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REACTIONS OF 2,3-BIS(METHYLENE)BUTADIENE DIANION

THE UNIVERSITY OF ARIZONA

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REACTIONS OF 2,3-BIS(METHYLENE)BUTADIENE DIANION

by

Jim White

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A Thesis Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements  
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 8 3

STATEMENT BY AUTHOR

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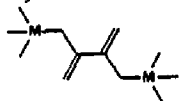
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## ABSTRACT

2,3-Bis(methylene)butadiene dianion was prepared from 2,3-dimethyl-1,3-butadiene and Lochmann's base. This dianion was reacted with a number of electrophiles to generate various symmetrically substituted 1,3-butadienes. Included were reactions with  $\alpha,\omega$ -dibromoalkanes to generate 1,2-bis(methylene)cycloalkanes with ring sizes five through fourteen and sixteen, and in some cases corresponding dimers and trimers.

It was surmised that three competing mechanisms were involved in substitution reactions with 2,3-bis(methylene)butadiene dianion:  $S_N2$ ,  $S_{RN}1$  and halogen-metal exchange.

A number of interesting side products were obtained in these reactions, all resulting from base-catalyzed cleavage of the solvent, tetrahydrofuran.

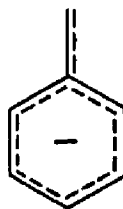
The conformations of the dienes were analyzed using UV and  $^1H$  NMR spectroscopy. 1,2-Bis(methylene)cycloalkanes display cisoid conformations in small rings and transoid conformations in larger rings. The corresponding dimers and trimers permitted study of the change in conformations from "acyclic transoid" in very large rings to "cyclic transoid" in smaller rings.

## INTRODUCTION

Allylic and benzylic anions, generated by proton abstraction from alkenes and alkylbenzenes, are known to be excellent synthons [1]. These anions are characterized by having an all carbon skeleton with delocalization of charge. The simplest examples are allyl anion 2 and benzyl anion 3 [2, 3].



2



3

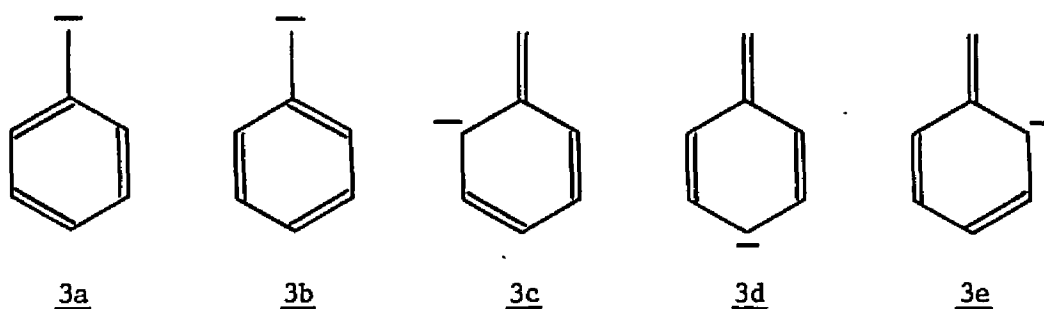
This charge delocalization can be visualized through resonance structures 2a and 2b for allyl anion and resonance structures 3a-e for benzyl anion.



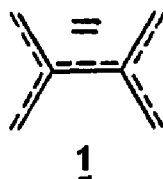
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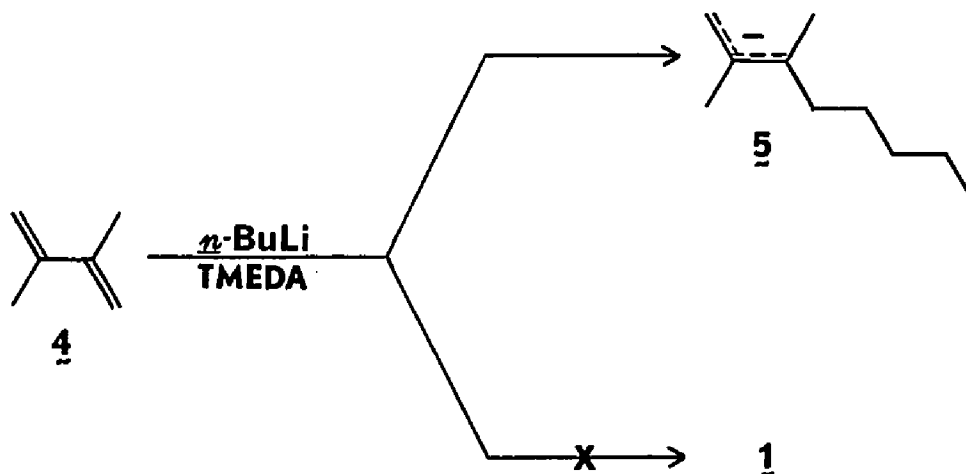
2b



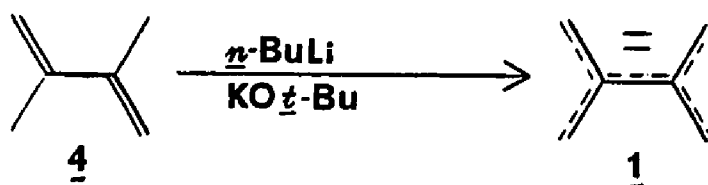
A number of benzylic and allylic dianions have been recently synthesized [4-6]. Of these, 2,3-bis(methylene)butadiene dianion 1 will be the focal point of this work.



Synthesis of these carbanions requires a strong metalating system. Unconjugated olefins are commonly metalated using n-butyllithium/tetramethylethylenediamine (TMEDA). However, conjugated dienes cannot be metalated using this system, as allylic proton abstraction is much slower than addition to the conjugated diene [5]. Dianion 1 cannot be generated from 2,3-dimethyl-1,3-butadiene (4) using n-BuLi/TMEDA; monoanion 5 is instead the product [6]. Nevertheless, dimetalation of 4 is achieved using Lochmann's base



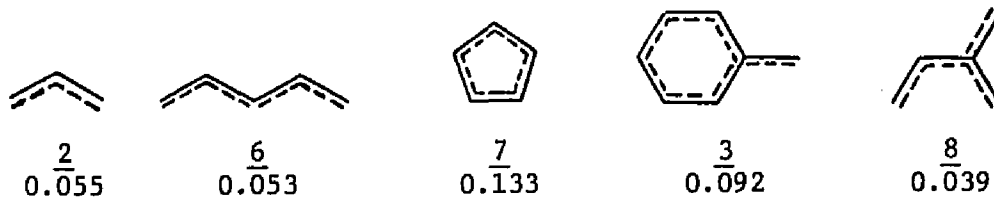
( $n$ -butyllithium/potassium  $t$ -butoxide) [6-8]. Presumably, this metalating system works with  $\text{KO}t\text{-Bu}$  acting as the kinetic base and the butyllithium acting as the thermodynamic base. Dianion **1** is generated in 73% yield with this system [6]. Orange dianion **1** precipitates as a dipotassium salt and lithium  $t$ -butoxide is washed away with pentane.



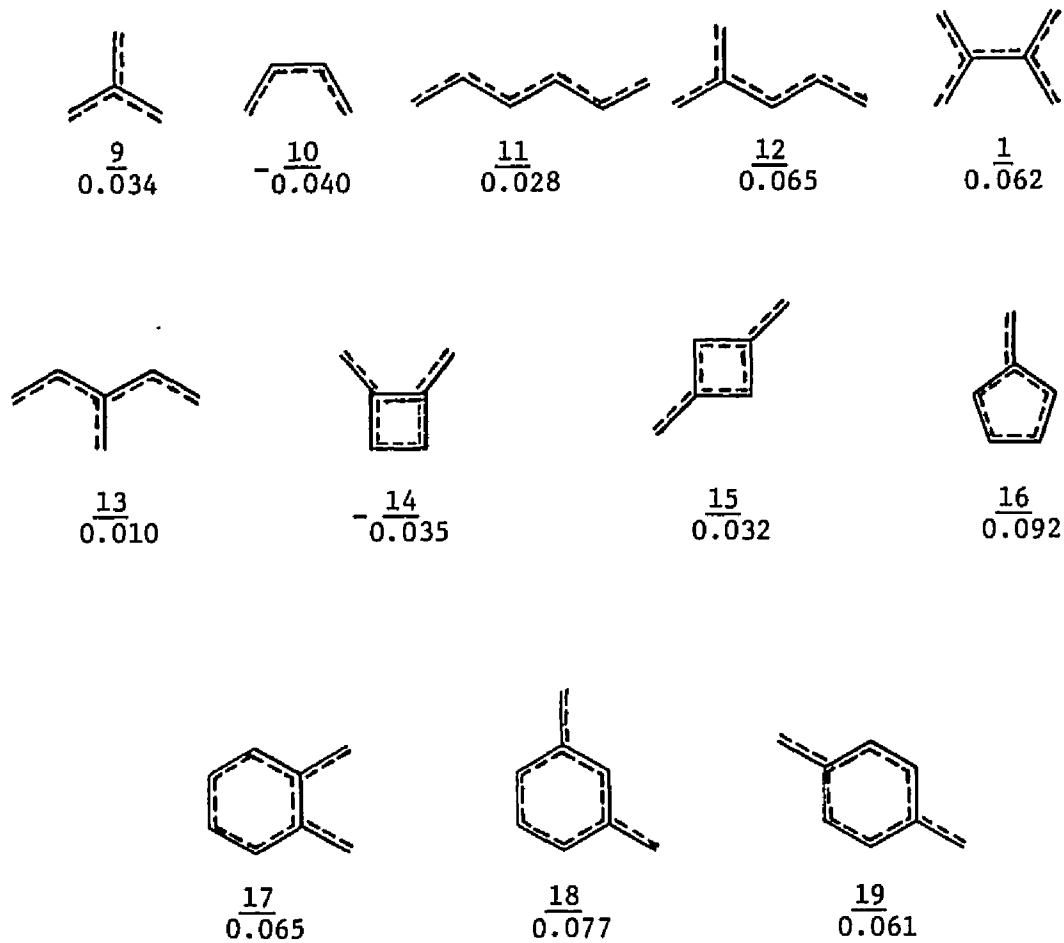
The relative stabilities of a number of allylic and benzylic carbanions have been calculated [9]. These have been expressed in terms of resonance energy per atom (REPA). The REPA's of a number of mono and dianions are given in Table 1 with units in terms of the Hückel parameter  $\beta$ .

Table 1. REPA's of Selected Carbanions (in  $\beta$  Units)

## Monoanions:



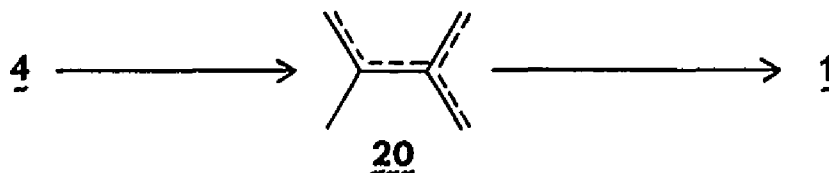
## Dianions:





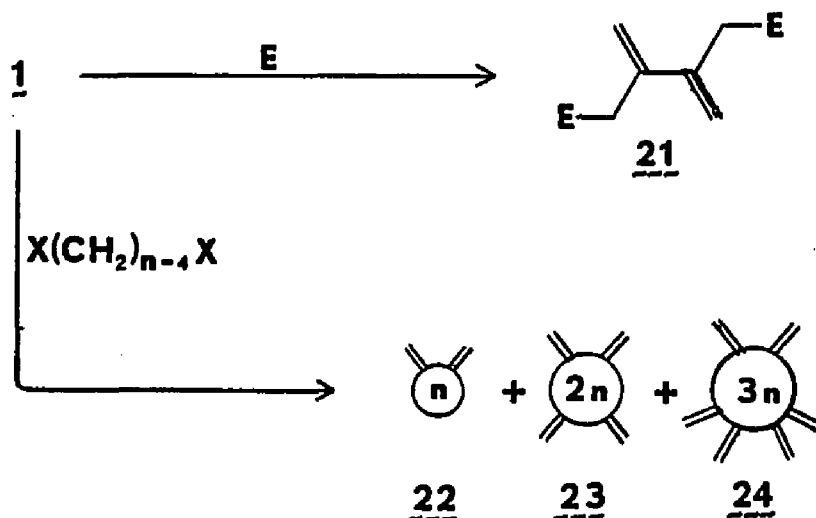
Dianions 1 [6], 11 and 12 [5] can be thought of as two allyl anions, linked middle to middle (1), end to end (11), and middle to end (12) through a  $\sigma$  bond. Stability of these dianions relative to allyl anion (2) is a function of the extent of  $\pi$ -delocalization across this bond. Dianion 11 is less stable than 2, while dianions 1 and 12 are more stable than 2.

Formation of dianion 1 must proceed via intermediate monoanion 20. However, a monoanion 20 has not been prepared in high concentration. When one equivalent of base is reacted with 4, no monoanion 20 is found, but instead half an equivalent of dianion 1. Monoanion 20 is very similar to isoprene anion 8 and would be expected to have an REPA very close to that of 8 for its  $\pi$ -system. In terms of REPA dianion 1 is 0.024  $\beta$  more stable than monoanion 8. This difference shows that dianion 1 is considerably more stable than monoanion 20. Therefore, monoanion 20 cannot be generated in high concentration as it would disproportionate to parent diene 4 and dianion 1. This is consistent with what is observed.

