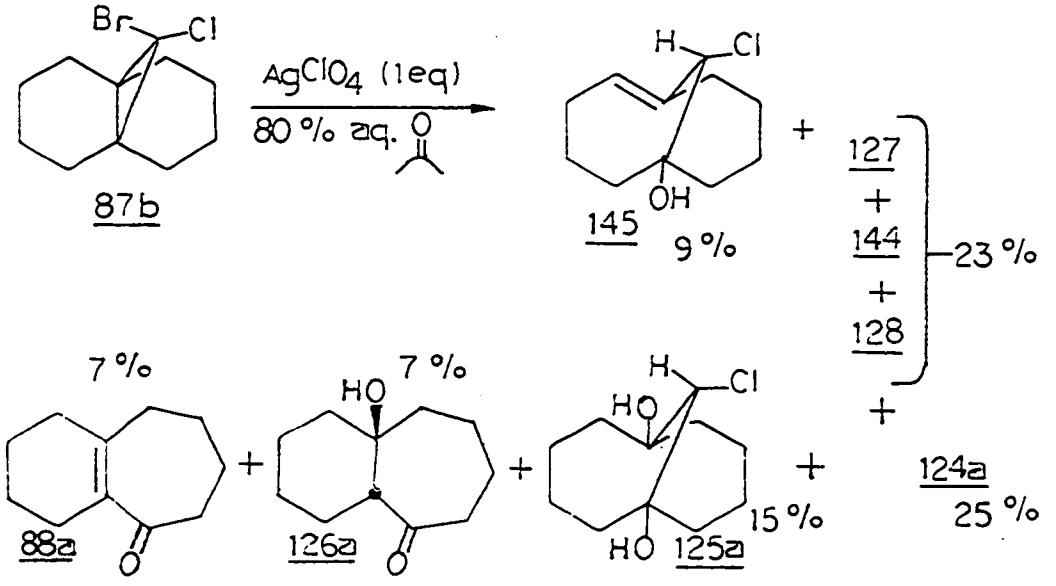


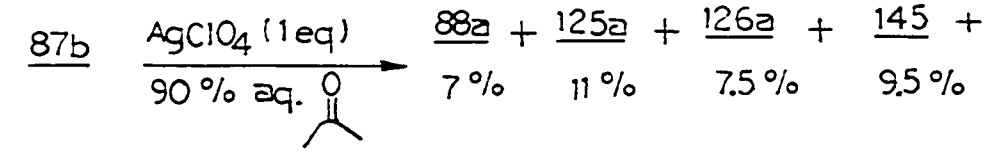
Figure 17. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of anti-11-chloro-6-hydroxybicyclo-[4.4.1]undec-1(2)-ene (145)

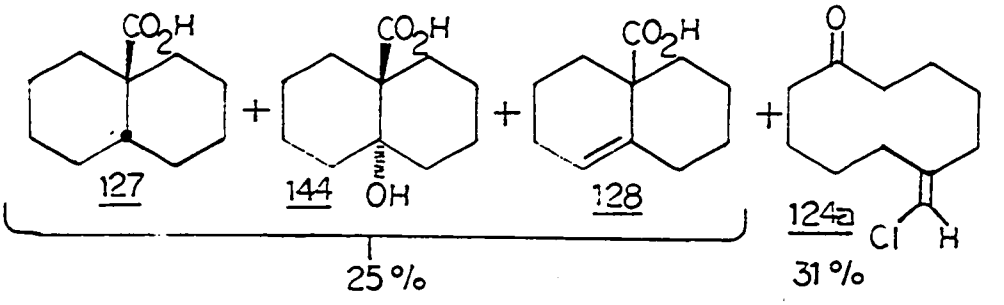
ion 123a. Treatment of 125a under the reaction conditions gave hydroxyketone 126a and a small amount of enone 88a.



(6)

The acidic products were similar to those isolated by Warner and Lu (117a), but their ratio was not measured. The stereochemistry of 145 is based on a similar elimination in the solvolysis of 99 and 109 and other results to be discussed herein. The solvolysis of 87b was also investigated in 90% aqueous acetone (Equation 7). The amount

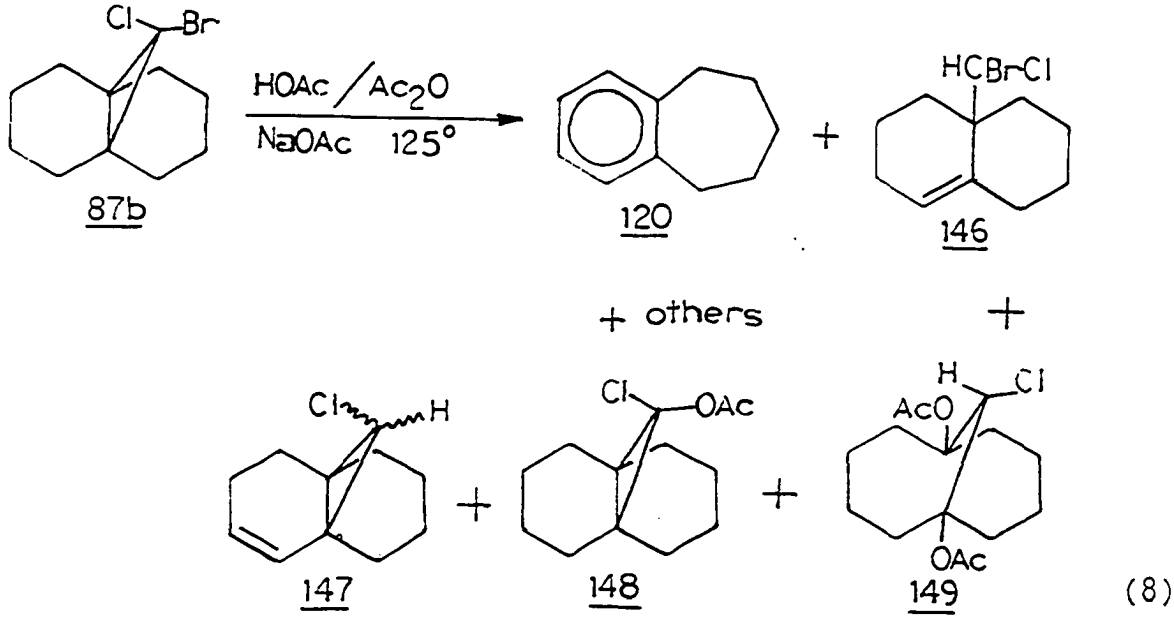




(7)

of fragmentation of 123a to 124a is greater in a medium where less water is available to trap 123a to give 125a (and, after further solvolysis, 126a and 88a (117)).

The acetolysis of 87b was also investigated in buffered acetic acid with varying amounts of water. Although some of the products were not fully characterized, they are similar to the products observed in the silver-assisted solvolysis of 87b and the acetolysis of 99 and 109. When the acetolysis was performed in acetic acid with acetic anhydride, the major products were different from those in aqueous acetone (Equation 8). Benzocycloheptene (120) (131) was isolated



(8)

from the acetolysis of 87a; it is the major product in the absence of a buffer (117). Compounds 146 (Figure 18) and 148 are analogous to 116 and 114 isolated in the acetolysis of 109. While 146 has been fully characterized, the

assignment of 148 is based on the infrared absorption at 1775 cm^{-1} as well as the lack of any aldehyde products which were isolated in the acetolysis of 87b with small amounts of water. Diacetate 149 (Figure 19) is similar to 125a to which it was converted with alkaline aqueous methanol. Compound 147 (Figure 20) was isolated, characterized and converted to 120 and two other unidentified components (in equal amounts to 120) under the reaction conditions. Possible mechanisms (117) for the production of 120, 147 and 146 are illustrated in Scheme 10. Pathway b of Scheme 10 has analogy in the similar [4.3.1]propellane series (114) (Scheme 6) and in some steroid and sesquiterpene work (132). Pathways a and b seem likely, since in the solvolysis of 87a the proportion of 120 increases sharply upon solvolysis in unbuffered acetic acid, a phenomenon which we attribute to HBr-catalyzed addition of acetic acid to 87a (117b). Pathway c has analogy in the [4.3.1]propellane series (114) and pathway d is similar to pathway a except the bromine has been replaced by an acetate group. A control experiment, wherein 146 is subjected to the acetolysis conditions, would serve to determine whether or not pathways other than a and b are necessary to account for the production of 120 and 147.

When the acetolysis of 87b was undertaken in buffered acetic acid without acetic anhydride, the amount of 148

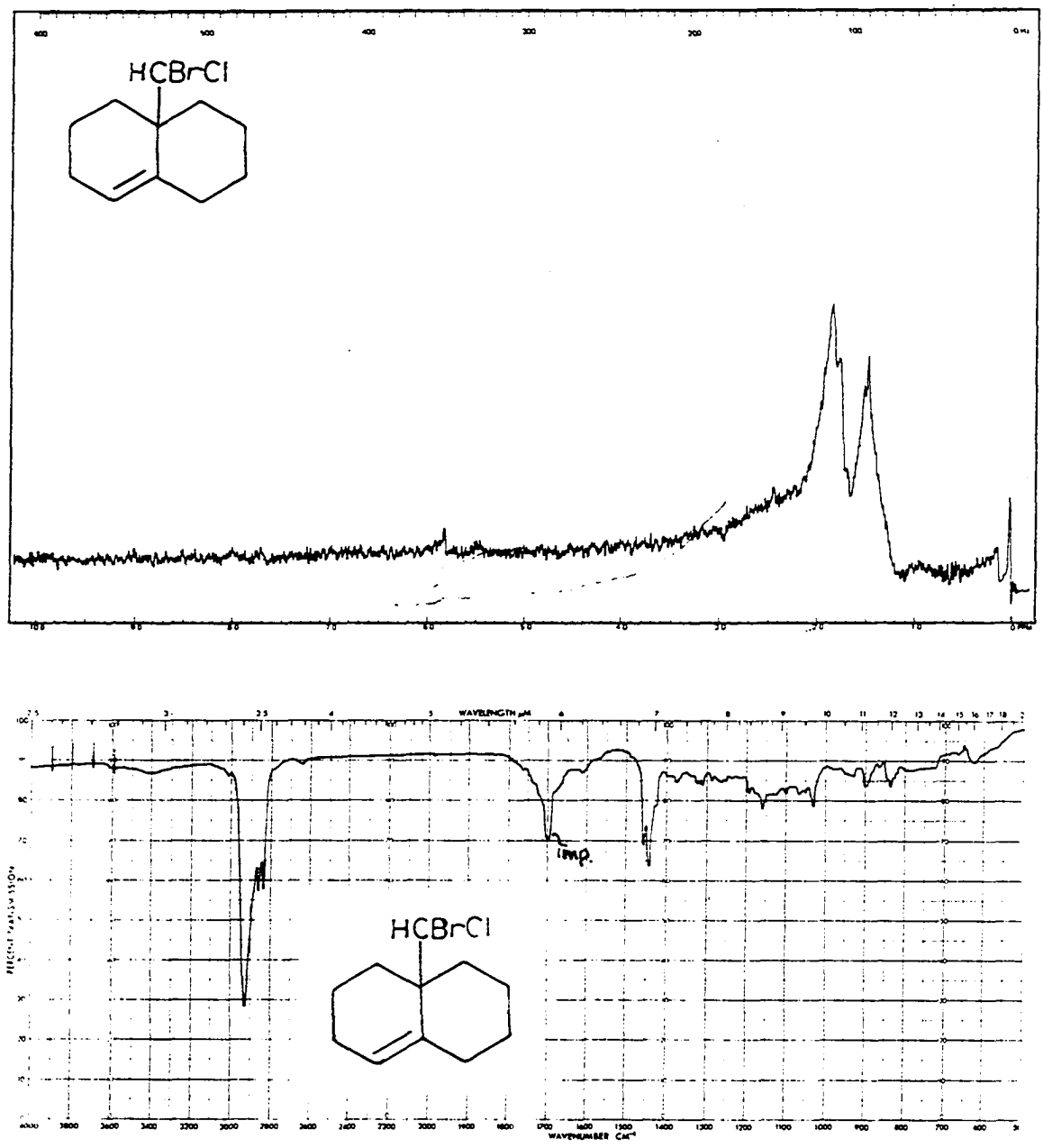


Figure 18. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of 1-bromochloromethylbicyclo[4.4.0]-dec-5-ene (146)

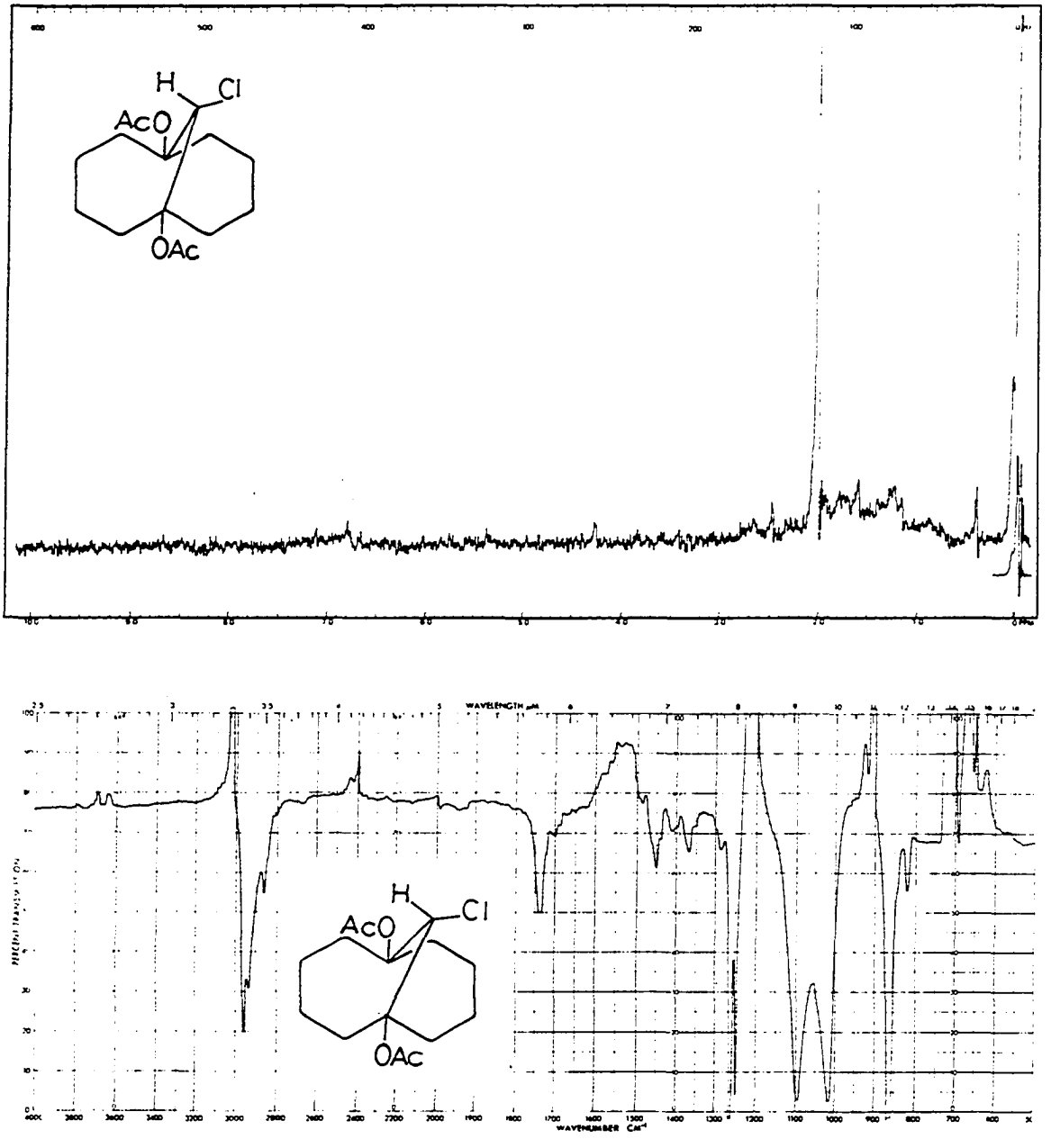


Figure 19. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of 11-chloro-1,6-diacetoxybicyclo-[4.4.1]undecane (149)

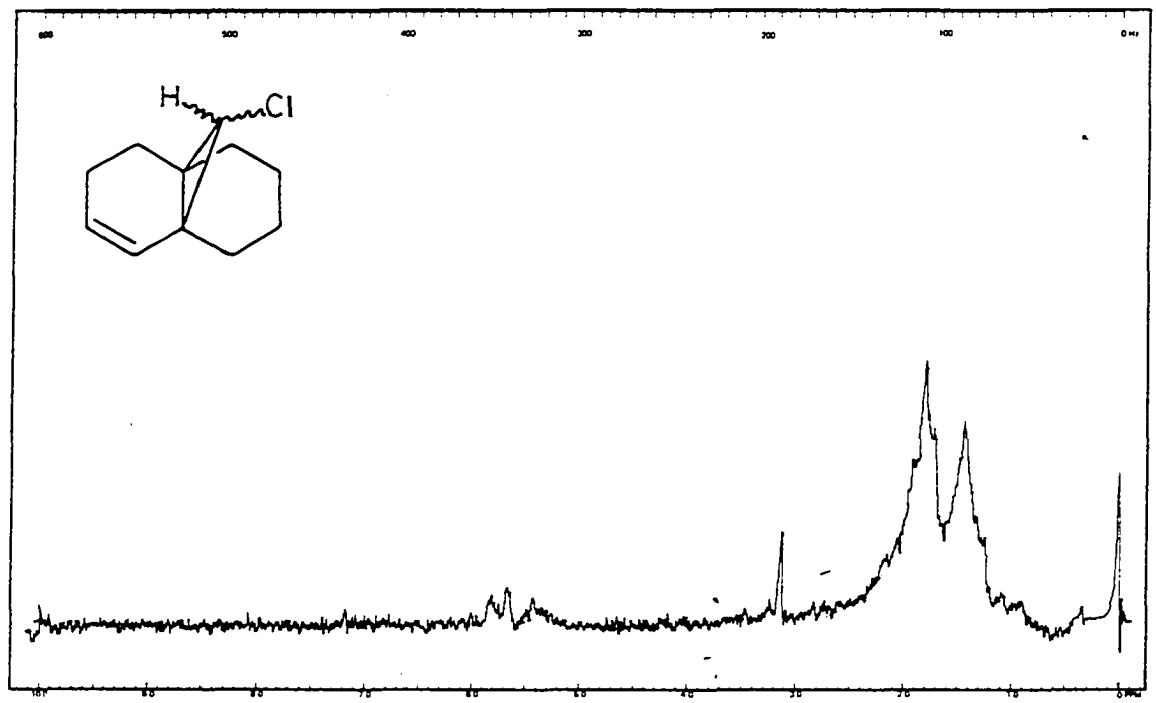
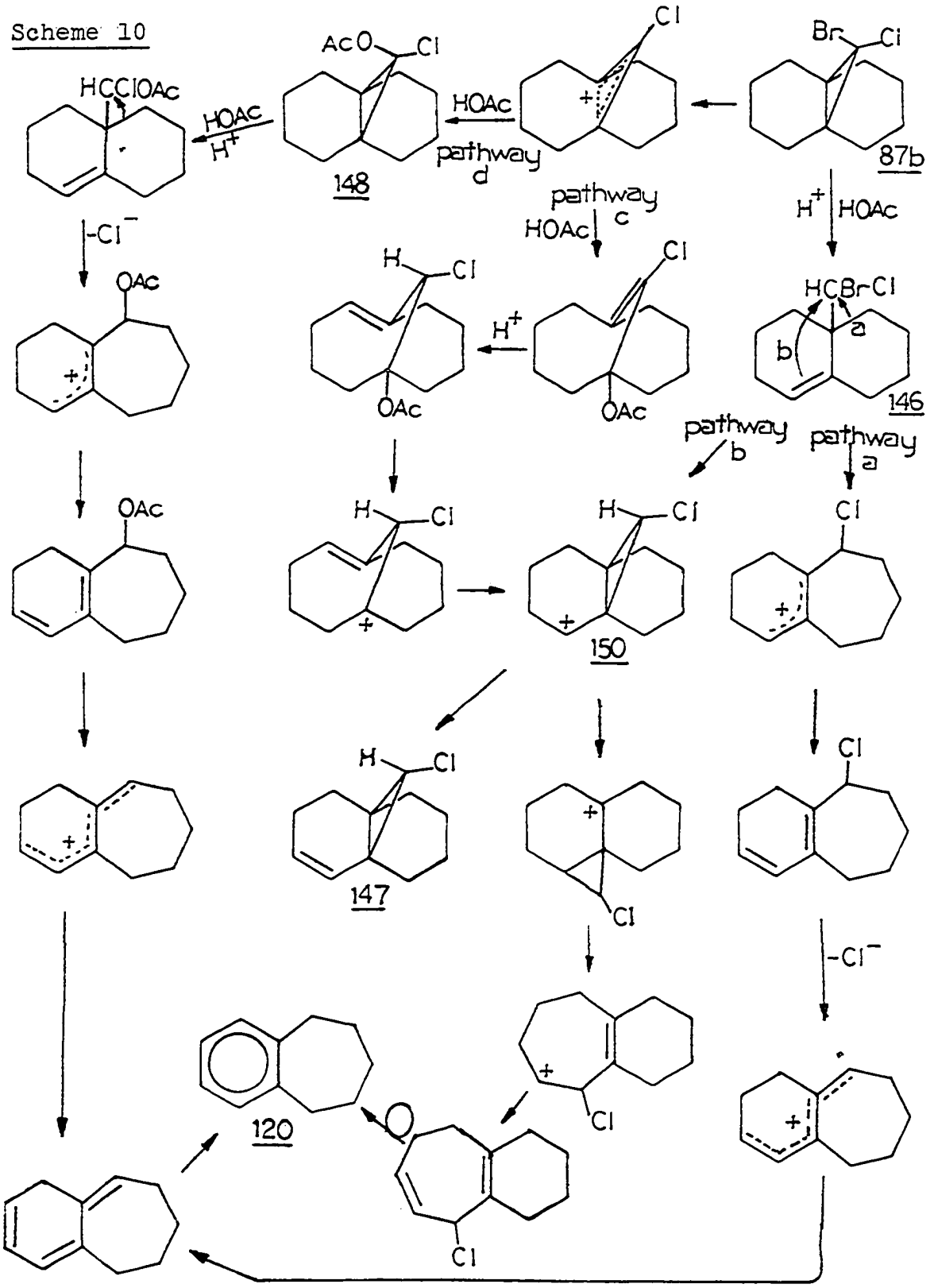
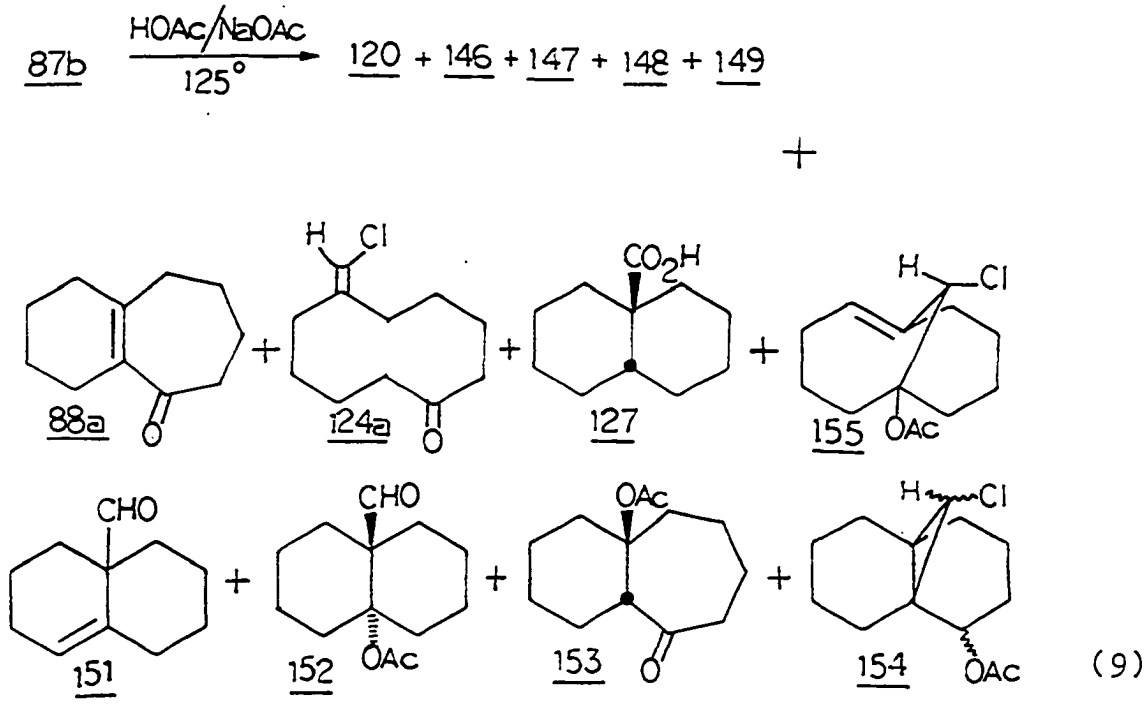


Figure 20. ^{1}H NMR (60 Mcps) spectrum of 11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-2-ene (147)

Scheme 10


HCClOAc
HOAc
H+
AcO
Cl
148
HOAc
pathway
d
Cl
Br
Cl
87b
H+
HOAc
pathway
c
HOAc
-Cl−
OAc
H
Cl
H+
OAc
OAc
HCBr-Cl
a
b
146
pathway
b
pathway
a
OAc
H
Cl
H
Cl
Cl
150
H
Cl
147
Cl
Cl
-Cl−
120
O
Cl

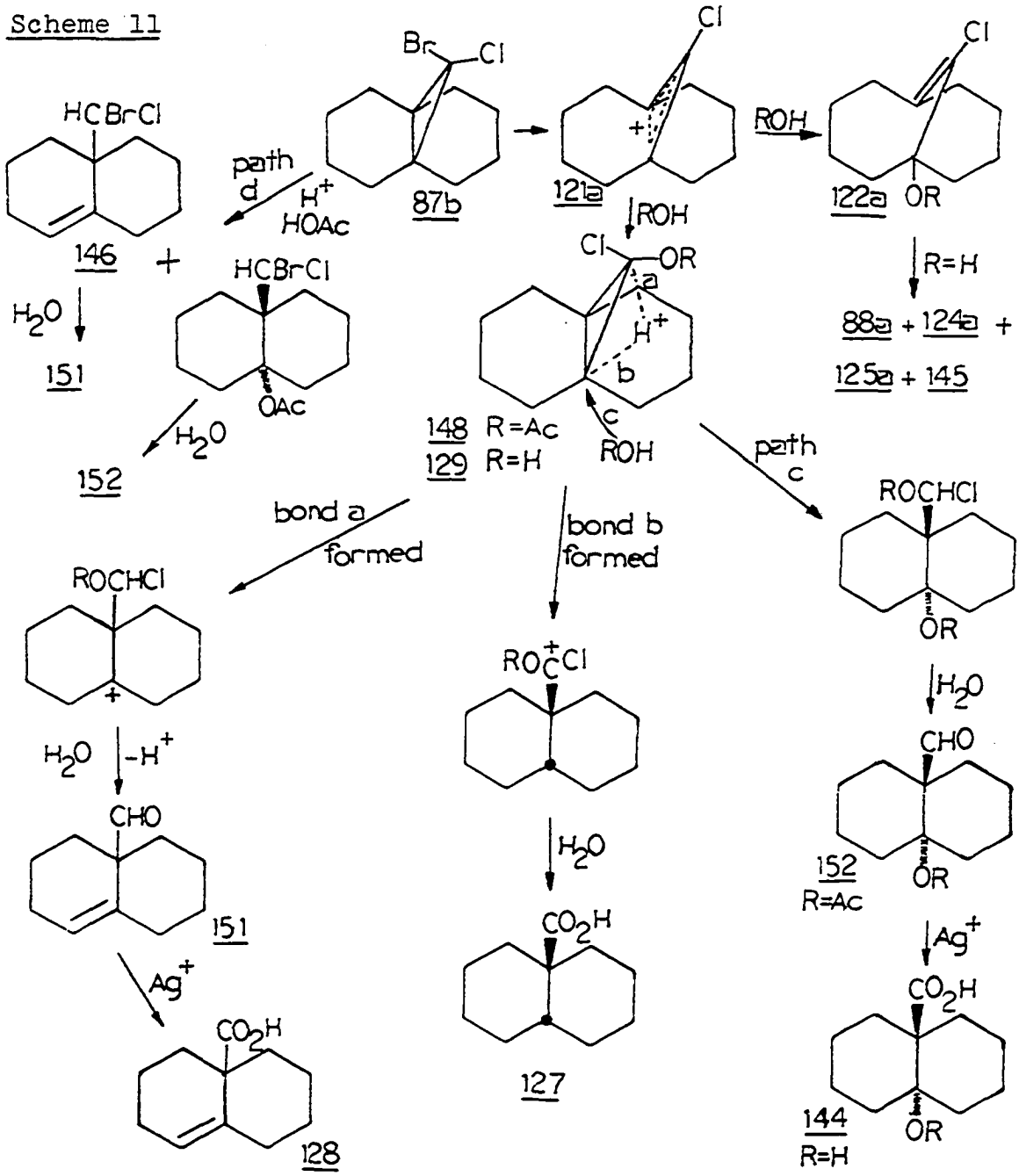
decreased (from IR band), but two new compounds, 151 (Figure 21) and 152, were observed along with acid 127 (Equation 9). Compounds 151 and 153 (Figure 22) were



(9)

isolated and characterized, whereas 152 was isolated as a mixture with 88a and 124a (the trans stereochemistry of 152 was assumed). Compounds 151 and 152 complement the mechanistic scheme used to explain the formation of the acidic products (127, 128 and 144) in the silver-assisted solvolysis of 87a and 87c (117) (Scheme 11). Thus, when the silver ion is removed from the medium, the aldehydes (151 and 152) are isolated because the Tollen's oxidation to acids (128 and 144 respectively) does not occur. In a separate experiment, 151 was oxidized to 128 under the silver-assisted hydrolysis conditions. Compound 148 is relatively stable

Scheme 11



in the absence of water (acetic acid with acetic anhydride), but with a trace of water present, 129 is formed and converted to 127 and aldehydes 151 and 152. The water must come from the supposedly glacial acetic acid.

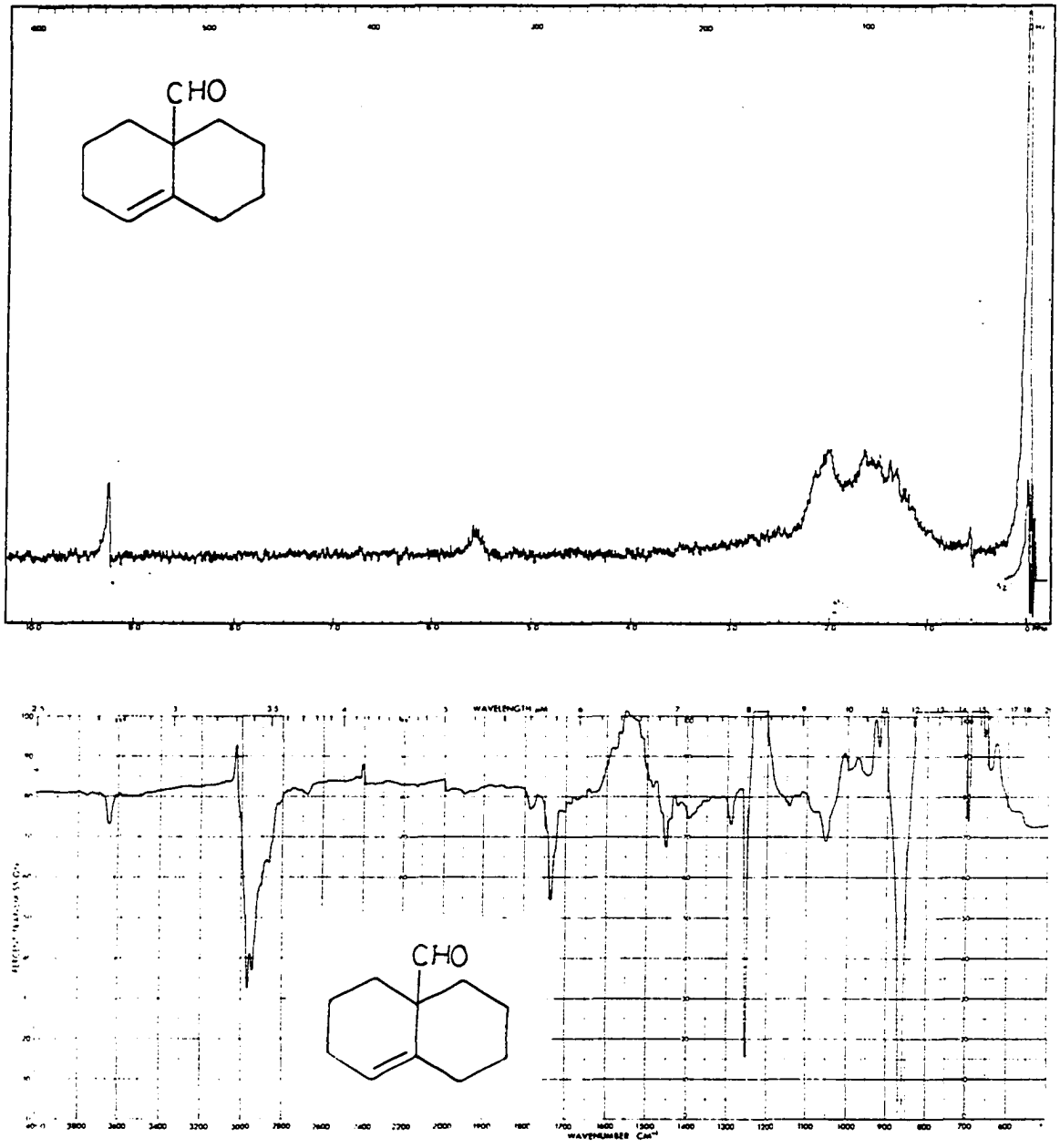


Figure 21. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of bicyclo[4.4.0]dec-5-ene-1-carboxaldehyde (151)

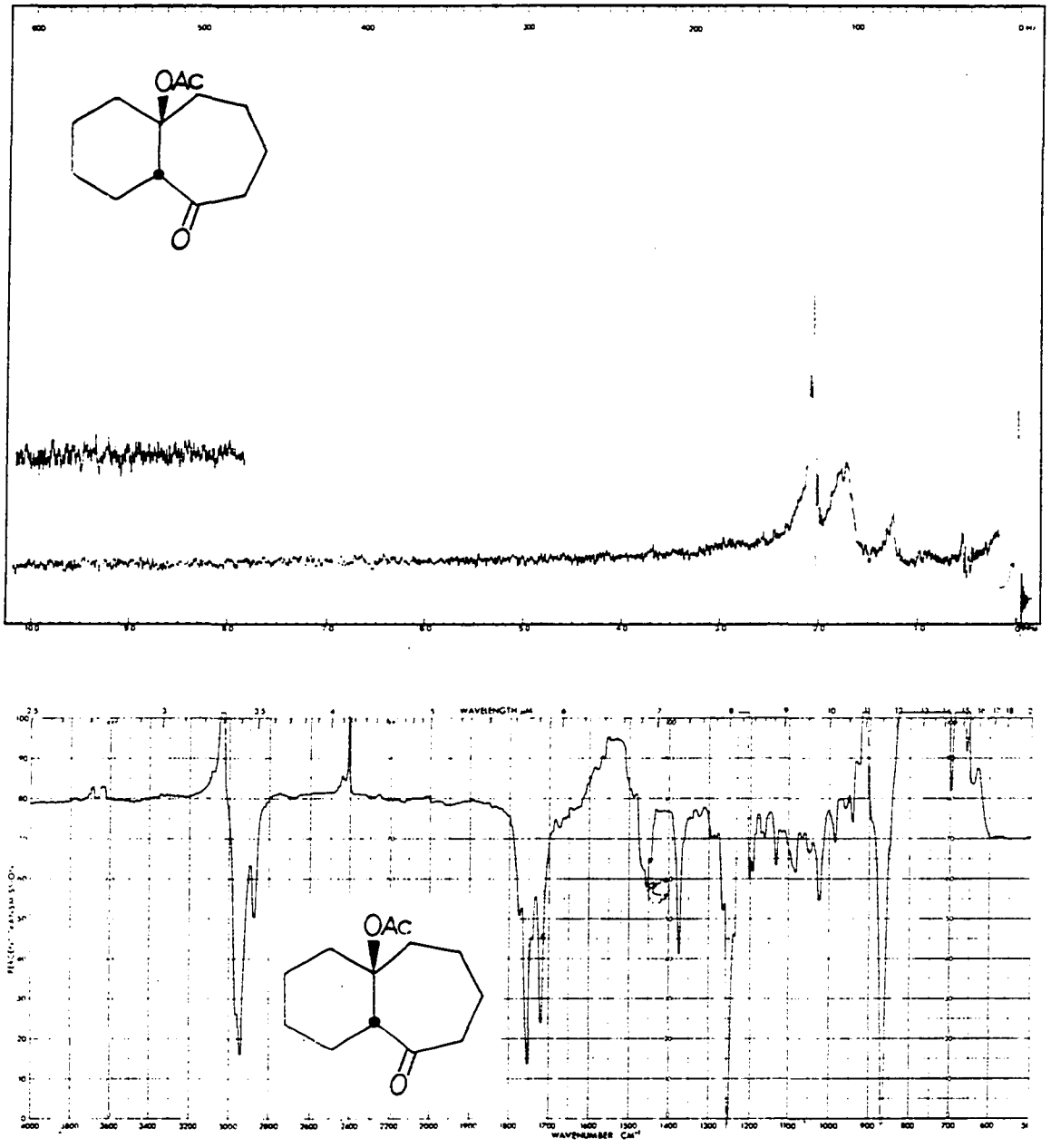
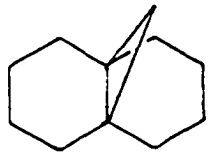
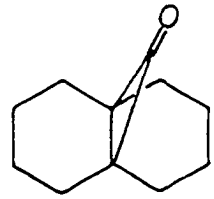


Figure 22. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of 7-acetoxybicyclo[5.4.0]undecan-2-one (153)



156

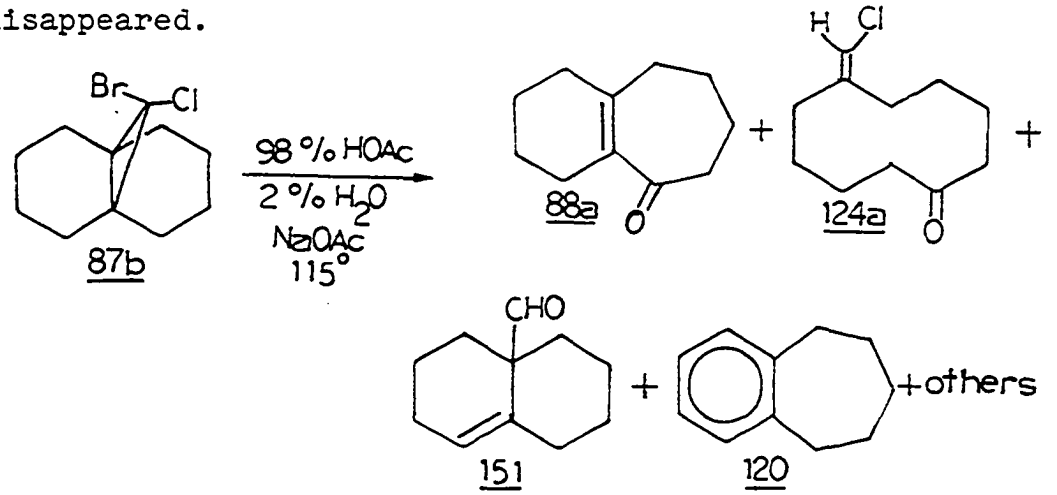


157

Protonic cleavage of 87a (Scheme 11, path d) in the silver-assisted solvolysis was ruled out by Warner and Lu (117a) because of the finding that 87a was recovered unchanged after treatment under the acidic solvolysis conditions at room temperature. They also showed that silver catalyzed cleavage was doubtful since [4.4.1]propellane (156) remained largely unchanged after treatment with Ag^+ under the acidic solvolysis conditions. The intermediacy of a cyclopropanone (157) was not conclusively proven, although one was isolated in the solvolysis of 9,9-dibromotricyclo[3.3.1.$0^{1,5}$]nonane (138) (121). A peak at 1835 cm^{-1} (appropriate for a cyclopropanone) was noticed in the infrared spectrum of the crude products resulting from the acetolysis of 87b with acetic anhydride.

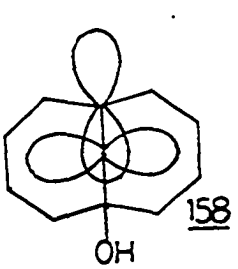
The two epimeric acetates (154) and the isomeric acetate 155 (analogous to 145) were isolated together and gave the correct mass spectral data. The structure was assigned based on analogous products isolated from the acetolysis of 109 (115a and 115b) and from the acetolysis of 99 (108 and 108b) (114), as well as the infrared spectra. Compounds 124a and 88a were again major products when the

acetolysis was conducted in 98% aqueous acetic acid (Equation 10). Benzocycloheptene (120) was still a major product, while most of the acetate containing products essentially disappeared.

