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Preparation and ^{13}C NMR investigation of 1,1-dilithioalkenes, 1,2-dilithioalkenes, 1-lithiocyclopropenes and 1,2-dilithiocyclopropenes

Hon-Wah Man
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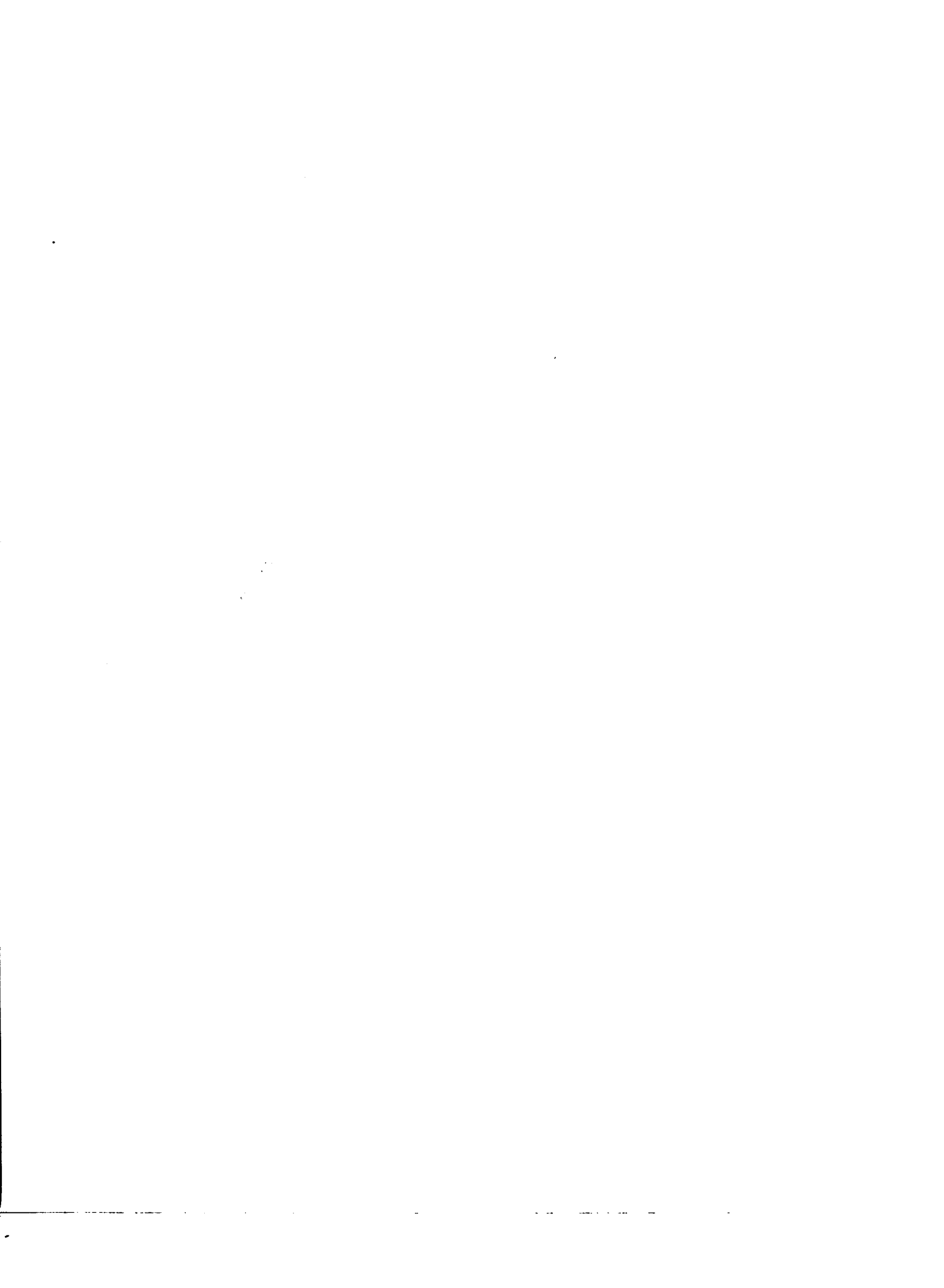
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**Preparation and ^{13}C NMR investigation of 1,1-dilithioalkenes,
1,2-dilithioalkenes, 1-lithiocyclopropenes and 1,2-dilithiocyclopropenes**

Man, Hon-Wah, Ph.D.

Iowa State University, 1990

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1,2-dilithioalkenes, 1-lithiocyclopropenes
and 1,2-dilithiocyclopropenes

by

Hon-Wah Man

A Dissertation Submitted to the
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For the Graduate College

Iowa State University
Ames, Iowa

1990

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INTRODUCTION

Literature

Since Schlenk and Holtz¹ discovered that methyllithium (MeLi) behaved like a Grignard reagent in 1917, the chemistry of organolithiums has been widely developed. There are a number of pertinent reviews and books on aspects of the chemistry of organolithiums. General aspects of organolithiums are featured in a book by Wakefield.² Reviews by Wardell³ and Oliver⁴ give general consideration to organoalkali metal compounds. Related subjects are also discussed in a chapter of the book "Organometallic Compounds".⁵

Earlier works on preparations of organolithiums are included in reviews by Gilman and Morton,^{6a} and by Jones and Gilman.^{6b} The new book by Wakefield⁷ and volumes 3 and 4 of "Organometallic Syntheses"⁸ include many new experimental techniques for handling organolithium compounds.

Heteroatom substituted organolithium compounds are featured in other reviews.⁹ Polylithiation of propargyl compounds by alkyllithium has already been reviewed by West¹⁰ and Klein.¹¹ Polylithiated aliphatic hydrocarbons which cannot be obtained by simple metalation reactions are featured in a review by Maercker and Theis.¹²

Several reviews of X-ray¹³ and NMR¹⁴ studies of organolithiums have been published. Schleyer¹⁵ published two reviews concerning the structures and thermodynamics of organolithiums and polylithiated compounds from the calculational viewpoint.

The effects of ion pairing in carbanionic, including aromatic radical anion and dianion, species have also been discussed.¹⁶

A survey of organolithium compounds in the book "Dictionary of Organometallic Compounds"¹⁷ provides an excellent reference for specific compounds. Finally, annual surveys of the literature appear in the series "Organometallic Chemistry"¹⁸ and in the Journal of Organometallic Chemistry.¹⁹

Theoretical Results

Structural studies of organolithiums are always complicated, because they are normally aggregated.² Polyolithiated organic compounds are even harder to study directly, since they neither can be prepared by simple metalation reactions nor dissolve easily in organic solvents. Tantalizingly, *ab initio* MO calculations indicate highly unusual structures, sometimes with anti-vant Hoff geometries, for polyolithiated organic compounds. Calculations have been done mainly by Schleyer¹⁵, Schleyer and coworkers,²⁰ but also by Streitwieser.²¹ Most striking among these are instances of square planar tetra-coordinate carbon^{22,23} and 90°-twisted alkenes.²⁴ These entirely new organic structures induced by lithium substitution have attracted the interest of not only theoretical chemists, but also spectroscopists,²⁵ physical organic²⁶ and physical inorganic²⁷ chemists.

Bridging and simultaneous σ -donor and π -acceptor abilities are the two general properties used to explain the unusual structures of organolithiums. Both theoretical and experimental results indicate

that lithium atoms prefer bridging positions in organolithiums,^{15a} intermolecularly or intramolecularly. Lithium atoms use their free p orbitals to reach a higher coordination number which is energetically favorable. Moreover, since association energies of organolithium compounds are quite large and double bridging within a polylithium compound can be considered to be the intramolecular equivalent of association, it is no surprise that polylithium compounds have stable bridged structures. At the same time, electrostatic interactions may also be responsible for bridging.

The simultaneous σ -donor and π -acceptor abilities are also very important in controlling the structure as discussed below. The empty p orbitals of the lithium atom can accept electron density by forming a π -bond with a neighbor atom. Since lithium is an electropositive element, the σ -bond between lithium and carbon is fairly polar.

It was also calculated (STO-3G) that lithium substitution would reduce the strain energy in cyclic and polycyclic small ring systems.²⁸ Examples of the reduction in strain energy by lithium mono-substitution are 19 KCal mol⁻¹ in 1-lithiocyclopropane and 40 KCal mol⁻¹ in 1-lithiobicyclobutane.

Planar Tetracoordinate Carbon

Collins and coworkers²² reported an exciting result from a calculational investigation of lithiated organic compounds. The energy differences between the tetrahedral and the planar structures of tetracoordinate carbon decrease with increasing lithiation as shown in Table 1. The results were confirmed recently by a

reexamination of the structures and bonding in dilithiomethane by Bachrach and Streitwieser²⁹ using electron density analysis, and Alvarado-Swaisgood and Harrison³⁰ with multi-configuration SCF calculations. Collins et al.²², Chandrasekhar and Schleyer³¹ also calculated that the planar geometry of 1,1-dilithiocyclopropane was 7 KCal mol⁻¹ more stable than its tetrahedral geometry at the STO-3G/STO-3G level. 3,3-Dilithiocyclopropene is even more favorable in its preference for the planar geometry.

Table 1. Calculated planar-tetrahedral energy differences (KCal mol⁻¹) (RHF)^{23a}

| Molecule | STO-3G | 4-31G |
|---|--------|-------|
| CH ₄ | 240 | 168 |
| CH ₃ Li | 52 | 42 |
| CH ₂ Li ₂ (trans) | 54 | 47 |
| CH ₂ Li ₂ (cis) | 17 | 10 |
| CHLi ₃ | 10 | 7 |
| CLi ₄ | 22 | 16 |
| Lithiocyclopropane | 65 | 52 |
| 1,1-Dilithiocyclopropane | -7 | -- |
| 3,3-Dilithiocyclopropene | -10 | -- |

The stabilization of planar carbon by lithium substitution is explained by two reasons. Firstly, the carbon lone pair electron delocalizes to empty p orbitals in the lithium atoms by π -conjugation

to form a cyclopropenium-type aromatic system as shown in Figure 1. Secondly, lithium atoms provide electron density to carbon by σ -donation to balance the electron density in the carbon atom. In the cyclopropyl system, lithiation reduces the strain energy, which is an additional important factor for stabilization of the planar 1,1-dilithiocyclopropane.

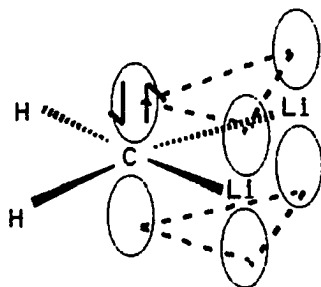


Figure 1. The planar dilithiomethane

Dimerization of dilithiomethane was also studied by Jemmis, Schleyer and Pople³² (4-31G/5-21G(Li)) and by Nilssen and Skancke²³ (RHF/STO-3G-RHF/4-31G). The most stable dimer is the head to head dimer of planar monomers as shown in Figure 2. The four lithium atoms are bridging two perpendicular CH_2 units. The dimerization energy relative to the energy of two tetrahedral monomers is 37 KCal mol^{-1} from both reports.

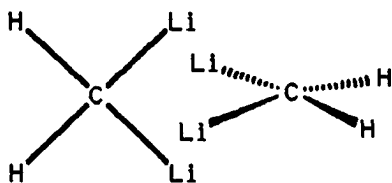


Figure 2. The dimer of dilithiomethane

1,1-Dilithioethene

Several experimental³³ and theoretical³⁴ treatments have been made on the rotational barriers around carbon-carbon double bonds. The barrier was calculated as 63.7 KCal mol⁻¹ (*ab initio*),^{34a} 63.2 KCal mol⁻¹ (*ab initio*)^{34b} and 63.9 KCal mol⁻¹ (MNDO/3)^{34c} for ethylene itself. They are in excellent agreement with the experimental value (65 KCal mol⁻¹).^{33a} π -Donor and π -acceptor substituents can reduce the rotational barrier significantly, since either the biradical or the dipolar configuration of the perpendicular form will be stabilized by electron delocalization.³⁵ Bulky substituents also destabilize the planar ground state.³⁶ Recently Sakurai reported unusual properties for tetrakis(trimethylsilyl)ethylene due to $\sigma(\text{Si-C})$ - π mixing from the distorted non-planar structure in the ground state.³⁷ Distortion of double bonds also appears in bridgehead double bond systems.³⁸

The reduction of the rotational barrier in 1,1-dilithioethylene is remarkable. Molecular calculation by several groups^{24,39-41} found that not only was the rotational barrier very low (< 0.6 KCal mol⁻¹) or non-existent, but also the perpendicular geometry (1) might actually be more stable than the planar geometry (2). 1,1-Dilithioethene prefers a triplet ground state with perpendicular geometry followed energetically by the planar triplet with the relative energy of 1.1 KCal mol⁻¹. The twisted singlet (34.3 KCal mol⁻¹) was calculated to be only slightly less stable than the planar singlet (33.5 KCal mol⁻¹), as shown in Table 2. However, the higher

level of calculations (SCF and SCF(CI)) showed that the planar singlet was a bit higher (0.9 and 1.5 KCal mol⁻¹, respectively) in energy than the twisted singlet.

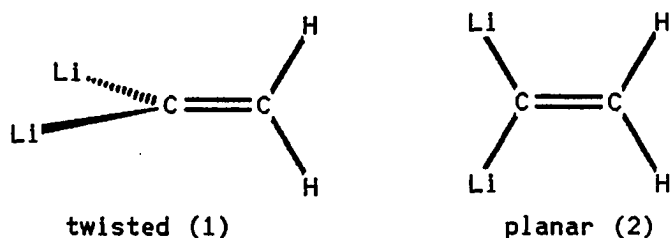


Table 2. Relative energies for 1,1-dilithioethenes (KCal mol⁻¹)

| Molecule | STO-3G | 4-31G | SCF | SCF(CI) |
|-----------------|--------|-------|------|---------|
| twisted triplet | 0.0 | 0.0 | 0.0 | 0.0 |
| twisted singlet | 26.8 | 34.3 | 28.4 | 14.0 |
| planar triplet | 2.1 | 1.1 | 1.2 | 1.4 |
| planar singlet | 36.7 | 33.5 | 29.3 | 15.5 |

The reasonably high stability of the singlet perpendicular form is due to the combination of the σ -donor and π -acceptor character of lithium atoms. This can be visualized with the zwitterion structure for the singlet perpendicular species as shown in Figure 3. The carbanion center (C_1) is stabilized by the delocalization of the two p_y -electrons on C_1 into the lithium p -orbitals in a cyclopropenium-type aromatic system. The cationic center (C_2) is stabilized by strong hyperconjugation of the p_x -orbitals on C_2 across the C-C bond with the two coplanar C-Li σ bonds and thus balances the

transfer of electrons from C_1 to the lithium atoms. As a result of this back-donation, 1,1-dilithioethylene is only slightly polarized. Even in the perpendicular form, the calculation indicated that the $C_1=C_2$ bond length was essentially double.

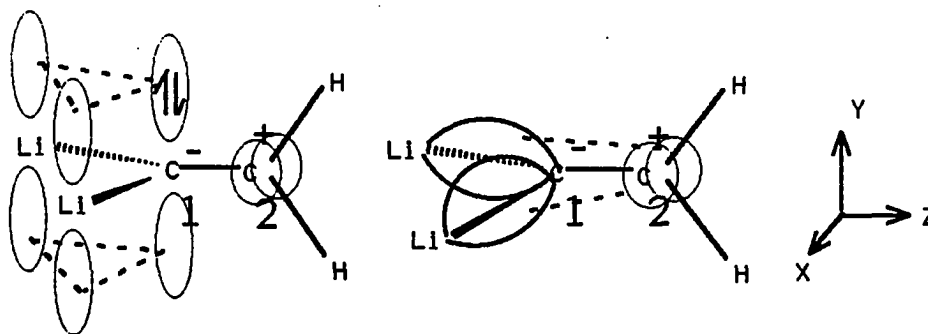
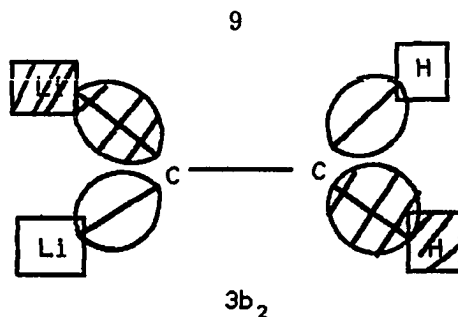


Figure 3. The twisted form of 1,1-dilithioethene

The surprising stabilization of the perpendicular triplet was explained as involving transfer of one of the p_y -electrons on C_1 , with spin inversion, to a σ -orbital which binds the two lithium atoms. Similarly in the planar triplet, an electron transfers from the singlet highest occupied molecular orbital (HOMO), which is a $3b_2$ σ -orbital bonding the two lithium atoms to C_1 but having an anti-bonding character between the two lithium atoms, to another σ bonding orbital which does have bonding character between the two lithium atoms. A further shortening of the Li-Li distance in the planar and the twisted triplets compared with the singlets results. This unoccupied low energy σ -type bonding orbital between lithium atoms is occupied by a formerly π -electron in the triplet state. Contrast this with the fact that an electron occupies the π^* antibonding orbital in planar triplet ethylene.



1,2-Dilithioalkenes

Apeloig et al.⁴¹ and Schleyer et al.⁴² have carried out extensive *ab initio* calculations on 1,2-dilithioethylenes. In their latest report, all $C_2H_2Li_2$ structures have been reoptimized with the polarized split valence 6-31G* basis set, and the relative energies have been calculated at the corrected MP2/6-31G*//6-31G* level with zero-point energy corrections at 3-21G//3-21G. As shown in Figure 4, the (partially bridged) trans isomer (3) was found to be 1.6 KCal mol⁻¹ more stable than the (doubly bridged) cis bridged isomer (4). The classical cis-non-bridged ethylene isomer (5), which was calculated to be a transition state structure, was some 20 KCal mol⁻¹ higher in energy than the cis-bridged isomer (4).

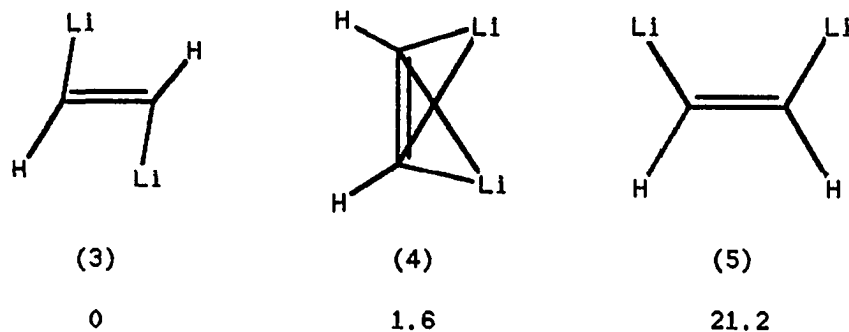


Figure 4. Relative energies of 1,2-dilithioethylene isomers
(KCal mol⁻¹)

The only substituted case of 1,2-dilithioalkenes which has been treated theoretically is 1,2-dilithiocyclopropene.⁴³ At the STO-3G//STO-3G level, the doubly bridged form (6) is more stable than the classical structure (7) by 9.7 KCal mol⁻¹. However, when the split-valence 4-31G/5-21G(Li) basis set was employed, the relative energies reversed as shown in Figure 5.

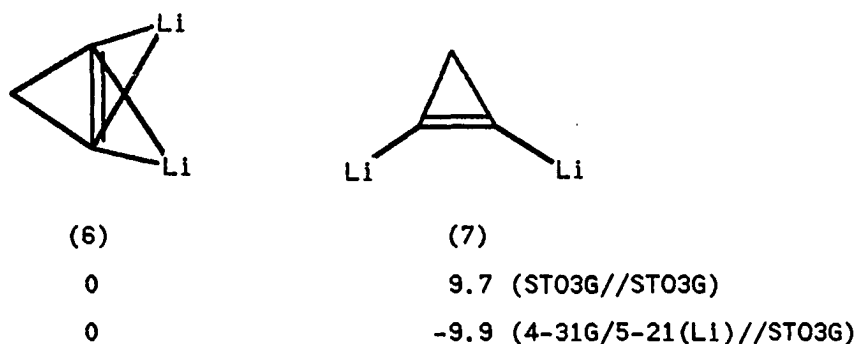


Figure 5. Relative energies of 1,2-dilithiocyclopropene isomers
(KCal mol⁻¹)

Jemmis et al.^{43a} and Schleyer et al.^{43b,44} have also evaluated the stabilities of various organolithiums relative to methyllithium as a standard, by means of an isodesmic reaction (eq. 1).



While formation of 1-lithiocyclopropene is 20.7 KCal mol⁻¹ exothermic, formation of 1,2-dilithiocyclopropene is only 8.3 KCal mol⁻¹ exothermic at the 4-31G//STO-3G level. However, the isodesmic reaction energy of ethylene relative to methyllithium was calculated to be 0.8 KCal mol⁻¹ endothermic. These results indicate that 1,2-dilithiocyclopropene may be accessible by direct metalation with

methyl lithium.

1-Lithiocyclopropene was also calculated by Schleyer, Kaufmann and Spitznagel.⁴⁴ They found that the charge in 1-lithiocyclopropene actually was delocalized, as indicated by Mulliken population analysis. At all level studied, C₃ has the largest negative charge of any of the carbon atoms, including C₁, where the lithium is attached. The situation can be explained by the resonance formalism shown in Figure 6. The calculations also predicted that 1-lithiocyclopropene should have an elongated C₁-C₃ bond (1.57-1.77 Å) due to an in-plane interaction.⁴⁵

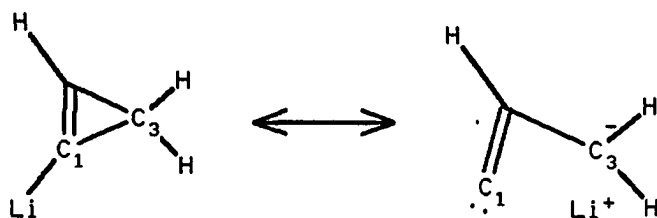


Figure 6. Resonance structures of 1-lithiocyclopropene

Structures of C₂Li₂,⁴⁶ LiCH₂CH₂Li,⁴⁷ C₃Li₄,⁴⁸ C₃H₅Li,⁴⁹ LiCH₂CH₂CH₂Li,⁵⁰ C₄Li₄⁵¹ and LiCH₂C(O)CH₂Li⁵² were also calculated, and bridged forms were predicted.

Experimental Results

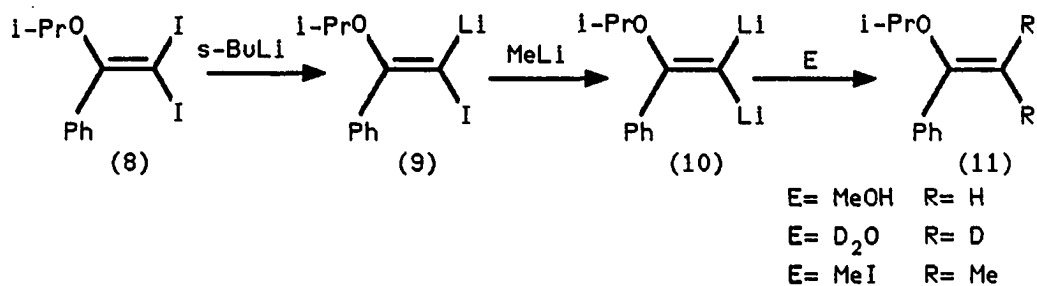
Syntheses

Theoretical calculations predict that polylithium organic compounds have many interesting features as mentioned above. Experimental chemists have tried to prepare these polylithium compounds to test these predictions. Although polylithium organic

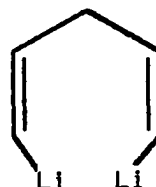
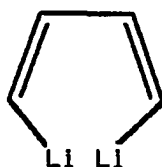
compounds are not easily synthesized via classical synthetic methods, many techniques have been attempted.

lithium-halogen exchanges Lithium-halogen exchange is a powerful and simple method for the synthesis of organolithium compounds. The reaction is rapid but reversible. Therefore, the organic group which can better support a negative charge ends up as the organolithium compound. However, since α , β , or γ elimination of lithium halide after the first exchange may be faster than the second exchange, the synthesis of polylithium organic compounds from lithium-halogen exchange is not popular. 1,4-Dilithiobutane and higher $1,\omega$ -dilithioalkanes, $\text{Li}(\text{CH}_2)_n\text{Li}$ ($n \geq 4$), were prepared by lithium-halogen exchange but not 1,2-dilithioethane and 1,3-dilithiopropane.⁵³ The other drawback of this exchange is the competition with metalation and alkylation.

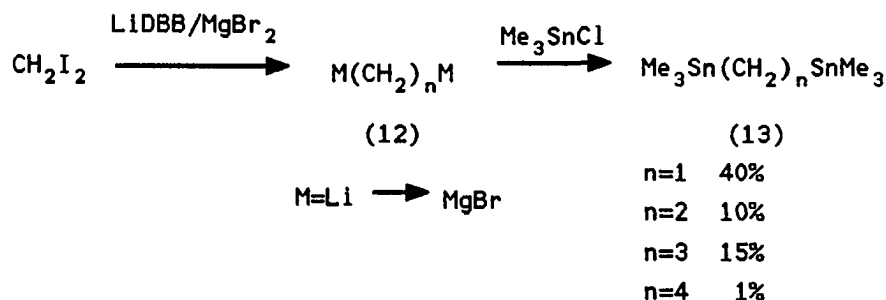
Since iodine exchanges faster than bromine, several polylithium organic compounds have been synthesized this way. Barluenga et al.⁵⁴ were able to prepare 1,1-dilithio-1-alkenes (10) in high yield by treatment of 1-iodo-1-lithio-1-alkenes (9) with methyllithium. Compound (9) was the product of the lithium-iodine exchange reaction of diiodide (8) with sec-butyllithium (s-BuLi).



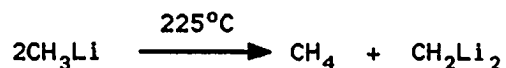
(Z,Z)-1,4-Dilithio-1,3-butadiene⁵⁵ and (Z,Z)-1,5-dilithio-1,4-pentadiene⁵⁶ have also been prepared by lithium-iodine exchange reaction of diiodide analogues with alkyllithium.



van Eikema Hommes, Bickelhaupt and Klumpp⁵⁷ synthesized some α,ω -dilithioalkanes ((12), M = Li) as intermediates, which were trapped *in situ* by MgBr_2 to give α,ω -bis(bromomagnesium)alkanes ((12), M = MgBr), from diiodomethane and lithium-4,4'-di-tert-butylbiphenyl (LiDBB) in the presence of MgBr_2 . Those organomagnesium compounds were trapped by trimethyltin chloride to yield the corresponding organotin compounds (13).

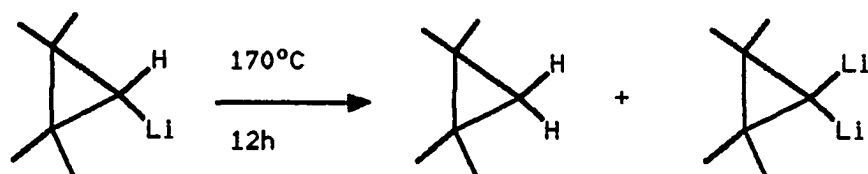


Pyrolysis reactions Ziegler and coworkers⁵⁸ demonstrated that halide free methyllithium upon pyrolysis disproportionates into methane and dilithiomethane in excellent yield.



Kawa, Manley and Lagow^{59a} applied this reaction technique to

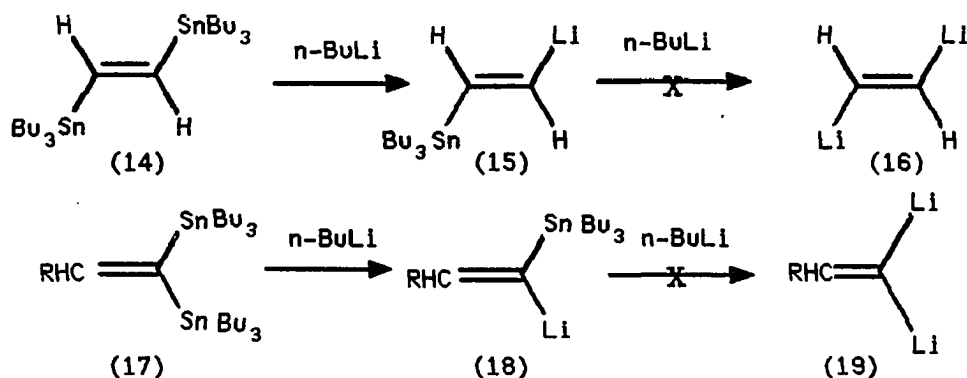
prepare 1,1-dilithio-2,2,3,3-tetramethylcyclopropane. However, this report lacks full credibility since the product was reported to be soluble in benzene. Kawa, Chinn and Lagow^{27a} also reported several preparations of gem-dilithium organic compounds utilizing pyrolysis. Recently, pyrolysis of 9-lithiofluorene at 180°C provided 9,9-dilithiofluorene.^{59b} However, no polyolithium vinyl compound has been reported as made by this method.



Transmetalation reactions A transmetalation⁶⁰ reaction is an excellent way to produce unstable organolithium compounds from other stable organometallic compounds, such as organotins, organomercurials, organoborons, etc.

Tin-lithium exchange works only for the preparation of organolithium compounds which are more stable than n-butyllithium (n-BuLi). Since dilithioethylenes may be less stable than n-butyllithium, neither trans-1,2-dilithioethylene (16)⁶¹ nor 1,1-dilithio-1-alkenes (19)⁶² can be generated by tin-lithium exchange. Only one stannyl moiety can be replaced by lithium.

Although t-butyllithium (t-BuLi) is a stronger base than n-butyllithium, due to steric hindrance t-butyllithium cannot be used to replace tin. Dimercury compounds will undergo mercury-lithium exchange with t-butyllithium or lithium powder. Maercker employed

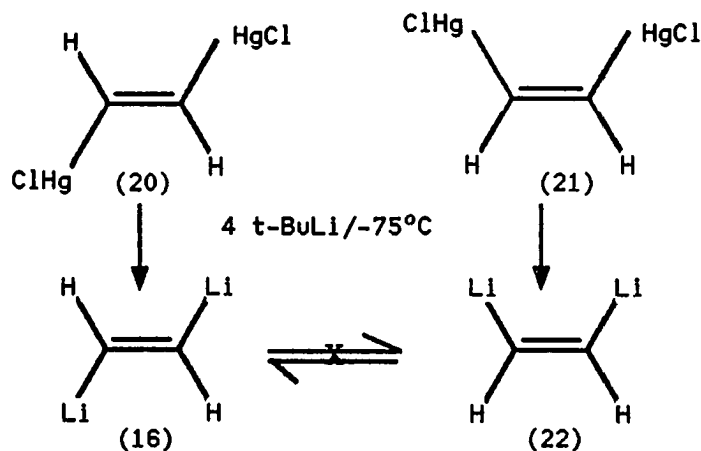


this reaction to prepare many isocentric polylithium compounds which were not available by other methods. Examples are CH_2Li_2 ,⁶³ ClLi_4 ,⁶⁴ CH_3CHLi_2 ,⁶³ $\text{CH}_2=\text{CHCH}_2\text{CHLi}_2$,¹² $(\text{CH}_3)_2\text{C}=\text{CLi}_2$ ⁶⁵ and $(\text{Li})\text{HC}=\text{CH}(\text{Li})$,⁶⁶ which were generated from reactions of the corresponding organomercury compounds with either lithium metal or *t*-butyllithium.

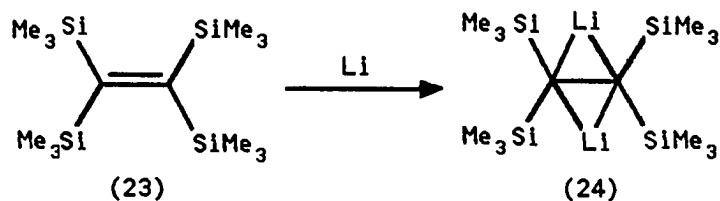
An interesting result from Maercker, Graule and Demuth⁶⁶ was that there was no interconversion between *cis*- and *trans*-1,2-dilithioethylene. Doubly deuterated *cis*-1,2-dilithioethylene and doubly deuterated *trans*-1,2-dilithioethylene were each prepared, as outlined in Scheme 1. They were allowed to react in the form of a 4:1 *cis*-*trans* mixture consisting of $[\text{D}_2]$ -*trans* (20) + *cis* (21) and *trans* (20) + $[\text{D}_2]$ -*cis* (21), respectively, with *t*-butyllithium. In both cases, the isotopic composition of *trans*-1,2-dilithioethylene was not enriched in the reaction mixture. This result is in contrast with the low calculated rotational barrier between *cis*- and *trans*-1,2-dilithioethylene in the gas phase. On the other hand, *cis*-dilithiocinnamitrile rearranges to *trans*-dilithiocinnamitrile exclusively even at low temperature,

as discussed below.

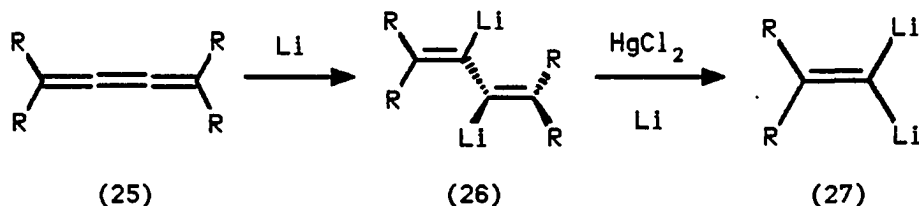
Scheme 1.



Addition to carbon-carbon multiple bonds Activated alkenes, alkynes and cumulenes are known to react with metallic lithium to yield dilithiated hydrocarbons via a radical pathway. Recently, Sekiguchi et al.⁶⁷ reported the synthesis and characterization of 1,2-dilithio-[tetrakis(trimethylsilyl)]ethane (24), the first stable alkyl-substituted 1,2-dilithioethane derivative. It was prepared from reduction of tetrakis(trimethylsilyl)ethylene (23) with excess lithium metal. A doubly bridged 1,2-dilithioalkane was observed by X-ray crystallography and NMR.



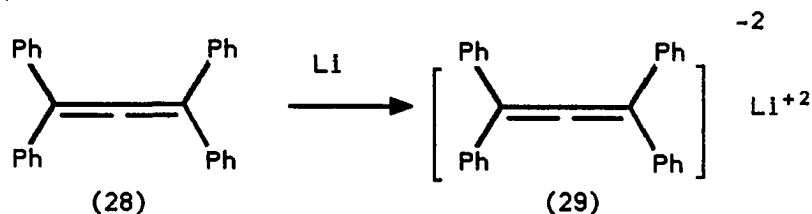
Maercker and Dujardin⁶⁸ found that the addition of lithium to the central double bond of butatrienes (25) gave 2,3-dilithio-1,3-butadienes (26), which, interestingly, were stable towards excess lithium, but were cleaved to 1,1-dilithio-1-alkenes (27) in the presence of mercury (II) chloride.



R=Me

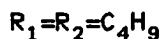
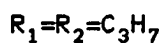
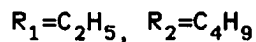
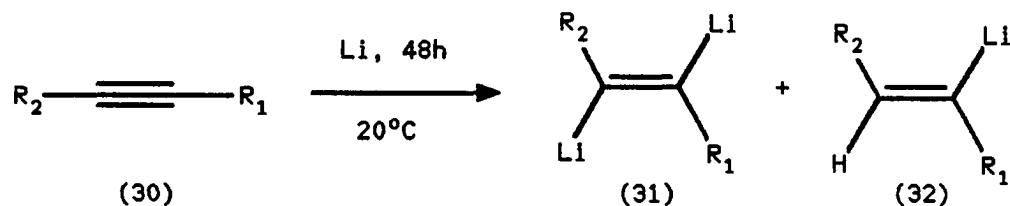
R,R=(CH₂)₅

Lithium can add to allene to yield both a monoanion and a dianion. Rajca and Tolbert^{26b} reported the preparation of dilithium tetraphenylallene (29) through this method.

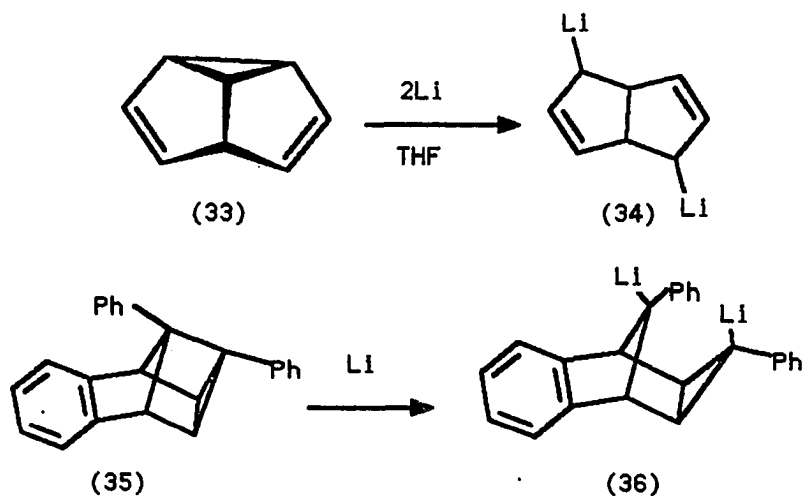


1,2-Dilithioalkenes were reportedly prepared by reactions of alkynes with lithium by Maercker and coworkers.⁶⁹ Lithium was added to the triple bond of cyclooctyne at -35°C to give cis-1,2-dilithiocyclooctene. Trans-addition of lithium to open-chain aliphatic alkynes (30) was also observed. Vicinal trans-1,2-dilithioalkenes (31), which were insoluble in diethyl

ether, along with monolithioalkenes (32) resulted.