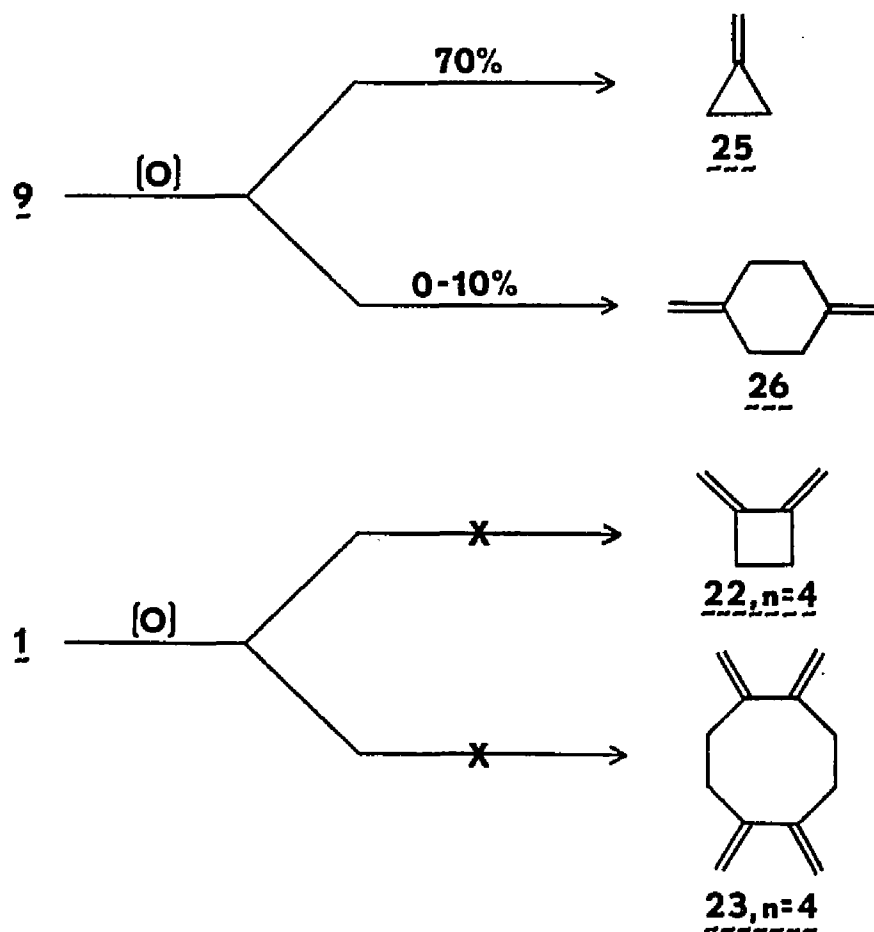


Dianion 1 reacts with electrophiles to yield symmetrical 2,3-disubstituted-1,3-butadienes 21 [6, 10]. Reaction of dianion 1 with  $\alpha,\omega$ -dihaloalkanes generates 1,2-bis(methylene)cycloalkanes 22; the

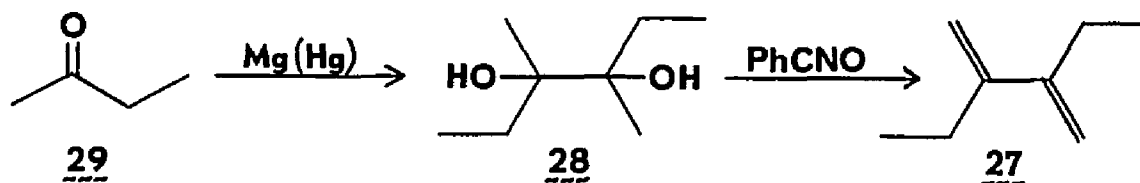
corresponding dimers 23 and trimers 24 might have been expected but were not found.



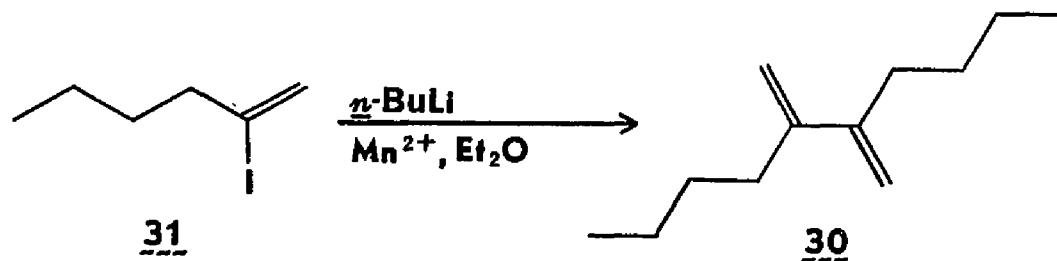
Oxidation of dianion 1 would be expected to produce 1,2-bis(methylene)cyclobutane 22,  $n=4$  in high yield analogously to the oxidation of isobutylene dianion 9 to methylenecyclopropane 25 in 70% yield [11], possibly accompanied by the dimeric product 23,  $n=4$ . Oxidation of dianion 9 under a variety of conditions gave a maximum of 10% yield of the analogous dimer 26 [11, 12]. However, no volatile products were reported from the oxidation of 1 [10]. In general, the syntheses of the compounds just discussed from dianion 1 are superior to previous preparations using other methods, and we wished to see if 1 was a superior precursor to certain other 2,3-disubstituted-1,3-butadienes.



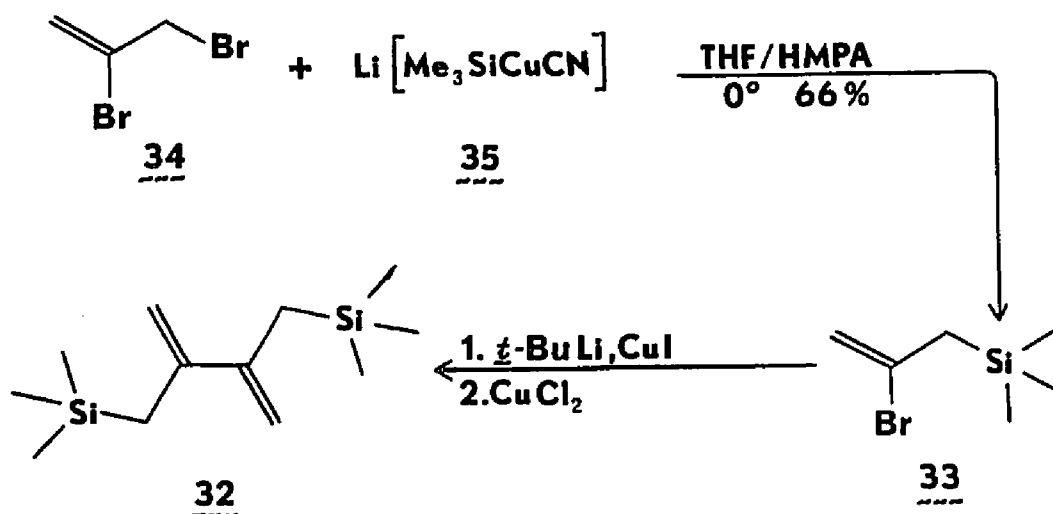
For example, 3,4-bis(methylene)hexane (27), which might be readily prepared from the methylation of dianion 1, had previously been prepared in 28% yield with a mixture of isomers from the dehydration of a mixture of *dl*- and *meso*-pinacol 28, which is prepared from 2-butanone (29) [13].



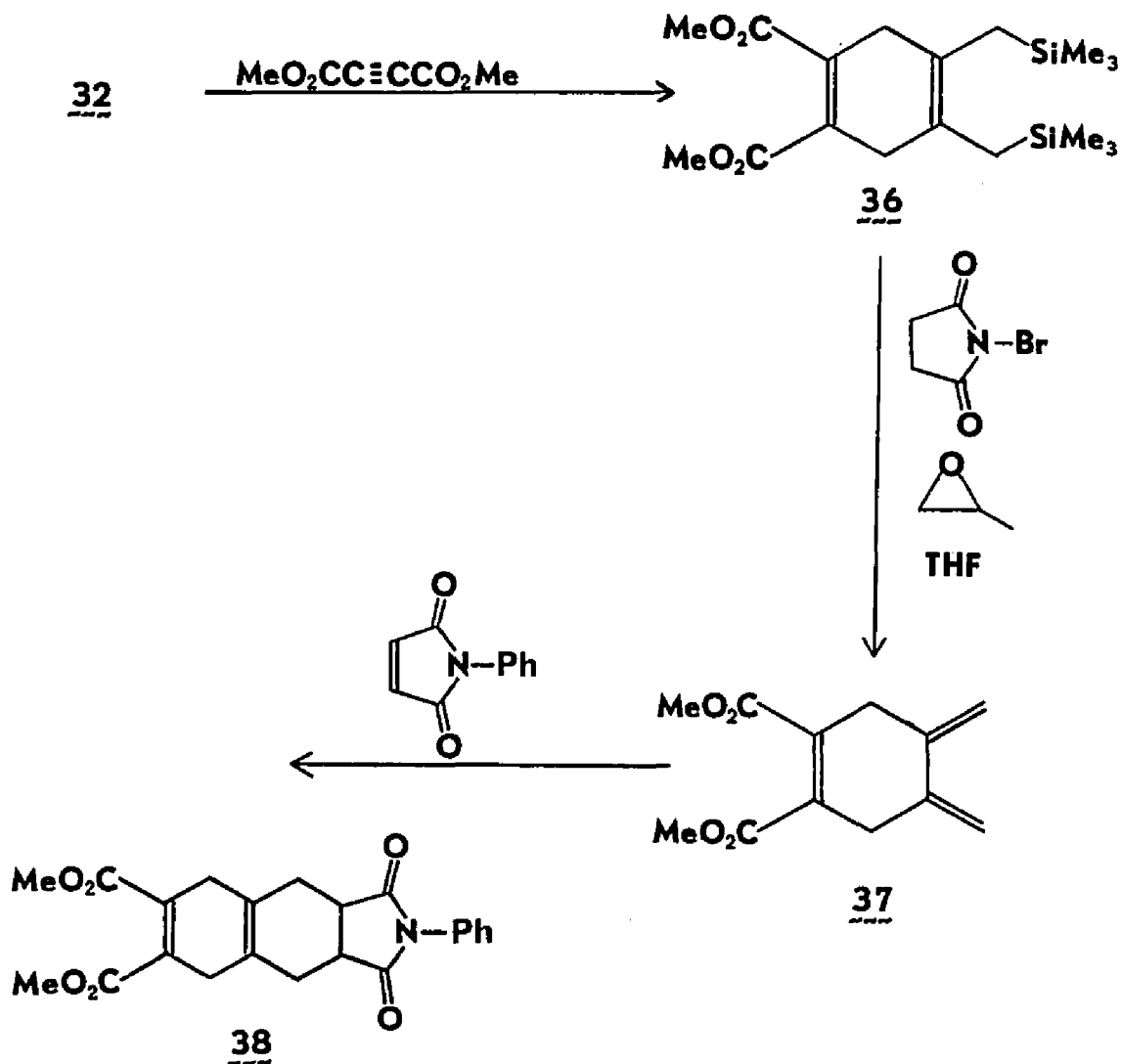
5,6-Bis(methylene)decane (30), which might be readily prepared from butylation of dianion 1, had been previously prepared in 70% yield by the coupling of 2-iodo-1-hexene (31) with *n*-butyllithium and catalytic amounts of manganese (II) salts [14].



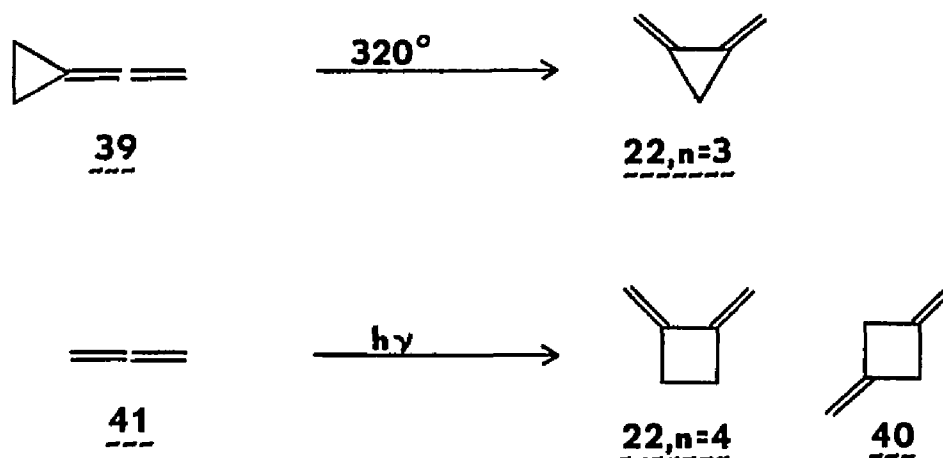
2,3-Bis(trimethylsilylmethyl)-1,3-butadiene (32), which should be easily made from trimethylsilylation of dianion 1, has been prepared in 70-88% yield from (2-bromoallyl)-trimethylsilane (33) by oxidative coupling of its corresponding cuprate [15]. The high yield for this reaction is deceptive because the starting material 33 is prepared in only 66% yield from the reaction of 2,3-dibromopropene (34) with lithium (trimethylsilyl)cyanocuprate (35) [16].



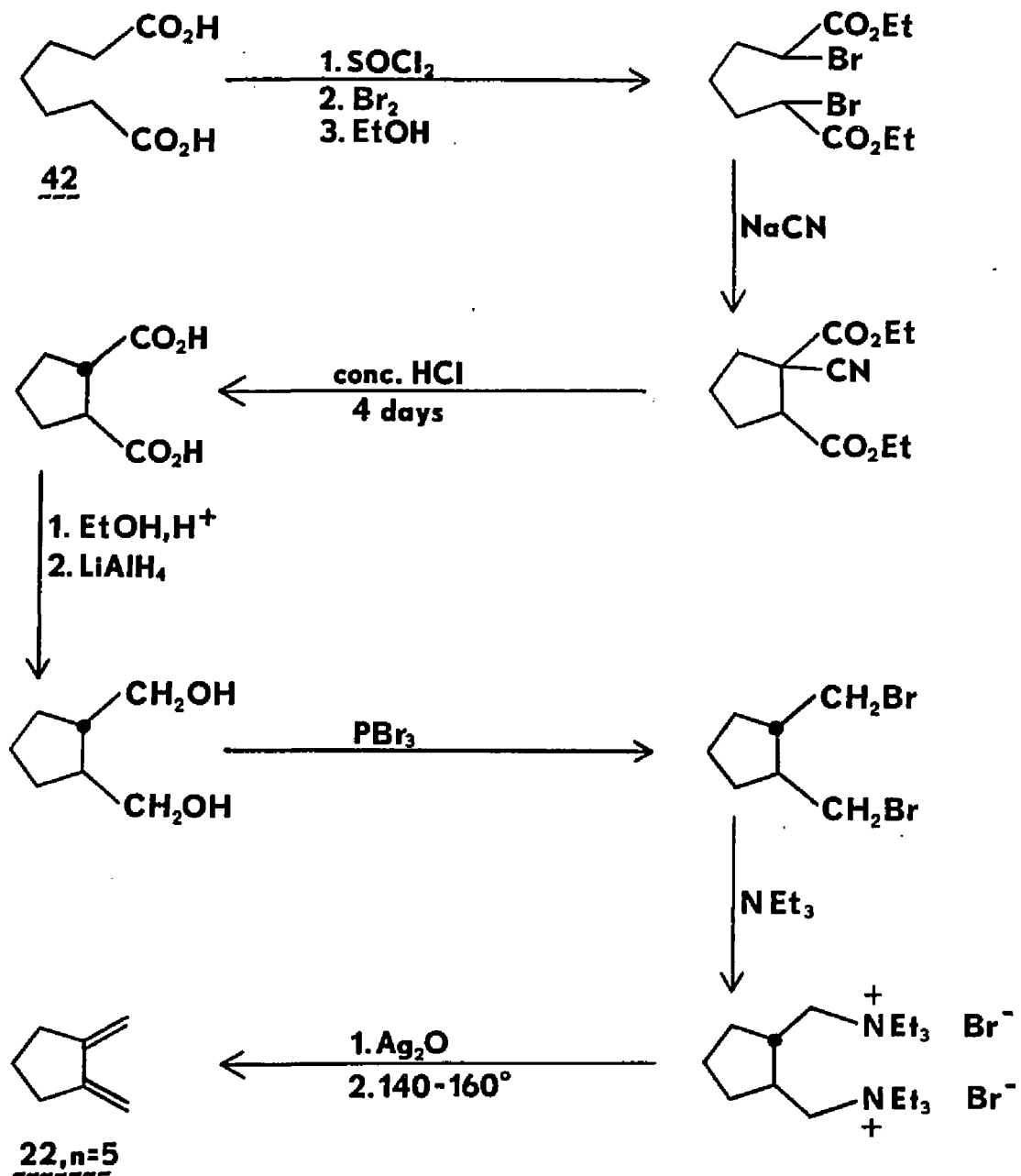
Diene 32 has been shown to be an important synthon by Trost and Shimizu [15] as a "conjunctive reagent for tandem Diels-Alder reactions." In the example below, 32 was reacted with dimethyl acetylenedicarboxylate to produce adduct 36 in 80% yield which was oxidatively bis-desilylated with NBS and propylene oxide to diene 37, which was then reacted with N-phenylsuccinimide to give adduct 38 in 43% yield from 36. These reactions were done successively in a single reaction vessel.