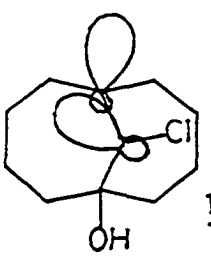


(10)

As shown by the labeling study of Warner and Lu (117a) and the solvolysis of 87b (107b), the solvolysis proceeds via a bridgehead olefin (122a). The products isolated arise via protonation of this intermediate to yield 123a, which either fragments to 124a or adds water to give 125a and then 126a and 88a or deprotonates to give 145. What is the nature of 122a? Is it symmetrical as in 158 (whereby its ground state would be a triplet) or is it unsymmetrical, possibly rehybridized as shown in 159? The solvolysis of



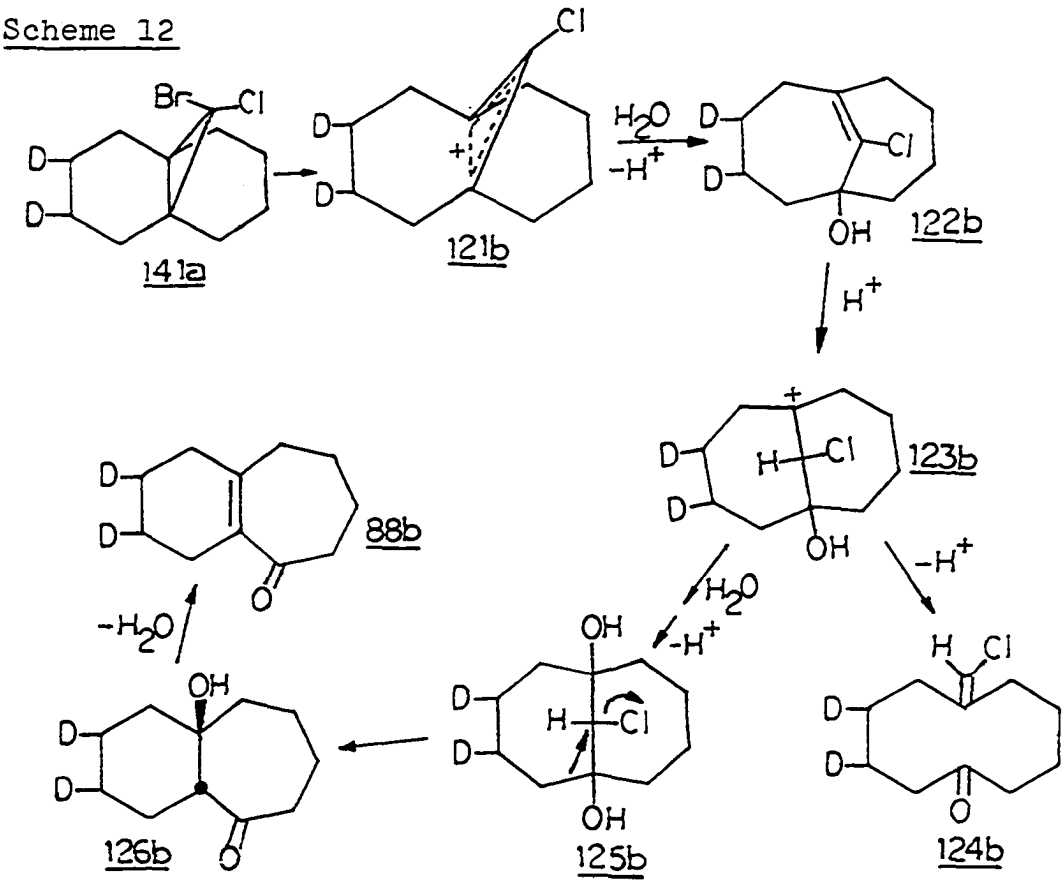
158



159

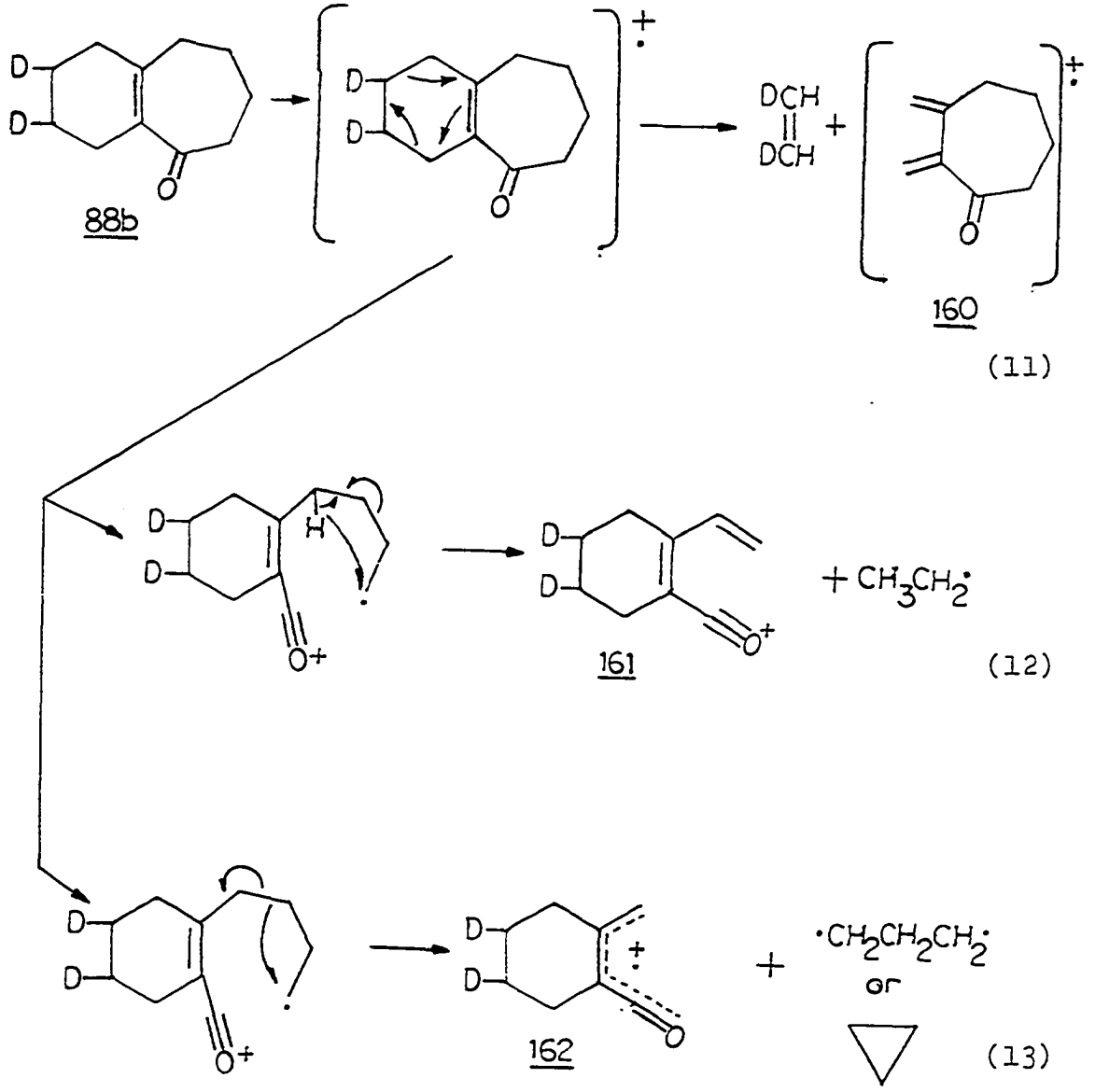
141a and 141b should provide an answer, as shown for 141a in Scheme 12. The loss of bromide and ring opening according to the Woodward-Hoffmann-DePuy rules would give the partially-opened cyclopropyl cation 121b which would collapse with

Scheme 12



water to the bridgehead olefin 122b with the deuterium in the "cis-cycloheptene" ring. If the olefin is symmetrical as in 158, protonation would occur equally from both sides. If the bridgehead olefin is unsymmetrical as in 159, protonation should occur from the deuterated ring side (attacking the large lobe of a rehybridized orbital). Thus,

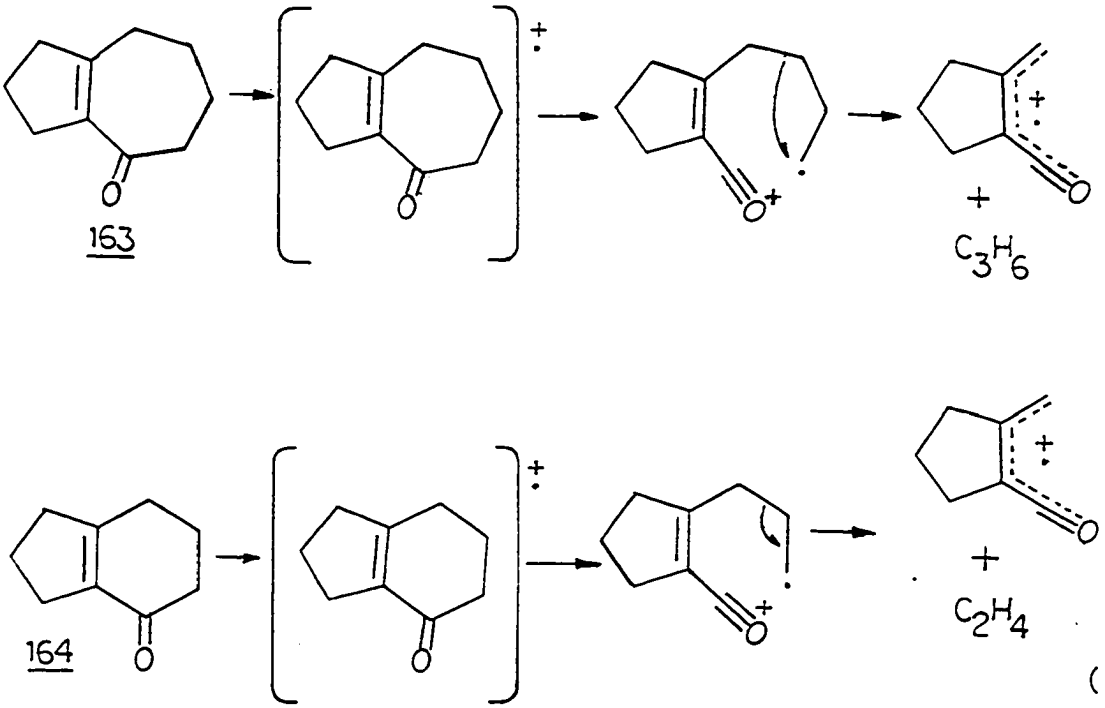
hydrogen would replace the bromine with retention to give 123b, which fragments to 124b or adds water to give 125b and then 126b and 88b. Since the ^{13}C NMR of 124a shows 11 distinct peaks, incorporation of deuterium into 2 or 4 carbons would be easily differentiated. But since all the carbon shift assignments could not be made, analysis of 124b could not be used to distinguish between retentive or invertive proton attack on 122b. On the other hand, analysis of 88b by mass spectrometry should prove more informative if the fragmentation modes can be identified. Fragmentation of the radical cation of 88b might be expected to proceed via a retro Diels-Alder reaction to give 160 and ethylene (Equation 11). A complicating fragmentation however, is the loss of ethyl radical from the cycloheptenone ring to generate a resonance stabilized cation (161); this process has been documented in the literature (Equation 12) (133). This, combined with the observed loss of carbon monoxide from 88b, makes analysis of the retro Diels-Alder fragmentation rather hopeless. Fortunately, the base peak corresponds to the loss of C_3H_6, which can be rationalized by a fragmentation to 162 (Equation 13). This assignment is supported by the mass spectrum of 163, where the loss of C_3H_6 is also the base peak (Equation 14), and that of 164, where the loss



of C_2H_4 is the base peak (Equation 15). Thus, the base peak from 88b would contain 2 deuteriums, while that from 88c would contain none.

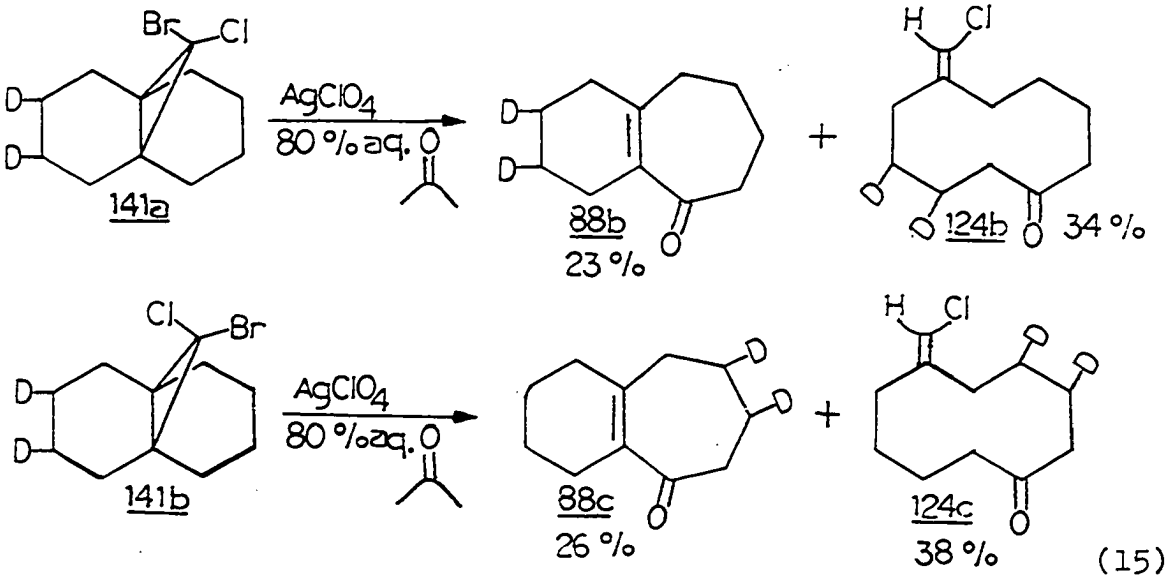
The silver-assisted solvolysis of 141a (1st trial) and 141b were performed in 80% aqueous acetone with five

equivalents of $AgClO_4$ to insure conversion of 125a and 126a to 88a. The effect of silver ion upon the reaction



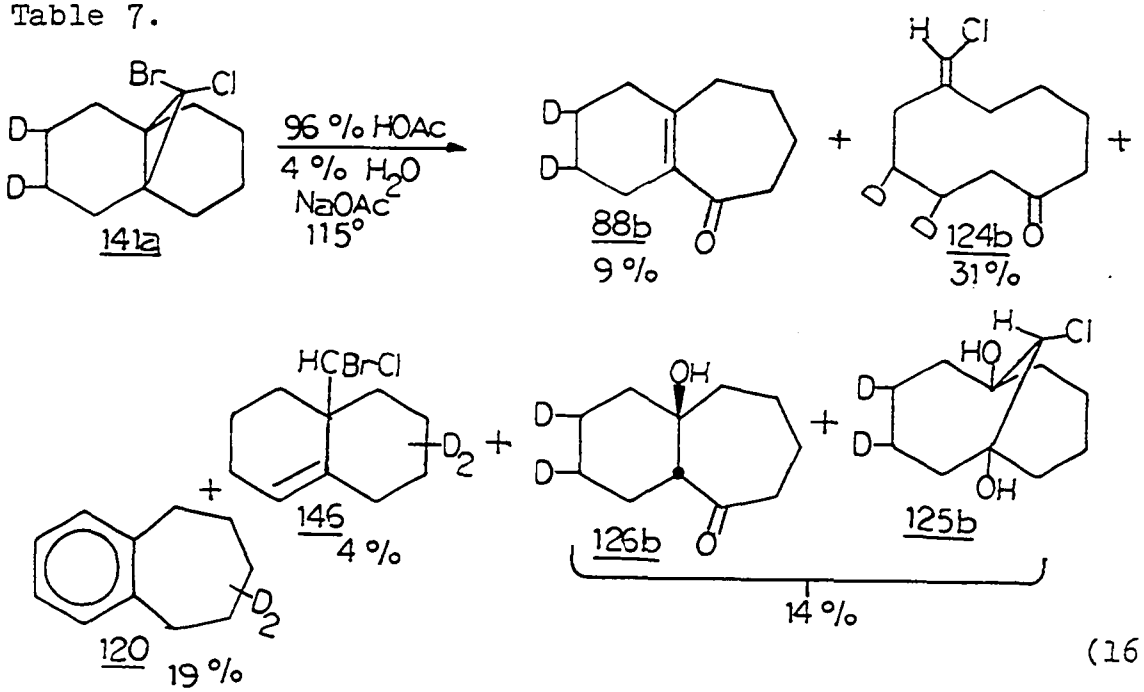
(14)

is unknown, although some anomalous effects have been observed (see Part II). In order to avoid any Ag^{+} induced



(15)

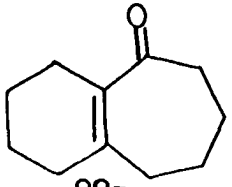
effects, the solvolysis of 141a (2nd trial) was also carried out in 96% aqueous acetic acid (Equation 16). The mass spectral data for enones 88a, 88b, 88c and 88b-acetolysis are listed in Table 6 and the ^{13}C NMR data for monocyclic ketones 124a, 124b, 124c and 124b-acetolysis are listed in Table 7.



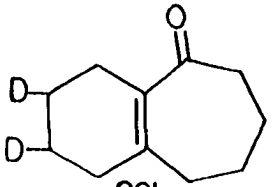
(16)

If the reaction had proceeded as indicated in Scheme 12 for 141a, all the deuterium in 88b would be located in the six-membered ring. The radical cation 162 should have an m/e of 124 rather than the 122 observed for 88a. As seen in Table 6, this was indeed the case (cf. Equation 13). Correspondingly, the enone (88c) derived from 141b should give rise to an undeuterated version of 162 (m/e 122); that this was observed can be seen from the data in Table 6.

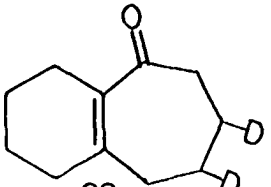
Table 6. Mass spectral intensities for enones at 70 ev



88a



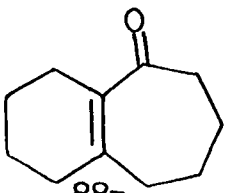
88b



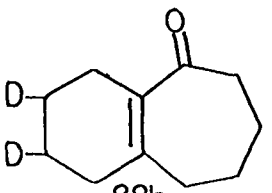
88c

m/e peak	88a (Average of 4)	88% of 88a & 12% of 124a (Average of 5)	88b (1st trial) (Average of 4)	88b (2nd trial) (Average of 5)	88c (Average of 7)	Formulas of Ions of Interest
141	0.4		---	---	---	
140	0.06		---	---	---	
139	0.2		2.1	1.3	---	
138	0.2		13.3	11.5	16.5	
137	1.1		45.6	55.9	56.0	
136	11.7		22.9	29.7	62.7	
135	41.9		5.1	13.1	12.2	
134	1.1		1.8	1.3	2.8	
133	1.8		3.7	8.2	8.2	
132	0.9		---	---	---	
131	2.6		---	---	---	
129	0.8		---	---	---	
128	1.2		---	---	---	
127	0.4		.74	---	---	
126	0.2	0.6	1.3	1.1	---	
125	0.2	3.4	9.9	17.0	4.6	$C_8H_7D_3O$

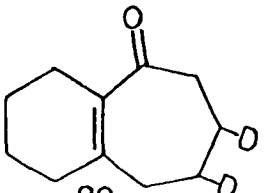
Table 6. (Continued)



88a



88b



88c

m/e peak	88a (Average of 4)	88% of 88a & 12% of 124a (Average of 5)	88b (1st trial) (Average of 4)	88b (2nd trial) (Average of 5)	88c (Average of 7)	Formulas of Ions of Interest
124	0.9	8.4	(100)[a]	(100)[a]	11.5	$C_8H_8D_2O$
123	9.3	19.8	24.7	33.2	18.2	C_8H_9DO
122	(100)[a]	(100)[a]	20.4	15.1	(100)[a]	$C_8H_{10}O$
121	10.1	18.4	4.3	7.1	22.5	
120	3.3	6.2	---	---	---	
119	1.3	2.8	---	---	---	

[a]Base peak.

But let us compare, in detail, the mass spectra obtained from 88a and 88c. According to the above "first-order" analysis, these should be identical in the m/e 121-125 range; as can be seen in Table 6, this is not the case. One possible source of the discrepancy could be the presence of 88b, formed from the 0-2% of 141a present in the starting 141b and, possibly, some scrambling due to symmetrization of the bridgehead olefin intermediate (122c). However, the presence of 88b should decrease the intensity of the ion at m/e 121, whereas the experimental facts are just the opposite! An alternate source of the aforementioned discrepancy is the unfortunate presence of ca. 10% of 124c in the sample of 88c (these were difficult to separate by the column chromatography utilized in this study). In fact, the mass spectrum of an 88:12 mixture of 88a and 124a (Table 6, column 2) matched the mass spectrum of 88c almost perfectly (within mass spectral experimental error) in the m/e 121-125 range.

Analysis of the mass spectral data for 88b (both trials) is made virtually futile because it is impossible to know how much of the intensity at m/e 120 arose from ions derived from the 124b impurity in the sample. If it is assumed that the fragmentation of 124b retained the deuterium in the daughter ion at m/e 122, then the intensity at m/e 120 for the mixture (Table 6, column 2) must be subtracted from the intensity at m/e 122 for 88b. Thus for 88b (1st trial), the

resultant intensity at m/e 122 is 14.2; from this must be subtracted an additional 6 to 4 [due to the 6 to 4% of epimer 141b present in the 141a (1st trial) utilized to get 88b (1st trial)], leaving a residual intensity of 7.8 at m/e 122. This means that there could have been as much as 15% scrambling (i.e., 15% of a symmetrical bridgehead olefin intermediate, or its equivalent, giving 7.5% each of 88b and 88c) in the reaction of 141a (1st trial) to give 88b (1st trial); however, the ^{13}C NMR data indicate this is too high (vide infra). A similar analysis for 88b (2nd trial) leads to a maximum of 4% scrambling. [Interestingly, the data for 88b (2nd trial) would indicate substantial amounts of d_1 and d_3 ions - more than from 88b (1st trial) - but the relative amount of d_0 ion is smaller than from 88b (1st trial). This probably signifies that no great reliance should be placed on scrambling percentages obtained mass spectroscopically in these experiments.]

The ^{13}C NMR data (Table 7) provided a more quantitative answer to how stereospecific the hydrolysis and acetolysis of 141a and 141b had been. The carbon assignments are based on the observations from the mass spectral data (Table 6) which showed that protonation of the bridgehead olefin intermediate occurred from the side of the cis-cycloheptene ring (i.e., the proton replaced the bromine with retention). Thus, in 124b no area was observed for C_8 and C_9 since the

deuterium splits this peak into a triplet which was too small to integrate. Similarly, in 124c no area was observed for C_3 and C_4. As noted before (Table 5), some scrambling of the deuterium into C_2 and C_5 of 141a, and C_7 and C_{10} of 141b, had occurred. The assignments of C_{10}, C_2, C_7 and C_5 are based upon the slightly lower areas in the ^{13}C NMR (Table 7) due to this deuterium scrambling. In 124c, C_2 and C_5 should have a small amount of deuterium due to this scrambling during incorporation of the deuterium into 141b, and the area of these carbons were consequently lower than what was expected based on comparison of areas with the undeuterated 124a. In 124b, C_7 and C_{10} should have lower areas than expected based on comparison of areas with the undeuterated 124a. It should be emphasized that the determination of stereospecificity (below) is independent of the correctness of the above assignments.

If the reaction proceeded with scrambling of the label between C_3, C_4 and C_8, C_9, the areas of these carbons would be reduced. It is obvious from the data (Table 7) that the reaction was largely stereospecific, and by comparison of the area of the deuterated samples (124b and 124c) to the undeuterated sample (124a) it could be established how stereospecific. Thus for 124b (1st trial) the following ratios were calculated: (C_3/C_{10})124b/(C_3/C_{10})124a x (C_{10}/C_2)124b/(C_{10}/C_2)124a = 97.9%; (C_4/C_{10})124b/(C_4/C_{10})124a x

Table 7. ^{13}C NMR data for monocyclic ketones 124 a-c

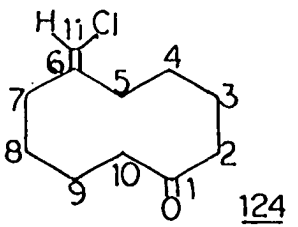
	C_1	C_{11}	C_6	C_{10}	C_2	C_7	C_5	C_8	C_3	C_4	C_9
δ(ppm)	214.3	141.4	113.1	43.1	37.8	31.2	30.9	24.5	23.2	22.8	22.4
124a											
area	805	781	1534	1435	1428	1492	1341	1662	2019	1508	1413
C_x/C_{10} [a]	0.561	0.544	1.069	(1.0)	0.995	1.040	0.934	1.158	1.407	1.051	0.985
C_x/C_2 [a]		0.547	1.074	1.005	(1.0)	1.045	0.939	1.164	1.414	1.056	0.989
124b (1st trial)											
area	541	1015	1716	1055	1061		2595[c]	---	1495	1054	---
C_x/C_{10} [a]	0.513	0.962	1.626	(1.0)	1.006				1.417	0.999	
C_x/C_2 [a]	0.510	0.957	1.617	0.994	(1.0)				1.409	0.993	
124b (2nd trial)											
area	---[b]	---[b]	---[b]	1263	1351		3549[c]	---	1709	1341	---
C_x/C_{10} [a]				(1.0)	1.070				1.353	1.062	
C_x/C_2 [a]				0.935	(1.0)				1.265	0.993	

124c area	1311	1461	2738	3033	2955	3274	3158	3310	---	---	3001
C_x/C_{10} [a]	0.432	0.482	0.903	(1.0)	0.974	1.079	1.041	1.091			0.989
C_x/C_2 [a]	0.444	0.494	0.926	1.026	(1.0)	1.108	1.069	1.120			1.016

[a]Ratio of area.

[b]This peak was not integrated.

[c]These peaks were not resolved so reported area is the combined area.



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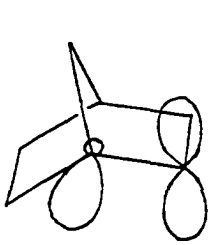
(C_{10}/C_2)124b/(C_{10}/C_2)124a = 96.8%; (C_3/C_2)124b/(C_3/C_2)124a = 95.1%; (C_4/C_2)124b/(C_4/C_2)124a = 94.0%; the average of these percentages was 96.0%, with a standard deviation of 1.7%. The factor (C_{10}/C_2)124b/(C_{10}/C_2)124a was included in the first two calculations since, as noted earlier, C_{10} of 124b contained a small amount of deuterium from scrambling during the deuterogenation step; thus, this factor is necessary to correct for said scrambling. The above-utilized syn-11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89b) contained 4 to 6% of epimer 89c (estimated from the ^{13}C NMR data). Thus C_3, C_4 should have contained 4-6% deuterium; from the above data, C_3, C_4 are calculated to have contained 4% $\pm$1.7% deuterium. Clearly, within experimental error, the reaction was 100% stereospecific (i.e., stereoretentive). The same calculations as above for 124b (2nd trial) from acetolysis gave the following percentages: 93.7%, 92.7%, 94.0% and 94.0%, which when averaged gave 93.6% with a standard deviation of 0.6%. The starting 89b contained 6.6% of the epimer 89c (calculated from ^{13}C NMR data). Thus, in this case, C_3, C_4 should have contained 6.6% deuterium; from the above data, C_3, C_4 are calculated to have contained 6.4% $\pm$0.6% deuterium. Again, within the experimental error of ^{13}C NMR area determination, the reaction was 100% stereoretentive. For 124c the following ratios were calculated:

(C_8/C_{10})124c/(C_8/C_{10})124a = 94.2%; (C_9/C_{10})124c/(C_9/C_{10})124a = 100.4%; (C_8/C_2)124c/(C_8/C_2)124a x (C_2/C_{10})124c/(C_2/C_{10})124a = 94.2%; (C_9/C_2)124c/(C_9/C_2)124a x (C_2/C_{10})124c/(C_2/C_{10})124a = 100.6%; the average of these percentages was 97.4% with a standard deviation of 3.6% (again note the adjustment for the slight deuterium incorporation into C_2 during deuterogenation). The starting isomer 89c contained 0 to 2% of epimer 89b (estimated from ^{13}C NMR data). Thus, in this experiment, C_8, C_9 should have contained 0-2% deuterium; from the above data, C_8, C_9 are calculated to have contained 2.6% $\pm$3.6% deuterium. Within the experimental error (albeit unfortunately large in this case) the reaction was $\geq$98% stereoretentive. This could correspond to as much as 4% symmetrization of the bridgehead olefin intermediate.

The primary conclusion is that the intermediate bridgehead olefin (122a) was not symmetrical as in 158, but was unsymmetrical. Rehybridization at both carbon atoms of the double bond was not demanded (as in 159). Keese and Krebs (41), in their calculations on 1-norborene (48), found the structure (165), in which the bridgehead carbon had s character mixed into the p-orbital, but the C_2 carbon retained the p-orbital, favored. This structure (166) for bridgehead olefin (122a) might account for the results by causing the bridge (C_{11}) to lean toward one side, thereby

blocking attack from that side. The authors (41) found that a charge separation occurred in structure (165);



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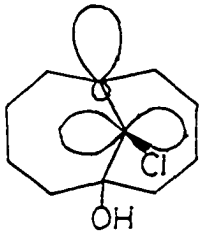

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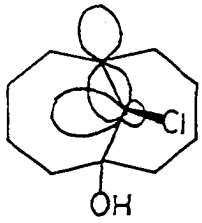

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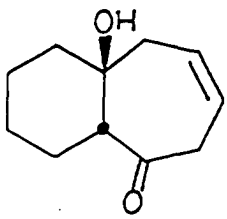
an ylid structure (62a) for 122a would place positive charge on C_{11}, which would make it difficult to explain the regiospecificity of the subsequent protonation in this system (117) and similar systems (114, 115, 118-21) including those without halogens (9, 17, 59). The other alternative (167) could account for the stereospecificity of the reaction, and the calculated charge separation would favor ylid structure 62b where the orbital at the bridgehead would be a p-orbital, and mixing of s character into the p-orbital at C_{11} would occur. This would explain the direction of protonation in these systems, although in either of these structures the dihedral angle between the two orbitals would still be large (based on examination of models) and thus the bond energy should still be smaller than for a structure like 159. Clearly, detailed, system specific,

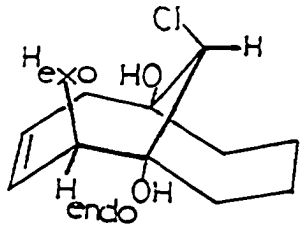
calculations should be undertaken, but the inescapable conclusion is that 122a does not symmetrize, probably because of rehybridization of the p-orbitals, as supported by calculations (73-75) and x-ray structures of similar systems (79-84).

Solvolysis of 11-Bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene

The silver-assisted solvolysis of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c) was executed in 90% aqueous acetone. Since the separation of the epimers was difficult, they were solvolyzed together and the yields reported are an average of two runs where the ratio of 89b to 89c varied (Equation 17); (the ratio of 89b:89c was 1 to 2). Benzocycloheptenone (91) and tetralin (168) were previously identified by Ledlie and Knetzer (109) as products in the solvolysis of 89a. The diols (176 and 177) were analogous to 125a isolated in the solvolysis of 87b;



180



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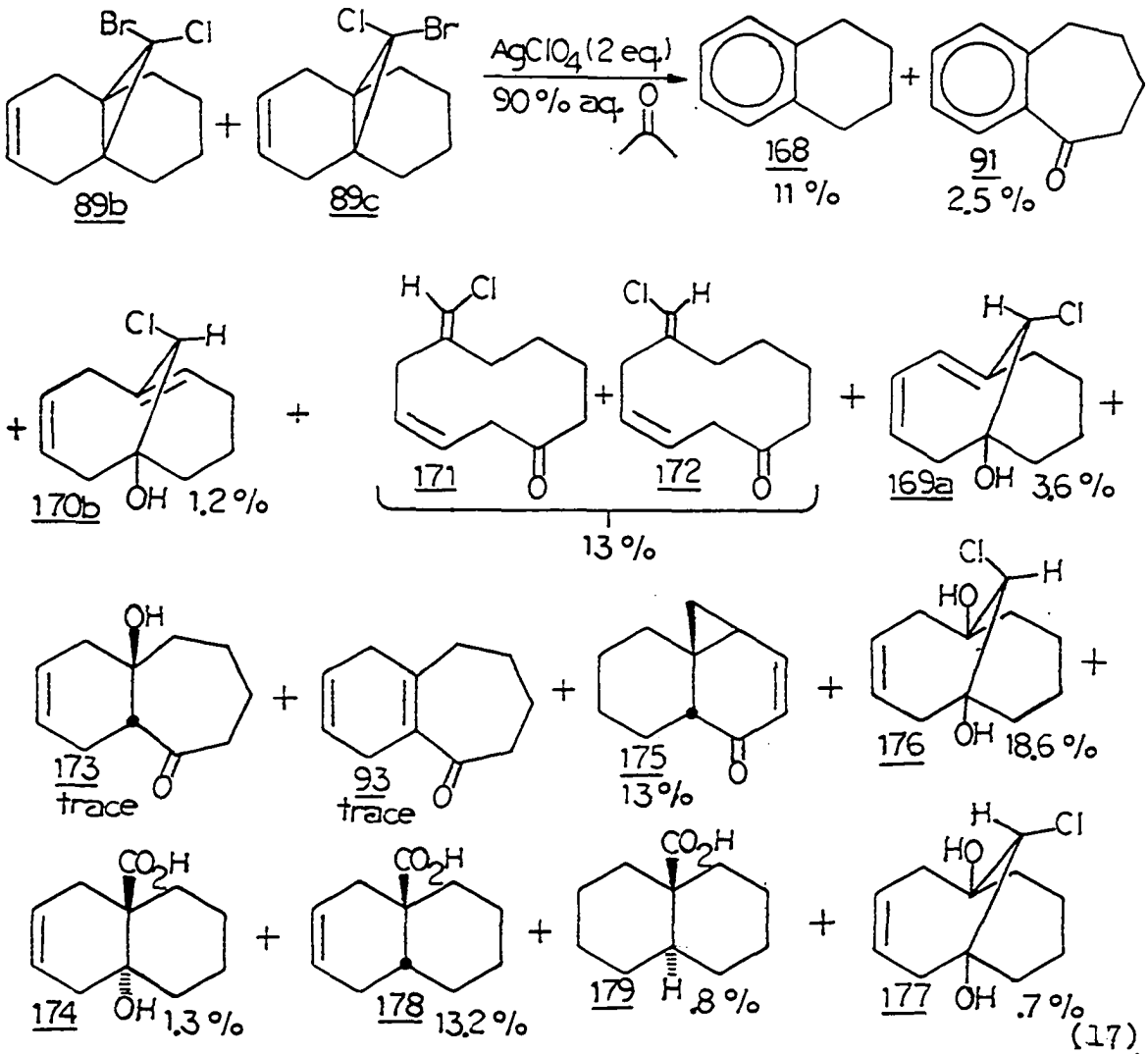
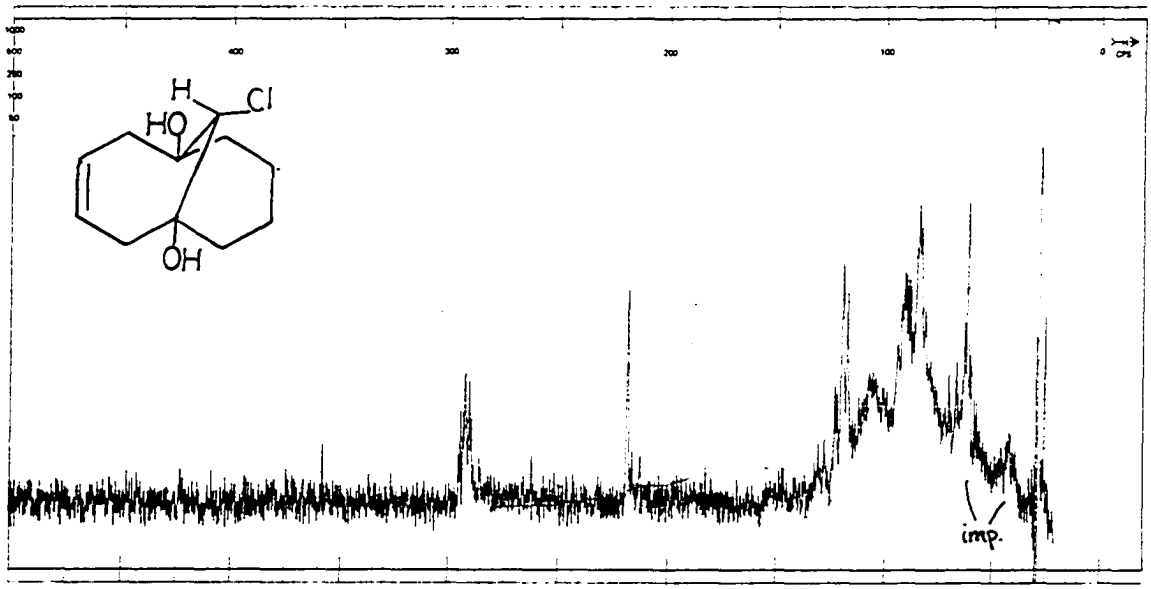
they were hydrogenated over platinum on carbon to give 125a. It was shown that 177 (Figure 23), which was isolated in low yield, could be rearranged to 173 and a trace of 93 and/or 91 under the hydrolysis conditions. In contrast, 176 was stable under the reaction conditions, while under forcing conditions (70°, sealed tube for 23 days) it gave three products, one of which was identified as hydroxyketone (180) (Figure 24). The stereochemistry of 176 (Figure 25) was





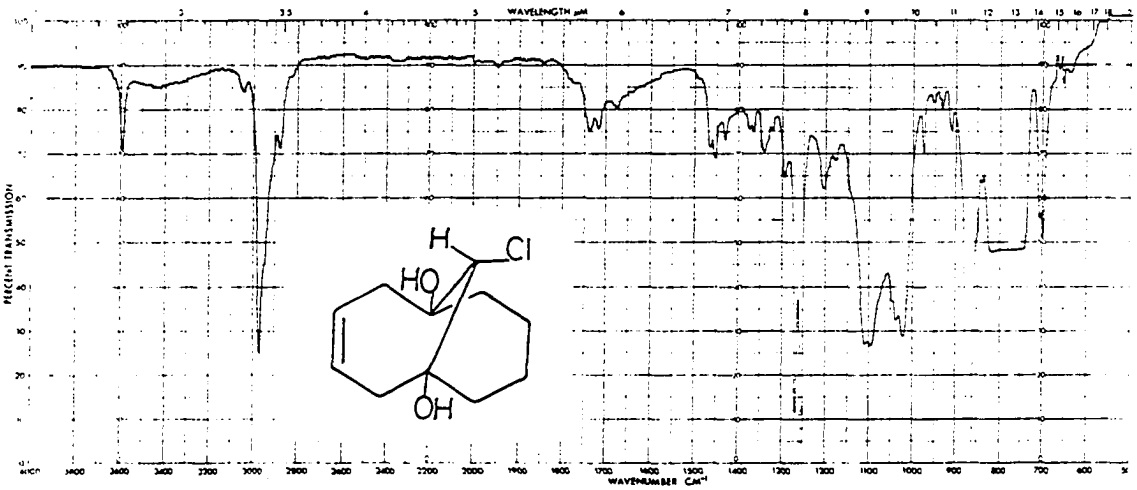


Figure 23. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of anti-11-chloro-1,6-dihydroxybicyclo-[4.4.1]undec-3-ene (177)

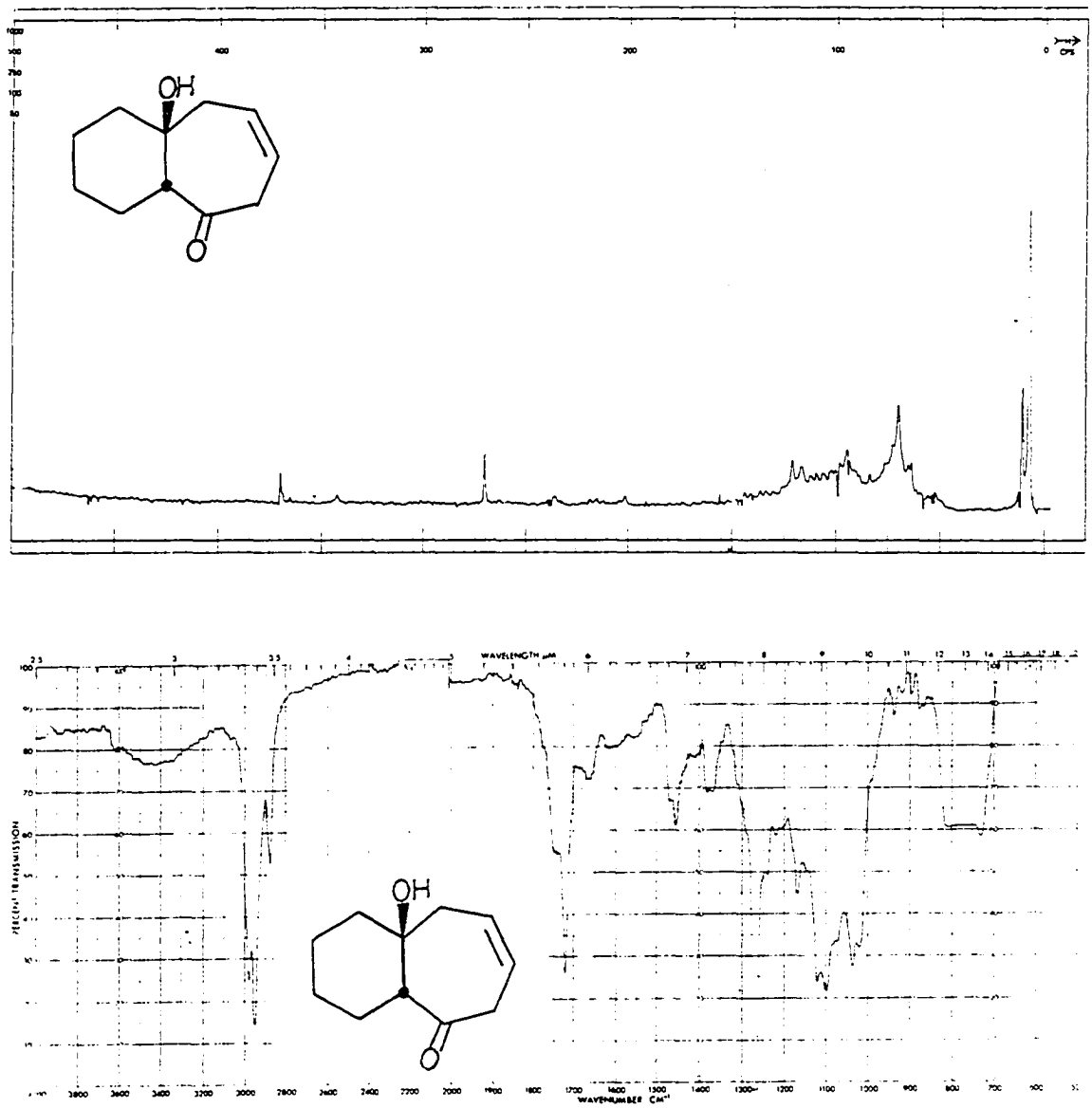


Figure 24. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of cis-7-hydroxybicyclo[5.4.0]undec-4-en-2-one (180)

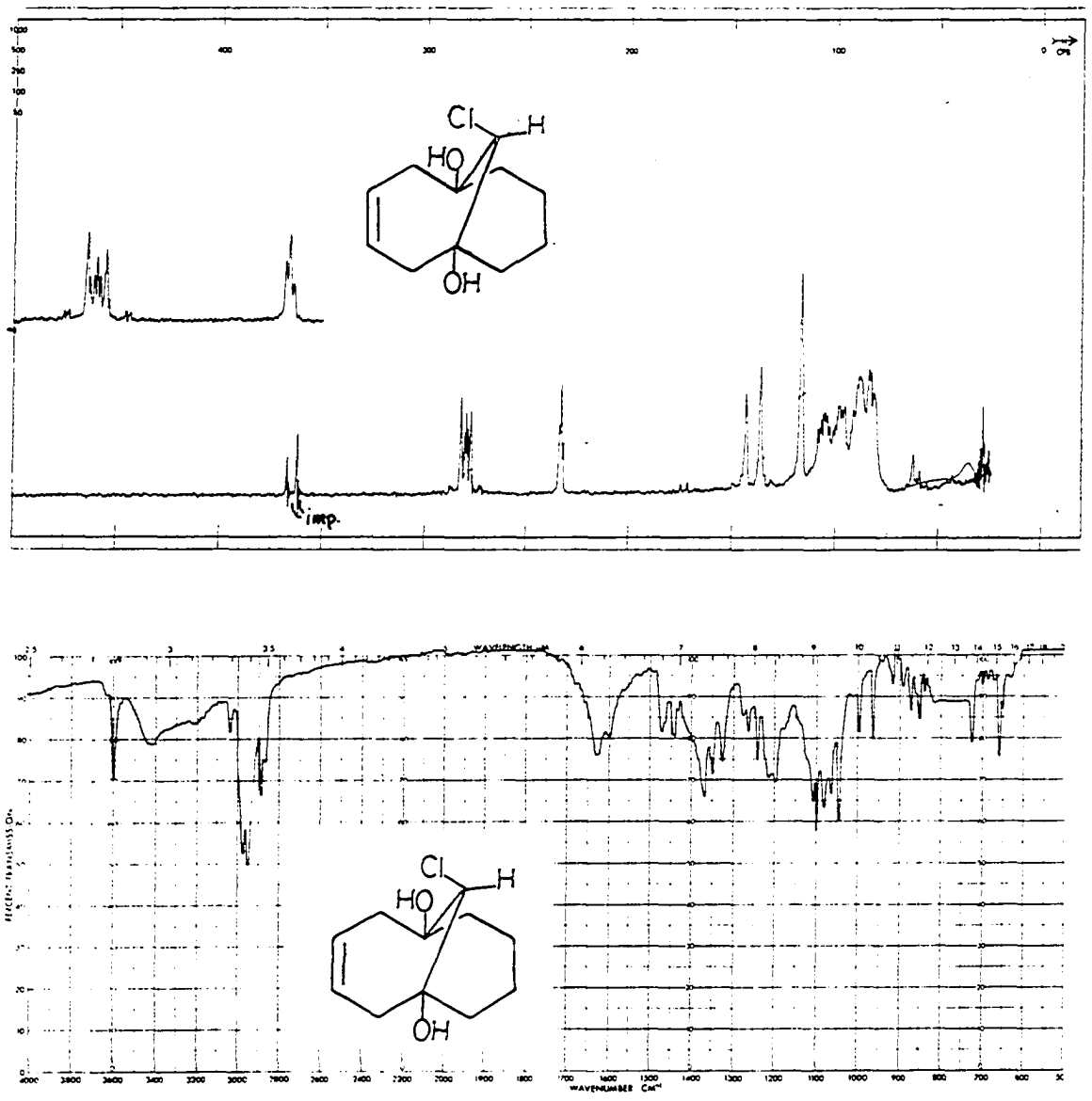
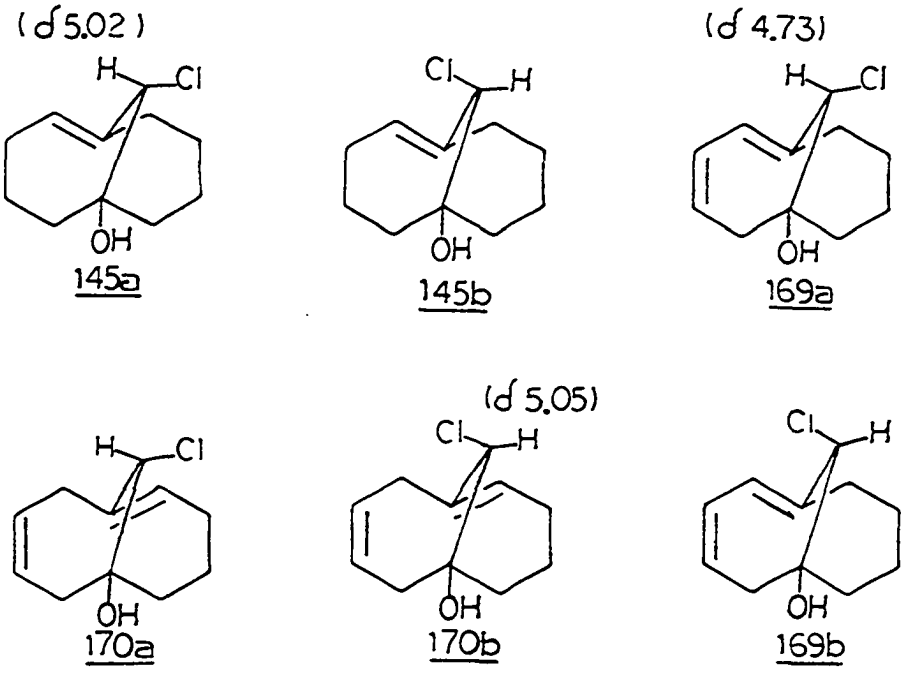


Figure 25. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of syn-11-chloro-1,6-dihydroxybicyclo-[4.4.1]undec-3-ene (176)

verified by ^{1}H NMR decoupling experiments, where long range coupling between the hydrogen on C_{11} and the endo-hydrogens on $C_{2,5}$ was observed. As was also the case for 112 (114), this was expected, since in conformation 181 (the saturated ring may be in a chair, rather than a boat, conformation) these hydrogens are in a "W" relationship. Contrariwise, in both 177 and 125a the hydrogen on C_{11} appeared as a singlet; in these cases, smaller or zero long-range coupling was predictable due to the less rigid conformation of the saturated 7-membered ring.