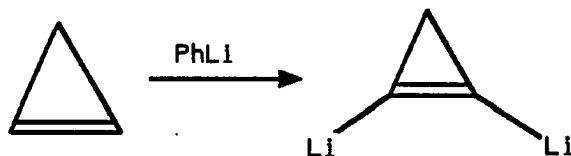
A single bond sometimes can be reductively cleaved by lithium. Goldstein and coworkers⁷⁰ obtained two diastereoisomeric dimers of "dilithium semibullvalenide" on treating semibullvalene with lithium in tetrahydrofuran (THF) at -78°C . The dilithium species (36) was also prepared by lithium reduction of the hydrocarbon (35).⁷¹



Metalation reactions

Metalation of acidic hydrocarbons is an equilibrium reaction, with the more acidic hydrocarbon largely converted to the organometallic compound. Propargylic, allylic and benzylic compounds react with alkyllithiums to give polyolithium

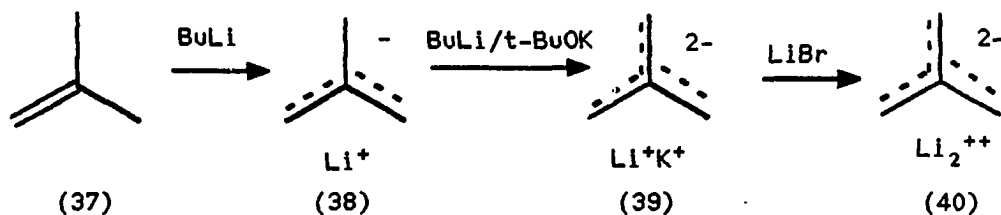
compounds.^{10,11} For example, propyne can be perlithiated with n-butyllithium in hexane to give the "lithiocarbon" C_3Li_4 .⁷² 1,2-Dilithiocyclopropene was thought to have been generated from the metalation of cyclopropene by phenyllithium in low yield.⁷³



The reactivities of organolithiums rise either with increasing Lewis basicity of the solvent, or by mixing with potassium t-butoxide (t-BuOK). The solvent effect is probably due to the deaggregation of the organolithium aggregates which increases the carbanionic character, and also due to the increasing stabilization of the transition state.⁷⁴ Benzene can be readily lithiated by a mixture of n-butyllithium and N,N,N',N'-tetramethylethylenediamine (BuLi/TMEDA). Linear and branched alkenes, for example, propene,⁷⁵ isobutylene⁷⁶ and 2-butene,⁷⁷ can also be polyolithiated by treatment with BuLi/TMEDA.

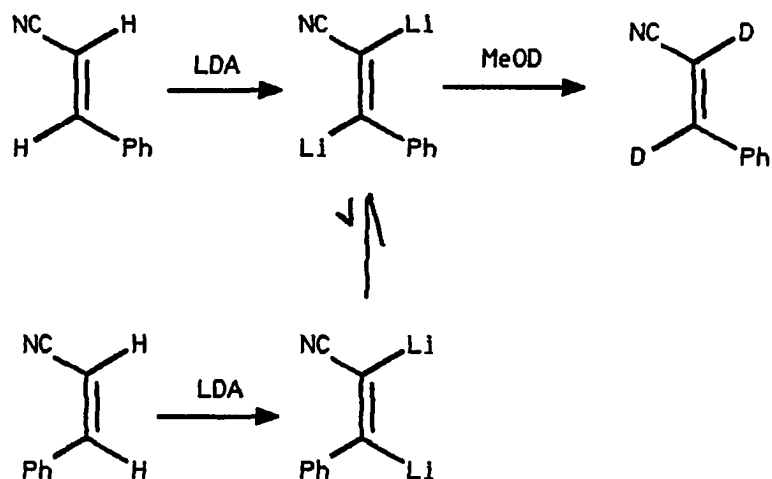
The combination of BuLi/t-BuOK has been employed to dilithiate isobutene and methylallylbenzenes.⁷⁸ It is effective because a stronger metalation agent, butylpotassium is formed. The dianion (39) can undergo lithium-potassium exchange with lithium bromide to yield the dilithium (40).⁷⁹

Generally, lithium dialkyl amines, $LiNR_2$, are more effective lithiating agents than the thermodynamically more basic alkylolithiums. Especially, for hydrocarbons which have $pK_a < 30$,

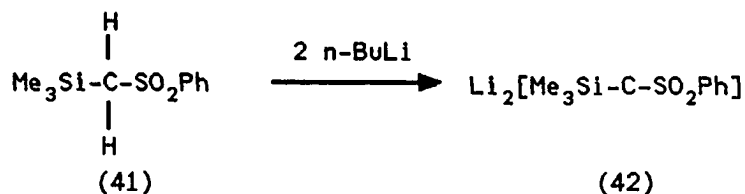


LiNR_2 are ideal lithiating agents. The effectiveness is due to an increased kinetic basicity which comes about via the use of the nitrogen lone pair in the four-centered transition state for the lithiation. Recently, Feit and coworkers⁸⁰ found that α,β -dilithiocinnamionitrile could be prepared by treating cis- or trans-cinnamionitrile with an excess of lithium diisopropyl amine (LDA). An interesting result is that cis-dilithiocinnamionitrile will convert to trans-dilithiocinnamionitrile exclusively even at low temperature. As mentioned above, 1,2-dilithioethylene does not exist as a cis-trans equilibrium mixture.⁶⁶ The activating group might have a profound influence regarding the preferred structure of the derived dilithioalkenes in solution.⁸¹

Dimetalation of disubstituted activated methanes by butyllithium is also possible. Vollhardt, Gais and Lukas⁸² reported the synthesis of dilithium trimethyl((phenylsulfonyl)methyl)-silane (42), which was prepared by metalation of trimethyl((phenylsulfonyl)methyl)-silane (41) with two equiv. of n-BuLi in THF. Gais and coworkers investigated the structure of (42) by X-ray and NMR⁸³. The dilithiosulfone (42) does not have a planar tetracoordinate carbon in the solid state. The crystal is a hexamer with a formula

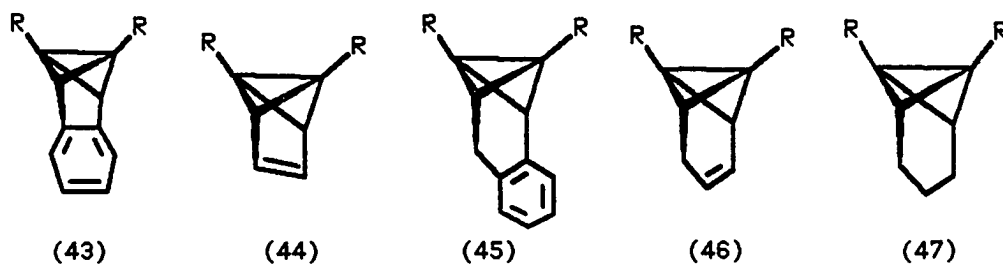


$(\text{Li}_2[\text{Me}_3\text{SiCSO}_2\text{Ph}])_6 \cdot \text{Li}_2\text{O} \cdot (\text{THF})_{10}$ as discussed below.



Several bicyclobutane derivatives (43-47) were lithiated at the bridgehead carbon with *n*-BuLi in ether at 20°C.⁸⁴ Those monolithiated bicyclobutane derivatives (43'-47') were assigned to be dimers (48-49) or trimers (50) in solution, as shown in Figure 7. A broad ¹³C NMR resonance ($W_{1/2} > 190$ Hz) of the "dianion" (44'') was recorded when (44) was treated with two equiv. of *n*-BuLi.

Lithium vapor Chung and Lagow⁸⁵ developed a general technique for preparing polyolithium compounds using lithium vapor. Halocarbons were reacted with lithium vapor to yield polyolithiated alkanes. Abstraction of chlorine from chlorides (RCl) by lithium is



R=H, H (43)
 R=H, Li (43')
 R=Li, Li (43'')

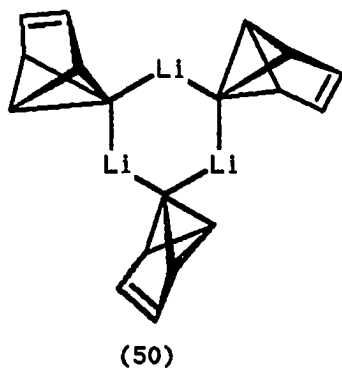
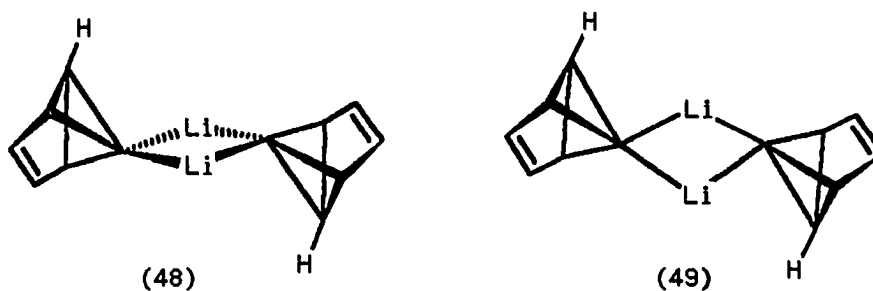
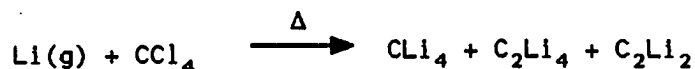


Figure 7. Some bicyclobutanes and the dimes (48), (49) and trimer (50) of (44')

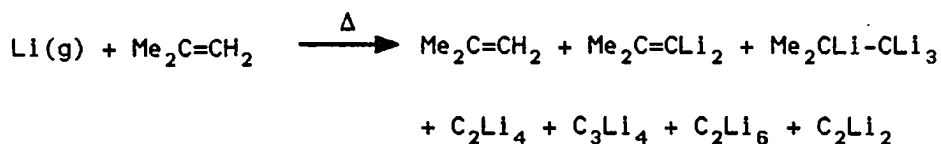
an extremely exothermic reaction ($\sim 109 \text{ KCal mol}^{-1}$) and the subsequent reaction of the free radical ($\text{R}\cdot$) with lithium forms a $\sim 56 \text{ KCal mol}^{-1}$ bond. Therefore, the product is vibrationally excited, which allows

the reaction to proceed to substitution of all the hydrogens by lithium.



When the reaction temperature is controlled at 750°C, dilithiomethane and tetralithiomethane can be obtained in 65.7% and 40.5% yield, respectively.⁸⁶ Diethylmercury provides the purest C_2Li_6 (99% purity) on treatment with lithium vapor at 800°C.⁸⁷

A mixture of polyolithiated alkenes and alkanes is obtained from the reaction of alkenes, such as isobutene, butadiene, trans-2-butene and 1,3-cyclohexadiene, with lithium vapor.⁸⁸ The major reaction is substitution of hydrogen by lithium and the minor pathway is addition of lithium to the double bond.



Reaction of carbon vapor with lithium atoms was reported to give C_3Li_4 as the major product. The side products were CLi_4 , C_2Li_2 and C_2Li_4 .⁸⁹

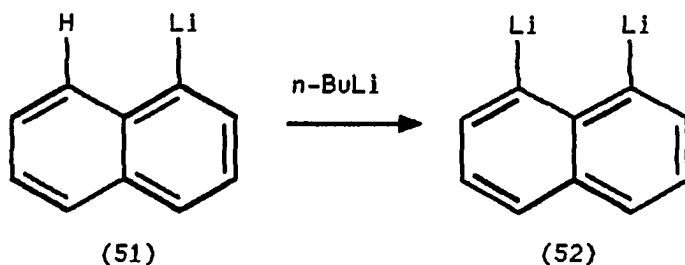
van Eikema Hommes, Bickelhaupt and Klumpp⁹⁰ reported that 1,2-dilithioethane and 1,4-dilithiobutane were formed when lithium vapor was condensed onto a glass composed of ethylene and dimethyl ether at -196°C. After the intermediates were treated with gaseous carbon dioxide and subjected to reaction with diazomethane, dimethyl succinate and dimethyl adipate were found in 8% yield each. This result demonstrates that even at very low temperature, the lithium

vapor is still active enough to react with organic compounds.

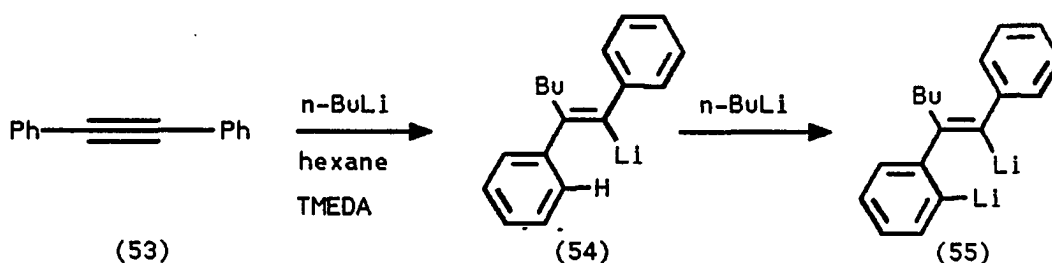
This non-solution method has several advantages. Firstly, the reactivity of lithium vapor is very high. Secondly, the rapid quenching of the products onto a cold finger reduces the rearrangement and secondary reactions. Thirdly, techniques have been developed to separate the polyolithiated products from lithium and lithium chloride, the side product from lithium-chlorine exchange. Unfortunately, two drawbacks limit the usefulness of this method. First of all, a special stainless steel reactor is required to generate lithium vapor, but it is not a common instrument in a normal laboratory. Secondly, methods have not yet been developed to separate one lithium substituted hydrocarbon from a mixture of others, so a mixture of polyolithiated products always results.

Metalation by agostic activation When a hydrogen atom in an organolithium compound is located close to a lithium atom, an agostic interaction may exist. The interaction can be identified by ^6Li , ^1H heteronuclear Overhauser spectroscopy (HOESY). A cross peak is recorded when the distance between lithium and hydrogen is short. The lithium atom often directs further metalation to that position. 1-Lithionaphthalene (51), in which H_8 has an agostic interaction with the lithium atom, can be converted to 1,8-dilithionaphthalene (52) by treatment with $n\text{-BuLi}$.⁹¹

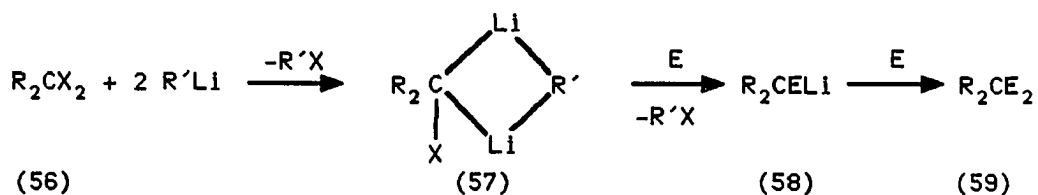
Reaction of a solution of diphenylacetylene in hexane with $n\text{-BuLi}$ in the presence of TMEDA yields the dilithium derivative (55).⁹² The ^6Li , ^1H HOESY indicates a short Li-H_8 distance in the



monolithium (54).⁹³ Therefore, the regiochemistry is controlled by the agostic interaction.

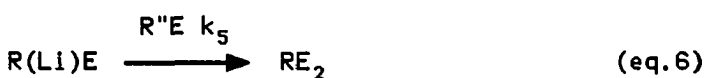
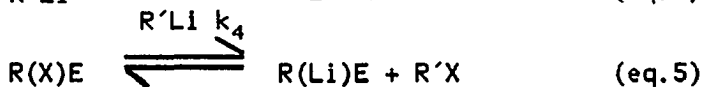
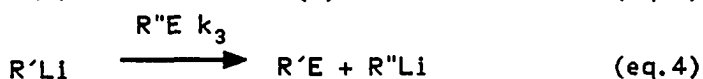
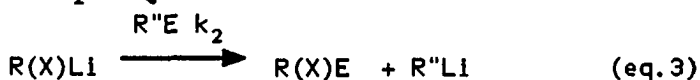
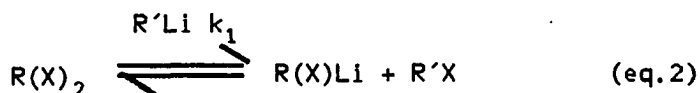


Stepwise quenching The "dilithium" species prepared from the above methods may not always be a real "dilithium"; it is important to obtain NMR or other direct detection data. As discussed by Crowley et al.⁹⁴ a monoanion-organolithium mixed dimer (57) might result after the first lithiation. During anion quenching by MeOD or other electrophiles, a rapid intraaggregate lithiation may occur to give the "second lithiation" product (58), which is trapped subsequently to provide disubstituted organic compounds (59).



Seyferth and Vick⁶¹ also provided a similar explanation for

possible stepwise quenching. When disubstituted organic compounds ($R(X)_2$), in which substituents can exchange with lithium, are treated with excess lithiated agent ($R'Li$), then during the quenching period the following reactions may coexist.



If k_3 (eq. 4) is slower than k_4 (eq. 5), the slow addition of trapping agent allows reaction of the monolithium compound ($R(X)Li$) with trapping agent ($R''E$) and subsequent lithiation of the product ($R(X)E$) (eq. 5) to occur. This process is in successful competition with the slow reaction, namely reaction of the lithiating agent with trapping agent (eq. 4). The monolithiated product ($R(Li)E$) will be trapped to yield a "dilithium derivative" (RE_2) (eq. 6). Several examples have been reported in which stepwise quenching existed.^{61, 94, 84}

To avoid possible stepwise quenching, the organolithium compounds should be added to the trapping agent. However, if the organolithium is labile to heat, the transfer may cause decomposition. The other method is to use more reactive trapping

agents. However, direct detection, for example by NMR or X-ray, is required to prove the existence of dilithium species.

Direct detection

Many polyolithium compounds have been detected directly by NMR, X-ray, UV, IR and/or mass spectroscopy. The objectives of these studies include to learn about: (1) the aggregation of organolithium compounds, and (2) the geometry of the carbon-bearing-lithium atom. Spectral studies of monolithium organic compounds have been investigated extensively and systematically, but that of polyolithium organic compounds are very limited. It is because polyolithium organic compounds appear to be electron-deficient polymeric materials that are highly associated in the solid state. Generally, they neither dissolve in solvent nor easily crystallize.

Aggregation Organolithium compounds exist as oligomers in solution and the solid state as determined by such methods as cryoscopy, ebullioscopy, X-ray crystallography and NMR spectroscopy. The aggregation of organolithium compounds affects the reactivity. Generally, a lesser extent of aggregation will raise the reactivity of the organolithium compound. For example, 3-lithio-1,5-dimethoxypentane (dimer) reacts with benzaldehyde about 10 times faster than 3-lithio-1-methoxybutane (tetramer). Moreover, understanding the degree of aggregation is important in kinetic studies. The kinetic expressions of (eq. 7) and (eq. 8) are definitely different. The correct aggregation state of the organolithium compound which is the actual reactant is needed to

obtain kinetically significant results.



The extent of aggregation of organolithium compounds depends upon the steric requirements of the alkyl group and the solvent in solution. Temperature and concentration also play important roles.

More branching near the carbon-bearing-lithium atom results in smaller aggregation. For example, ethyl- and n-butyllithium are hexameric in cyclohexane and benzene, but t-butyllithium is tetrameric in the same solvents. The bulky organolithium $\text{LiCH}(\text{SiMe}_3)_2$ is monomeric in the gas phase.⁹⁵ Recently, 1,2-dilithio-[tetrakis(trimethylsilyl)]ethane was reported to be monomeric either in THF solution or in the solid state.⁶⁷ Moreover, if the carbanion is stable, the degree of aggregation is low.

In better coordinating solvents, the extent of aggregation of organolithium compounds decreases.⁹⁶ THF is commonly used to deaggregate organolithium compounds. t-BuLi is a nice example. It is tetrameric in non-polar solvents (aliphatic and aromatic hydrocarbons), dimeric in a more donating solvent (diethyl ether) and monomeric in the less crowded donating solvent (THF). In addition, n-BuLi is a mixture of dimer and tetramer in THF solution.⁹⁷ Most organolithium compounds form 1:1 complexes with TMEDA, whereby n-BuLi, for example, is a mixture of dimer and monomer.⁷⁴ Addition of the tridentate ligand, N,N,N',N'',N''-pentamethyldiethylenetriamine

(PMDTA), can convert most dimeric alkyllithium compounds to monomers.^{98,99} For example, phenyllithium is a monomer-dimer mixture in THF, but it is solely monomeric in the presence of PMDTA. There is one notable exception, methyllithium. In both solid state and solution, although TMEDA is the coordinating agent, methyllithium is still a tetrameric complex. TMEDA acts as a bridge connecting two tetramers of methyllithium as shown in Figure 8. If the organolithium compound contains intramolecular chelating groups, the degree of aggregation is lowered, as discussed below.

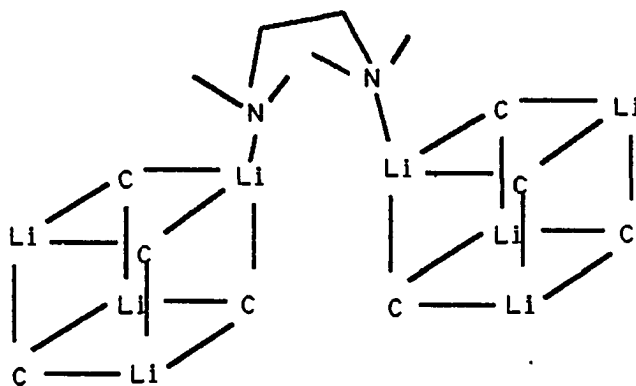


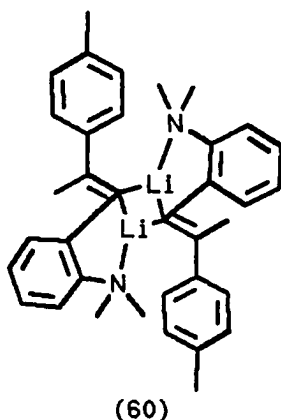
Figure 8. Tetrameric MeLi in TMEDA

Predictably, the degree of aggregation rises with increasing concentration of organolithium compounds. For instance, both isopropyl- and trimethylsilylmethyl lithium are reported to change from tetramers to hexamers as the concentration is increased.¹⁰⁰

Lowering the temperature usually results in an increase in the degree of aggregation. Fraenkel and coworkers¹⁰¹ found that propyllithium in cyclopentane solution existed not only as a hexamer, but also an octamer and three different nonamers. While the hexamer

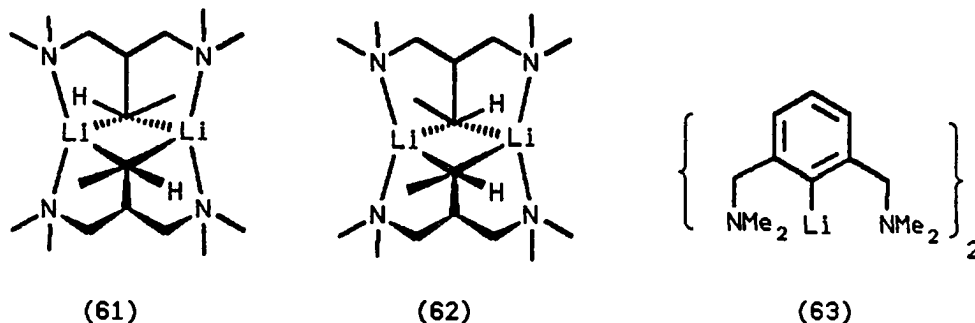
predominates above 250 K, the other aggregates are present in appreciable amounts at lower temperature.

Intramolecular chelation Intramolecular chelation can not only reduce the degree of aggregation, but also stabilize the organolithium compound. In terms of deaggregation, trans-1-propenyllithium is tetrameric in diethyl ether, while the organolithium (60), which has an intramolecular donor dimethylamino group, is dimeric in benzene by cryoscopy.¹⁰²



Vos et al.¹⁰³ showed that 3-lithio-1,5-dimethoxypentane was dimeric in hydrocarbon solution by ¹³C NMR. Moene et al.¹⁰⁴ also reported the X-ray data for a dimeric alkyllithium crystal obtained from a solution of 1,1-bis((dimethylamino)methyl)-2-propyllithium (61) in pentane. In this structure, the two lithium atoms are bridged by the two α -carbons, and they are tetracoordinated with two carbon atoms and two dimethylamino groups. Two dimers (61) and (62) are present in n-pentane-d₁₂ in a 67:33 ratio at 245 K on the basis of ¹³C NMR analysis. The crystalline structure (61) with

trans-positioned α -methyl groups is assigned to the major dimer. The 2,6-bis((dimethylamino)methyl)phenyllithium (63) is also dimeric in the solid state.¹⁰⁵

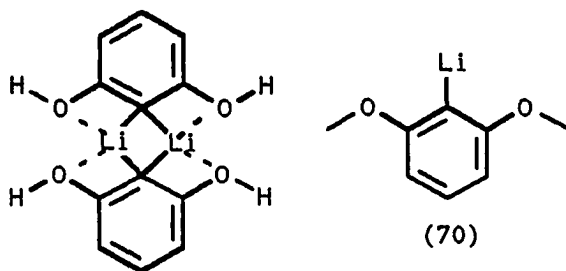


The second advantage of intramolecular chelation is that it may lead to stabilization of organolithium compounds. Heats of reaction, $\Delta H_{r, s-BuOH}(25^\circ C)$, of ca. 10^{-3} M benzene solutions of several organolithium compounds with or without an intramolecular methoxy group have been studied by Geurink and Klumpp.¹⁰⁶ The results are shown in Table 3. The enthalpy of intramolecular etheration (ΔH_{intra}) can be calculated from the difference between the heats of formation of related organolithium compounds.

The results indicate that intramolecular chelation reduces the enthalpy of formation for organolithium compounds. The enthalpy of intramolecular etheration (ΔH_{intra}) is ca. 10 KCal mol⁻¹. It is slightly larger than the enthalpy of intermolecular etheration, (ΔH_{inter}) which is 8.6 KCal mol⁻¹, obtained from the formation of $i-Pr_4Li_4 \cdot THF$ in benzene.¹⁰⁰ It is understandable that intermolecular chelation is sterically more demanding than intramolecular chelation. In the cases of the primary organolithiums ((65) and (68), (66) and

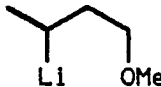
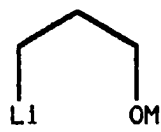
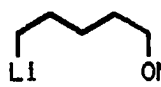
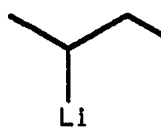
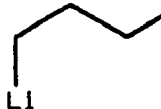

(69)), their different aggregations in benzene must be considered. (65) and (66) are tetramers, which (68) and (69) are hexamers. When the enthalpy of deaggregation (hexamer to tetramer, 3 KCal mol⁻¹) is taken into account, ΔH_{intra} is again about 10 KCal mol⁻¹.

Intramolecular chelation affects the geometry of the carbon-bearing-lithium atom. A good example is given by the Schleyer group. Harder et al.¹⁰⁷ performed MNDO calculations on the dimer of 2,6-dihydroxyphenyllithium. The effectiveness of oxygen-lithium chelation makes the planar tetracoordinate geometry more stable than the tetrahedral geometry by 28 KCal mol⁻¹.



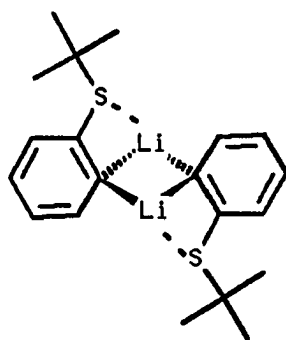
Experimentally, Harder et al.¹⁰⁷ and Dietrich et al.¹⁰⁸ simultaneously showed that 2,6-dimethoxyphenyllithium (70) had a local environment of the α carbon which approaches the planar tetracoordinate geometry. The crystal structure of (70) is tetrameric, where there are two interacting dimeric units. In the dimer units, the twist angles between the planes C-C(ipso)-C' and Li-C(ipso)-Li' are in the range of 6.0(4)^o-16.8(4)^o (average 11.1^o). The C-Li distance within the dimers (average 2.285(9) Å) is shorter than that between the dimers (average 2.349(9) Å). The Li-Li distances within and between the dimers are 2.74(1) Å and 2.68(1) Å,

Table 3. Heats of reactions ($\Delta H_{r, s-BuOH}$) (KCal mol⁻¹) at 25°C in benzene

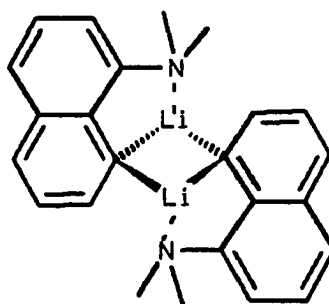
| Organolithiums | | $\Delta H_{r, s-BuOH}$ |
|---|------|------------------------|
|  | (64) | -47.4 ± 1 |
|  | (65) | -45.2 ± 0.5 |
|  | (66) | -45.2 ± 0.7 |
|  | (67) | -57.2 ± 1.2 |
|  | (68) | -52.1 ± 0.5 |
|  | (69) | -52.6 ± 0.7 |

respectively. The septet pattern in the ¹³C NMR spectrum of the lithiated carbon of (70) in toluene-d₈ indicates a tetrameric structure. In THF-d₈ solution, a monomeric structure was found by cryoscopy. In toluene-d₈, two different magnitudes of ¹³C-⁶Li coupling constants (3.5, 4.9 Hz) were observed by ⁶Li NMR

spectroscopy. This suggests that the solid state tetrameric structure is retained in the apolar solvent. On the other hand, the X-ray structures of dimers for both phenyllithium/TMEDA¹⁰⁹ complex and 2,3,5,6-tetrakis[(dimethylamino)methyl]phenyllithium¹⁰⁵ indicated that the perpendicular form was favored. Other organolithium compounds with intramolecular chelating groups, (71)¹¹⁰ and (72),¹¹¹ show some tetrahedral-planar distortion of the carbon atom bearing the lithium atom. The twist angles between the aryl ring and the C-Li-C-Li four membered ring are 47.6° and 41.3° for (71) and (72), respectively.



(71)



(72)

NMR spectroscopic results

NMR spectroscopy is the most powerful method for observing the structures and aggregation states of organolithium compounds in solution. The signal multiplicity and the magnitude of the C-Li coupling constant provide important information for solving the aggregation problem. ¹³C-⁷Li coupling was used early to establish the tetrahedral structure of methyllithium tetramers.¹¹² But the short ⁷Li relaxation time normally broadens out the multiplicity to give a broad singlet. In

1978, Wehrli¹¹³ recognized that the ${}^6\text{Li}$ nucleus had a relatively relaxation time in organolithium compounds. The narrower linewidth for both ${}^{13}\text{C}$ and ${}^6\text{Li}$ spectra made the observation of ${}^{13}\text{C}$ - ${}^6\text{Li}$ coupling easier. The development of 2D NMR techniques also increased the applicability of NMR spectroscopy to organolithium chemistry. ${}^6\text{Li}$, ${}^1\text{H}$ Nuclear Overhauser enhancements have been used to study molecular geometry.¹¹⁴ Moskau and coworkers also developed ${}^6\text{Li}$, ${}^{13}\text{C}$ shift correlation¹¹⁵ and ${}^6\text{Li}$, ${}^6\text{Li}$ COSY techniques.^{25c}

Due to fast carbon-lithium bond exchanges within and between aggregates, ${}^{13}\text{C}$ NMR spectra of organolithium compounds are temperature dependent. At higher temperature, an average spectrum of different aggregates may be obtained. Generally, the coupling pattern may be resolved at low temperature due to the slowing down of the exchange process. Since the total spin numbers (I) of the quadrupolar isotopes ${}^6\text{Li}$ ($I = 1$; 7.4%) and ${}^7\text{Li}$ ($I = 3/2$; 92.6%) are different, the signal multiplicities of ${}^{13}\text{C}$ - ${}^6\text{Li}$ and ${}^{13}\text{C}$ - ${}^7\text{Li}$ are different. Following the $(2nI+1)$ multiplicity rule, for example, when two ${}^6\text{Li}$ nuclei bond with one carbon ($n = 2$, $I = 1$), a quintet splitting is observed in ${}^{13}\text{C}$ NMR spectra. However, a septet is obtained when two ${}^7\text{Li}$ nuclei are bonded to one carbon ($n = 2$, $I = 3/2$). Therefore, from the splitting pattern of a ${}^{13}\text{C}$ NMR signal split due to coupling to ${}^6\text{Li}$ or ${}^7\text{Li}$, the degree of aggregation of the organolithium compound can be assigned as shown in Table 4.

Table 4. The coupling pattern of different organolithium aggregates

| Oligomers | Isotope of Li bonded | Number of line |
|----------------------------------|----------------------|----------------|
| monomer | 6 | 3 |
| monomer | 7 | 4 |
| dimer | 6 | 5 |
| dimer | 7 | 7 |
| tetramer(static) ^a | 6 | 7 |
| tetramer(static) ^a | 7 | 10 |
| tetramer(fluxional) ^b | 6 | 9 |
| tetramer(fluxional) ^b | 7 | 13 |
| hexamer | 6 | 13 |

^aA static aggregate, assuming coupling to three equivalent Li nuclei.

^bA fluxional aggregate, coupling to all Li nuclei within the aggregate.

The magnitudes of ^{13}C - $^{6,7}\text{Li}$ coupling constants depend on three factors:

- (1) The degree of aggregation.
- (2) Intramolecular lithium bridging.
- (3) The bonding nature of carbon-lithium bond.

Due to the major ionic character of the carbon-lithium bond, spin polarization may be responsible for the observed coupling.

Bauer, Winchester and Schleyer⁹⁸ summarized values of ^{13}C - $^{6,7}\text{Li}$ coupling constants for many organolithium compounds, as shown in Table 5.

Table 5. ^{13}C - $^6,^7\text{Li}$ Coupling constants (Hz) of some organolithiums


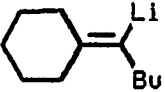
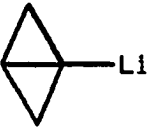
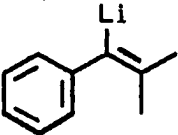
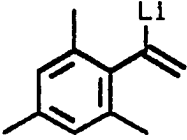
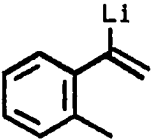
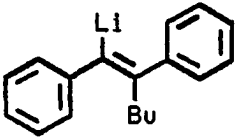
| Organolithiums | Agg. ^a | $J(^{13}\text{C}, ^6\text{Li})$ | $J(^{13}\text{C}, ^7\text{Li})$ |
|--|-------------------|---------------------------------|---------------------------------|
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$ | n ^b | 2.22 | (5.86) |
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$ | o ^b | 2.48 | (6.55) |
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$ | h ^b | 3.25 | (8.58) |
| s-BuLi | h ^b | 3.35 | (8.85) |
| t-BuLi | t ^b | 5.4 | (14.3) |
| t-BuLi | t ^c | 4.1 | (10.8) |
| n-BuLi | t | (5.5) | 14.6 |
| s-BuLi | t | 6.1 | (16.1) |
| CH_3Li | t | (5.5) | 14.5 |
| t-BuCCLi | t | 6 | 16 |
| $\text{CH}_2=\text{CHLi}$ | t | (5.8) | 15.4 |
| t-BuLi | d | (7.6) | 20 |
| PhLi | d | 8 | 20 |
| n-BuLi | d | 7.8 | (20.6) |
| PhCCLi | d | 8.2 | (21.7) |

^aAgg.=aggregation, n=nonamer, o=octamer, h=hexamer, t=tetramer, d=dimer, m=monomer.

^bFluxional.

^cStatic.

Table 5. (Continued)

| Organolithiums | Agg. ^a | J(¹³ C, ⁶ Li) | J(¹³ C, ⁷ Li) |
|---|-------------------|--------------------------------------|--------------------------------------|
|  | d | 9.7 | (25.6) 10.8 |
|  | d | 9.0 | (23.8) |
|  | d | 10.3 | (27.2) |
|  | m | 12 | (31.7) |
|  | m | 11 | (29.0) |
|  | m | 12 | (31.7) |
|  | m | 10.8 | (28.5) |

Coupling constants of the two isotopes are related to each other by their gyromagnetic ratios (γ) according to the following equation (eq. 9).

$$J(^{13}\text{C}-^7\text{Li}) = (\gamma(^7\text{Li})/(^6\text{Li})) J(^{13}\text{C}-^6\text{Li}) = 2.64 J(^{13}\text{C}-^6\text{Li}) \quad (\text{eq. 9})$$

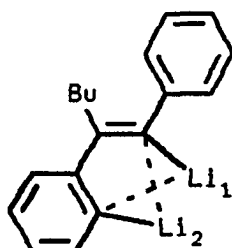
With the same degree of aggregation, the differences between the magnitudes of $^{13}\text{C}-^6,^7\text{Li}$ coupling constants for different hybridizations of lithiated carbon atoms are very small. The coupling constants ($^{13}\text{C}-^6\text{Li}$; $^{13}\text{C}-^7\text{Li}$) for the tetramers of methyllithium (5.5; 14.5 Hz), vinylithium (5.8; 15.4 Hz) and lithio-3,3-dimethylbutyne (6; 16 Hz) are nearly identical. The magnitudes of the $^{13}\text{C}-^6,^7\text{Li}$ coupling constants roughly follow two equations (eq. 10 and eq. 11), in which n equals the number of lithium atoms directly bonded to carbon (or the number of carbon atoms which share an electron pair with the coupled lithium) on the NMR time scale: $n = 1$ (monomer), 2 (dimer), 3 (static tetramer), 4 (fluxional tetramer), 6 (hexamer), 8 (octamer), or 9 (nonamer).

$$J_{^{13}\text{C},^6\text{Li}} = 1/n (17 \pm 2) \text{ Hz} \quad (\text{eq. 10})$$

$$J_{^{13}\text{C},^7\text{Li}} = 1/n (45 \pm 5) \text{ Hz} \quad (\text{eq. 11})$$

Interestingly, even when the lithium bridge is intramolecular the $^{13}\text{C}-^6,^7\text{Li}$ coupling constants follow the equations well.¹¹⁵ For instance, the $^{13}\text{C}-^6\text{Li}$ coupling constants of Li_1 and Li_2 in monomeric (55) are 5.9 and 7.6 Hz, respectively. They are close to the expected values for dimeric organolithiums (6-8 Hz).

$^{13}\text{C}-^6,^7\text{Li}$ coupling constants of monomeric organolithium



(55)

compounds show significant deviations from the generalizations given in eqs. 10 and 11. For instance, the ^{13}C - ^6Li coupling constants for monomeric *t*-BuLi and *s*-BuLi are 11.9 and 14.0 Hz, respectively. They are smaller than the expected 17 Hz. Most monomeric carbenoids have larger ^{13}C - ^6Li coupling constants (16.3-17 Hz). Monomeric vinyl lithium derivatives have lower than expected ^{13}C - $^6,7\text{Li}$ coupling constants (10-12 Hz) as shown in Table 5. The reason is thought to be related to the ionic nature of the carbon-lithium bond, which, in monomers, should be more ionic in some instances than others. For compounds with completely ionic carbon-lithium bonds, such as benzyl lithium, no carbon-lithium coupling is seen, even at very low temperature.

Recently, Thomas and coworkers¹¹⁶ observed ^{13}C - ^6Li coupling for branched-chain alkyllithium compounds, but not for straight-chain alkyllithium compounds in cyclopentane solution. The rapid interaggregate exchange between higher aggregates (hexamer, octamer and nonamer) of straight-chain alkyllithium compounds may be responsible for the unresolved signals. Since the branched-chain alkyllithium compounds are hexameric or tetrameric in the hydrocarbon solvent, the interaggregate exchange can be frozen at low

temperature, whereby ^{13}C - ^6Li coupling is detected.