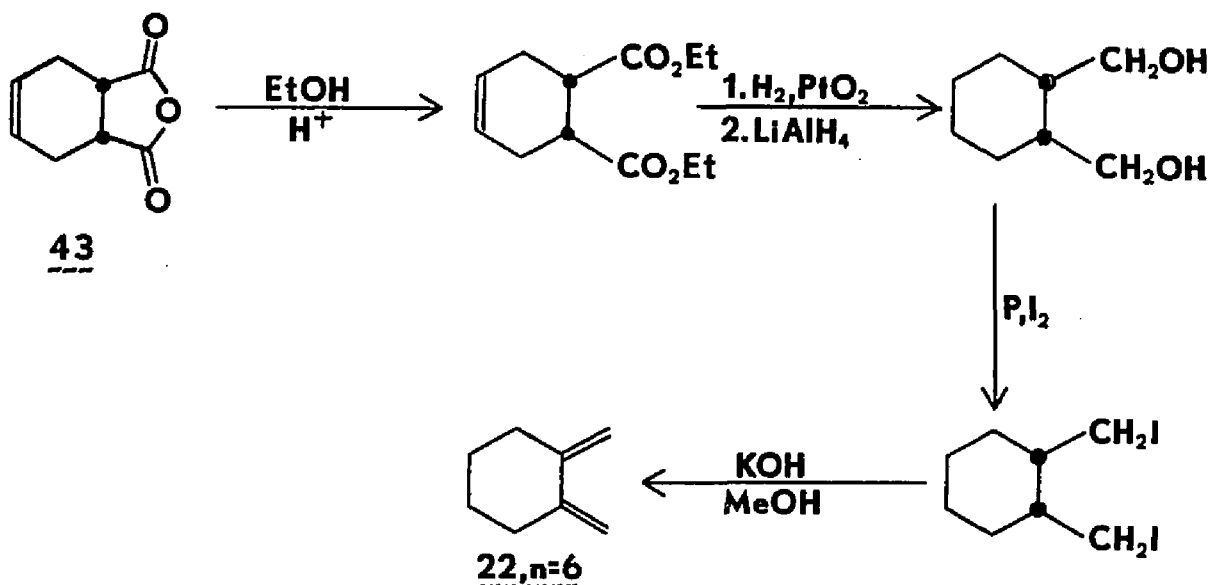
1,2-Bis(methylene)cycloalkanes 22, of which ring sizes  $n=7-10$  have been made by the reaction of dianion 1 with dibromoalkanes [10], have been synthesized using other methods for ring size  $n=3-8,12$  [17-19]. 1,2-Bis(methylene)cyclopropane (22,n=3) has been generated in 30% yield by heating vinylidenecyclopropane (39) [17]. 1,2-Bis(methylene)cyclobutane (22,n=4) has long been known (along with its 1,3-isomer 40) as a dimer of allene (41) [18, 19] and has not been made



from dianion 1. 1,2-Bis(methylene)cyclopentane (22,n=5) is prepared in eleven steps from pimelic acid (42) in an overall yield of 25% [20-22]. The scheme for this synthesis is shown below:

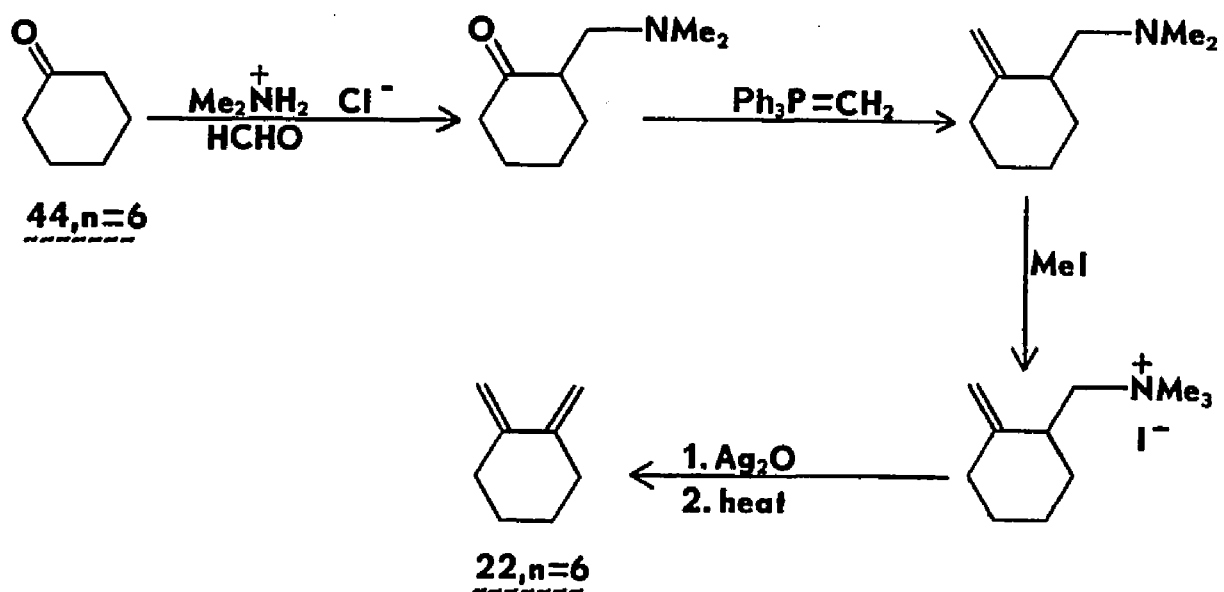


Compounds 22,n=4 and 22,n=6 have also been prepared in this manner [23, 24], but these syntheses are inferior to shorter syntheses which use more readily available starting materials. For example, the Diels-Alder adduct 43 of 1,3-butadiene and maleic anhydride has been used to generate 22,n=6 in the scheme shown below [25].

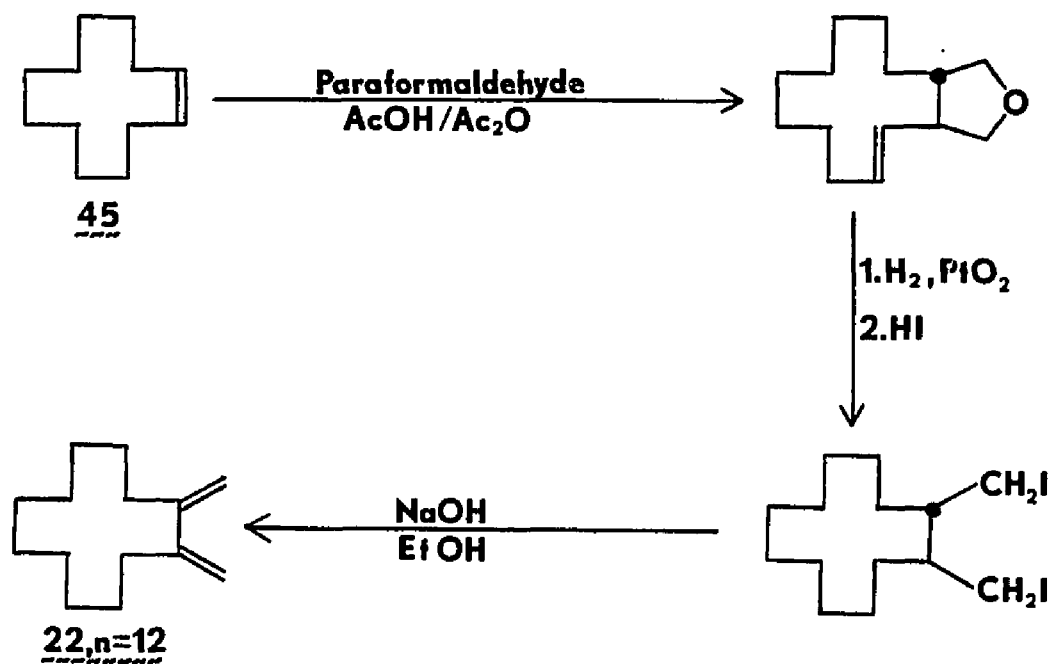


A more general method of preparing 1,2-bis(methylene)-cycloalkanes (22) from cycloalkanones (44) has been used to prepare ring sizes n=6, 7, 8, 12 [26-28]. The yields of 22 were 10% for n=6, 30% for n=7, 25% for n=8 and 50% for n=12. 1,2-Bis(methylene)-cyclododecane (22,n=12) has been made by two other methods as well

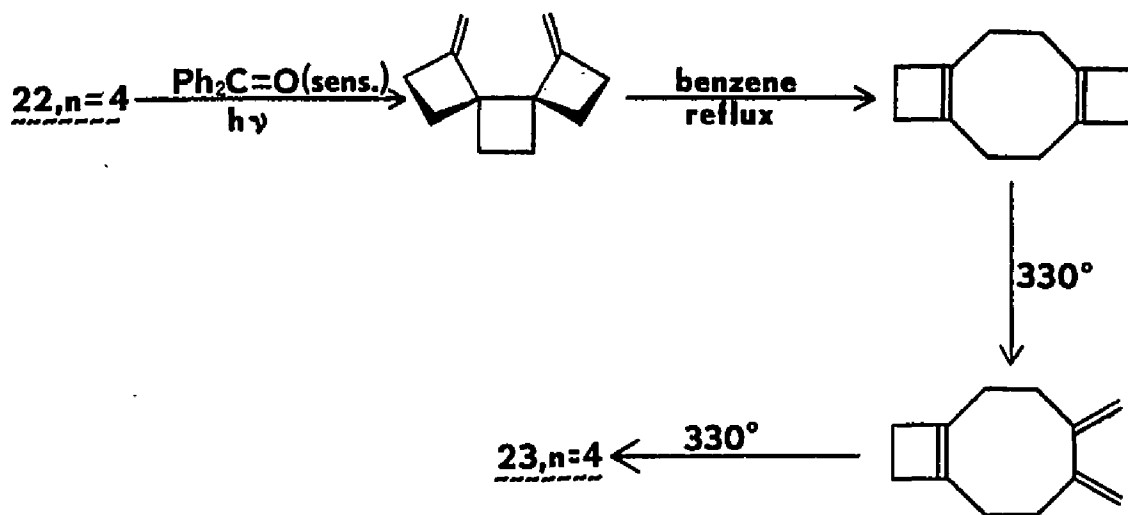




[29, 30]. A 22% yield of **22,n=12** was obtained from cyclododecene (**45**) using the following scheme [29].

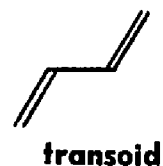


23,n=4, the oxidative dimer from dianion 1, has been generated from the dimerization of 22,n=4. A yield of 51% was achieved using the scheme below [31].



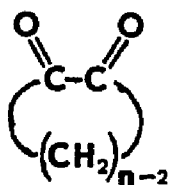
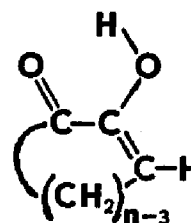
In addition to being useful synthons in electrocyclic reactions, 2,3-disubstituted 1,3-butadienes are useful as polymethization monomers.

Another reason for interest in 1,2-bis(methylene)butadienes (22) is to study the conformation of the diene moiety as a function of ring size. The two limiting conformations are the s-cis or cisoid conformation with a dihedral angle of  $0^\circ$  and the s-trans or transoid conformation with a dihedral angle of  $180^\circ$ . These two coplanar conformations are shown below:



The diene moiety in the smaller rings is fixed in the cisoid conformation [32]. In very large rings, the conformation would be expected to be transoid as in acyclic 2,3-disubstituted butadienes [33].

Close analogs to 1,2-bis(methylene)cycloalkanes (22) are the 1,2-dicycloalkanediones (46). A complication is that 1,2-diketones form an equilibrium with their tautomers, ketoenols 47. In the case of five- and six-membered rings (46, n=5,6; 47, n=5,6), the equilibrium lies in favor of the enol forms. However, in larger rings the equilibrium favors the keto forms with the enol forms in relatively negligible amounts [34].