The compound 11-chlorobicyclo[4.4.1]undeca-1,3-dien-6-ol (169) (Figure 26) was found to be conjugated on the basis of its UV absorption (λmax = 2417Å, ε = 5700; note the

reduced extinction coefficient which is appropriate for a twisted diene) and its ^{1}H NMR olefinic absorptions at δ 6.13, while 11-chlorobicyclo[4.4.1]undeca-1(10),3-dien-6-ol (170) (Figure 27) was unconjugated, as shown by only end absorption in its UV spectrum and its ^{1}H NMR olefinic absorptions at δ 5.5. The stereochemistry at C_{11} for alcohols 145, 169 and 170 was assigned as follows. There are 2 possible stereoisomers for each of 145, 169 and 170, and these fall into 2 series: 145a, 169a, 170b and 145b, 169b, 170a. Since H_{11} of 169 is deshielded relative to H_{11} of 145, the structure of the former must be 169a, since H_{11} of 169b should not be deshielded by the $\Delta^{3,4}$ double bond. On the other hand, H_{11} of 170 has the same chemical shift as H_{11} of 145, whereby 170 must be 170b, with H_{11} anti to the $\Delta^{3,4}$ double bond. Further support for these chemical shift arguments came from the spectra of 177, 176 and 125a, where H_{11} of 177 (δ 4.39) is deshielded relative to H_{11} of 176 (δ 4.64) or 125a (δ 4.61). Finally, what is the structure of 145? It is known that a double bond oriented as in 145a deshields the proton above it (H_{11}). It seems inconceivable that H_{11} oriented as in 145b could have the same chemical shift as H_{11} of 170b. Therefore it seems certain that 145 has structure 145a, which is also in accord with mechanistic expectations. Both 169a and 170b were stable under the hydrolysis conditions.

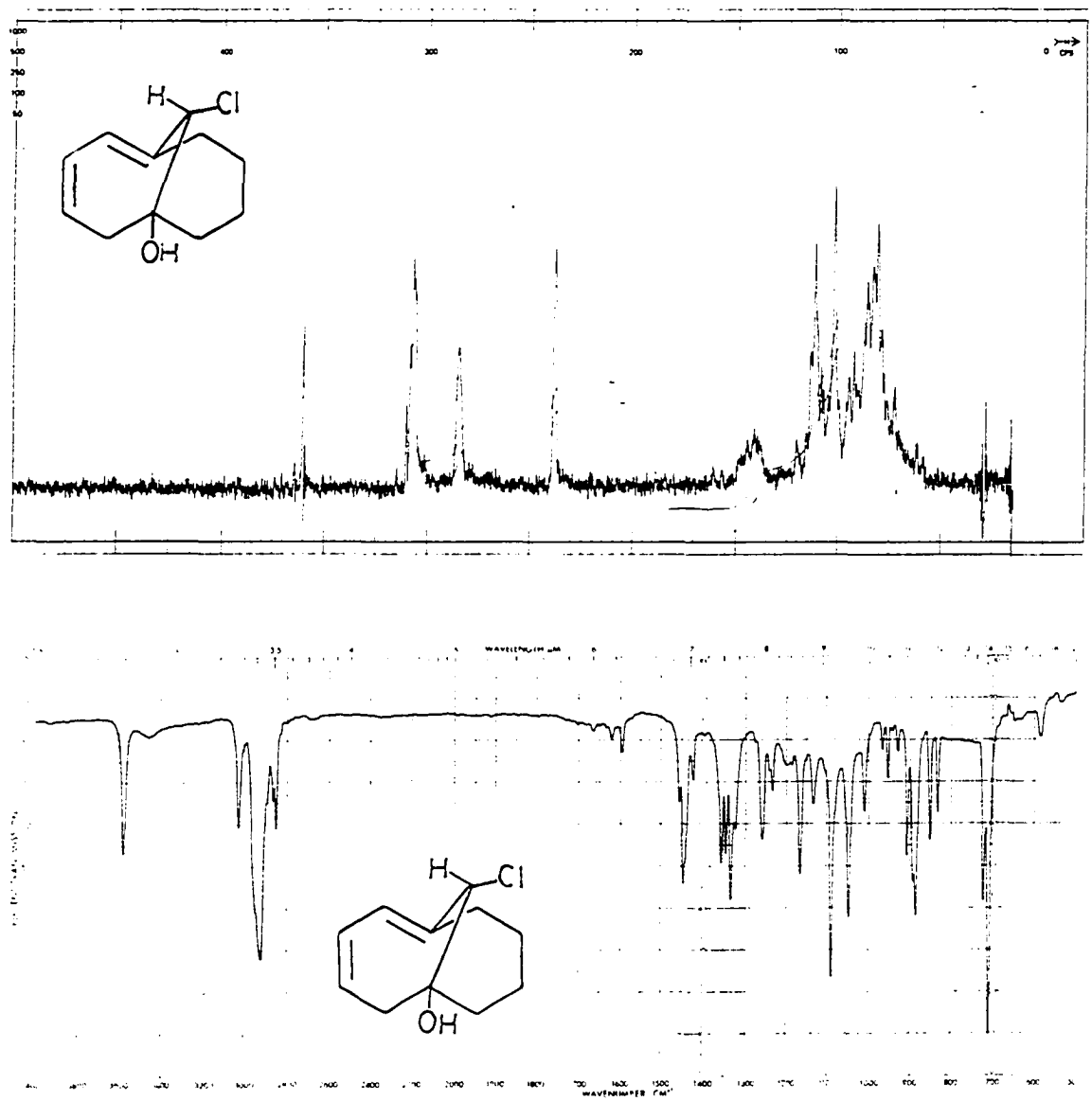
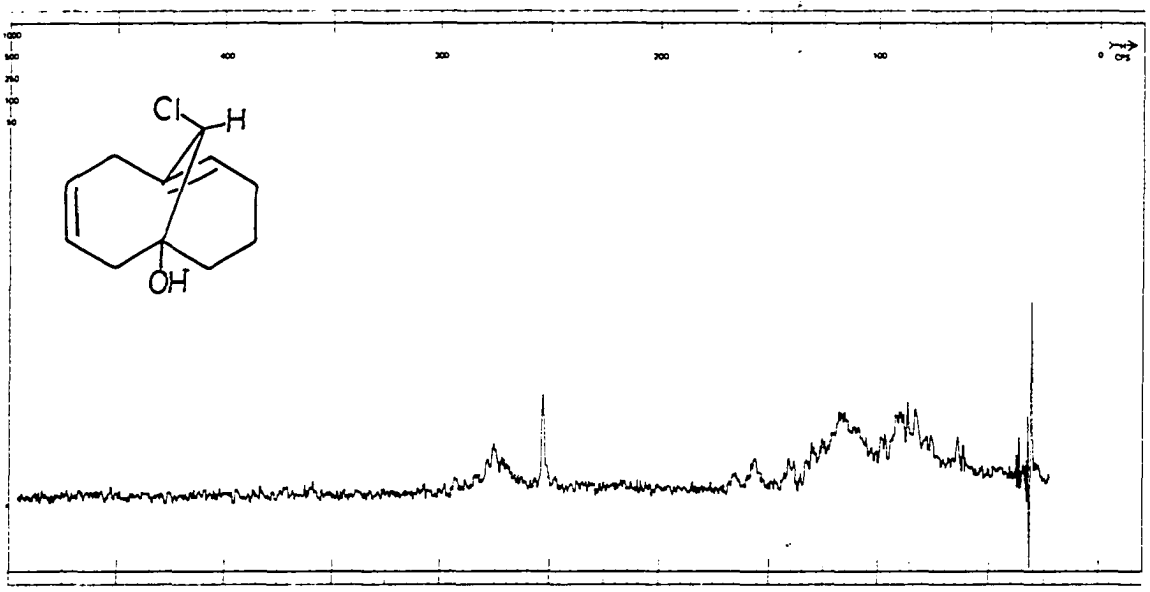


Figure 26. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of anti-11-chlorobicyclo[4.4.1]undec-1,3-dien-6-ol (169a)



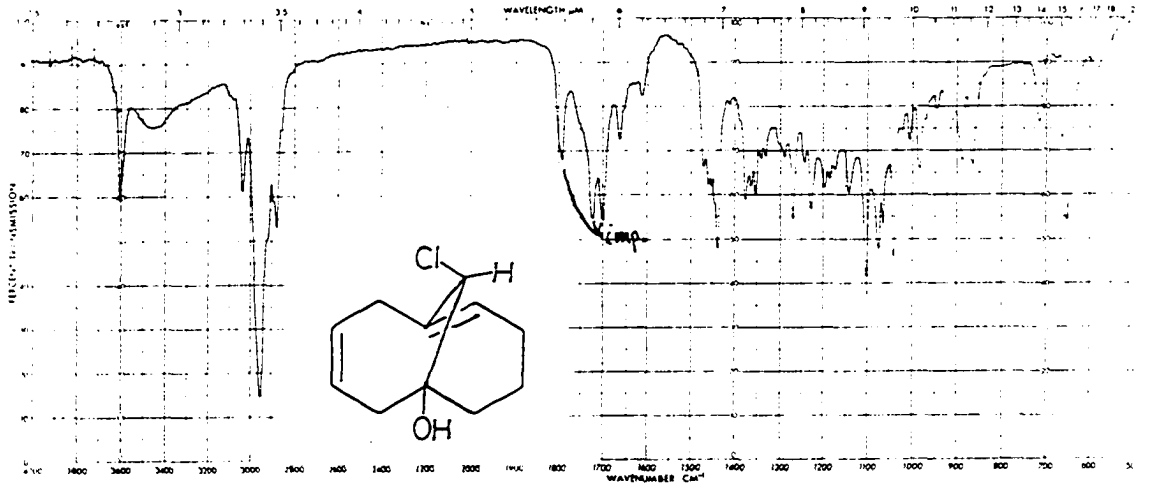


Figure 27. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of (11R, 6S) and (11S, 6R)-11-chlorobicyclo[4.4.1]undec-1(10),3-dien-6-ol (170b)

The isomeric monocyclic ketones 171 and 172 (Figure 28) were isolated as a mixture, with 172 predominant (see later for isolation of pure 171); their structures were assigned from their similarity to 124a. Both 173 (Figure 29) and 93 (Figure 30) were isolated in low yields and in some runs were not found at all. Their structures are based upon their spectral properties and their conversion to 93 and 91 respectively. The lack of a product (182) analogous to 93 was puzzling at first, but the stability of 176 and the isolation of 175 provided the keys to understanding the reaction paths involved. While it is difficult to precisely assess the reasons for the solvolytic stability of 176 vs. the reactivity of 177, it is noteworthy that the rearrangement of 177 involves the migration of an allyl group, which should be more prone to migration than the saturated group which must migrate in the rearrangement of 176 (e.g., under forcing conditions).

The structure of the cyclopropyl product (175) (Figure 31) was assigned from its spectra, in particular ^{1}H NMR decoupling experiments which provided an answer to the stereochemistry of the hydrogen alpha to the ketone. Irradiation of the absorption at δ 1.04 (which at first was attributed to a cyclopropyl hydrogen) caused the collapse of the alpha hydrogen (H_1) to a broad singlet. In conformer 183, the axial hydrogen on C_{11} is in the shielding cone of

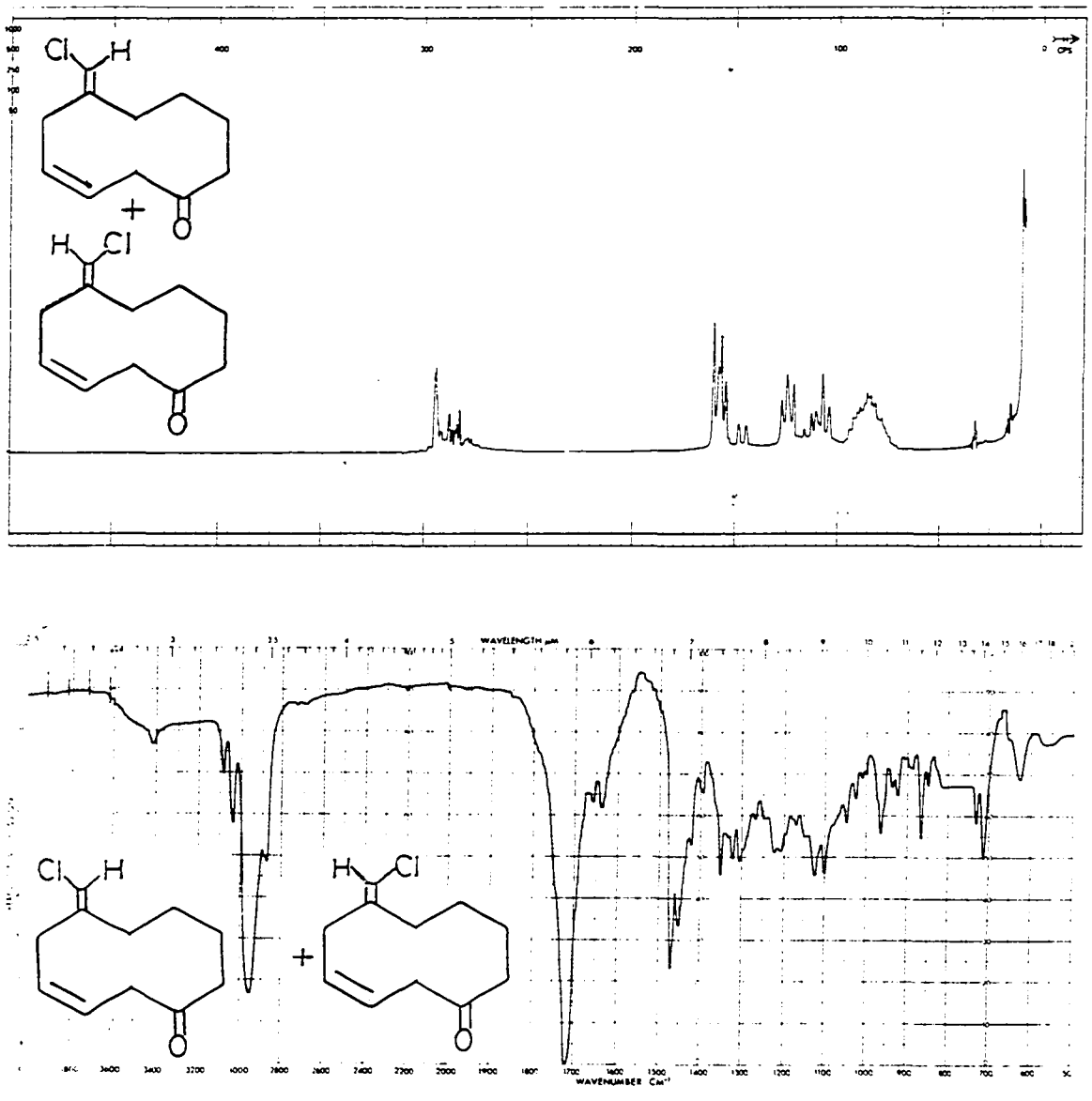


Figure 28. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of 6-chloromethylenecyclodec-3-enone (171 and 172)

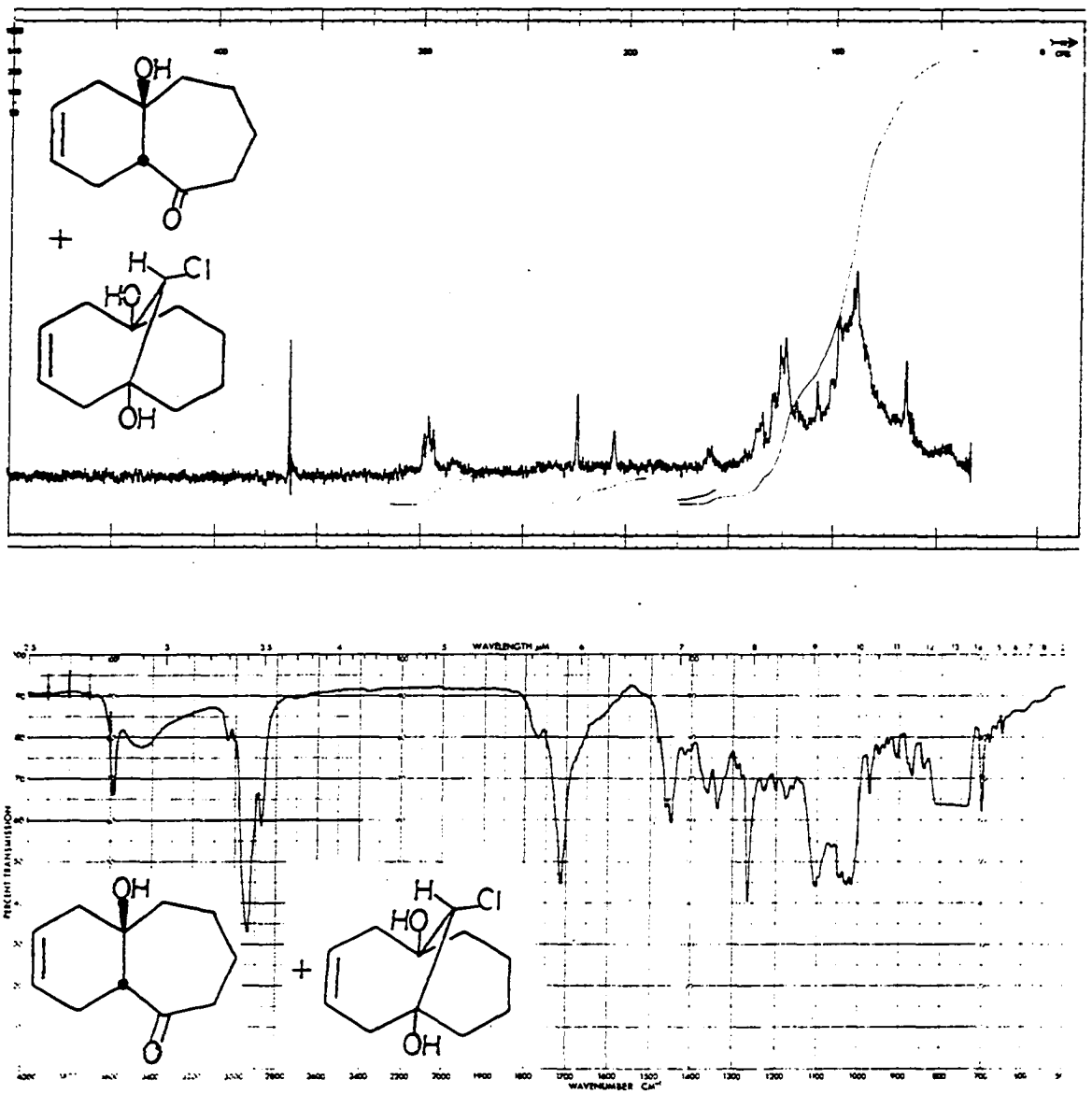


Figure 29. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of a mixture of cis-7-hydroxybicyclo-[5.4.0]undec-9-en-2-one (173) and anti-11-chloro-1,6-dihydroxybicyclo[4.4.1]undec-3-ene (177)

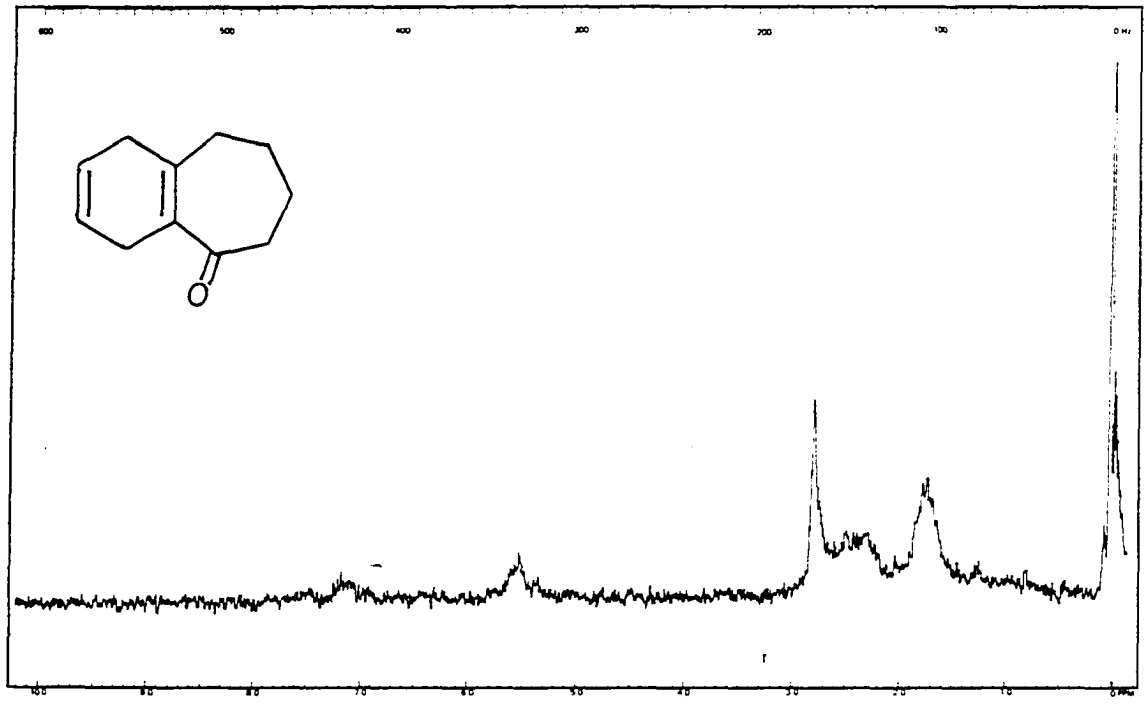


Figure 30. ^{1}H NMR (60 Mcps) spectrum of bicyclo[5.4.0]-undec-1(7),9-dien-2-one (93)

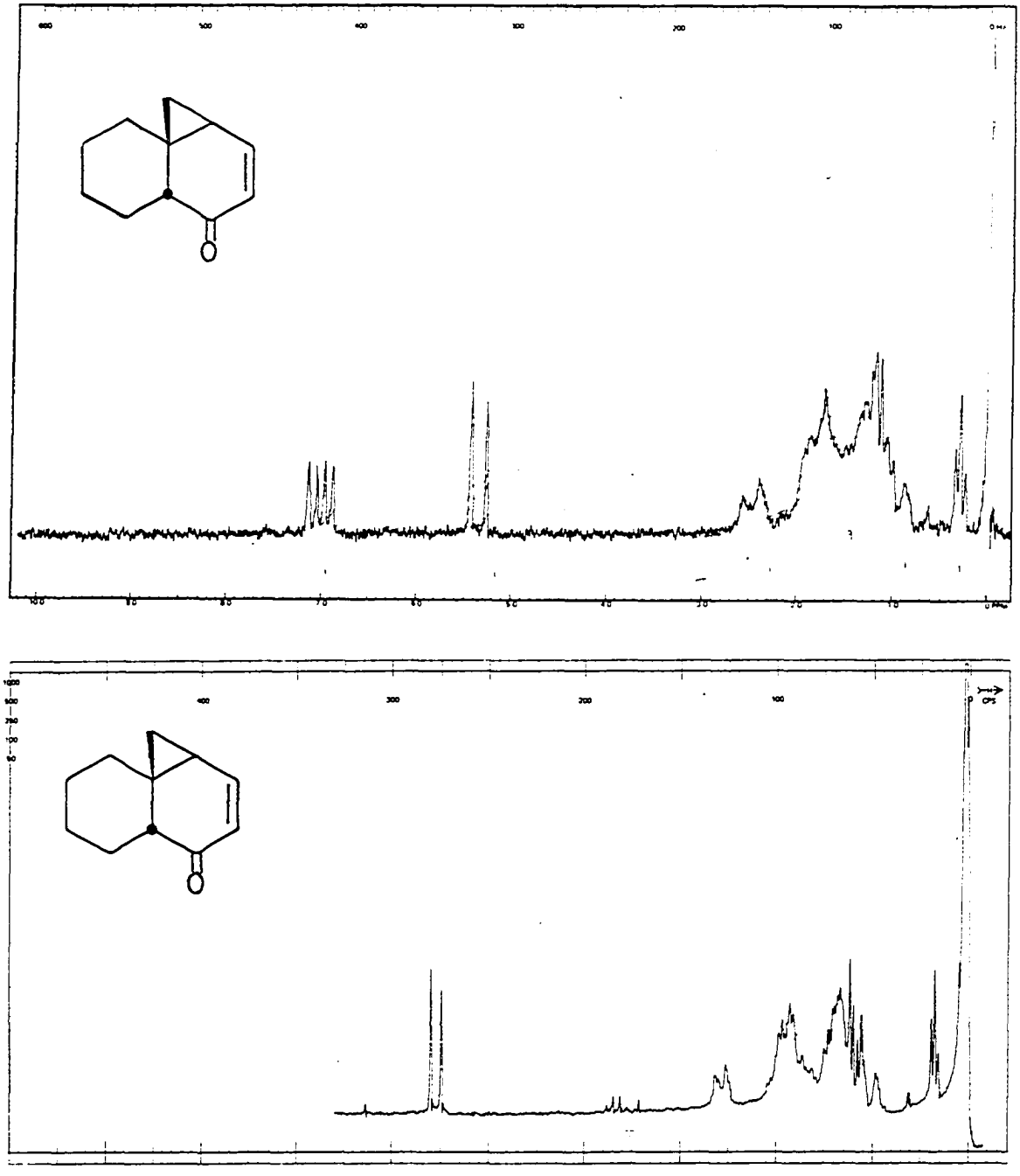
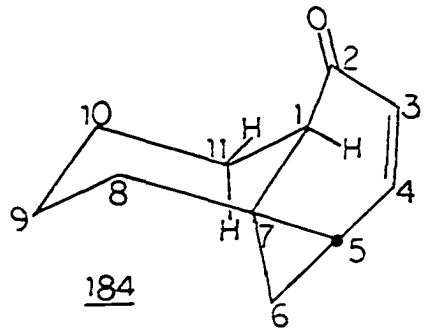


Figure 31a. ^{1}H NMR (top, 60 Mcps and bottom, 100 Mcps) spectra of cis-tricyclo[5.4.0.$0^{5,7}$]undec-3-en-2-one (175)



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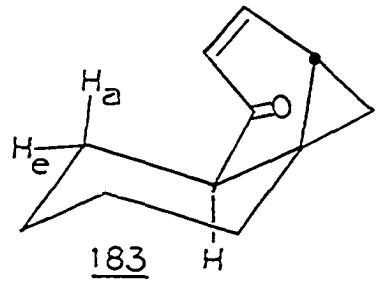

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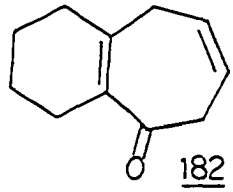

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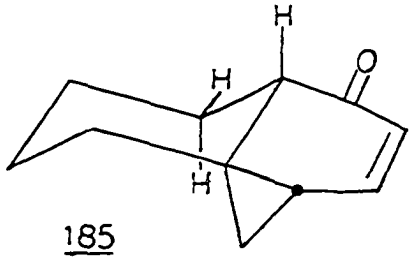

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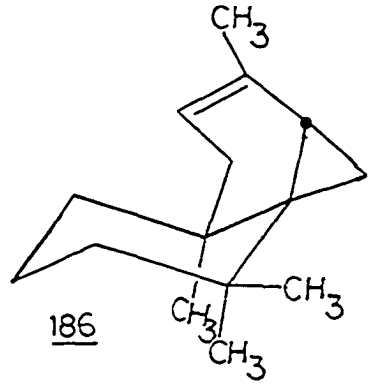


186

the double bond and would thus be shifted upfield; the absorption at δ 1.04 can thus be assigned to H_{11a}. The dihedral angle between H_{11a} and H_1 in 183 is 180°, which, from the Karplus relationship, should result in a coupling constant of about 10 Hz, which is close to the observed J=11Hz. In the other cis conformer (184), the dihedral angle between each proton at C_{11} and H_1 is about 45°, which should result

in a coupling constant of only ca. 4 Hz. The trans isomer (185) would have a dihedral angle of 180° between H_{11a} and H_1, but it is impossible to explain the observed upfield chemical shift of H_{11a} (δ 1.04) on the basis of the nuclear relationship present in 184. Of the two cis conformers (183 and 184), 183 has the C_1-C_2 bond in an equatorial position while in 184 it is axial; thus 183 should be favored, as was observed. A similar conformation of the natural product thujopsene (186) has been used to explain its ^1H NMR spectrum and photooxidation products (134). The

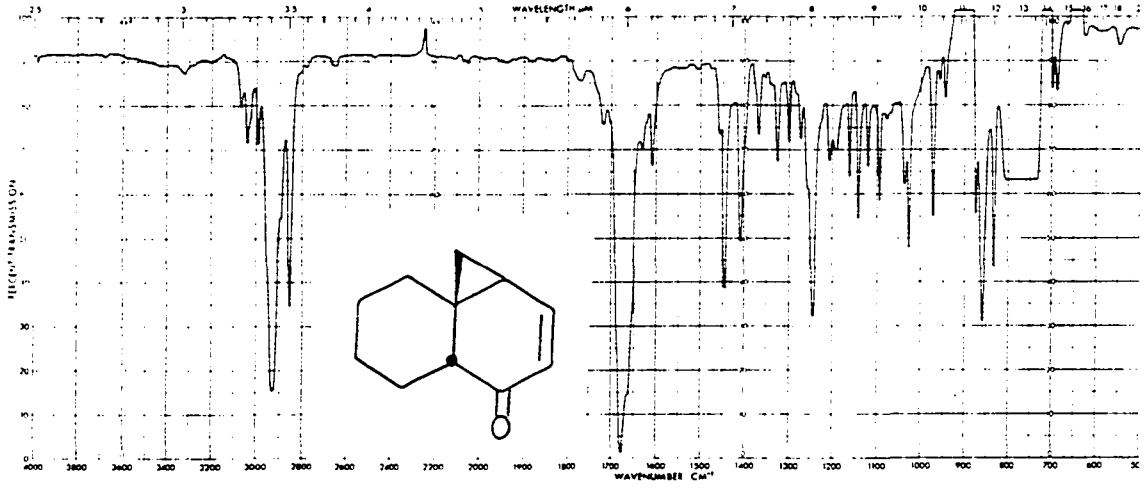
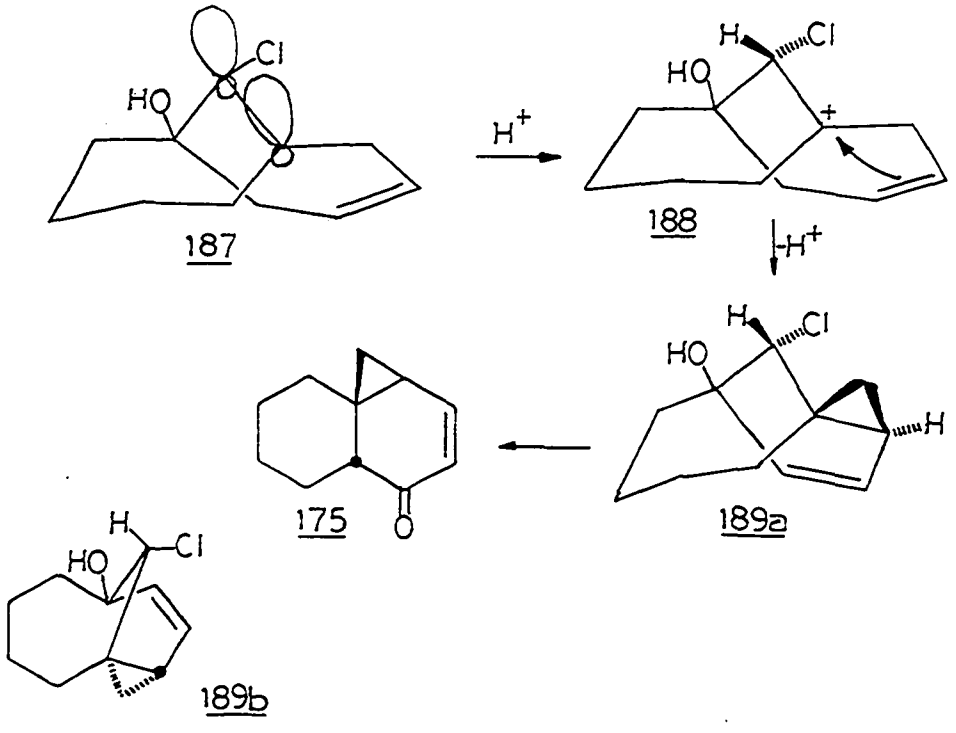


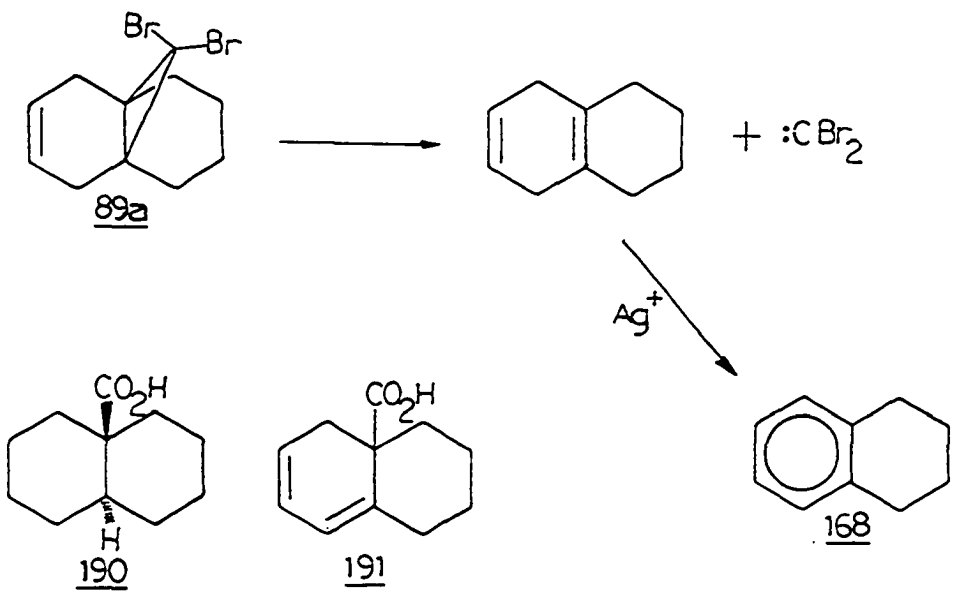
Figure 31b. Infrared spectrum of cis-tricyclo[5.4.0.$0^{5,7}$]-undec-3-en-2-one (175)

only reasonable mode for the formation of 175 is via solvolytic rearrangement of 189a. This postulate also nicely explains the stereochemistry of 175, for the precursor required to generate the trans isomer (185) is 189b, which would not be expected to form since it is an inside-outside bicyclic molecule (see below for details of 189a formation).



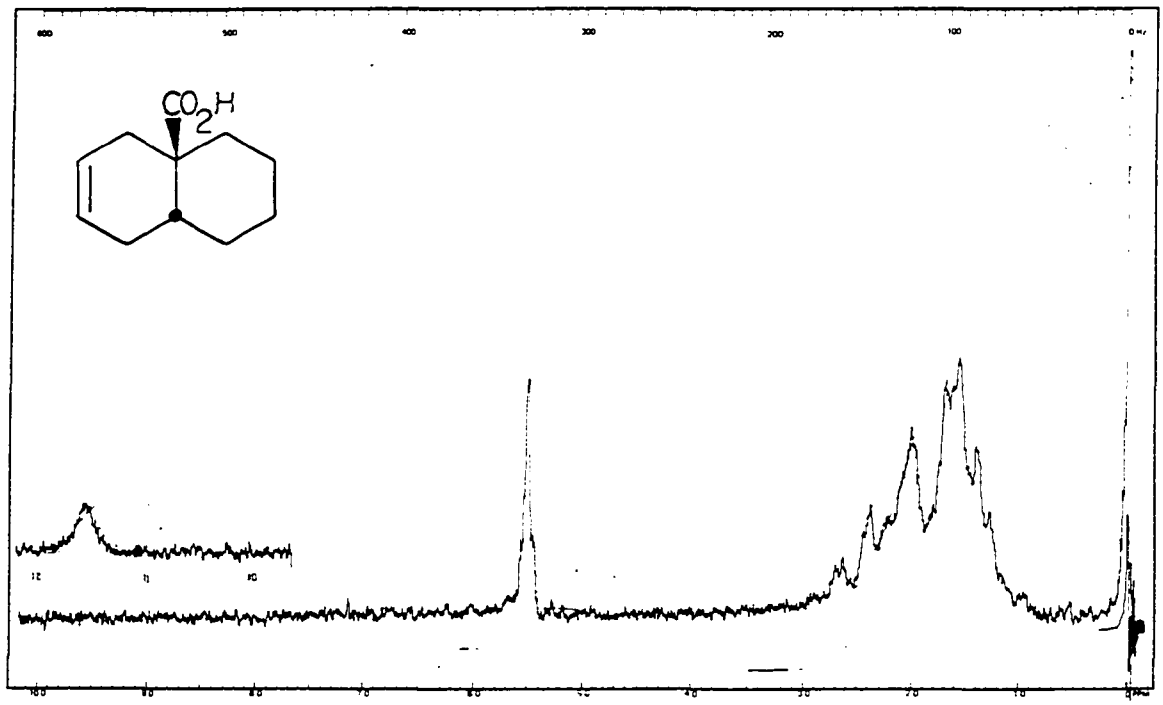
The isomeric acids 178 and 179 were identified by hydrogenation to the known cis- and trans-decalin-9-carboxylic acids (127 and 190), and comparison of their infrared spectra (135). The characteristic infrared peak at 11.5 μ for 178 (Figure 32) was close to the 11.26 μ peak for 127 and, correspondingly, the infrared peak at

9.8 μ for 179 (Figure 33) was similar to the 10.29 μ peak for 190. The hydroxy acid 174 (Figure 34) was isolated in low yield, and upon hydrogenation gave the known saturated hydroxy acid 144 (117). It is interesting that no acid (191) similar to 128 was isolated. Ledlie and Knetzer (109) postulated that the tetralin (168) formed in the reaction arose from a retro-carbene cleavage of 89a, followed by silver ion oxidation to the aromatic species (110) (Equation 18); Ledlie and Knetzer actually demonstrated the



(18)

second step of their proposed sequence. However, the retro-carbene reaction reported in the literature (136), which produces naphthalene directly, and the retro-carbenic decomposition of 192 observed in this laboratory (Equation 19) both require temperatures in excess of 100°. In contrast, 89a, 89b, 89c and 89d were all purified by



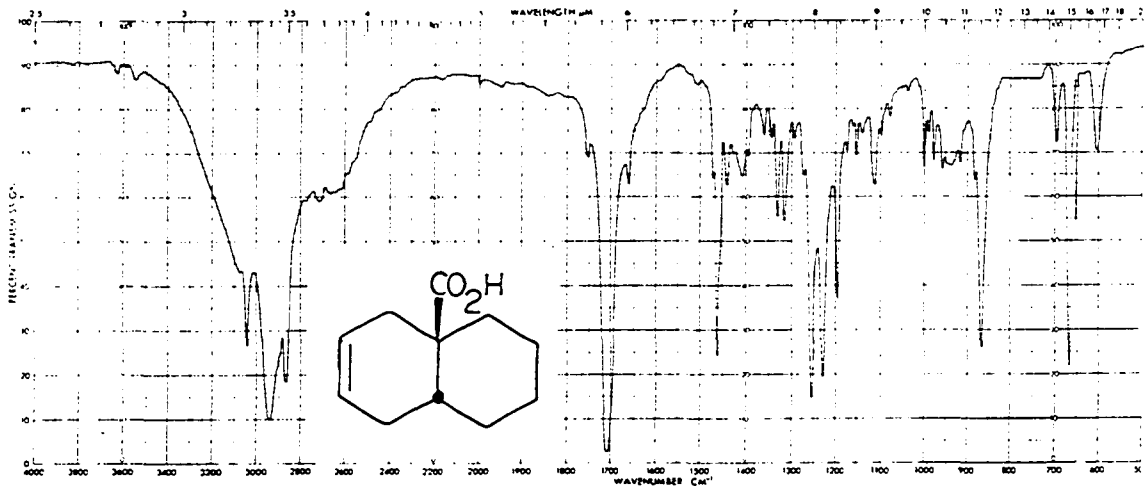


Figure 32. ^{1}H NMR (top, 60 Mcps) and infrared (bottom) spectra of cis-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (178)