Although the magnitudes of ^{13}C - $^6,7\text{Li}$ coupling constants do not correlate with the hybridization of the carbon atom bearing the lithium atom, different types of organolithium compounds are categorized according to the chemical shift differences $\Delta\delta(\text{H,Li})$ between them and their hydrocarbon analogs. Seebach and coworkers⁹⁷ studied the ^{13}C NMR spectra of many lithiated hydrocarbons. They divided the organolithium compounds into four categories. Some examples are given in Table 6.

In category A are lithiated alkanes and cyclopropanes. Their $\Delta\delta(\text{H,Li})$'s are small ($\sim \pm 15$ ppm), because of the high degree of aggregation. An increase in charge density leads to an upfield shift for lithiated alkanes. However, a downfield shift is observed in lithiocyclopropane systems.

Category B includes σ -bonded vinyl, aryl and allenyl systems. Their $\Delta\delta(\text{H,Li})$'s are between 50 to 65 ppm and a downfield shift results. The ^{13}C -deshielding is related to the polarization of the π -electrons. Lithium substitution increases the σ -electron density on the α carbon. The result is a decrease of the π -electronic excitation energy. According to eq. 12, derived by Karplus and Pople,¹¹⁷ the paramagnetic shielding term σ^{para} increases with a decreasing average electronic excitation energy, ΔE . Since σ^{para} is a negative value, a deshielding results.

$$\sigma^{\text{para}} = - \frac{e^2 h^2}{m^2 c^2} \Delta E^{-1} \gamma_{2p}^{-3} [Q_{AA} + \sum Q_{AA}] \quad (\text{eq. 12})$$

Table 6. The ^{13}C chemical shifts of organolithium ($\delta(\text{C}(\text{Li}))$) and their hydrocarbon analogues ($\delta(\text{C}(\text{H}))$), and their differences ($\Delta\delta(\text{H},\text{Li})$)


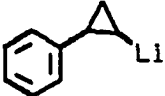
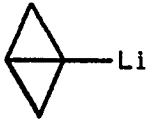
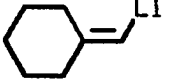
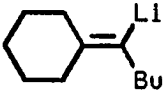
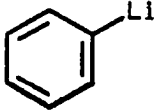
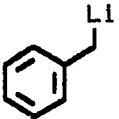
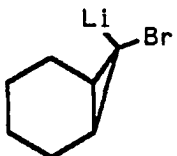
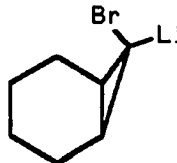
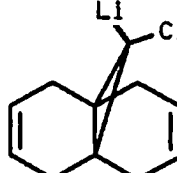
| Organolithiums | $\delta(\text{C}(\text{H}))$ | $\delta(\text{C}(\text{Li}))$ | $\Delta\delta(\text{H},\text{Li})$ |
|---|------------------------------|-------------------------------|------------------------------------|
| n-BuLi | 14.5 | 12.4 | -1.9 |
|  | 10.6 | 11.9 | 1.3 |
|  | 10.7 | 22.4 | 11.7 |
|  | -4.0 | -14.9 | -10.9 |
|  | 107.5 | 162.0 | 54.5 |
|  | 122.0 | 173.5 | 51.5 |
|  | 128.6 | 188.9 | 60.3 |
| $\text{CH}_3(\text{CH}_2)_5\text{C}\equiv\text{CLi}$ | 70.7 | 118.8 | 48.1 |
| $(\text{CH}_3)_3\text{CC}\equiv\text{CLi}$ | 67.0 | 115.0 | 48.0 |
|  | 24.0 | 37.4 | 13.4 |

Table 6. (Continued)

| Organolithiums | $\delta(\text{C(H)})$ | $\delta(\text{C(Li)})$ | $\Delta\delta(\text{H,Li})$ |
|---|-----------------------|------------------------|-----------------------------|
| $(\text{Ph})_2\text{-CHLi}$ | 42.1 | 80.8 | 38.7 |
| $(\text{Ph})_3\text{-CLi}$ | 56.8 | 90.4 | 33.6 |
| LiCHCl_2 | 55.5 | 105.5 | 50.0 |
| LiCHBr_2 | 22.5 | 101.3 | 78.8 |
| LiCHI_2 | -55.0 | 61.0 | 126.0 |
| LiCCl_3 | 80.0 | 145.9 | 65.9 |
| LiCBr_3 | 9.7 | 152.2 | 142.5 |
| LiCI_3 | -138.0 | 142.0 | 280.0 |
| $\text{CH}_3\text{CBr}_2\text{Li}$ | 42.6 | 148.1 | 105.5 |
|  | 25.8 | 87.7 | 62.0 |
|  | 34.7 | 90.7 | 56.0 |
|  | 43.5 | 86.0 | 42.5 |

Category C contains α -heterosubstituted organolithium compounds. They usually are monomeric in solution, so a large ^{13}C - ^6Li coupling constant of ca. 17 Hz is observed. The range of $\Delta\delta(\text{H,Li})$ is very large (40 ~ 280 ppm). In all cases, the α carbon is deshielded, probably due to the increased s-character at the α carbon. This may also be represented by a "cationic" resonance form for the carbenoid, as shown in Figure 9.

Category D includes π -bonded allylic and benzylic systems. A downfield shift results due to the lithium substitution. The rehybridization of carbon in these species from sp^3 to more or less sp^2 might be the reason for the downfield ^{13}C shift. The charge delocalization increases the deshielding of the α carbon.

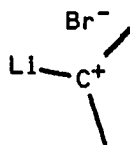
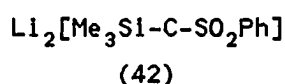


Figure 9. Cationic form of carbenoid

Several ^{13}C NMR spectra of polylithium compounds have been reported recently. Gurak et al.¹¹⁸ recorded an excellent solid state ^{13}C NMR spectrum of CH_2^6Li_2 , using the cross polarization magic angle spinning technique with ^6Li decoupling as well as ^1H decoupling. A sharp singlet 26.5 ppm downfield from CH_3^6Li was observed. It implies that the symmetry of solid aggregate $(\text{CH}_2\text{Li}_2)_n$ is very high, and only one carbon environment exists in the solid state. The other

surprising observation is the downfield ^{13}C shift of CH_2^6Li_2 , even though an increase in charge density at the methylene carbon with increasing lithium substitution should result in shielding. The downfield shift may be due to rehybridization of carbon in CH_2Li_2 from sp^3 to more or less sp^2 .

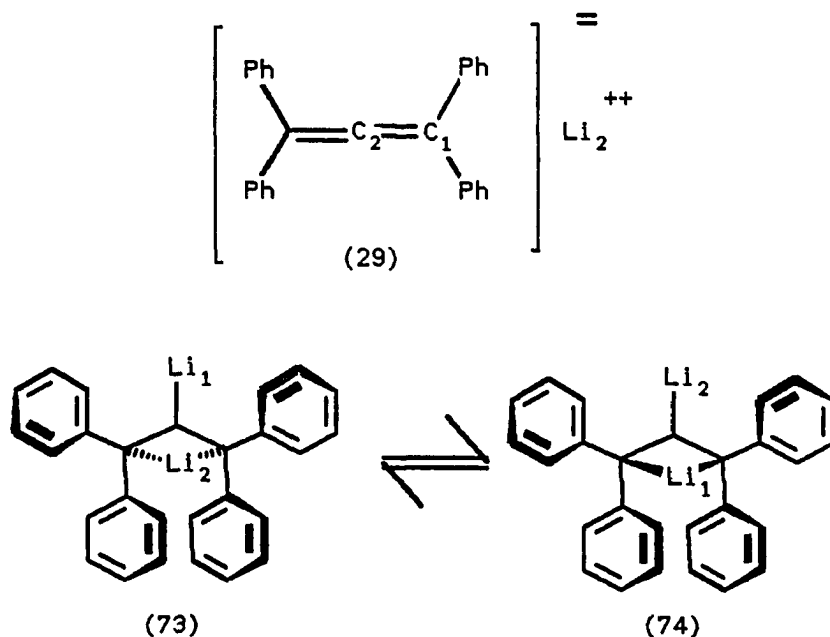
Gais and coworkers⁸³ obtained ^{13}C and ^6Li NMR spectra of dilithiosulfone (42) in THF solution.



Because of fast inter- and/or intraaggregate exchange processes, a single line was observed in the ^{13}C NMR spectrum of (42) at room temperature. Upon lowering the temperature to about -60°C , five signals (δ 51.36, 49.92, 54.53, 53.88, 38.16 ppm) appeared in the ^{13}C NMR spectrum and seven signals were observed in the ^6Li NMR spectrum. All of them were split by ^{13}C - ^6Li coupling with different coupling constants. They represent the α carbon of (42) either in different aggregates, or in different conformational environments in a hexamer, the aggregate state of (42) in the solid. Using 2D NMR techniques, ^6Li , ^6Li COSY and ^{13}C , ^6Li shift correlation experiments, they demonstrated that when a carbon atom carries two lithium atoms in a single molecule, two different ^{13}C - ^6Li coupling constants may arise.

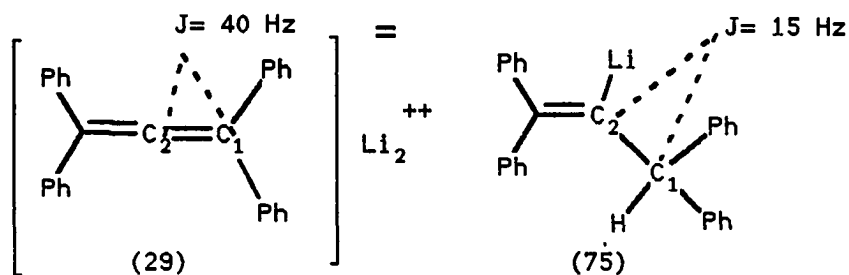
Bernard, Schnieders and Müllen¹¹⁹ utilized ^1H , ^{13}C and ^7Li NMR spectroscopies to study the structure of dilithium tetraphenylallene (29). Rajca and Tolbert^{26b,120} reported a similar result by using the ^{13}C , ^6Li labelling technique. The

terminal carbon resonances remain equivalent and uncoupled to lithium even at -140°C . The center carbon resonance is a quintet with a 9 Hz splitting due to ^{13}C - ^6Li coupling. The ^6Li NMR spectrum of $^{13}\text{C}_2$ -(29) exhibits a well resolved doublet with a 9 Hz splitting at -115°C . Moreover, the $^1J(\text{C}_1\text{-C}_2)$ is 40 Hz, in the range typical for $\text{sp}^3\text{-sp}^2$ carbon-carbon bonds. According to the spectroscopic results and the *ab initio* calculations on 2,3-dilithiopropenes,¹²¹ they concluded that the exchange process between (73) and (74) is fast in the NMR time scale, and (29) is monomeric in solution at low temperature.



As mentioned above, the downfield shifts of allylic and benzylic lithiated carbons are due to rehybridization of the carbon. This lithium induced rehybridization has been demonstrated by Rajca and Tolbert.¹²⁰ The $^1J(\text{C}_1\text{-C}_2)$ of 1,2,3-tri ^{13}C -(29) and 1,2-di ^{13}C -(75) are 40 Hz and 15 Hz, respectively. The $^1J(\text{C}_1\text{-C}_2)$ of the

corresponding propene, allyllithium and allene are 44, 67 and 103 Hz, respectively. The coupling constants reflect an increase of p character between C_1 and C_2 . It is expected that the carbon lithium bond would have greater s character due to the polar nature of that bond. One interesting result is that (75) is monomeric in THF solution, probably due to the steric effect of the four phenyl groups. A triplet with a 15 Hz splitting was observed for C_2 due to the ^{13}C - ^6Li coupling.



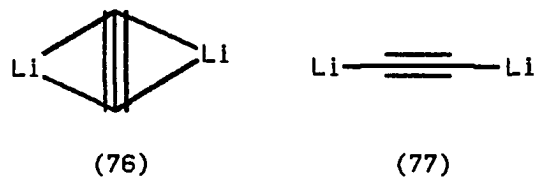
X-Ray Crystallography

X-ray crystallography provides the best information concerning structural details in the solid state.¹⁵ Almost all organolithium compounds have non-van't Hoff forms. Symmetrical multiple bridging either intermolecular or intramolecular is also quite common. Additionally, most of the reported X-ray structures have associated solvent molecules. Therefore, the crystal structures of these species may also be representative of the structures of solvated species in solution.

In 1963, Dietrich reported the first organolithium X-ray structure, ethyllithium tetramer.¹²² One year later, crystalline methyllithium was also determined as tetrameric.¹²³ Recently, numerous structures have been determined by Lappert et al.,¹²⁴

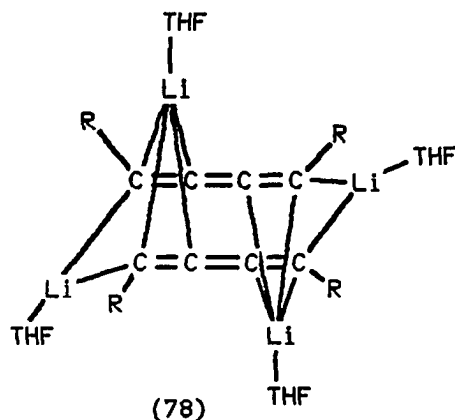
Amstutz et al.,¹²⁵ Klumpp et al.,¹²⁶ Schleyer,¹⁵ and other groups.¹²⁷

The few known X-ray structures of polylithium compounds are in good agreement with theoretical calculations where calculations on those systems have been performed. According to theoretical calculations by Schleyer,^{15b} dilithioacetylene in the gas phase may prefer a bridged structure (76) rather than the conventional linear structure (77). Interestingly, the unit cell of dilithioacetylene was shown by X-ray to be built of formally bicyclic C_2Li_2 units, instead of linear ones,¹² as shown in Figure 10.

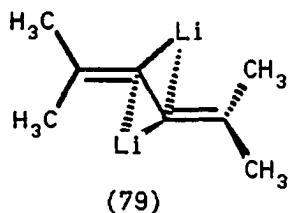


From MNDO calculations, 1,4-dilithiobutatriene has a dimeric cis-structure (78) with two different kinds of lithium atoms and a true butatriene geometry.¹²⁸ The crystal of 1,4-bis(*t*-butyl)-1,4-dilithiobutatriene ($R = t\text{-Bu}$) turns out to have a structure in agreement with the predicted one.

2,3-Dilithio-1,1,4,4-tetramethyl-1,3-butadiene (79) is tetrameric in both the solid state¹² and solution.^{25c,115} As shown in Figure 10, four lithium atoms form a tetralithiocyclobutane skeleton. Two crystallographically different diene molecules are present in different environments. According to the C-C bond lengths, (79) is a true butadiene derivative with $C_1-C_2 = C_3-C_4 = 1.40 \text{ \AA}$ and $C_2-C_3 = 1.50 \text{ \AA}$ on average. The structure of (79) was also

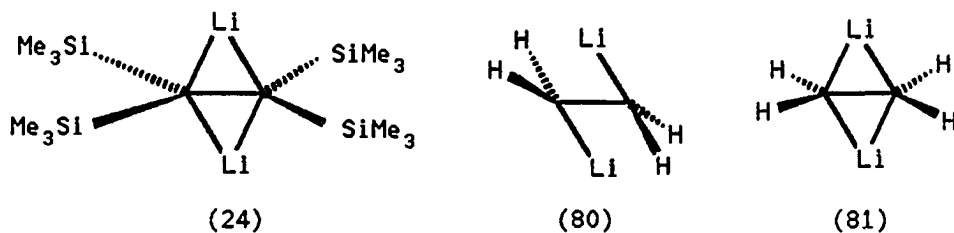


identified by NMR. Two signals were recorded in the ^6Li NMR spectrum of (79). They are coupled with each other, as shown by a ^6Li , ^6Li COSY experiment.^{25c} This suggests that the two lithium atoms are present in the same molecule.

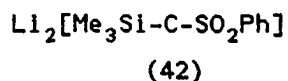


Recently Sekiguchi et al.⁶⁷ reported the crystal structure of 1,2-dilithio[tetrakis(trimethylsilyl)]ethane (24). Theoretical calculations⁴⁷ on 1,2-dilithioethane indicate that a trans conformation (80) (C_{2h}) with a partially bridged geometry is the most stable one. However, it is also suggested that the symmetrically trans bridged structure (81) (D_{2h}) is only 1.9 KCal mol⁻¹ higher in energy than the most stable one. The lithium atoms in the crystal of monomeric (24) are tri-coordinated. They are each bonded to one THF molecule as well as to two carbon atoms. The X-ray result supports

the trans-lithium bridged structure.

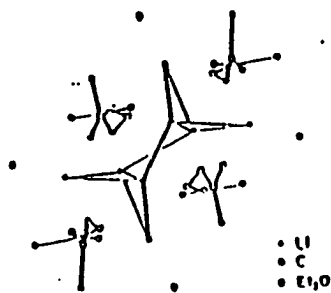


The complicated crystal structure of dilithium trimethyl((phenylsulfonyl)methyl)silane (42), a dilithiomethane derivative, was solved by Gais and coworkers.⁸³ As shown in Figure 10, the X-ray structure of $(42)_6 \cdot \text{Li}_2\text{O} \cdot \text{THF}_{10}$ shows a hexamer (C_1) with six THF and one Li_2O molecules. Four THF molecules lie between the hexamers. In the hexamer, there are three pairs of conformationally different dicarbanion carbons. Those three different dianionic carbon atoms are each coordinated to at least two lithium atoms. At the center of the hexamer, around the oxygen atom of Li_2O is an octahedral array of six lithium atoms. Only four of those lithium atoms contact the dianionic carbon.

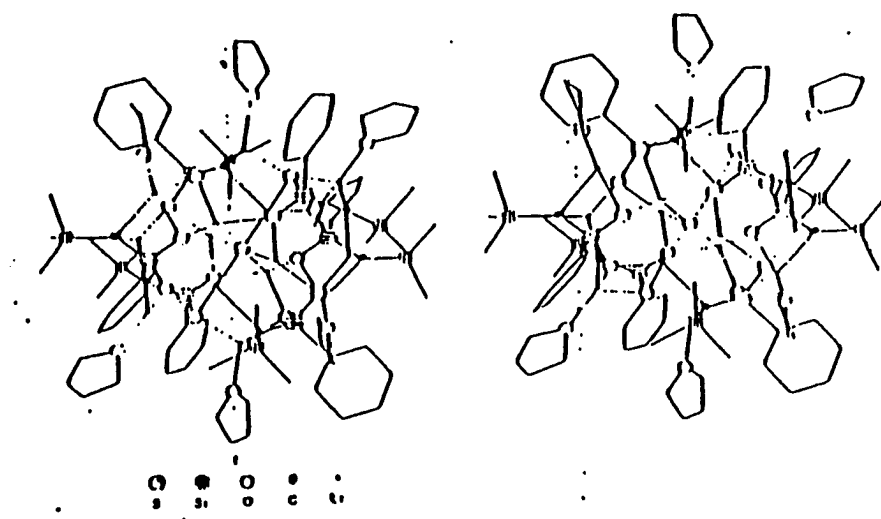




(76)



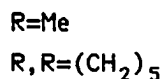
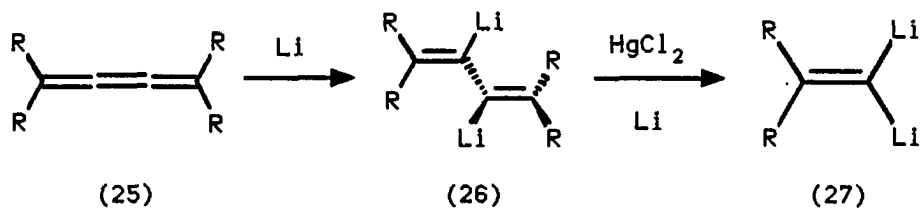
(79)



(42)

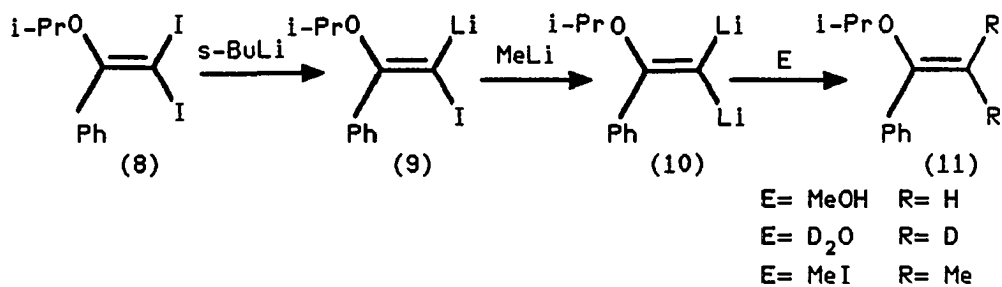
Figure 10. The crystal structures of compounds (76), (79) and (42)

Maercker and Dujardin⁶⁸ also found that the addition of lithium to the center double bond of butatrienes (25) resulted in dilithiums (26). The dienes (26) are stable towards excess lithium, but are cleaved to 1,1-dilithioalkenes (27) in the presence of mercury (II) chloride.

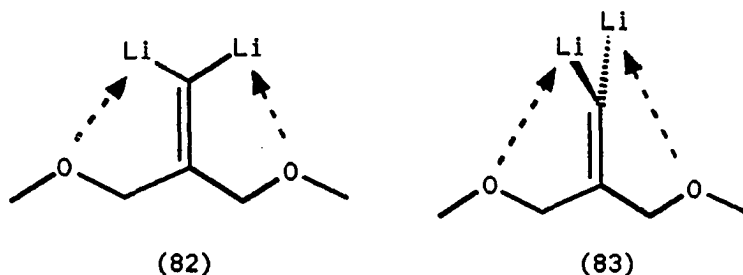


The available 1,1-dilithioethylene derivatives (27) neither dissolve in organic solvent nor crystallize out. Therefore, no structural information is available.

One more example of 1,1-dilithioethylene derivatives was presented by Barluenga and coworkers.⁵⁴ Carbenoid (9) is first prepared by the lithium-iodine exchange reaction of the diiodoalkene (8) with *s*-BuLi. Compound (9) reacts with excess MeLi to provide 1,1-dilithio-1-alkenes (10), which after trapping gives 1,1-disubstituted alkene (11) in high yield. However, diiodoalkene (8) is not a normal alkene but an enol ether. Stepwise quenching is a very possible reaction in this case rather than formation of 1,1-dilithio-1-alkene derivative (10). In addition, no structural studies have been performed.



The intramolecular chelation strategy was employed in an attempt to generate and study the structure of 1,1-dilithioethylene. In monomeric 1,1-dilithio-3-methoxy-2-methoxymethylpropene (82), coordination of the lithium atoms by oxygen should make the planar form (82) strongly preferred. The perpendicular conformer (83) can be excluded because it is too strained.

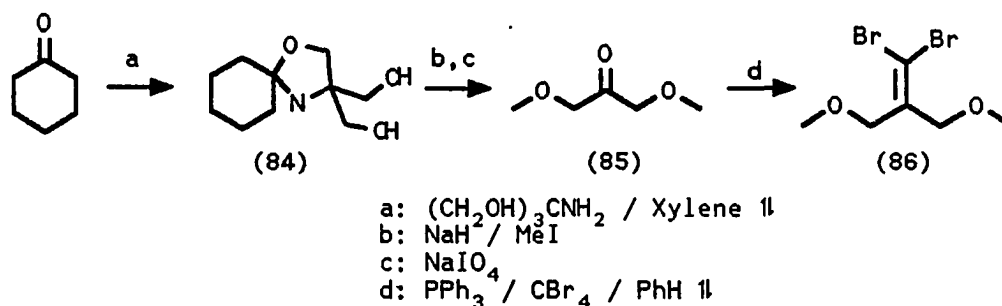


The Lithium-bromine Exchange Route

Synthesis

Since the lithium-bromine exchange is a very fast process even at low temperature, the first precursor of dilithium (82) tried was 1,1-dibromo-3-methoxy-2-methoxymethylpropene (86). The preparation of the dibromide (86) is outlined in Scheme 2.

Scheme 2.

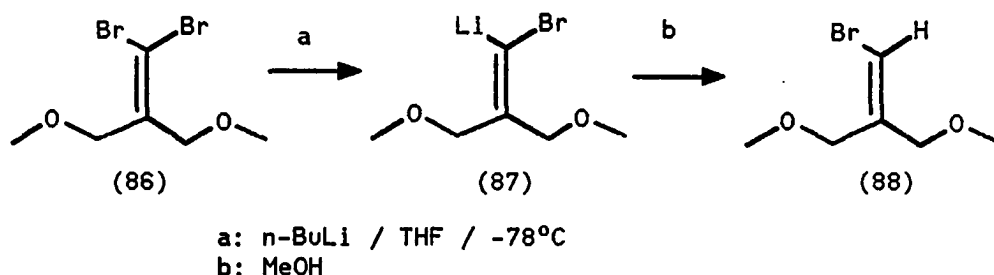


Treatment of cyclohexanone with (tris-(hydroxymethyl))-aminomethane (THAM) gave the diol (84).¹²⁹ A sequence of methylation of diol (84), followed by deprotection and oxidative cleavage of the corresponding dimethyl ether by sodium periodate, gave 1,3-dimethoxypropanone (85)¹³⁰ in 30% overall yield. Then ketone (85) was transformed into dibromide (86) via the procedure developed by Posner and coworkers^{131a} ($\text{CBr}_4/\text{PPh}_3$ in refluxing benzene) in 75% yield. If either the temperature of the oil bath was too high ($> 100^\circ\text{C}$) or the stirring inefficient, a thick gel was formed and the yield was low ($< 10\%$). An alternative method due to Corey and Fuchs,^{131b} using a 2:2:2 mixture of zinc dust, triphenylphosphine and carbon tetrabromide as reagents was tried, but the yield was lower (50%).

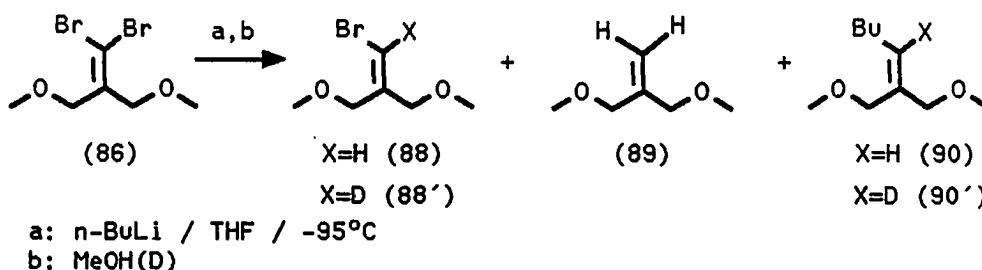
Results and discussions

Reaction of dibromide (86) with butyllithium Dibromide (86) was first treated with one equiv. of n-BuLi, followed by quenching with methanol. 1-Bromo-3-methoxy-2-methoxymethylpropene (88) resulted as the sole product. This indicated the accessibility of

stable lithio-bromocarbonoid (87) under these conditions.



When more than one equiv. of n-BuLi was added, three products were obtained after quenching with methanol. They were bromide (88), 3-methoxy-2-methoxymethylpropene (89) and 1-methoxy-2-methoxymethyl-2-heptene (90). The formation of alkene (89) suggested the possibility that 1,1-dilithioalkene (82) had been generated.



The results of reacting dibromide (86) with excess n-BuLi (2-12 equiv.), followed by quenching with methanol-OD (MeOD) are shown in Table 7. Since the M⁺ was not seen for alkene (89), and (M⁺-1) was of low intensity in the GC/MS spectrum, the deuterium content

calculated from the peaks due to the isotopomeric (M^+-1)'s was not reliable. However, the ratio of $d_0:d_1:d_2$ -(89), which was about 57:67:2, was estimated by comparing the area of fragmentation peaks (M^+-45 ((89)- CH_2OMe)). In all cases, the relative amount of isotopomers of alkene (89) was $d_0 = d_1 > d_2$. Contrariwise, the bromoalkene (88') and butylalkene (90') contained > 99% vinyl deuterium on the basis of GC/MS and NMR data.

Table 7. The relative yield of the products quenched by MeOD (from GC area ratio)

| Equiv. of n-BuLi | (88) | (89) | (90) |
|------------------|------|------|------|
| 2 | 90% | 6% | 4% |
| 4 | 83% | 12% | 5% |
| 12 | 78% | 16% | 6% |

Since n-BuLi may not have been strong enough to perform the second lithium-bromine exchange, t-BuLi was studied. As shown in Table 8, the yield of alkene (89) increased. From GC/MS data, the ratio of $d_0:d_1:d_2$ -(89) after MeOD quenching was about 18:62:18, with 6 equiv. of t-BuLi. The presence of t-butyl substituted product in the product mixture remains uncertain, since it has the same GC retention time as an impurity present in t-BuLi. These two compounds are separable only by the GC/MS single ion chromatography technique. However, as discussed below when the reaction was quenched with dimethyl disulfide (Me_2S_2), the t-butyl substituted alkene (93) was

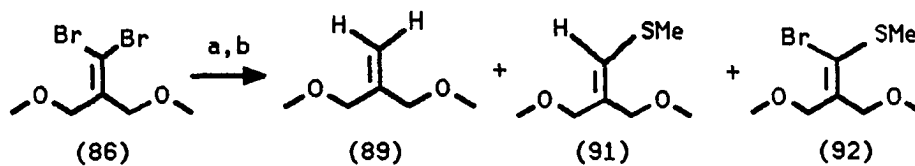
obtained.

Since the isotopomeric content of alkene (89) was not easily obtainable from GC/MS data, another trapping agent was used to examine the problem. Dimethyl disulfide is known as an excellent organolithium trap.

Table 8. The relative yield of the products quenched by MeOD (from GC area ratio)

| Equiv. of t-BuLi | (88) | (89) |
|------------------|------|------|
| 2 | 96% | 4% |
| 6 | 12% | 87% |

After the reaction mixture was quenched by Me₂S₂, five products were obtained as shown in Table 9. The relative amount of alkenes (89), (91) and (94) is (91) > (89) ≅ (94). This is consistent with the result from the MeOD quench. The formation of 3-methoxy-2-methoxymethyl-1,1-bis(methylthio)propene (94) suggested the presence of 1,1-dilithioalkene (82), but in a relatively small amount. Not excluded, however, is a sequential quenching/exchange/quenching process. Also, the formation of compound (93) attested to alkylation of carbenoid (87), perhaps via addition/elimination, by t-BuLi.



a: $t\text{-BuLi}$ / THF / -78°C

b: Me_2S_2

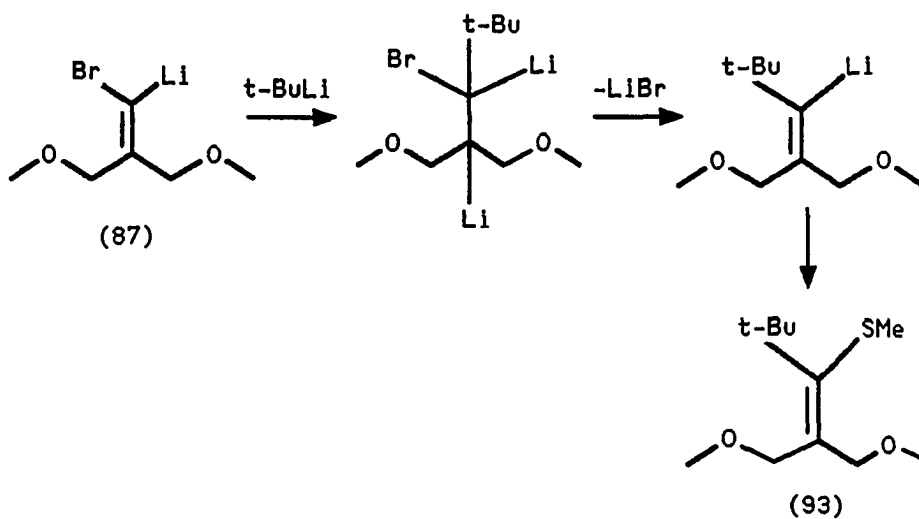
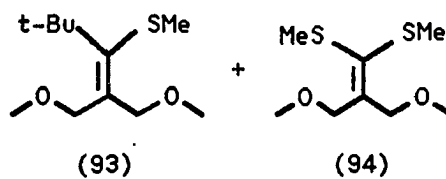


Table 9. The relative yield of the products quenched by Me_2S_2 (from NMR area ratio)

| Equiv. of $t\text{-BuLi}$ | (89) | (91) | (92) | (93) | (94) |
|---------------------------|------|------|------|------|------|
| 4 | 14% | 57% | 14% | 3% | 11% |
| 7 | 21% | 34% | 34% | 2% | 8% |

Reduction of carbenoid (87) by butyllithium The isotopomeric ratio of alkene (89) from carbenoid (87) must be explained. Although the reaction mixture was quenched with MeOD, d_0 - and d_1 -(89) were the major isotopomers of alkene (89) formed. Three possible explanations for the formation of d_0 - and d_1 -(89) are as follows:

(1) The MeOD contained MeOH or other proton sources.

(2) Proton abstraction from solvent or butyl bromide by the carbenoid (87).

(3) Hydride transfer from butyllithium to the carbenoid (87).

The first explanation can be easily ruled out by noting the formation of fully deuterated bromoalkene (88') and butylalkene (90'). If there had been any proton sources in the MeOD, bromoalkene (88') and butylalkene (90') should have contained some of the d_0 isotopomer. In addition, the Me_2S_2 quench gave alkene (89) and sulfide (91), but no bromide (88) and butylalkene (90). Therefore, the Me_2S_2 was not wet either.

The second explanation can be ruled out by the results with one equiv. of butyllithium. When one equiv. of butyllithium was reacted with the dibromide (86), followed by a MeOD quench, no alkene (89) or bromide (88) was detected, but rather only bromide (88'). The result suggests that the carbenoid (87) did not abstract a proton from the solvent or bromobutane.

The last explanation seems to be the most likely one. Since alkene (89) is obtained only when excess butyllithium is added, the mechanism must involve butyllithium. There are several reports

concerning the reducing ability of organolithium compounds.

Thioaldehydes can be reduced to thioethers by $n\text{-BuLi}$.¹³² Majewski¹³³ reported that lithium diisopropylamide could reduce aldehydes to the corresponding alcohols. The mechanism of the reduction is not firmly established.

The reaction can be rationalized by assuming that a mixed aggregate (dimer or tetramer) of butyllithium and the carbenoid exists in solution, as shown in Figure 11.

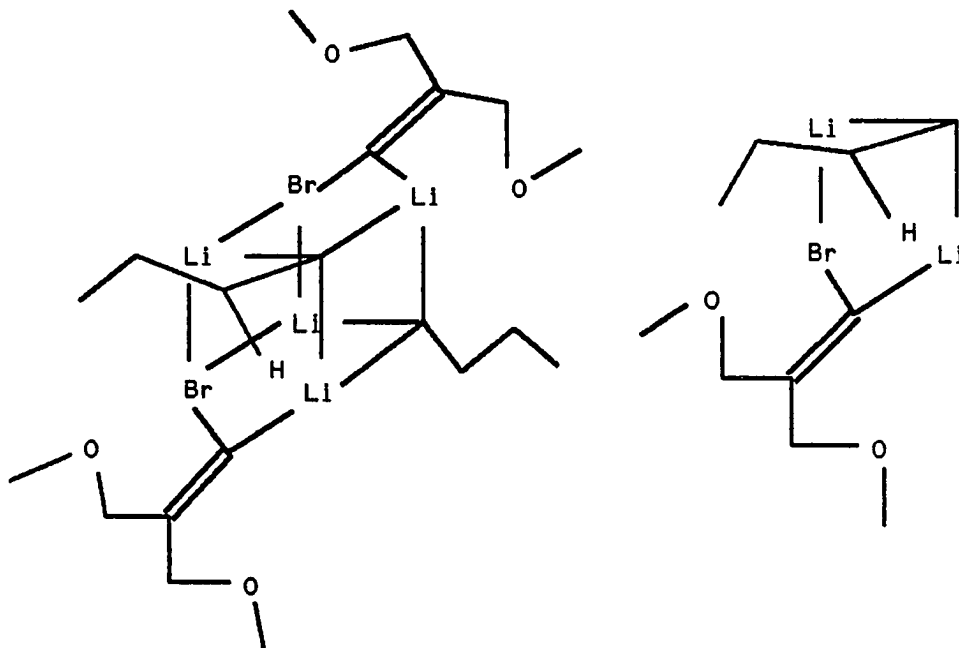
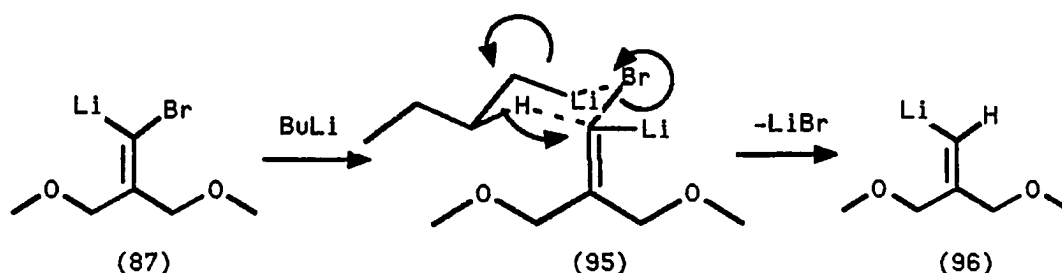


Figure 11. The mixed aggregates (tetramer and dimer) of carbenoid (87) and $n\text{-BuLi}$

The β -hydrogen of butyllithium may transfer to the carbenoid center via a six membered ring transition state (95) to give lithium (96), butene and LiBr . The formation of d_0 -(89) can be explained in

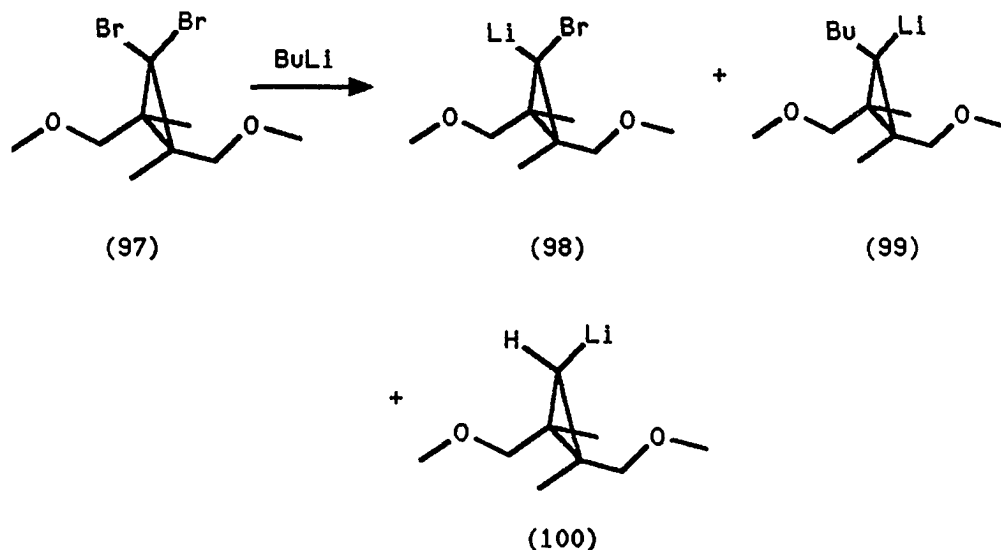
a different manner. Compound (96) acts as a base to abstract the β -hydrogen from butylbromide to provide d_0 -(89). When *t*-BuLi was used, most *t*-butylbromide would be consumed by reaction with *t*-BuLi, then less compound d_0 -(89) was resulted. This mechanism was confirmed by treating bromide (88) with 1 equiv. of *n*-BuLi, followed by a MeI quench, from which a 1:1 mixture of compound d_0 -(89) and 1-methoxy-2-methoxymethyl-2-butene was obtained.