4647

Because of the polarity of the carbon-oxygen double bond, the dipole moment of a molecule of 46 provides a means to determine its conformation. A molecule with a cisoid conformation would have a large dipole moment and a molecule with a transoid conformation would have a small dipole moment. The dipole moments and UV spectra of a series of 1,2-cycloalkanediones 46, n=5-12 have been measured and are listed along with dihedral angles as calculated from dipole moments in Table 2 [34]. It is well known that when the dihedral angle is 90° the absorption maximum in the UV occurs at the shortest wavelengths

Table 2. 1,2-Cycloalkanediones (46)

n	$\lambda_{\text{max}}^{\text{EtOH}}$ (nm)	$\epsilon_{\text{max}}^{\text{EtOH}}$	Dipole Moment (D)	Dihedral Angle, °
5	253	9410	2.21	
6	267	7440	2.92	
7	267	129	3.74	89.5
8	272	148	3.47	93.7
9			2.89	107.5
10			2.04	128.7
11	269	162	1.87	133.2
12			1.86	133.5
biacetyl	275		1.22	150

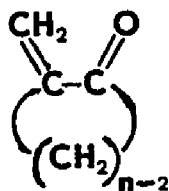
and that cisoid and transoid coplanar conformations (dihedral angle =  $0^\circ$  or  $180^\circ$ ) have UV absorption maxima at the longest wavelengths [35]. The data in Table 2 are somewhat ambiguous with respect to UV; however, the dipole moments show a gradual shift from high dipole moments in cisoid systems to lower dipole moments in transoid systems. Nevertheless, 46,n=12, which might be expected to be transoid, has a dipole moment somewhat less than acyclic biacetyl. It was suggested that "considerable oscillation" was occurring in these molecules [34]. Biacetyl's dihedral angle as calculated from its dipole moment was  $150^\circ$ , not the expected  $180^\circ$ .

Other close analogs to 1,2-bis(methylene)cycloalkanes (22) are the 2-methylenecycloalkanones (48). These compounds, unlike 1,2-cycloalkanediones (46), enolize only to a small extent and therefore enols do not interfere with UV and dipole moment measurements. However, the differences between the dipole moments of cisoid and transoid are somewhat less in 48 than in 46. Cisoid conformations have higher dipole moments than transoid conformations in 48 as with 46. The dipole moments and UV spectra of a series of 2-methylene-cycloalkanones 43,n=5-10,12,16 have been measured and are listed in Table 3 [36]. It is known that in 48 molecules with cisoid conformations absorb at higher wavelengths than molecules with transoid conformations. Also, molecules with planar cisoid or transoid conformations absorb more strongly than those twisted from planarity, with a dihedral angle of  $90^\circ$  again being the minimum [37]. UV data listed in Table 3 show an uneven decrease in  $\lambda_{\max}$  from the cisoid five-membered ring (48,n=5) to the presumably transoid sixteen-membered

Table 3. 2-Methylenecycloalkanones (48)

n	$\lambda_{\text{max}}^{\text{EtOH}}$ (nm)	$\epsilon_{\text{max}}^{\text{EtOH}}$	Dipole Moment (D)
5	232	8130	3.02
6	231	3240	
7	230	4470	2.89
8	233	4370	2.91
9	228	3980	2.88
10	231	4270	2.58
12	229	4790	2.40
16	225	6920	2.36

ring (48,n=16). The extinction coefficients show a maximum with 48,n=5 decreasing to a minimum at 48,n=9 followed by an increase to another maximum at 48,n=16. The dipole moment shows a steady, if slightly uneven, decline from cisoid 48,n=5 to transoid 48,n=16.



48

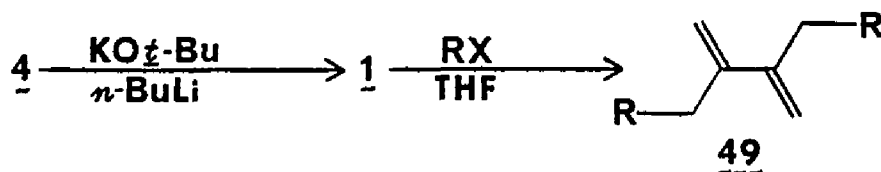
In summary, compounds 46 and 48 display a nearly planar cisoid conformation in five-membered rings. The six-, seven- and eight-membered rings show twisted cisoid conformations. The nine-, ten- and eleven-membered rings have twisted conformations intermediate between

cisoid and transoid. The twelve-membered rings (46, $n=12$ ; 48, $n=12$ ) are interesting in that they are large enough to easily accommodate a transoid conformation, yet the data point to a dihedral angle considerably less than  $180^\circ$ . 48, $n=16$  appeared to be in a slightly twisted transoid conformation, but with a deviation from  $180^\circ$  that is more than that of transoid acyclic 2-methyl-1-butenone, which had a  $\lambda_{\text{max}}$  of 217.8 nm compared to the calculated  $\lambda_{\text{max}}$  of 219 nm [37].

It is expected that the changes observed as a function of ring size in 1,2-bis(methylene)cycloalkanes (22), will be similar to those found in the study of 46 and 48. Dipole moments in 22 would be likely to exhibit only small differences between cisoid and transoid and their measurement would not be useful. Thus, 1,2-bis(methylene)-cycloalkanes will be studied using primarily high resolution  $^1\text{H}$  NMR and UV.

## RESULTS

2,3-Bis(methylene)butadiene dianion 1 was prepared from 2,3-dimethyl-1,3-butadiene (4) with Lochmann's base. Dianion 1 was reacted with a variety of organic halides to yield a number of disubstituted products 49. The reported yields of products are based on starting diene 4 and not on dianion 1 which is obtained from 4 in 73% yield [6, 10].

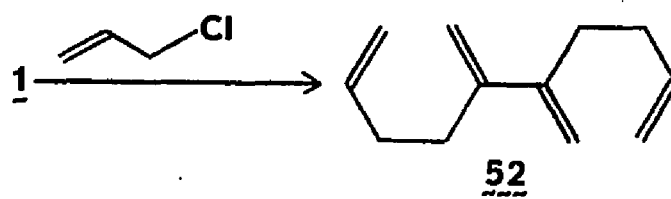
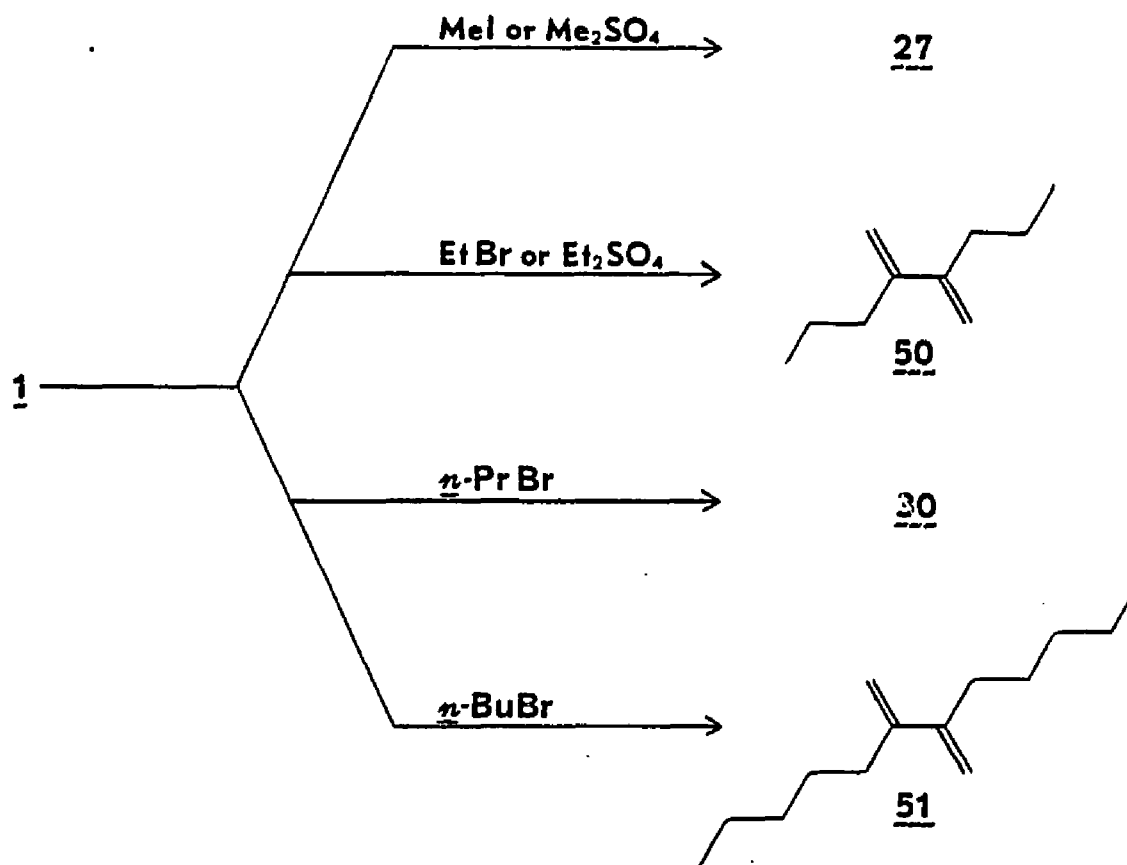


Dianion 1 reacted with primary alkyl halides and sulfates to generate the expected products. 1 reacted with methyl iodide and dimethyl sulfate to produce 3,4-bis(methylene)hexane (27) in 43% and 61% yields, respectively. 1 reacted with ethyl bromide to generate 4,5-bis(methylene)octane (50) in 43% yield. The reaction of 1 with diethyl sulfate gave 50 in 71% yield [6, 10]. Dianion 1 reacted with 1-borompropane to give the expected 5,6-bis(methylene)decane (30) in 34% yield. The reaction of 1 with 1-bromobutane generated 6,7-bis(methylene)dodecane (51) in 30% yield.

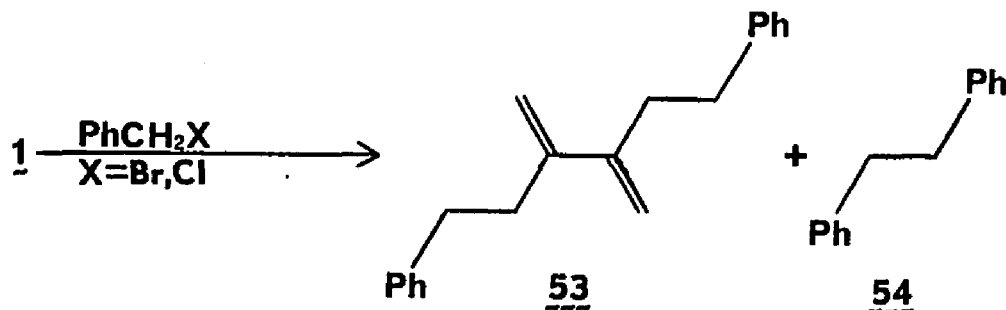
Allyl chloride reacted with dianion 1 to give a 70% yield of 5,6-bismethylene-1,9-decadiene (52).

Benzyl chloride reacts with dianion 1 to give the expected disubstitution product 53 in 53% yield and also 1,2-diphenylethane (54)

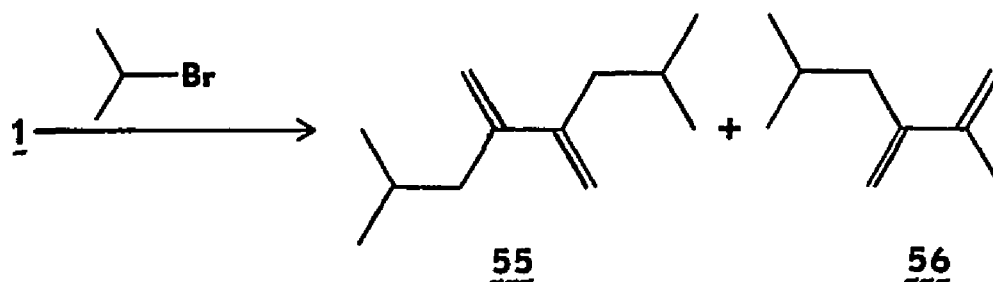




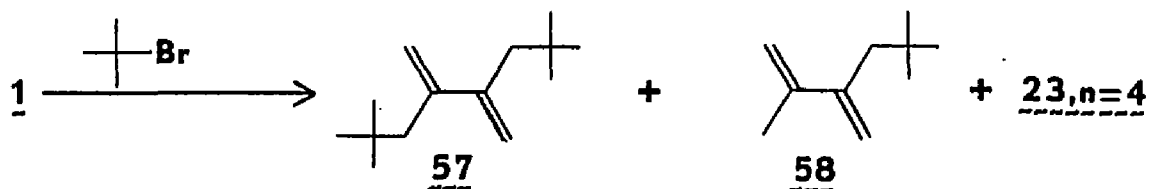
in 22% yield. However, the reaction of 1 with benzyl bromide generated 54 as the major product in 30% yield and 53 as the minor product in 21% yield.



Dianion 1 reacted with 2-bromopropane, a secondary halide, to produce a 41% yield of disubstitution product 55 and a 2% yield of monosubstitution product 56.



Surprisingly, dianion 1 reacted with t-butyl bromide to generate disubstitution product 57, monosubstitution product 58 and dimeric oxidation product 23,n=4, each in 15% yield. However, the reaction of 1 with t-butyl chloride produced none of these products.



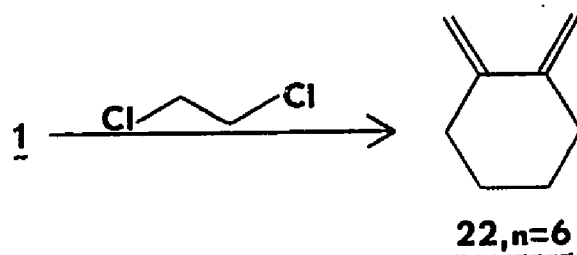
A summary of the yields of disubstitution products 49 of dianion 1 is listed in Table 4.

Table 4. Disubstitution Products of Dianion 1

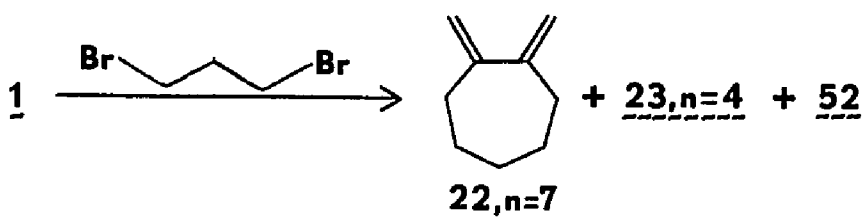
R	X	% Yield	Product
Me	I	43	<u>27</u>
Mr	MeSO <sub>4</sub>	61	<u>27</u>
Et	Br	43	<u>50</u>
Et	EtSO <sub>4</sub>	71	<u>50</u>
<u>n</u> -Pr	Br	34	<u>30</u>
<u>n</u> -Bu	Br	30	<u>51</u>
<u>i</u> -Pr	Br	41	<u>55</u>
<u>t</u> -Bu	Br	15	<u>57</u>
<u>t</u> -Bu	Cl	0	<u>57</u>
H <sub>2</sub> C=CHCH <sub>2</sub>	Cl	70	<u>52</u>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Br	21	<u>53</u>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Cl	53	<u>53</u>
Me <sub>3</sub> Si	Cl	47	<u>32</u>
Me <sub>3</sub> Ge	Br	54	<u>59</u>
Me <sub>3</sub> Sn	Cl	32	<u>60</u>
Me <sub>3</sub> Pb	Cl	30	<u>61</u>

Cyclizations were performed using the reaction of dianion 1 with dihalides. Reaction of dichloromethane with dianion 1 generated 1,2-bis(methylene)cyclopentane (22,n=5) in 12% yield. The reaction of 1 with dibromomethane produced 22,n=5 in 5% yield but also gave the dimeric product 23,n=4 in 11% yield.