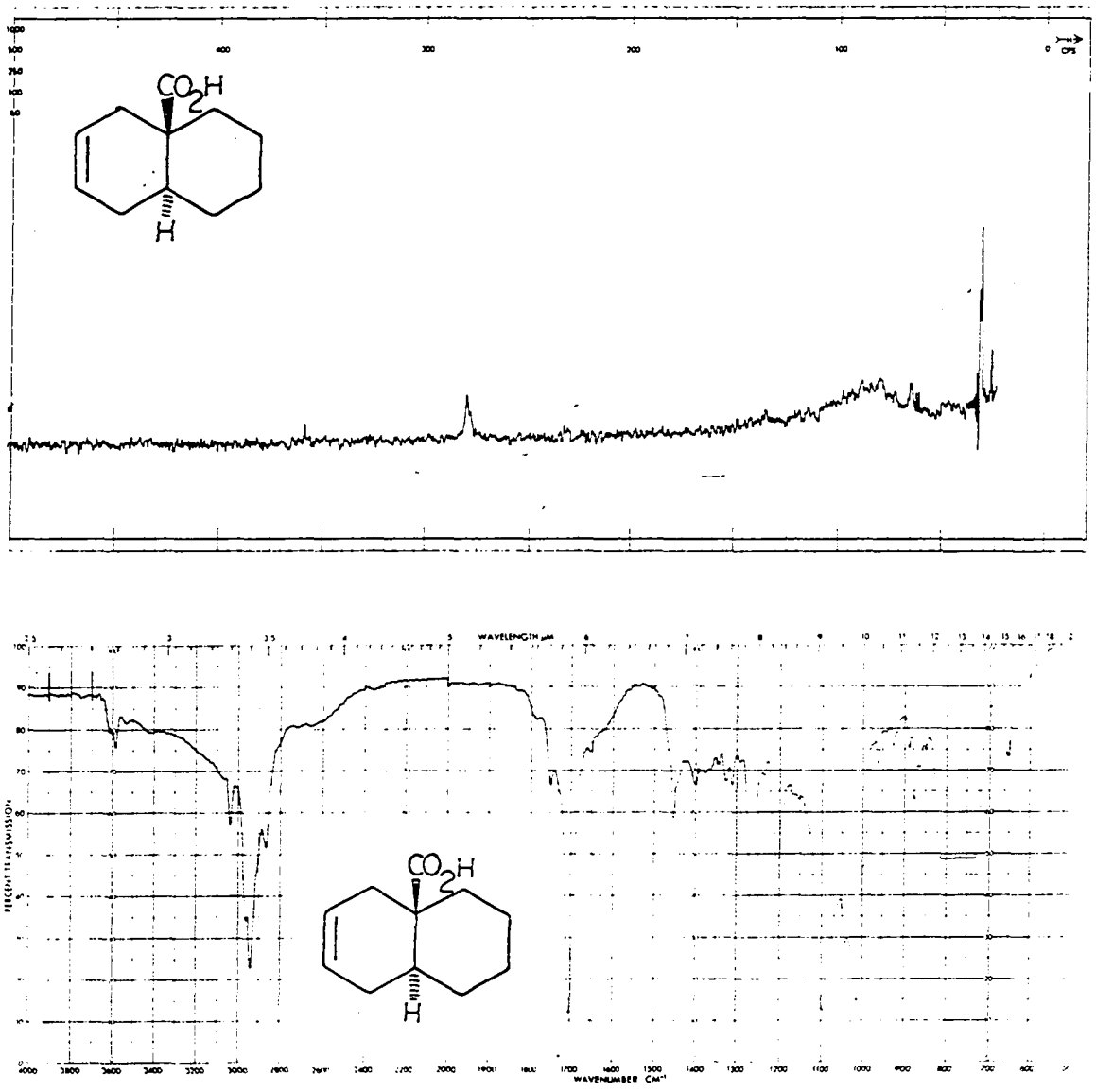


Figure 33. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of trans-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (179)

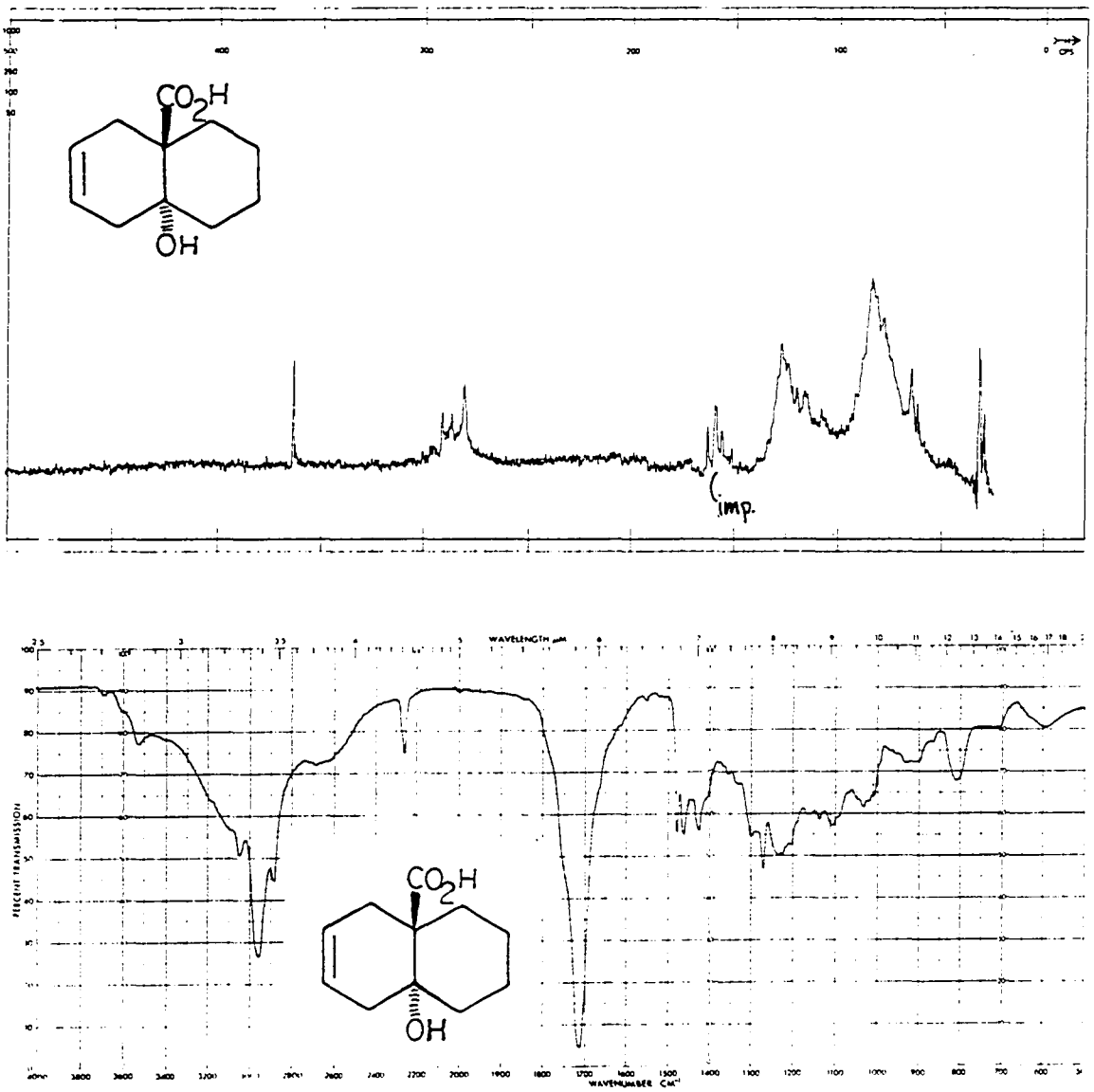
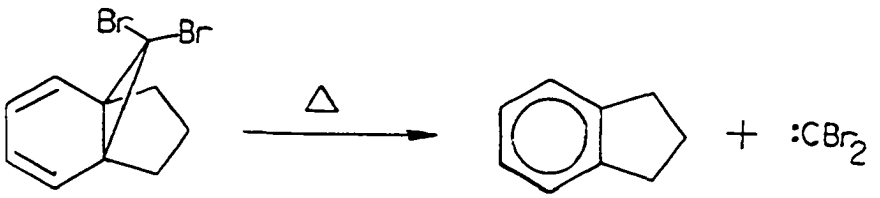


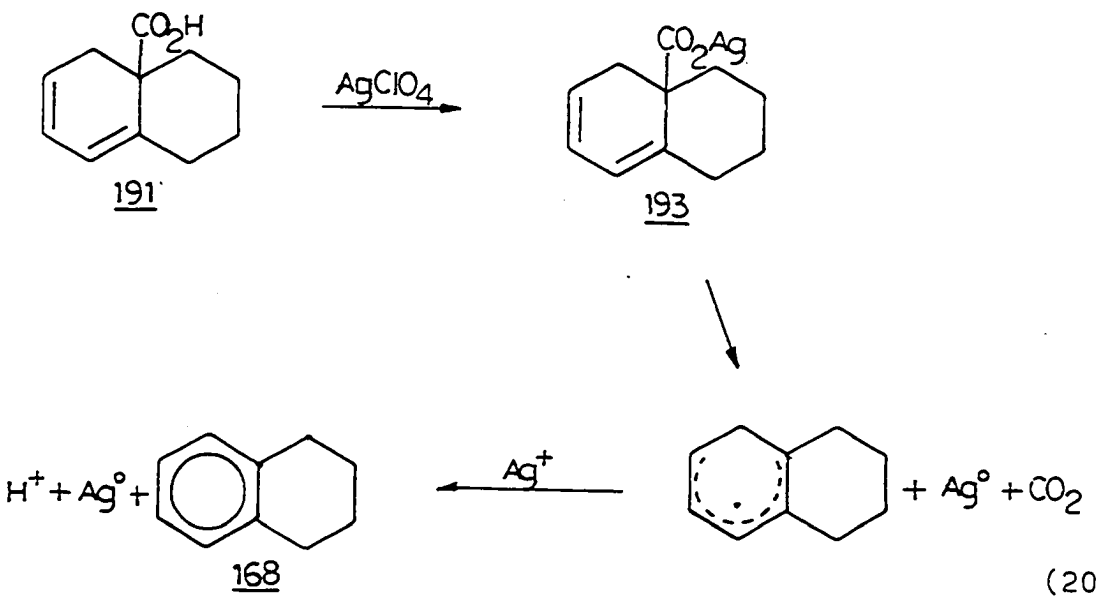
Figure 34. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of trans-6-hydroxybicyclo[4.4.0]dec-3-ene-1-carboxylic acid (174)

distillation under reduced pressure at 75-90° with no apparent decomposition. Thus it seems unlikely that the



192 (19)

tetralin (168) arose as indicated by Ledlie and Knetzer (109), especially at room temperature. It seems reasonable that a silver carboxylate (193) could form which would decompose to give tetralin and elemental silver (Equation 20).



191 193 168 (20)

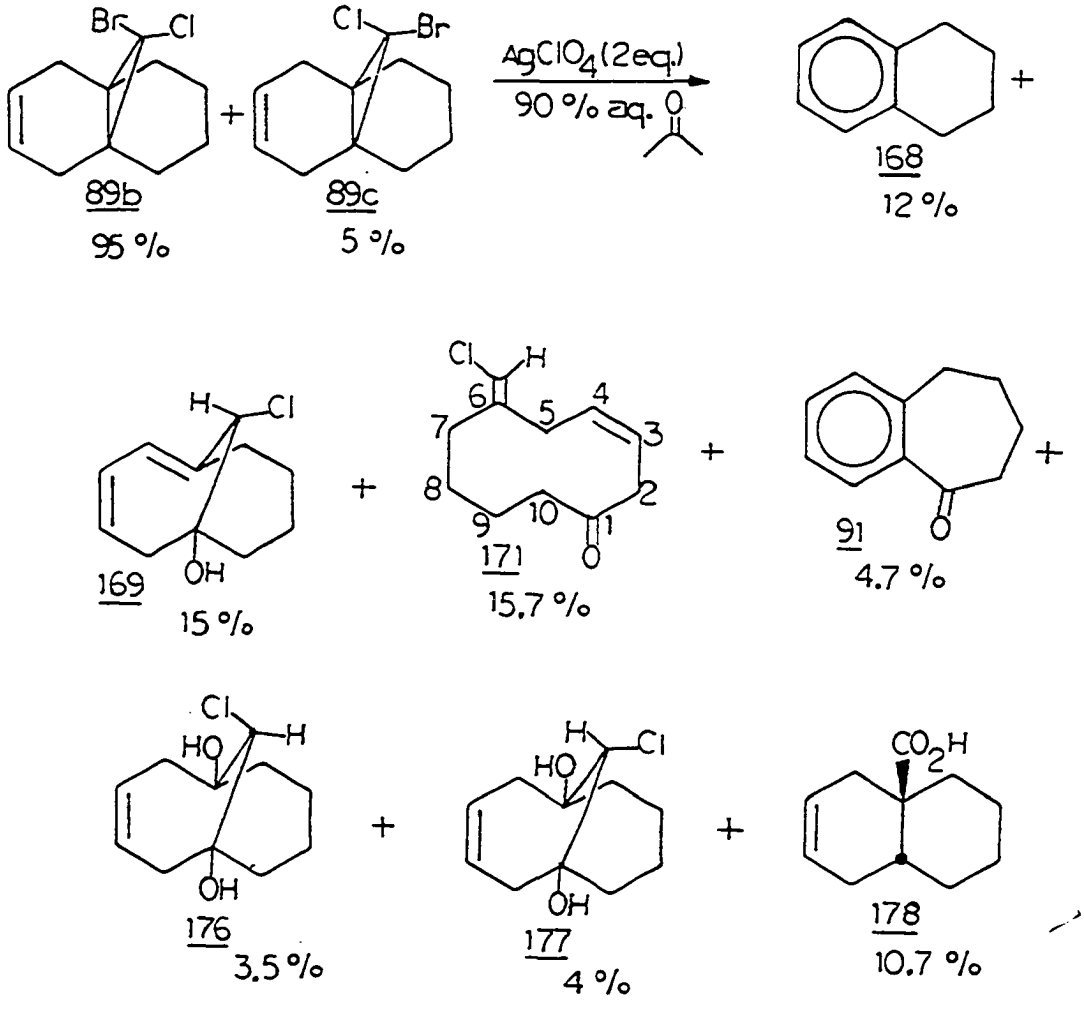
This decomposition of the silver carboxylate is similar to the process which occurs in the Hunsdieker reaction (137), and there is some evidence for the formation of silver carboxylates in acidic solutions (137c). The presence of finely divided silver metal was in fact observed in the reaction, but it could also have resulted from the oxidation of 93 to 91.

After solvolysis of the synthetic mixture, the recovered 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene was enriched in epimer 89b, which resulted in the separation technique used to obtain pure 89b. This observation was contrary to the reported silver-assisted solvolysis rates observed by Ledlie et al. (119) for 89e and 89f, where the syn-bromide (89e) was 3 times more reactive than the anti-bromide (89f). It was also contrary to the results obtained with dibromide 89a, where the major product (91) arose from ionization of the bromine syn to the double bond (i.e., 91 was obtained from 89b, but not 89c). Because of the relative rate anomalies, the monobromides (89e and 89f) were investigated further. They (89e and 89f) were synthesized and the original structure assignment (125) verified by a ^{13}C NMR study. Next the methanolysis rates of 89e and 89f were determined (using Ledlie's conditions - a 20 fold excess of silver ion (119)), and 89e was again found to be more reactive than 89f (by a factor of 2); the same results

obtained in 90% aqueous acetone with 5 eq of silver ion. But the solvolyses of 89b and 89c were conducted with only 2 eq of silver ion. When 89e and 89f were methanolyzed with 1 eq of silver ion, 89f was more reactive! This reactivity reversal may be due to the complex kinetic role of silver ion, where at high silver ion concentrations 2 or more silver ions may be involved in the transition state, whereas at low concentrations, the reaction becomes first-order in silver ion. Certainly complexation of the double bond does occur (114a). In any event, anomalous effects with silver ion have been observed in other systems (vide infra).

Silver-assisted solvolysis of 89b (95%) and 89c (5%) in 90% aqueous acetone gave the products illustrated in Scheme 13. Only one monocyclic ketone (171) (Figure 35) was isolated; its purity was indicated by its ^{13}C NMR (only 11 lines after 28,672 scans) and its ^{1}H NMR. The stereochemistry was assigned from the deshielding by Cl of the allylic protons on C_7 (δ 2.20), whereas in 172 the allylic protons on C_5 are deshielded (δ 3.12) by the chlorine atom, as well as the results in other systems (114b) (vide supra the solvolyses of 141a and 141b). Diene 169 was isolated in 15% yield, to the exclusion of any other dienes. Diols 177 and 176 (176 was the major product in the solvolysis of a mixture of 89b and 89c)

Scheme 13



were isolated in about equal yields. This indicated that 176 arose from 89c and is the only bridgehead olefin mediated product isolated from the 5% of 89c present in the starting material (Scheme 13). The absence of diene 170 (and isomeric dienes 189 or 190) implies that 89b gave conjugated diene 169, while 89c gave the unconjugated diene 170 (but in lower yield).

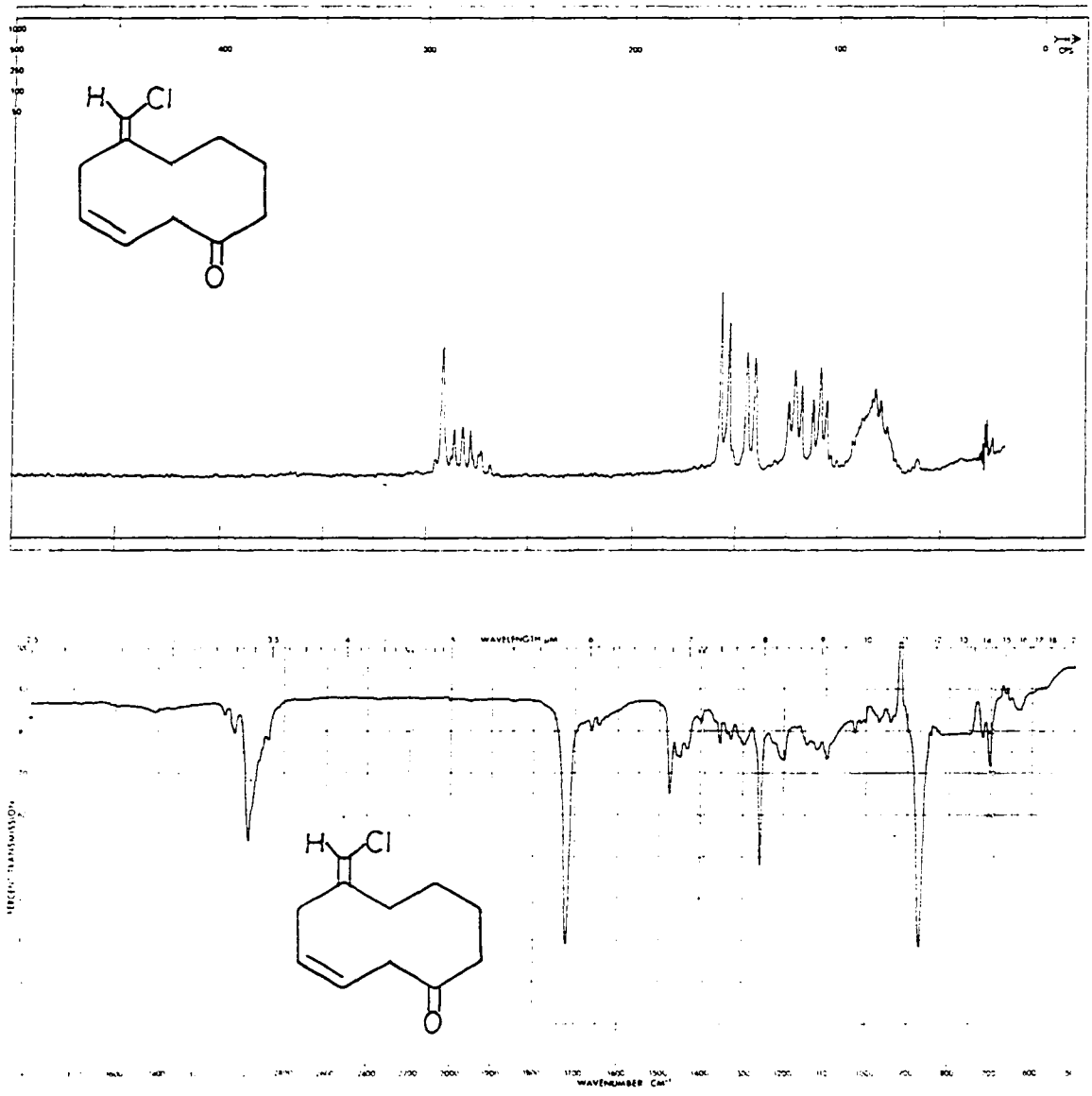
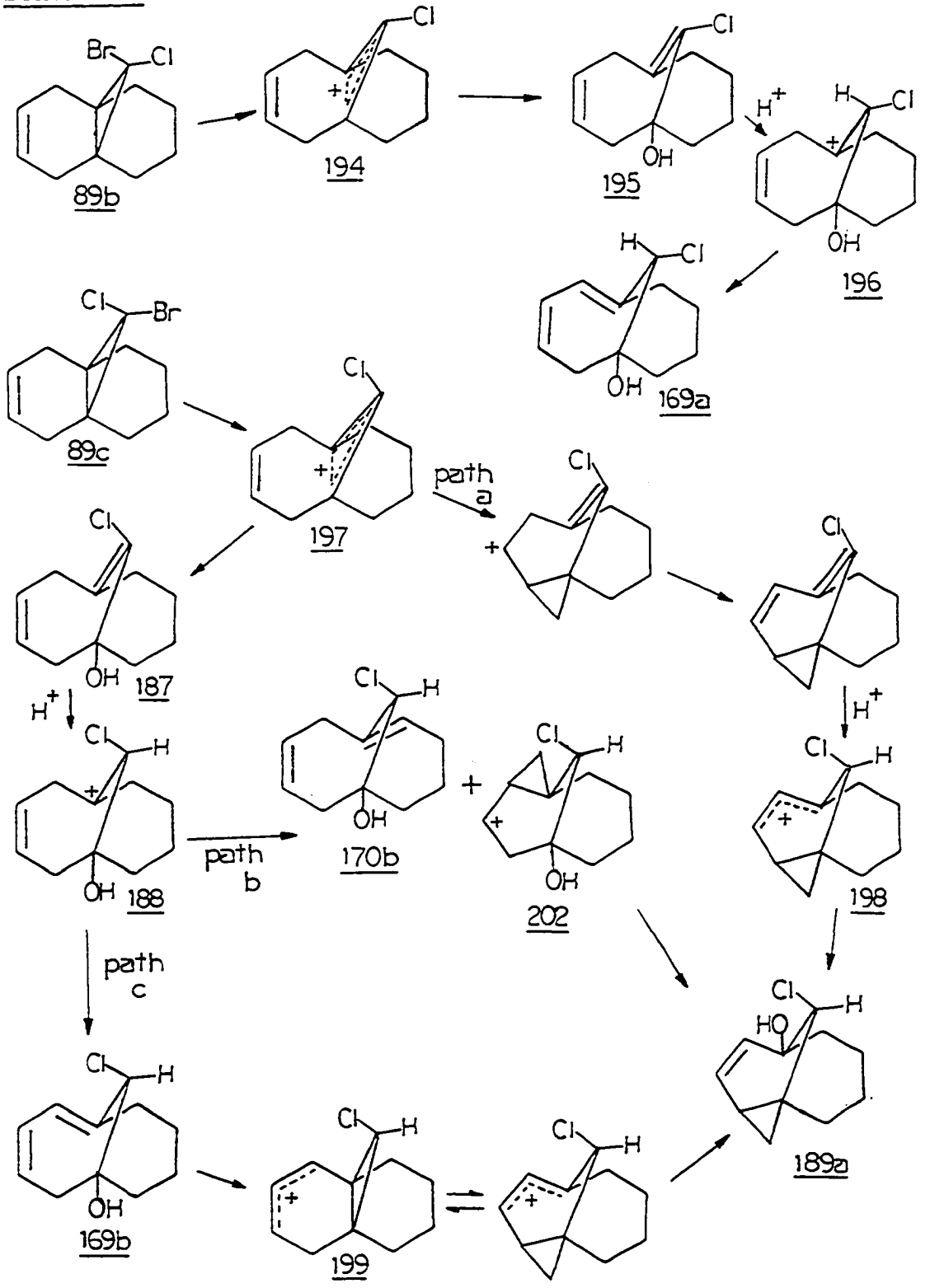


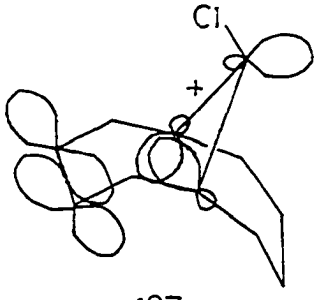
Figure 35. ^{1}H NMR (top, 100 Mcps) and infrared (bottom) spectra of 6-chloromethylenecyclodec-3-enone (171)

The stereospecific formation of monocyclic ketones 171 and 172 and of bicyclic diols 176 and 177 was expected based on the deuterium labeling studies. However, how can the stereospecificity and regiospecificity in the formation of 169a and 170b be explained? Also, why did 175 form uniquely from 89c? First let us consider the overall mode of formation for 169a, 170b and 189a (the previously discussed source of 175) (Scheme 14). Clearly, 169a and 170b must stem from the protonation-deprotonation of bridgehead olefins 195 and 187, respectively. The pathway to 189a is less certain. The route indicated as path c (Scheme 14), i.e., passing through unobserved diene 169b, can be eliminated from consideration not because of the observed stability of 169a and 170b, but rather due to the stability of 200 (114). Path a is less readily dismissed. Certainly the double bond in 197 is oriented favorably for interaction with the bridgehead (see 197a), but such interaction should be antihomoaromatic (if symmetrical) in nature. Yet the double bond of 89c is less decelerative than that of 89b, the cation from which has a parallel (noninteractive) alignment of π and bridgehead orbitals (see 194a). In the absence of sophisticated calculations, the precise significance of these observations cannot be ascertained. As for path a, it certainly seems likely that were it operative,

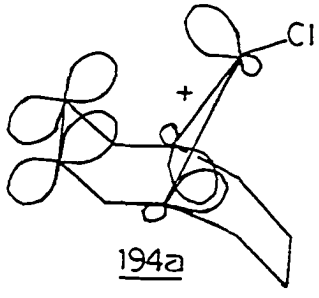
Scheme 14


Br
Cl
89b
194
195
196
169a
89c
197
path a
187
path b
188
170b
202
198
path c
169b
199
189a
H+
OH
HO

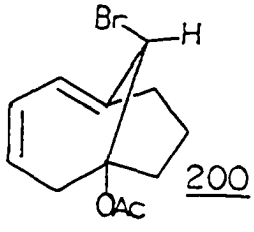
intermediate ion 198 would revert to 199 and produce some cycloheptatriene product 201, which is not observed. This



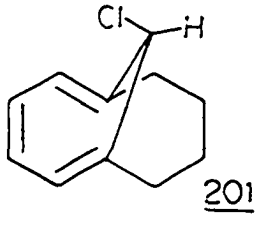
197a



194a



200

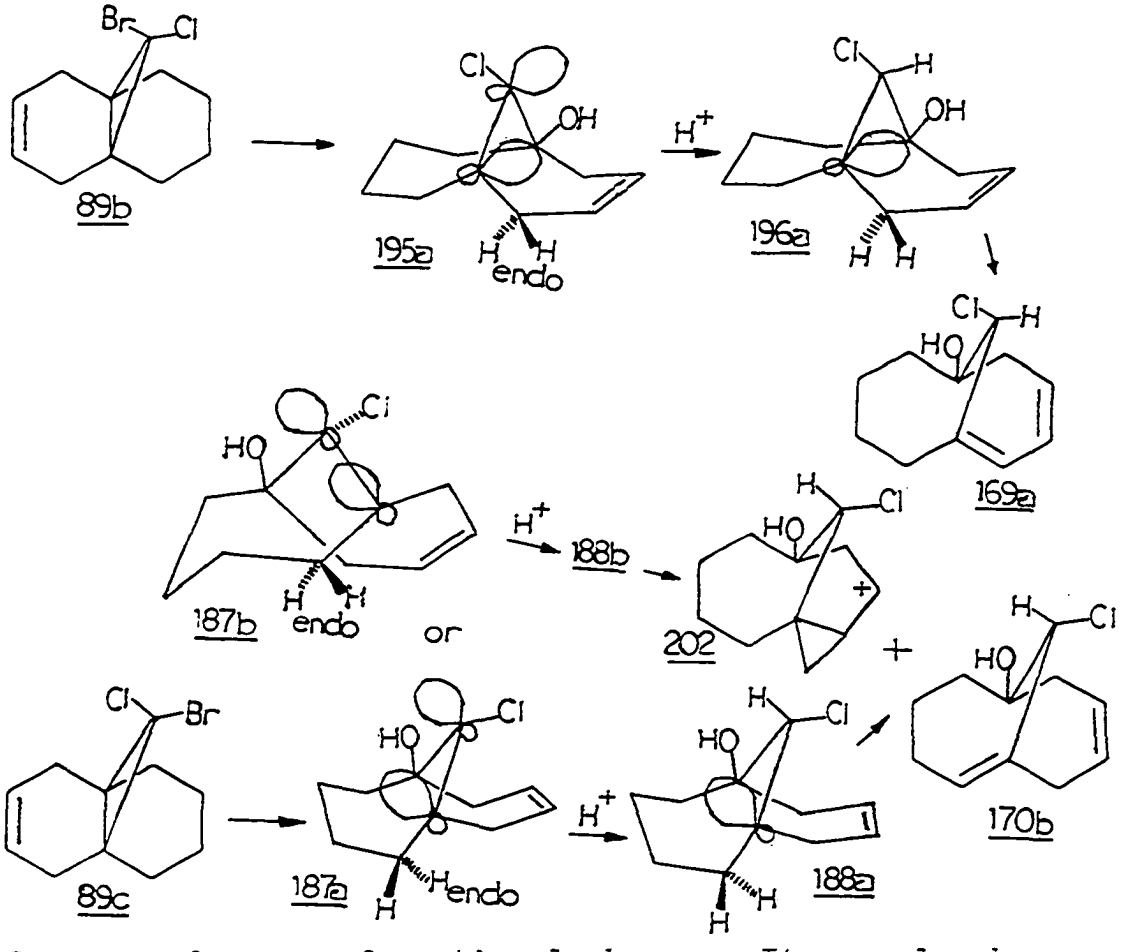


201

leaves path b as "most likely" the route to 189a; path b would be favored by the principle of "Okham's Razor", if by nothing else.

But why are 169a and 170b formed to the exclusion of 169b and 170a, and why does ion 188 decay to ion 202, whereas ion 196 does not undergo a similar process? Answers to these questions are best obtained by considering the detailed structures of bridgehead olefins 187 and 195 and ions 188 and 196. If models of 187 and 195 are constructed with rehybridized orbitals at C_{11}, with or without rehybridization at C_1 (of course, rehybridization at C_1 affords better π overlap), it is found that the best overlap is obtained when the unsaturated seven-membered

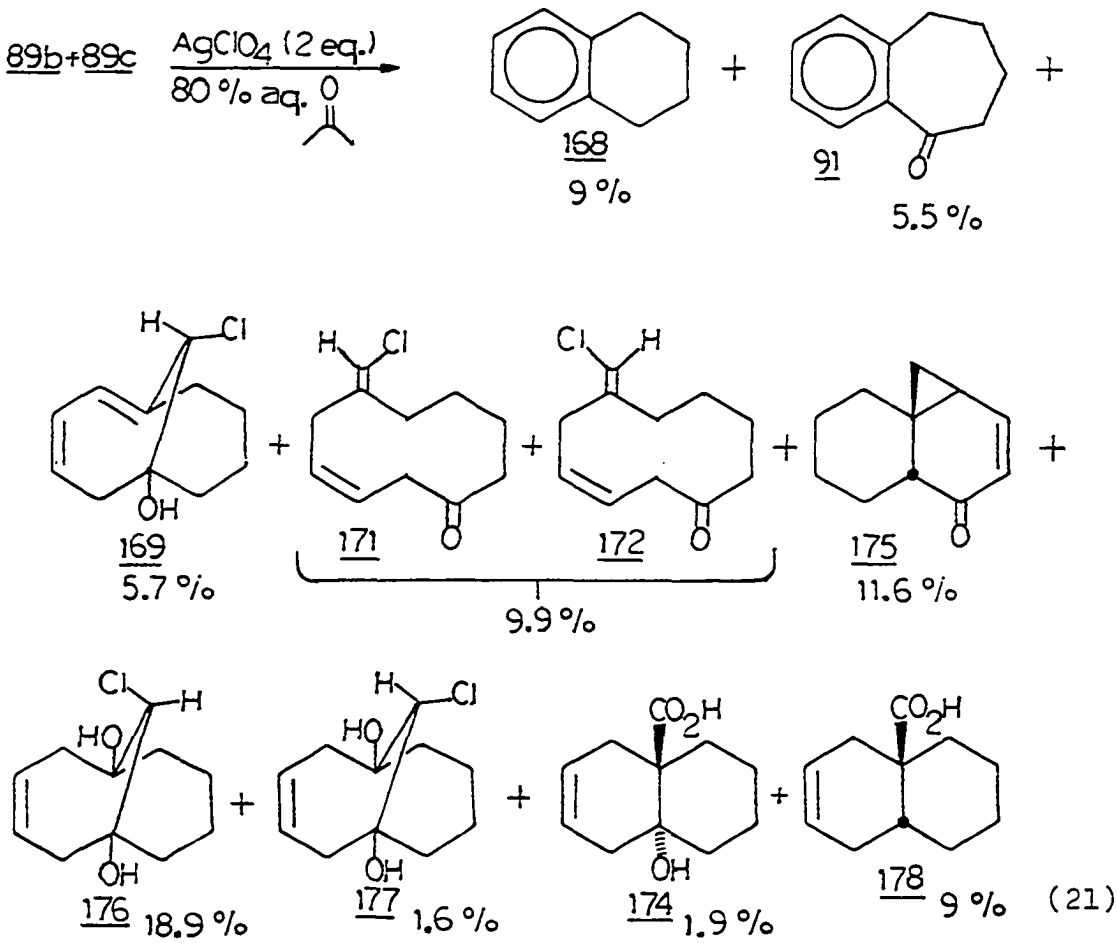
ring is in a twisted boat conformation (195a), wherein the dihedral angle between H_2endo and the π-bonded bridgehead orbital is ca. 180°. This alignment, favorable for elimination if maintained in cation 196, is obtained even when the conformation of the other seven-membered ring is altered. On the other hand, the hydrogens on C_{10} are never perfectly aligned for elimination. The results suggest cation 196a is



slow to undergo conformational change. It can also be seen that the π orbitals of the $\Delta^{3,4}$ double bond of 196a are not properly aligned for interaction with the cationic center.

A similar analysis of a model of 187 indicates that the conformations shown in 187a and 187b afford the best π overlap. Now H_{10}endo is aligned for elimination, just as H_2endo was in 195a. For simplicity, it should be noted that 187b leads to ion 188 in the conformation shown in 188b (187b should also be favored on steric grounds), where this ion may either eliminate (to 170b) or undergo π participation to afford ion 202. The relatively smaller amount of elimination from ion 188 as compared to ion 196 may reflect product diene stabilities, as well as more, subtle energy factors (such as conformational flexibilities). Of course, in addition to the processes discussed above, ion 196 affords 171 and 177 while ion 188 yields 172 and 176. When the silver-assisted hydrolysis of 89b and 89c was conducted in 80% aqueous acetone (Equation 21), the same products were obtained as in 90% aqueous acetone, but the percentages of 171 and 172 decreased at the expense of diols 176 and 177 (this is in accord with previous results) (114, 117). This means that ions 188 and 196 have significant lifetimes, in that they are capable of waiting around for solvent water. Their apparent failure to reorganize conformationally may well be reasonable for their lifetimes, but one cannot exclude the possibility that more complex factors, possibly involving silver ion are at play. It would be worthwhile to

investigate the solvolyses of 89b and 89c in the absence of silver ion.

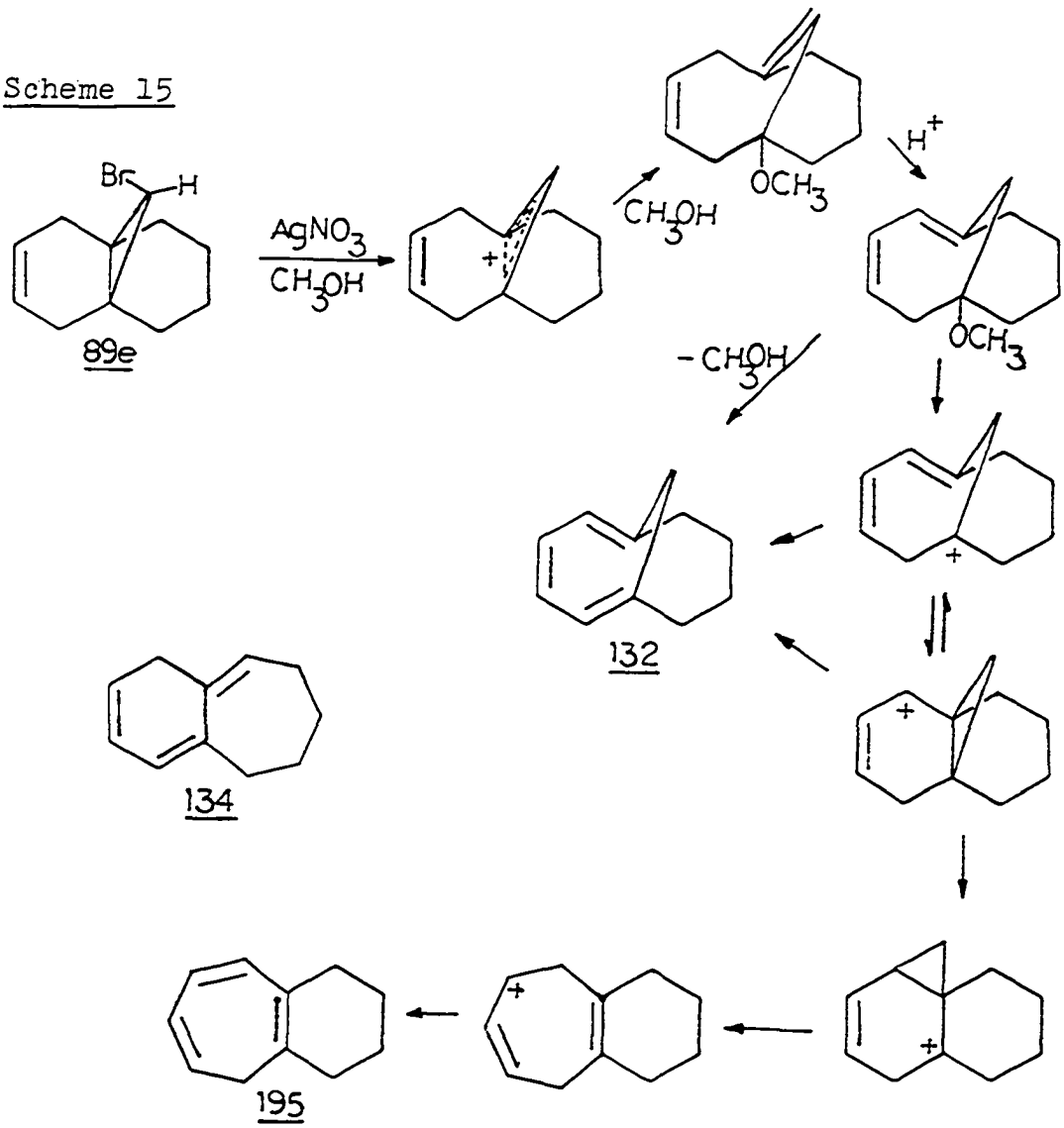


(21)

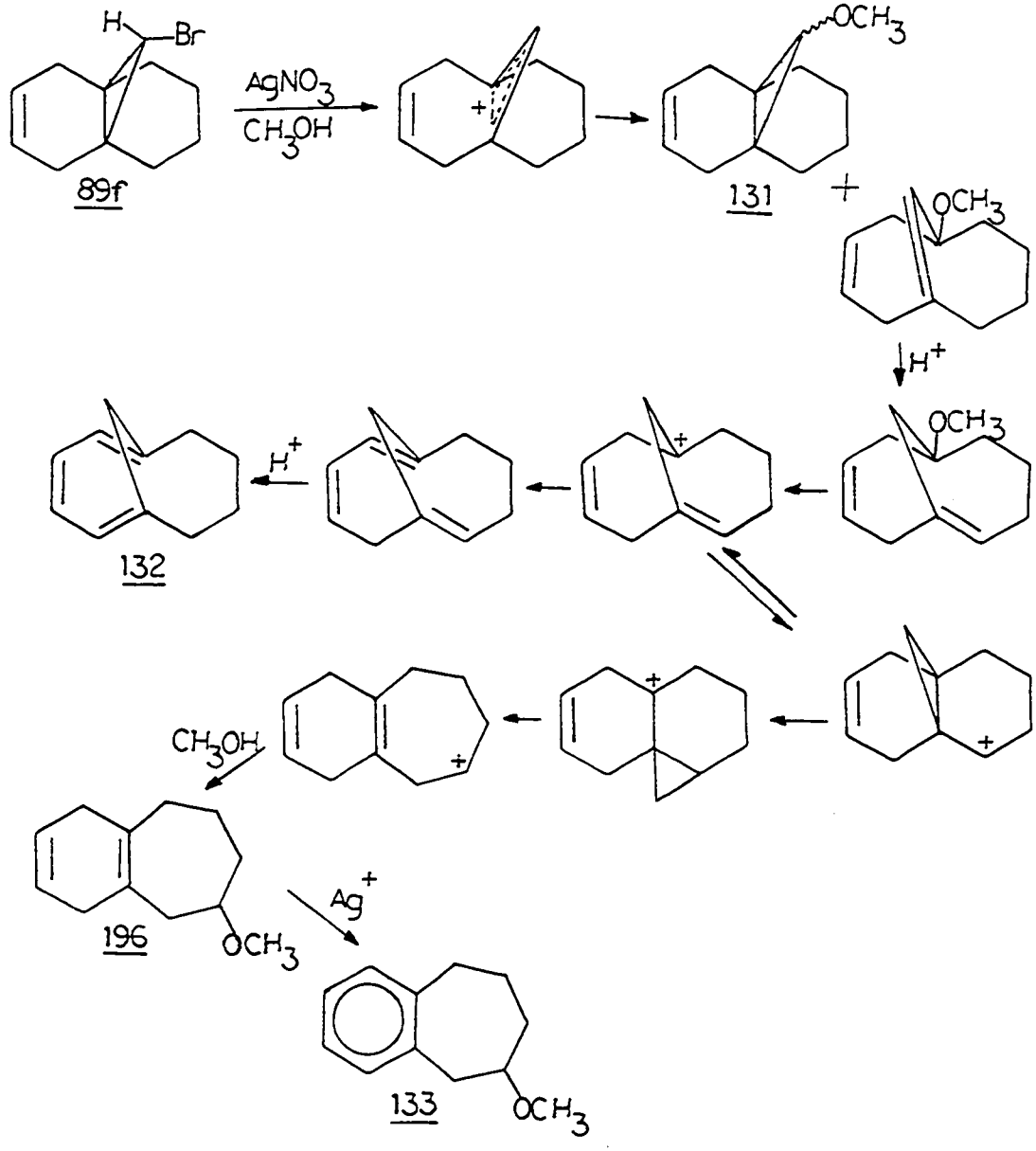
Ledlie et al. (119) reported the products obtained in the silver-assisted solvolysis of 89e and 89f in methanol (both refluxing and at room temperature). These products can be readily rationalized by considering the conformers of the intermediate bridgehead olefins (Scheme 15). It is obvious that the product (134) was misassigned and is actually 195. It is absurd to assume that 134 would not aromatize to benzocycloheptene (120) under the reaction conditions, since 133 was obtained from 196 by oxidation

with silver ion. Thus, elimination from the protonated bridgehead olefins occurred into the ring in which the precursor bridgehead olefin had been cisoid. These results again support a bridgehead olefin which is rehybridized since the conformations necessary for this preferential elimination are best obtained with sp^3 hybridization at the bridgehead carbon and C_{11}.

Scheme 15



Scheme 15 (Continued)



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 and Hitachi Perkin-Elmer R-20B 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 spectrometer equipped with a Nicolet Model 1089 data package. The mass spectral studies were conducted using Atlas CH-4, AEI High Resolution MS-902 and Perkin-Elmer 270 GLC-mass spectrometers. GLC analyses were conducted on a Varian Aerograph Model 90-P gas chromatograph. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by the Ilse Beetz Microanalytical Laboratory, Kronach, West Germany and Spang Microanalytical Laboratory, Ann Arbor, Michigan.

The following GLC columns were utilized. All the columns listed are glass columns and the inlet port of the Varian Aerograph Model 90-P contained a glass insert to insure no contact with a metal surface.