As discussed herein, MeLi does not reduce the carbenoid (87). It may be due to the lack of any β -hydrogens in MeLi. In the mixed tetramer, it is clear that the α -hydrogen is too far away from the carbenoid center.

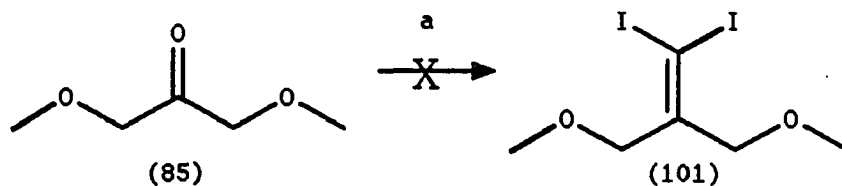
A similar result has been found previously by our group. In the effort of Warner, Chu and Brendel, reaction of 1,1-dibromo-2,3-bismethoxymethyl-2,3-dimethylcyclopropane (97) with excess butyllithium in THF gave a mixture of carbenoid (98), lithiobutylcyclopropane (99) and lithiocyclopropane (100). These were observed by ^{13}C NMR and also suggested by the quenching products. In addition, butene was observed in low temperature ^{13}C NMR analysis. In addition, a mixed aggregate between butyllithium and carbenoid (98) may have been observed by ^{13}C NMR. However, no

direct evidence for (95) or 1-butene was obtained in this case.



The preparation of 1,1-dilithioalkene (82) was then attempted via the method developed by Barluenga and coworkers.⁵⁴

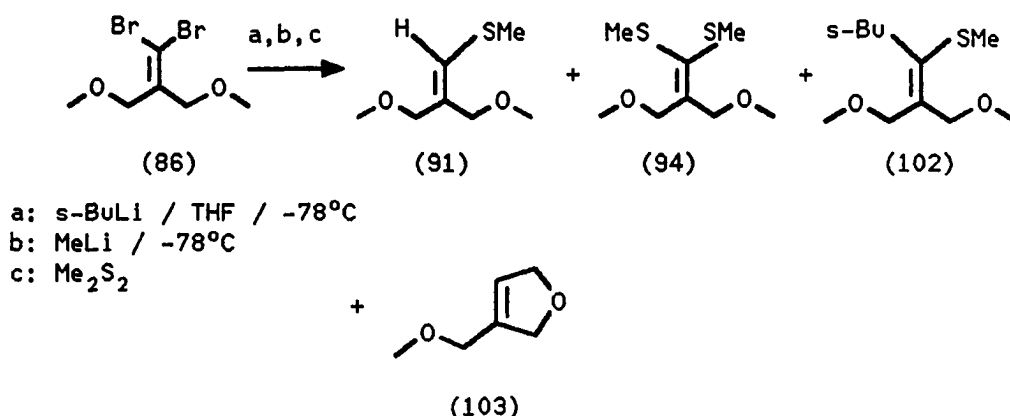
Unfortunately, 1,1-diiodo-3-methoxy-2-methoxymethylpropene (101) could not be prepared by the reaction of carbon tetraiodide and triphenylphosphine with (85).



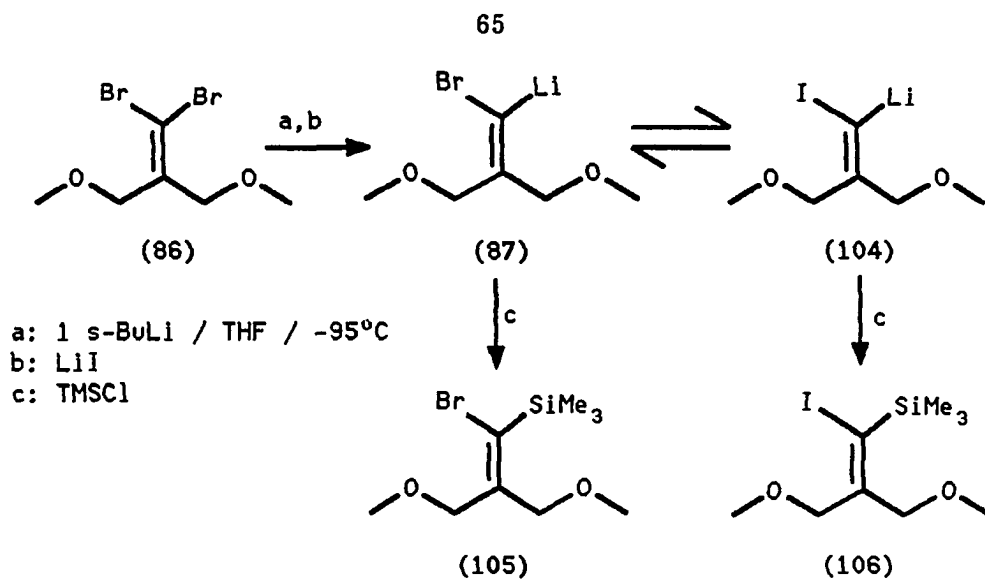
a: Cl_4 / PPh_3 / Ph \ddagger

As an alternative, the method⁵⁴ was applied to dibromide (86). Dibromide (86) was treated with 3 equiv. of *s*-BuLi in THF at -78°C , followed by the addition, after 30 min., of 3 equiv. of MeLi in ether. The solution was then quenched with Me_2S_2 . The product ratio of (91) to (94) was about 1:1. In comparison to the results in Table

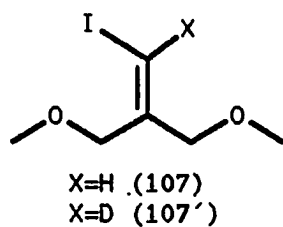
9, the proportion of (94) increased significantly. But, (94), possibly the product from the 1,1-dilithioalkene (82), was still not the major products. Instead, the butylated product (102) and the carbenoid insertion product, 3-methoxymethyl-2,5-dihydrofuran (103), were the major products. The formation of (103) can be attributed to the higher temperature reached in this case, as discussed below. Interestingly, no carbenoid quenching product (92) was obtained.



Since lithio-halovinylidenoids were known¹³⁴ to undergo halogen exchange with lithium halide, we hoped that lithio-iodocarbenoid (104) would be accessible via this approach. To test this idea, dibromide (86) was reacted with one equiv. of *s*-BuLi in THF at -95°C, followed by the addition of lithium iodide. The reaction mixture was quenched with trimethylsilyl chloride (TMSCl), which led to a mixture of 1-bromo-3-methoxy-2-methoxymethyl-1-trimethylsilylpropene (105) and 1-iodo-3-methoxy-2-methoxymethyl-1-trimethylsilylpropene (106) in a ratio of about 1:4. The bromine in carbenoid (87) obviously exchanged with iodide to give carbenoid (104), although the exchange was not complete.

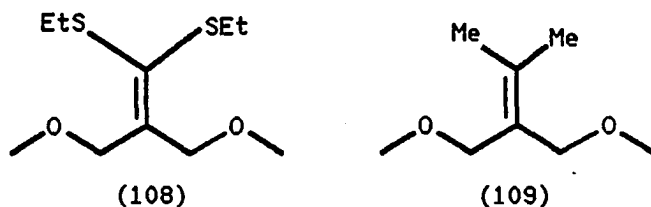


Next, dibromide (86) was treated with 1.1 equiv. of s-BuLi in the presence of 3 equiv. of lithium iodide at -78°C, followed by the addition of 3 equiv. of MeLi at -70°C. The reaction mixture was then quenched by either MeOD or Me₂S₂. In the Me₂S₂ case, the product contained only (94) and (103). When MeOD was used, the product contained (88'), 1-deutero-1-iodo-3-methoxy-2-methoxymethylpropene (107'), and (103).



Other quenching agents were also used, including methyl iodide, diethyl disulfide and TMSCl. Among these quenching agents, MeOD and TMSCl, which are "strong" electrophiles, provide a mixture of carbenoids quenching products ((88') and (107')); (105) and (106),

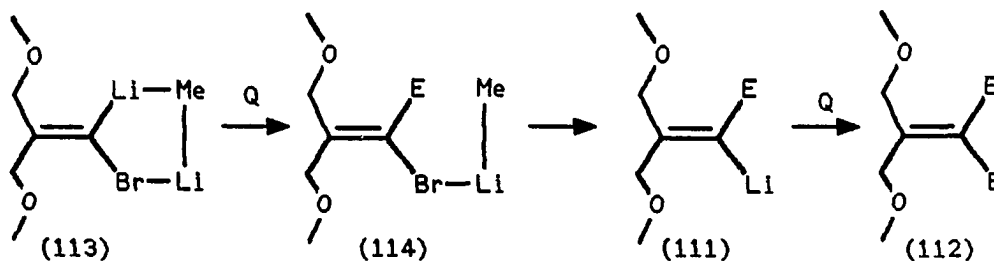
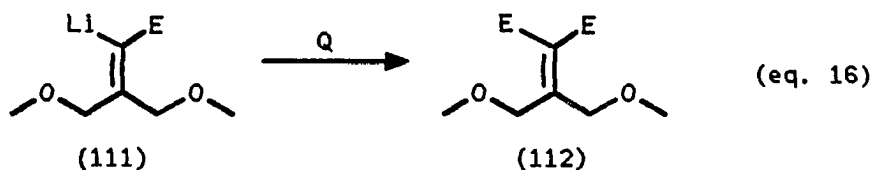
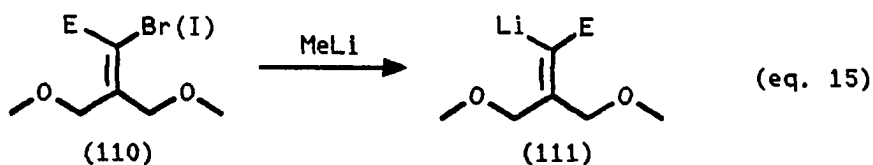
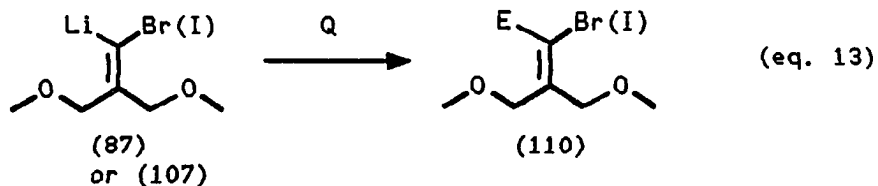
respectively) and (103). However, dimethyl disulfide, diethyl disulfide, and methyl iodide, which are "weak" electrophiles, lead to (94), (108), and (109), respectively, and also (103).



These contrasting results can be rationalized by assuming that a stepwise quenching process occurs with "weak" electrophiles. The reaction of those "weak" electrophiles with MeLi (eq. 14) is slower than the reaction of the first carbenoid quenching product (110) with MeLi (eq. 15). After compound (110) is formed (eq. 13), reaction to give compound (111) follows. Therefore, products equivalent to those expected from a dilithio derivative result. The "strong" electrophiles use up the excess MeLi without the occurrence of the reaction shown in (eq. 15). Stepwise quenching occurs with excess MeLi, but not with butyllithiums, since the reactivity of MeLi is lower than that of butyllithiums.

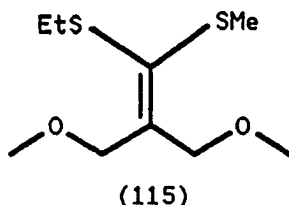
It is possible that formation of mixed aggregates of methyllithium and carbenoid (87), as shown in Figure 11, can account for the rapid second exchange. With "weak" electrophiles, carbenoid (87) gives (114), which undergoes intraaggregate lithiation to give (111). On the other hand, the "strong" electrophiles react with both the carbenoid (87) and the MeLi left in complex (113).

It has been claimed that dimethyl disulfide is a better lithium



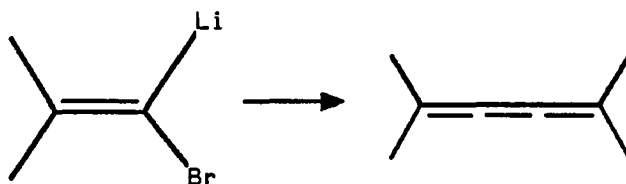
trap than TMSCl , but our results indicate the reverse. One possible explanation is that carbenoid (87) inserts into the S-S bond to give (94) directly. This explanation can be ruled out by the following control reaction. Under the same conditions, the reaction mixture was quenched with a 1:1 mixture of dimethyl disulfide and diethyl disulfide. The product mixture contained (94), (108) and 1-ethylthio-3-methoxy-2-methoxymethyl-1-methylthiopropene (115) in a ratio of about 1:1:2. The formation of (115) and the product ratio

point to stepwise quenching rather than insertion. Were insertion to have occurred, (94) and (108) are the only two expected products.



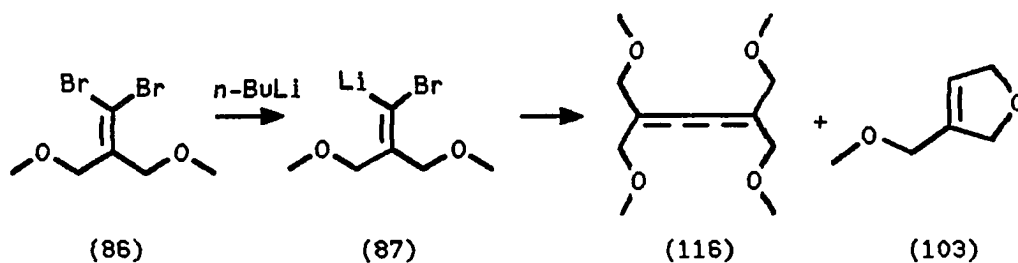
The Butatriene Route

Since the double lithium-bromine exchange did not provide any 1,1-dilithioalkene (82), other routes, similar to Maercker's strategy were attempted. Köbrich and coworkers prepared 1,1,4,4-tetramethyl-1,2,3-butatriene from the thermal dimerization of 1-bromo-1-lithio-2-methylpropene.



Similarly, treatment of a solution of dibromide (86) in THF with 1 equiv. of *n*-BuLi at -95°C , followed by warming to higher temperature, gave insertion product¹³⁵ (103) and dimerization product (116) (1,6-dimethoxy-2,5-bismethoxymethyl-2,3,4-hexatriene), from the intermediate carbenoid (87).

The relative amounts of (116) and (103) depended on the temperature at which the reaction was performed, as shown in Table 10. The results show that the yields of both (116) and (103) increased with increasing reaction temperature. When the temperature



went to or above -60°C , the amount of (103) increased significantly, but that of (116) did not. The best way to produce (116) was to run the reaction at -80°C for 2 hours, although (103) was still not completely eliminated.

Table 10. Relative amounts of (88), (103) and (116) in the product mixture from quenching of carbenoid (87)

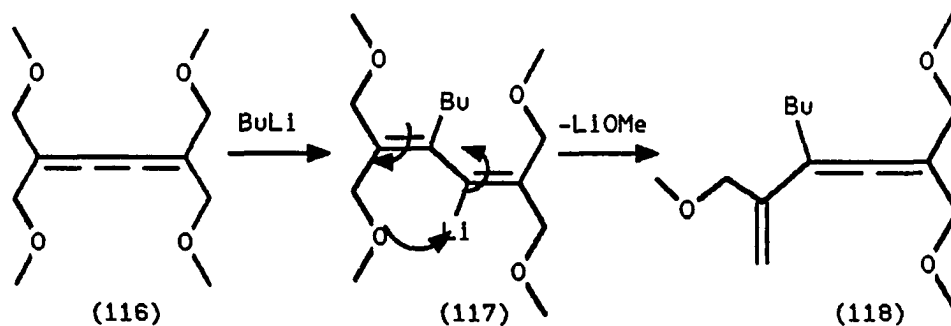
| Temp. ($^\circ\text{C}$) | (88) | (103) | (116) |
|----------------------------|------|-------|-------|
| -80 | 97% | 1% | 2% |
| -70 | 76% | 6% | 18% |
| -60 | 38% | 35% | 27% |
| -50 | 14% | 51% | 27% |
| -40 | 9% | 59% | 31% |

The amount of $n\text{-BuLi}$ used in the reaction was also very critical. If more than 1 equiv. of $n\text{-BuLi}$ was added, a secondary product from (116) was obtained. The product was assigned as allene (118) on the basis of MS and ^1H NMR analysis. A mechanism for the formation of (118) is outlined in Scheme 3. Addition of $n\text{-BuLi}$ to the cumulene system is known.^{2,136} Addition of $n\text{-BuLi}$ at the center

bond of (116) would provide (117). Elimination of lithium methoxide, perhaps via a six-membered ring transition state, would give the product (118). Because, the maximum yield of (116) was less than 50%, a small molar excess of n-BuLi is sufficient to largely convert (116) to (118).

Treatment of (116) with lithium metal under a variety of conditions did not produce the 1,1-dilithioalkene (82). Irrespective of the form of lithium (wire, dispersion, powder), solvent (ether, THF), temperature (room temperature, reflux), presence or absence of mercury (II) chloride or an ultrasonic bath or time (few minutes, few days) employed, (116) either did not react or decomposed. It should be noted that (116) decomposed after a few days in the freezer.

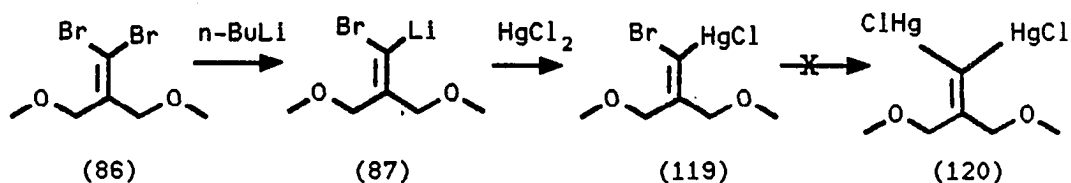
Scheme 3.



The Lithium-mercury Exchange Route

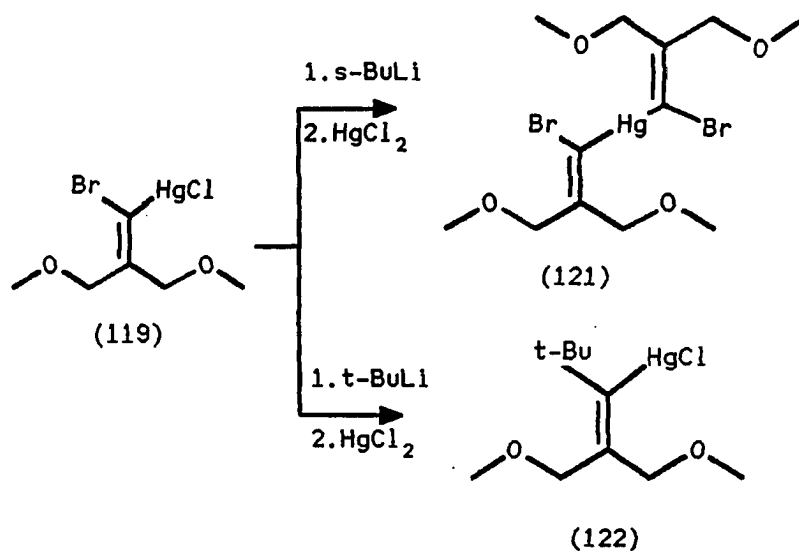
The preparation of 1,1-dimercuroalkene (120) was first tried via a short-cut. Treatment of the dibromide (86) with n-BuLi in THF, followed by quenching with mercury (II) chloride, led to

1-bromo-1-chloromercurio-3-methoxy-2-methoxymethylpropene (119) in good yield (75%). Compound (119) was apparently derived by reaction of carbenoid (87) with mercury (II) chloride. The high-resolution mass spectrum showed that the product also contained some amount of 1-bromo-1-bromomercurio-3-methoxy-2-methoxymethylpropene, although the ^1H and ^{13}C NMR spectra did not serve to distinguish the bromo and chloromercurials. The spectra revealed only two different methylene and two different methyl proton and carbon resonances. The proton methylene resonances appear at δ 4.20 ($J_{\text{H-Hg}} = 20$ Hz) and δ 4.08 ($J_{\text{H-Hg}} = 40$ Hz).

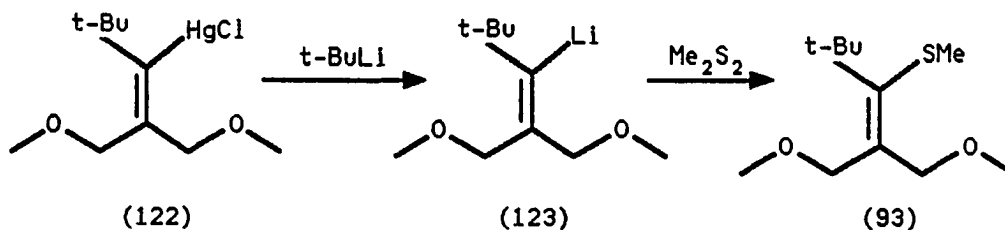


Interestingly, reactions of (119) with *s*-BuLi or *t*-BuLi, respectively, produced different products. When (119) was treated with *s*-BuLi, followed by quenching with mercury (II) chloride, dimer (121) was produced. When (119) was treated with *t*-BuLi, followed by quenching with mercury (II) chloride, *t*-butyl substituted alkene (122) was obtained. The reason for these different results is unclear, but may relate to the different aggregation states of the various butyllithiums, or the different base strengths of the lithium reagents employed. Another possibility is that *t*-BuLi reacts with (119) via an SET mechanism, whereas *s*-BuLi does not.

The mass spectrum of (121) showed an envelop of ions due to the

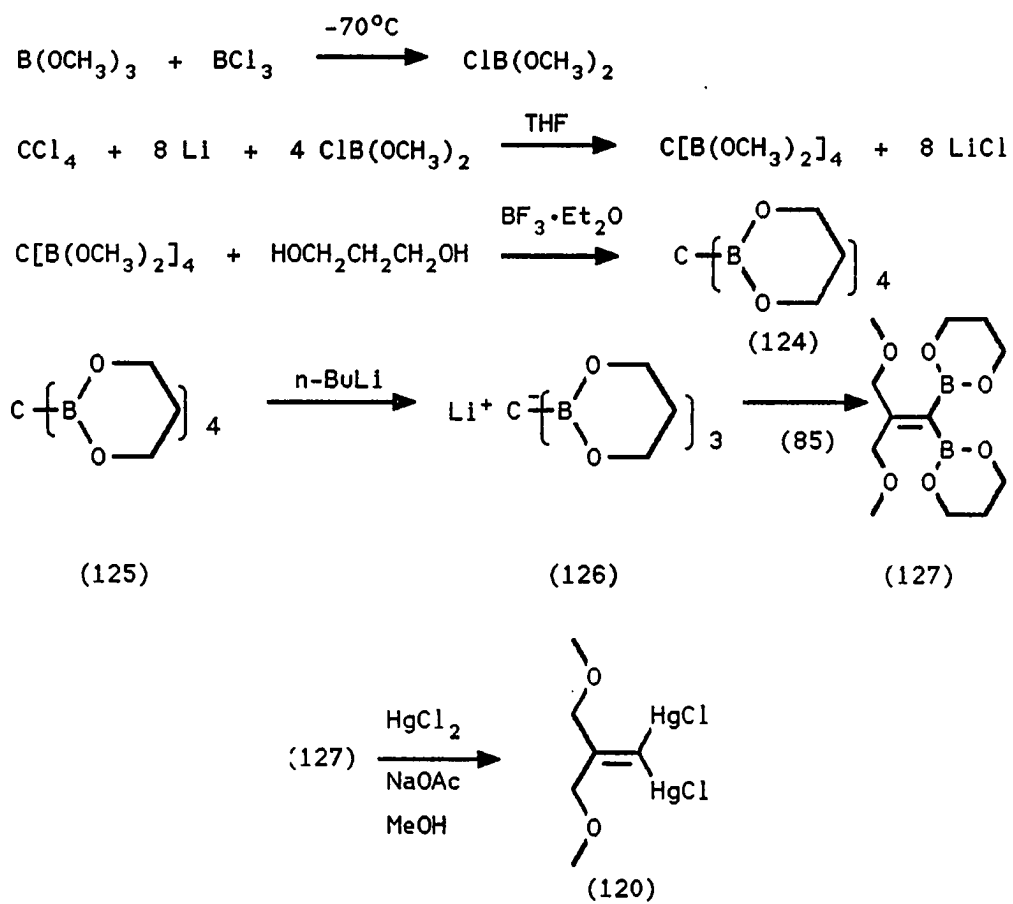


isotopes of mercury and bromine atoms around m/e 588, which is the molecular weight of dimer (121) (^{202}Hg , ^{79}Br). In the ^1H NMR spectrum of (121), two types of methylene hydrogens appear at δ 4.24 and 4.10 ppm. The latter resonance has a 22 Hz H-Hg coupling constant. The mass spectrum of (122) showed an envelop of ions around m/e 408 (^{202}Hg , ^{35}Cl). The ^1H NMR spectrum of (122) showed two kinds of methylene resonances at δ 4.07 ($J_{\text{H-Hg}} = 17$ Hz) and δ 3.97 ($J_{\text{H-Hg}} = 39$ Hz). When t-BuLi was added to (122) in THF at 0°C , followed by quenching with dimethyl disulfide, (93) was obtained as the sole product. The reaction consisted of lithium-mercury exchange to the vinyl lithium (123), which was trapped by Me_2S_2 to give (93).



Since this "short-cut" did not lead to the desired product (120), the original synthetic pathway¹³⁷ was then followed. The synthesis is outlined in Scheme 4. Reaction of trimethyl borate with boron trichloride at -70°C yielded dimethoxyboron chloride. This was added to a mixture of lithium, carbon tetrachloride and trimethyl borate to give octamethylmethanetetra boronate.^{137a} A ligand exchange reaction provided tetrakis(trimethylenedioxyboryl)methane, which reacted with n-BuLi to yield lithium tris(trimethylenedioxyboryl)methide.^{137b} Reaction of ketone (85) with lithium tris(trimethylenedioxyboryl)methide led to (127). Without further purification, (127) was converted to (120) by reaction with mercury chloride and sodium acetate in aqueous methanol.^{137c} Compound (120) was characterized by high-resolution MS, ¹H and ¹³C NMR. The resonance of the methylene protons appears at δ 3.93 ($J_{H-Hg} = 34$ Hz). Unfortunately, (120) did not dissolve in ether or THF. A suspension of (120) and lithium metal in ether remained unchanged even after a few days. Further efforts with the dibromo or diiodo analogs of (120) might prove fruitful.

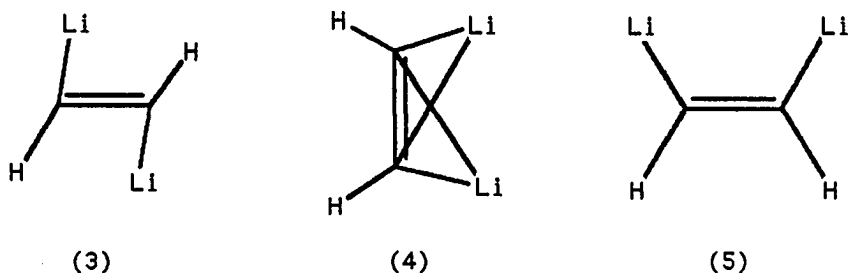
Scheme 4.



1,2-DILITHIOALKENES

Background

Ab initio calculations^{41,42} on 1,2-dilithioethylenes indicated that the partially bridged trans isomer (3) was 1.6 KCal mol⁻¹ more stable than the doubly bridged cis isomer (4). In addition, the classical cis-nonbridged isomer (5), which was confirmed to be a transition-state structure, was some 20 KCal mol⁻¹ higher in energy than the cis-bridged isomer (4).



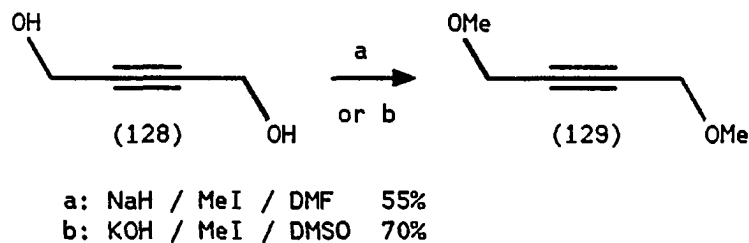
Maercker and Dujardin⁶⁸ were able to synthesize trans-1,2-dilithioethylene derivatives from the reduction of alkyne with lithium metal. Unfortunately, the solubility of those dilithium compounds were so low that solution NMR spectra could not be obtained. They also prepared a 1,2-dilithioethylene from lithium mercury exchange on the corresponding 1,2-bis(chloromercuro)ethylene with *t*-butyllithium.⁶⁶ The same lack of solubility prevented any NMR study. Recently, Fiet and coworkers⁸⁰ prepared α,β -dilithiocinnamitriles by treating cis- or trans-cinnamotrile with an excess of LDA but they did not report any structural studies.

Our approach is to introduce intramolecular chelating groups to increase the solubility of organolithium compounds in organic

solvents. An ether chain, which is known to increase the stability, solubility and deaggregation of organolithium compounds, was our first candidate. Crown ethers are known to be highly effective at solvating metal ions. Thus a polyether chain might be employed advantageously for intramolecular chelation. A series of alkoxyalkynes were synthesized to test this hypothesis.

Synthesis

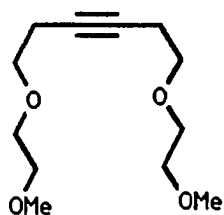
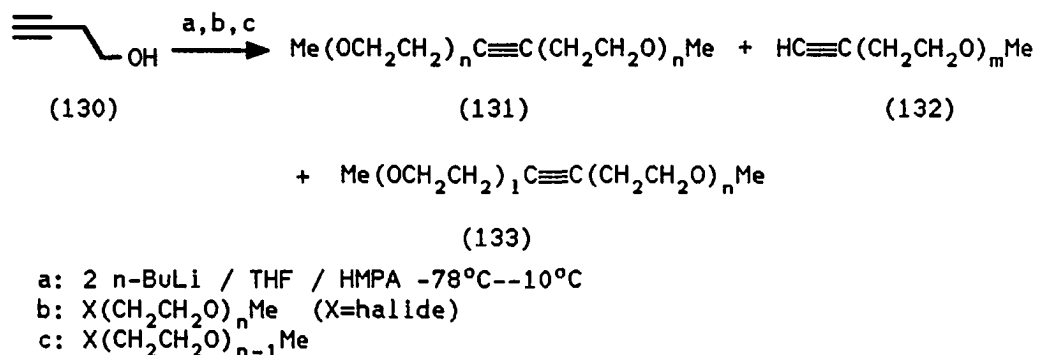
The first alkoxyalkyne, 1,4-dimethoxybut-2-yne (129), was prepared by the following method. Etherization of but-2-yn-1,4-diol (128) with methyl iodide and sodium hydride in dimethyl formate (DMF) gave (129) in 55% yield. A better yield, 70%, was obtained by treatment of (128) with methyl iodide and potassium hydroxide in dimethyl sulfoxide (DMSO).



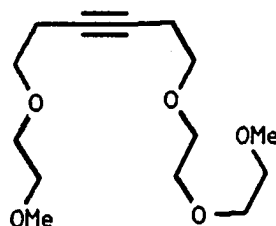
Other alkoxyalkynes in the series were prepared by the approach as shown in Scheme 5.¹³⁸ For example, treatment of a THF solution of but-1-yn-4-ol (130) with 2 equiv. of *n*-BuLi in the presence of HMPA was followed by addition of 2-bromoethyl methyl ether. After the reaction mixture was left at room temperature overnight, methyl iodide was added to yield three products: 1,6-dimethoxy-3-hexyne ((131), *n* = 1) (20% yield), 4-(2-methoxyethoxy)-1-butyne ((132), *m* =

2) (10% yield) and 6-methoxy-1-(2-methoxyethoxy)-3-hexyne ((133), $l = 2$, $n = 1$) (8% yield). Other alkoxyalkynes, such as 1,6-bis(2-methoxyethoxy)-3-hexyne (134) (19% yield) and 6-(2-methoxyethoxy)-1-(2-(2-methoxyethoxy)ethoxy)-3-hexyne (135) (6% yield) were similarly prepared beginning with the appropriate haloether. Finally, the synthesis of 1,6-bis(2-(2-methoxyethoxy)ethoxy)-3-hexyne ((131), $n = 3$) was unsuccessful.

Scheme 5.

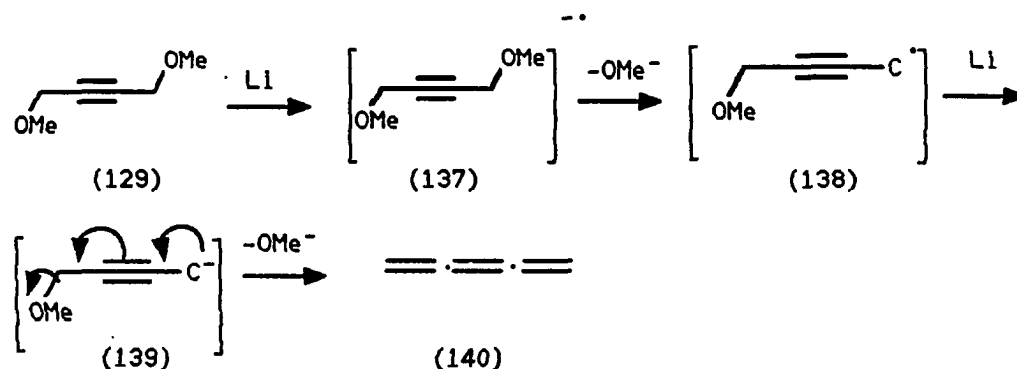


(134)

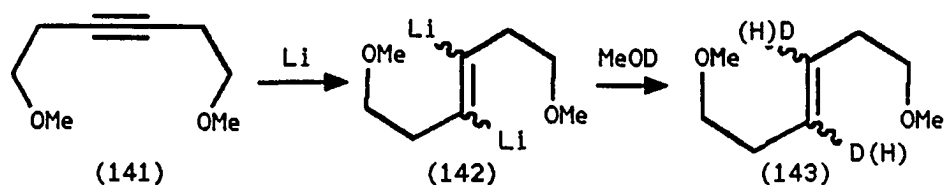


(135)

The variety of products may be explained by assuming the formation of dianion (136) is formed in the presence of HMPA at temperature above -10°C . Since the alkynide anion is more



1,6-dimethoxy-2-hexene (143). Two stereoisomers, presumably the E/Z pair, were observed by GC in 50:1 ratio. The major isomer was assigned as the E (trans) isomer on the basis of the work by Maercker and Dujardin.⁶⁸ Since the molecular ion of (143) was not observable from GC/MS, the deuterium content was calculated on the basis of a GC/MS/CI analysis. The ratio of $d_0:d_1:d_2$ for the major isomer of (143) was about 25:16:59. In the broadband decoupled ^{13}C NMR spectrum of (143), the vinyl carbon bearing deuterium showed a triplet at δ 127 ppm with a 28 Hz C-D coupling. In addition, the vinyl carbon bearing hydrogen showed a singlet at δ 128 ppm. Therefore, the quenching result suggests that 1,2-dilithioalkene (142) may have been one of the intermediates.



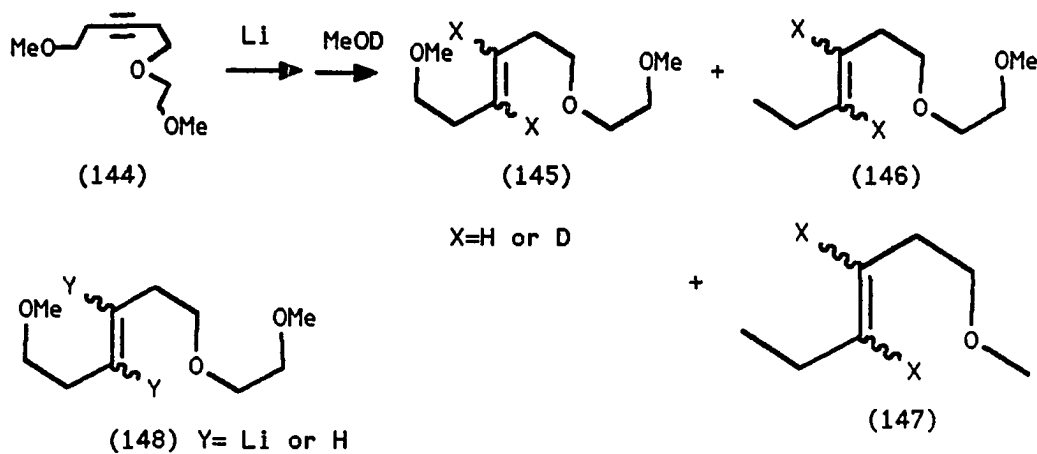
The reaction was then run in a sealed NMR tube and followed by NMR. The ^{13}C and ^1H NMR signals broadened, and the lock was lost

after six hours due to the formation of a lot of solid. The dilithioalkene (142) was a solid, as demonstrated by the following experiment. After the reaction was complete, the mixture was filtered through a filter funnel under argon. The filtrate, the residue in the reaction flask and the residue in the filter funnel were separately quenched by MeOD. Reduced alkene (143) was the major component in the product from all three. According to the GC/MS data, no d_2 -(143) was found in the filtrate, but rather only d_0 -(143) was obtained. However, d_2 -(143) was the major component of the product from the material in the funnel and the reaction flask. This indicated that (142) was a solid which did not pass through the filter.