1,2-Bis(methylene)cyclohexane (22,n=6) was obtained in 19% yield from the reaction of 1 with 1,2-dichloroethane. However, the reaction of 1 with 1,2-dibromoethane yielded neither 22,n=6 nor the dimeric oxidation product 23,n=4.



The reaction 1 with 1,3-dibromopropane generated the expected 22,n=7 in 18% yield in addition to a 6% yield of side product 52 and a trace of oxidative dimer 23,n=4.



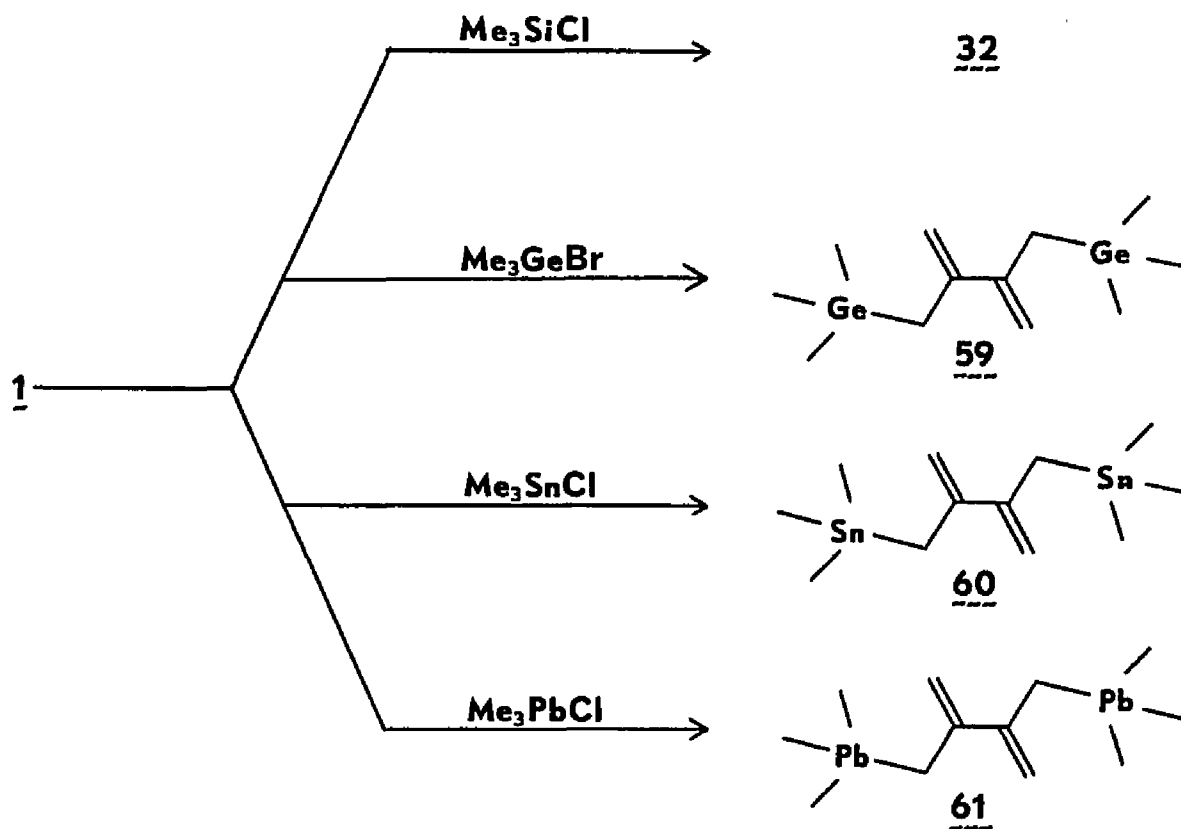
Dianion 1 was reacted with all the  $\alpha,\omega$ -dibromoalkanes from 1,4-dibromobutane to 1,10-dibromodecane as well as 1,12-dibromododecane to generate 1,2-bis(methylene)cycloalkanes (22,n=8-14, 16). In cases where the products were isolated by LC, dimers 23,n=11-14,16 and trimers

24, n=12-14, 16 were also obtained. The % yields of these products are listed in Table 5, which summarizes the reactions of dianion 1 with  $\alpha, \omega$ -dihaloalkanes.

Table 5. Reactions of Dianion 1 with  $\alpha, \omega$ -Dihaloalkanes

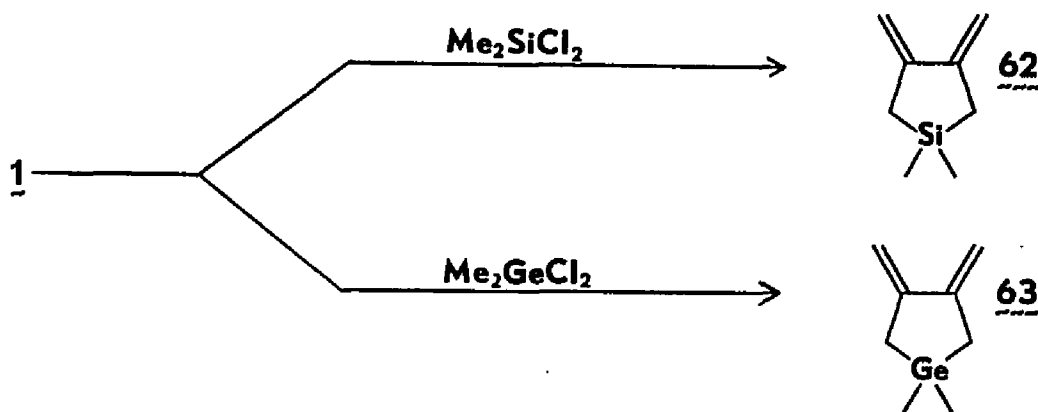
Dihalide	% Yield	Product
CH <sub>2</sub> Br <sub>2</sub>	5	<u>22, n=5</u>
	11	<u>23, n=4</u>
CH <sub>2</sub> Cl <sub>2</sub>	12	<u>22, n=5</u>
Br(CH <sub>2</sub> ) <sub>2</sub> Br	0	<u>22, n=6</u>
	0	<u>23, n=4</u>
Cl(CH <sub>2</sub> ) <sub>2</sub> Cl	19	<u>22, n=6</u>
Br(CH <sub>2</sub> ) <sub>3</sub> Br	18	<u>22, n=7</u>
	trace	<u>23, n=4</u>
	6	<u>52</u>
Br(CH <sub>2</sub> ) <sub>4</sub> Br	18	<u>22, n=8</u>
Br(CH <sub>2</sub> ) <sub>5</sub> Br	15	<u>22, n=9</u>
Br(CH <sub>2</sub> ) <sub>6</sub> Br	20	<u>22, n=10</u>
Br(CH <sub>2</sub> ) <sub>7</sub> Br	2	<u>22, n=11</u>
	2	<u>23, n=11</u>
Br(CH <sub>2</sub> ) <sub>8</sub> Br	2	<u>22, n=12</u>
	7	<u>23, n=12</u>
	3	<u>24, n=12</u>
Br(CH <sub>2</sub> ) <sub>9</sub> Br	4	<u>22, n=13</u>
	2	<u>23, n=13</u>
	1	<u>24, n=13</u>
Br(CH <sub>2</sub> ) <sub>10</sub> Br	5	<u>22, n=14</u>
	3	<u>23, n=14</u>
	1	<u>24, n=14</u>
Br(CH <sub>2</sub> ) <sub>12</sub> Br	8	<u>22, n=16</u>
	4	<u>23, n=16</u>
	2	<u>24, n=16</u>

Dianion 1 was reacted with trimethylsilyl chloride to yield the expected disubstitution product 32 in 47% yield. 1 also reacted with trimethylgermanium bromide, trimethyltin chloride and trimethyllead chloride to produce disubstitution products 59, 60 and 61 in 54%, 32% and 30% yields, respectively.

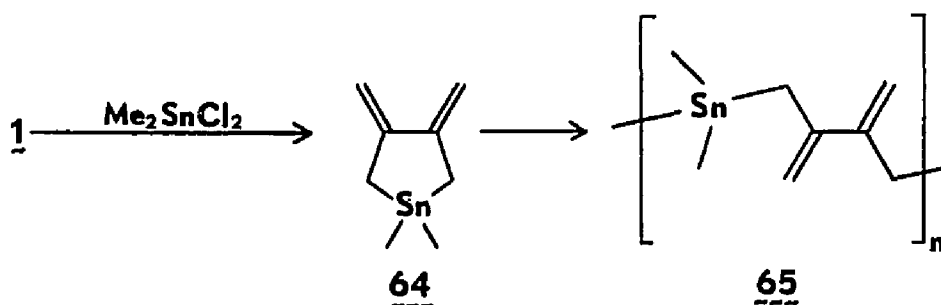


Dianion 1 was reacted with dimethyldichlorosilane and dimethyldichlorogermane to give heterocyclic compounds 62 and 63 in 30% and 32% yields, respectively.

When 1 was reacted analogously with dimethyltin dichloride, the expected heterocyclic tin compound 64 was formed. However, 64 is

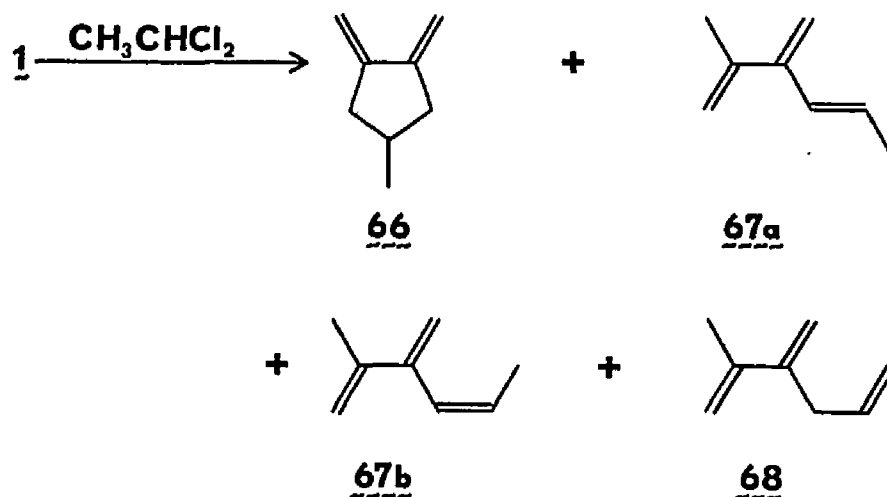


unstable at room temperature and decomposed steadily to its homopolymer 65, which was identified by the very close similarity of its  $^1\text{H}$  NMR spectrum to that of 60.



When dianion 1 was reacted with 1,1-dichloroethane, a number of products were generated. The anticipated cyclization product 66 was formed in 6.0% yield. In addition, isomeric products 67a, 67b and 68 were generated in 6.5%, 1.4% and 2.2% yields, respectively.

Reaction of 1 with iodine yielded oxidative dimer 23,n=4 in 3% yield. When 1 was reacted with hexachloroethane, 23,n=4 was generated in 11% yield. Oxidations of 1 with metal salts  $\text{CuBr}$ ,  $\text{CuBr}_2$  and  $\text{CdI}_2$  generated 23,n=4 in 8%, 17% and 11% yields, respectively, along with many other interesting products [38]. Although a GC standard was



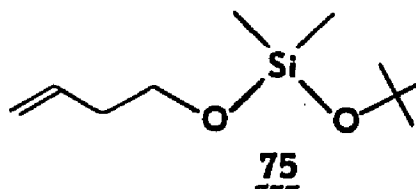
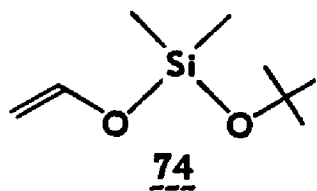
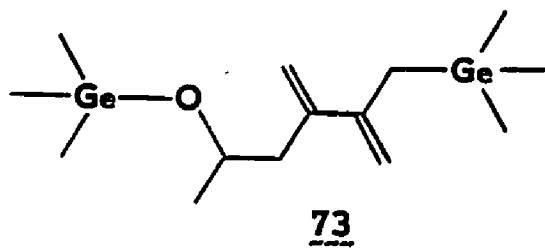
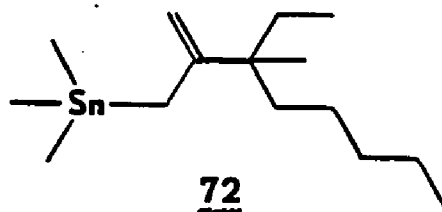
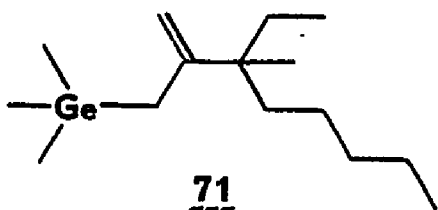
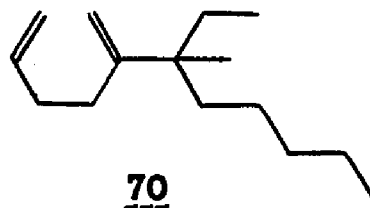
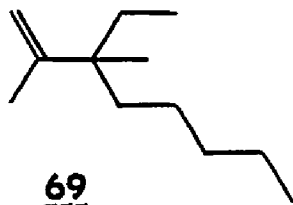
available for oxidative monomer 22,  $n=4$  and it was carefully searched for, it was never found in any reaction involving dianion 1.