A. 16 ft x 1/4 in 10% diisodecyl phthalate on Chromsorb W A/W 60/80 mesh

B. 16 ft x 1/4 in 10% FFAP on Chromsorb W A/W 60/80 mesh

C. 16 ft x 1/4 in 14% Carbowax 20M on Chromsorb W A/W 60/80 mesh

D. 26 ft x 1/4 in 10% DEGS on Chromsorb W A/W 60/80 mesh

E. 16 ft x 1/4 in 14% DEGS on Chromsorb W A/W 60/80 mesh

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

The [4.4.1]propellane System

11-Bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c)

In a 50 ml three-necked flask equipped with mechanical stirrer, addition funnel, gas inlet tube and drying tube which were flame dried while passing nitrogen through the apparatus, 10.78 g of a mixture of 80% 1,2,3,4,5,8-hexahydronaphthalene (123) and 20% of 1,2,3,4-tetrahydronaphthalene (64.4 mmol of 1,2,3,4,5,8-hexahydronaphthalene), 7.392 g (66.0 mmol) of potassium t-butoxide, and 100 ml of pentane were combined and cooled to -78° (dry ice/acetone).

The mixture was stirred while 13.42 g (64.4 mmol) of dibromochloromethane (Columbia Organic Chemicals Co.) dissolved in 45 ml of pentane was added dropwise over 1 1/4 hours. After the addition was complete, the solution was left stirring for 8 hours as it warmed up; 50 ml of H_2O was then added. The layers were separated, and the aqueous layer was extracted with 2 x 25 ml of pentane. The pentane layers were dried over Na_2SO_4 and concentrated to give a white solid which was removed before the remainder of the material was distilled. The first fraction (3.82 g, 22-25°, 0.06 torr) contained 1,2,3,4,5,8-hexahydronaphthalene, 1,2,3,4-tetrahydronaphthalene, and dibromochloromethane, while the second fraction (7.063 g, 42%, 78-80°, 0.18 torr) consisted of 89b, 89c and 140. The residue in the pot was identified as 139, as was the initially filtered white precipitate (3.5 g, 14%); ^1H NMR δ 2.7-2.3 (m), 2.05-1.65 (m), 1.50-1.25 (m). GLC columns A and F were used to separate the second fraction; (column at 142°, injector at 172°, collector at 146°, detector at 169°; Helium flow 20 ml/min at 30 psi) column F resolved the material into three components. The first (retention time of 170 minutes) consisted of 89b and 89c; these were collected and the ^{13}C NMR which was obtained showed the ratio of 89b:89c was 40:60. The other two fractions (retention times of 185 minutes and 195 minutes)

contained the epimeric end-adducts 140. The ratio of 89b and 89c to 140, as determined from GLC, was 77:23.

Separation of 89b, 89c and 140

Propellanes 89b and 89c were separated from the end-adducts (140) by recrystallization from ethyl acetate at -78° (123). Once a material which was solid at room temperature was obtained, 100% ethanol was used as the recrystallization solvent and 89c was obtained pure after 25-30 recrystallizations; m.p. 45.8-46.2° (100% ethanol); ^{1}H NMR: δ 5.35 (s, 2H), 2.7-2.2 (m, 4H), 2.00-1.45 (m, 8H), (see Figure 11a); IR (CCl_4): 2940 (strong), 1670 (weak, C=C) cm^{-1} (see Figure 11b); High resolution mass spectrum at 70 ev: Calc'd for $C_{11}H_{14}BrCl$ 261.9942, found m/e (rel. int.) 261.9961 (5, P), 181 (38, P-Br), 145 (45, P-Br-HCl); ^{13}C NMR ($CDCl_3$) (see Table 2). Preparative thin-layer chromatography (silica gel), column chromatography on neutral Woelm alumina, high pressure liquid chromatography on a Waters Associates Liquid Chromatograph using a 2' x 1/4" μ-porasil (normal phase) or a 4' x 1/2" bondapak C_{18}-porasil (reverse phase) column, columns A through F on the gas-liquid chromatograph, sublimation, and zone refining all failed to completely purify epimer 89b. Finally, partial solvolysis was tried. To a stirring solution of 0.748 g (2.98 mmol) of 89b and 89c in 42 ml of 90% aqueous acetone (by volume) was added dropwise a solution of 0.617 g

(2.98 mmol) of silver perchlorate in 10 ml of 90% aqueous acetone. After addition was complete, the mixture was stirred for 2 hours, following which the acetone was removed on the roto-evaporator. Subsequently 25 ml of ether and 25 ml of ice-water were added and the layers were separated. The aqueous layer was extracted with 2 x 25 ml of ether and the combined ether layers were washed with 2 x 10 ml of saturated Na_2CO_3 solution and 1 x 10 ml of saturated NaCl solution before drying over $MgSO_4$. Removal of the solvent gave 0.705 g which ^1H NMR analysis indicated contained a higher ratio of 89b:89c than was present in the starting material. This material was chromatographed on a 10% $AgNO_3$-silica gel column using hexane as the eluting solvent (50 ml fractions). Early fractions contained mainly 89c, while later fractions contained increasing amounts of 89b. Collection of these later fractions, followed by partial solvolysis and $AgNO_3$-silica gel column chromatography, resulted in pure 89b (∿0.1 g) after three such iterative processes; m.p. 30-31.5° (methanol); ^1H NMR: δ 5.36 (s, 2H), 2.34 (broad s, 4H), 1.90-1.35 (m, 8H) (see Figure 12a); IR (CCl_4): 2940 (strong), 1670 (weak, C=C) cm^{-1} (see Figure 12b); ^{13}C NMR: (see Table 2); High resolution mass spectrum at 70 ev: Calc'd for $C_{11}H_{14}BrCl$ 259.99674 found m/e (rel. int.) 259.99686 (6, P), 181 (46, P-Br).

Preparation of silver nitrate-silica gel column

A solution of silver nitrate in 100 ml of acetonitrile was added to 70 g of silica gel. The acetonitrile was removed on the rotoevaporator and the residue was placed in a vacuum oven for 6 hours at 75°. Hexane was used to prepare the column for use.

11-Bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undecane (87b)

A mixture of the 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undec-3-enes (89b and 89c, 7.26 g, 2.76 mmol) was dissolved in 15 ml of ether in a Parr shaker bottle. Then ca. 0.02 g of 5% platinum on carbon was placed in the bottle. The bottle was shaken under hydrogen (initial pressure ca. 30 psi) for 2 hours. Removal of the catalyst by filtration, and the ether by rotoevaporation gave 0.738 g (2.77 mmol, 100%) of 87b; m.p. 38-39.5° (methanol); ^{1}H NMR: δ 2.0-1.6 (m, 8H), 1.55-1.25 (m, 8H) (see Figure 11); IR (CCl_4): 2940 (strong), 1450 (medium) cm^{-1} (see Figure 13); High resolution mass spectrum at 70 ev: Calc'd for $C_{11}H_{16}BrCl$ 262.01239 found m/e (rel. int.) 262.01164 (2.5, P), 229 (10, P-Cl), 227 (10, P-Cl), 183 (65, P-Cl); ^{13}C NMR: (see Table 2).

11,11-Dibromotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89a)

Compound 89a was prepared from 1,2,3,4,5,8-hexahydronaphthalene and bromoform (Baker Chemical Co.) in the presence of potassium t-butoxide in pentane as described by

Vogel et al. (123); m.p. 24-25° (methanol); ^{1}H NMR: (see Figure 14); ^{13}C NMR: (see Table 2).

11,11-Dichlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89d)

Compound 89d was prepared from 1,2,3,4,5,8-hexahydronaphthalene and chloroform (Fisher Scientific Co.) in the presence of potassium t-butoxide in pentane as described by Vogel et al. (123); m.p. 49-50° (methanol); ^{1}H NMR: (see Figure 15); ^{13}C NMR: (see Table 2).

11,11-Dibromotricyclo[4.4.1.$0^{1,6}$]undecane (87a)

Compound 87a was prepared by hydrogenation of 89a over 5% platinum on carbon, and had properties identical to those reported in the literature (107, 108); ^{13}C NMR: (see Table 2).

11,11-Dichlorotricyclo[4.4.1.$0^{1,6}$]undecane 87c

Compound 87c was prepared by hydrogenation of 87d over 5% platinum on carbon, and had properties identical to those reported in the literature (117, 122); ^{13}C NMR: (see Table 2).

Anti and syn-11-bromotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89f and 89e, respectively)

The two epimeric monobromides (89e and 89f) were prepared by reduction of 89a with tri-n-butyltin hydride, as reported in the literature (125). Separation was effected on a Woelm neutral alumina (167.5 x 1.3 cm) column using hexane as the eluting solvent (30 ml fractions):

Fraction 12-18, anti-11-bromotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89f), ^{13}C NMR: (see Table 2); fraction 22-30, syn-11-bromotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89e), ^{13}C NMR: (see Table 2).

Attempted reduction of 11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c) with diimide (126)

A mixture of 89b and 89c (0.093 g, 0.373 mmol) and 0.218 g (1.12 mmol) of potassium azodicarboxylate were stirred together in 6 ml of methanol at room temperature. Acetic acid (0.134 g, 2.24 mmol) in 4 ml of methanol was added over a 10 minute period and the mixture was allowed to stir for 2 1/2 hours. Water was then added and the mixture was extracted with pentane (3 x 10 ml), and the combined pentane extracts dried over $MgSO_4$. The pentane was evaporated to give 0.090 g of material which was starting material as indicated by ^{1}H NMR. GLC analysis on column F (helium flow of 40 ml/min at 50 psi, column at 148°, collector at 140°, detector at 163°, and injector at 164°) indicated that ca. 5% reduction to 87b (retention time of 1.42 hr) had occurred.

Attempted reduction of 89b and 89c with diborane followed by protonolysis

A 25 ml three-necked R. B. flask equipped with magnetic stirrer, gas inlet tube, condenser, rubber septum and drying tube was flame dried while flushing with nitrogen. Next,

0.303 g (1.16 mmol) of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undec-3-ene (89b and 89c) and 7 ml of diglyme (distilled from $LiAlH_4$) were injected through the septum. While stirring, 0.60 ml (1.2 mmol) of a BH_3·THF solution was then injected into the mixture, and the resulting solution stirred for 2 1/2 hours. Then 0.3 ml (4.08 mmol) of propionic acid was added through the septum and the resulting mixture refluxed (pot temp. 170°) for 5 1/2 hours. Upon cooling, 3 M sodium hydroxide solution was added until the mixture was basic, followed by an equal volume of pentane; the layers were then separated. The aqueous layer was extracted with 2 x 10 ml of pentane and the combined pentane layers were washed with 2 x 10 ml of water before drying over $MgSO_4$. Concentration gave 0.143 g of dark material which was chromatographed on a silica gel (1.2 x 50 cm) column using hexane as the eluting solvent (25 ml fractions). Fractions 3-6 consisted of 0.108 g (35.4%) of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undecane (87b), as identified by gas chromatography on column F.

Homogeneous hydrogenation with "Wilkinson's Catalyst" (128c)

To a 50 ml three-necked flask equipped with magnetic stirrer, constant pressure addition funnel, gas inlet tube, side arm and drying tube, was added 4 ml of benzene (distilled from sodium) after the apparatus had been flame dried while flushing with nitrogen. Tris(triphenylphosphine)rhodium chloride (0.02 g, 0.022 mmol) was placed in the side arm.

The benzene and the apparatus were degassed by four freeze-thaw cycles, following which hydrogen gas was admitted into the flask. While flushing the system with hydrogen gas, 0.102 g (0.405 mmol) of 11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c) dissolved in 2 ml of benzene was placed in the addition funnel. The addition funnel was connected *via* a drying tube to a mercury bubbler (to maintain about atmospheric hydrogen pressure during the reaction). The side arm was rotated to add the catalyst to the solution and the contents of the addition funnel were slowly added to the vigorously stirring solution. The mixture was left stirring for 4 hours before the benzene was removed on the rotoevaporator and the resulting mixture was column chromatographed on Woelm neutral alumina (1.0 x 38.5 cm) using hexane as the eluting solvent (25 ml fractions). Fractions 2 and 3 contained 0.099 g (96%) of 87b; no other organic fraction was found. The material was identical to a known sample (analysis by ^{1}H NMR, IR and gas chromatography). The reaction was repeated using identical conditions and amounts of starting materials, except it was allowed to stir for only 1 hour. Analysis by GLC showed a 95% yield of 87b and 5% of unreduced 89b and 89c. The reaction was repeated with deuterium gas, using 0.099 g (0.379 mmol) of 89b and 89c while maintaining the other quantities of reactants as above; the reaction time was

2 1/2 hours. Since analysis of the product showed the incorporation of two deuteriums, the above procedure was repeated individually with the purified epimers, 89b and 89c.

Homogeneous hydrogenation of 89b with deuterium gas

Compound 89b (0.204 g, 0.780 mmol) which contained 6.4% of epimer 89c (as determined from ^{13}C NMR data) was deuterated using "Wilkinson's Catalyst" via the procedure outlined above; a reaction time of 2 3/4 hours was used. A total of 0.175 g (0.664 mmol, 85%) of 141a (1st trial) was isolated from fractions 2-4 (column chromatography). Additionally, 0.021 g (0.080 mmol) of unreduced 89b was recovered in fractions 6-9. Mass spectral data for 141a (1st trial) are listed in Table 8; ^{13}C NMR: (see Table 4). The reaction was repeated with 0.140 g (0.535 mmol) of 89b in order to obtain material for use in acetolysis experiments. The procedure was the same as before; the reaction time was 2 3/4 hours. A total of 0.128 g (0.486 mmol, 91%) of 141a (2nd trial) was isolated from fractions 2-4 (column chromatography). Fractions 6-9 contained an unidentified material with olefinic ^{1}H NMR absorptions. Mass spectral data for 141a (2nd trial) are listed in Table 8; ^{13}C NMR: (see Table 4).

Homogeneous hydrogenation of 89c with deuterium gas

Compound 89c (0.201 g, 0.769 mmol) which contained 2.0% of epimer 89b (as determined from ^{13}C NMR data) was deuterated

using "Wilkinson's Catalyst" *via* the procedure outlined above; a reaction time of 2 1/2 hours was used. A total of 0.144 g (0.546 mmol, 71%) of 141b was isolated from fractions 4-5 (column chromatography). Additionally, 0.056 g (0.214 mmol) of unreduced 89c was recovered from fractions 8-11. Mass spectral data for 141b are listed in Table 8; ^{13}C NMR: (see Table 4).

Determination of the amount of deuterium incorporated into 141a (1st and 2nd trials) and 141b

Comparison of the (P-Br) peaks in the mass spectra of the parent compound (87b) and the deuterated analogues (141a and 141b) showed that mainly two deuteriums were incorporated into the molecule (comparison of the parent ions was impossible due to their weak intensity) (Table 8). By subtracting out the background peak at m/e 182 in the mass spectrum of 87b from the corresponding peak at m/e 184 in 141a and 141b, it was deduced what portion of this peak was due to the species $C_{11}H_{15}D^{35}Cl$. The analogous subtraction was done for each peak to arrive at the data in Table 9. Since virtually all the peak intensity at m/e 184 (Table 9) was due to $C_{11}H_{15}DCl$ and that at m/e 188 was due to $C_{11}H_{13}D_3{}^{37}Cl$, one could utilize their intensities to obtain the D_1 and D_3 percentages shown in Table 3 (by method A, i.e., $\%D_1 = I(m/e\ 184)\cdot 100/[100+I(m/e\ 184)+I(m/e\ 188)/0.325]$; $\%D_3 = [I(m/e\ 188)/0.325]\cdot 100/[100+I(m/e\ 184)+I(m/e\ 188)/0.325]$;

Table 8. Mass spectral intensities for 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undecane (average of five runs)

m/e	87b	(theor.)	141a (1st trial)	141a (2nd trial)	141b (2nd trial)	Major Ions (^{13}C ions not listed)
189			---	---	---	$C_{11}H_{12}D_4{}^{37}Cl$
188			5.3	6.3	4.5	$C_{11}H_{13}D_3{}^{37}Cl$
187			33.1	37.0	32.3	$C_{11}H_{14}D_2{}^{37}Cl$, $C_{11}H_{12}D_4{}^{35}Cl$
186	5.9	(3.9)	19.8	19.2	15.5	$C_{11}H_{15}D{}^{37}Cl$, $C_{11}H_{13}D_3{}^{35}Cl$, $C_{11}H_{13}D_2{}^{37}Cl$
185	35.0	(32.8)	100	100	100	$C_{11}H_{14}D_2{}^{35}Cl$, $C_{11}H_{16}{}^{37}Cl$
184	15.1	(14.0)	8.8	9.2	7.8	$C_{11}H_{15}D{}^{35}Cl$, $C_{11}H_{13}D_2{}^{35}Cl$ $C_{11}H_{15}{}^{37}Cl$
183	100	(100)	0.13	---	---	$C_{11}H_{16}{}^{35}Cl$
182	6.2					$C_{11}H_{15}{}^{35}Cl$
181	---			---		

Table 9. Intensities (I) of ions containing other than 2 deuterium atoms I[deuterated m/e(M)]-I[undeuterated m/e(M-2)]

M (m/e)		141a (1st trial) subtraction of data in Table 8[a]	141a (1st trial) calculated from M=184[b]	141a (2nd trial) subtraction of data in Table 8[a]	141a (2nd trial) calculated from M=184[b]	141b subtraction of data in Table 8[a]	141b calculated from M=184[b]
	189	---		---		---	
$C_{11}H_{13}D_3{}^{37}Cl$	188	-0.6	1.3 D_3	0.4	1.0 D_3	-1.4	0.0 D_3
$C_{11}H_{12}D_4{}^{35}Cl$	187	-1.9		2.0		-2.7	
$C_{11}H_{13}D_3{}^{35}Cl$,			3.9 D_3		3.1 D_3		-0.1 D_3
$C_{11}H_{15}D^{37}Cl$	186	4.7	0.8 D_1	4.1	1.0 D_1	0.4	0.5 D_1
	185	(0.0)		(0.0)		(0.0)	
$C_{11}H_{15}D^{35}Cl$	184	2.6	2.6 D_1	3.0	3.0 D_1	1.6	1.6 D_1
$C_{11}H_{16}{}^{35}Cl$	183	0.13		---	---	---	

[a]Method A; see text for explanation.

[b]Method B.

negative intensities assumed to be zero). It was obvious that a different result would be obtained by considering the peak intensity at m/e 186 which was due to a combination of $C_{11}H_{15}D^{37}Cl$ and $C_{11}H_{13}D_3{}^{35}Cl$ ions. The percentages obtained by method B (Table 3) were calculated by assuming the accuracy of the m/e 184 peak (due to $C_{11}H_{15}D^{35}Cl$), where from the expected intensity of the $C_{11}H_{15}D^{37}Cl$ contribution to the m/e 186 peak can be calculated. The remaining intensity at m/e 186 was then due to $C_{11}H_{13}D_3{}^{35}Cl$ (Table 9, second column of entries below each compound) from which the intensity of m/e 188 ($C_{11}H_{13}D_3{}^{37}Cl$) was calculated; this intensity was always greater than that actually observed. The difference was well within the experimental error (probably $\pm$2%) as seen from the intensities of the "$C_{11}H_{12}D_4{}^{35}Cl$" ion listed in Table 9. From the above calculated intensities, the data in Table 3 were derived (method B, i.e., $\%D_1 = I(m/e\ 184)\cdot 100/\left[100+I(m/e\ 184)+I(m/e\ 186\ [D_3])\right]$; $\%D_3 = I(m/e\ 186\ [D_3])\cdot 100/\left[100+I(m/e\ 184)+I(m/e\ 186\ [D_3])\right]$, where $I(m/e\ 186\ [D_3])$ is the fraction of the intensity at m/e 186 due to $C_{11}H_{13}D_3{}^{35}Cl$). It seems likely that Table 3 presents maximal amounts of D_1 and D_3 material, as no attempt has been made to eliminate the errors inherent in the mass spectral data.

The ^{13}C NMR data for 141a (1st and 2nd trials), 141b and 89b are listed in Table 4. By calculating and comparing ratios of the areas of $C_{2,5}$ and $C_{7,10}$ to $C_{1,6}$ in the

deuterated and undeuterated samples (Table 10), it was possible to conclude that there was some incorporation of deuterium into $C_{2,5}$ in 141a and $C_{7,10}$ in 141b; these percentages are listed in Table 5 (i.e. %D in $C_{2,5}=100\cdot(x^{87b} - [y^{87b} \cdot x^{141a}/y^{141a}])/x^{87b}$; %D in $C_{7,10}=100\cdot(y^{87b} - [x^{87b} \cdot y^{141b}/x^{141b}])/y^{87b}$). The negative percentage for 141b (Table 5) was due to the error (probably $\pm$2%) in the ^{13}C NMR areas.

Table 10. Ratio of areas (from Table 4) of ^{13}C NMR data

Ratio of areas in carbons	87b	141a (1st trial)	141a (2nd trial)	141b
$x=C_{2,5}/C_{1,6}$	2.29	2.45	3.59	3.60
$y=C_{7,10}/C_{1,6}$	2.36	2.64	3.87	3.79

Silver-assisted solvolysis of 11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undecane (87b)

To a stirring solution of 0.092 g (0.348 mmol) of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undecane (87b) in 15 ml of 80% aqueous acetone (by volume) was added dropwise a solution of 0.361 g (1.74 mmol, 5 eq.) of silver

perchlorate in 5 ml of 80% aqueous acetone. After addition was complete, the solution was stirred at room temperature for 4 hours, and then the acetone was removed on the roto-evaporator, following which 20 ml of ether and 10 ml of ice-water were added and the layers separated. The aqueous layer was extracted with 2 x 10 ml of ether and the combined ether layers were washed with 2 x 10 ml of saturated Na_2CO_3 solution and 1 x 10 ml of saturated NaCl solution before drying over $MgSO_4$. Removal of the solvent gave 0.054 g of crude product. Chromatography on a silica gel column (1.0 x 41 cm) gave the following results (eluting solvent: 99% ethereal hexane for fractions 1-30, 98% ethereal hexane for fractions 31-45; 10 ml fractions):

Fraction 2-4, 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undecane 87b; 0.004 g.

Fraction 24-29, 6-chloromethylenecyclodecanone (124a); 0.020 g (30%); m.p. 44-45.5° (aq. methanol); ^{1}H NMR: δ 5.87 (s, 1H), 2.6-1.5 (m, 16H); IR (CCl_4): 1710 (C=O), 1620 (C=C) cm^{-1}. These data were identical in all respects to that reported before (117).

Fraction 33-35, bicyclo[5.4.0]undec-1(7)-en-2-one (88a); 0.004 g (7%); ^{1}H NMR: δ 2.75-1.95 (m, 8H), 1.9-1.4 (m, 8H); IR (CCl_4): 1662 (C=O), 1632 (C=C) cm^{-1}. This compound was identical to that reported in the literature (107, 108).

Fraction 43-45, 7-hydroxybicyclo[5.4.0]undecan-2-one (126a); 0.006 g (9%); ^{1}H NMR: δ 3.8 (m, OH), 2.7-1.0 (m, 17H); IR (CCl_4): 3450 (OH), 1705 (C=O) cm^{-1}. This compound was identical to that reported in the literature (117). No other fraction was collected, but 0.004 g of material failed to dissolve in the 99% ethereal hexane used to put the material on the column. This amount, together with the material that failed to elute off the column, totals 20-32% of unrecovered products (depending upon the molecular weight of the unrecovered products, which is unknown).

Treatment of the base (Na_2CO_3) extracts with concentrated hydrochloric acid until acidic, followed by extraction with 3 x 10 ml of ether, drying and evaporation of solvent, resulted in the isolation of 0.012 g (18% if solely 127) of acidic products.

Solvolysis of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undecane (87b) with 1 equivalent of $AgClO_4$

To a stirring solution of 1.298 g (4.94 mmol) of 87b in 100 ml of 80% aqueous acetone was added dropwise a solution of 1.02 g (4.94 mmol) of $AgClO_4$ in 20 ml of 80% aqueous acetone. The resulting solution was stirred for 2 days, and the acetone was then removed on the roto-evaporator. The mixture was extracted with 4 x 15 ml of

ether and the combined ether extracts were washed with 2 x 20 ml of saturated Na_2CO_3 solution and 1 x 20 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 0.898 g of material, to which p-dibromobenzene was added and the following yields determined by ^1H NMR: 124a, 24.7%; 125a, 10.2%; 145, 9.7%. The crude oil was then chromatographed on a silica gel column (1.4 x 70 cm) using hexane initially as the eluting solvent (50 ml fractions). Elution with a mixture of ether and hexane (1/99 for fractions 4-8; 2/98 for fractions 9-15; 4/96 for fractions 16-24; 8/92 for fractions 25-28; 12/88 for fractions 29-32; 16/84 for fractions 33-40; 32/68 for fractions 41-49; 64/36 for fractions 50-59) afforded the following products:

Fraction 2-3, 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undecane (87b); 0.508 g.

Fraction 17-20, mixture of 6-chloromethylenecyclodecanone (124a) and anti-11-chloro-6-hydroxybicyclo-[4.4.1]undec-1(2)-ene (145); 0.210 g. Subsequently, 0.047 g of the mixture was put on a preparative thin layer silica gel plate and advanced with an 80/20 mixture of hexane and acetone. The first band with R_f=0.568 was 145, 0.0125 g (9%); ^1H NMR: δ 5.28-5.44 (m, 1H), 5.02 (s, 1H), 2.56-2.88 (broad m, 1H), 2.54-1.3 (m, 14H) (see Figure 15); IR (CCl_4): 3590 (sharp,

OH), 2940, 1645 (C=C) cm^{-1} (see Figure 15); ^{13}C NMR ($CDCl_3$), rel. area): δ 125.0 (4.18), 117.1 (1), 88.6, 73.6 (4.14), 40.4 (5.84), 37.0 (4.26), 32.8 (4.09), 26.5 (4.74), 24.9 (4.82), 22.1 (5.84), 19.3 (3.34); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{17}OCl$ 200.09680, found m/e (rel. int.) 200.09642 (0.8, P), 184 (10, P-16), 182 (30.8, P-18), 165 (28.1, P-35), 164 (100, P-36), 158 (11.9, P-42), 147 (55.1, P-53), 146 (12.6, P-54), 136 (16.6, P-64), 135 (46.7, P-65), 133 (40, P-67). The second band, with R_f=0.459, was 124a, 0.033g (25%).

Fraction 22-26, bicyclo[5.4.0]undec-1(7)-en-2-one (88a); 0.034 g (7%).

Fraction 32-34, 7-hydroxybicyclo[5.4.0]undecan-2-one (126a); 0.038 g (7%).

Fraction 36-39, 11-chloro-1,6-dihydroxybicyclo[4.4.1]-undecane (125a); 0.098 g (15%); m.p. 93-94° (CCl_4); ^1H NMR: δ 4.61 (s, 1H), 2.54-2.8 (broad s, 2H), 2.2-1.2 (m, 16H) (see Figure 14); IR (CCl_4): 3600 (sharp, OH), 2940, 1255, 1125 cm^{-1} (see Figure 14); High resolution mass spectrum at 70 ev: 218 (0.7, P), calc'd for $C_{11}H_{17}OCl$ 200.09680; found m/e (rel. int.) 200.09644 (3,P-18, no exact mass could be obtained on the parent ion), 182 (22, P-36), 164 (45, P-54), 147 (35, P-71); ^{13}C NMR ($CDCl_3$, rel. area): δ 84.2 (1, $C_{1,6}$), 74.7 (1.73, C_{11}), 39.9 (2.14), 39.4 (2.18, $C_{2,5}$ and $C_{7,10}$),

23.5 (2.19), 23.3 (1.97, $C_{3,4}$ and $C_{8,9}$). Anal. calc'd for $C_{11}H_{19}O_2Cl$: C, 60.40; H, 8.76, found: C, 60.54; H, 8.62.

Acidification of the basic extracts with conc. HCl, followed by extraction with ether (4 x 10 ml), drying ($MgSO_4$) and removal of solvent, gave 0.129 g of acidic products (23% if solely 127). The ^1H NMR and infrared spectrum showed the presence of the three previously observed acids (127, 128 and 144) (117).

Solvolysis of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undecane (87b) in 90% aqueous acetone

To a solution of 1.176 g (4.09 mmol) of 87b in 90 ml of 90% aqueous acetone was added dropwise a solution of 0.847 g (4.09 mmol) of $AgClO_4$ in 10 ml of 90% aqueous acetone. The resulting solution was stirred for 2 days before the acetone was removed on the rotoevaporator. The residue was diluted with 10 ml of H_2O and extracted with 4 x 15 ml of ether. The combined ether layers were washed with 2 x 15 ml of saturated Na_2CO_3 solution and 15 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 0.886 g; ^1H NMR of this crude material (p-dibromobenzene standard) indicated the following yields: 124a, 30.1%; 125a, 10.2%; 145, 10.2%. The oil was chromatographed on a silica gel column (1.4 x 122 cm) using hexane initially as

the eluting solvent (50 ml fractions) followed by a mixture of ether and hexane (1/99 for fractions 20-41; 2/98 for fractions 42-47; 4/96 for fractions 48-59; 5/95 for fractions 60-77; 8/92 for fractions 79-95; 10/90 for fractions 96-102; 12/88 for fractions 103-116); the following products were obtained:

Fraction 2-3, 11-bromo-11-chlorotricyclo[4.4.1.0]undecane (87b); 0.657 g.

Fraction 28-33, mixture of 6-chloromethylenecyclodecanone (124a); 0.122 g (31%) and anti-11-chloro-6-hydroxybicyclo-[4.4.1]undec-1(2)-ene (145); 0.038 g (9.5%). The determination of the amount of each isomer was effected by integration of the δ 5.87 singlet of 124a vs. the δ 5.02 singlet of 145.

Fraction 40-46, bicyclo[5.4.0]undec-1(7)-en-2-one (88a); 0.023 g (7%).

Fraction 61-64, 7-hydroxybicyclo[5.4.0]undecan-2-one (126a); 0.027 g (7.5%).

Fraction 105-111, 11-chloro-1,6-dihydroxybicyclo[4.4.1]-undecane (125a); 0.047 g (11%).

Acidification of the basic extracts with conc. HCl, followed by extraction with 3 x 15 ml of ether, drying ($MgSO_4$) and solvent evaporation, gave 0.094 g of acidic products (25% if solely 127).

Solvolysis of 11-chloro-1,6-dihydroxybicyclo[4.4.1]undecane (125a)

To a stirring solution of 0.088 g (0.425 mmol) of $AgClO_4$ in 3 ml of 90% aqueous acetone was added 0.040 g (0.325 mmol) of 2-bromopropane (to generate $HClO_4$), and the resulting solution stirred for 30 minutes. Then a solution of 0.016 g (0.0728 mmol) of 125a in 1 ml of 90% aqueous acetone was added, and the resulting mixture stirred for 13 days. At this point, 5 ml of saturated NaCl solution and 10 ml of ether were added and the layers were separated. The aqueous layer was extracted with 3 x 10 ml of ether and the combined ether layers were washed with 1 x 10 ml of saturated Na_2CO_3 solution and 1 x 10 ml of saturated NaCl solution before drying over $MgSO_4$. Removal of the ether gave 0.016 g of material which by ^1H NMR and infrared spectroscopy consisted of 125a, 126a and a trace of 88a. Analysis on the GLC (column F, column at 155°, collector at 150°, injector at 173°, detector at 173°, flow of helium of 30 ml/min. at 50 psi) showed the presence of 88a (retention time of 0.78 hr) and 126a (retention time of 0.94 hr).

Buffered acetolysis of 87b

In a sealed tube, 0.418 g (1.59 mmol) of 87b and 0.261 g (3.18 mmol) of sodium acetate were dissolved in 11 ml of glacial acetic acid and the solution heated to 125°

for 2 days. After cooling, the tube was opened and poured into an ice-cold solution of Na_2CO_3; the resulting mixture was extracted with 4 x 10 ml of ether. The combined ether extracts were washed with 1 x 10 ml of saturated NaCl solution before drying over $MgSO_4$. Removal of the solvent gave 0.218 g of a black material which was chromatographed on a silica gel column (1.3 x 104 cm) using hexane as the initial eluting solvent (30 ml fractions), followed by a mixture of ether and hexane (1/99 for fractions 31-44, 2/98 for fractions 45-51, 4/96 for fractions 52-62, 8/92 for fractions 63-72, 12/88 for fractions 73-100). The following products were obtained:

Fraction 3-5, mixture of 120, 87b, 147 and 146; 0.122 g. This material was rechromatographed on a neutral alumina (Woelm) column (1.0 x 41 cm) using hexane as the eluting solvent (25 ml fractions): fraction 3'-4', 87b: 0.059 g; fraction 5', mixture of 87b and 146: 0.011 g; fraction 6', 1-bromochloromethylbicyclo[4.4.0]dec-5-ene (146): 0.008 g (~4%); ^1H NMR: δ 5.83 (s, 1H), 5.48 (m, 1H), 2.5-1.3 (m, 14H) (see Figure 16); High resolution mass spectrum at 70 ev [m/e (rel. int.)]: 264 (0.2, P, no exact mass could be obtained), calc'd for $C_{11}H_{16}Br$ 227.0435, found 227.04344 (21.1, P-37), 229 (20.2, P-35), 183 (26.6, P-81), 185 (10, P-79), 147 (55.2, P-117), 91 (100, P-164);

fraction 7', mixture of 146 and 147: 0.004 g; fraction 8', mixture of 147 and unidentified product: 0.002 g; fraction 9', 11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-2-ene (147): 0.012 g (~7%); ^{1}H NMR: δ 5.73 (m, 1H), 5.43 (m, 1H), 3.12 (s, 1H), 2.2-1.3 (m, 12H) (see Figure 18); Mass spectrum: m/e (rel. int.) 182 (23.2, P), 147 (100, P-35), 119 (28.4, P-63), 105 (36.8, P-77), 91 (81.4, P-91); fraction 10', mixture of 147 and 120: 0.005 g; fraction 11'-13', benzocycloheptene (120) (131): 0.020 g (~12%); ^{1}H NMR: δ 6.95 (br.s, 4H), 2.70 (m, 4H), 1.7 (m, 6H); IR (film): 3040, 1500, 1460, 750 cm^{-1}. Fraction 29-30, bicyclo[4.4.0]dec-5-ene-1-carboxaldehyde (151); 0.006 g (4%); ^{1}H NMR: δ 9.25 (s, 1H), 5.56 (m, 1H), 2.25-1.1 (m, 14H) (see Figure 19); IR (CCl_4): 2960 (strong), 1730 (C=O), 1250 cm^{-1} (see Figure 19); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{16}O$: 164.12012, found m/e (rel. int.) 164.11868 (10.4, P), 150 (48.7, P-14), 136 (16.4, P-28), 135 (31.0, P-29), 134 (16.1, P-30), 123 (17.3, P-41), 122 (64.6, P-42), 91 (75.8, P-73), 79 (100, P-85). Fraction 33-35; 0.005 g of an unidentified material which might be 148 and products derived therefrom; several absorptions in the 1775-1675 cm^{-1} region of the infrared, including one at 1775 (rel. int. 1, probably 148) and others at 1735 (rel. int. 2) 1707 (rel. int. 2) and 1675 (rel. int. 1) cm^{-1}.

Fraction 40-43, mixture of 11-chloro-6-acetoxybicyclo-[4.4.1]undec-1-ene (155) and exo- and endo-11-chloro-2-acetoxytricyclo[4.4.1.$0^{1,6}$]undecane (154); 0.013 g (4%); ^{1}H NMR: δ 5.05 (s), 3.20 (s), 3.31 (s), 2.4-1.3 (m, except for broad acetate singlet at δ 2.05); IR (CCl_4): 2940 (strong), 1740 (C=O of 155), 1735 (C=O of 154), 1260 (C-O of 155), 1238 (C-O of 154-exo), 1248 (C-O of 154-endo) (114c); High resolution mass spectrum at 70 ev [m/e (rel. int.)]: 242 (0.3, P, too small for exact mass measurement), calc'd for $C_{12}H_{17}OCl$, 212.0963, found 212.09199 (5.0, P-30), 207 (6.2, P-^{35}Cl), 202 (4.2, P-40), 200 (12.0, P-42), 182 (17.0, P-60), 181 (5.9, P-61), 165 (17.9, P-79), 164 (12.7, P-80), 151 (48, P-91), 147 (56.5, P-95), 91, (100, P-151). Some of the above spectral assignments are based upon analogous data obtained for compounds 115a and 115b (114c). The relative intensities of the hydrogen on C_{11} in the ^{1}H NMR were as follows: 155 one isomer 2, 155 other isomer 1 and 154 1.

Fraction 45, 11-chloro-1,6-diacetoxybicyclo[4.4.1]undecane (149); 0.006 g (2%); ^{1}H NMR: δ 4.30 (s, 1H), 2.03 (s, 6H), 2.2-1.2 (m, 16H) (see Figure 17); IR (CCl_4): 2960, 1740 (C=O), 1260 (C-O) cm^{-1} (see Figure 17); High resolution mass spectrum at 70 ev [m/e (rel. int.)]: 302 (0.15, P, too small for exact mass measurement), calc'd for $C_{13}H_{21}O_3Cl$, 260.0814, found 260.0787 (1.6, P-42), 204

(5.6, P-98), 200 (3.9, P-102), 182 (8.3, P-120), 181 (8.3, P-121), 175 (7.7, P-127), 165 (9.7, P-137), 164 (10.5, P-138), 158 (15.7, P-142), 147 (22.8, P-155), 145 (30.0, P-157), 144 (100, P-158), 129 (71.3, P-173).

Fraction 47-50, mixture of 88a, 124a and trans-6-acetoxybicyclo[4.4.0]decane-1-carboxaldehyde (152); 0.020 g; 88a and 124a were identified from their ^{1}H NMR and infrared spectra and retention time (0.78 hr for 88a, 1.625 hr for 124a) on GLC column F (flow rate of 30 ml/min at 50 psi of helium, column at 155°, collector at 150°, injector at 173° and detector at 173°); 152: ^{1}H NMR: δ 10.01 (s), 2.0 (s); IR (CCl_4): 2930, 2840, 1720 (C=O) cm^{-1}.

Fraction 58-61, 7-acetoxybicyclo[5.4.0]undecan-2-one (153); 0.009 g (3%); ^{1}H NMR: δ 2.07 (s, 3H), 2.4-1.2 (m, 17H) (see Figure 20); IR (CCl_4): 2930, 1745 (acetate C=O), 1708 (ketone C=O), 1245 (C-O) cm^{-1} (see Figure 20); High resolution mass spectrum at 70 ev: calc'd for $C_{13}H_{20}O_3$, 224.14125, found m/e (rel. int.) 224.14299 (0.2, P), 182 (3.3, P-42), 164 (16.4, P-60), 136 (100, P-88), 135 (30.8, P-89), 121 (21.8, P-103), 111 (45, P-113), 107 (23.8, P-117).

Fraction 73-83, cis-decalin-9-carboxylic acid 127; 0.011 g (5%); m.p. 119-121° (acetone, lit. (135) 121.8-123°); the compound had similar spectral characteristics to that reported in the literature (135), particularly the peak at 1255 cm^{-1} in the infrared spectrum.

Fraction 90-96, unidentified material; 0.013 g; ^{1}H NMR: δ 2.1-1.1 (m); IR (CCl_4): 2950 (strong), 1730 (weak) cm^{-1}.

Hydrolysis of 11-chloro-1,6-diacetoxybicyclo[4.4.1]undecane (149)

To 0.5 ml of 90% aqueous methanol (by volume) which was 0.4M in KOH was added 0.006 g (0.020 mmol) of 149 and the resulting solution stirred at room temperature for 2 hours. Neutralization was achieved by adding 0.5M HCl, following which the solution was diluted with 3 ml of H_2O and 5 ml of ether. Separation of the layers and extraction of the aqueous layer with 2 x 5 ml of ether, followed by drying of the combined ether layers ($MgSO_4$) and solvent evaporation afforded ca. 0.002 g (46%) of 11-chloro-1,6-dihydroxybicyclo-[4.4.1]undecane (125a). This material was spectroscopically identical to that isolated before (vide supra).

Treatment of 11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-2-ene (147) under acetolysis conditions

In a sealed tube were placed 0.011 g (0.0604 mmol) of 147, 2.5 ml of glacial acetic acid and 0.010 g (0.121 mmol) of sodium acetate, and the mixture was heated to 115° for 10 days. The tube was then cooled and its contents poured into 15 ml of saturated Na_2CO_3 solution at ice-water temperature. This mixture was extracted with 4 x 8 ml of ether and the combined ether extracts dried over $MgSO_4$. Removal of

the ether gave 0.007 g of material, one component of which was benzocycloheptene (120) as determined from the ^{1}H NMR spectrum and GLC analysis on column F (column at 160°, injector at 178°, detector at 175°, collector at 150°, flow of 31.3 ml/min. at 50 psi of helium gas). Besides compounds 120 and 147 (retention times of 0.297 and 0.523 hours) two other unidentified components (retention times of 0.285 and 0.743 hours) were observed (all three products had approximately equal peak areas on GLC while 147 was twice the area of any product).

Buffered acetolysis of 87b with acetic anhydride

In a sealed tube, 0.383 g (1.46 mmol) of 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undecane, 0.244 g (2.98 mmol) of NaOAc, 8 ml of glacial acetic acid and 1/2 ml of acetic anhydride were combined and heated to 125° for 2 1/2 days. After cooling, the tube was broken open and its contents poured into an ice-cold saturated Na_2CO_3 solution. This mixture was extracted with 4 x 12 ml of ether and the combined ether layers were washed with 1 x 10 ml of a saturated NaCl solution before drying over $MgSO_4$. Removal of the solvent gave 0.222 g of crude material, the infrared spectrum of which showed a peak at 1775 cm^{-1} as its most intense carbonyl absorption. The product was then chromatographed on a silica gel column (1.0 x 39 cm). Initially, hexane was

used as the eluting solvent (25 ml fractions), followed by a mixture of ether and hexane (1/99 for fractions 20-25, 2/98 for fractions 26-31); the following products were obtained:

Fraction 1-3, mixture of 120, 146, 147, 87b and ≥ 1 unidentified component; 0.169 g. These products were identified from comparison of ^{1}H NMR and infrared spectra and comparison of GLC traces on column F. The retention times (the retention times of compounds 146 and 87b were 1.44 and 0.938 hours, respectively) and conditions are listed in the experimental section on the buffered acetolysis of 147.

Fraction 10-13, mixture of 148 and unidentified components; 0.011 g (8%). As noted before, 148 was identified by its infrared absorption at 1775 cm^{-1}; also, its order of elution from the column was similar to that reported for 114 (114). Other carbonyl absorptions were also present, some of which could have been products derived from 148.

Fraction 21-24, mixture of 155 and the two epimeric acetates (154); 0.013 g (9%); identified by comparison of ^{1}H NMR and infrared spectra with those of samples isolated before (vide supra).

Fraction 27-28, 11-chloro-1,6-diacetoxybicyclo[4.4.1]-undecane (149); 0.005 g (3%); spectroscopically (^{1}H NMR and IR) identical to the previously isolated sample (vide supra).

Although no other products were isolated, 124a was identified (^{1}H NMR and IR) as a minor component of the crude reaction material.

Acetolysis of 87b in 98% aqueous acetic acid

In a test tube, 0.250 g (0.949 mmol) of 87b, 0.156 g (1.90 mmol) of sodium acetate and 12 ml of 98% aqueous acetic acid (by volume) were combined and the tube was sealed and heated to 115° for 8 days. The tube was cooled, opened and its contents poured into an ice-cold saturated Na_2CO_3 solution and the resulting mixture extracted with 4 x 10 ml of ether. The combined ether extracts were dried over $MgSO_4$ and concentrated to afford 0.097 g of a black material which was chromatographed on a silica gel column (1.3 x 103 cm). Hexane was used as the initial eluting solvent (50 ml fractions), followed by a mixture of ether and hexane (1/99 for fractions 4-37 and 2/98 for fractions 38-48); the following products were isolated:
Fraction 2-3, mixture of 120 and 87b; 0.038 g; identified from ^{1}H NMR and infrared spectra. Although it was impossible to exclude the presence of 146, 147 or other unidentified components, 120 and 87b were the major ones.
Fraction 7-8, unidentified material; 0.008 g; ^{1}H NMR: δ 2.8-1.1 (m with singlet at δ 2.4 and 2.3 (acetate?)); IR (CCl_4): 2940 (strong), 1740 (medium), 1715, 1220 cm^{-1}.