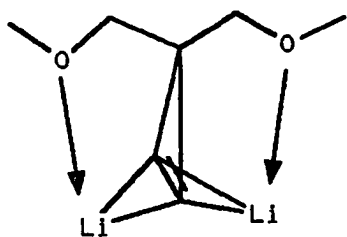
The reaction with lithium was faster in THF solution. The reaction remained incomplete after 3 days in ether, but it was over within five hours in THF. A similar filtering experiment showed that the 1,2-dilithioalkene (142) was also insoluble in THF. An attempt to dissolve (142) in TMEDA led to ether cleavage products. It is known that ether cleavage by lithium occurs more readily in polar solvents.¹³⁹

Interestingly, when 6-methoxy-1-(2-methoxyethoxy)-3-hexyne (144) was treated with lithium in ether, followed by a MeOD quench, more d_2 -(145) was observed. The ratio of $d_0:d_1:d_2$ was about 8:12:79 on the basis of GC/MS/CI data. The result suggests that more ether groups may increase the yield of the dilithioalkene (148). However, the big drawback was that the ether cleavage reaction was also

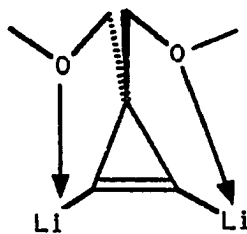
promoted. Two ether cleavage products (146) and (147) were obtained along with (145). Moreover, the lithio-intermediate (148) was a solid ether, so no solution NMR experiment could be performed. In the cases of higher alkoxyalkynes, both alkynes (134) and (135) gave not only more d_2 -alkene, but also more products similar to (146) and (147) from ether cleavage.



Although the 1,2-dilithioalkenes produced did not dissolve in organic solvents, the study showed that intramolecular chelating groups promote the lithiation of alkynes.



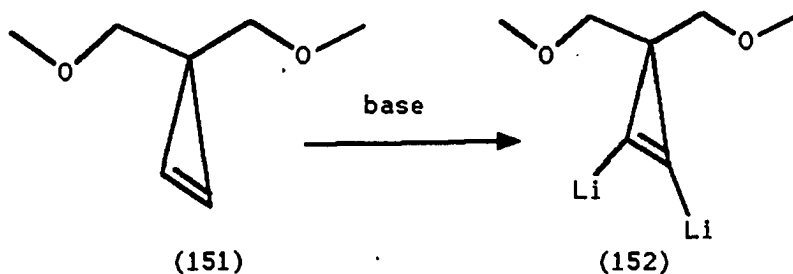
(149)



(150)

Synthesis

Our first approach involved the generation of 3,3-bismethoxymethylcyclopropene (151), followed by the lithiation of (151) by base to produce 1,2-dilithio-3,3-bismethoxymethylcyclopropene (152).



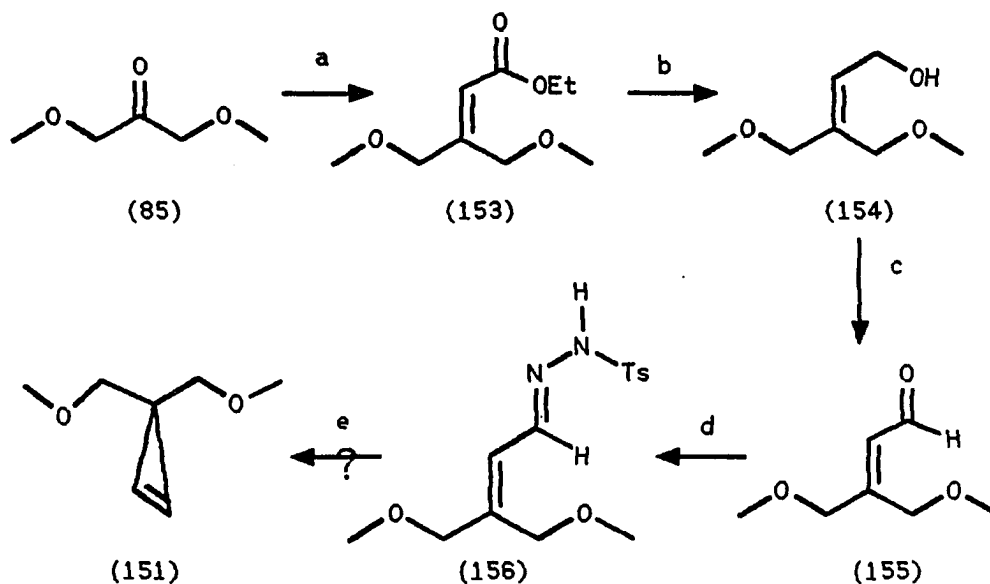
(151)

(152)

The failed attempt to prepare (151) via intramolecular allylidene insertion¹⁴⁰ is outlined in Scheme 6. The problem seemed to be that purification of (151) required distillation, and the temperature (> 200°C) required was so high that decomposition or polymerization occurred before collection.

An alternate approach was then used, based on prior work by Baird and coworkers, who reported a series of papers concerning reactions of methyllithium with 1,1,2-trihalocyclopropanes.¹⁴¹ Reaction of 1,1,2-tribromo-3,3-dimethylcyclopropane (157) with two

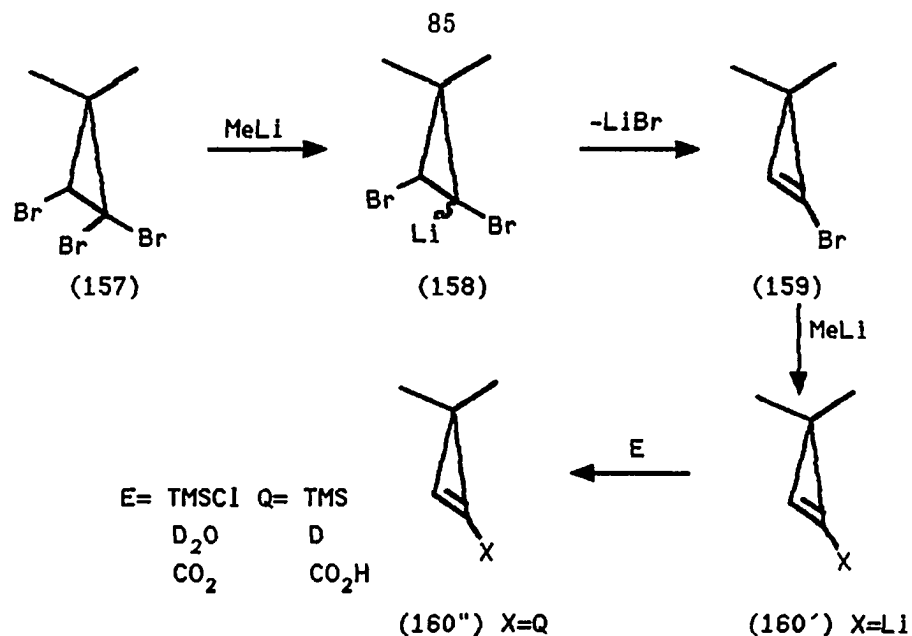
Scheme 6.



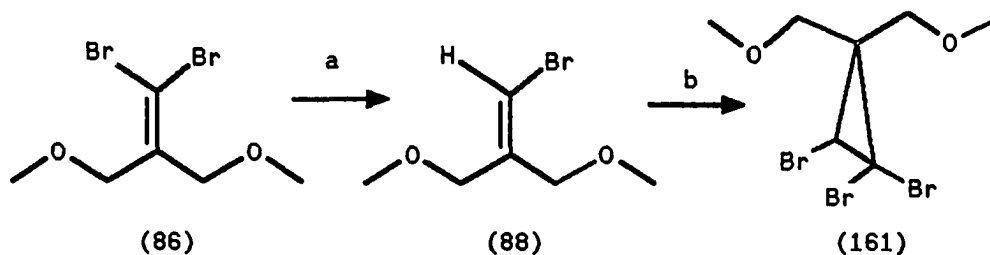
a: $(\text{EtO}_2\text{C})\text{C}=\text{P}(\text{OEt})_2$
 b: DIBAL
 c: PCC
 d: TsNH_2NH_2
 e: Δ/MeONa

equiv. of MeLi was reported to give 1-lithio-3,3-dimethylcyclopropene (160') in moderate yield. The presumed reaction course involves formation of the carbenoid (158) by lithium-bromine exchange, followed by the elimination of lithium bromide to give 1-bromo-3,3-dimethylcyclopropene (159). A second lithium-bromine exchange with excess MeLi produces (160'), which was trapped by TMSCl, D_2O or CO_2 .

By changing the methyl groups to methoxymethyls, we were able to prepare 1,2-dilithio-3,3-bismethoxymethylcyclopropene (152) from the reaction of 1,1,2-tribromo-3,3-bismethoxymethylcyclopropane (161) with excess MeLi at low temperature. The synthesis of (161) was



effected as follows. Reduction of the dibromide (86) with one equiv. of tributyltin hydride afforded bromide (88) in 70% yield.¹⁴² Phase transfer dibromocarbene cyclopropanation of bromide (88) with bromoform using cetrinide as catalyst yielded tribromide (161) in 12% yield.¹⁴³

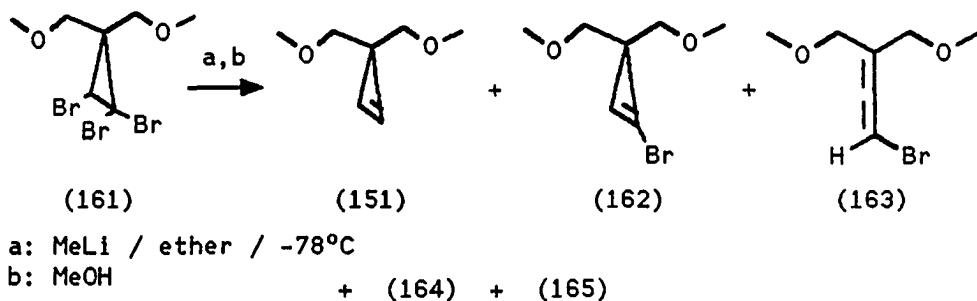


a: $n\text{-Bu}_3\text{SnH} / 0^\circ\text{C}$
 b: $\text{CHBr}_3 / 50\% \text{ NaOH}_{(\text{aq})} / \text{cetrinide}$

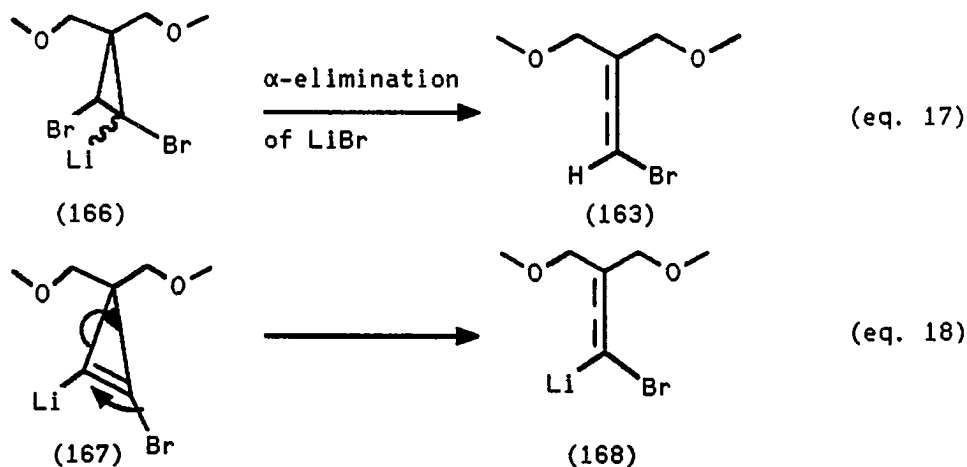
Reaction Of Tribromide (161) With 1 Equiv. Of MeLi

Treatment of tribromide (88) with 1 equiv. of MeLi in ether at -60°C followed by a methanol quench gave a mixture of (151), 1-bromo-3,3-bismethoxymethylcyclopropene (162),

1-bromo-4-methoxy-3-methoxymethyl-1,2-butadiene (163) and two unidentified isomers, (164) and (165).



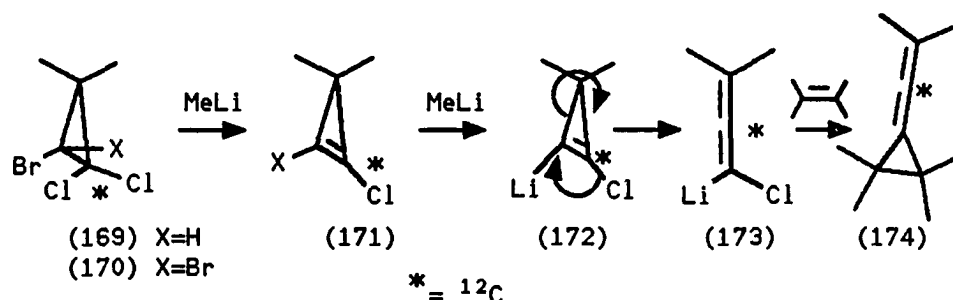
Two possible mechanisms could lead to bromoallene (163). They are ring-opening of carbenoid (166) (eq. 17), and rearrangement of 1-bromo-2-lithio-3,3-bismethoxymethylcyclopropene (167) (eq. 18).



According to the study by Baird and coworkers,^{141a} reaction of 1-bromo-2,2-dichloro-3,3-dimethylcyclopropane (169) or 1,1-dibromo-2,2-dichloro-3,3-dimethylcyclopropane (170) with excess MeLi led to 3-methyl-1,2-butadienylidene (173) by the rearrangement of 1-chloro-2-lithio-3,3-dimethylcyclopropene (172). The mechanism was

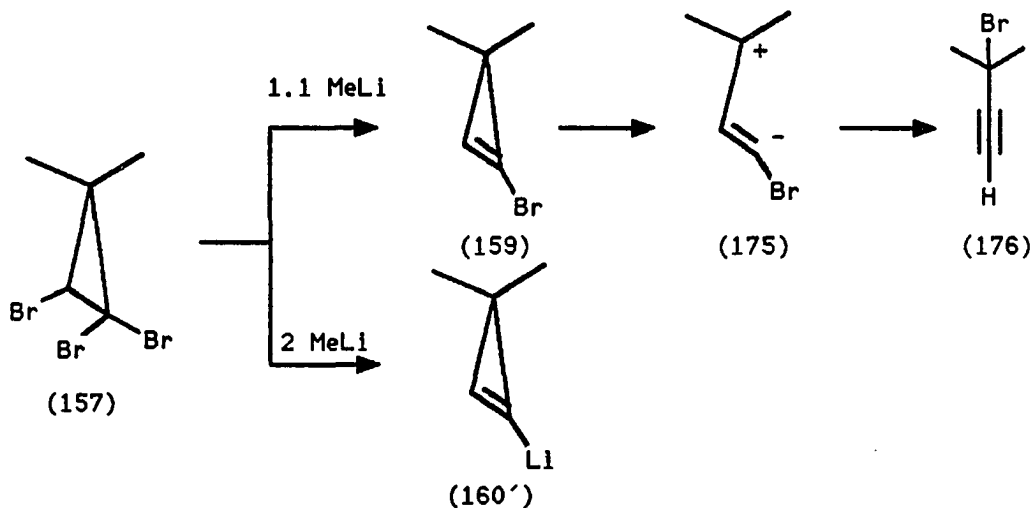
supported by a ^{12}C labelling experiment, as shown in Scheme 7.^{141b} When the carbon bearing chlorine atoms was labelled, the labelled carbon ended up on the center carbon of the allenylidene adduct (174).

Scheme 7.



However, reaction of tribromide (157) with a slight excess of MeLi in ether at -40°C led to 3-bromo-3-methyl-1-butyne (176).¹⁴⁴ The bromocyclopropene (159) was shown to be converted to (176) in polar solvents, for example, DMSO at room temperature. Thus, a polar intermediate (175) was proposed. Interestingly, when (157) was treated with 2 equiv. of MeLi starting at -78°C and ending at 20°C ,^{141a} the major product was not the propargylic bromide (176) but rather the lithiocyclopropene (160'), which is the lithium bromine exchange product. Formation of (160') was confirmed by trapping with several electrophiles, as mentioned above. Since the lithium bromine exchange is faster than the lithium hydrogen exchange, the second equiv. of MeLi gave (160') instead of 1-lithio-2-bromo-3,3-dimethylcyclopropene (which could rearrange to

the allenylidene).



In the case of (166), we were concerned that the presence of the ether groups might stabilize it, and promote the ring opening. Several experiments were performed to test this concern, and the results are shown in Table 11. Reaction of tribromide (161) with less than 1 equiv. of MeLi afforded the bromocyclopropene (162) as the sole product. It was essential to use a slightly more than one equiv. of MeLi to obtain bromoallene (163). This result ruled out the carbenoid ring opening mechanism, because that mechanism required formation of (163) independent of the amount of MeLi. Therefore, (163) must be a secondary product from (162).

Quenching of the reaction mixture with MeOD gave both deuterated (162) and (163), according to GC/MS/CI data. This supported the rearrangement of lithiocyclopropene (167) to (168). Since the rearrangement is slow at -75°C , both (167) and (168) were trapped by

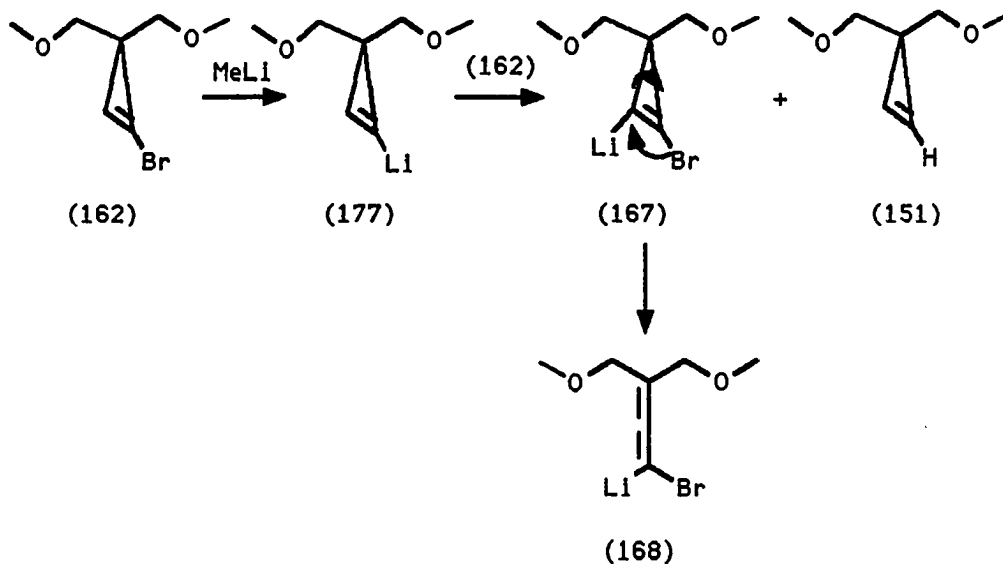
Table 11. The relative yields of products from the reaction of tribromide (161) with MeLi

| Temp.(°C) | MeLi(eq.) | (151) | (162) | (163) | (164) | (165) |
|-----------|-----------|-------|-------|-------|-------|-------|
| -60 | 1.2 | 10% | 47% | 14% | 24% | 5% |
| -75 | 1.2 | 3% | 86% | 3% | 3% | 5% |
| -75 | 0.6 | --a | 100% | --a | --a | --a |

^aNot detectable.

MeOD. In addition to those two products, d_0 and d_1 cyclopropene (151) was observed by GC/MS.

The result indicated that the lithium-hydrogen exchange process might have been faster than the lithium-bromine exchange. This is in contrast to the finding of Baird. However, as discussed below, when tribromide (161) was reacted with 2 equiv. of MeLi, all of bromocyclopropene (162) was converted to the lithiocyclopropene (177), contrary to the expectation of transformation of (162) to (168). An explanation may be as follows. The excess MeLi does, in fact, react with bromocyclopropene (162) to give lithiocyclopropene (177) via lithium-halogen exchange. When there is only a small excess of MeLi present, the (177) formed has the chance to deprotonate (162) to give (167) and (151), of which the former rearranges to (168).



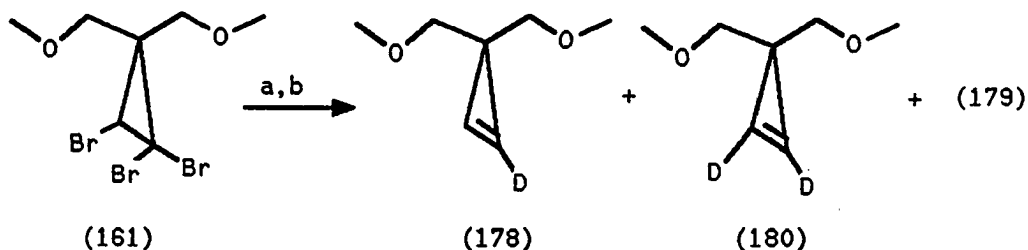
Reaction of Tribromide (161) with 2 Equiv. of MeLi

Treatment of tribromide (161) with 2 equiv. of MeLi in THF at -100°C for 30 minutes, followed by a MeOD quench, led to a mixture containing bromocyclopropene (162) and unreacted tribromide (88). The lithiocyclopropene (177), together with a volatile product, can be generated by warming the solution from -100°C to -30°C . Compound (177) was trapped by MeOD to give 1-deutero-3,3-bismethoxymethylcyclopropene (178). The volatile product was characterized as 3-methoxymethylbut-3-enyne (179) by ^1H NMR and MS. A reasonable route leading to (179) is the elimination of lithium methoxide from (177) as shown in Scheme 8. This type of elimination appears to be very common in this system. For example, lithiodiene (117) undergoes a similar elimination to give (118), as discussed earlier in this thesis.

Reaction of Tribromide (161) with More Than 2 Equiv. of MeLi

Formation of 1,2-dilithio-3,3-bismethoxymethylcyclopropene

Treatment of tribromide (161) with excess MeLi (5-10 equiv.) in THF from -100°C to -30°C , followed by a MeOD quench, produced a mixture of (178) and (180) in the ratio of 40:60 on the basis of GC/MS/CI data; enyne (179) was also formed. The molecular ion of cyclopropene (151) was not observed under our GC/MS conditions, so the ratio of (178) to (180) was estimated from GC/MS/CI data. Unfortunately, even when the reaction was kept at -30°C for 15 hours, the proportion of (180) did not increase significantly.

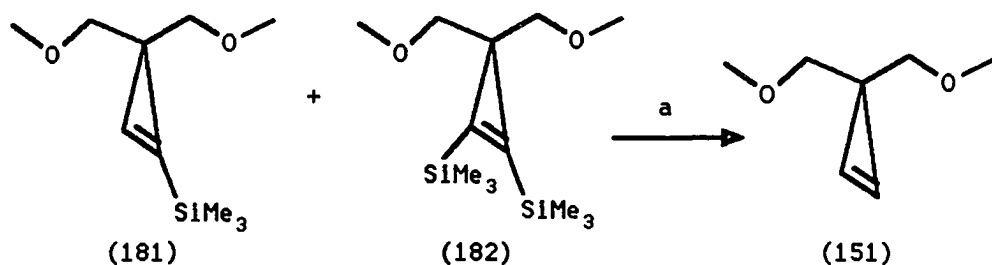


a: xs' MeLi
b: MeOD

Since the deuterium content of cyclopropene (151) (i.e., (157):(178):(180)) could not be determined easily by mass spectroscopy, trimethylsilyl chloride was used to quench the reaction. Two products, 3,3-bismethoxymethyl-1-trimethylsilylcyclopropene (181) and 3,3-bismethoxymethyl-1,2-bistrimethylsilylcyclopropene (182) were obtained. The structures were confirmed by reaction of each with potassium fluoride/crown ether in acetonitrile to give 3,3-bismethoxymethylcyclopropene (151).¹⁴⁵ The ratio of (181) to

(182) varied from 1:1 mixture to 100% (182) depending on the rate of addition of TMSCl. Slower addition gave more (182). This indicated that stepwise quenching was likely involved, even though TMSCl is known to be an excellent organolithium quenching agent.

Nevertheless, as discussed later, the 1,2-dilithiocyclopropene (152) was observed by low temperature NMR. Therefore, some of the 1,2-disubstituted cyclopropene did derive from (152).

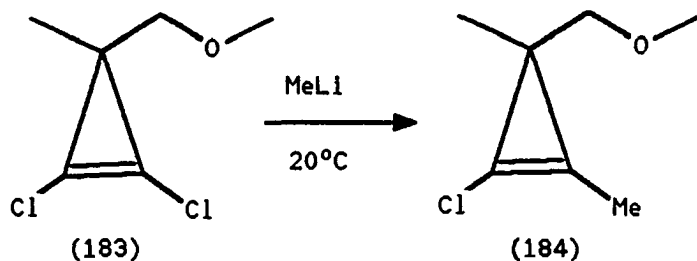


a: KF/ CH₃CN / 18-C-6 / r.t.

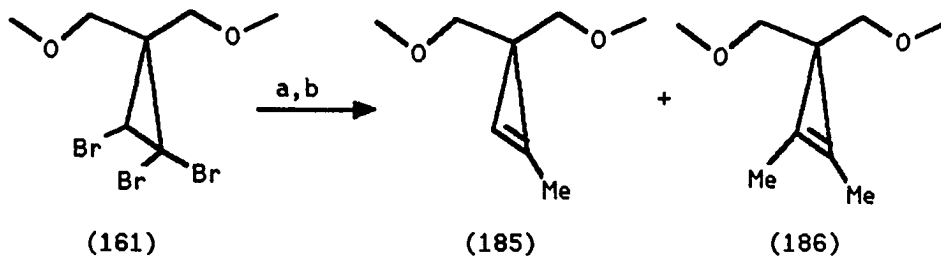
Addition of MeLi to cyclopropenes

Several additions of organometallic compounds to cyclopropenes have been reported. Grignard reagents¹⁴⁶ and organoboranes¹⁴⁷ add to the double bond of cyclopropenes to give cis adducts in good yield. Stoll and Negishi¹⁴⁸ reported that cyclopropenes would react with DIBAH, allylzinc bromide and n-PrCu·MgBr₂ to give the corresponding cyclopropane via cis addition. However, the addition reactions of cyclopropenes with organolithiums are very slow and proceed in low yield, although with high cis stereoselectivity.¹⁴⁹ Magid and Welch^{149a} reported the addition of phenyllithium to cyclopropene to give 2-phenylcyclopropyllithium in only 3% yield but with >99%

(Z)-stereochemistry. Baird and Al-Dulayymi^{141c} reported that the addition of MeLi to the dichlorocyclopropene (183), with subsequent elimination of lithium chloride, gave 1-chloro-2-methylcyclopropene (184) at room temperature. When the methoxy group was replaced by chlorine, no addition reaction of cyclopropene occurred.



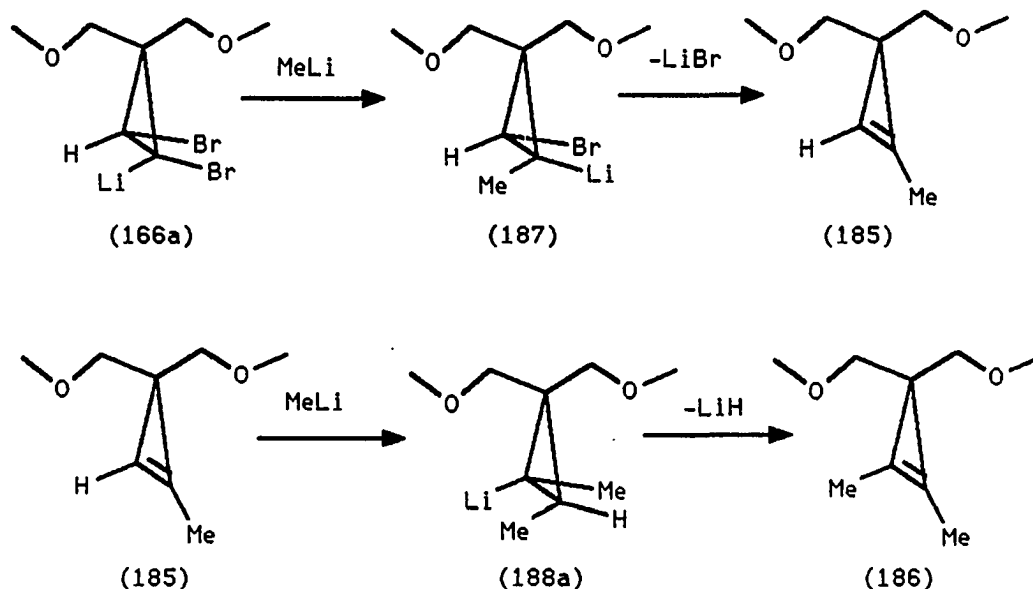
Treatment of tribromide (161) with excess MeLi (2-5 equiv.) above -20°C , followed by a methanol quench, led to two products, 3,3-bismethoxymethyl-1-methylcyclopropene (185) and 3,3-bismethoxymethyl-1,2-dimethylcyclopropene (186).



a: xs^r MeLi
b: MeOH

Several possible mechanisms for the formation of methylated products (185) and (186) are outlined below. First of all, the stereoisomer of carbenoid (166) expected to be formed first (166a) may rapidly react with MeLi to give 1-bromo-2-lithio-3,3-bismethoxymethyl-2-methylcyclopropane (187).

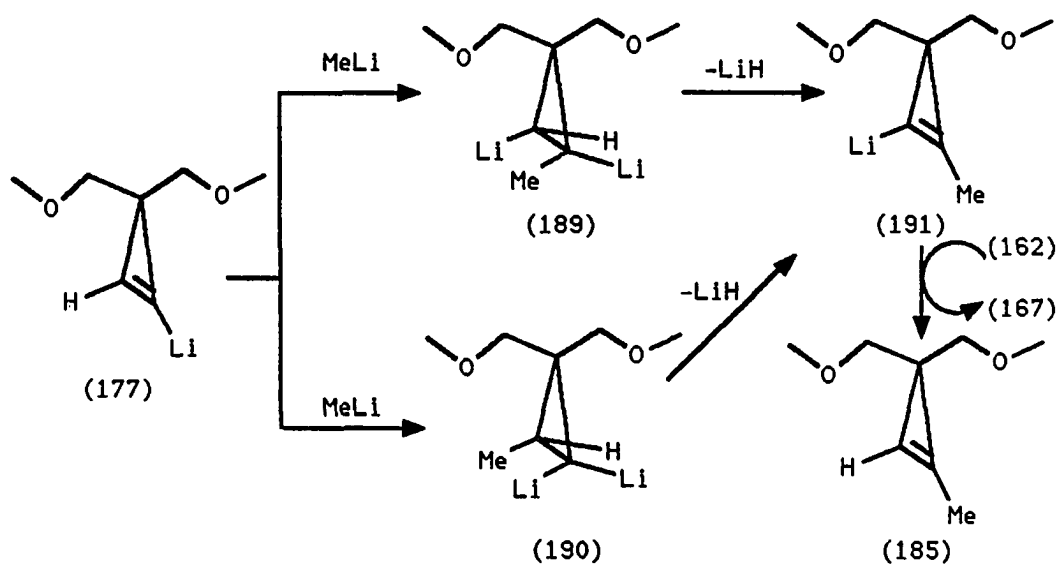
This corresponds to a standard carbenoid alkylation. Subsequent cis elimination of lithium bromide would give (185). Cis addition of MeLi to (185) could provide (188a), which could lose lithium hydride to give (186). This last step, however, requires a disfavored trans elimination.



A problem with this mechanism is that it requires that alkylation of (166a) be more rapid than isomerization to its epimer, (166b), and subsequent loss of LiBr to give bromocyclopropene (162). Indeed, when (162), formed by treatment of tribromide (161) with less than one equiv. of MeLi at -20°C , was reacted with two more equiv. of MeLi at -20°C , methylcyclopropenes (185) and (186) were produced. The first mechanism is ruled out by this observation.

A second possibility is that lithiocyclopropene (177) may be the methylcyclopropene precursor. The cis addition of MeLi to (177) may lead to two products, (189) and (190). Addition reactions of

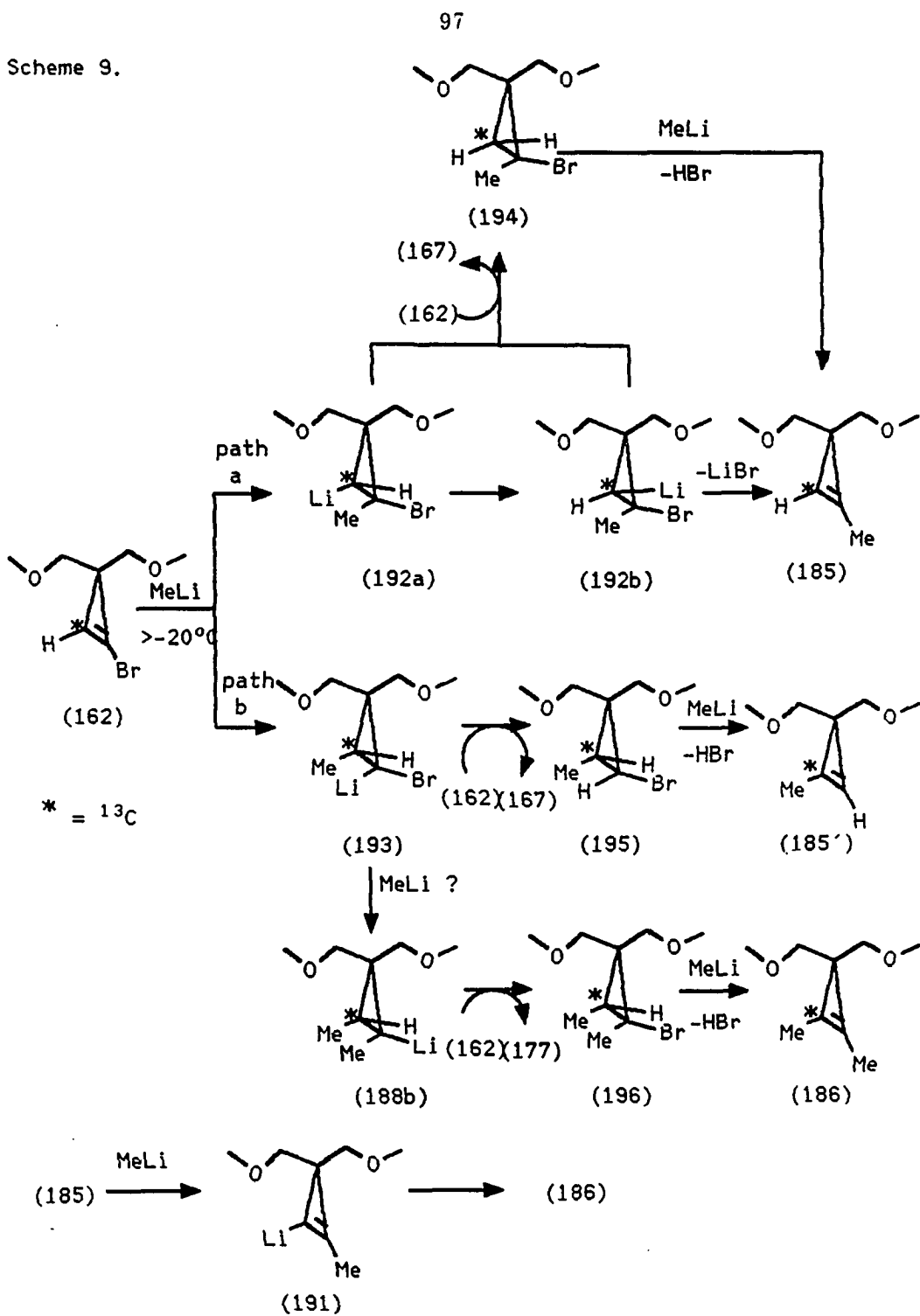
organolithiums to cyclopropenes normally occur with highly regioselectivity, such that the more stable anion is formed. If so, (190) may not form. 1,2-Dilithiocyclopropane (189) might lose lithium hydride via cis elimination to yield (191). Elimination of lithium hydride from (190), were it formed, would also lead to (191). From (191), one could envision reaction with (162) to give (185) and (167), or with either MeBr or MeLi to eventually give (186).



As a test, lithiocyclopropene (177) was generated below -40°C from the reaction of tribromide (161) with 3 equiv. of MeLi, after which the solution was allowed to warm to room temperature. Even at room temperature, however, compound (177) did not react further with MeLi, a finding which ruled out this mechanism.

A third possibility is that MeLi added directly to bromocyclopropene (162). As shown in Scheme 9, cis addition of MeLi to the double bond can give two possible adducts, (192a) and (193).

Scheme 9.



Although (193) looks to be the more stable adduct, the polarization of the double bond of (162) might actually favor addition to (192a) as the kinetic product, as discussed below. Whatever the case, compound (192a) would probably be configurationally labile at $>-20^{\circ}\text{C}$, and equilibration with (192b) should occur, where from cis elimination of LiBr would afford (185). Another route to (185) involves protonation of (192) by (162) to give (194) and (167). Simple base-promoted (MeLi) elimination of HBr from (194) would give (185). The fate of (167), which would surely isomerize to (168), is unknown and undetected. Carbenoid (193) might be rapidly protonated by (162) to afford (195) and (167). Subsequent elimination of HBr from (195) would again give (185), but now with a different labelling pattern (vide infra). Although allene formation from (193a) was not observed (direct synthesis of (193) is in progress), which is understandable, alkylation by MeLi would give (188b). Since (188b) is a tertiary alkyl lithium, it might undergo lithium-halogen exchange with (162) to give (196) and (177); indeed, some (151) was also observed in this reaction, and (177) would give (151). Loss of HBr from (196) would provide (186).

Another route to (186), currently being subjected to direct testing, is the further reaction of (185) with MeLi. Proton abstraction would give (191), which could react in $\text{S}_{\text{N}}2$ fashion with MeBr generated in the first step.

To test whether or not the methyl group in (185) was scrambled between the two vinylic positions, the following labelling experiment

was performed.

1,1,2-Tribromo-3,3-bismethoxymethyl-2- ^{13}C -cyclopropane ($^{13}\text{C}_2$ -(161)) was synthesized, as discussed below. Treatment of this compound with one equiv. of MeLi in d_8 -THF gave 1-bromo-3,3-bismethoxymethyl-2- ^{13}C -cyclopropane ($^{13}\text{C}_2$ -(162)), which was observed by ^{13}C NMR (enhancement of the peak at δ 114.6 ppm, as shown in Table 12).