A number of strange side products were found in these reactions. The most consistent side product was 3-ethyl-2,3-dimethyl-1-octene (69), which was obtained in the reactions of 1 with 1,2-dibromoethane, 1,4-dibromobutane, dimethyldichlorogermane, isopropyl bromide and t-butyl bromide in 12%, 2%, 3%, 1% and 12% yields, respectively. The reaction of 1 with allyl chloride generated side product 70 in 10% yield. Trimethylgermyl bromide and trimethyltin chloride yielded side products 71 and 72 in 5% and 6% yields, respectively. 70, 71 and 72 may be considered derivatives of 69.

The reaction of 1 with trimethylgermyl bromide produced the bizarre side product 73 in 4% yield.

When dianion 1 was prepared in the presence of excess  $\text{KOt-Bu}$ , its reaction with dichlorodimethylsilane yielded side products 74 and 75, which are unrelated to 1.





Three methods of addition were used in these reactions:

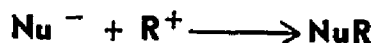
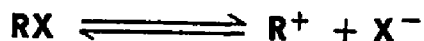
1. Direct addition
2. Inverse addition
3. Simultaneous addition

The first involves the addition of electrophile directly to the dianion. The yields obtained from this method for 22,n=7-9 and for 50 were virtually the same as yields obtained from the other methods. Direct addition was inferior to the other methods in the synthesis of larger ring systems in 22,n=10,13. Direct addition of 1 to benzyl bromide generated primarily bibenzyl 54 and only a trace of disubstitution product 53. The second method involves the addition of the dianion to a solution of the electrophile. This is generally the best method for monofunctional electrophiles, although in most cases it offers no advantage over direct addition. The third method involves the simultaneous addition of the dianion and the electrophile to a dilute THF solution. This method was necessary to achieve reasonable yields for the formation of larger rings (22,n $\geq$ 10). In the case of smaller rings, this method provided no advantage over inverse or direct addition.

## DISCUSSION

Substitution reactions of dianion 1 may result from a number of possible mechanisms and we believe we have observed at least three of them. The first mechanism discussed involves the ionization of the electrophile to generate an alkyl cation, which then rapidly couples with the anion nucleophile,  $\text{Nu}^-$ ). This is the  $\text{S}_{\text{N}}1$  mechanism.

$\text{S}_{\text{N}}1$ :



The  $\text{S}_{\text{N}}1$  mechanism is favored only when the R group is capable of stabilizing a positive charge; this is not the case for most of the alkyl halides reacted. Also the  $\text{S}_{\text{N}}1$  mechanism is not favored in strongly basic systems while the mechanisms about to be discussed are favored. It is therefore doubtful that the  $\text{S}_{\text{N}}1$  mechanism is involved in any of the reactions of 1.

The next mechanism involves backside attack by the anion (nucleophile,  $\text{Nu}^-$ ) on the alkyl halide with simultaneous expulsion of a halide ion. This is the well-known concerted  $\text{S}_{\text{N}}2$  mechanism.

$\text{S}_{\text{N}}2$ :

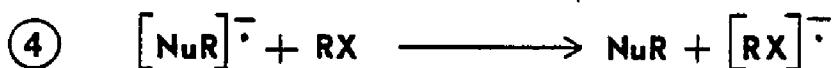
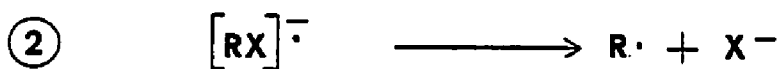
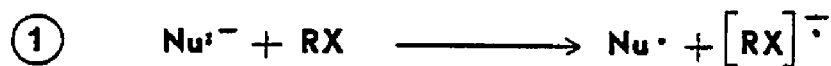


When the electrophile is an allyl halide then  $\gamma$ -attack via an  $S_N2'$  mechanism is also a possibility [39].

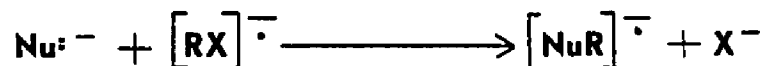
$S_N2'$



The  $S_N2$  and  $S_N2'$  mechanisms involve formal transfer of two electrons, but single electron transfer (SET) is also possible. Several possible mechanisms involve SET as the initial step. The  $S_{RN}1$  reaction as described by Bunnett [40] and Galli and Bunnett [41] is well known in the reactions of aryl halides with anions. This is a chain mechanism with initiation, propagation and termination steps. In the cases studied by Bunnett, the initiation step involved an external electron source. In the case of the reactions of 1, the anion itself acts as the electron source. The mechanisms are identical except for the involvement of the radical resulting from the loss of an electron by the nucleophile. Propagation step 2 occurs very rapidly and is common to the 2-3-4 and 2-5-6 propagation sequences. Propagation steps 3 and 4 result in substitution while propagation steps 5 and 6 result in dimerization of the nucleophile. To the extent that this dimerization occurs, this modified  $S_{RN}1$  mechanism would lead to lower yields of substitution products than would the  $S_N2$  mechanism. Dimerization of the R group, on the other hand, can only occur through termination step 9 and the resulting product would be expected to be found only in trace amounts, if at all, with the  $S_{RN}1$  mechanism.

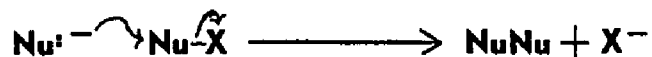
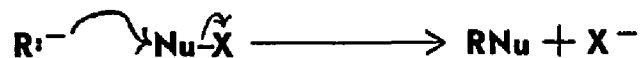
**S<sub>RN</sub>1:**

If the second and third steps of the S<sub>RN</sub>1 mechanism are merged into a single concerted step, the mechanism becomes S<sub>RN</sub>2 [41]. This is essentially the same as having the nucleophile react with the anion radical in a solvent "cage" [42].

**S<sub>RN</sub>2 (steps 2 and 3 of S<sub>RN</sub>1 merged):**

The  $S_{RN}2$  mechanism is unlikely in SET reactions because it requires a negatively charged anion to attack an also negatively charged anion radical. The resulting coulombic repulsion makes this mechanism improbable and it has been ruled out in aryl halide reactions [41]. In addition, step 2 is believed to be very rapid when X = halide, so it is unlikely that the anion radical would wait for a collision with another negatively charged species before splitting into  $R\cdot$  and  $X^-$ . If, for some reason, radical to anion coupling (steps 3 and 5) is disfavored, the SET mechanism becomes a non-chain radical-radical coupling (RRC) mechanism consisting of steps 1, 2, 7, 8 and 9. However, the concentration of the anions is very much greater than that of any of the radicals, making radical-anion coupling a very much more likely event than radical-radical coupling.

The last mechanistic possibility to be considered is that of substitution by halogen-metal exchange (HME) [43] followed by subsequent  $S_N2$  reactions. HME may be concerted or stepwise involving SET. HME involves equilibria favoring the thermodynamically most stable anion. Therefore, it can be ruled out in most cases involving the reaction of dianion 1 because the anion that would result from the exchange is much less stable than dianion 1. In a few cases where the resulting anion is of the same order of stability as 1, this mechanism is very likely important. In addition to substitution products, coupling of the electrophile with its conjugate anion to give R-R would be expected.

**HME:**

Bordwell and Clemens [44] have given some rules involving factors that determine whether the reactions of carbanions with electrophiles will tend to go by  $\text{S}_{\text{N}}2$  or SET mechanisms. The factors which favor an SET mechanism over an  $\text{S}_{\text{N}}2$  mechanism are:

1. A poor leaving group, X
2. Steric hindrance in RX
3. A strong electron acceptor in R
4. Increasing basicity in the reacting anion

The REPA's of the anions are an excellent measure of the basicity of the anions. Although factors may favor one mechanism or the other, it is quite likely that in most reactions two (or more) mechanisms are competing.

Primary alkyl halides and sulfates react with dianion 1 primarily by the  $\text{S}_{\text{N}}2$  mechanism. However, the difference in yields between halides and sulfates suggests some SET in the reactions with halides which may lead to side products. SET would be expected to be

avored in the series  $I > Br > Cl \gg RSO_4$ . The sulfate is an excellent leaving group and SET is strongly disfavored. The reactions of primary iodides with alkylolithiums are known to show CIDNP effects when the reactions are monitored by  $^1H$  NMR [45, 46].

The reaction of 1 with allyl chloride can go by either the  $S_N2$  or  $S_N2'$  mechanisms (or both). The high yield of the disubstitution product 52 suggests that SET and HME are not important in this case.

HME is apparently important in the reaction of dianion 1 with benzyl halides. Bibenzyl (54) was obtained in addition to disubstitution product 53; this tends to favor HME over  $S_{RN}1$ . The absence of oxidative dimer 23,n=4 also argues against the  $S_{RN}1$  mechanism; this can be rationalized in the HME scheme in two ways: first, initial coupling leading to dimer requires dianion 1 to react with a mono-anionic halide, which is a problem for coulombic reasons. The intermediate must then undergo another HME, after which two ends must couple before reacting with other molecules. Therefore, these reactions most likely go by competing HME and  $S_N2$  mechanisms, the  $S_N2$  mechanism being favored with benzyl chloride and the HME mechanism being favored with benzyl bromide.

Disubstitution of 1 using secondary halide 2-bromopropane went in reasonable yield. This moderately-hindered secondary alkyl halide probably goes primarily by the  $S_N2$  mechanism with some competitive SET.

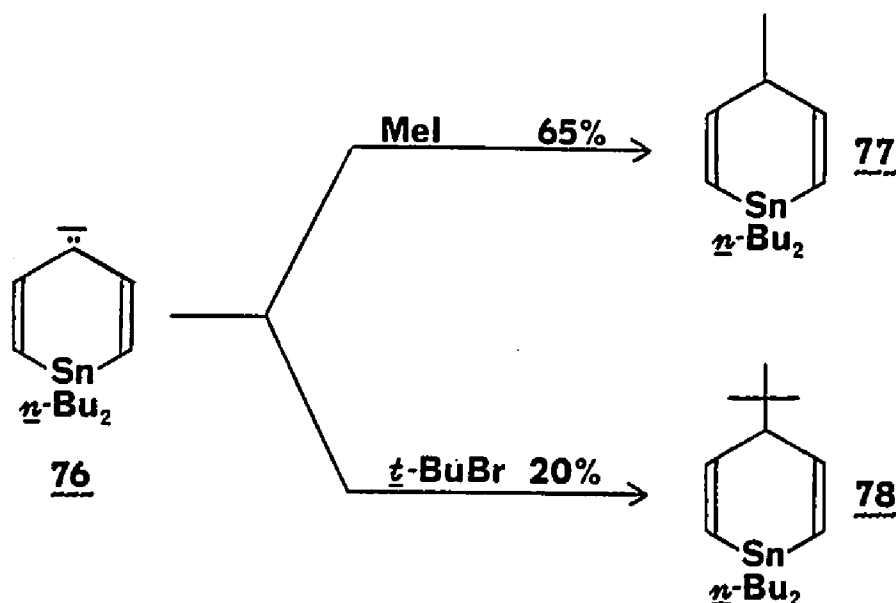
Because of steric hindrance, disubstitution of t-butyl groups cannot go by an  $S_N2$  mechanism. The results point strongly to the  $S_{RN}1$  mechanism: disubstitution product 57 and oxidative dimer 23,n=4 were formed in equal yields while 2,2,3,3-tetramethylbutane was not



found. The presence of monosubstitution product 58 in 15% yield is probably due to hydrogen abstraction by the intermediate radical or anion from THF or t-BuBr. It is interesting that the reaction of dianion 1 with t-BuCl generated neither 57 nor 23,n=4. Apparently, dianion 1 is not a strong enough electron donor to transfer an electron to the chloride. Dianion 13, which has a much lower REPA than 1, readily undergoes SET with chlorides [12].

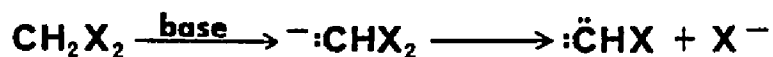
Substitution reactions of carbanions with tertiary halides are uncommon because the anion may abstract  $\alpha$ -hydrogens of the tertiary halide, leading to E2 elimination. An early example of an anion reacting with a tertiary halide involved an intramolecular reaction to yield a three-membered ring [47]. t-Butylation of O- and N-stabilized carbanions is known only in a few cases [48, 49]. Sodium cyclopentadienide undergoes substitution with t-butyl bromide [50] as does lithium di-n-butylstannacyclohexadienide (76) [51]. Monoanion 76 would be expected to have an REPA similar to pentadienyl anion 6 which has an REPA lower than but closer to that of dianion 1. Indeed, anion 76 reacts similarly to 1 with methyl iodide to generate 77 and with t-butyl bromide to generate 78. The formation of 57 from dianion 1 is the first example of di-t-butylation of a dicarbanion.

Dianion 1 may undergo  $S_N2$  reactions with  $Me_3SiCl$ ,  $Me_3GeBr$ ,  $Me_3SnCl$  and  $Me_3PbCl$  because the diameters of the central heteroatoms are much greater than that of carbon, allowing room for backside attack by the anion. Another mechanistic possibility for these reactions is a pentavalent intermediate analogous to the transition state in  $S_N2$  reactions.



Oxidation of dianion 1 to 23,n=4 most likely occurs by the SET mechanism shown in Fig. 1. The most likely path involves coupling of anions with radicals in the  $S_{RN}1$  manner.

Dianion 1 reacted with dichloromethane and dibromomethane to yield 22,n=5, while only dibromomethane yielded oxidative dimer 23,n=4. The dichloromethane probably reacts by consecutive  $S_N2$  mechanisms, while the  $S_{RN}1$  mechanism becomes involved in the dibromomethane case. Dihalomethanes are known to generate carbenes in the presence of strong base in the manner shown below [52]. This of course lowers the yields of the cyclization products.