Fraction 9-11, bicyclo[4.4.0]dec-5-ene-1-carboxaldehyde (151); 0.003 g (2%); identified by comparison of its ^{1}H NMR and infrared spectra with those of previously isolated 151 (vide supra).

Fraction 12-13, mixture of 148 and unidentified compound(s); 0.003 g (1.4%).

Fraction 17-19, mixture of 155 and 154; 0.005 g (2%); identified by comparison of ^{1}H NMR and infrared spectra with those of previously isolated 154 and 155 (vide supra).

Fraction 28-32, 6-chloromethylenecyclodecanone (124a); 0.028 g (16%); identified by comparison of its ^{1}H NMR and infrared spectra with those of a known sample of 124a (vide supra).

Fraction 37-41, bicyclo[5.4.0]undec-1(7)-en-2-one (88a); 0.010 g (7%); identified by comparison of its ^{1}H NMR and infrared spectra with those of a known sample of 88a (107). A total of 0.094 g of the 0.097 g originally placed on the column were recovered.

Silver-assisted solvolysis of 141a (1st trial)

To a stirring solution of 0.106 g (0.399 mmol) of syn-11-bromo-11-chloro-3,4-dideuterotricyclo[4.4.1.0^{1,6}]-undecane (141a, 1st trial) in 12 ml of 80% aqueous acetone was added dropwise a solution of 0.413 g (1.99 mmol) of $AgClO_4$ in 2 ml of 80% aqueous acetone. The resulting mixture was stirred for 5 1/2 hours, following which the

acetone was evaporated and the residue extracted with 4 x 15 ml of ether. The combined ether extracts were washed with 2 x 15 ml of saturated Na_2CO_3 solution and 15 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 0.063 g of material which was chromatographed on a silica gel column (1.0 x 40 cm) using hexane as the initial eluting solvent, with increasing amounts of ether used to elute later fractions (25 ml fractions). The following products were obtained:

Fraction 2-3, syn-11-bromo-11-chloro-3,4-dideuterotricyclo-[4.4.1.$0^{1,6}$]undecane (141a, 1st trial); 0.018 g.

Fraction 20-25, 3,4-dideutero-6-chloromethylenecyclodecanone (124b); 0.023 g (34%); ^{13}C NMR: (see Table 7).

Fraction 27-30, 9,10-dideuterobicyclo[5.4.0]undec-1(7)-en-2-one (88b); 0.012 g (23%); mass spectrum: (see Table 6).

Silver-assisted solvolysis of 141b

To a stirring solution of 0.114 g (0.43 mmol) of anti-11-bromo-11-chloro-3,4-dideuterotricyclo[4.4.1.$0^{1,6}$]-undecane (141b) in 13 ml of 80% aqueous acetone was added dropwise a solution of 0.446 g (2.15 mmol) of $AgClO_4$ in 1 ml of 80% aqueous acetone. The resulting mixture was stirred for 5 hours, following which the acetone was evaporated and the residue extracted with 3 x 15 ml of ether. The combined ether extracts were washed with 2 x 15 ml of saturated Na_2CO_3 solution and 15 ml of saturated

NaCl solution before drying over $MgSO_4$. Concentration gave 0.059 g of material which was chromatographed on a silica gel column (1.0 x 42 cm), using hexane as the initial eluting solvent, with increasing amounts of ether in later fractions (25 ml fractions); the following products were obtained:
Fraction 3-4, anti-11-bromo-11-chloro-3,4-dideuterotricyclo-[4.4.1.$0^{1,6}$]undecane (141b); 0.003 g.
Fraction 30-33, 3,4-dideutero-6-chloromethylenecyclo-decanone (124c); 0.033 g (38%); ^{13}C NMR: (see Table 7).
Fraction 35-40, 4,5-dideuterobicyclo[5.4.0]undec-1(7)-en-2-one (88c); 0.018 g (26%); mass spectrum: (see Table 6).

Acetolysis of 141a (2nd trial)

In a sealed tube, a solution of 0.091 g (0.344 mmol) of syn-11-bromo-11-chloro-3,4-dideuterotricyclo[4.4.1.$0^{1,6}$]-undecane (141a, 2nd trial) and 0.056 g (0.688 mmol) of NaOAc in 7.5 ml of 96% aqueous acetic acid was heated to 115° for 9 3/4 days. The tube was then cooled, opened and the contents poured into 25 ml of an ice-cold saturated Na_2CO_3 solution; the resulting mixture was extracted with 4 x 10 ml of ether. The combined ether extracts were dried over $MgSO_4$ and concentrated to yield 0.060 g of a black material. This was chromatographed on a silica gel (1.0 x 105 cm) column, using hexane as the initial eluting solvent; later fractions contained up to 2% ether (25 ml fractions).

The following products were obtained:

Fraction 3, syn-11-bromo-11-chloro-3,4-dideuterotricyclo-[4.4.1.$0^{1,6}$]undecane (141a, 2nd trial); 0.017 g; there also could have been some 147 present.

Fraction 4-5, n-deuterobenzocycloheptene (120); 0.008 g (19%); this could also have included some 141a (2nd trial) and 147.

Fraction 15, unidentified compound(s); 0.003 g; probably consisted of 151, 154 and 155.

Fraction 21-24, 3,4-dideutero-6-chloromethylenecyclo-decanone (124b); 0.018 g (31%); ^{13}C NMR: (see Table 7).

Fraction 25-26, 9,10-dideuterobicyclo[5.4.0]undec-1(7)-en-2-one (88b); 0.004 g (9%); mass spectrum: (see Table 6).

Fraction 42-49, mixture of 126b and 125b; 0.008 g (14%, based on a 1:1 mixture).

Silver-assisted solvolysis of 11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c)

To a stirring solution of 2.062 g (7.88 mmol) of 89b and 89c in 120 ml of 90% aqueous acetone was added dropwise a solution of 3.27 g (15.76 mmol) of $AgClO_4$ in 30 ml of 90% aqueous acetone. After stirring the resulting mixture in the dark for 13 days, during which time a blackish precipitate appeared, it was quenched with ca. 0.5 g of sodium chloride, following which the acetone was evaporated. The residue was extracted with 4 x 25 ml of ether and the

combined ether extracts were washed with 25 ml of saturated Na_2CO_3 solution and 15 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 1.397 g of material which was chromatographed on a silica gel column (1.3 x 120 cm) using hexane as the initial eluting solvent. However, 0.115 g of 176 failed to dissolve in hexane and hence was isolated without chromatography. It was recrystallized from CCl_4 and the mother liquid was added to the column with the rest of the crude material. Elution with hexane, then a mixture of ether and hexane (1/99 for fractions 6-20; 2/98 for fractions 21-40; 4/96 for fractions 41-50; 8/92 for fractions 51-70; 16/84 for fractions 71-90; 20/80 for fractions 91-100), then acetone and hexane (15/85 for fractions 100-126) and finally methanol and hexane (15/85 for fractions 127-134), afforded the following products (50 ml fractions): Fraction 3-4, 11-bromo-11-chlorotricyclo[$4.4.1.0^{1,6}$]-undec-3-ene (89b and 89c) and tetralin (168); 0.835 g. Analysis of the mixture by ^1H NMR with an internal standard (dibromobenzene), and removal of the tetralin by distillation, indicated 0.075 g (11.4%) of tetralin present. A ^{13}C NMR of the propellanes (89b and 89c) showed that the mixture was enriched in 89b relative to the starting material. Fraction 33-35, 1-benzosuberone (91); 0.020 g (2.5%); the ^1H NMR and IR spectra were identical to those reported before (109, 138).

Fraction 36, anti-11-chlorobicyclo[4.4.1]undec-1,3-dien-6-ol (169); 0.012 g (1.2%); m.p. 90-91.5 (hexane); ^{1}H NMR: δ 6.15 (broad s, 2H), 5.70 (broad s, 1H), 4.73 (s, 1H), 2.88 (broad, OH), 2.30-1.30 (m, 10H) (see Figure 26); IR (CCl_4): 3580 (sharp, OH), 2920, 1620, 1595 (weak, C=C), 1090 (strong) cm^{-1} (see Figure 26); ^{13}C NMR ($CDCl_3$, rel. area): δ 131.8 (1.73), 131.2 (1.38), 125.2 (too small to measure), 87.8 (too small to measure), 71.6 (too small to measure), 40.9 (1), 36.7 (1.07), 32.9 (1.35), 23.2 (1.88), 22.5 (1.98), C_1 was not observed; High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{15}OCl$ 198.08115, found m/e (rel. int.) 198.0804 (0.5, P), 180 (8, P-18), 163 (16, P-35), 162 (22, P-36), 91 (40, P-107); UV (95% C_2H_5OH): 2417 Å (ε=5700).

Fraction 37-38, mixture of 6-chloromethylenecyclodec-3-enone (171 and 172), (11R, 6S) and (11S, 6R)-11-chlorobicyclo[4.4.1]undec-1(10),3-dien-6-ol (170) and 169; 0.097 g. Part of the mixture (0.049 g) was put on a preparative thin-layer silica gel plate and advanced with an 80/20 mixture of hexane/acetone. The first band (R_f=0.589) was 169 (0.012 g, 2.4%). The second band (R_f=0.534) was 170 (0.006 g, 1.2%); ^{1}H NMR: δ 5.05 (s, 1H), 5.35-5.65 (m, 3H), 3.05-3.35 (m, 2H), 2.85-1.35 (m, 8H) (see Figure 27); IR (CCl_4): 3600 (sharp, OH), 2950, 1650,

1615 (C=C), 1100 (strong) cm^{-1} (see Figure 27); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{15}OCl$ 198.08115, found m/e (rel. int.) 198.0807 (2.0, P), 180 (8.3, P-18), 163 (21.4, P-35), 162 (35.4, P-36), 91 (100, P-107). The third band (broad, R_f=0.467) was a mixture of 171 and 172 (0.031 g, 6.3%); ^1H NMR of 172: δ 5.87 (s, 1H), 5.62 (m, 2H), 3.17 (d, 2H, J=7Hz), 3.12 (d, 2H, J=7Hz), 2.49 (t, 2H, J=7Hz), 2.14 (t, 2H, J=7Hz), 1.90-1.45 (m, 4H) (see Figure 28 for spectrum of 171 and 172); IR of 172 (CCl_4): 2940, 1707 (C=O), 1650, 1630 (C=C), 857 cm^{-1} (see Figure 28 for spectrum of 171 and 172); ^{13}C NMR of 172 ($CDCl_3$, rel. area): δ 212.6 (1.05, C_1), 140.0 (1, C_{11}), 130.0 (2.65), 124.9 (3.34), 113.7 (3.84), 42.4 (4.06), 40.3 (3.42), 31.8 (3.05), 28.5 (3.18), 26.2 (3.74), 24.7 (5.34); High resolution mass spectrum of 171 and 172 at 70 ev: calc'd for $C_{11}H_{15}OCl$ 198.08115, found m/e (rel. int.) 198.0804 (6.9, P), 200 (1.1, P+2), 180 (7.7, P-18), 163 (59.3, P-35), 162 (26.4, P-36), 145 (30.1, P-43), 134 (11.6, P-64), 133 (10.7, P-65), 117 (16.8, P-81), 109 (12.0, P-89), 107 (14.8, P-91), 106 (18, P-92), 105 (25.6, P-93), 104 (12.1, P-94), 97 (20.6, P-101), 93 (50.2, P-105), 91 (100, P-107). For spectra of 171 see silver-assisted solvolysis of syn-11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undec-3-ene (89b).

Fraction 39-41, mixture of the two isomers of 6-chloro-methylenecyclodec-3-enone (171 and 172); 0.066g (6.7%). Thus the total yield of 171 and 172 was 13%.

Fraction 43-47, cis-tricyclo[5.4.0.$0^{5,7}$]undec-3-en-2-one (175); 0.106 g (13.1%); ^{1}H NMR: δ 7.04 (dd, H_4, J=9.5, 5Hz), 5.37 (d, H_3, J=9.5 Hz), 2.48 (broad d, H_1, J=11Hz), 2.0-1.0 (m, 9H), 0.97 (broad d, H_{11}, J=11Hz), 0.30 (dd, H_5, J=5, 3Hz) (see Figure 31); IR (CCl_4): 2930, 2855, 1678 (C=O), 1630, 1610 (C=C), 1445, 1243 cm^{-1} (see Figure 31); ^{13}C NMR ($CDCl_3$, rel. area): δ 201.1 (1, C_2), 153.8 (4.34, C_4), 122.0 (4.18, C_3), 48.7 (4.09, C_1), 34.2 (4.48), 32.1 (5.02), 31.8 (4.01), 25.3 (4.47), 24.8 (4.51), 23.6 (1.93, C_7), 20.8 (4.26, C_6); High resolution mass spectra at 70 ev: calc'd for $C_{11}H_{14}O$, 162.10447, found m/e (rel. int.), 162.1062 (9, P), 134 (3, P-28), 133 (2, P-29), 129 (2.8, P-33), 105 (4, P-57), 91 (12, P-71), 28 (100, P-134).

Fraction 84-92, syn-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (176); 0.086 g (18.6% yield includes material insoluble in hexane before placing on column); m.p. 165-166.5 (CCl_4, sealed tube); ^{1}H NMR ($CDCl_3$): δ 5.58 (AB quartet split further by exo-hydrogens on $C_{2,5}$, J=8, 3Hz, 2H), 4.64 (t, 1H, J=2Hz), 2.79 (d, 2H, J=15Hz), 2.33 (s, 2H, OH), 2.02 (broad d, 2H, J=15Hz), 1.95-1.55 (m, 8H) (see Figure 25); IR (CCl_4): 3590 (sharp OH), 2950, 1670, 1645 (C=C), 1095, 1040 cm^{-1} (see Figure 25); ^{13}C NMR ($CDCl_3$,

rel. area): δ 127.4 (2.35, $C_{3,4}$), 84.6 (1, $C_{1,6}$), 74.3 (1.16, C_{11}), 37.7 (2.02), 33.7 (2.01), 17.6 (1.99, $C_{8,9}$); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{17}O_2Cl$, 216.09171, found m/e (rel. int.) 216.0908 (3, P), 218 (1, P+2), 198 (1, P-18), 180 (3, P-36), 163 (13, P-53), 161 (26, P-55), 125 (16, P-91), 97 (25, P-119), 91 (17, P-125), 28 (100, P-188); anal. calc'd for $C_{11}H_{17}O_2Cl$: C, 60.97; H, 7.91; found for $C_{11}H_{17}O_2Cl$: C, 60.83; H, 8.03.

Fraction 101-103, mixture of 7-hydroxybicyclo [5.4.0]undec-9-en-2-one (173) and 177; 0.005 g; ^1H NMR of 173: δ 5.65 (m, 2H), 3.18 (m, 1H), 2.75-1.4 (m, 13H) (see Figure 29); IR (CCl_4): 3450 (broad, 0H), 2930, 1707 (C=0), 1260 cm^{-1} (see Figure 29).

Fraction 104-106, anti-11-chloro-1,6-dihydroxybicyclo-[4.4.1]undec-3-ene (177); 0.007 g (0.7%); ^1H NMR: δ 4.39 (s, 1H), 5.87 (m, 2H), 2.61-1.3 (m, 12H), 2.95 (broad s, 2H) (see Figure 23); IR (CCl_4): 3590 (sharp, 0H), 2960, 1670, 1265, 1250 cm^{-1} (see Figure 23); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{17}O_2Cl$, 216.0917, found m/e (rel. int.) 216.0918 (1, P), 198 (1, P-18), 163 (5, P-53), 161 (9, P-55), 149 (4, P-67), 145 (4.5, P-71), 97 (8.5, P-119), 91 (9, P-125), 63 (100, P-153), 48 (100, P-168).

Fraction 120-129, unidentified mixture; 0.044 g of a red oil, insoluble in nonpolar solvents (CCl_4, $CDCl_3$, etc.)

but soluble in hydroxylic solvents (ethanol and methanol); ^{1}H NMR(methanol): δ 2.3-1.2 (m).

Treatment of the basic extracts (Na_2CO_3 extracts and NaCl wash) with concentrated hydrochloric acid (until acidic), followed by extraction with 4 x 10 ml of ether, drying ($MgSO_4$) and solvent evaporation resulted in the isolation of 0.188 g of a semisolid brown mixture. Chromatography on a silica gel column (1.0 x 40 cm, initial eluting solvent was 95% etheral hexane, followed by a 45/50/5 mixture of chloroform/hexane/ether after fraction 16, followed by methanol for fractions 32-36; 50 ml fractions) afforded the following products:

Fraction 4-7, cis-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (178); 0.119 g (13.2%); m.p. 128-129° (CCl_4); ^{1}H NMR: δ 11.55 (broad, OH), 5.51 (broad s, 2H), 2.8-1.1 (m, 13H) (see Figure 32); IR (CCl_4): 3360-2500, 1707 (C=O), 1460, 1255, 1230, 865 cm^{-1} (see Figure 32); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{16}O_2$, 180.11503; found m/e (rel. int.), 180.1145 (11.6, P), 162 (10.3, P-18), 135 (100, P-45), 134 (24.9, P-46), 132 (17.5, P-48), 128 (16.8, P-52), 105 (25.9, P-75), 104 (27.1, P-76), 92 (32.9, P-88), 91 (73.2, P-89).

Fraction 11-12, trans-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (179); 0.007 g (0.8%); ^{1}H NMR: δ 5.60 (broad s, 2H), 11.6 (broad s, OH), 2.8-1.15 (m, 13H) (see Figure 33);

IR (CCl_4): 3500-2600, 1705 (C=O), 1260, 1095, 1010 cm^{-1} (see Figure 33); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{16}O_2$, 180.11503; found m/e (rel. int.), 180.1144 (12.1, P), 163 (41.9, P-17), 162 (31.8, P-18), 161 (75.2, P-19), 150 (22.3, P-30), 148 (17.5, P-32), 146 (16.8, P-34), 142 (25.7, P-38), 134 (39.2, P-46), 133 (100, P-47), 132 (32.6, P-48), 125 (40.3, P-55), 124 (24.6, P-56), 91 (50.2, P-89).

Fraction 22-25, trans-6-hydroxybicyclo[4.4.0]dec-3-ene-1-carboxylic acid (174); 0.013 g (1.3%); ^1H NMR: δ 5.83-5.58 (m, 2H), 2.75-2.10 (m, 4H), 1.90-1.2 (m, 8H), 3.15 (m, 1H, alcohol), 11.6 (m, 1H, CO_2H) (see Figure 34); IR (CCl_4): 3530 (alcohol OH), 3450-2500 (acid OH), 1712 (C=O), 1270 cm^{-1} (see Figure 34); no mass spectrum was obtained, but 174 gave the known trans-6-hydroxybicyclo[4.4.0]decane-1-carboxylic acid (144) upon hydrogenation.

Fraction 32-35, unidentified mixture; 0.039 g of a red oil which was insoluble in nonpolar solvents; ^1H NMR (MeOH): δ 2.3-1.2 (m).

The above solvolysis was repeated several times; once a compound eluted from the column after the mixture of monocyclic ketones (171 and 172). It was identified as bicyclo-[5.4.0]undec-1(7),9-dien-2-one (93) from its spectral properties: 0.008 g (1%); ^1H NMR: δ 5.54 (m, 2H), 2.85-1.3 (m, 12H) (see Figure 30); IR (CCl_4): 2940, 1670, 1620, 1265 cm^{-1}

(see Figure 30); High resolution mass spectrum at 70 ev [m/e (rel. int.)]: 162 (3, P, too small for exact mass measurement), calc'd for $C_{11}H_{12}O$, 160.08881; found 160.0877 (31, P-2), 131 (23, P-31), 133 (11, P-29), 104 (27, P-58), 91 (28, P-71), 28 (100, P-134). Upon standing, 93 gave rise to the aromatic ketone, 91.

Hydrogenation of syn-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (176)

A solution of 0.060 g (0.277 mmol) of 176 in 14 ml of ether was placed in a Parr shaker bottle with 0.005 g of 5% platinum on carbon, and hydrogenated (30 psi H_2) for 3/4 hour. Removal of the catalyst by filtration, followed by concentration gave 0.059 g (0.27 mmol, 97.7%) of 11-chloro-1,6-dihydroxybicyclo[4.4.1]undecane (125a) which was identical to that isolated before (vide supra).

Hydrogenation of anti-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (177)

A solution of 0.010 g (0.046 mmol) of 177 in 4 ml of ether was placed in a Parr shaker bottle with 0.001 g of 5% platinum on carbon and hydrogenated (30 psi H_2) for 20 minutes. Removal of the catalyst by filtration, followed by concentration gave 0.010 g (0.046 mmol, 99.5%) of 11-chloro-1,6-dihydroxybicyclo[4.4.1]undecane (125a) which was identical to that isolated before (vide supra).

Treatment of anti-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (177) under the solvolysis conditions

In a 25 ml flask a solution of 0.009 g (0.042 mmol) of 177 and 0.043 g (0.208 mmol) of silver perchlorate in 2 ml of 90% aqueous acetone was stirred for 7 days. Sodium chloride was then added to quench the reaction, the acetone evaporated, 3 ml of water added and the mixture extracted with 4 x 5 ml of ether. The combined ether extracts were washed with 5 ml of saturated Na_2CO_3 solution and 5 ml of saturated NaCl solution before drying over $MgSO_4$. Evaporation of the ether gave 0.007 g of a yellow oil which showed the presence of starting material 177 (^{1}H NMR), hydroxyketone 173 (IR) and enone 91 or 93 (IR).

Treatment of syn-11-chloro-1,6-dihydroxybicyclo[4.4.1]undec-3-ene (176) under the solvolysis conditions

Simply stirring 176 with silver perchlorate with or without perchloric acid (generated from $AgClO_4$ and 2-bromopropane) in 90% aqueous acetone for 22 days at room temperature gave essentially quantitative recovery of starting material. However, under the following more vigorous conditions reaction was realized. A solution of 0.025 g (0.205 mmol) of 2-bromopropane and 0.188 g (0.906 mmol) of silver perchlorate in 1 ml of 90% aqueous acetone was allowed to stir for 30 minutes. Then 0.043 g (0.209 mmol) of 176

dissolved in 6.5 ml of 90% aqueous acetone was added, and the tube was sealed. The resulting mixture was heated to 70° for 23 days; upon cooling the tube was opened, the reaction quenched with NaCl and the acetone evaporated. After 5 ml of H_2O was added, the solution was extracted with 4 x 10 ml of ether. The combined ether extracts were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 0.048 g of a black solid which was chromatographed on a silica gel column (1.0 x 37 cm) to give 0.012 g of starting 176 and some other material. This material (0.020 g) was separated on a preparative thin-layer silica gel plate using a 80/20 mixture of hexane and chloroform as the eluent. The first component (R_f=0.35, 0.004 g) had the following spectral characteristics: ^1H NMR: δ 3.5 (d, rel. int. 3), 2.5-2.2 (m, rel. int. 2), 1.4 (s, rel. int. 1); IR (CCl_4): 3640, 2940, 1625, 1265 cm^{-1}. The second component (R_f=0.28, 0.005 g) had the following spectral properties: ^1H NMR: δ 7.37 (s, rel. int. 1), 6.52 (s, rel. int. 1), 5.40 (m, rel. int. 2), 3.5 (d, rel. int. 1), 2.32 (dd, rel. int. 4), 1.5-1.37 (m, rel. int. 4); IR (CCl_4): 2950, 1720, 1610, 1275 cm^{-1}. The third component (R_f=0.19, 0.010 g) was identified as cis-7-hydroxybicyclo[5.4.0]undec-4-en-2-one (180): ^1H NMR: δ 5.42 (s, 2H), 2.8-1.25 (m, 13H) (see Figure 24); IR (CCl_4): 3640-3200 (OH), 2940, 1710 (C=O),

1270, 1100 cm^{-1} (see Figure 24); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{16}O_2$ 180.11503, found m/e (rel. int.) 180.1157 (4.7, P), 152 (1.4, P-28), 150 (2.2, P-30), 125 (1.8, P-55), 107 (1.3, P-73), 95 (3.5, P-85), 94 (3.3, P-86), 58 (18.3, P-122), 44 (100, P-136, 28 (100, P-152).

Treatment of (11R,6S) and (11S,6R)-11-chlorobicyclo[4.4.1]-undec-1(10),3-dien-6-ol (170) under the solvolysis conditions

In a 10 ml flask a solution of 0.005 g (0.025 mmol) of 170 in 2 ml of 90% aqueous acetone was stirred while 0.010 g (0.050 mmol) of silver perchlorate was added. The resulting mixture was stirred for 13 days before quenching with NaCl and evaporation of the acetone. Water (2 ml) was added to the residue, and the resulting mixture extracted with 4 x 7 ml of ether. The combined ether extracts were washed with 7 ml of a saturated Na_2CO_3 solution and 7 ml of a saturated NaCl solution before drying over $MgSO_4$. Evaporation of the ether gave 0.006 g (120%) of an oil which was spectroscopically identical to the starting material (170).

Treatment of anti-11-chlorobicyclo[4.4.1]undec-1,3-dien-6-ol (169) under the solvolysis conditions

To a stirring solution of 0.044 g (0.211 mmol) of $AgClO_4$ in 1 ml of 90% aqueous acetone was added 0.017 g (0.137 mmol) of 2-bromopropane, and the resulting mixture allowed to stir

for another 0.75 hour. Then a solution of 0.007 g (0.036 mmol) of 169 in 1.5 ml of 90% aqueous acetone was added, and the resulting mixture stirred for 20.5 days. The reaction was then quenched with NaCl and the acetone evaporated. After 2 ml of water had been added to the residue, the mixture was extracted with 4 x 7 ml of ether. The combined ether layers were washed with 7 ml of saturated Na_2CO_3 solution and 7 ml of saturated NaCl solution before drying over $MgSO_4$. Removal of the ether gave 0.007 g (100%) of material spectroscopically identical to the starting alcohol, 169.

Hydrogenation of cis-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (178)

To a solution of 0.020 g (0.11 mmol) of 178 in 10 ml of ether was added 0.003 g of 5% of platinum on carbon. The mixture was hydrogenated (30 psi H_2) on a Parr shaker for 30 minutes. Removal of the catalyst by filtration, and the ether by evaporation, gave 0.020 g (0.107 mmol, 96.4%) of cis-decalin-9-carboxylic acid (127) (135).

Hydrogenation of trans-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (179)

To a solution of 0.007 g (0.039 mmol) of 179 in 7 ml of ether was added 0.002 g of 5% platinum on carbon. The mixture was hydrogenated (30 psi H_2) on a Parr shaker for

30 minutes. Removal of the catalyst by filtration, and the ether by evaporation, gave 0.007 g (0.039 mmol, 100%) of trans-decalin-9-carboxylic acid (186), the properties of which were identical to those reported in the literature (135).

Hydrogenation of trans-6-hydroxybicyclo[4.4.0]dec-3-ene-1-carboxylic acid (174)

A solution of 0.004 g (0.020 mmol) of 174 in 8 ml of ether was placed in a Parr shaker bottle with 0.002 g of 5% platinum on carbon, and the mixture hydrogenated (30 psi H_2) for 30 minutes. Removal of the catalyst by filtration, followed by concentration, gave 0.004 g (0.020 mmol, 100%) of trans-6-hydroxybicyclo[4.4.0]decane-1-carboxylic acid (144), identical to that isolated before (117).

Silver-assisted solvolysis of syn-11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89b)

In a 250 ml flask a solution of 0.712 g (2.72 mmol) of a 95% 89b and 5% 89c mixture (as determined by ^{13}C NMR) in 30 ml of 90% aqueous acetone (by volume) was stirred while a solution of 1.128 g (5.44 mmol) of $AgClO_4$ in 24 ml of 90% aqueous acetone was slowly added. The resulting mixture was stirred for 13 days and then quenched with NaCl before evaporating the acetone and adding 10 ml of H_2O. This mixture was then extracted with 4 x 15 ml of ether, and the combined

ether extracts were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 0.601 g of crude material which was chromatographed on a silica gel column (1.3 x 95 cm) using hexane as the initial eluting solvent, followed by a mixture of ether and hexane (0.5/99.5 for fractions 25-33; 1/99 for fractions 34-43; 2/98 for fractions 44-53; 4/96 for fractions 54-63; 8/92 for fractions 64-73; 16/84 for fractions 74-89; 32/68 for fractions 90-100 and 60/40 for fractions 100-125; 50 ml fractions); the following products were isolated:

Fraction 2-3, syn-11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]-undec-3-ene (89b) and tetralin (168); 0.485 g; the amount of tetralin was determined by NMR (with internal dibromobenzene) and by its distillative removal; 168 0.015 g (12%).

Fraction 22-24, benzosuberone (91); 0.007 g (4.7%).

Fraction 31, anti-11-chlorobicyclo[4.4.1]undec-1,3-diene-6-ol (169); 0.017 g (9.2%).

Fraction 32-33, mixture of 6-chloromethylenecyclodec-3-enone (171) and 169; 0.021 g. ^{1}H NMR (internal standard dibromobenzene) established the following amounts: 171: 0.011 g (6.0%); 169: 0.010 g (5.4%).

Fraction 34-36, 6-chloromethylenecyclodec-3-enone (171); 0.019 g (10.3%); a single isomer as established by ^{13}C NMR

and ^{1}H NMR; ^{1}H NMR: δ 5.86 (s, 1H), 5.66 (tt, 2H, J=7, 7Hz), 3.16 (d, 2H, J=7Hz), 2.90 (d, 2H, J=7Hz), 2.44 (t, 2H, J=7Hz), 2.20 (t, 2H, J=7Hz), 1.9-1.5 (m, 4H) (see Figure 35); IR (CCl_4): 2950, 1710 (C=O), 1650, 1630 (C=C), 1250, 860 cm^{-1} (see Figure 35); ^{13}C NMR ($CDCl_3$, rel. area): δ 212.6 (1.02, C_1), 140.4 (1, C_{11}), 130.6 (2.39), 125.4 (2.05), 113.8 (2.36), 42.4 (1.77), 40.8 (1.49), 33.6 (1.27), 26.4 (1.98), 25.0 (1.63), 24.6 (2.37); High resolution mass spectrum at 70 ev: calc'd for $C_{11}H_{15}OCl$ 198.08115, found m/e (rel. int.) 198.08013 (5.7, P), 200 (2.3, P+2), 180 (8.7, P-18), 163 (59, P-35), 162 (24.6, P-36), 145 (30, P-44), 135 (10.3, P-54), 134 (12.2, P-55), 133 (11.8, P-56), 131 (11.6, P-58), 117 (16.3, P-81), 106 (18.1, P-92), 105 (23.4, P-93), 104 (11.5, P-94), 93 (47.9, P-105), 92 (22.3, P-106), 91 (90.7, P-107), 54 (100, P-135).

Fraction 71-73, syn-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (176); 0.006 g (3.0%). Since 176 was formed to the extent of ∿18.5% from the solvolysis of the mixture of 89b and 89c (vide supra), it could be concluded that 176 arises largely or solely from 89c. Although it seemed unlikely (e.g., no other products derived from 89c were observed in this experiment), it was impossible to exclude the formation of some 176 from 89b because the ratio of 89b to 89c in the earlier solvolysis of the mixture was unknown (although it was thought to be between 1 and 2).

Fraction 78-81, anti-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (177); 0.008 g (4.0%).

Fraction 95-100, unidentified material; 0.006 g; ^{1}H NMR ($CDCl_3$): δ 2.2-1.2 (m). The acidic products (0.021 g) obtained from acidification (conc. HCl) of the Na_2CO_3 and NaCl washes, ether extraction (4 x 10 ml) and drying over $MgSO_4$ were added to the column during the collection of fraction 98.

Fraction 121-123, cis-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (178); 0.018 g (10.7%).

Silver-assisted solvolysis of 11-bromo-11-chlorotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c) in 80% aqueous acetone

To a stirring solution of 1.499 g (5.96 mmol) of 89b and 89c in 75 ml of 80% aqueous acetone was added dropwise a solution of 2.47 g (11.9 mmol) of silver perchlorate in 15 ml of 80% aqueous acetone. The resulting solution was stirred for 8 days, following which the acetone was evaporated and the residue extracted with 3 x 25 ml of ether. The combined ether extracts were washed with 3 x 15 ml of saturated Na_2CO_3 solution and 15 ml of saturated NaCl solution before drying over $MgSO_4$. The ether was then evaporated and the 1.020 g residue chromatographed on a silica gel column (1.4 x 107 cm); however, 0.084 g of 176 failed to dissolve in the hexane used initially as the eluent, so it was

recrystallized from CCl_4, and the mother liquor added to the column. Further elution was conducted with a mixture of ether and hexane (1/99 for fractions 5-24; 2/98 for fractions 25-49; 4/96 for fractions 50-59; 8/92 for fractions 60-69 and 16/84 for fractions 70-85; 50 ml fractions). The following products were obtained:

Fraction 3-4, 11-bromo-11-chlorotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89b and 89c) and tetralin (168); 0.559 g; the amount of each was determined by ^{1}H NMR (internal p-dibromobenzene standard) and also by distilling the tetralin away; 168: 0.045 g (9%). The recovered starting material was a 9:1 mixture of 89b and 89c (^{13}C NMR analysis).

Fraction 8-13, 1-benzosuberone (91); 0.033 g (5.5%).

Fraction 19-21, anti-11-chlorobicyclo[4.4.1]undec-1,3-dien-6-ol (169); 0.027 g (3.6%).

Fraction 22-23, mixture of 6-chloromethylenecyclodec-3-enones (171 and 172), 169 and 170; 0.091 g; amount of each determined by ^{1}H NMR (internal p-dibromobenzene standard); 171 and 172; 0.050 g (6.7%); 169; 0.016 g (2.1%); the amount of 170 was determined by the difference; 0.025 g (3%).

Fraction 24-27, 6-chloromethylenecyclodec-3-enones (171 and 172); 0.024 g (3.2%).

Fraction 28-32, cis-tricyclo[5.4.0.$0^{5,7}$]undec-3-en-2-one (175); 0.071 g (11.6%).

Fraction 37-39, unidentified material; 0.007 g.
Fraction 47-53, syn-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (176); 0.070 g (8.6%); the total yield of 176 (including the amount which crystallized out) was 18.9%.
Fraction 57-60, anti-11-chloro-1,6-dihydroxybicyclo[4.4.1]-undec-3-ene (177); 0.013 g (1.6%). Acidification of the Na_2CO_3 and NaCl washes with concentrated hydrochloric acid, extraction with 3 x 10 ml of ether, drying ($MgSO_4$) and solvent evaporation gave 0.083 g of material which was placed on the column during the collection of fraction 56.
Fraction 62-66, cis-bicyclo[4.4.0]dec-3-ene-1-carboxylic acid (178); 0.062 g (9.0%).
Fraction 72-74, trans-6-hydroxybicyclo[4.4.0]dec-3-ene-1-carboxylic acid (174); 0.015 g (1.9%).

Separation of solvolysis products on the GLC

On column F (column at 175°, collector at 158°, detector at 196°, injector at 194°, helium flow at 17 ml/min at 40 psi) the solvolysis products were separated with the following retention times: 175, 57.5 minutes; 91, 67.5 minutes; 169, 87.7 minutes; 171 and 172, 128.8 minutes.

Competitive Rate Studies of the Solvolysis of syn- and anti-11-bromotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89e and 89f)

General considerations

Each solvolysis was followed by removing aliquots at measured time intervals, quenching with sodium chloride, and injecting into column F of the GLC (column at 175°, injector at 186°, detector at 187°, collector at 159°, He flow of 30.6 ml/min at 50 psi). The retention times for the compounds used were as follows: syn-11-bromotricyclo-[4.4.1.$0^{1,6}$]undec-3-ene (89e), 32.2 minutes; anti-11-bromotricyclo[4.4.1.$0^{1,6}$]undec-3-ene (89f), 29.1 minutes biphenyl (internal standard), 23.1 minutes. The correction factors, defined as the (peak wt of biphenyl)(wt of compound)/(wt of biphenyl)(peak wt of compound), were 3.01 for 89e and 3.00 for 89f. Thus for each aliquot, the amount of the unknown compound (either 89e or 89f) was found by the following computation: (correction factor)(peak wt of compound)(wt of biphenyl)/(peak wt of biphenyl)=wt of compound.

Methanolysis with a 20 fold excess of silver perchlorate

To a stirring solution of 0.023 g (0.084 mmol) of 89e, 0.0310 g (0.136 mmol) of 89f and 0.0151 g of biphenyl (internal standard) in 6 ml of methanol was added a solution of 0.913 g (4.4 mmol) of silver perchlorate in 16 ml of methanol and the resulting mixture stirred at room

temperature. After each time interval given in Table 11, a 1 ml aliquot was removed, quenched with NaCl and the components present analyzed by GLC. The listed weights of 89e and 89f obtained as described above are the average of two GLC traces. Treatment of the data as if the reaction were

Table 11. Weights (in grams) of 89e and 89f obtained from methanolysis with 20 fold excess silver perchlorate

	3 hrs	7 hrs	21.5 hrs	67 hrs	69 hrs	102 hrs	121.5 hrs
wt 89e	0.0182	0.0156	0.0145	0.0086	0.0095	0.0051	-----
wt 89f	0.0328	0.0285	0.0285	0.0240	0.0208	0.0164	0.0153

pseudo first-order gave the following results (139): 89e: $k=2.9\times10^{-6}$ sec^{-1} with a correlation coefficient of $r=0.955$ (defined as $r=m\sigma_x/\sigma_y$, m=slope and $(\sigma_x)^2=\sum_{i=1}^{N} X_i^2/N-\bar{X}^2$); 89f: $k=1.58\times10^{-6}$ sec^{-1} with a correlation coefficient of $r=0.970$. Dividing these rate constants by the silver concentration gave the following second-order rate constants: 89e: $k=1.45\times10^{-5}$ $M^{-1}sec^{-1}$; 89f: $k=7.89\times10^{-6}$ $M^{-1}sec^{-1}$.

Methanolysis with a stoichiometric amount of silver perchlorate

To a stirring solution of 0.0282 g (0.124 mmol) of 89e, 0.0342 g (0.151 mmol) of 89f and 0.0174 g of biphenyl (internal standard) in 4 ml of methanol was added a solution of 0.0571 g (0.275 mmol) of silver perchlorate in 6 ml of methanol and the resulting solution stirred at room temperature. After each of the time intervals given in Table 12, a 1 ml aliquot was removed, quenched with NaCl and the components present analyzed by GLC. The data was treated as if the reaction followed second-order kinetics (139), although this required the assumption that the available silver ion concentration was at all times equal to the sum of the 89e and 89f concentrations. The following results were obtained: 89e: $k=6.13\times10^{-7}$ $M^{-1}sec^{-1}$ with a correlation coefficient of $r=0.968$; 89f: $k=6.40\times10^{-7}$ $M^{-1}sec^{-1}$ with a correlation coefficient of $r=0.968$. From a simple comparison of the data, it is obvious that under these conditions 89f reacted faster than 89e.

Hydrolysis in 90% aqueous acetone

To a stirring solution of 0.0189 g (0.083 mmol) of 89e, 0.0277 g (0.122 mmol) of 89f and 0.0191 g of biphenyl in 7 ml of 90% aqueous acetone (by volume) was added a solution of 0.2127 g (1.025 mmol) of silver perchlorate in 8 ml of 90% aqueous acetone and the resulting mixture

Table 12. Weights (in grams) of 89e and 89f obtained from methanolysis with stoichiometric amount of silver perchlorate

	30 hrs	65.5 hrs	93 hrs	120.75 hrs	142 hrs	239 hrs	389 hrs	978 hrs
wt 89e	0.0284	0.0274	0.0268	0.0250	0.0250	0.0260	0.0238	0.0164
wt 89f	0.0340	0.0330	0.0315	0.0295	0.0294	0.0304	0.0278	0.0184

stirred at room temperature. After each of the time intervals given in Table 13, a 1 ml aliquot was removed, quenched with NaCl and the components present analyzed by GLC. The data were treated as if the reaction followed second-order

Table 13. Weights (in grams) of 89e and 89f obtained from hydrolysis with 5 fold excess of silver perchlorate

	29 hrs	92 hrs	119.75 hrs	141 hrs	238 hrs	385 hrs	977 hrs
wt 89e	0.0151	0.0119	0.0153	0.0127	0.0124	0.0107	0.0091
wt 89f	0.0173	0.0170	0.0212	0.0191	0.0175	0.0148	0.0145

kinetics (139), although it is probably more complex (see Part II of this work). This treatment required the assumption that the available silver ion concentration was at all times equal to the sum of the 89e and 89f concentrations plus four times the sum of the initial 89e and 89f concentrations. The following results were obtained: 89e: $k=1.89\times10^{-6}$ $M^{-1}sec^{-1}$ with correlation coefficient of r=0.866; 89f: $k=1.09\times10^{-6}$ $M^{-1}sec^{-1}$ with correlation coefficient of r=0.678. If the data were treated as if the reaction were pseudo

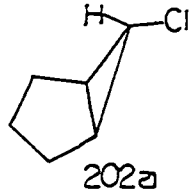
first-order, the following results were obtained: 89e: $k=1.34\times10^{-7}$ sec^{-1} with correlation coefficient of $r=0.862$; 89f: $k=7.93\times10^{-8}$ sec^{-1} with correlation coefficient of $r=0.699$. Dividing these rate constants by the silver concentration gave the following second-order constants: 89e: $k=1.96\times10^{-6}$ $M^{-1}sec^{-1}$; 89f: $k=1.16\times10^{-6}$ $M^{-1}sec^{-1}$.

PART II: THE EFFECT OF SILVER(I) ION UPON THE SOLVOLYSIS PRODUCTS IN THE DIBROMO- AND MONOBROMOBICYCLO-[6.1.0]NONANE SYSTEMS

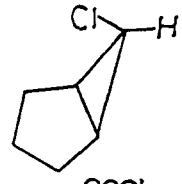
INTRODUCTION

The stereospecificity of the ring opening of cyclopropyl cations, according to the Woodward-Hoffmann-DePuy (90, 91) rules, spurred much research in the solvolysis of halogenocarbene adducts of olefins. For halogenocarbene adducts to cyclic olefins in medium-sized rings, solvolysis of the exo- halogen would result in the formation of reasonably stable derivatives of trans-cycloolefins.