Addition of two more equiv. of MeLi at -20°C , followed by a methanol quench, afforded two identifiable products, namely (185) and (186), each labelled. The ^{13}C NMR spectrum of the product mixture showed enhanced peaks at δ 106 (d, $J_{\text{C-H}} = 225$ Hz); 113 (s) and 124 (s) ppm, which were assigned as the ^{13}C -labelled carbon of methylated cyclopropenes $^{13}\text{C}_2$ -(185), ^{13}C -(186), and $^{13}\text{C}_1$ -(185), respectively, as shown in Figure 12.

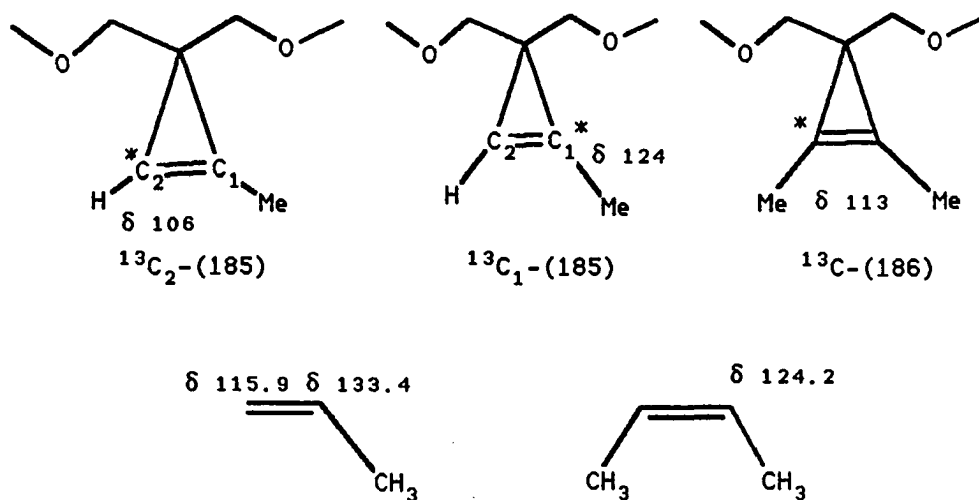
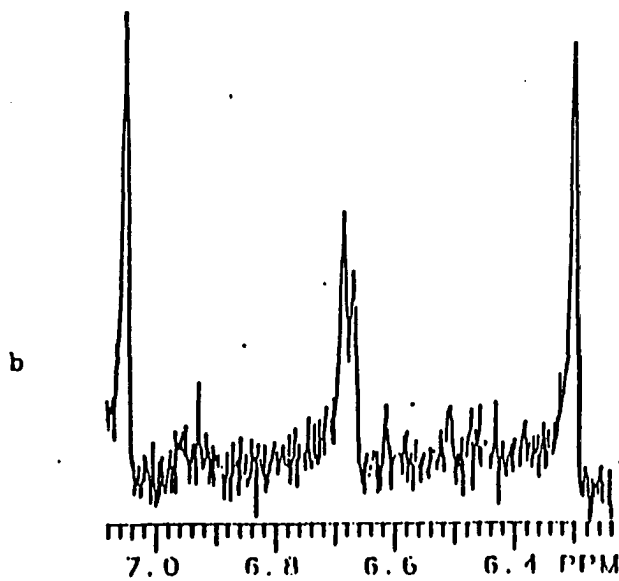
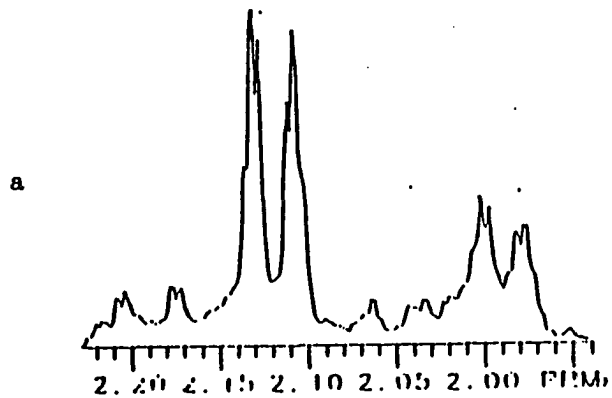


Figure 12. ^{13}C NMR resonances for methylated cyclopropenes (185) and (186)

The assignment of the δ 113 ppm peak to (186) and the δ 124 ppm peak to $^{13}\text{C}_1$ -(185) was made on the basis that the vinylic carbon of 1,2-disubstituted alkenes is normally upfield from the substituted carbon of monosubstituted alkenes. For example, in propene, the chemical shift of C_1 is 115.9 ppm, while that of C_2 is 133.4 ppm; in (Z)-2-butene, the vinyl carbon resonates at δ 124.2 ppm. These observations were substantiated by the ^1H NMR spectrum of the crude product. Centered around δ 6.7 ppm were two doublets with $J = 225$ Hz and $J = 5$ Hz, as shown in Figure 13. The former doublet is due to $^{13}\text{C}_2$ -(185), and its intensity indicates it is about twice as prevalent as $^{13}\text{C}_1$ -(185), which gives rise to the latter doublet. It is possible that (193) was formed in preference to (192a), but that it gave rise to less (185) than did (192a). The structural assignments were further confirmed by the ^1H NMR resonances of the methyl region, where two pairs of doublets were observed, as shown in Figure 13. In the case shown, (185) predominated over (186), but the proportion of (186) increased with increased amounts of MeLi used to effect the reaction. In the case of ^{13}C -(186), the hydrogens of Me_1 have a $^2J(^{13}\text{C}-^1\text{H})$ coupling with $^{13}\text{C}_1$, and the hydrogens of Me_2 have a $^3J(^{13}\text{C}-^1\text{H})$ coupling with $^{13}\text{C}_1$. Thus two doublets were expected, and were observed to be split by about the same amount (6.0, 6.3 Hz). There appears to be a slight (1.5 Hz) chemical shift difference between the Me groups due to the ^{13}C label. A similar coupling and chemical shift pattern was observed for the Me resonances of $^{13}\text{C}_1$ -(185) and $^{13}\text{C}_2$ -(185).



- a- Methyl proton resonances.
b- Cyclopropenyl proton resonances.

Figure 13. The methyl and cyclopropenyl proton resonances of a mixture of methylated cyclopropenes ^{13}C -(185) and (186)

One doublet is derived from ${}^3J({}^{13}\text{C}-{}^1\text{H})$ in ${}^{13}\text{C}_1$ -(185) and the other doublet from ${}^2J({}^{13}\text{C}-{}^1\text{H})$ in ${}^{13}\text{C}_2$ -(185). The observed ${}^{13}\text{C}$ scrambling indicated that the addition reaction of MeLi to (162) was not regiospecific.

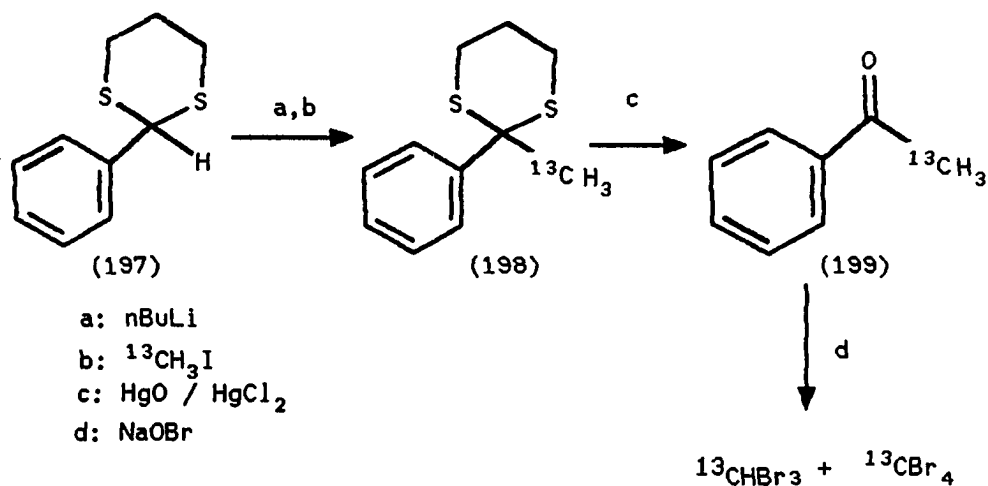
${}^{13}\text{C}$ NMR Studies of 1-Lithiocyclopropene (177) and
1,2-Dilithiocyclopropene (152)

Synthesis of labelled materials

The quenching result from the reaction of tribromide (161) with MeLi suggested that 1-lithiocyclopropene (177) and 1,2-dilithiocyclopropene (152) were intermediates. Since an attempt to observe these organolithium compounds by ${}^{13}\text{C}$ NMR using unlabelled material failed, ${}^{13}\text{C}$ -labelled tribromide (161) was prepared as follows.

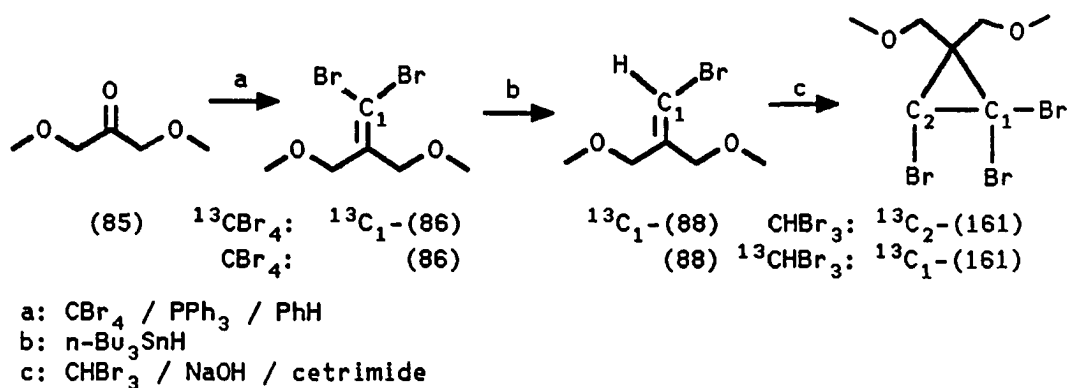
${}^{13}\text{C}$ -Labelled carbon tetrabromide and bromoform were prepared via the Siegel and Seebach method.¹⁵⁰ Methylation of lithiated 2-phenyl-1,3-dithiane (197) with ${}^{13}\text{C}$ -methyl iodide yielded 2-(${}^{13}\text{C}$ -methyl)-2-phenyl-1,3-dithiane (198). Hydrolysis of (198) with mercuric (II) chloride led to ${}^{13}\text{C}$ -methyl phenyl ketone (199). The haloform reaction on (199) gave either ${}^{13}\text{C}$ -carbon tetrabromide or ${}^{13}\text{C}$ -bromoform, depending on the reaction conditions. When the acetophenone was added to the NaOBr solution and a longer reaction time was used, carbon tetrabromide was obtained. However, inverse addition of a NaOBr solution to acetophenone, with cooling, afforded bromoform as the major product.

Utilizing either ${}^{13}\text{C}$ -carbon tetrabromide or ${}^{13}\text{C}$ -bromoform led to



1,1,2-tribromo-3,3-bismethoxymethyl-2- ^{13}C -cyclopropane ($^{13}\text{C}_2$ -(161))
 or 1,1,2-tribromo-3,3-bismethoxymethyl-1- ^{13}C -cyclopropane
 ($^{13}\text{C}_1$ -(161)), respectively, as shown in Scheme 10.

Scheme 10.



The ^{13}C -tribromide (^{13}C -(161)) was added to various amounts of MeLi in d₈-THF solution at -100°C, after which the solution was warmed up to -30°C for 1 hour. The solution was transferred to

either a 5 mm or 8 mm NMR tube through a two way needle, and was subjected to low temperature NMR observation. When less than 5 equiv. of MeLi was used, after quenching with MeOD or D₂O, the product contained only the monodeuterated cyclopropene ¹³C-(178). When more than 10 equiv. of MeLi was used, D₂O quenching gave a mixture of deuterio- and dideuterocyclopropene (¹³C-(178) and ¹³C-(180), respectively). Therefore, the major new signals in the low temperature NMR spectra prior to quenching are the resonances of the 1-lithio- and/or the 1,2-dilithiocyclopropene (¹³C-(177) and ¹³C-(152), respectively).

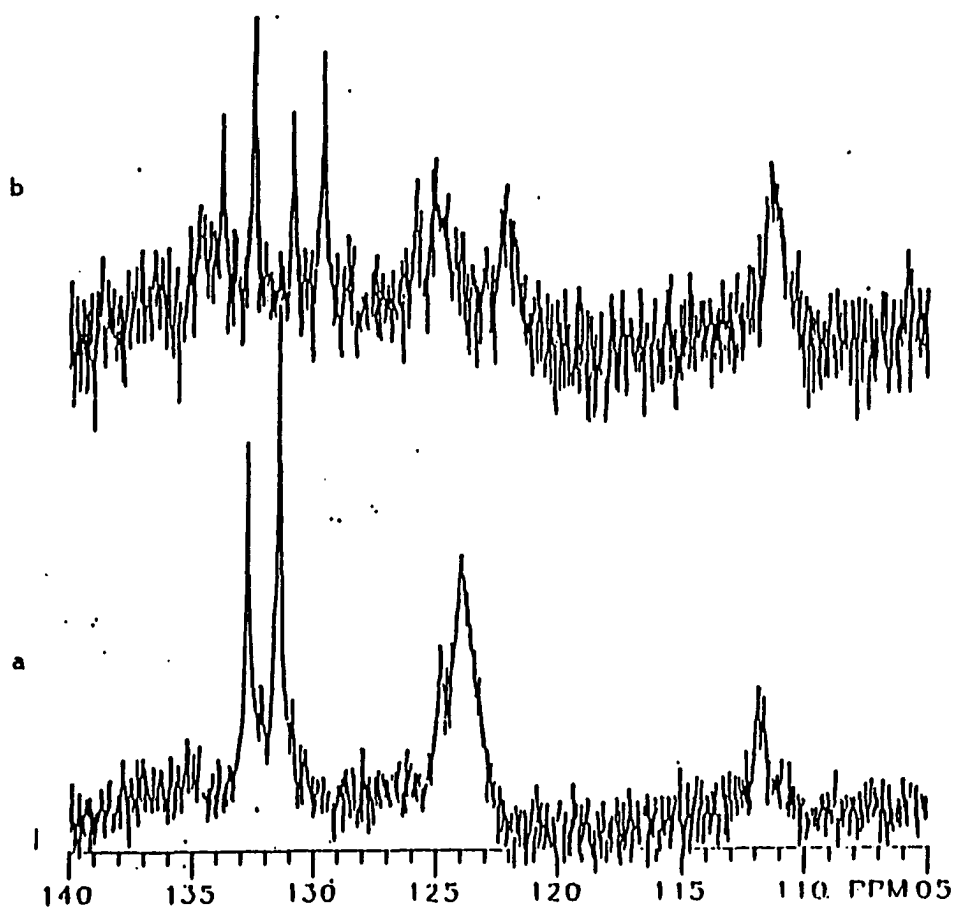
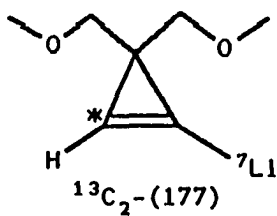
¹³C NMR of 1-lithio-3,3-bismethoxymethylcyclopropene (177)

When ¹³C₂-(161) was reacted with excess Me⁷Li in d₈-THF, 1-lithiocyclopropene (¹³C₂-(177)) was presumably formed. The resulting ¹³C NMR spectra are shown in Figure 14. Two peaks appeared at δ 131.4 and 132.7 ppm in the proton decoupled spectrum below -70°C. In the ¹H-coupled spectrum, each became a doublet (J = 216 Hz) due to the C-H coupling, which is in the expected range for a cyclopropene (210-230 Hz). They were thus both assigned to C₂ of ¹³C₂-(177). These signals indicated the presence of at least two different stereoisomers or aggregates of (177) in THF solution, and were consistent with results to be described later. Two other broad signals (δ 124 and 110 ppm) were also recorded. The former signal split into a doublet in the absence of proton decoupling, but the coupling constant, although in the range of 210-230 Hz, could not be precisely measured due to the ⁷Li coupling-induced signal breadth;

the latter signal did not split when the decoupler was turned off, meaning that it was not due to a carbon bearing a hydrogen. These results showed the presence of five different species (counting the shoulder to low field of the δ 124 peak), of which the three major ones were coupled to a single proton, as required for ($^{13}\text{C}_2$ -(177)) (the shoulder at ca. δ 125 ppm appears to also be coupled to one proton). While structure assignments are deferred until after the description of the following labelling experiments, it is noteworthy that the δ 124 peak appears to be due to a cyclopropenic carbon bearing both a proton and a lithium atom.

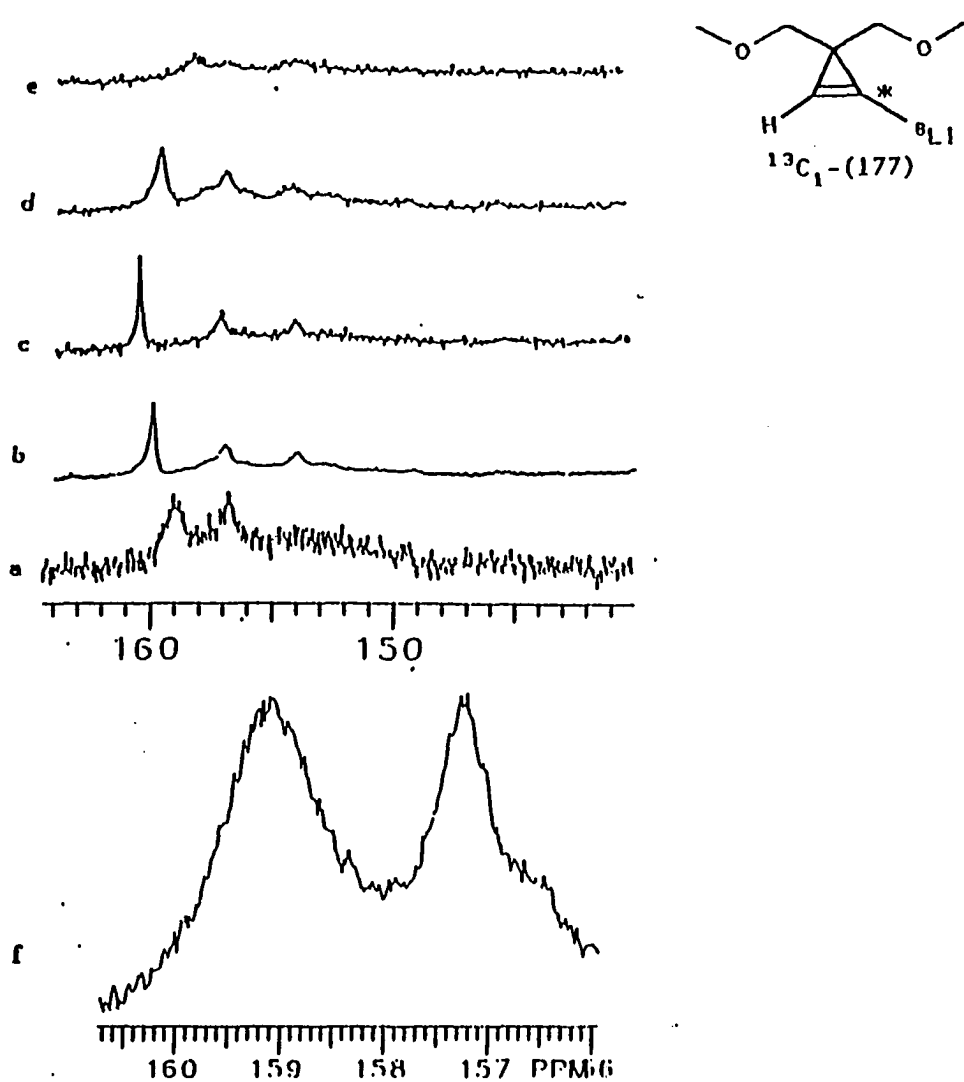
When $^{13}\text{C}_1$ -(177) was treated with excess Me^6Li in d_8 -THF, there resulted the ^{13}C NMR spectra shown in Figure 15. The main features were three broad peaks between δ 150 and δ 160 ppm at $\leq -80^\circ\text{C}$. The broadening from ^6Li coupling was expectedly less severe than with ^7Li , but the coupling pattern could not be ascertained (i.e., the peaks remained unresolved), even at -107°C . When the initial concentration of $^{13}\text{C}_1$ -(177) was doubled to 0.06 M, treatment with excess Me^6Li generated a ^{13}C NMR spectrum with 3-5 additional broad peaks in the 150-160 ppm region, as shown in Figure 16. All of these peaks coalesced (reversibly) into a single broad peak at -40°C . Thus they appear to be all due to aggregates, mixed aggregates, or diastereomers of (177). The three major peaks presumably correlate with the three major peaks observed from $^{13}\text{C}_2$ -(177), which are shown in Figure 14.

The ^{13}C chemical shifts of the vinyl carbon atoms in ^{13}C -(177)



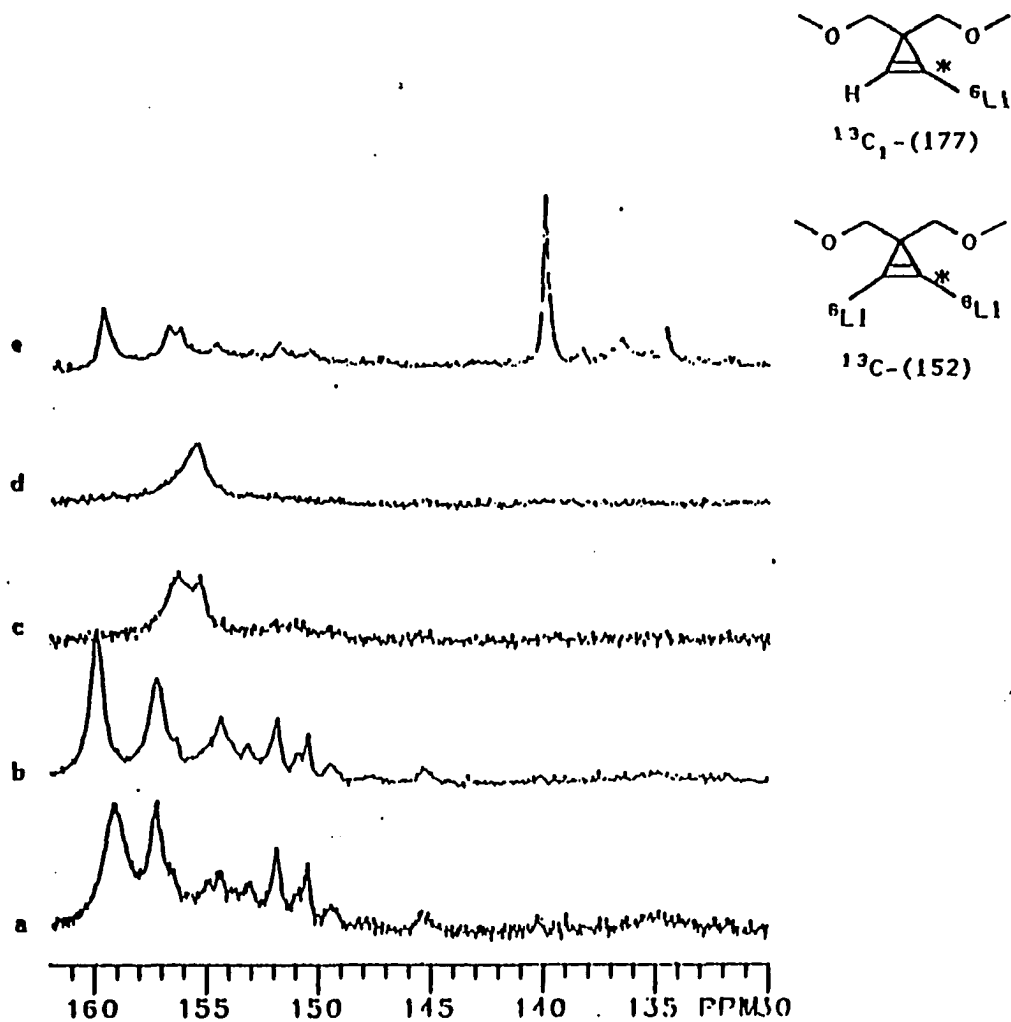
a- Broadband decoupled ^{13}C NMR.
 b- ^1H coupled ^{13}C NMR.

Figure 14. ^{13}C NMR spectra of lithiocyclopropene $^{13}\text{C}_2$ -(177) at -80°C



- a-c- Temperature were at -70 , -90 and -100°C , respectively.
 d- The solution was warmed to -80°C .
 e- PMDTA (10 equiv.) was added at -80°C .
 f- Blow-up of ^6Li -coupled peaks showing unresolved ^6Li - ^{13}C coupling.

Figure 15. ^{13}C NMR spectra of lithiocyclopropene $^{13}\text{C}_1$ -(177) at various temperatures (0.03M)



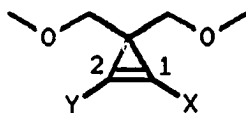
- a-b- Temperatures were at -80 and -90°C , respectively.
 c- The solution was warmed to -40°C .
 d- MeLi (10 equiv.) was added at -30°C .
 e- Temperature was at -90°C

Figure 16. ^{13}C NMR spectra of the mixture of lithiocyclopropene $^{13}\text{C}_1$ -(177) and 1,2-dilithiocyclopropene ^{13}C -(152) at various temperature (0.06M)

are at lower field (δ 150-160 ppm for the lithiated carbon; δ 124-132 ppm for the proton-bearing carbon) than that of the vinyl carbon atom in cyclopropene (151) (δ 116 ppm), as shown in Table 12. The downfield shift is due to the increased σ -electron density around the lithiated vinyl carbon.⁹⁴ The charge polarization decreases the mean excitation energy ΔE , in the paramagnetic shielding term, σ^{para} . Therefore, a downfield shift occurs. As mentioned earlier, the chemical shift difference between a σ -bonded vinyl lithium and the corresponding hydrocarbon, $\Delta\delta(\text{H, Li})$, is generally 50 to 65 ppm. For example, the ^{13}C chemical shift of the lithiated carbon of vinyl lithium is δ 186.3 ppm, and that of its non-lithiated carbon is δ 132.5 ppm. The ^{13}C chemical shift of the vinyl carbon of ethene is δ 123.5 ppm. The $\Delta\delta(\text{H, Li})$ of the lithiated carbon in (177) is unusually small ($\Delta\delta$ 34-44 ppm). This may be due to the unusual nature of the double bond of cyclopropene, which is more acetylenic than vinylic.

The inability to observe the ^6Li - ^{13}C coupling of the lithiated carbon in $^{13}\text{C}_1$ -(177) could be due to any of several reasons, including:

- (1) Poor spectrometer shimming or sample.
- (2) Rapid interaggregate exchange relative to the coupling.
- (3) Rapid relaxation of the ^6Li nuclei.
- (4) Overlap among aggregates.
- (5) Mixed aggregate formation with MeLi or lithium bromide.

Table 12. The ^{13}C chemical shifts (ppm) for some cyclopropenes

| Compounds | X,Y | C_1 | C_2 |
|-----------|-------|--------------|--------------|
| (151) | H,H | 116 | |
| (152) | Li,Li | 134, 140 | |
| (162) | Br,H | 108.3 | 114.6 |
| (177) | Li,H | 150-160 | 124-132 |
| (185) | Me,H | 124 | 106 |
| (186) | Me,Me | 113 | |

The chemical shift is reference to d_8 -THF ($\delta = 67.4$ ppm) at all temperature.

The first reason can be ruled out on the basis of the narrow lines of the remaining carbon atoms in the ^{13}C NMR spectrum. Moreover, the remaining MeLi was observed as a septet with a 5.5 Hz ^{13}C - ^6Li coupling. An interaggregate exchange process does occur, since the peaks coalesced at higher temperature, but separated at low temperature. Although the exchange process was slow below -80°C , below which base line separation was recorded, any couplings of those peaks were still unresolved. The spin-lattice relaxation times for the ^6Li nuclei are probably too long to have averaged out the coupling, even at low temperature. For example, only one lithiated

carbon¹¹⁵ out of two was resolved in
2,3-dilithio-1,1,4,4-tetramethyl-1,3-butadiene.

Overlap among aggregates and/or mixed aggregates may be present in this case. There are various possible conformers of 1-lithiocyclopropene (177), even in the dimer, and these may have very similar chemical shifts. Two reasonable dimers are shown in Figure 17. The overlap of chemical shifts would make the peaks very complicated and broad.

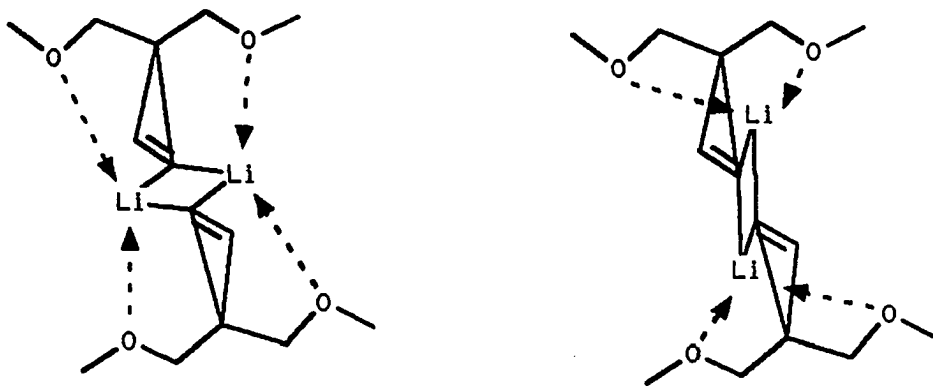
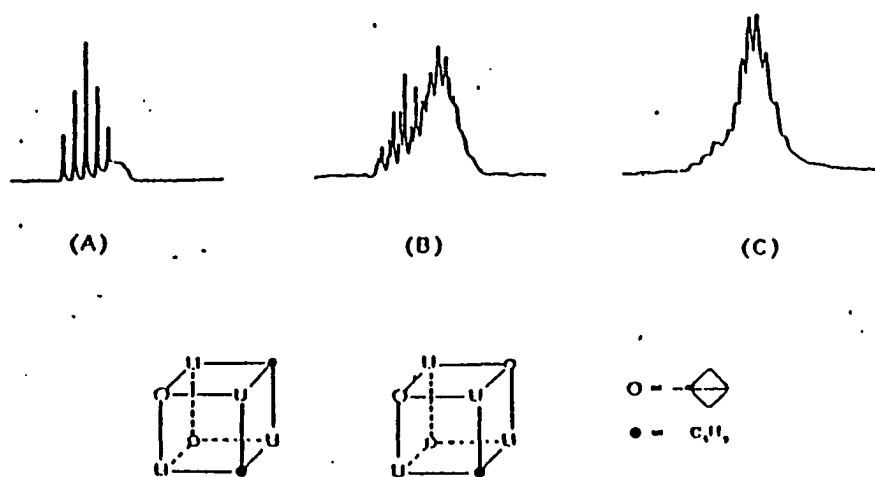


Figure 17. Two possible dimers of 1-lithiocyclopropene (177)

According to Seebach, the lithiated carbon in 1-lithiobicyclobutane appeared as a quintet with a 10.3 Hz ^{13}C - ^6Li coupling, in the absence of *n*-BuLi. The coupling pattern became very complicated in the presence of excess *n*-BuLi as shown in Figure 18. This was explained in terms of mixed aggregates of 1-lithiobicyclobutane and *n*-BuLi.

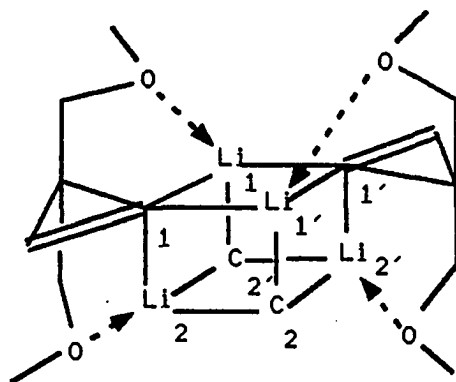
In the present case, MeLi was in large excess and lithium bromide was also present in excess. Either or both may have formed mixed aggregates with lithiocyclopropene (177). The coupling



- (A)- 1-Lithiobicyclobutane.
 (B)- 1-Lithiobicyclobutane with 1 equiv. n-BuLi.
 (C)- 1-Lithiobicyclobutane with 2.5 equiv. n-BuLi.

Figure 18. ^{13}C NMR spectra of different mixed aggregates of
 1-lithiobicyclobutane with n-BuLi

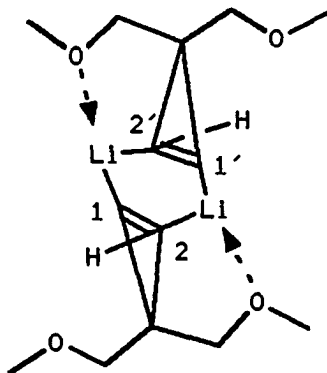
constants between different carbons and lithium atoms inside the aggregate may be different and complicated or unresolved signals may result.⁹³ For example, as shown below, Li_1 and $\text{Li}_{1'}$ are chemically equivalent but, Li_1 and Li_2 are different. Therefore, $J(\text{C}_1-\text{Li}_1)$ and $J(\text{C}_1-\text{Li}_2)$ may be different, and a complicated or unresolved line shape should appear.



An attempt to deaggregate and thereby resolve the signals by addition of N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDTA) failed. The signals remained unresolved even in the presence of 10 equiv. of PMDTA, as shown in Figure 15e.

The species responsible for the peak at δ 124 ppm in Figure 14 is especially interesting, since it represents a compound with a carbon bearing both a proton and a lithium. Since quenching gave ^{13}C -(178) clearly, and the "lithiated" carbon of this compound coalesced with the other "lithiated" carbons as shown in Figure 16, the δ 124 peak must be due to a compound with the carbon framework of (177). The structure shown below is a possibility. This dimer would have an apparently unprecedented bridging pattern for a vinyl lithium.

Perhaps the structure is "chelation induced", as each Li atom can be chelated by a methoxymethyl group from the half of the dimer to which it is bridged (i.e., from the half where it is not "primarily" bound).

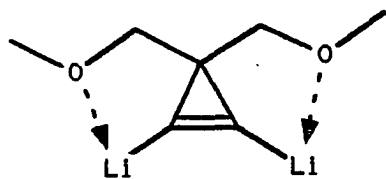


^{13}C NMR of 1,2-dilithio-3,3-bismethoxymethylcyclopropene (152)

1,2-Dilithiocyclopropene ^{13}C -(152) was presumably formed from the reaction of tribromide $^{13}\text{C}_2$ -(161) with 15 equiv. of Me^6Li . The ^{13}C NMR spectrum of the solution in d_8 -THF showed two broad peaks at δ 140 and 134 ppm, as shown in Figure 20. They remained unchanged when the proton decoupling was turned off, so no hydrogens were bonded to these carbons. When tribromide $^{13}\text{C}_1$ -(161) was used, the same two signals appeared in the ^{13}C NMR spectrum, together with those of $^{13}\text{C}_1$ -(177), as shown in Figure 16. Thus, the δ 134 and 140 peaks were assigned as due to the lithiated carbons of 1,2-dilithiocyclopropene ^{13}C -(152), presumably in differently aggregated forms. Unfortunately, the signal at δ 140 ppm remains unresolved even at -107°C . Resolution enhancement techniques did not

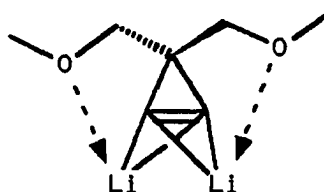
help to resolve the signal even after 10000 scans. However, the signal at δ 134 ppm was resolved, and it has a 5.2 Hz ^{13}C - ^6Li coupling. The number of lines is uncertain due to the noise, but could well be seven, as shown in Figure 21. Figure 19 shows some reasonable structures, and their expected ^{13}C NMR patterns. Clearly the resolved peak at δ 134 does not correspond to either monomer (149) or (150). Also, aggregates or mixed aggregates of structure (200) or (201) do not fit, although they could be appropriate for the δ 140 peak. A bridged dimeric structure like (202) or (203) does fit the observed coupling at δ 134; structure (202) is "pseudo-tetrameric" in the sense that it is similar to the MeLi tetramer. The δ 140 peak could conceivably be due to a monomer ((149) or (150)), since deaggregation generally leads to a downfield shift.⁹⁵ For example, the lithiated carbon of monomeric phenyllithium appears at lower field than the corresponding carbon in the tetramer.