1,2-Dichloroethane reacted in a presumably  $S_N2$  manner to give 22,n=6. However, 1,2-dibromoethane yielded neither 22,n=6 nor 23,n=4, but instead gave a 12% yield of 51 and assorted side products which corresponded to 1 coupling with two molecules of THF and varying

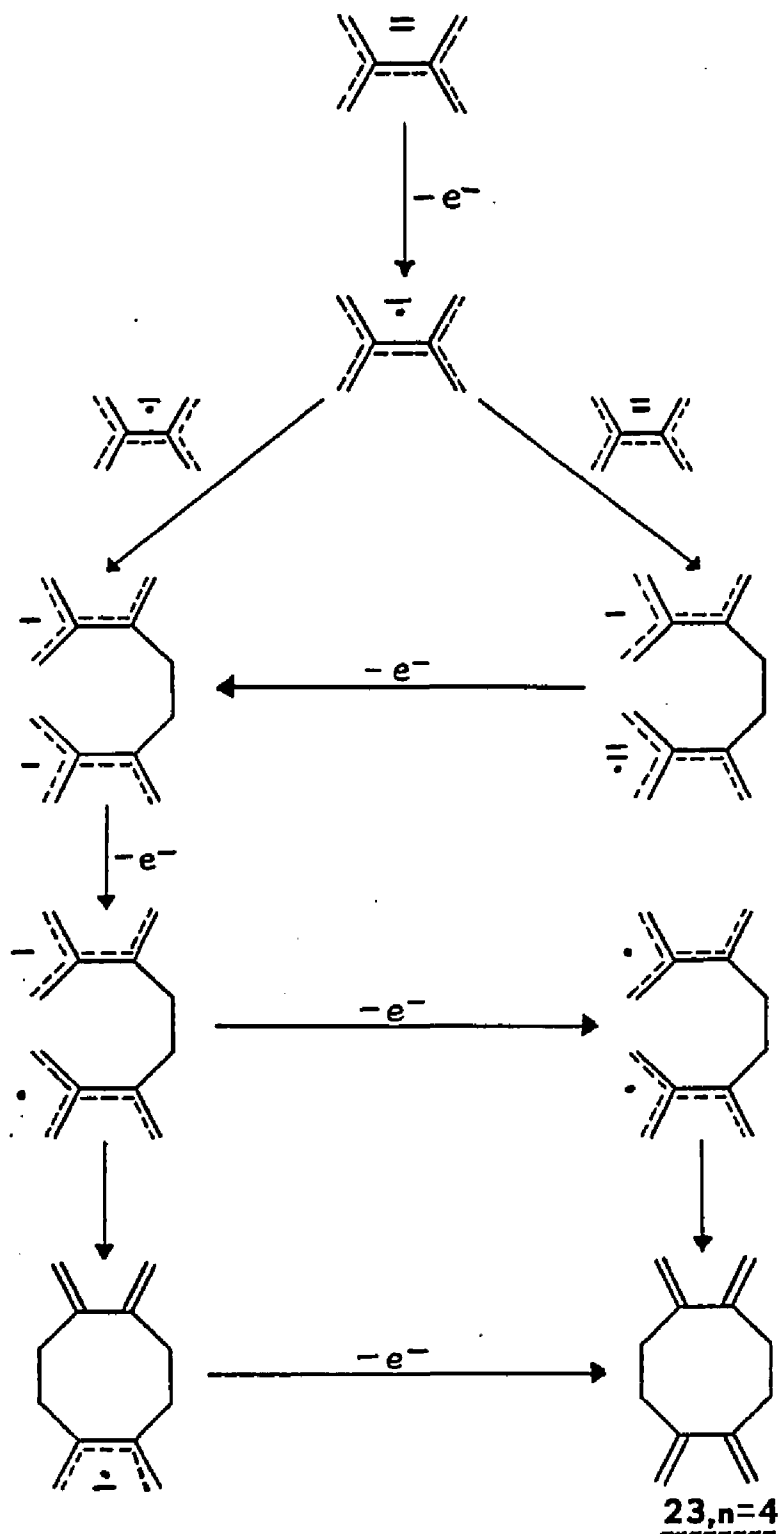
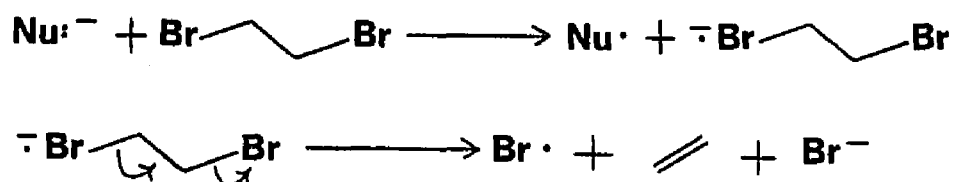


Fig. 1. Mechanism of formation of  $23, n=4$ .

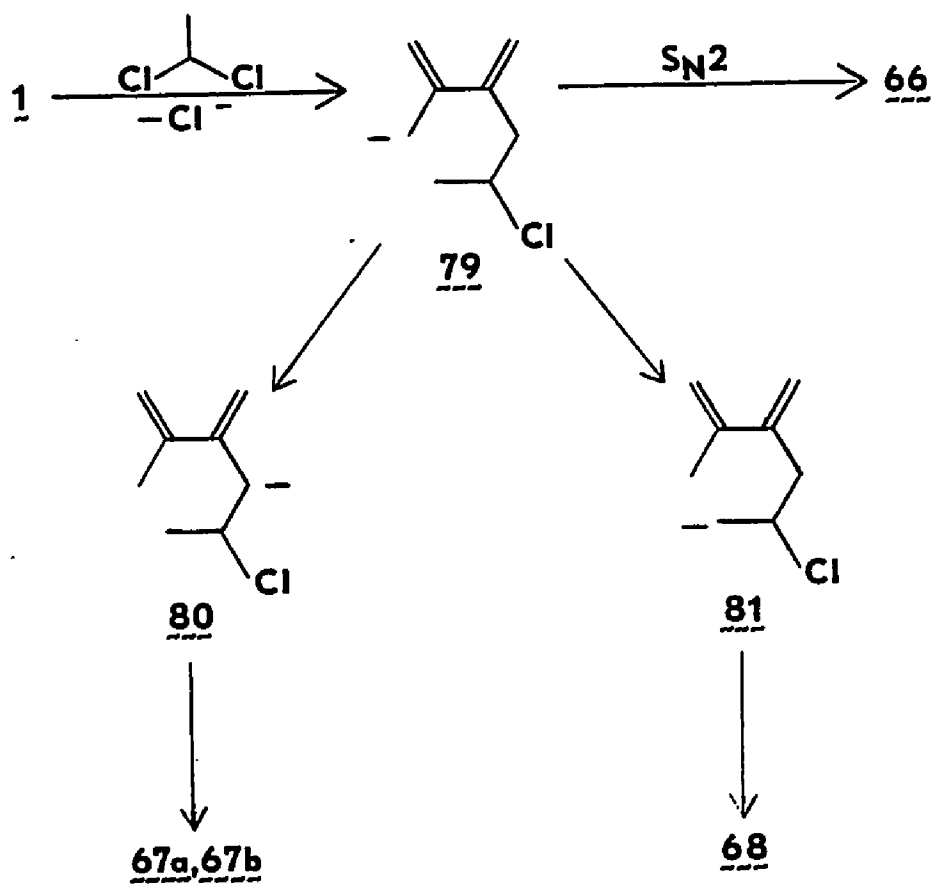
numbers of ethylene molecules (GC/MS). 1,2-Dibromoethane is a well-known oxidant probably reacting by the SET mechanism shown below to generate ethylene.



1,1-Dichloroethane reacts with 1, probably by an  $\text{S}_{\text{N}}2$  mechanism, to generate intermediate 80 which may undergo a subsequent  $\text{S}_{\text{N}}2$  reaction to yield cyclization product 66. Intermediate 79 can also undergo intramolecular proton transfer to generate intermediate 80 and to a lesser extent intermediate 81. Chloride may be eliminated from 80 to yield trans/cis isomers 67a and 67b. Elimination in the case of 81 leads to product 68.

1,3-Dibromopropane reacts with 1 to give the expected cyclization product 22, n=7 by sequential  $\text{S}_{\text{N}}2$  mechanisms. Side product 52 is probably formed in a similar manner to side products 67a, 67b and 68 from 1,1-dichloroethane. The presence of 23, n=4 shows that the  $\text{S}_{\text{RN}}1$  mechanism is probably competing.

Larger rings were prepared from 1 with the corresponding  $\alpha, \omega$ -dibromoalkanes. It should be noted that the major products of these reactions are polymers. In the reactions in which the products were separated by LC (n=11-14,16), dimers 23 were isolated as well as monomers 22, but generally in lower yield. If the yields of 22 are plotted as a function of ring-size as in Fig. 2, we can see that a minimum occurs at n=11-12. Interestingly, for n=12, the dimer



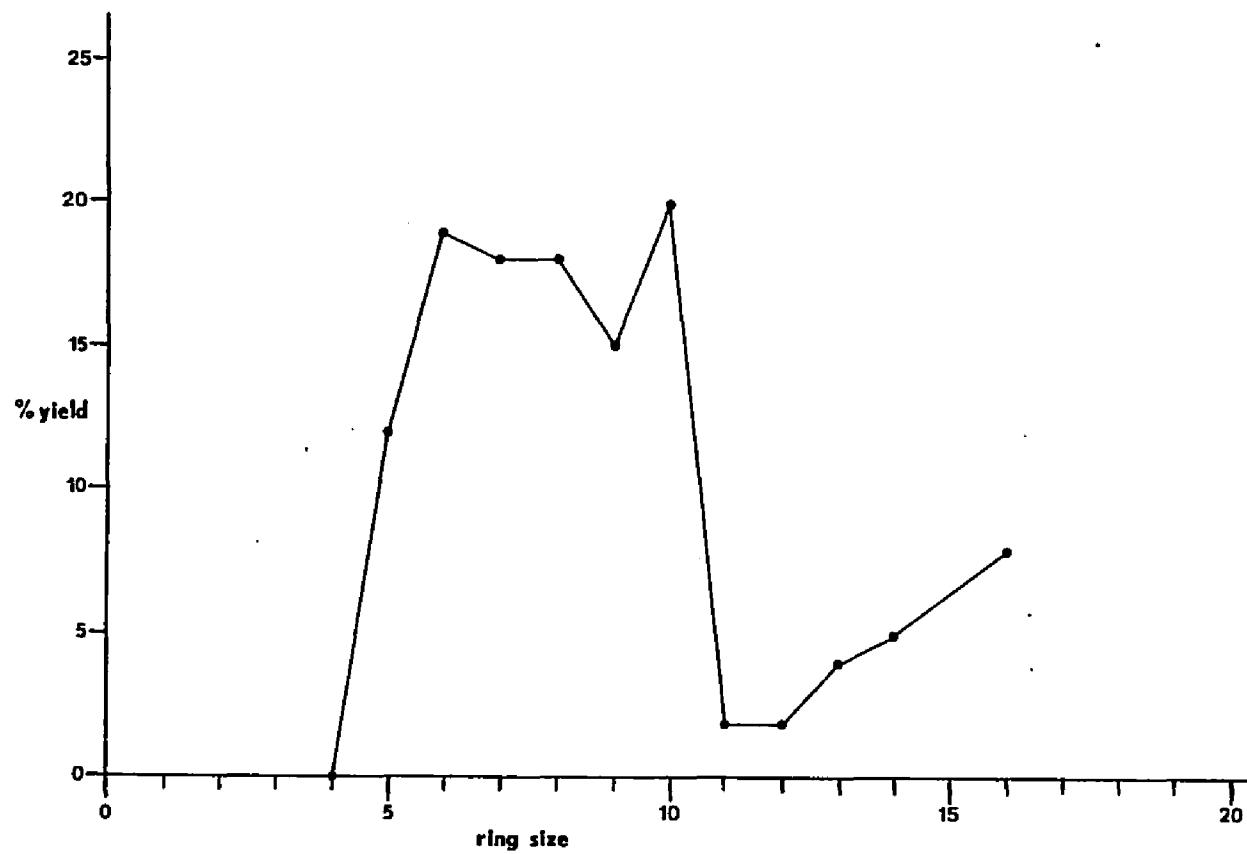
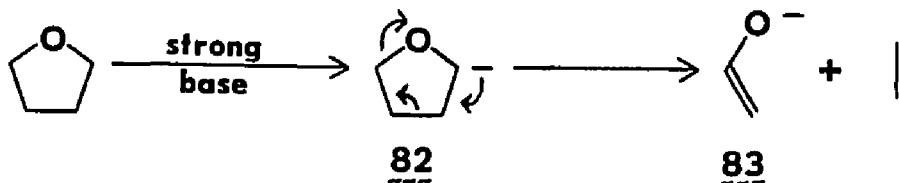


Fig. 2. % yield of 22 as a function of ring size.

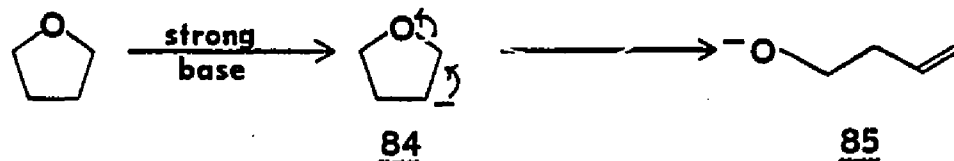
23,n=12 was formed in more than three times the yield of 22,n=12. The dimers are interesting in that when n is even, isomorphous crystalline compounds with the same melting point are formed, while if n is odd, the dimers are oils. In some cases even trimers 24,n=12-14,16 were isolated, in 1-3% yields. The presence of methyl groups (NMR) in side products is best explained by primary alkyl radicals abstracting hydrogen atoms. These methylated side products increase as a function of ring size. This shows that the  $S_{RN}1$  mechanism is once again competing to some extent.

Cyclizations of dianion 1 with  $Me_2SiCl_2$ ,  $Me_2GeCl_2$  and  $Me_2SnCl_2$  generated 5-membered heterocycles 62, 63 and 64, probably via consecutive  $S_N2$  reactions. However, the pentavalent intermediate described previously must also be considered. Monomeric 64 rearranges to its homopolymer 65 at room temperature with a half-life of about 10 minutes. Presumably this polymerization results from the cleavage of the allyl-tin bond due to ring strain in 64. This cleavage results in either a diradical or a zwitterionic intermediate, either of which could lead to polymerization.

Side products 70-76 have in common that they all involve reactions of the solvent, THF. Strong base is known to generate THF  $\alpha$ -anion 82 which eliminates ethylene to generate enolate anion 83 [53, 54].