Baird et al., after providing evidence for a concerted ring-opening in the solvolysis of exo- and endo-6-chlorobicyclo[3.1.0]hexane (202a and 202b) (140), investigated the halocarbene adducts of cycloheptene and cis-cyclooctene. Both epimers of 8-bromobicyclo[5.1.0]octane (203a and 203b) rearranged to cis, cis-cycloocta-1,3-diene

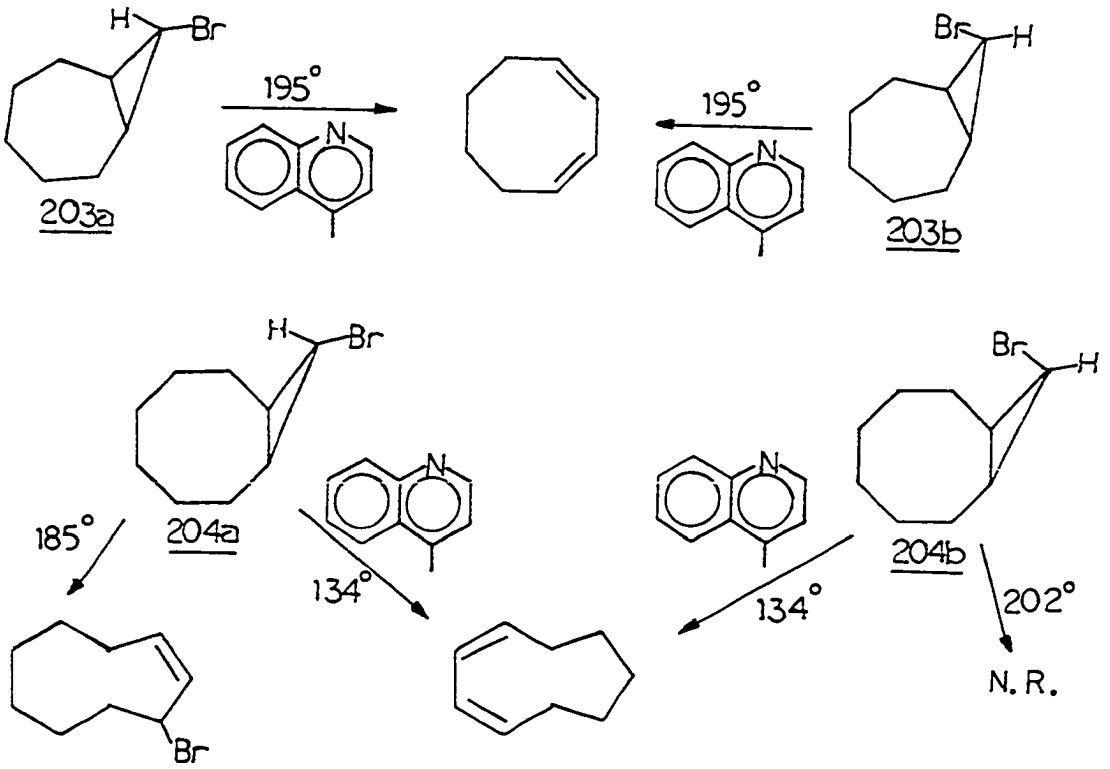


202a

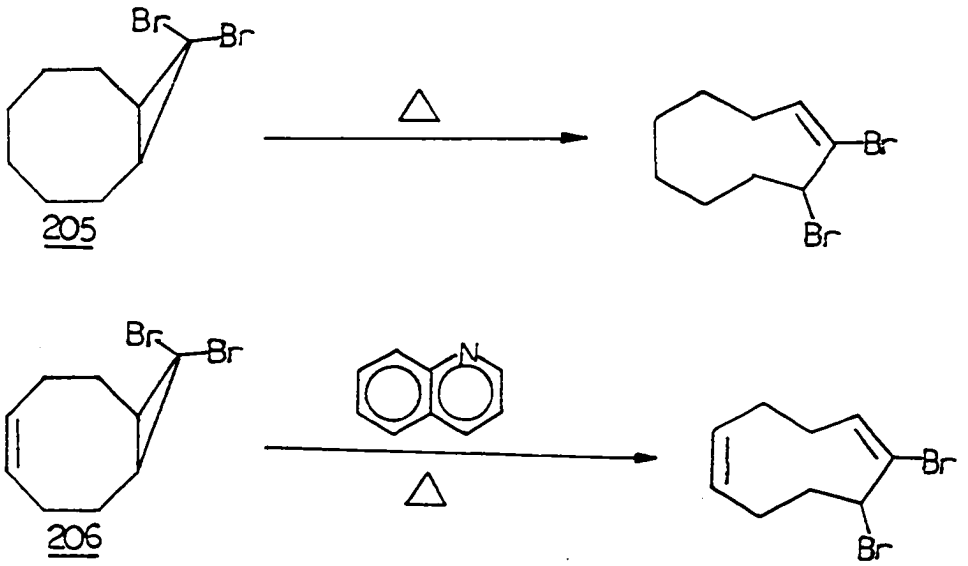


202b

upon heating to 195° in 4-methylquinoline. Upon heating exo-9-bromobicyclo[6.1.0]nonane (204a) to 185°, cis-3-bromocyclononene was obtained, while endo-9-bromobicyclo[6.1.0]-nonane (204b) remained unchanged at higher temperatures.

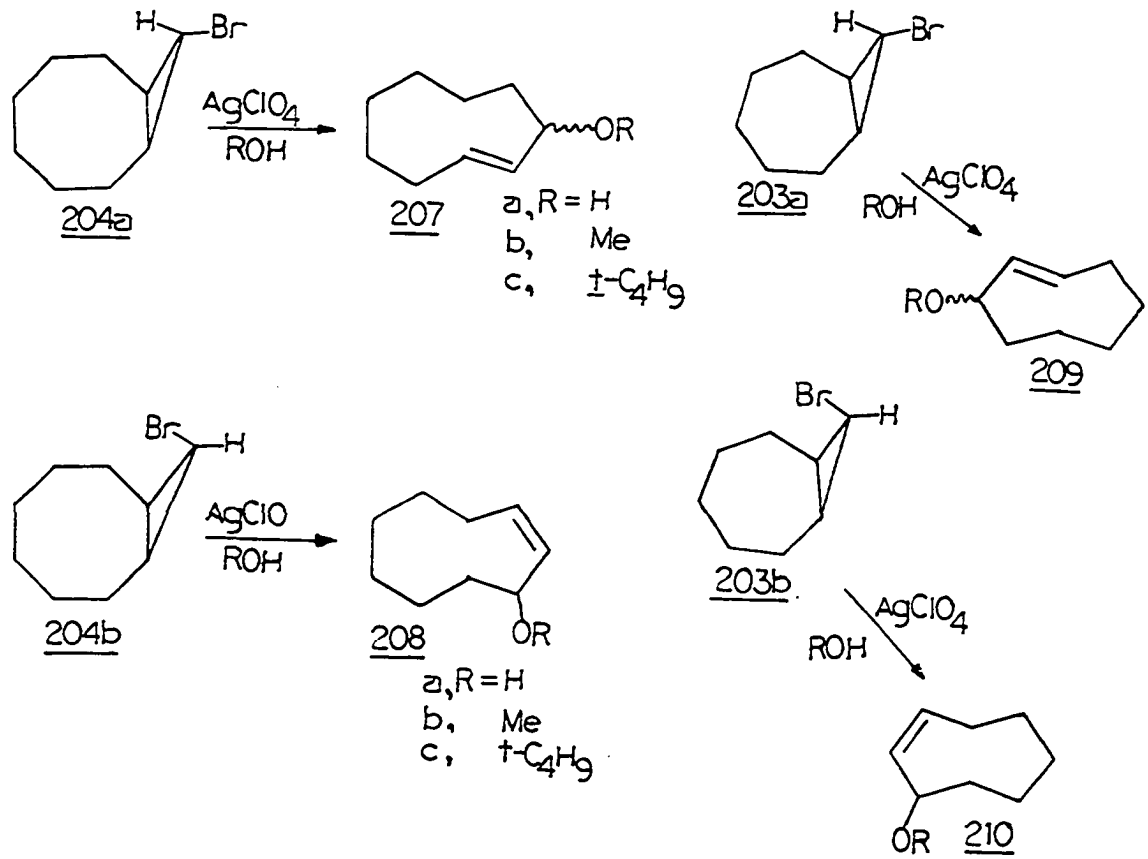


Heating of either isomer in 4-methylquinoline gave cis, cis-cyclonona-1,3-diene. Baird and Reese (141) also showed that 9,9-dibromobicyclo[6.1.0]nonane (205) rearranged to

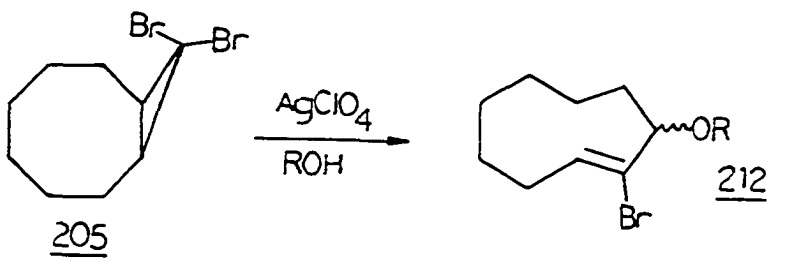


cis-1,9-dibromocyclononene upon heating, and 9,9-dibromobicyclo[6.1.0]non-4-ene (206) isomerized in hot quinoline solution to cis, cis-1,9-dibromocyclonona-1,5-diene. The authors concluded that it was unclear whether the reactions proceeded in a nonconcerted or concerted fashion, with isomerization possible at the trans-olefin product or the intermediate trans, trans-allyl cation stage.

After work by Duffin and Sutherland (142) had indicated that silver-assisted solvolysis of halogenocarbene adducts of 1,5-cyclooctadiene proceeded stereospecifically,

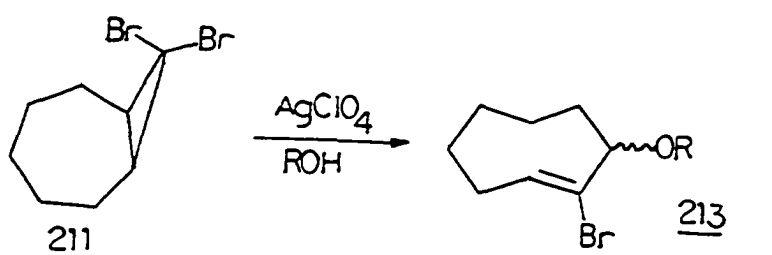


Baird and Reese observed similar results (143). Reese and Shaw (144a) reported silver-assisted solvolyses of exo- and endo-9-bromobicyclo[6.1.0]nonane (204a and 204b) in 95% aqueous methanol, which gave trans-3-hydroxycyclononene (207a) and cis-3-hydroxycyclononene (208a), respectively. Similar stereospecific solvolysis results were obtained with the exo and endo epimers of 8-bromobicyclo[5.1.0]-octane (203a and 203b) under similar conditions. When the reactions were conducted in methanol, stereospecific formation of the corresponding methoxy ethers was observed. The silver-assisted solvolysis of 9,9-dibromobicyclo[6.1.0]-nonane (205) and 8,8-dibromobicyclo[5.1.0]octane (211)



205 212

a, R = H
b, Me
c, t-C4H9
d, Ts

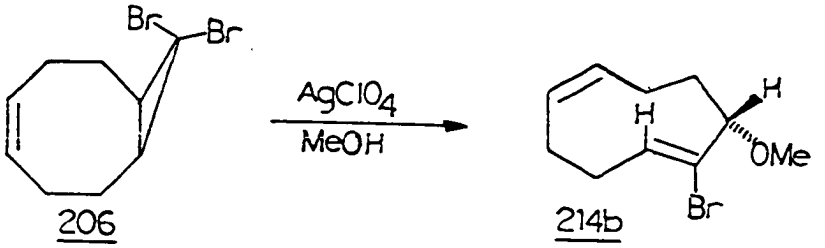


211 213

a, R = H
b, Me
c, t-C4H9

reportedly gave trans-2-bromocyclononene (212) and trans-2-bromocyclooctene (213) derivatives, respectively.

Reese and Shaw (144b) reported the formation of only one diastereomer in the silver-assisted hydrolysis or methanolysis of the dibromo-, dichloro-, and exo-monobromocarbene adducts of cycloheptene and the dibromo- and dichlorocarbene adducts of 1,5-cyclooctadiene. The dihalogenocarbene adducts were more stereospecific than the monhalogenocarbene adducts, and the authors established the configuration of the 2-bromo-3-methoxy-cis, trans-cyclonona-1,6-diene (214b) generated from 206. The diastereomers obtained from the silver-assisted hydrolysis



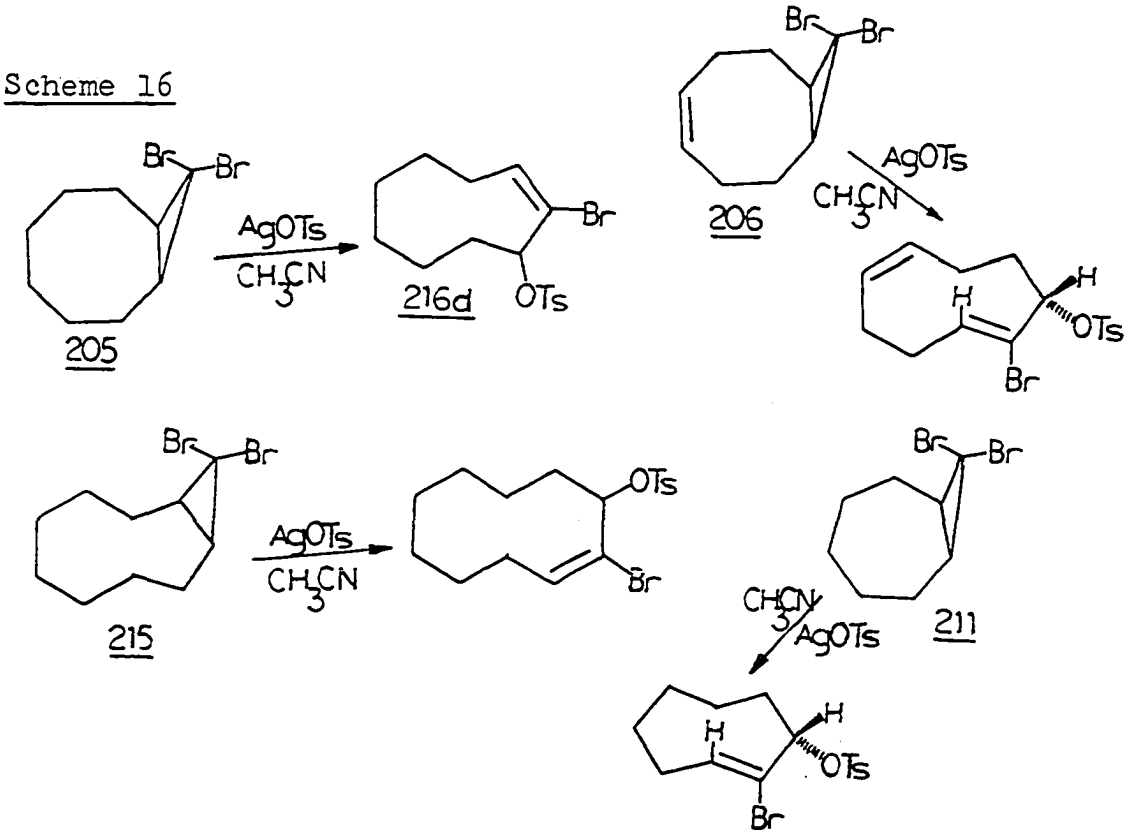
206 214b

or methanolysis of the dibromo-, dichloro- and exo-monobromocarbene adducts of cyclooctene equilibrated at room temperature, although absorptions for each diastereomer could be observed in the ^1H NMR spectra (144). Cope et al. (145) found that the energy of activation (E_a) for the racemization of trans-cyclononene was 20 $\pm$2 kcal/mole, and estimated that the half-life of this process would be 6 seconds at 30°.

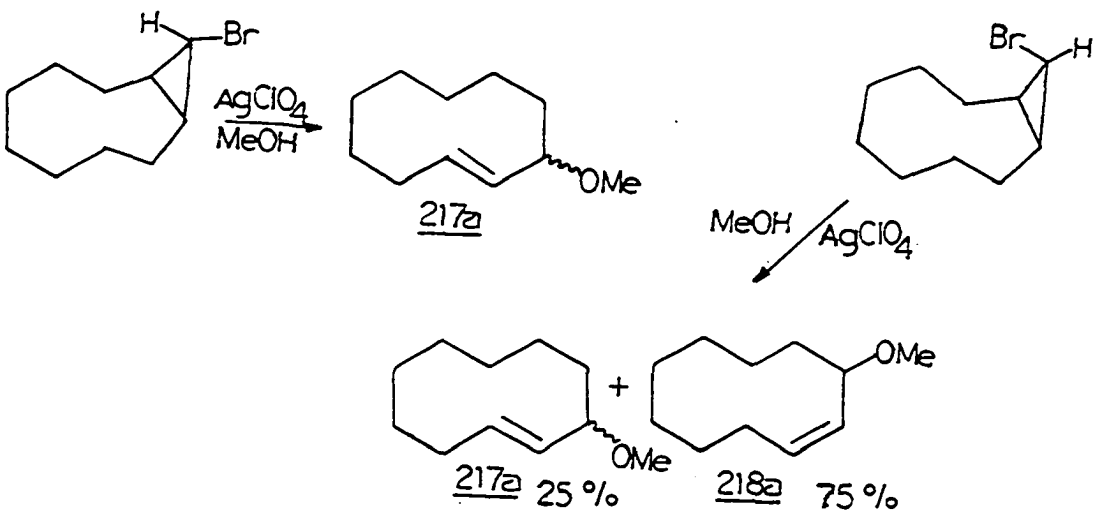
In their major paper on these solvolyses (106c), Reese and Shaw emphasized the importance of high concentrations of silver(I) ions for a fast and stereospecific reaction. They point out that isomerization from trans to cis-olefins, as observed by Whitham and Wright (146), was promoted by silver ions under the conditions they used for solvolysis, but that no isomerization was observed in the experiments conducted by Reese and Shaw.

Recently, Loozen et al. (147a) investigated the ring-opening of geminal dibromocyclopropanes with silver tosylate in refluxing acetonitrite (Scheme 16). In the larger ring

Scheme 16



compounds (205 and 215) only the cis-allylic tosylates were isolated, while only one trans-diastereomer was isolated in the solvolyses of 206 and 211. These authors also repeated the silver perchlorate assisted hydrolysis of 205 and 215 in order to obtain trans-1-bromo-9-hydroxycyclononene (212a) and trans-1-bromo-10-hydroxycyclodecene for preparation of authentic samples of the corresponding tosylates. Unexpectedly, they observed the formation of 30% of the cis-isomer in both cases, which in the case of 9,9-dibromobicyclo[6.1.0]nonane (205) was contrary to the Reese and Shaw results. Reese and Shaw noted 30% of the cis-1-bromo-10-hydroxycyclodecene, but only 5% of cis-1-bromo-9-hydroxycyclononene (this disappeared upon hydrolyzing the reaction mixture at 0°) in the silver-assisted hydrolyses of 215 and 205, respectively. Reese and Shaw also observed the formation of 25% of trans-3-methoxycyclodecene (217a) and 75% of the cis-isomer (218a) in the

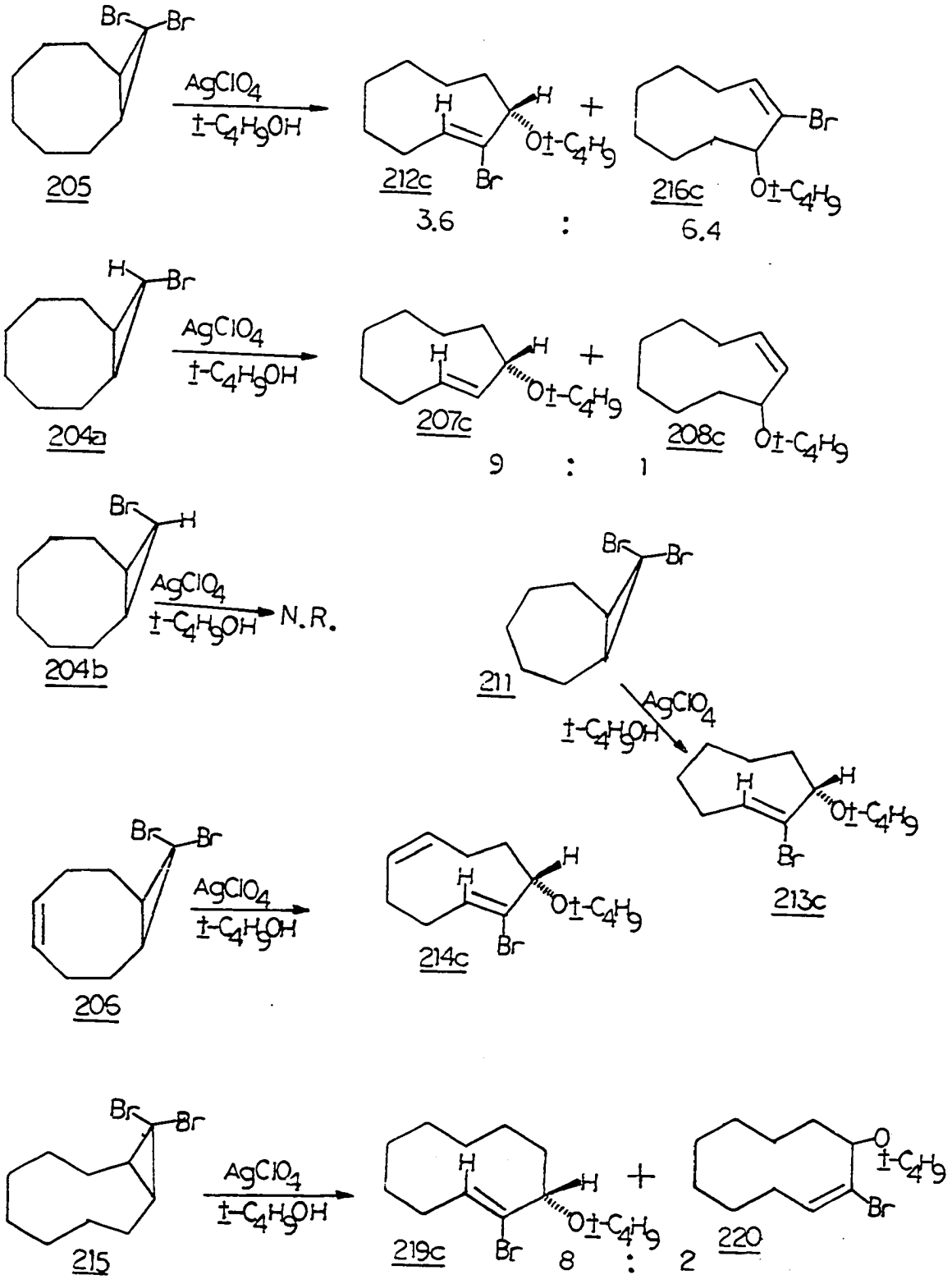


silver-assisted methanolysis of endo-10-bromobicyclo[7.1.0]-decane, while the exo-isomer gave the expected stereospecific trans product (217a) (106c). As regards the discrepancy between Loozen's and Reese's results, it should be noted that Loozen et al. used only 1 equivalent of silver perchlorate, while Reese and Shaw used 5 equivalents in less solvent.

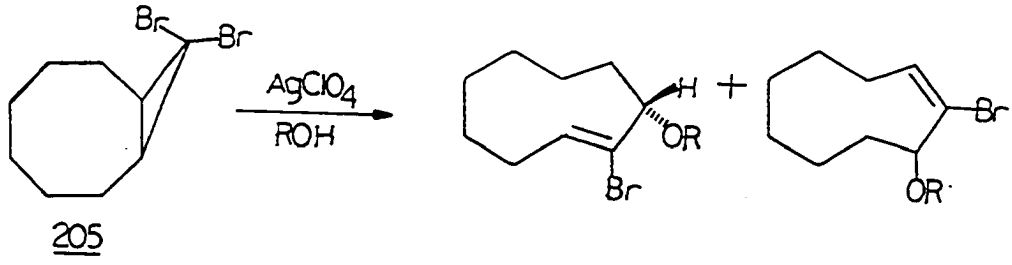
Loozen et al. (147b) reinvestigated the silver-assisted solvolysis of these geminal dibromocyclopropanes in tert-butyl alcohol at 40°. t-Butyl alcohol was chosen as the solvent since it is more nucleophilic than tosylate, and thus would hopefully trap the intermediate allylic cations before isomerization occurred. The results with exo- and endo-9-bromobicyclo[6.1.0]nonane (204a and 204b) indicated that the exo-bromide in 205 was ionizing (Scheme 17). They also performed the solvolysis of 205 in a series of alcohols. Since the most nucleophilic alcohol (methanol) gave the smallest amount of cis-olefin, it was concluded that the intermediate allyl cation was isomerizing (Scheme 18). It should be noted that it is a mistake to indicate just one trans-diastereomer, since even Loozen et al. note that equilibration occurred at room temperature, as reported by Reese and Shaw (144).

Blackburn and Ward (148) reported a kinetic study of the silver-assisted methanolysis of 205 and 206. They

Scheme 17


Br
Br
AgClO4
t-C4H9OH
205
H
H
+
Ot-C4H9
212c
Br
Br
216c
Ot-C4H9
3.6 : 6.4
H
Br
204a
207c
208c
9 : 1
204b
N.R.
211
213c
206
214c
215
219c
8 : 2
220

Scheme 18



205

R = Me	90	:	10
C_2H_5	61	:	39
i-C_3H_7	47	:	53
t-C_4H_9	36	:	64

reported both a first- and second-order dependence on silver(I) ion for the methanolysis rates of both 205 and 206; the rate of methanolysis of the olefinic substrate (206) was an order of magnitude greater than 205. Bach and Willis (149) have also reported both a first- and second-order dependence upon silver ion in the reaction of 2-bromooctane with silver perchlorate, although other workers have in general reported complex rate laws with nonintegral dependence on silver(I) ion (150). The observed data could be accounted for by use of an equilibrium as in Equation 22, but there is no precedent for such

complex ion formation in the case of silver perchlorate. Silver(I) salts are known to catalyze the rearrangement of small ring organic molecules, but not in a simple substituted cyclopropane at room temperature (151). Neither of the

$$2Ag^{+} + ClO_4^{-} \rightleftharpoons Ag_2ClO_4^{+} \qquad (22)$$

groups commented upon the variation of the trans/cis ratio apparent from comparison of the data obtained by Reese and Shaw (144), and Loozen et al. (147). The trans isomer (212a) predominated at high silver ion concentrations. There was apparently no silver ion catalyzed isomerization to the thermodynamically more stable cis isomer (216a) (152). By assuming that the pathway with the second-order dependence in silver generated only trans isomer (212a) while the first-order pathway generated both cis (216a) and trans (212a), one can derive a simplified expression for the ratio of trans (212a)/cis (216a) (Equation 23). Therefore, we chose to study the silver-assisted solvolysis of 205 under the

$$\frac{d[cis]}{dt} \propto k_1[Ag^+] \qquad \frac{d[trans]}{dt} \propto k_i[Ag^+] + k_2[Ag^+]^2;$$

$$\therefore \quad \frac{[trans]}{[cis]} = \frac{k_i + k_2[Ag^+]}{k_1} = \frac{k_i}{k_1} + \frac{k_2}{k_1}[Ag] \qquad (23)$$

conditions reported by Reese and Shaw, and Loozen et al., to establish if there was a product dependence upon silver(I) concentration, and if this can be expressed as a function of the *trans*/*cis* ratio.

RESULTS AND DISCUSSION

Synthesis

9,9-Dibromobicyclo[6.1.0]nonane (205) was synthesized by the addition of dibromocarbene to cis-cyclooctene according to the published procedure (153). Endo-9-bromobicyclo[6.1.0]nonane (204b) was prepared via tri-n-butyltin hydride reduction (154) of 205, while exo-9-bromobicyclo-[6.1.0]nonane (204a) was prepared from 205 by reduction with sodium in dimethylsulfoxide (155).

Silver-Assisted Solvolysis of 9,9-Dibromobicyclo[6.1.0]nonane

The silver-assisted hydrolysis of 205 was initially performed under the conditions reported by Reese and Shaw (144), and Loozen et al. (147), to verify their results. Since the results reported by both sets of authors were found to be correct, the experimental conditions must have resulted in the different product ratios (212/216) observed. The silver-assisted methanolysis of 205 was then performed, and results similar to the hydrolysis were obtained. Namely, at high silver ion concentrations, only trans-1-bromo-9-methoxycyclononene (212b) was observed, but on lowering the silver ion concentration, cis-1-bromo-9-methoxycyclononene (216b) was also observed. Thus the rate

data (148) obtained in methanol was not an artifact caused by the solvent.

The silver-assisted solvolysis of 205 was performed under varying silver concentrations in methanol and in 95% aqueous acetone in order to establish if there was a relationship between silver ion concentration and the product ratio (212/216). These results suggested that indeed the trans-olefin (212) was the major, if not only, product at high silver(I) concentrations, while increasing amounts of the cis-olefin were obtained on lowering the silver ion concentrations. The stabilities of trans-1-bromo-9-hydroxycyclononene (212a) (Figure 36) and cis-1-bromo-9-hydroxycyclononene (216a) (Figure 37) were checked under the reaction conditions at high silver ion concentration; neither showed isomerization or decomposition. Also, in one reaction mixture, the product ratio (212a/216a) was checked periodically over 30 days; no change occurred during this period.

Equation 23 predicts that a plot of the (212a/216a) ratio versus the silver ion concentration should be a straight line with an intercept of $\frac{k_i}{k_1}$ and a slope of $\frac{k_2}{k_1}$. A series of silver-assisted hydrolyses of 205 was performed at constant ionic strength (utilizing $LiClO_4$) in 95% aqueous acetone at room temperature (Table 14). A linear least squares fit of the data was obtained and the

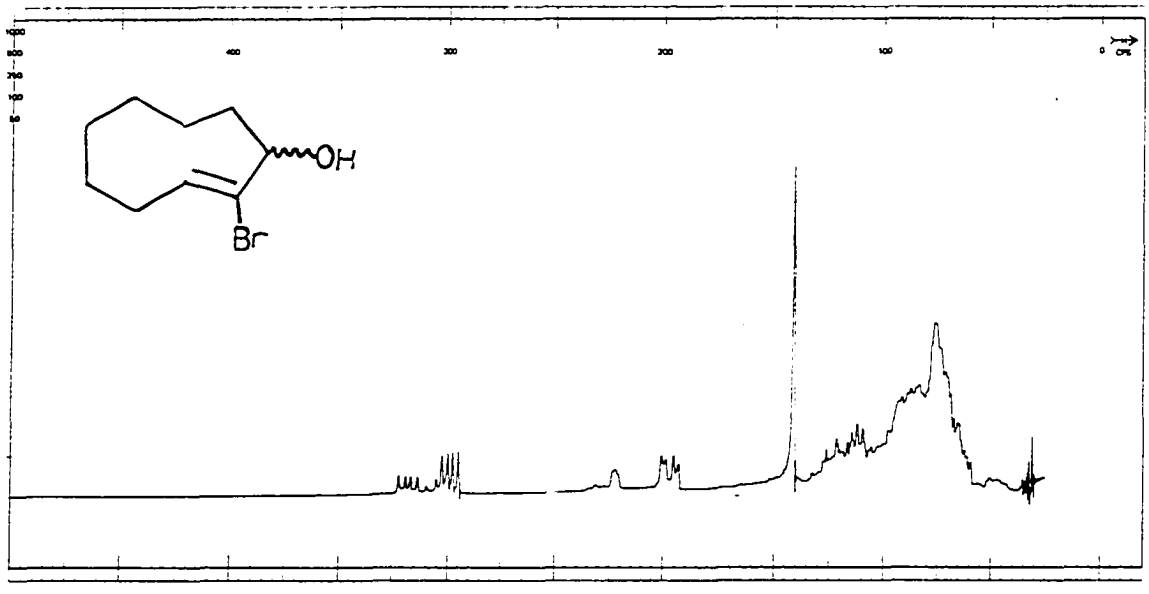


Figure 36. ^{1}H NMR spectrum (100 Mcps) of trans-1-bromo-9-hydroxycyclononene (212a)

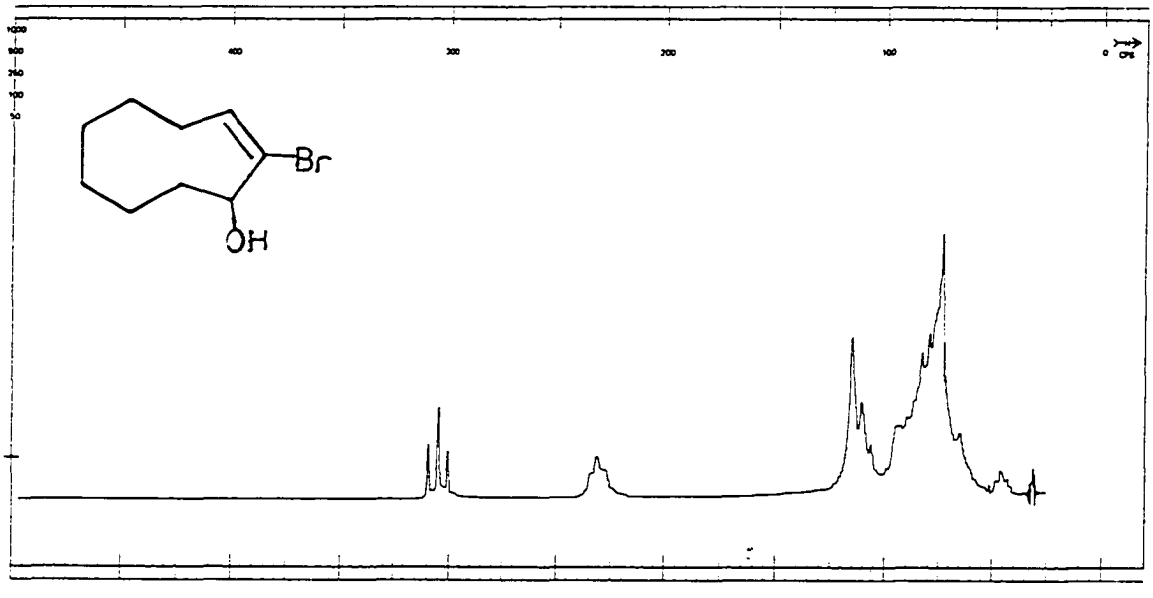


Figure 37. ^{1}H NMR spectrum (100 Mcps) of cis-1-bromo-9-hydroxycyclononene (216a)

Table 14. Silver-assisted solvolysis of 205 in 95% aqueous acetone

$[AgClO_4]$	$[LiClO_4]$	[205]	212a % trans[a]	216a % cis[a]	212a/216a	correlation coeff.	slope	intercept	
0.10	1.40	0.010	34.3	62.7	0.557	0.997	2.93	0.165	
0.40	1.10	0.010	53.8	45.9	1.171				
0.70	0.80	0.010	63.4	28.7	2.21				
1.00	0.50	0.010	74.5	23.0	3.24				all 10 points r=0.997 s=3.05 i=0.115
1.50	---	0.010	72.8	16.1	4.52				
0.10	1.40	0.010	28.3	61.7	0.46	0.998	3.17	0.064	
0.40	1.10	0.010	55.8	43.6	1.28				
0.70	0.80	0.010	65.8	30.2	2.15				
1.00	0.50	0.010	71.6	21.5	3.33				
1.50	---	0.010	79.4	16.5	4.81				
0.15	0.35	0.010	43.7	55.8	0.78	0.989	2.10	0.426	
0.20	0.30	0.010	43.3	54.7	0.79				
0.30	0.20	0.010	51.6	49.6	1.04				
0.40	0.10	0.010	52.9	40.6	1.30				
0.50	---	0.010	56.5	38.6	1.46				
0.20	1.40	0.10	47.2	48.4	0.98	0.996	5.29	-0.228	
0.40	1.20	0.10	58.9	38.5	1.53				
0.80	0.80	0.10	78.9	18.4	4.29				
1.60	---	0.10	85.8	10.5	8.17				

[a]These are absolute yields.

correlation coefficient, slope and intercept are reported for each set of data. A similar series of silver-assisted hydrolyses of 205 was carried out in 90% aqueous acetone (Table 15). The fit of the data to a straight line as indicated by Equation 23 is excellent in most cases (Figure 38 and Figure 39). The mechanistic significance of these results could not be immediately ascertained. For instance it was uncertain as to whether solvolysis of 9,9-dibromobicyclo[6.1.0]nonane (205) always involved ionization of the exo-bromine atom, or whether some endo-bromine loss could have occurred. Thus the study of the monobromo analogs of 205 was undertaken.

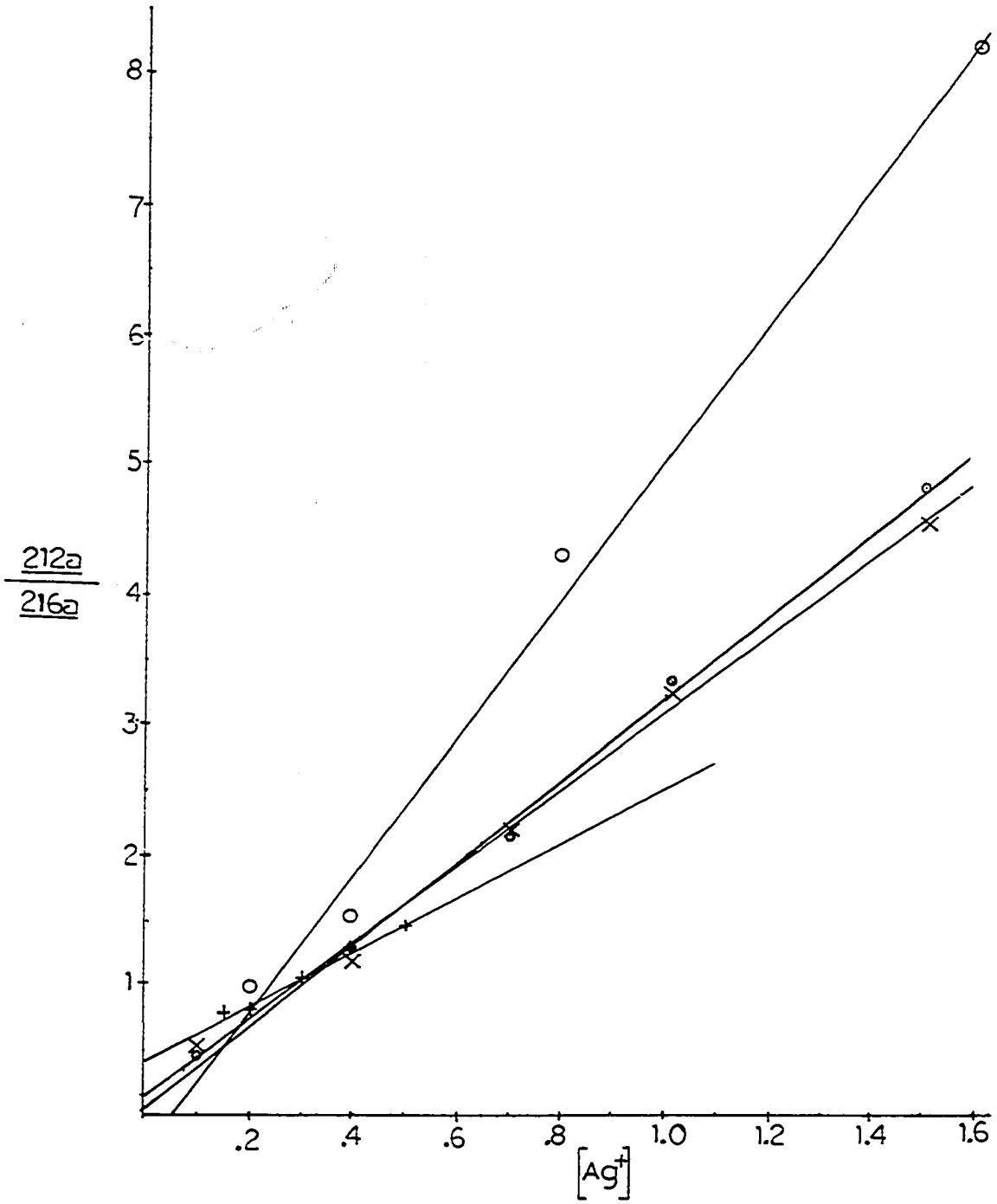
Silver-Assisted Solvolysis of exo-9-Bromobicyclo[6.1.0]nonane

Studies of the silver-assisted hydrolyses of exo-9-bromobicyclo[6.1.0]nonane (204a) and endo-9-bromobicyclo-[6.1.0]nonane (204b) were performed under the conditions reported by Reese and Shaw (106c). While each isomer gave the expected stereospecific products, solvolysis of 204a at low silver concentrations resulted in the formation of some cis-3-hydroxycyclononene (208a) (Figure 40) as well as the expected trans-3-hydroxycyclononene (207a) (Figure 41). These results paralleled those obtained by Loozen et al. (147b) in the silver-assisted solvolysis of 204a

Table 15. Silver-assisted solvolysis of 205 in 90% aqueous acetone

$[AgClO_4]$	$[LiClO_4]$	[205]	% 212a[a]	% 216a[a]	212a/216a	correlation coeff.	slope	intercept	
0.10	1.40	0.010	43.5	56.2	0.78	0.996	3.83	0.594	all 10 points r=0.988 s=3.88 i=0.402
0.40	1.10	0.010	67.2	28.0	2.40				
0.70	0.80	0.010	74.9	22.7	3.30				
1.00	0.50	0.010	78.2	17.9	4.37				
1.50	---	0.010	85.3	13.5	6.32				
0.10	1.40	0.010	45.5	59.4	0.77	0.987	3.92	0.209	
0.40	1.10	0.010	65.3	35.3	1.85				
0.70	0.80	0.010	70.3	29.8	2.36				
1.00	0.50	0.010	78.3	17.6	4.45				
1.50	---	0.010	86.3	14.1	6.12				

[a]These are absolute yields.