The ^{13}C chemical shifts of the lithiated carbons in (152) (δ 134, 140 ppm) are upfield relative to those from (177) (δ 150-160 ppm), due to the increased charge in (152). This happens in other cases; for example, the ^{13}C resonance of the alkynyl carbon of 1-lithiooctyne resonates at δ 119 ppm, while that of dilithioacetylene is at δ 75 ppm. In addition, if ^{13}C -(152) has a doubly bridged structure, the chemical shift of the lithiated carbon will move upfield, as this effectively corresponds to intramolecular "aggregation".⁹



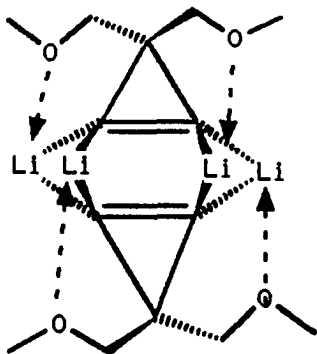
(149)

$J(^{13}\text{C}-^6\text{Li})$: 17 Hz
 Pattern: 1:1:1 triplet



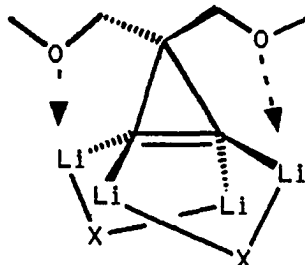
(150)

8 Hz
 pentuplet



(200)

$J(^{13}\text{C}-^6\text{Li})$: 8 Hz
 Pattern: pentuplet



X= Me or Br

(201)

8 Hz
 pentuplet

Figure 19. Some possible structures for lithiocyclopropene (152) with predicted ^{13}C NMR patterns

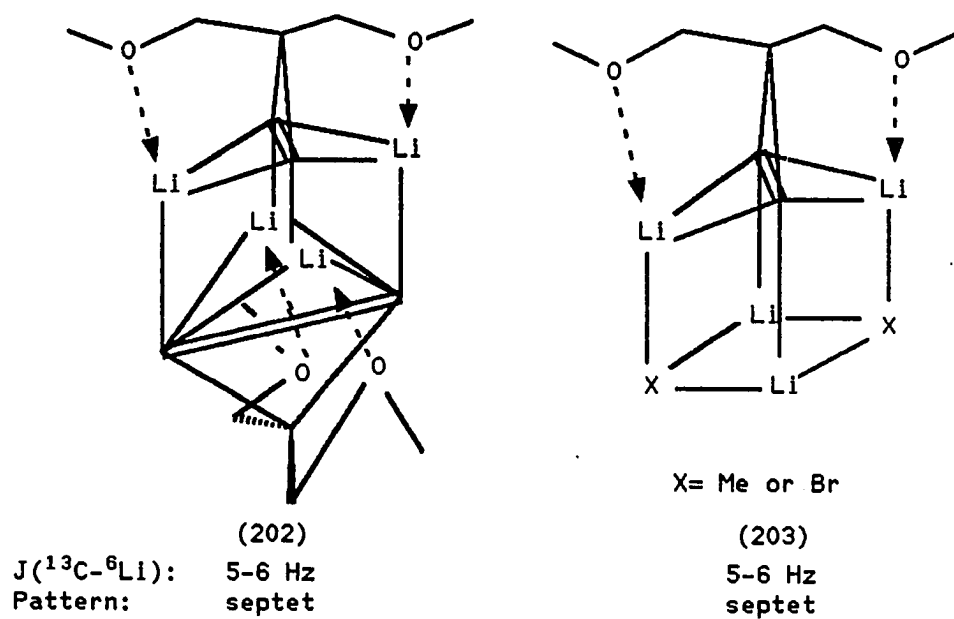
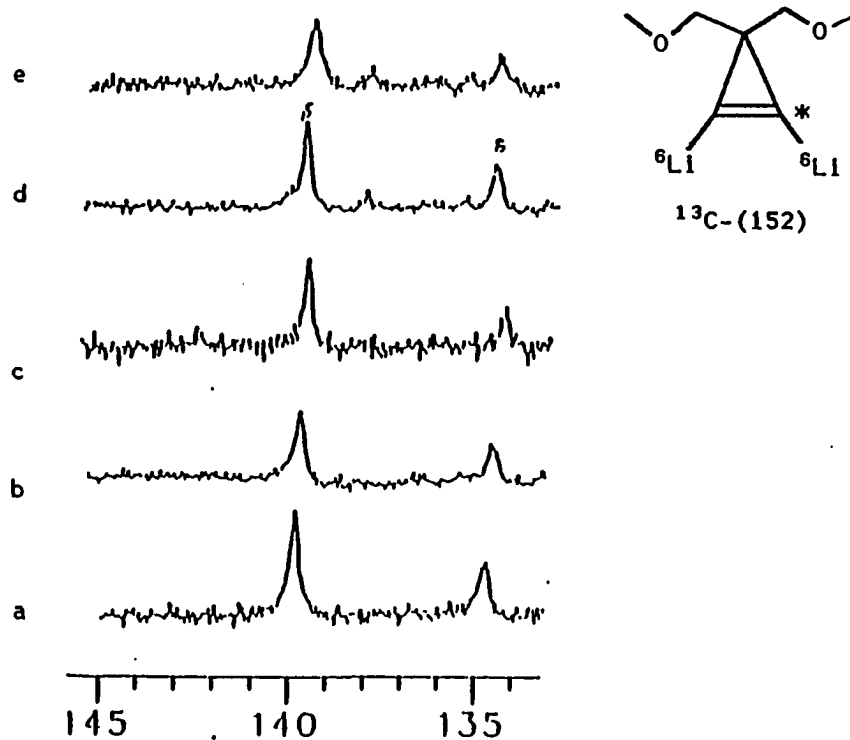


Figure 19. (Continued)



a-c- Temperatures were at -80 , -90 and -100°C , respectively.
 d-e- The solution was warmed to -80°C (d) and then to -90°C (e).

Figure 20. ^{13}C NMR spectra of 1,2-dilithiocyclopropene ^{13}C -(152) from reaction of tribromide $^{13}\text{C}_2$ -(161) with 15 equiv. of MeLi in d_8 -THF

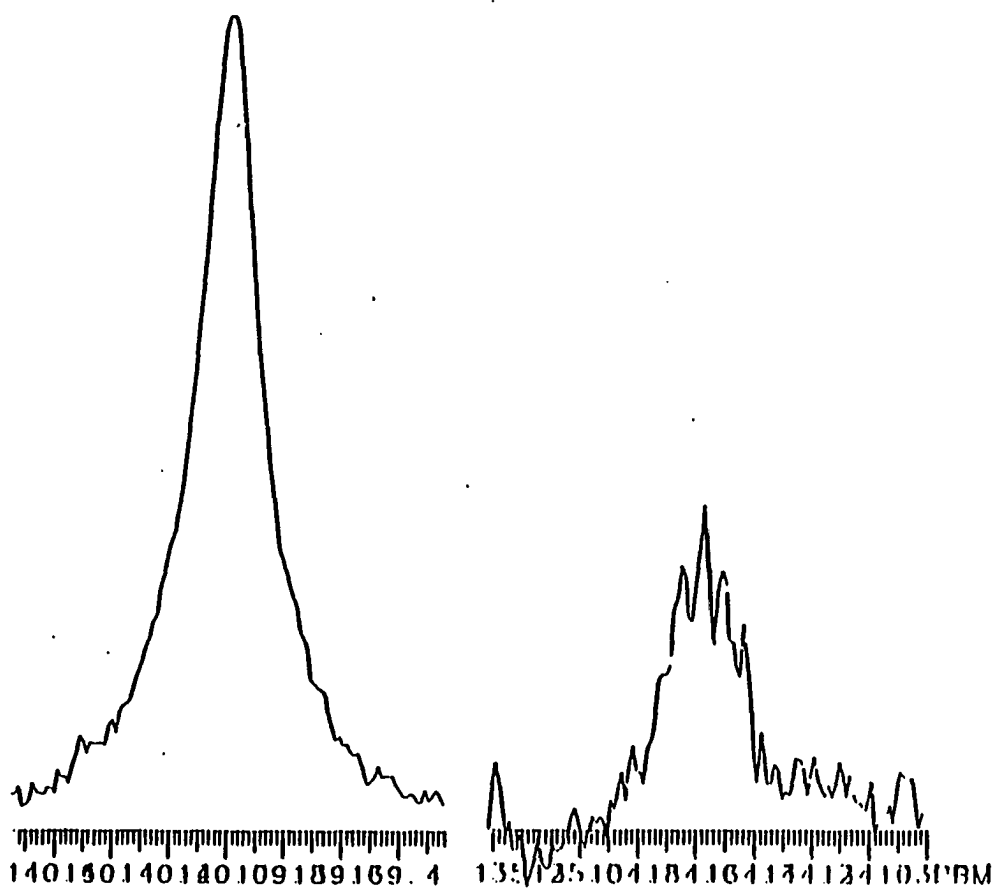
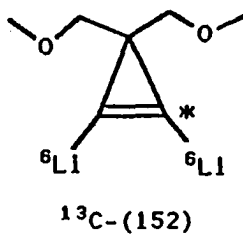


Figure 21. The ¹³C NMR spectra of ¹³C-(152) at δ 134 and 140 ppm

EXPERIMENTAL

General

Infrared spectra were recorded on an IBM FT-IR 98 spectrophotometer, or on a Mattson 4020 Galaxy Series FT-IR spectrophotometer, using a potassium bromide pellet for solid samples, and neat for liquid samples. GC/FT-IR spectra were obtained on a Mattson 4020 Galaxy Series FT-IR spectrophotometer, which was equipped with a Hewlett-Packard HP-5890 series II Gas Chromatograph with a 30 meter DB-5 capillary column. The nuclear magnetic resonance spectra were recorded on Varian EM-360, Varian XL-300, Nicolet 300 and Bruker WM-300 NMR Spectrometers, using CDCl_3 as solvent and internal standard ($\delta = 7.24$ ppm), unless otherwise mentioned. Exact mass and GC exact mass spectra were recorded on a High Resolution Finnigan MS-50 Mass Spectrometer at 70 eV, unless otherwise mentioned. GC/MS spectra were recorded on a Perkin-Elmer Ion-Trap Detector, which was equipped with a Perkin-Elmer 8420 Gas Chromatograph with a 30 meter DB-1 or DB-5 capillary column. GC analysis was performed on a Hewlett-Packard HP-5890 Gas Chromatograph, which was fitted with a 30 meter DB-1 or DB-5 capillary column and a flame ionization detector. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Cetrimide is cetylammonium bromide.

Synthesis and Reaction

3,3-Bis(hydroxymethyl)-4-aza-1-oxaspiro[4.5]decane (84)

In a three-necked flask equipped with a Dean-Stark Trap and a reflux condenser, a solution of cyclohexanone (19.8 g, 0.2 mol) and tris(hydroxymethyl)aminomethane (THAM) (26.7 g, 0.22 mol) in 140 mL of xylene was refluxed for 8 hours. Then 200 mL of acetone was added to the reaction mixture, and the unreacted THAM filtered off. After removal of the solvents, recrystallization from anhydrous acetone afforded (84) (mp, 118°-120°C, 24 g, 60% yield).

1,3-Dimethoxypropanone (85)

To a solution of (84) (7.6 g, 38 mmol) in 100 mL of DMF, sodium hydride (1.4 g, 58 mmol) was slowly added with ice-cooling. After addition of NaH, methyl iodide (3 mL, 48 mmol) was added dropwise. After 1 hour in an ice-water bath, more NaH (2.5 g, 100 mmol) and MeI (5 mL, 80 mmol) were slowly added to the mixture. After 4 hours, 3 mL of methanol and 200 mL of ether were added to the mixture. The precipitate was then filtered off, and the solution concentrated. Chloroform was added to the liquid, and the resulting solution was washed twice with 100 mL portions of water. After concentrating the solution, the resulting oil was dissolved in 400 mL of 3 M HCl. The solution was heated at 50°C for 5 hours, and then solid Na₂CO₃ was added to the brown oil until the evolution of carbon dioxide ceased. The reaction mixture was extracted three times with 100 mL portions of CHCl₃. The aqueous layer was diluted with water to 100 mL, and then treated with sodium metaperiodate (8.7 g, 41 mmol) below 20°C.

After 2 hours, the precipitate was filtered off, and the solution was extracted six times with 100 mL portions of CHCl_3 . The combined organic layers were dried over Na_2SO_4 . After removal of the solvent, distillation afforded (85) (bp, $102^\circ\text{--}104^\circ\text{C}/60$ Torr, 2.3 g, 52% yield).

HRMS (m/e): $\text{C}_5\text{H}_{10}\text{O}_3$ (M^+)- 118.06300(calculated).

118.06298(found).

^1H NMR (δ = ppm): 4.15(s, 4H), 3.4(s, 6H).

^{13}C NMR (δ = ppm): 205.3, 73.8, 59.1.

IR (neat, cm^{-1}): 2935, 2827, 1736, 1676, 1452, 1389, 1200, 1120, 984, 939.

IR (GC, cm^{-1}): 3003, 2934, 2841, 1752, 1459, 1204, 1111.

1,1-Dibromo-3-methoxy-2-methoxymethylpropene (86)

A mixture of (85) (3.0 g, 26 mmol), triphenylphosphine (26.3 g, 104 mmol) and CBr_4 (17.2 g, 52 mmol, which was passed through a short pad of Alumina with benzene beforehand) was dissolved in 300 mL of benzene and refluxed for 14 hours. After the solution was cooled to room temperature, 500 mL of pentane was added. The precipitate was filtered through a short pad of Florisil. After removal of the solvents, the solid was dissolved in a minimum amount of CH_2Cl_2 , and then precipitated out by addition of pentane. The resulting white solid was filtered, and the remaining solution concentrated. The process was repeated four times to remove the solid. Distillation afforded (86) (bp, $56^\circ\text{--}58^\circ\text{C}/0.25$ Torr, 4.4 g, 60% yield).

GC/MS (m/e): 244(16), 242(57), 240(13), 231(43), 229(85), 227(38),

114(100).

$^{13}\text{C}_1$ -(86): 245(33), 243(52), 241(21), 232(58) 230(97),
228(51), 134(97), 115(100).

HRMS (m/e): $\text{C}_6\text{H}_{10}\text{Br}_2\text{O}_2$ (M^+)- 271.90475(calculated).

271.90527(found).

^1H NMR (δ = ppm): 4.11(s, 4H), 3.32(s, 6H).

$^{13}\text{C}_1$ -(86): 4.11(d, $J(\text{C-H}) = 7.5$ Hz), 3.32(s).

^{13}C NMR (δ = ppm): 139.5, 94.4, 71.6, 58.3.

$^{13}\text{C}_1$ -(86): (139.5), 94.5(^{13}C), 71.6(d, $J(\text{C-C}) =$
3.5 Hz), 58.4.

IR (neat, cm^{-1}): 2986, 2928, 2822, 1624, 1585, 1452, 1379, 1285,
1250, 1209, 1101, 955, 910, 802.

General procedure for the reaction of dibromide (86) with
alkyllithium (reaction 1)

To a solution of (86) (30 mg, 0.11 mmol) in 1 mL of dry THF, alkyllithium (n-BuLi or t-BuLi) was slowly added via syringe at the desired temperature under argon. After one hour, a quenching agent (MeOH, MeOD, Me_2S_2 or TMSCl) (> 10 equiv.) was added to the solution at low temperature. The mixture was then allowed to warm to room temperature. Ether was added to the solution, and the organic layer washed with NH_4Cl , water and brine. The products were analyzed by GC and GC/MS.

General procedure for the reaction of dibromide (86) with mixed alkyllithiums (reaction 2)

To a solution of (86) (30 mg, 0.11 mmol) in 1 mL of dry THF, s-BuLi (0.35 mL, 0.97 M, 0.33 mmol) was slowly added via syringe at -95°C under argon. After 30 min, MeLi (0.25 mL, 1.4 M, 0.33 mmol) was slowly added to the solution via syringe. The solution was allowed to stir at -70°C for 30 min. A quenching agent (MeOH, MeOD, Me₂S₂, Et₂S₂, MeI or TMSCl) (> 10 equiv.) was then added to the solution at -70°C. The resulting mixture was allowed to warm to room temperature. Ether was added to the solution, and the organic layer washed with NH₄Cl, water and brine. The products were analyzed by GC and GC/MS.

General procedure for the reaction of dibromide (86) with mixed alkyllithiums in the presence of LiI (reaction 3)

To a solution of (86) (30 mg, 0.11 mmol) and LiI (45 mg, 0.33 mmol) in 1 mL of dry THF, s-BuLi (0.35 mL, 0.97 M, 0.33 mmol) was slowly added via syringe at -95°C under argon. After 30 min, MeLi (0.25 mL, 1.4 M, 0.33 mmol) was slowly added to the solution via syringe. The solution was allowed to stir at -70°C for 30 min. A quenching agent (MeOH, MeOD, Me₂S₂, Et₂S₂, MeI, TMSCl or Me₂S₂/Et₂S₂) (> 10 equiv.) was added to the solution at -70°C. The mixture was then warmed to room temperature. Ether was added to the solution, and the organic layer washed with NH₄Cl, water and brine. The products were analyzed by GC and GC/MS.

Products from reactions 1-3 are as follows.

1-Bromo-3-methoxy-2-methoxymethylpropene (88)

GC/MS (m/e): 164(25), 162(29), 151(43), 149(39), 115(58), 85(58),
83(70), 55(100).

HRMS (m/e): $C_6H_{11}O_2^{81}Br$ (M^+)- 195.99220(calculated).
195.99230(found).

1H NMR (δ = ppm): 6.38(s, 1H), 4.11(s, 2H), 3.95(s, 2H), 3.32(s, 6H).

$^{13}C_1$ -(88): 6.38(d, $J(C-H) = 197$ Hz), 4.11(d,
 $J(C-H) = 5.7$ Hz), 3.94(d, $J(C-H) = 81$ Hz), 3.31(s).

^{13}C NMR (δ = ppm): 138.7, 107.4, 72.6, 69.7, 58.1.

^{13}C -(88): 138.8(d, $J(C-C) = 80$ Hz), 107.5(^{13}C),
73.7(d, $J(C-C) = 5.5$ Hz), 69.7, 58.2.

IR (GC, cm^{-1}): 3088, 3000, 2932, 2836, 1636, 1460, 1372, 1196, 1116.

3-Methoxy-2-methoxymethylpropene (89)

GC/MS (m/e): 117(1), 84(42), 71(89), 45(100), 41(92).

HRMS (m/e): $C_6H_{12}O_2$ (M^+)- 116.08373(calculated).
116.08348(found).

1H NMR (δ = ppm): 5.16(t, $J = 0.9$ Hz, 2H), 3.91(m, 4H), 3.32(s, 6H).

IR (neat, cm^{-1}): 2986, 2928, 2820, 1659, 1452, 1398, 1194.

3-Methoxy-2-methoxymethyl-1-methylthiopropene (91)

GC/MS (m/e): 162(18), 117(75), 99(20), 45(100).

HRMS (m/e): $C_7H_{14}O_2S$ (M^+)- 162.07146(calculated).
162.07120(found).

1H NMR (δ = ppm): 6.18(s, 1H), 4.01(s, 2H), 3.91(d, $J = 0.9$ Hz, 2H),
3.07(s, 3H), 3.05(s, 3H), 2.28(s, 3H).

1-Bromo-3-methoxy-2-methoxymethyl-1-methylthiopropene (92)

GC/MS (m/e): 242(8), 240(8), 208(6), 210(6), 197(39), 195(50), 5(32),
45(100).

¹H NMR (δ = ppm): 4.24(s, 2H), 4.19(s, 2H), 3.34(s, 3H), 3.32(s, 3H),
2.37(s, 3H).

1-(t-Butyl)-3-methoxy-2-methoxymethyl-1-methylthiopropene (93)

GC/MS (m/e): 218(1), 186(11), 171(52), 156(31), 139(13), 57(100).

¹H NMR (δ = ppm): 4.41(s, 2H), 4.13(s, 2H), 3.33-3.32(m, 6H), 2.18(s,
3H), 1.25(s, 9H).

3-Methoxy-2-methoxymethyl-1,1-bis(methylthio)propene (94)

GC/MS (m/e): 208(8), 177(76), 163(87), 145(100), 91(90).

¹H NMR (δ = ppm): 4.29(s, 4H), 3.32(s, 6H), 2.29(s, 4H).

3-Methoxymethyl-2,5-dihydrofuran (103)

GC/MS (m/e): 114(10), 85(31), 71(18), 57(30), 43(100).

GC/MS/CI(i-butane) (m/e): 115(M+1).

¹H NMR (δ = ppm): 5.74(m, 1H), 4.63-4.57(m, 4H), 4.01(s, 2H), 3.31(s,
3H).

¹³C NMR (δ = ppm): 137.5, 122.7, 75.7, 75.4, 68.0, 58.2.

IR (neat, cm⁻¹): 2986, 2928, 2949, 1452, 1381, 1196, 1105, 1069,
1018, 943.

1-Bromo-3-methoxy-2-methoxymethyl-1-trimethylsilylpropene (105)

GC/MS (m/e): 253(20), 251(20), 223(70), 221(70), 45(100).

¹H NMR (δ = ppm): 4.24(s, 2H), 3.99(s, 2H), 3.35(s, 3H), 3.30(s, 3H),
0.290(s, 9H).

IR (neat, cm⁻¹): 2957, 2929, 2820, 1600, 1452, 1375, 1252, 1101, 872,

843, 760.

1-Iodo-3-methoxy-2-methoxymethyl-1-trimethylsilylpropene (106)

GC/MS (m/e): 314(5), 299(38), 200(35), 187(45), 89(60), 73(52),
45(100).

¹H NMR (δ = ppm): 4.20(s, 2H), 4.00(s, 2H), 3.36(s, 3H), 3.29(s, 3H),
0.304(s, 9H).

1,1-Bisethylthio-3-methoxy-2-methoxymethylpropene (108)

GC/MS (m/e): 236(16), 191(32), 175(30), 173(50), 45(100).

¹H NMR (δ = ppm): 4.32(s, 4H), 3.31(s, 6H), 2.76(q, J = 7.5 Hz, 4H),
1.19(t, J = 7.5 Hz, 6H).

1-Methoxy-2-methoxymethyl-3-methyl-2-butene (109)

GC/MS (m/e): 144(1), 112(35), 99(100).

1-Ethylthio-3-methoxy-2-methoxymethyl-1-methylthiopropene (115)

GC/MS (m/e): 222(15), 177(37), 159(40), 45(100).

1,6-Dimethoxy-2,5-bismethoxymethyl-2,3,4-hexatriene (116)

To a solution of (86) (500 mg, 1.8 mmol) in 10 mL of dry THF, n-BuLi (1.7 mL, 1.1 M, 1.8 mmol) was slowly added via syringe at -80°C under argon. After two hours, MeOH was added to the solution at -80°C. The resulting mixture was allowed to warm to room temperature. Ether was then added to the solution, and the organic layer washed with NH₄Cl, water and brine. After removal of solvent, followed by column chromatography (SiO₂, ether/hexanes 1:3), (103) (35 mg, 17% yield) (see characterization above) and (116) (80 mg, 38% yield) were obtained.

GC/MS (m/e): 228(1), 183(20), 152(12), 151(12), 121(20), 73(100).

HRMS (m/e): $C_{12}H_{12}O_4$ (M^+)- 228.13616(calculated).

228.13655(found).

1H NMR (δ = ppm): 4.08(s, 4H), 3.36(s, 6H).

^{13}C NMR (δ = ppm): 159.8(s), 116.0(s), 72.2(t), 57.9(q).

IR (neat, cm^{-1}): 2984, 2928, 2854, 1641, 1450, 1366, 1192, 1097, 908.

3-(n-Butyl)-6-methoxy-2,5-bismethoxymethyl-1,3,4-hexatriene (118)

To a solution of (86) (500 mg, 1.8 mmol) in 10 mL of dry THF, n-BuLi (2.0 mL, 1.1 M, 2.2 mmol) was slowly added via syringe at $-80^\circ C$ under argon. After two hours, MeOH was added to the solution at $-80^\circ C$. The resulting mixture was allowed to warm to room temperature. Ether was then added to the solution, and the organic layer washed with NH_4Cl , water and brine. After removal of solvent, followed by column chromatography (SiO_2 , ether/hexanes 1:3), (103) (30 mg, 14% yield) (see characterization above) and (118) (50 mg, 20% yield) were obtained.

GC/MS (m/e): 254(2), 209(10), 91(22), 75(55), 45(100).

GC/MS/CI(i-butane) (m/e): 255(M+1).

1H NMR (δ = ppm): 5.21(bs), 5.18(s), 3.98(s), 3.93(s), 3.33(s),
3.31(s), 2.22(t, $J = 6.9$ Hz), 1.29-1.46(m), 0.88(t,
 $J = 7.2$ Hz).

IR (neat, cm^{-1}): 2957, 2924, 2854, 1450, 1259, 1194, 1092, 1018.

1-Bromo-1-chloromercuro-3-methoxy-2-methoxymethylpropene (119)

To a solution of (86) (200 mg, 0.72 mmol) in 5 mL of dry THF, n-BuLi (0.75 mL, 0.97 M, 0.72 mmol) was slowly added via syringe at $-95^\circ C$ under argon. After 30 min, $HgCl_2$ (200 mg, 0.72 mmol) in 0.5 mL

of dry THF was slowly added to the solution via syringe. The solution was then allowed to stir at -95°C for 30 min. The mixture was warmed to room temperature, ether added to the solution, and the organic layer washed with NH_4Cl , water and brine. After removal of the solvent, followed by column chromatography (SiO_2 , ether/hexanes 1:3), (119) (230 mg, 75% yield) was obtained.

HRMS (m/e): $\text{C}_6\text{H}_{10}\text{O}_2^{79}\text{Br}^{35}\text{Cl}^{199}\text{Hg}$ (M^+)- 426.92349(calculated).

426.92316(found).

^1H NMR (δ = ppm): 4.20(s, 2H), 4.09(s, 2H), 3.46(s, 3H), 3.33(s, 3H).

^{13}C NMR (δ = ppm): 146.8, 130.2, 72.7, 72.6, 58.9, 58.4.

Bis(1-bromo-3-methoxy-2-methoxymethylpropenyl)mercury (121)

To a solution of (119) (200 mg, 0.46 mmol) in 5 mL of dry THF, *s*-BuLi (0.46 mL, 1.0 M, 0.46 mmol) was slowly added via syringe at -95°C under argon. After 30 min, HgCl_2 (200 mg, 0.72 mmol) in 0.5 mL of dry THF was slowly added to the solution via syringe. The solution was then allowed to stir at -95°C for 30 min. The mixture was warmed to room temperature, ether added to the solution, and the organic layer washed with NH_4Cl , water and brine. After removal of solvent, followed by column chromatography (SiO_2 , ether/hexanes 1:3), (121) (82 mg, 60% yield) was obtained.

MS (m/e): 588(^{202}Hg , ^{79}Br , a cluster), 556, 543.

MS-CI(*i*-butane) (m/e): 589(M+1).

^1H NMR (δ = ppm): 4.24(s, 2H), 4.10(s, $J(\text{H}-\text{Hg}) = 22$ Hz, 2H), 3.43(s, 3H), 3.33(s, 3H).

^{13}C NMR (δ = ppm): 146.6, 74.0, 72.88, 58.9, 58.2.

1-(t-Butyl)-1-chloromercuro-3-methoxy-2-methoxymethylpropene (122)

To a solution of (119) (200 mg, 0.46 mmol) in 5 mL of dry THF, t-BuLi (0.35 mL, 1.3 M, 0.46 mmol) was slowly added via syringe at -95°C under argon. After 30 min, HgCl₂ (200 mg, 0.72 mmol) in 0.5 mL of dry THF was slowly added to the solution via syringe. The solution was then allowed to stir at -95°C for 30 min. The mixture was warmed to room temperature, ether added to the solution, and the organic layer washed with NH₄Cl, water and brine. After removal of the solvent followed by column chromatography (SiO₂, ether/hexanes 1:3), (122) (115 mg, 61% yield) was obtained.

MS (m/e): 408(²⁰²Hg, ³⁵Cl, a cluster).

¹H NMR (δ = ppm): 4.07(s, J(H-Hg) = 17 Hz, 2H), 3.97(s, J(H-Hg) = 40 Hz, 2H), 3.42(s, 3H), 3.31(s, 3H), 1.25(s, 9H).

¹³C NMR (δ = ppm): 165.0, 138.8, 74.1, 70.7, 58.3, 58.4, 37.8, 34.3.

1,1-Bis(chloromercuro)-3-methoxy-2-methoxymethylpropene (120)

A suspension of tetrakis(trimethylenedioxyboryl)methane (400 mg, 1.1 mmol) in 5 mL of dry THF was stirred at -70°C. To the mixture, MeLi (0.78 mL, 1.4 M, 1.1 mmol) was added via syringe. After the mixture was allowed to warm to 0°C and recooled to -70°C, ketone (85) (120 mg, 1.1 mmol) was added. The mixture was then stirred at room temperature for 16 hours. After removal of the solvent under reduced pressure, the residue was treated with 50 mL of chloroform/ether (1:2). The solid was filtered off, and the solution was concentrated on a rotary evaporator. The resulting crude oil was dissolved in 10 mL of MeOH, to which a mixture of mercury (II) chloride (610 mg, 2.2

mmol) and sodium acetate (185 mg, 2.2 mmol) in 5 mL of 50% aqueous MeOH was added. A white solid (120) precipitated immediately and, after stirring for a few min, was filtered and washed with several portions of MeOH.

HRMS (m/e): $C_6H_{10}O_2Cl_2Hg_2$ (M^+)- 585.94468(calculated).

585.94375(found).

1H NMR (d_6 -DMSO) (δ = ppm): 3.93(s, $J(H-Hg)$ = 34 Hz, 4H), 3.25(s, 6H).

^{13}C NMR (d_6 -DMSO) (δ = ppm): 159.5, 151.8, 75.5($J(C-Hg)$ = 191, 355.2 Hz), 57.7.

1,4-Dimethoxy-2-butyne (129)

Two methods were used to prepare (129).

Method a: To a mixture of NaH (3 g, 50% in mineral oil, 62.5 mmol) in 10 mL of DMF, was added but-2-yn-1,4-diol (2.12 g, 24.6 mmol) at 0°C under nitrogen. After the addition, methyl iodide (3.9 mL, 62.6 mmol) was added. The solution was allowed to stir at 0°C for 3 hours. Then 10 mL of methanol was added slowly, followed by 100 mL of ether. The reaction mixture was then filtered through a short pad of celite. The resulting solution was washed with water, brine, and dried over Na_2SO_4 . After removal of the solvent, followed by column chromatography (SiO_2 , ether/hexanes 1:2), (129) (1.55 g, 55% yield) was obtained.

Method b: To a suspension of KOH (5.2 g, 82.8 mmol) in 50 mL of DMSO, was added but-2-yn-1,4-diol (1.11 g, 12.9 mmol) dropwise. After the subsequent addition of methyl iodide (3 mL, 48.2 mmol), the

mixture was allowed to stir at room temperature for 30 min. The mixture was then poured into water, and the aqueous layer extracted six times with 30 mL of CH_2Cl_2 . The combined organic layers were washed six times with 30 mL of water, twice with 30 mL of brine twice, and dried over Na_2SO_4 . After removal of the solvent, followed by column chromatography (SiO_2 , ether/hexanes 1:2), (129) (1.29 g, 70% yield) was obtained.

GC/MS (m/e): 114(5), 99(61), 71(50), 69(50), 53(61), 45(100), 39(79).

^1H NMR (δ = ppm): 4.13(s, 4H), 3.37(s, 6H).

^{13}C NMR (δ = ppm): 82.3, 59.9, 57.7.

1,6-Dimethoxy-3-hexyne (141)

To a solution of butyn-4-ol (1 mL, 13.2 mmol) in 15 mL of dry THF and 6 mL of HMPA, was added dropwise n-BuLi (10.8 mL, 2.5 M, 27 mmol) in hexanes at -78°C under argon. The solution was then warmed to -10°C for 45 min. Bromoethyl methyl ether (1.4 mL, 14.4 mmol) was then added dropwise to the mixture at -10°C . After the addition, the solution was allowed to stir at room temperature for 18 hours. To the resulting red solution was added MeI (1 mL, 16 mmol) dropwise at room temperature. After 2 more hours, the mixture was poured into water and the aqueous layer extracted three times with 30 mL of ether. The combined organic layers were washed twice each with water and brine, and dried over Na_2SO_4 . After removal of the solvent, followed by column chromatography (SiO_2 , CH_2Cl_2 /hexanes 1:5), (141) was obtained (370 mg, 20% yield).

GC/MS (m/e): 141(2), 127(47), 97(100), 67(40).

GC/MS/CI(NH₃) (m/e): 143(M+1).

¹H NMR (δ = ppm): 3.45(t, J = 6.9 Hz, 4H), 3.34(s, 6H), 2.42(t, J = 6.9 Hz, 4H).

Two side products, (132) and (144) were also obtained in 10% and 8% yield, respectively.

4-(2-Methoxyethoxy)-1-butyne (132)

GC/MS (m/e): 89(80), 59(100), 53(92), 45(52).

GC/MS/CI(NH₃) (m/e): 129(M+1).

¹H NMR (δ = ppm): 3.64-3.58(m, 4H), 3.55-3.52(m, 2H), 3.37(s, 3H), 2.48(td, J = 7.2, 2.7 Hz, 2H), 1.954(t, J = 2.7 Hz, 1H).

IR (neat, cm⁻¹): 3292, 2920, 2878, 2117, 1678, 1115.

1-Methoxy-6-(2-methoxyethoxy)-3-hexyne (144)

GC/MS (m/e): 171(1), 141(10), 89(30), 59(100).

GC/MS/CI(NH₃) (m/e): 204(M+NH₄⁺).

¹H NMR (δ = ppm): 3.61-3.49(m, 6H), 3.44(t, J = 6.9 Hz, 2H), 3.36(s, 3H), 3.34(s, 3H), 2.47-2.39(m, 3H).

IR (neat, cm⁻¹): 2980, 2924, 2827, 1456, 1383, 1358, 1227, 1115, 1063.

1,6-Bis(2-methoxyethoxy)-3-hexyne (134)

To a solution of butyn-4-ol (1 mL, 13.2 mmol) in 15 mL of dry THF and 6 mL of HMPA, was added dropwise n-BuLi (10.8 mL, 2.5 M, 27 mmol) in hexanes at -78°C under argon. The solution was then warmed to -10°C for 45 min. Then 2-(2-bromoethoxy)ethyl methyl ether (2.6 g, 14.4 mmol) was then added dropwise to the mixture at -10°C. After

the addition, the solution was allowed to stir at room temperature for 18 hours. To the resulting red solution was added dropwise 2-bromoethyl methyl ether (1.4 mL, 14.4 mmol) at room temperature. After 2 more hours, the mixture was poured into water, and the aqueous layer extracted three times with 30 mL portions of ether. The combined organic layers were washed twice each with water and brine, and dried over Na_2SO_4 . After removal of the solvent, followed by column chromatography (SiO_2 , CH_2Cl_2 /hexanes 1:5), (134) and (135) were obtained (570 mg, 19% yield; 320 mg, 9%, respectively).

1,6-Bis(2-methoxyethoxy)-3-hexyne (134)

GC/MS (m/e): 230(1), 185(5), 123(22), 89(22), 59(100).

GC/MS/CI(i-butane) (m/e): 231(M+1).

^1H NMR (δ = ppm): 3.60-3.49(m, 12H), 3.35(s, 6H), 2.44-2.39(m, 4H).

^{13}C NMR (δ = ppm): 77.5, 71.6, 69.840, 69.848, 58.7, 19.8.

6-(2-Methoxyethoxy)-1-(2-(2-methoxyethoxy)ethoxy)-3-hexyne (135)

GC/MS (m/e): 153(2), 133(10), 103(11), 59(100).

GC/MS/CI(i-butane) (m/e): 275(M+1).

^1H NMR (δ = ppm): 3.63-3.49(m, 16H), 3.35(s), 3.348(s), 2.44-2.38(m, 4H).

^{13}C NMR (δ = ppm): 71.88, 71.80, 70.5, 70.1, 70.0, 69.87, 69.82, 58.9, 20.0.

Reaction of 1,6-dimethoxy-3-hexyne (141) with lithium (reaction 4)

To a suspension of lithium metal (100 mg, 14 mmol) in 10 mL of ether, was added (141) (550 mg, 3.5 mmol) at room temperature under argon. After 2 days, MeOD or MeOH was then added to the mixture at

0°C. The organic solution was washed twice each with 1 M HCl, water and brine, and dried over Na₂SO₄. After removal the solvent, followed by column chromatography (SiO₂, CH₂Cl₂/hexanes 1:5), (143) (310 mg, 60% yield) was obtained.

1,6-Dimethoxy-3-hexene (143)

GC/MS (m/e): d₀-(143): 112(72), 97(40), 84(40), 68(100), 67(62).

GC/MS/CI(NH₃) (m/e): d₀-(143): 162(M+NH₄).

d₂-(143): 164(M+NH₄).

¹H NMR (δ = ppm): a mixture of d₀, d₁, d₂-(143): 5.46(m), 3.35(t, J = 6.9 Hz), 3.29(s), 2.24(t, J = 6.9 Hz).

¹³C NMR (δ = ppm): a mixture of d₀, d₁, d₂-(143): 128.4, 127.9(t, J(C-D) = 22.8 Hz), 72.4, 58.5, 32.8.

Reaction of 1-Methoxy-6-(2-methoxyethoxy)-3-hexyne (144) with lithium (reaction 5)

To a suspension of lithium metal (60 mg, 8.5 mmol) in 10 mL of ether, was added (144) (350 mg, 1.9 mmol) at room temperature under argon. After 2 days, MeOD or MeOH was then added to the mixture at 0°C. The organic solution was washed twice each with 1 M HCl, water and brine, and dried over Na₂SO₄. After removal the solvent, followed by column chromatography (SiO₂, CH₂Cl₂/hexanes 1:5), (145) (230 mg, 63% yield) was obtained.

1-Methoxy-6-(2-methoxyethoxy)-3-hexene (145)

GC-MS (m/e): a mixture of d₀, d₁, d₂-(145): 114(10), 113(5), 112(4), 89(35), 59(100).

GC-MS-CI(i-butane) (m/e): d₂-(145): 191(M+1).

^1H NMR (δ = ppm): a mixture of d_0 , d_1 , d_2 -(145): 5.39-5.43(m),
3.51-3.43(m), 3.39(t, J = 7.2 Hz), 3.29(s),
3.24(s), 2.24-2.15(m).

Ethyl 4-methoxy-3-methoxymethylbut-2-enoate (Ethyl
 β,β -bismethoxymethylacrylate) (153)

A mixture of (85) (0.4 g, 0.34 mmol) and carbethoxymethylenetriphenylphosphorane (2.4 g, 0.68 mmol) in 30 mL of benzene was refluxed under argon for 5 hours. After cooling the mixture to room temperature, 50 mL of pentane was added and the solid removed via suction filtration. The solvent was removed on a rotary evaporator. The resulting solid was extracted five times with pentane. The combined organic layers were dried over Na_2SO_4 . Removal of the solvent afforded a colorless liquid, (153) (0.41 g, 65% yield).

GC/MS (m/e): 156(50), 143(22), 127(60), 96(82), 45(100).

GC/MS/CI(NH_3) (m/e): 189(M+1).

^1H NMR (δ = ppm): 6.00(m, 1H), 4.54(s, 2H), 4.14(q, J = 7.2 Hz, 2H),
4.09(m, 2H), 3.37(s, 3H), 3.32(s, 3H), 1.26(t, J =
7.2 Hz, 3H).

^{13}C NMR (δ = ppm): 165.8(s), 154.6(s), 115.4(d), 72.1(t), 69.2(t),
59.7(t), 58.4(q), 14.0(q).

IR (neat, cm^{-1}): 2982, 2930, 2820, 1715, 1655, 1319, 1221, 1146,
1115, 1043.

1-Methoxy-2-methoxymethylbut-2-en-4-ol (154)

To a solution of (153) (1.39 g, 7.4 mmol) in 50 mL of CH₂Cl₂, was added dropwise DIBAL (15 mL, 1 M, 1.5 mmol) in hexanes at -78°C under argon. After 2 hours, methanol was added to the solution at -78°C, whereafter the solution was then allowed to warm to room temperature. Then 1 mL of 1 M HCl was slowly added to the solution. The resulting solution was filtered through a short pad of Florisil; after removal of the solvent, (154) (1.05 g, 98% yield) was obtained. GC/MS (m/e): 145(1), 128(10), 114(10), 85(50), 69(50), 55(50), 45(100).

GC/MS/CI(i-butane) (m/e): 147(M+1).

HRMS (m/e): C₇H₁₁O₂ (M⁺-18)- 128.08373(calculated).
128.08364(found).