× - first set of data

∘ - second set of data

+ - third set of data

o - fourth set of data

Figure 38. Plot of data in Table 14

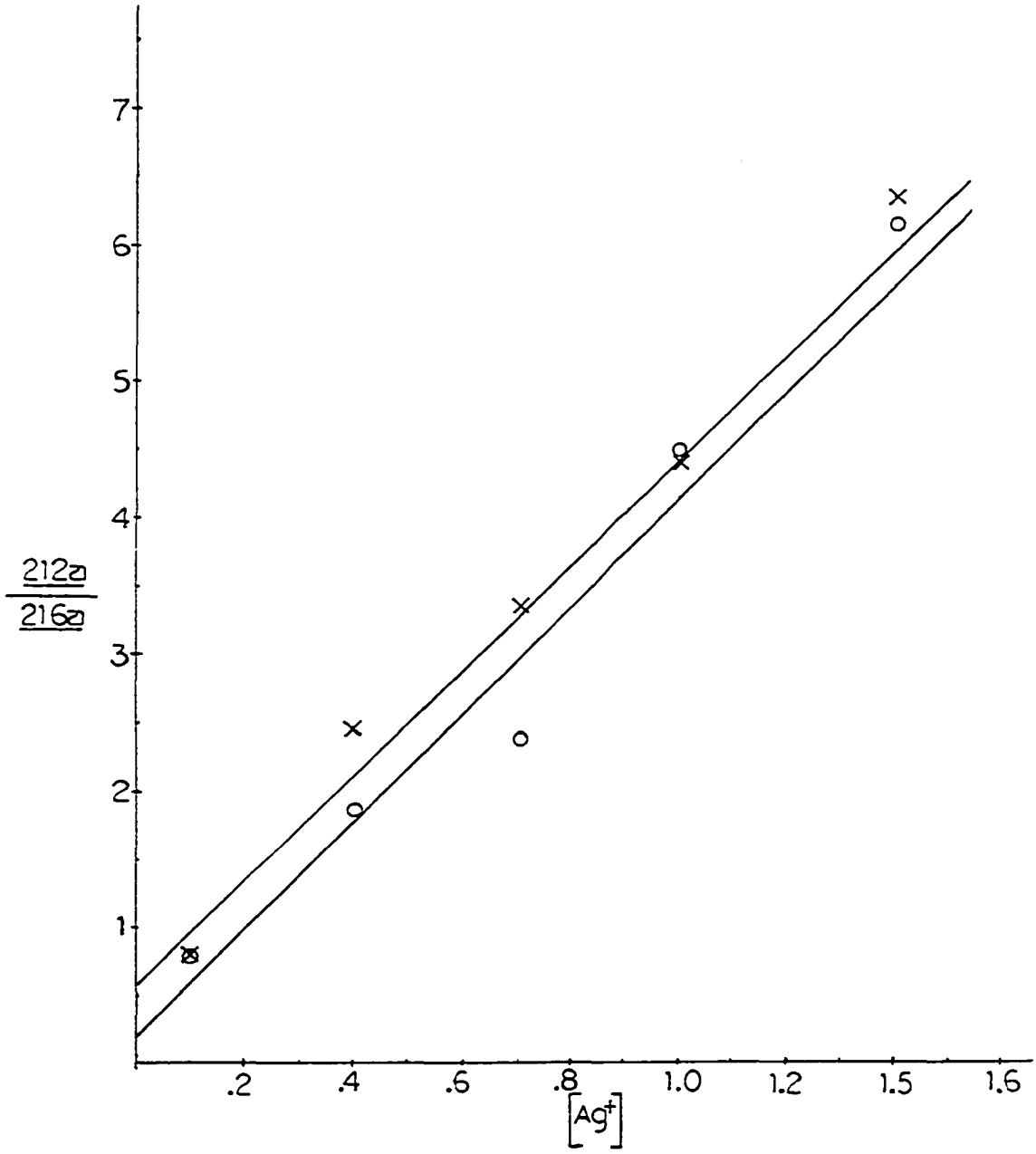


Figure 39. Plot of data in Table 15

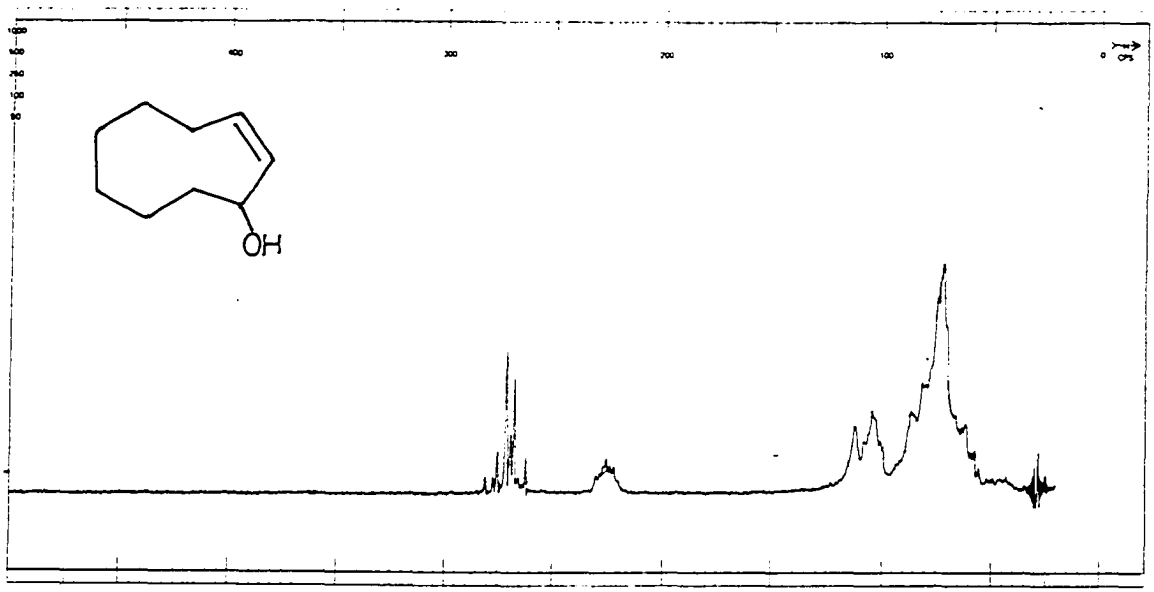


Figure 40. ^{1}H NMR spectrum (100 Mcps) of cis-3-hydroxycyclononene (208a)

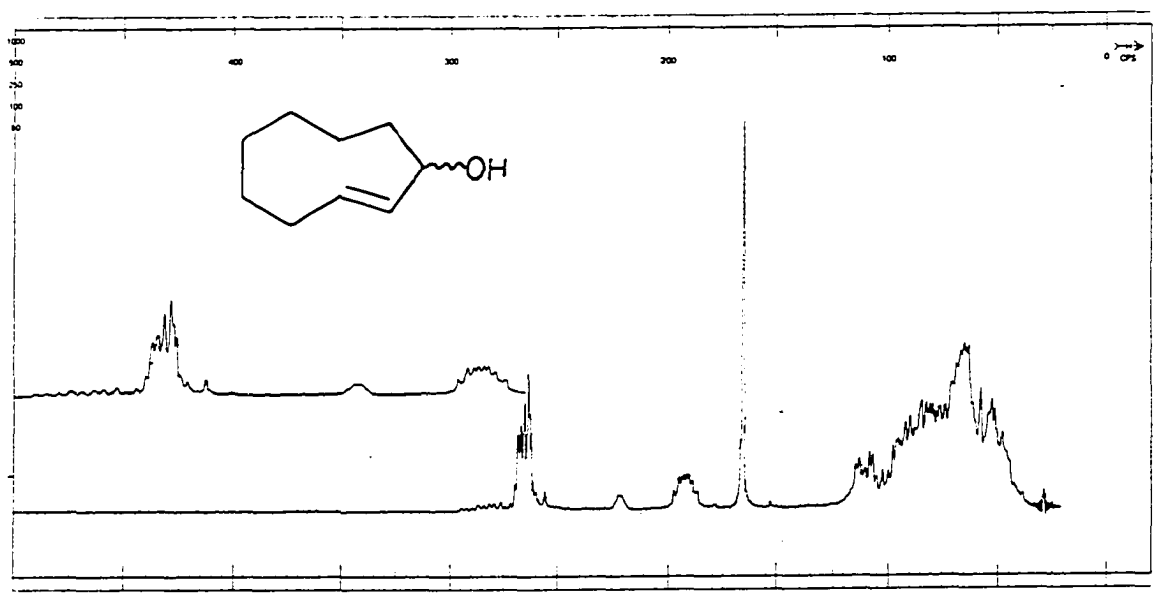


Figure 41. ^{1}H NMR spectrum (100 Mcps) of trans-3-hydroxycyclononene (207a)

in t-butyl alcohol. The solvolysis of 204b gave only the expected cis-olefin (208a), and the solvolysis of 204b was several orders of magnitude slower than that of 204a. No isomerization of the cis-olefin (208a) or trans-olefin (207a) was observed under the reaction conditions, but perchloric acid did catalyze the isomerization of 207a to 208a as well as the decomposition of 207a and 208a. However, these processes were slow under the reaction conditions utilized. A series of silver-assisted hydrolyses of 204a at room temperature was performed at constant ionic strength (utilizing $LiClO_4$) in 95% aqueous acetone (Table 16). The conditions for the formation of any cis-3-hydroxycyclononene (208a) were limited, as demonstrated by the data obtained (Figure 42). All attempts to solvolytically generate the cis-olefin (208a) from 204a in 90% aqueous acetone failed. The ionic strength as well as the concentration of 204a had to be high for the formation of any of the cis-olefin (208a). However, if the concentrate of 204a was too high, the perchloric acid formed destroyed and isomerized the products. The lability of 207a and 208a was in contrast to the stability of 212a and 216a.

Mechanistic Scheme

The observed dependence of the product olefin geometry on the silver ion concentration for the hydrolysis of

Table 16. Silver-assisted solvolysis of 204a

$[AgClO_4]$	$[LiClO_4]$	[204a]	% 208a[a]	% 207a[a]	207a/208a	correlation coeff.	slope	intercept
0.10	1.4	0.010	51.6	37.5	0.73	0.984	6.68	-.0012
0.20	1.3	0.010	38.8	53.5	1.38			
0.30	1.2	0.010	36.3	61.7	1.70			
0.40	1.1	0.010	23.5	67.7	2.88			
0.50	1.0	0.010	19.4	64.2	3.31			
0.20	2.80	0.020	10.7	80.0	7.48			
0.40	2.60	0.020	5.3	83.5	15.75			
0.60	2.40	0.020	1.7	91.5	53.8			
0.80	2.20	0.020	1.5	95.1	63.4			
1.00	2.00	0.020	1.0	98.8	98.8			
0.10	0.40	0.010	---	90.1	---			
0.50	---	0.010	---	92.3	---			
0.050	0.700	0.0050	---	89.4	---			
0.750	---	0.0050	---	87.6	---			

[a]These are absolute yields.

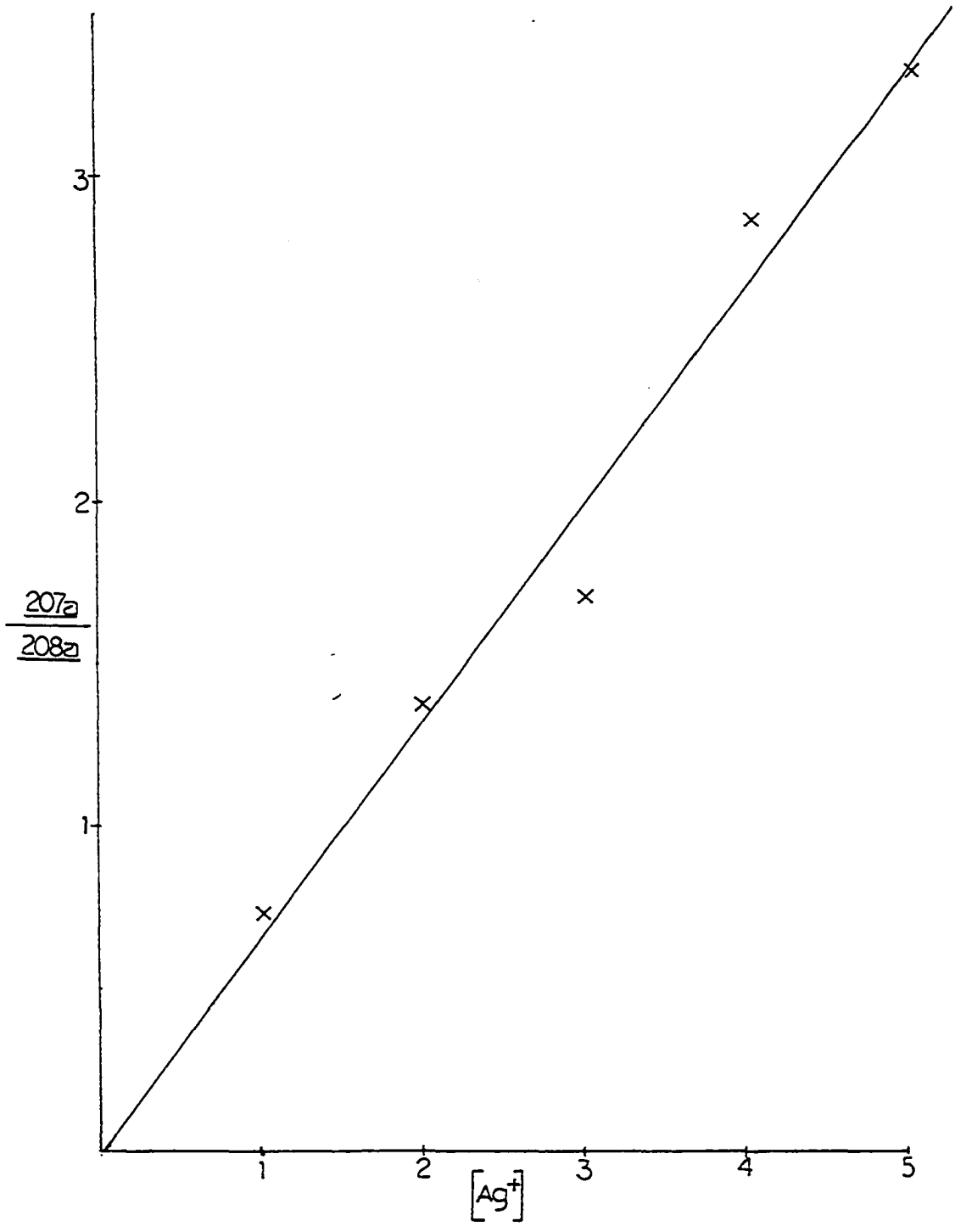
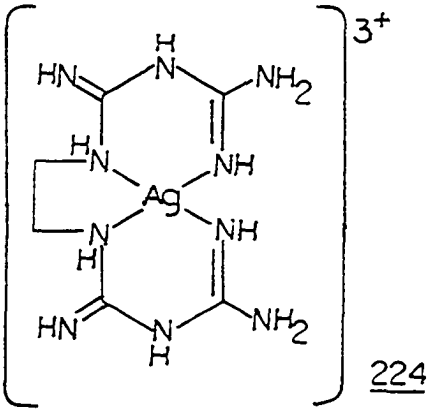


Figure 42. Plot of data in Table 16

monobromide 204a means that other than Woodward-Hoffman-DePuy-type stereochemical results can be obtained in these solvolyses. Thus it is perfectly reasonable to assume that the solvolysis of 205 always proceeds via ionization of the exo bromine atom. Further precise mechanistic deductions become complex, since several kinetically equivalent schemes can be concocted.

Loozen et al. (147b) found that decreased solvent nucleophilicity led to increased proportions of cis olefin formation (from 205). Those results are most easily understood in terms of initial trans, trans allyl cation (221) formation, followed by competitive nucleophilic attack to yield trans olefin (212) vs. rotational isomerization to give the cis, trans allyl cation (222), which in turn affords cis olefin product (216). As expected, the data amassed herein support such a scheme, since more trans olefin (212a) was formed in 90% aqueous acetone than in 95% aqueous acetone. It is attractive to assume that the product dependence upon silver ion concentration is due to complexation of the trans, trans allylic ion (221); such silver complexation would serve to prevent isomerization of 221 to 222, leading to enhanced production of trans olefin 212 at high silver ion concentrations. However, any scheme proposed must account for both the product dependence on silver ion concentration, and the first and second order

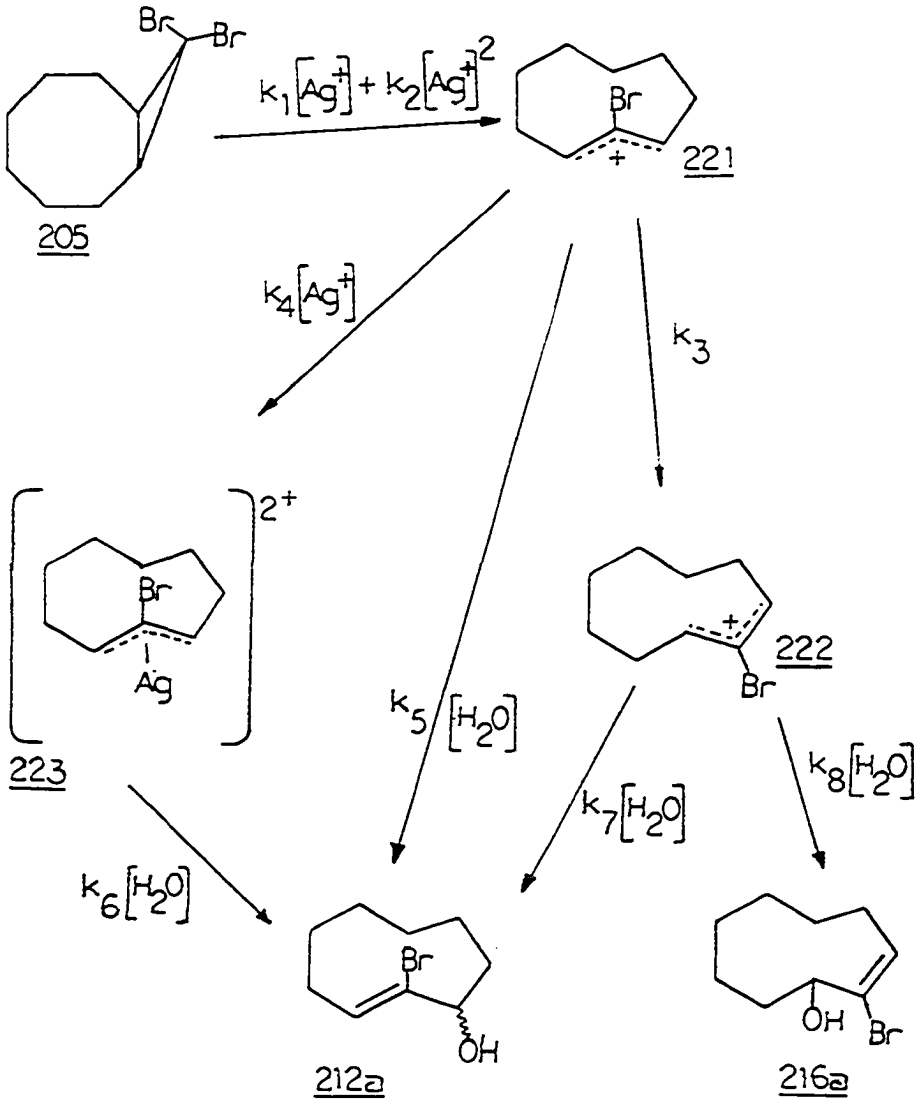


224

rate dependence on silver ion for the disappearance of 205 (148). Schemes 19 and 20 display the most reasonable kinetic possibilities.

The fundamental difference between the two proposed mechanisms is that in the former there is only one primary cation formed (221), and it is unassociated with silver ion (at least unassociated in a significant fashion), while the latter proposal envisions two primary products, one of which is the complexed ion 223. Although there are numerous examples of the complexation of silver(I) ion with olefins (156-159), the complexation of an allylic cation system with silver(I) ion has no verified precedent. The oxidation state of silver in 223 must be greater than (I), although whether it is (II) or (III) (as in ethylenedibiguanide, 224 (160)) is conjectural. Regardless, a considerable energy input would be necessary to complex the silver(I) ion with an allylic cation. Nickel (161), palladium (162) and platinum (163) all readily form π-allyl complexes (164).

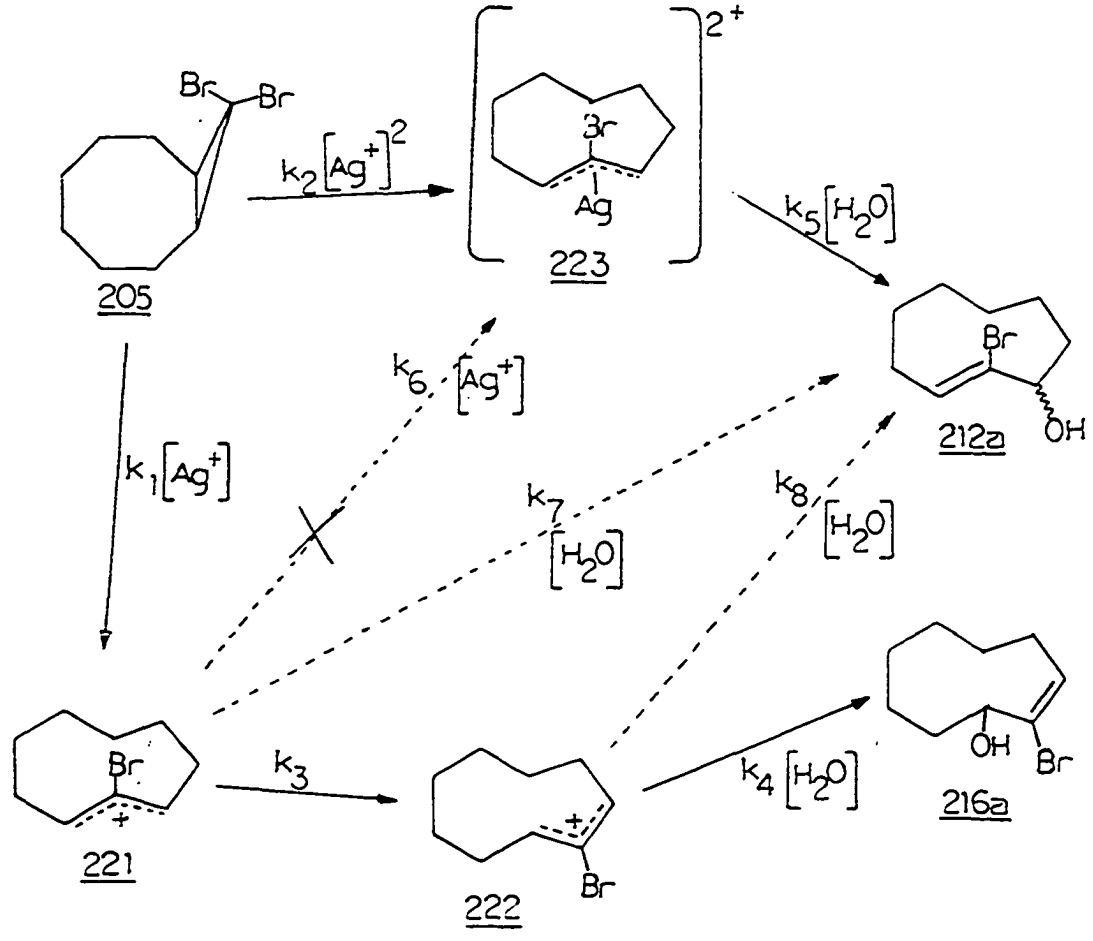
Scheme 19



$$\frac{[212a]}{[216a]} = \frac{k_4[Ag^+] + k_5[H_2O] + k_3k_7/(k_7 + k_8)}{k_3k_8/(k_7 + k_8)}$$

(Note: Formation of 221 is rate-determining step)

Scheme 20



$$\frac{[212a]}{[216a]} = \frac{k_2}{k_1}[Ag^+] \qquad k_6,\ k_7,\ k_8 \approx 0$$

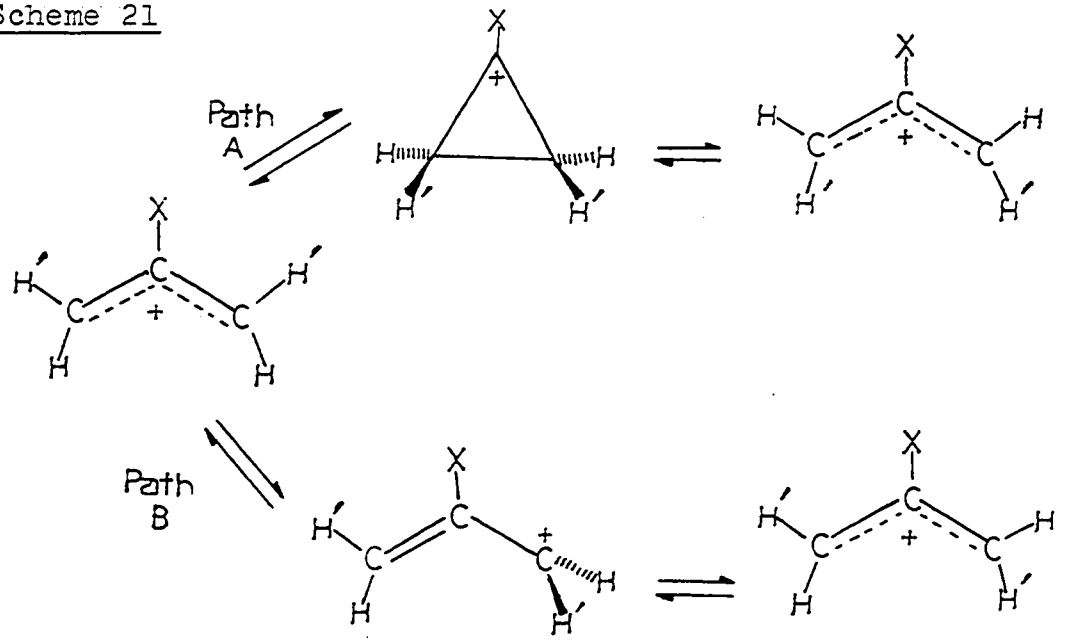
$$\frac{[212a]}{[216a]} = \frac{k_2[Ag](k_3 + k_7[H_2O]) + k_1k_7[H_2O] + k_1k_3k_8/(k_4 + k_8)}{k_1k_3k_4/(k_4 + k_8)}, \qquad k_6 \approx 0$$

(Note: If $k_6 \neq 0$, $\frac{[212a]}{[216a]}$ will not be linear in Ag^+)

The energy required to increase the oxidation state of silver(I) ion may well be provided by the stabilization afforded the strained allylic cation. Strained olefins form more stable complexes with silver(I) ion as shown by the separation of trans-cyclooctene from cis-cyclooctene (159). It is noteworthy that the intermediacy of a complexed ion analogous to 223 can nicely account for the observation of only one trans diastereomer in the silver-assisted solvolyses of each of 211, 203a and 206. From the available data, it is impossible to determine which (if either) scheme is operational in this bicyclo[6.1.0]-nonane system.

In both Schemes 19 and 20, the isomerization of trans, trans allyl cation 221 to cis, trans allyl cation 222 is proposed to occur via rotation around the C_2-C_3 bond. However, from calculations on substituted cyclopropyl cations, Radom et al. (165) concluded that stereomutation of allyl cations could take place via disrotatory ring closure to a cyclopropyl cation followed by disrotatory ring opening in the opposite sense (Scheme 21, Path A). For the parent cyclopropyl cation (X=H), they concluded a simple stepwise rotation of the terminal methylene groups (i.e., isomerization via a perpendicular allyl cation) would be favored (Scheme 21, Path B). But when X was CH_3, NH_2, OH and F, pathway A was predicted to be favored. Recently, these

Scheme 21



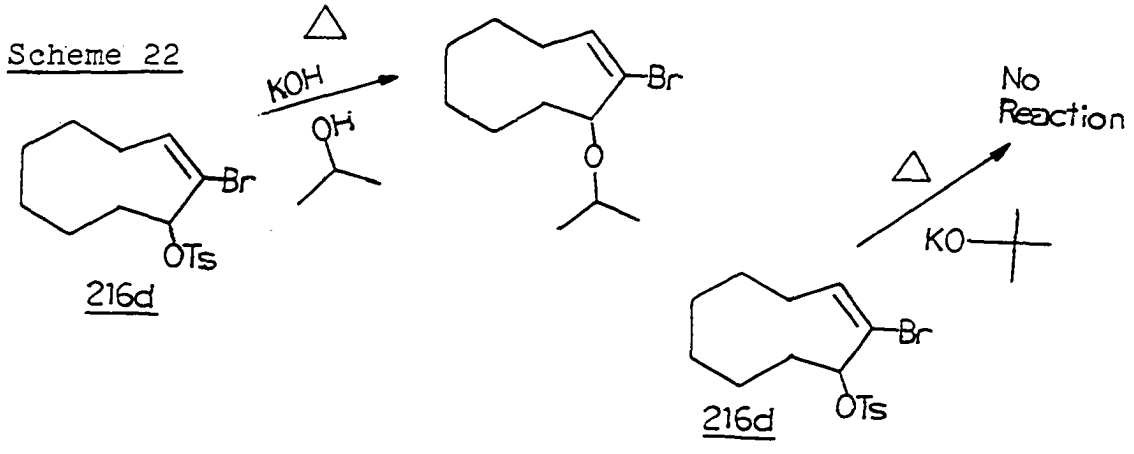
calculations have been questioned by Allinger and Siefert (166) who calculated a lower barrier for the rotation of the terminal methylene group. Some experimental results (167) showed that substitution of methyl groups on C_1 and C_3 stabilize the perpendicular allyl cation, thus lowering the energy of this species by half the amount predicted by the calculations by Radom et al.

Loozen et al. (147) noticed isomerization in 215 and 205, but not in 211, which implied that rotation to a cis, trans allyl cation could occur in the larger rings. From examination of models, it appears that a cis, trans allyl cation in an eight-membered ring is strained, but this is not the case for such an ion in nine- and ten-membered rings. The cis, cis allyl cation can be accommodated in an

eight-membered ring as readily as in a nine- or ten-membered ring. Thus isomerization should have occurred in the solvolysis of 211, were it occurring by Path A. It is also noteworthy that the trans-diastereomers (213) from 211 are readily separately observed, but that they interconvert rapidly in the nine- and ten-membered rings (212 and 219, respectively). This isomerization involves a rotation of the alkyl bridge about the trans-double bond, which is more facile in larger rings. Isomerization of the trans, trans allyl cation by rotation should occur more readily in larger rings, which is consistent with what is observed.

Finally, the possibility that elimination from an allyl cation (presumably 221) to a 1,3-cyclononadiene, followed by silver-promoted addition of water to the diene (resulting in 212a and 216a) was occurring, was considered. All attempts to prepare a 1,3-cyclononadiene from 216d failed (Scheme 22). Even refluxing 216d in potassium

Scheme 22



t-butoxide for 3 hours resulted in the recovery of starting material. Calculations have indicated that 1,3-cyclononadienes are more strained than either cis or trans-cyclononene (152b). Baird and Reese's results on the pyrolysis of 205, 204a and 204b indicated that these dienes are only obtained when a nitrogen base is used as the solvent (141). Thus 1,3-cyclononadienes are not viable intermediates in these solvolyses.

EXPERIMENTAL

General

9,9-Dibromobicyclo[6.1.0]nonane (205)

Addition of dibromocarbene to cis-cyclooctene according to the published procedure (153) gave 205 in 86% yield, b.p. 60-65° (0.13-0.14 torr); ^{1}H NMR: δ 2.25-1.20 (m, 14H).

endo-9-Bromobicyclo[6.1.0]nonane (204b)

Reduction of 205 with tri-n-butyltin hydride according to the published procedure (154) gave 204b in 71% yield, b.p. 35-38° (0.07 torr). Chromatography through neutral alumina (Woelm) resulted in the destruction of the small amount of the exo-9-bromobicyclo[6.1.0]nonane isomer which was also present; ^{1}H NMR: δ 3.14 (t, 1H, J=7.5Hz), 2.3-0.80 (m, 14H).

exo-9-Bromobicyclo[6.1.0]nonane (204a)

Reaction of 205 with sodium in dimethyl sulfoxide according to the published procedure (155) gave 204a in 49% yield, b.p. 43-47° (0.14 torr). GLC analysis on column C (column at 128°, detector at 175°, injector at 172°, collector at 150°, helium gas flow of 29 ml/min at 27 psi) showed the presence of 204a (98.5%; retention time, 7.2 min) and 204b (1.5%; retention time, 8.9 min); ^{1}H NMR: δ 2.21 (m, 3H), 1.95-0.85 (m, 12H).

Solvolysis of 9,9-dibromobicyclo[6.1.0]nonane (205) in 95% aqueous acetone with 5 eq. $AgClO_4$

To a stirring solution of 0.435 g (1.61 mmol) of 205 in 3 ml of 95% aqueous acetone (by volume) was added a solution of 1.670 g (8.05 mmol) of silver perchlorate in 2 ml of 95% aqueous acetone. After stirring the resulting mixture for 2 hours, the acetone was removed and the residue was extracted with 4 x 10 ml of ether. The combined ether layers were washed with 10 ml of saturated sodium carbonate solution and 10 ml of sodium chloride solution before drying over $MgSO_4$. Evaporation of the ether gave 0.264 g (75%) of trans-1-bromo-9-hydroxycyclononene (212b), along with a trace of the cis alcohol as noted by Reese and Shaw (144, 106c); ^1H NMR: δ 6.23 (dd, J=6Hz, J=10.5Hz), 5.86 (dd, J=6Hz, J=11Hz) vinyl hydrogen, 4.37 (m, 1H, OH), 3.94 (m), 3.77 (m) methine hydrogen, 2.5-1.2 (m, 12H) (Figure 36).

Solvolysis of 9,9-dibromobicyclo[6.1.0]nonane (205) in 95% aqueous acetone with 1 eq. $AgClO_4$

To a stirring solution of 3.256 g (12.0 mmol) of 205 in 40 ml of 95% aqueous acetone was added a solution of 2.49 g (12.0 mmol) of silver perchlorate in 20 ml of 95% aqueous acetone. After stirring the resulting mixture for 3 hours, the acetone was removed and the

residue was extracted with 4 x 20 ml of ether. The combined ether extracts were washed with 20 ml of saturated Na_2CO_3 solution and 20 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration gave 1.997 g (76%) of a mixture of cis and trans-1-bromo-9-hydroxycyclononene. Column chromatography on a silica gel column (1.4 x 93 cm) using a mixture of ether and hexane as the eluent (1/99 for fractions 1-7; 2/98 for fractions 8-16; 4/96 for fractions 17-23; 8/92 for fractions 24-30; 16/84 for fractions 31-38; 50 ml fractions) gave the following eluates:

Fraction 22-24, cis-1-bromo-9-hydroxycyclononene (216a); 0.320 g (12.2%); m.p. 72-74° (hexane); ^1H NMR: δ 6.09 (t, 1H, J=9.5Hz), 4.67 (m, 1H), 2.55-1.2 (m, 13H) (Figure 37) (147a).

Fraction 25-27, mixture of cis- and trans-1-bromo-9-hydroxycyclononene (216a and 212a); 0.559 g (21.3%).

Fraction 28-31, trans-1-bromo-9-hydroxycyclononene (212a); 1.110 g (42.2%).

Silver-assisted methanolysis of 9,9-dibromobicyclo[6.1.0]-nonane (205)

To a stirring solution of 0.379 g (1.40 mmol) of 205 in 2 ml of methanol was added a solution of 1.45 g (7 mmol) of silver perchlorate in 2 ml of methanol. Evaporation of the methanol and extraction of the residue with 4 x 10 ml

of ether, drying and concentration gave 0.264 g (81%) of trans-1-bromo-9-methoxycyclononene (212b), identical to that isolated before (106c).

Silver-assisted methanolysis and hydrolysis of (205)

The silver-assisted hydrolysis and methanolysis of 205 were performed as outlined above. The ratio of 212/216 was determined by injection into column B on the gas chromatograph (column at 172°, collector at 165°, injector at 188°, detector at 190°, flow of 45 ml/min of He at 50 psi). The retention times were for 212a: 64.7 minutes, and for 216a: 59.4 minutes. At high concentrations of silver(I) ion only the trans olefin was observed, but on lowering the silver ion concentration, increasing amounts of the cis olefin were observed (147b).

Treatment of trans-1-bromo-9-hydroxycyclononene (212a) under the reaction conditions

A solution of 1.25 g (6.02 mmol) of silver perchlorate in 4 ml of 95% aqueous acetone was stirred while 0.005 g (0.041 mmol) of 2-bromopropane (to generate perchloric acid) and 0.008 g of biphenyl (as an internal standard) were added. After 1 hour, 0.009 g (0.041 mmol) of 212a was added and the resulting mixture stirred for

11 days at room temperature in the dark. Quenching with NaCl was followed by injection into the gas chromatograph (using column B and the conditions outlined before); the analysis indicated the presence of only 212a (96%).

Treatment of cis-1-bromo-9-hydroxycyclononene (216a) under the reaction conditions

A solution of 1.83 g (8.82 mmol) of silver perchlorate in 6 ml of 95% aqueous acetone was stirred while 0.007 g (0.057 mmol) of 2-bromopropane and 0.009 g of biphenyl (internal standard) were added. After 1 hour, 0.013 g (0.059 mmol) of 216a was added and the resulting mixture stirred for 11 days at room temperature in the dark. Quenching with NaCl was followed by injection into the gas chromatograph (column B); the analysis indicated the presence of only 216a (97%).

Stability of cis- and trans-1-bromo-9-hydroxycyclononene (212a and 216a) under prolonged reaction conditions

In a 100 ml flask, 0.122 g (0.433 mmol) of 205 dissolved in 8.3 ml of 95% aqueous acetone was stirred while 8.984 g (43.3 mmol) of silver perchlorate dissolved in 35 ml of 95% aqueous acetone were added. The resulting solution was stirred for 32 days, with 0.025 g of biphenyl as an internal standard. After 19 hours, 45 hours, 6 1/2 days, 8 1/2 days, 11 1/2 days, 14 days and

32 days, 3 ml was removed, quenched with NaCl, extracted with CH_2Cl_2 and injected into the gas chromatograph (column B, conditions outlined before). The ratio of 212a/216a was an essentially constant 7.77 $\pm$ 0.21, with little loss in yield (the yield diminished by ~3% after 32 days).

Silver-assisted solvolyses of (205) used to construct Table 14

The general procedure used was as follows. In 100 ml flasks, the measured amount of 9,9-dibromobicyclo-[6.1.0]nonane (205) and biphenyl (internal standard) were dissolved in the measured amount of 95% aqueous acetone (by volume) and stirred while the measured $AgClO_4$ and $LiClO_4$ dissolved in 95% aqueous acetone were added. The resulting solutions were stirred for 8 days (first set of data), 7 days (second and third sets of data), and 5 hours (fourth set of data) before NaCl was added to quench the reactions. In each case, the acetone was then removed and the residue was combined with ~10 ml of water before extracting with 4 x 10 ml of ether. The combined ether layers were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration followed by injection into the gas chromatograph (column C, column at 127°, collector at 150°, detector at 175°, injector at 172° and

He gas flow of 32 ml/min at 30 psi) gave the results in Table 14. The retention time of cis-1-bromo-9-hydroxycyclononene (216a) was 98 minutes, that of trans-1-bromo-9-hydroxycyclononene (212a) was 110 minutes, and that of biphenyl was 34 minutes. The correction factors were for 213a: 1.98; for 207a: 2.04. The amount of each component was calculated as described before (Experimental section of Part I). For each reaction mixture the ratio of 212a/216a was determined as the average of at least two GLC traces.

Silver-assisted solvolysis of (205) used to construct Table 15

The general procedure used was identical to that used to construct Table 14, except that the reactions from which was generated the first set of data were stirred for 7 days before work-up, while those for the second set were stirred for 10 days; 90% aqueous acetone was used throughout this set of experiments.

Silver-assisted hydrolysis of exo-9-bromobicyclo[6.1.0]-nonane (204a)

In a 25 ml flask, 0.319 g (1.57 mmol) of 204a dissolved in 3 ml of 95% aqueous acetone were stirred while 1.63 g (7.85 mmol) of silver perchlorate dissolved in 3 ml of 95% aqueous acetone was added. The reaction

mixture was stirred for 1 day before NaCl was added, and the acetone was evaporated. The residue was combined with 5 ml of water before extracting with 4 x 10 ml of ether. The combined ether layers were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration was followed by chromatography through a short silica gel column (1.0 x 35 cm) using hexane for fractions 1-4 and 10% ether/90% hexane for the other fractions (25 ml fractions). There resulted trans-3-hydroxycyclononene (207a, 0.171 g, 78%) as a white solid; ^1H NMR: δ 5.9-5.1 (m, 2H), 4.43 (m), 3.84 (m, methine hydrogen), 3.31 (s, 1H, OH), 1.3-0.8 (m, 12H) (Figure 41) (106c).

Silver-assisted hydrolysis of endo-9-bromobicyclo[6.1.0]-nonane (204b)

In a 25 ml flask, 0.327 g (1.61 mmol) of 204b dissolved in 3 ml of 95% aqueous acetone was stirred while 1.67 g (8.05 mmol) of silver perchlorate dissolved in 3 ml of 95% aqueous acetone was added. The reaction mixture was then stirred for 3 days before NaCl was added, and the acetone was evaporated. The residue was combined with 5 ml of water and extracted with 4 x 10 ml of ether. The combined ether layers were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying

over $MgSO_4$. Removal of the ether followed by chromatography through a short silica gel column (1.0 x 38 cm, hexane for fractions 1-4, 10% ether/90% hexane for the remaining fractions; 25 ml fractions) gave cis-3-hydroxycyclononene (208a), 0.122 g (87%) and 0.124 g of starting 204b. ^1H NMR: δ 5.62-5.24 (m, 2H), 4.50 (m, 1H), 2.35-1.20 (m, 13H) (Figure 41) (106c).

Treatment of trans-3-hydroxycyclononene (207a) under the reaction conditions

To a stirring solution of 0.020 g (0.143 mmol) of 207a in 0.15 ml of 95% aqueous acetone was added a solution of 1.482 g (7.14 mmol) of silver perchlorate, 1.521 g (14.3 mmol) of lithium perchlorate and 0.014 g of biphenyl (internal standard) in 7 ml of 95% aqueous acetone. The resulting mixture was stirred for 3 days. Then 0.020 g (0.163 mmol) of 2-bromopropane was added and the mixture was allowed to stir for another 15 minutes. Then ∿3.5 ml of the solution was removed, quenched with NaCl and the acetone evaporated. The residue was combined with ∿5 ml of water and extracted with 4 x 5 ml of ether. The combined ether extracts were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration followed by analysis on GLC column D indicated the presence of only 207a (96%).

The remaining reaction mixture was allowed to stir for another 4 days, and then it was worked up as described for the aliquot. The results of the GLC trace showed the presence of 207a (95.6%) and 208a (1.7%).

Treatment of trans-3-hydroxycyclononene (207a) under the acidic reaction conditions

To a stirring solution of 0.023 g (0.167 mmol) of 207a in 0.35 ml of 95% aqueous acetone was added a solution of 1.734 g (8.36 mmol) of silver perchlorate, 1.78 g (16.7 mmol) of lithium perchlorate and 0.011 g of biphenyl (internal standard) in 8 ml of 95% aqueous acetone. Subsequently, 0.033 g (0.266 mmol) of 2-bromopropane was added to generate perchloric acid. The mixture was then stirred for 1 day, after which it was worked up as described for the previous experiment. The results of the GLC analysis showed the presence of 207a (48.9%) and 208a (6.4%), with no other identifiable components.

Silver-assisted hydrolysis of (204a) used to construct Table 16

The general procedure used was as follows. In 100 ml flasks, the measured amounts of 204a and biphenyl (internal standard) were dissolved in the measured amount of 95% aqueous acetone and stirred while the measured amount of $AgClO_4$ and $LiClO_4$ in 95% aqueous acetone was

added. The reaction mixtures were then stirred for 1 day (first set of data), 3 3/4 hours (second set of data), 2 1/2 days (third set of data), and 3 days (fourth set of data), after which they were quenched with NaCl, and the acetone evaporated. The residue was combined with ∿10 ml of water before extracting with 4 x 10 ml of ether. The combined ether extracts were washed with 10 ml of saturated Na_2CO_3 solution and 10 ml of saturated NaCl solution before drying over $MgSO_4$. Concentration and injection into column D on the gas chromatograph (column at 115°, collector at 145°, detector at 168°, injector at 170° with a He gas flow of 18.75 ml/min at 40 psi) produced the results reported in Table 16. The retention times of trans-3-hydroxycyclononene (207a), cis-3-hydroxycyclononene (208a), and biphenyl were 171 minutes, 161 minutes, and 252 minutes, respectively. The correction factors were for 207a: 1.51; for 208a: 1.59, and the ratio of 207a/208a was determined from at least two GLC traces for each reaction mixture.

Separation of cis- and trans-1-bromo-9-hydroxycyclononene (212a and 216a)

A solution of 1.634 g of a mixture of 212a (52%) and 216a (48%) in 10 ml of hexane was extracted with 6 x 7 ml of an aqueous 20% (by weight) • $AgNO_3$ solution. The combined $AgNO_3$ extracts were washed with 2 x 5 ml of hexane,

and the wash combined with the original hexane solution. The combined hexane layers were then washed with 10 ml of saturated NaCl solution before drying over $MgSO_4$. Solvent evaporation afforded 1.562 g (96%) of a mixture of 212a and 216a. The $AgNO_3$ extract was added slowly to 17 ml of cold concentrated NH_4OH solution and the resulting solution was extracted with 3 x 8 ml of hexane and 2 x 8 ml of ether. The combined organic extracts were washed with 10 ml of saturated NaCl solution and dried over $MgSO_4$. Concentration afforded 0.062 g (7% of available 212a, 4% of total material) of pure trans-1-bromo-9-hydroxycyclononene (212a).

Attempted elimination of cis-1-bromo-9-tosyloxycyclononene (216d) in isopropyl alcohol

A solution of 0.860 g (2.3 mmol) of 216d (prepared according to the published procedure (147a)) in 15 ml of isopropyl alcohol was stirred with 0.216 g (5.4 mmol) of sodium hydroxide at room temperature for 2 hours. The mixture was then heated to reflux for 1 1/2 hours and, upon cooling, 5 ml of water was added. The mixture was extracted with 4 x 10 ml of hexane and the combined hexane layers were dried over $MgSO_4$. Concentration gave 0.566 g of material which was chromatographed on a silica gel column (1.0 x 38 cm) using hexane with increasing amounts of chloroform as the eluent (25 ml fractions).

Fraction 4-7, cis-2-bromo-3-isopropoxycyclononene; 0.258 g (64%). This material was identical to that reported by Loozen et al. (147b).

Fraction 9-12, cis-2-bromo-3-tosyloxycyclononene (216d); 0.267 g.

Attempted elimination of cis-1-bromo-9-tosyloxycyclononene (216d) with potassium t-butoxide

A solution of 0.209 g (0.56 mmol) of 216d in 5 ml of dry tetrahydrofuran was stirred while 0.0672 g (0.6 mmol) of potassium t-butoxide was added. The resulting mixture was stirred for 8 hours at room temperature before refluxing for another 3 hours. The tetrahydrofuran was then evaporated, and 5 ml of water and 10 ml of ether added, and the layers separated. The aqueous layer was extracted with 3 x 10 ml of ether. The combined ether layers were washed with 5 ml of saturated ammonium chloride solution before drying over $MgSO_4$. Concentration gave 0.184 g of a slightly yellow solid, which ^1H NMR analysis indicated consisted of essentially only starting material 216d.

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ACKNOWLEDGMENTS

I wish to express my appreciation to Dr. Philip M. Warner for his advice, assistance and encouragement which made this research and manuscript possible.

A very special acknowledgement is conveyed to my wife and child who endured much during the course of this research and its conclusion, but always offered their loving support.

I also wish to thank my parents, brothers and sister whose enthusiastic support and love contributed to the completion of this study.

Finally, all members of the Warner group contributed with their innumerable discussions and suggestions which facilitated the research described herein.