HRMS-CI (i-butane) (m/e): C₇H₁₅O₃ (M⁺+1)- 147.10213(calculated).
147.10196(found).

¹H NMR (δ = ppm): 5.86(t, J = 6.3 Hz), 4.17(t, J = 6.3 Hz), 3.94(s), 3.87(s), 3.29(s), 3.28(s), 2.52(t, J = 6 Hz).

¹³C NMR (δ = ppm): 134.5(s), 131.1(d), 74.3(t), 67.6(t), 57.8(two q), 57.6(t).

IR (neat, cm⁻¹): 3418, 2980, 2926, 2820, 1680, 1450, 1379, 1192, 1101, 1015, 953, 912.

4-Methoxy-3-methoxymethylbut-2-enal (β,β-Bismethoxymethylacrolein) (155)

To a mixture of PCC (1.86 g, 8.6 mmol) and sodium acetate (0.16 g, 1.95 mmol) in 20 mL of CH₂Cl₂, was added (154) (0.62 g, 4.25 mmol)

in 5 mL of CH_2Cl_2 at room temperature under argon. After 3 hours, the black mixture was washed five times with 20 mL portions of ether. The combined organic layers were filtered through a short pad of Florisil. After removal of the solvent, distillation afforded (155) (bp, 105°-107°C/15 Torr, 0.48 g, 79% yield).

GC/MS (m/e): 144(10), 112(50), 97(15), 82(50), 45(100).

HRMS (m/e): $\text{C}_7\text{H}_{12}\text{O}_3$ (M^+)- 144.07865(calculated).

144.07860(found).

^1H NMR (δ = ppm): 10.08(d, J = 7.8 Hz, 1H), 6.14-6.18(m, 1H), 4.34(s, 2H), 4.07(m, 2H), 3.36(s, 3H), 3.35(s, 3H).

^{13}C NMR (δ = ppm): 190.5(d), 156.2(s), 126.5(d), 72.5(t), 68.3(t), 58.3(q).

IR (neat, cm^{-1}): 2990, 2934, 2826, 1676, 1616, 1452, 1393, 1200, 1115, 997, 957, 932.

4-Methoxy-3-methoxymethylbut-2-enal tosylhydrazone (156)

To a solution of p-toluenesulfonylhydrazide (0.84g, 4.5 mmol) in 10 mL of methanol, was added (155) (0.67 g, 4.7 mmol) at 40°C. After 30 min at 40°C, the solution was placed in the freezer (-23°C) for 14 hours. The resulting mixture was column chromatographed (SiO_2 , ethyl acetate/hexane 1:1), whereby a yellow oil (156) (1.4 g, 91% yield) was obtained.

GC/MS (m/e): 312(2), 157(60), 125(100), 91(50), 65(50).

^1H NMR (δ = ppm): 8.00(m, 1H), 7.88(d, J = 9.9 Hz, 1H), 7.79(d, J = 8.4 Hz, 2H), 7.28(d, J = 8.4 Hz, 2H), 6.26(d, J = 9.9 Hz, 1H), 4.02(s, 2H), 3.92(s, 2H), 3.29(s, 3H),

3.27(s, 3H), 2.40(s, 3H).

^{13}C NMR (δ = ppm): 145.2(d), 143.7(s), 142.2(s), 135.0(s), 123.3(d),
127.5(d), 124.8(d), 73.7(t), 68.1(t), 57.9(q),
21.3(q).

IR (neat, cm^{-1}): 3196, 2928, 2893, 1600, 1450, 1364, 1329, 1167,
1094, 916, 816, 706, 667.

1-Bromo-3-methoxy-2-methoxymethylpropene (88)

Tributyltin hydride (1.9 mL, 7.1 mmol) was added dropwise to neat (86) (2 g, 7.3 mmol) at 0°C. The resulting mixture was then allowed to stir at room temperature for 1 day. Distillation under reduced pressure afforded (88) (bp, 20°C/4 Torr, 1 g, 70% yield) (see characterization above).

1,1,2-Tribromo-3,3-bismethoxymethylcyclopropane (161)

To a solution of (88) (500 mg, 2.5 mmol) and cetrimide (50 mg) in bromoform (10 mL), was added aqueous sodium hydroxide (7 mL, 100%) at 4-10°C. The resulting solution was stirred for one day. Chloroform was then added to the solution, the organic layer washed twice each with water and brine, and dried over Na_2SO_4 . The resulting brown mixture was heated to 40°C under reduced pressure (0.2 Torr) to remove excess bromoform. After the residue was column chromatographed (SiO_2 , CH_2Cl_2 /hexanes 1:3), (161) (200 mg, 21% yield) was obtained.

GC/MS (m/e): 292(38), 290(46), 288(38), 257(50), 255(100), 253(46),
207(60), 205(53).

GC/MS/CI(i-butane) (m/e): 365(M+1).

^1H NMR (δ = ppm): 3.68(d, J = 12.9 Hz, 1H), 3.65(d, J = 12.9 Hz, 1H),
3.63(d, J = 10.2 Hz, 1H), 3.59(s, 1H), 3.53(d, J =
10.2 Hz, 1H), 3.39(s, 3H), 3.36(s, 3H).

$^{13}\text{C}_1$ -(161): 3.68-3.51(m), 3.39(s), 3.36(s).

^{13}C NMR (δ = ppm): 73.0, 72.7, 59.2, 58.9, 37.2, 36.2, 35.7.

$^{13}\text{C}_1$ -(161): 73.0, 72.6, 59.2, 58.9, (37.2),

36.2(^{13}C), (35.7).

$^{13}\text{C}_2$ -(161) (d_8 -THF): 73.7, 73.2, 59.1, 58.9,

38.0(^{13}C), (36.2), (35.7).

IR (GC, cm^{-1}): 2995, 2934, 2833, 1467, 1389, 1196.

Reaction of tribromide (161) with 1 equiv. of MeLi in ether (reaction 6)

To a solution of MeLi (0.95 mL, 1.0 M, 0.95 mmol) in 2 mL of ether, was slowly added a solution of (161) (50 mg, 0.14 mmol) in 1 mL of ether at the desired temperature under argon (Table 11). After 45 min, the solution was quenched with MeOH (≥ 10 equiv.). After the solution was warmed to room temperature, ether was added to the mixture. The organic solution was then washed with NH_4Cl solution and brine. The product ratio of (162) and (163) were analyzed by GC and GC/MS.

1-Bromo-3,3-bismethoxymethylcyclopropene (162)

GC/MS (m/e): 208(30), 206(25), 177(21), 175(18), 127(38), 59(100).

GC/MS/CI(NH_3) (m/e): 226, 224(M+1), 209, 207.

^1H NMR (δ = ppm): 7.30(s, 1H), 3.50(d, J = 10.5 Hz, 2H), 3.43(d, J =
10.5 Hz, 2H), 3.31(s, 6H).

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^{13}C NMR (δ = ppm): 113.1, 107.6, 75.8, 58.9, 35.4.

IR (GC, cm^{-1}): 3003, 2944, 2840, 1648, 1592, 1464, 1248, 1140.

1-Bromo-4-methoxy-3-methoxymethyl-1,2-butadiene (163)

GC/MS (m/e): 132(18), 130(22), 97(80), 52(100).

GC/MS/CI(NH_3) (m/e): 209, 207(M+1).

^1H NMR (δ = ppm): 6.12(m, 1H), 4.04(d, J = 1.8 Hz, 4H),

3.35(s, 6H).

General procedure for the reaction of tribromide (161) with excess MeLi in THF (reaction 7)

To a solution of MeLi (0.95 mL, 1.0 M, 0.95 mmol) in 2 mL of dry THF, was slowly added a solution of (161) (50 mg, 0.14 mmol) in 1 mL of dry THF at -100°C under argon. After 45 min, the solution was allowed to warm to -30°C , whereafter it was stirred at that temperature for 1 hour. A quenching agent (MeOD, MeOH or TMSCl) (> 10 equiv.) was then added at -70°C . When the solution had warmed to room temperature, ether was added to the mixture. The organic solution was washed with NH_4Cl solution and brine. The products were analyzed by GC and GC/MS.

3,3-Bismethoxymethylcyclopropene (151)

GC/MS (m/e): 127(2), 97(28), 83(49), 67(74), 53(91), 45(90), 39(100).

GC/MS/CI(NH_3) (m/e): 129(M+1).

^1H NMR (δ = ppm): 7.31(s, 1H), 3.38(s, 4H), 3.30(s, 6H).

^{13}C NMR (δ = ppm): 115.2(d), 78.3(t), 58.3(q).

^2H NMR (δ = ppm) (ether): d_1 -(151): 7.3(s).

IR (GC, cm^{-1}): 2988, 2887, 2828, 1644, 1467, 1374, 1196, 1111.

3,3-Bismethoxymethyl-1-trimethylsilylcyclopropene (181)

GC/MS (m/e): 200(1), 155(13), 89(67), 73(100).

^1H NMR (δ = ppm): 7.89(s, 1H), 3.32(AB, 2H), 3.24(AB, 2H), 3.228(s, 6H), 0.176(s, 9H).

^{13}C NMR (δ = ppm): 129.6, 80.0, 58.4, 1.26.

IR (GC, cm^{-1}): 2972, 2903, 2833, 1683.

3,3-Bismethoxymethyl-1,2-bistrimethylsilylcyclopropene (182)

GC/MS (m/e): 272(1), 241(12), 227(14), 89(75), 73(100).

^1H NMR (d_6 -acetone) (δ = ppm): 3.25(s, 4H), 3.23(s, 6H), 0.15(s, 18H).

^{13}C NMR (d_6 -acetone) (δ = ppm): 140.6, 80.6, 58.4, -1.15.

IR (GC, cm^{-1}): 2965, 2903, 2828, 1721.

2-(^{13}C -Methyl)-2-phenyl-1,3-dithiane (198)

To a solution of 2-phenyl-1,3-dithiane (7.0 g, 35.5 mmol) in 60 mL of dry THF, was slowly added n-BuLi solution (2.4 M, 14.7 mL, 35.0 mmol) in hexane at -78°C under argon, and the solution stirred at -78°C for 1 hour. Neat ^{13}C -methyl iodide (5.0 g, 35.0 mmol) was then added slowly at -78°C . After the solution had stirred at -30°C overnight, it was allowed to warm to room temperature, whereupon 25 mL of dilute HCl (3 mL 37% HCl in 100 mL of water) and 100 mL of water were added. The aqueous phase was extracted three times with 50 mL portions of CH_2Cl_2 /pentane (1:1). The combined organic layers were washed twice each with 75 mL portions of water and brine, and dried over Na_2SO_4 . After removal of the solvent, a pale yellow liquid (198) (7.0 g, 93% yield) was obtained.

GC/MS (m/e): 211(100), 195(20), 137(23), 121(65).

^1H NMR (δ = ppm): 7.94(d, J = 8.1 Hz, 2H), 7.38(t, J = 7.5 Hz, 2H),
7.26(t, 2H), 2.72-2.75(m, 4H).

^{13}C NMR (δ = ppm): (144.0), (132.5), (127.7), (126.9), (55.73(d,
 $J(\text{C-C})$ = 36 Hz), 32.7(^{13}C), (28.0), (24.6).¹⁵⁰

^{13}C -Methyl phenyl ketone (199)

To a solution of crude (198) (7.0 g, 33.2 mmol) in 200 mL of 95% methanol, were added HgCl_2 (18 g, 66.1 mmol) and red HgO (6.7 g, 30.9 mmol) at room temperature. The resulting mixture was refluxed for 5 hours. The white precipitate was filtered, and the filter cake carefully extracted twice with 50 mL portions of CH_2Cl_2 . After the resulting CH_2Cl_2 solution was concentrated to ca. 50 mL, it was stirred with aqueous NH_4OAc solution (50 g in 200 mL of water). The aqueous solution was then extracted three times with 50 mL portions of CH_2Cl_2 /pentane (1:1). The combined organic layers were washed twice with 75 mL portions of water and with 150 mL portions of brine. After drying the solution over Na_2SO_4 , and removal of the solvent, distillation afforded (199) (bp, 94°-96°C/15 Torr, 3.0 g, 74% yield).

GC/MS (m/e): 121(9), 105(100), 77(92), 51(62).

^1H NMR (δ = ppm): 8.00-7.90(m), 7.59-7.50(m), 7.5-7.40(m), 2.57(d,
 $J(\text{C-H})$ = 126 Hz).

^{13}C NMR (δ = ppm): (197.3(d, $J(\text{C-C})$ = 43 Hz)), (137.5), 133.0, 128.4,
128.2, 26.5(^{13}C).¹⁵⁰

IR (GC, cm^{-1}): 3081, 1706, 1351, 1259.

¹³C-Carbon tetrabromide

To an ice-cooled NaOBr solution prepared from NaOH (13 g, 0.32 mol), 90 mL of water and Br₂ (6.0 mL, 0.12 mol), was added neat (199) (2.7 g, 0.022 mol) dropwise. After removing the cooling bath, the emulsion was stirred for 12 hours. The aqueous solution was then extracted three times with 30 mL portions of ether. The combined organic layers were washed twice each with Na₂S₂O₄ solution (1 g in 150 mL of water) and 100 mL portions of brine, and then dried over Na₂SO₄. After concentration of the solution, it was filtered through a short pad of alumina, with hexanes as solvent. After removal of the solvent, ¹³C-carbon tetrabromide (4.4 g, 60% yield) was obtained. GC/MS (m/e): 256(29), 254(100), 252(100), 250(30), 94(37), 92(39), 81(75), 79(74).

¹³C NMR (δ = ppm): 29.8.¹⁵⁰

IR (GC, cm⁻¹): 3588, 1764.

¹³C-Bromoform

An ice-cooled NaOBr solution was prepared from NaOH (10 g, 250 mmol), 48 mL of water and Br₂ (3.83 mL, 74 mmol). This cold solution ($\leq 5^{\circ}\text{C}$) was added dropwise to the ice-cooled neat (199) (3.0 g, 25 mmol) with vigorous stirring. A slightly yellow solution resulted while the temperature in the reaction flask rose from 6°C to 11°C. The cooling bath was removed and the solution was allowed to warm to room temperature. A colorless emulsion resulted. Then 30 mL of ether was added to the solution. The aqueous layer was extracted three times with 30 mL portions of ether. The combined organic

layers were washed with $\text{Na}_2\text{S}_2\text{O}_4$ solution (1 g in 150 mL of water) once and twice with 100 mL portions of brine, and then dried over Na_2SO_4 . After removal of the solvent and distillation under reduced pressure, ^{13}C -bromoform (bp, $46^\circ\text{C}/14$ Torr, 3.8 g, 60% yield) was obtained.

GC/MS (m/e): 257(0.9), 255(0.9), 176(51), 174(100), 172(40).

^1H NMR (δ = ppm): 6.80(d, $J(\text{C-H}) = 204$ Hz).¹⁵⁰

^{13}C NMR (δ = ppm): 9.67.¹⁵⁰

IR (GC, cm^{-1}): 3040, 1144.

Reaction of tribromide $^{13}\text{C}_2$ -(161) with MeLi at $\geq -20^\circ\text{C}$ (reaction 8)

In a flame dried 8-mm NMR tube was placed a solution of $^{13}\text{C}_2$ -(161) (50 mg, 0.14 mmol) in 1 mL of d_8 -THF. MeLi (0.1 mL, 1.1 M, 0.11 mmol) was then added to the solution at -100°C under argon. The resulting solution was subjected to ^{13}C NMR analysis. The resonances of C_2 in $^{13}\text{C}_2$ -(162) was observed. After the solution was allowed to warmed to -20°C , more MeLi (0.3 mL, 3.3 mmol) was added to the solution via syringe. The ^{13}C NMR spectrum showed a mixture of $^{13}\text{C}_1$ -(185), $^{13}\text{C}_2$ -(185) and ^{13}C -(186).

1-Bromo-3,3-bismethoxymethyl-2- ^{13}C -cyclopropene $^{13}\text{C}_2$ -(162)

^{13}C NMR (δ = ppm): 114.6(^{13}C , $J(\text{C-H}) = 232$ Hz), (107.6), 76.2, 58.9, (35.4).

A mixture of 1-methyl-3,3-bismethoxymethylcyclopropene (185) and 1,2-dimethyl-3,3-bismethoxymethylcyclopropene (186)

GC-MS (m/e): (185): 127(5), 97(100).

^{13}C -(185): 128(4), 112(11), 98(100), 82(47), 80(45).

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(186): 111(100), 96(12), 81(10), 79(12), 77(18).

^{13}C -(186): 112(100), 96(23), 82(15), 80(24), 78(30).

GC-MS-CI(NH_3) (m/e): (185): 143(M+1).

(186): 157(M+1).

^1H NMR (δ =ppm): (a mixture of (185) and (186)): 6.70(s), 3.37(s),
3.28(s), 3.27(s), 2.12-2.11(m), 1.99(s).

Reaction of tribromide ^{13}C -(161) with MeLi: NMR experiment

$\text{Me}^{6.7}\text{Li}$ was placed in a flame dried flask under argon. The solvent was evaporated in vacuo (0.25 Torr) at room temperature. The resulting solid was dissolved at -78°C in 1 mL of d_8 -THF. After the resulting solution was cooled to -100°C , a solution of $^{13}\text{C}_1$ - or $^{13}\text{C}_2$ -(161) (50 mg, 0.14 mmol) in 1 mL of d_8 -THF was added via syringe. The solution was then allowed to warm to -30°C for 1 hour. The solution was transferred to a flame dried 8-mm NMR tube via a double-tipped needle. Then the red mixture was subjected to low temperature NMR analysis

REFERENCES

1. Schlenk, W.; Holtz, J. *Chem. Ber.* 1917, 50, 262.
2. Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974.
3. Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982, p 43.
4. Oliver, J. P. *Adv. Organomet. Chem.* 1977, 15, 235.
5. Coates, G. E., Green, M. L. H., Wade, K. *Organometallic Compounds*; Methuen: London, 1967, Vol. 1, Chap. 1.
6. a) Gilman, H.; Morton, J. W., Jr. *Org. React.* 1954, 8, 158.
b) Jones, R. G.; Gilman, H. *Org. React.* 1951, 6, 339.
7. Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988.
8. a) King, R. B., Eisch, J. J., Eds.; *Organometallic Syntheses*; Elsevier: New York, 1986, Vol. 3.
b) King, R. B., Eisch, J. J., Eds.; *Organometallic Syntheses*; Elsevier: New York, 1988, Vol. 4.
9. a) Krief, A. *Tetrahedron* 1980, 36, 2531.
b) Gschwerd, H. W.; Rodriguez, R. *Org. React.* 1976, 26, 1.
10. West, R. *Adv. Chem. Ser.* 1974, 130, 211.
11. a) Klein, J. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978, p 343.
b) Klein, J. *Tetrahedron* 1983, 39, 2733.
12. Maercker, A.; Theis, M. *Top. Curr. Chem.* 1987, 138, 1.

13. Setzer, W.; Schleyer P. v. R. *Adv. Organomet. Chem.* 1985, 24, 153.
14. a) O'Brien, D. H. In *Comprehensive Carbanion Chemistry*; Buncl, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980, vol. 1.
b) Fraenkel, G. In *Lithium: Current Applications in Science, Medicine, and Technolgy*; Bach, R. O., Ed.; Wiley: New York, 1985.
15. a) Schleyer, P. v. R. *Pure Appl. Chem.* 1984, 56, 151.
b) Schleyer, P. v. R. *Pure Appl. Chem.* 1983, 55, 355.
16. a) Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* 1977, 15, 154.
b) Szwarc, M., Ed.; *Ions and Ion-Pairs in Organic Reactions*; Wiley: London, 1972, Vol. 1.
c) Szwarc, M., Ed.; *Ions and Ion-Pairs in Organic Reactions*; Wiley: London, 1974, Vol. 2.
d) Szwarc, M. *Prog. Phys. Org. Chem.* 1968, 6, 323.
17. *Dictionary of organometallic compounds*; Chapman and Hall Ltd.: London, vols. 1-3 and supplements.
18. Wardell, J. L. In *Organometallic Chemistry*; Stone, F. G. A., Abel, E. W., Eds.; Royal Society of Chemistry: London, 1980, vol. 9, 1.
20. a) Schleyer, P. v. R.; Würthwein, E. -U.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* 1983, 105, 5930.
b) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1984, 106, 1856.
c) Houk, K. N.; Rondan, N. G.; Schleyer, P. v. R.; Kaufmann,

- E.; Clark, T. *J. Am. Chem. Soc.* 1985, 107, 2827.
- d) Kaufmann, E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1985, 107, 5560.
21. Streitwieser, A., Jr. *Acc. Chem. Res.* 1984, 17, 353.
22. Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* 1976, 98, 5419.
23. Nilssen, E. W.; Skancke, A. *J. Organomet. Chem.* 1976, 116, 251.
24. Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* 1976, 98, 4332.
25. a) Manceron, L.; Andrews, L. *J. Am. Chem. Soc.* 1985, 107, 563.
b) Fracnkel, G.; Halasa, A. F.; Mochel, V.; Stumpe, R.; Tate, D. *J. Org. Chem.* 1985, 50, 4563.
c) Günther, H.; Moskau, D.; Dujardin, R.; Maercker, A. *Tetrahedron Lett.* 1986, 27, 2251.
26. a) Maercker, A.; Thies, M. *Angew. Chem. Int. Ed. Engl.* 1984, 23, 995.
b) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* 1985, 107, 2969.
27. a) Kawa, H.; Chinn, J. W., Jr.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* 1984, 24, 1664.
b) Edlund, U.; Lejon, T.; Venkatachalam, T. K.; Buncel, E. J. *Am. Chem. Soc.* 1985, 107, 6408.
28. Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* 1979, 101, 6814.
29. Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1984,

- 106, 5818.
30. Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* 1985, **89**, 62.
 31. Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* 1981, **21**, 260.
 32. Jemmis, E. D.; Schleyer, P. v. R.; Pople, J. A. *J. Organomet. Chem.* 1978, **154**, 327.
 33. a) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* 1955, **23**, 315.
b) Kalinowski, H. -O.; Kessler, H. *Top. Stereochem.* 1973, **7**, 295.
 34. a) Buenker, R. J.; Peyerimhoff, S. D.; Hsu, H. L. *Chem. Phys. Lett.* 1971, **11**, 65.
b) Wood, M. H. *Chem. Phys. Lett.* 1974, **14**, 239.
c) Bingnam, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, **97**, 1294.
 35. a) Salem, L.; Stohrer, W. D. *J. Chem. Soc., Chem. Commun.* 1975, **15**, 140.
b) Salem, L.; Leforestier, C.; Segal, G.; Wetmore, R. *J. Am. Chem. Soc.* 1975, **97**, 479.
 36. Almmon, H. L.; Wheeler, G. L. *J. Am. Chem. Soc.* 1975, **97**, 2326.
 37. a) Sakurai, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* 1980, **21**, 3077.
b) Sakurai, H.; Tobita, H.; Kira, M.; Nakadaira, Y. *Angew. Chem. Int. Ed. Engl.* 1980, **19**, 620.

- c) Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* 1982, 104, 300.
- d) Sakurai, H.; Nakadaira, Y.; Tobita, H. *Chem. Lett.* 1982, 771.
38. Warner, P. M. *Chem. Rev.* 1989, 89, 1067.
39. Nagase, S.; Morokuma, K. *J. Am. Chem. Soc.* 1978, 100, 1661.
40. Laidig, W. D.; Schaefer III, H. F. *J. Am. Chem. Soc.* 1979, 101, 7184.
41. Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R. *Israel J. Chem.* 1980, 20, 43.
42. Schleyer, P. v. R.; Kaufmann, E.; Kos, A. J.; Clark, T.; Pople, J. A. *Angew. Chem. Int. Ed. Engl.* 1986, 25, 169.
43. a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1979, 101, 2848.
- b) Schleyer, P. v. R.; Chandrasekhar, J.; Kos, A. J.; Clark, T.; Spitznagel, G. W. *J. Chem. Soc., Chem. Commun.* 1981, 21, 882.
44. Schleyer, P. v. R.; Kaufmann, E.; Spitznagel, G. W. *Organometallics* 1986, 5, 79.
45. Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1984, 106, 4412.
46. Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Jorgensen, W. L. *Tetrahedron Lett.* 1976, 3923.
47. Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R.; Gleiter, R.; Fihbch, U.; Pople, J. A. *J. Am. Chem. Soc.* 1981, 103, 4996.

48. Jemmis E. D.; Poppinger, D.; Schleyer, P. v. R.; Pople, J. A. J. *Am. Chem. Soc.* 1977, 99, 5796.
49. Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. J. *Organomet. Chem.* 1978, 150, 1.
50. Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. J. *Am. Chem. Soc.* 1983, 105, 7617.
51. a) Rausher, G.; Clark, T.; Poppinger, D.; Schleyer, P. v. R. *Angew. Chem. Int. Ed. Engl.* 1978, 17, 276.
b) Ritchie, J. P. J. *Am. Chem. Soc.* 1983, 105, 2083.
c) Disch, R. L.; Schulman, J. M.; Ritchie, J. P. J. *Am. Chem. Soc.* 1984, 106, 6246.
52. Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Angew. Chem. Int. Ed. Engl.* 1984, 23, 620.
53. West, R.; Rochow, E. G. J. *Org. Chem.* 1953, 18, 1739.
54. Barluenga, J.; Rodriguez, M. A.; Campso, P. J.; Asensio, G. J. *Am. Chem. Soc.* 1988, 110, 5567.
55. Ash III, A. J.; Drone, F. J. *Organometallics* 1985, 4, 1478.
56. Jutzi, P.; Baungärtner, J.; Schraut, W. J. *Organomet. Chem.* 1977, 132, 333.
57. a) van Eikema Hommes, N. J. R.; Bickelhaupt, F.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* 1988, 107, 393.
b) van Eikema Hommes, N. J. R.; Bickelhaupt, F.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* 1987, 106, 514.
58. Zieglere, K.; Nagel, K.; Patheiger, M. Z. *Anorg. Allg. Chem.* 1955, 282, 345.

59. a) Kawa, H.; Manley, B. C.; Lagow, R. J. *J. Am. Chem. Soc.* 1985, 107, 5313.
b) Chauhan, H. P. S.; Kawa, H.; Lagow, R. J. *J. Org. Chem.* 1986, 51, 1632.
60. a) Kauffmann, T. *Top. Curr. Chem.* 1980, 92, 109.
b) Kauffmann, T. *Angew. Chem. Int. Ed. Engl.* 1982, 21, 410.
61. Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* 1978, 144, 1.
62. Mitchel, T. N.; Amamria, A. *J. Organomet. Chem.* 1983, 252, 47.
63. Maercker, A.; Theis, M.; Kos, A. J.; Schleyer, P. v. R. *Angew. Chem. Int. Ed. Engl.* 1983, 22, 733.
64. Maercker, A.; Theis, M. *Organometallic Syntheses* 1986, 3, 378.
65. a) Maercker, A.; Dujardin, R. *Angew. Chem. Int. Ed. Engl.* 1984, 23, 224.
b) Maercker, A.; Dujardin, R. *Organometallic Syntheses* 1986, 3, 356.
66. Maercker, A.; Graule, T.; Demuth, W. *Angew. Chem. Int. Ed. Engl.* 1987, 26, 1032.
67. Sekiguchi, A.; Nakanishi, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* 1989, 111, 3748.
68. Maercker, A.; Dujardin, R. *Angew. Chem. Int. Ed. Engl.* 1984, 24, 571.
69. Maercker, A.; Graule, T.; Girreser, U. *Angew. Chem. Int. Ed. Engl.* 1986, 25, 167.
70. a) Goldstein, M. J.; Wenzel, T. T.; Whittaker, G.; Yates, S. F. *J. Am. Chem. Soc.* 1982, 104, 2669.

- b) Goldstein, M. J.; Wenzel, T. T. *J. Chem. Soc.; Chem. Commun.* 1984, 1654; 1655.
71. Hoell, D.; Lex, J.; Müllen, K. *J. Am. Chem. Soc.* 1986, 108, 5983.
72. a) West, R.; Carney, P. A.; Mines, I. C. *J. Am. Chem. Soc.* 1965, 87, 3788.
- b) West, R.; Jones, P. C. *J. Am. Chem. Soc.* 1969, 91, 6156.
73. Applequist, D. E.; Saurborn, E. G. *J. Org. Chem.* 1972, 37, 1676.
74. Langer, A. W. *Adv. Chem. Ser.* 1974, 130.
75. Klein, J.; Medlik-Balan, A. *J. Chem. Soc.; Chem. Commun.* 1974, 877.
76. Klein, J.; Medlik-Balan, A.; Meyer, A. Y.; Chorev, M. *Tetrahedron* 1976, 32, 1839.
77. Bates, R. B.; Beavers, W. A.; Greene, M. G.; Klein, J. H. *J. Am. Chem. Soc.* 1974, 96, 5640.
78. Trepka, W. J.; Favre, J. A.; Sonnenfeld, R. J. *J. Organomet. Chem.* 1973, 55, 221.
79. Kulik, W.; Verkruijsse, H. D.; de Jong, R. L. P.; Hommes, H.; Brandsma, L. *Tetrahedron Lett.* 1983, 2203.
80. Feit, B. A.; Haag, B.; Schmidt, R. R. *J. Org. Chem.* 1987, 52, 5825.
81. a) Lafont, D.; Hoch, M.; Schmidt, R. R. *J. Carbohydr. Chem.* 1986, 5, 601.
- b) Feit, B. A.; Melamed, U.; Speer, H.; Schmidt, R. R. *J. Chem. Soc.; Perkin Trans. I.* 1984, 775.

82. Vollhardt, J.; Gais, H. -J.; Lukas, K. L. *Angew. Chem. Int. Ed. Engl.* 1985, 24, 696.
83. Gais, H. -J.; Vollhardt, J.; Günther, H.; Moskau, D.; Lindner, H. J.; Braun, S. J. *Am. Chem. Soc.* 1988, 110, 978.
84. Schlüter, A. -D.; Huber, H.; Szeimies, G. *Angew. Chem. Int. Ed. Engl.* 1985, 24, 404.
85. Chung, C.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* 1972, 1078.
86. Landro, F. J.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Organomet. Chem.* 1983, 249, 1.
87. Shimp, L. A.; Lagow, R. J. *J. Am. Chem. Soc.* 1979, 101, 2214.
88. Morrison, J. A.; Chung, C.; Lagow, R. J. *J. Am. Chem. Soc.* 1975, 97, 5015.
89. Shimp, L. A.; Lagow, R. J. *J. Am. Chem. Soc.* 1973, 95, 1343.
90. van Eikema Hommes, N. J. R.; Bickelhaupt, F.; Klumpp, G. W. *Angew. Chem. Int. Ed. Engl.* 1988, 27, 1083.
91. Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1987, 109, 970.
92. Mulvaney, J. E.; Newton, D. J. *J. Org. Chem.* 1969, 34, 1936.
93. Bauer, W.; Feigel, M.; Müllen, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1988, 110, 6033.
94. Crowley, P. J.; Leach, M. R.; Meth-Cohn, O.; Wakefield, B. J. *Tetrahedron Lett.* 1986, 2909.
95. Atwood, J. L.; Fjeldberg, T.; Lappert, M. F.; Luong-Thi, N. T.; Shakir, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* 1984, 1163.

96. Brown, T. L. *Pure Appl. Chem.* 1977, 15, 235.
97. Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* 1983, 66, 308.
98. Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* 1987, 6, 2371.
99. Schumann, U.; Kopf, J.; Weiss, E. *Angew. Chem. Int. Ed. Engl.* 1985, 24, 215.
100. Quirk, R. D.; Kester, D. E. *J. Organomet. Chem.* 1977, 127, 111.
101. Fraenkel, G.; Henricks, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. *J. J. Am. Chem. Soc.* 1980, 102, 3345.
102. Ten Hoedt, R. W. M.; van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* 1979, 170, 131.
103. Vos, M.; de Kanter, F. J. J.; Schakel, M.; van Eikema Hommes, N. J. R.; Klumpp, G. W. *J. Am. Chem. Soc.* 1987, 109, 2187.
104. Moene, W.; Vos, M.; de Kanter, F. J. J.; Klumpp, G. W. *J. Am. Chem. Soc.* 1989, 111, 3463.
105. Smeets, W. J. J.; Spek, A. L.; v. D. Zeyden, A. A. H.; van Koten, G. *Acta Crystallogr.* 1987, C43, 1429.
106. Geurink, P. J. A.; Klumpp, G. W. *J. Am. Chem. Soc.* 1986, 108, 538.
107. Harder, S.; Boersma, J.; Brandsma, L.; Heteren, A. v.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1988, 110, 7802.
108. Dietrich, H.; Mahdi, W.; Storck, W. *J. Organomet. Chem.* 1988, 349, 1.

109. Thoennes, D.; Weiss, E. *Chem. Ber.* 1978, 111, 3157.
110. a) Harder, S.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1987, C43, 1535.
- b) Bauer, W.; Klusener, P.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics* 1988, 7, 552.
111. Jastrzebski, J. T. B. H.; van Koten, G. J. *Organomet. Chem.* 1983, 246, C75.
112. Mckeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* 1968, 90, 3244.
113. Wehrli, F. W. *J. Magn. Reson.* 1978, 30, 193.
114. Avent, A. G.; Eaborn, C.; El-Kheli, M. N. A.; Molla, M. E.; Smith, J. D.; Sullivan, A. C. *J. Am. Chem. Soc.* 1986, 108, 3854.
115. Moskau, D.; Brauers, F.; Günther, H.; Maercker, A. *J. Am. Chem. Soc.* 1987, 109, 5532.
116. Thomas, R. D.; Jensen, R. M.; Young, T. C. *Organometallics* 1987, 6, 565.
117. Karplus, M.; Pople, J. A. *J. Chem. Phys.* 1963, 38, 2803.
118. a) Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J.; Steinfink, H.; Yannoni, C. S. *Inorg. Chem.* 1984, 23, 3717.
- b) Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J.; Kendrick, R. D.; Yannoni, C. S. *Inorg. Chim. Acta* 1985, 96, L75.
119. Bernard, J.; Schnieders, C.; Müllen, K. *J. Chem. Soc., Chem.*

Commun. 1984, 12.

120. Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* 1987, 109, 1782.
121. Rajca, A.; Streitwieser, A., Jr.; Tolbert, L. M. *J. Am. Chem. Soc.* 1987, 109, 1790.
122. a) Dietrich, H. *Acta Crystallogr.* 1963, 16, 681.
b) Dietrich, H. *J. Organomet. Chem.* 1981, 205, 291.
123. a) Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* 1964, 2, 197.
b) Weiss, E.; Hencken, G. *J. Organomet. Chem.* 1970, 21, 265.
c) Köster, H.; Thönnies, D.; Weiss, E. *J. Organomet. Chem.* 1978, 160, 1.
124. a) Lappert, M. F.; Raston, C. L.; Shelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1982, 14.
b) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1983, 1323.
125. a) Amstutz, R.; Seebach, D.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Angew. Chem.* 1980, 92, 59.
b) Amstutz, R.; Dunitz, J. D.; Seebach, D. *Angew. Chem.* 1981, 93, 487.
c) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* 1981, 64, 2617.
126. Klumpp, G. W.; Geurink, P. J. A.; Spek, A. L.; Duisenberg, A. *J. M. J. Chem. Soc., Chem. Commun.* 1983, 814.
127. a) Butler, I. R.; Cullen, W. R.; Reglinski, J.; Rettig, S. J. *J. Organomet. Chem.* 1983, 249, 183.

- b) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* 1983, 105, 5320.
128. Neugebauer, W.; Geiger, G. A. P.; Kos, A. J.; Stezowski, J. J.; Schleyer, P. v. R. *Chem. Ber.* 1985, 118, 1504.
129. Pierce, J. S.; Lunsford, C. D.; Raiford, R. W., Jr.; Rush, J. L.; Riley, D. W. *J. Am. Chem. Soc.* 1951, 73, 2595.
130. Araki, Y.; Nagasawa, J.; Ishtdo, Y. *J. Chem. Soc.* 1981, 12.
131. a) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* 1975, 1373.
- b) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* 1972, 3769.
132. Wilson, S. R.; Georgiadis, G. M.; Khatri, H. N.; Bartmess, J. E. *J. Am. Chem. Soc.* 1980, 102, 3377.
133. Majewski, M.; *Tetrahedron Lett.* 1988, 4057.
134. Köbrich, G. *Angew. Chem. Int. Ed. Engl.* 1972, 11, 473.
135. Buxton, S. R.; Holm, K. H.; Skattebol, L. *Tetrahedron Lett.* 1987, 2167.
136. Wakefield, B. J. In Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 7, p 1.
137. a) Castle, R. B.; Matteson, D. S. *J. Am. Chem. Soc.* 1968, 90, 2194.
- b) Matteson, D. S.; Hagelee, L. A. *J. Organomet. Chem.* 1975, 93, 21.
- c) Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* 1978, 152, 1.
138. Cossy, J.; Pete, J. P. *Tetrahedron Lett.* 1986, 573.

139. Maercker, A. *Angew. Chem. Int. Ed. Engl.* 1987, 26, 972.
140. a) Powell, J. W.; Whiting, M. C. *Tetrahedron* 1959, 305.
b) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* 1959, 81, 5512.
c) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* 1960, 82, 1002.
d) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* 1961, 83, 3159.
141. a) Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc.; Perkin Trans. I* 1986, 1845.
b) Baird, M. S. *Tetrahedron Lett.* 1984, 4829.
c) Baird, M. S.; Al-Dulayymi, J. *Tetrahedron Lett.* 1988, 6147.
142. Kuivila, H. G. *Synthesis* 1970, 499.
143. Baird, M. S.; Nethercott, W.; Slowey, P. D. *J. Chem. Res.(s)* 1985, 370.
144. Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* 1983, 605.
145. Maier, G.; Wolf B. *Synthesis* 1985, 871.
146. a) Lukina, M. Yu.; Rudavshevskaya, T. Y.; Nesmeyanova, O. A. *Dokl. Akad. Nauk SSSR* 1970, 190, 1109.
b) Lehmkuhl, H; Mehler, L. *Liebigs Ann. Chem.* 1978, 1841.
c) Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Dyachenko, A. I.; Saviilova, S. F.; Nefedov, O. M. *Synthesis*, 1982, 296.
147. Köster, R.; Arora, S.; Binger, P. *Angew. Chem. Int. Ed. Engl.* 1969, 8, 205.
148. Stoll, A. T.; Negishi, E. -I. *Tetrahedron Lett.* 1985, 26, 5671.

149. a) Magid, R. M.; Welch, J. G. *J. Am. Chem. Soc.* 1968, *90*,
5211.
- b) Fisher, F.; Applequist, D. A. *J. Org. Chem.* 1965, *30*, 2089.
- c) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* 1963, *83*,
2015.
150. Siegel, H.; Seebach, D. *J. Labelled Compd. & Radiopharm.* 1980,
279.

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