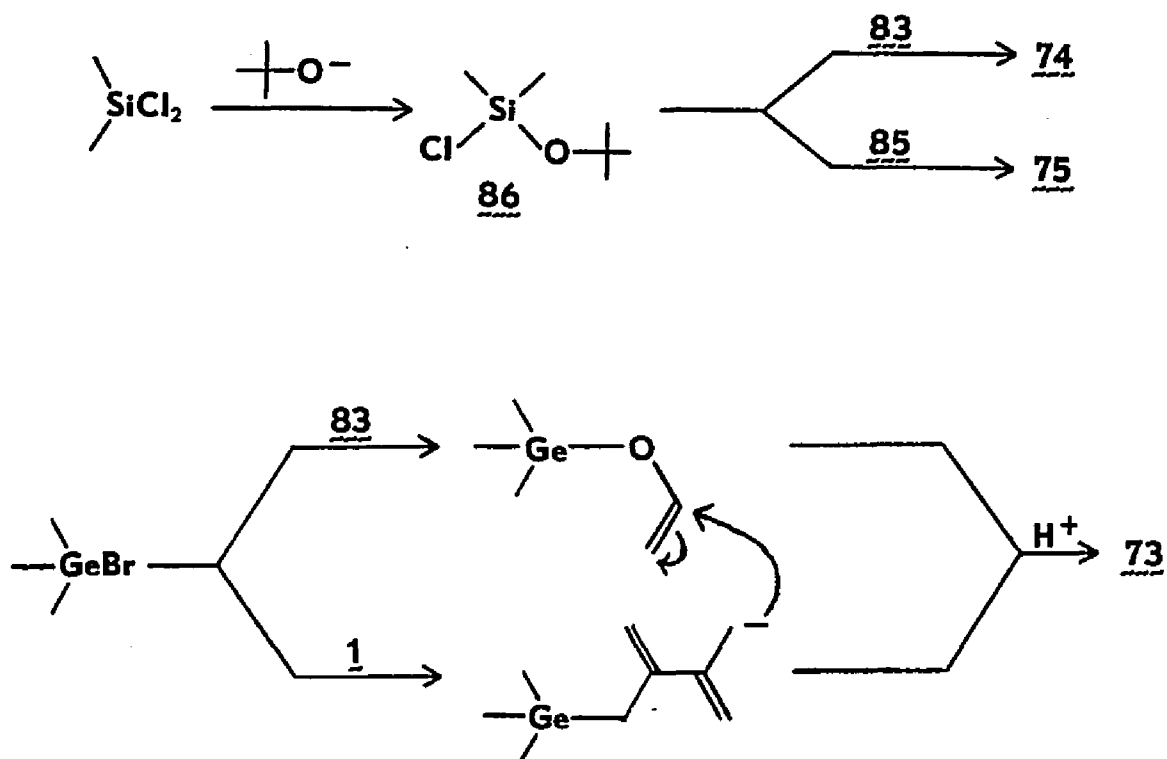
THF  $\beta$ -anion 84 is known for substituted THF's but not for THF itself. Anion 84 would be expected to undergo simple elimination to yield anion 85 [54].



Side products 74 and 75 result from dimethyldichlorosilane reacting with *t*-butoxide ion to yield intermediate 86 followed by reaction with anions 83 and 85, respectively. These products are surprising for two reasons, the first being the presence of 75, because anion 85 is not generated by the reaction of butyllithium with THF. The second reason is that the yields of 74 and 75 were considerably higher than those of other THF elimination products from reactions of dianion 1 in THF. Dimethyldichlorosilane was reacted with KO-*t*-Bu in THF to yield quantitatively di-*t*-butoxydimethylsilane. This showed that *t*-butoxide does not generate THF anions 82 or 84 in appreciable amounts. Therefore it is reasonable to assume that the mixture of 1 and KO-*t*-Bu form a very strong metallating system similar to Lochmann's base [6-8]. This would account for the increased yield of THF elimination product. Such a strong metallating system might be expected to be less selective, resulting in anions 84 and 85. However, 74 was favored over 75 by a ratio of six to one.

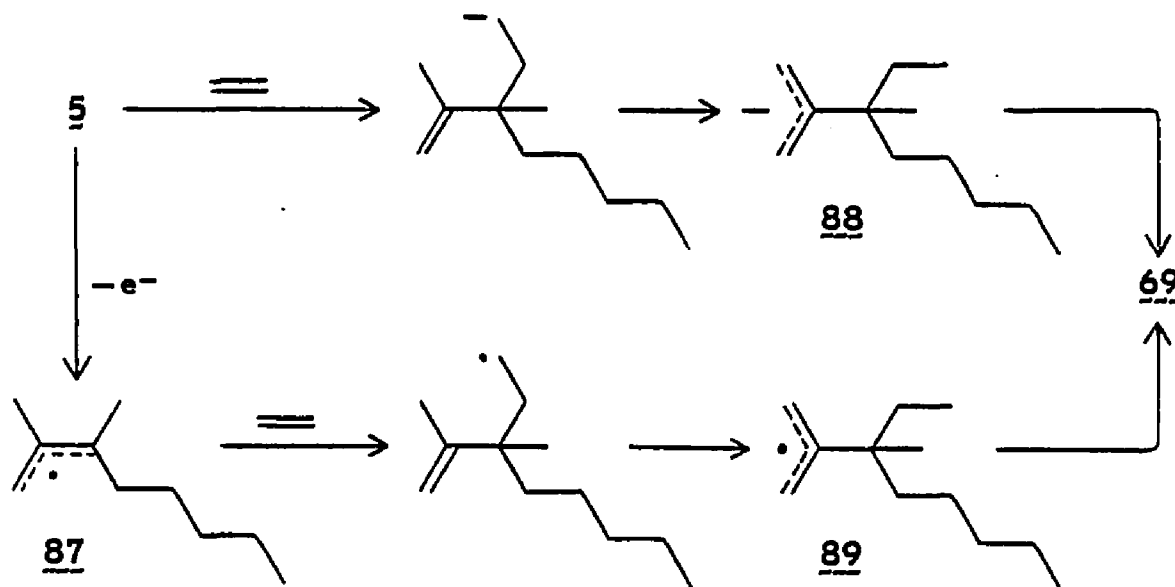
Bizarre side product 73 is probably generated as shown in the scheme below involving enolate anion 83.





Side product 76 is produced by the coupling of anion 5 with ethylene eliminated from THF. Anion 5 results from the addition of butyl anion to diene 4 and might be expected to be a side product in the preparation of dianion 1. Ethylene adds exclusively to the tertiary center in anion 5 rather than at the primary center. This addition may go either by an anionic or a radical mechanism or both.

There is precedent for an anion containing both primary and tertiary centers reacting exclusively at the tertiary center [55] and the presence of 70, 71 and 72 is more readily explained by substitution with 88 than with 89. The yields of 69 were highest when SET mechanisms were known to be operating in the cases of t-butyl bromide and



1,2-dibromoethane (which also acts as a source of ethylene). Anion 5, because of the tertiary charge-bearing carbon, would be expected to have a lower REPA than allyl anion 2 and therefore have greater tendency to undergo SET. Therefore, the radical mechanism via 87 is perhaps more likely when 69 is produced, while the anionic mechanism is probable when 70, 71 and 72 are generated.

UV and  $^1\text{H}$  NMR spectroscopy give information on the conformations of 2,3-disubstituted-1,3-butadienes, 49. The UV data for acyclic butadienes 4, 27, 30, 50 and 55 are listed in Table 6. These compounds are known to be transoid and compounds 30 and 50 provide good approximations for an infinitely large ring ( $22, n=\infty$ ). The  $\lambda_{\text{max}}$ 's of these compounds do not vary much. However, the molar extinction coefficient ( $\epsilon_{\text{max}}$ ) for 4 is considerably higher than those of the others. Therefore, 4 is not a good model for transoid systems. Compounds 32, 59 and 60 have  $\epsilon_{\text{max}}$ 's that indicate that they exist in transoid conformations; however, the  $\lambda_{\text{max}}$ 's of these compounds are higher than

Table 6. UV Data for 2,3-Disubstituted 1,3-Butadienes

Compound	$\lambda_{\max}^{\text{hexane}}$ (nm)	$\epsilon_{\max}^{\text{hexane}}$	Reference
<u>4</u>	228	21900	56
<u>27</u>	228	12800	
<u>50</u>	228 228 (EtOH)	12600 12000 (EtOH)	10
<u>30</u>	229	12000	
<u>55</u>	231	11700	

those of the dienes containing only carbon and increase from silicon to germanium to tin. The variance in  $\lambda_{\max}$  is probably due to an inductive effect involving the heteroatom rather than any change in conformation. The UV data for 32, 59 and 60 are listed in Table 7.

2,3-Disopropyl-1,3-butadiene 90 has a  $\lambda_{\max}$  of 223 nm and an  $\epsilon_{\max}$  of 6180. Evidently, steric bulk has forced the molecule into a twisted transoid conformation with the dihedral angle somewhat less than  $180^\circ$  [57]. When the steric bulk is increased further, the molecule is forced into a "skew" conformation where the dihedral angle is  $90^\circ$ . This is the case for 2,3-di-t-butyl-1,3-butadiene (91), which has a  $\lambda_{\max}$  of 185 nm and an  $\epsilon_{\max}$  of 6165 [58].

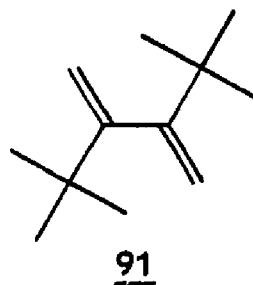
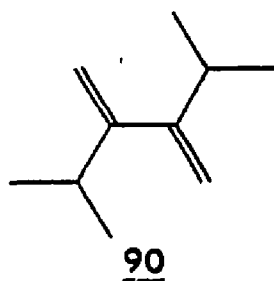
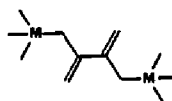


Table 7. UV Data for



Compound	M	$\lambda_{\text{max}}^{\text{hexane}}$	$\epsilon_{\text{max}}^{\text{hexane}}$
<u>32</u>	Si	240	11700
<u>59</u>	Ge	241	13800
<u>60</u>	Sn	247	12700

There is no good acyclic model for the planar cisoid conformation. Probably the best model is five-membered ring diene 22,n=5, although some ring strain is associated with this molecule. Three- and four-membered rings dienes 22,n=3,4 also have planar cisoid conformations, but much more ring strain is associated with these molecules.

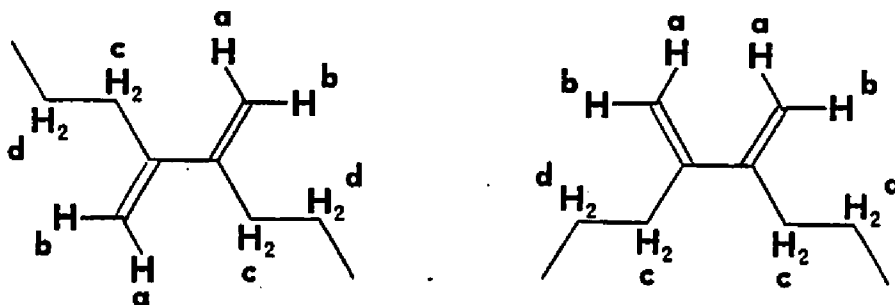
The UV data of 22,n=3-10,12 and 23,n=4,14 are listed in Table 8. Unlike 22,n=5, the six-membered ring, 22,n=6 is known to exist in a chair conformation with a dihedral angle of  $55^\circ$  [60]. Therefore, the UV spectrum of 22,n=6 exhibits a low  $\lambda_{\text{max}}$  and a low  $\epsilon_{\text{max}}$ . Compound 63, having a germanium atom incorporated into a five-membered ring has a ring size intermediate between 22,n=5 and 22,n=6. 63 has a  $\lambda_{\text{max}}$  of 227 and  $\epsilon_{\text{max}}$  of 6400; these values are slightly higher than 22,n=6, indicating a twisted cisoid conformation with a dihedral angle less than  $55^\circ$ . The seven- and eight-membered ring dienes 22,n=7,8 are puzzling in that they have higher absorption maxima than 22,n=6, indicating that the dihedral angles are less than in the six-membered ring,

Table 8. UV Data for 22, 23

Compound	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$	Solvent	Reference
<u>22, n=3</u>	232	11000	hexane	17
<u>22, n=4</u>	248	10100	EtOH	32
<u>22, n=5</u>	248	10500	Isooctane	22, 32, 59
<u>22, n=6</u>	220	6375	95% EtOH	59
	220	6400	EtOH	32
	220	5500	hexane	24, 27
<u>22, n=7</u>	235	5800	EtOH	10
<u>22, n=8</u>	229	3700	hexane	27
	233	5800	EtOH	10
<u>22, n=9</u>	225	7400	EtOH	10
<u>22, n=10</u>	233	6950	EtOH	10
<u>22, n=12</u>	230	7100	hexane	27
<u>23, n=8</u>	228	10000	hexane	31
<u>23, n=14</u>	228	24000	hexane	

but have extinction coefficients slightly less than that of 22,n=6, suggesting that the dihedral angles are larger than in the six-membered ring. However,  $\lambda_{\max}$  is usually the more reliable parameter as it is much easier to measure accurately than  $\epsilon_{\max}$ . The extinction coefficients for 22,n=9,10 are intermediate values and the values for  $\lambda_{\max}$  are not very informative. These rings probably have more than one important conformation. The UV data for 22,n=12 are closer to that of 22,n=10 than to those of acyclic transoid models. Therefore, 22,n=12 has not reached the planar transoid conformation. Dimeric 23,n=4 has a twisted cisoid conformation, the dihedral angles being similar to that of 22,n=6 based on an  $\epsilon_{\max}$  of 5000 per diene moiety. Twenty-eight-membered ring diene 23,n=14 matches transoid models 30 and 50 quite well with  $\lambda_{\max}$  228 nm and  $\epsilon_{\max}$  12000 per diene moiety.

$^1\text{H}$  NMR allows the examination of more parameters than UV ( $\lambda_{\max}$  and  $\epsilon_{\max}$  only). The chemical shifts of vinylic (a,b), allylic (c) and homoallylic (d) protons provide four parameters and coupling constants involving protons a-d give several more.  $^1\text{H}$  NMR data are listed in tables in Appendix A.



Acyclic butadienes 30 and 51 provide excellent transoid models and approximate an infinitely large ring 22, n=∞. The chain-ending methyl groups in 30 and 51 are distant enough to have virtually no effect on the parameters of interest.

In examining acyclic 2,3-disubstituted-1,3-butadienes, the chemical shifts of vinyl protons ( $\delta H_a$ ,  $\delta H_b$ ) and the coupling constant between these two protons ( $J_{ab}$ ) are the most useful parameters as they are least sensitive to shielding and deshielding effects of substituents. With these acyclic compounds we expect that increasing the steric bulk of the substituents forces the diene conformation out of transoid planarity and decreases the dihedral angle from  $180^\circ$  to a limit of  $90^\circ$  which occurs with the extreme steric bulk of *t*-butyl groups in 91. Transoid model 51 has the NMR parameters  $\delta H_a = 5.04$ ,  $\delta H_b = 4.91$  and  $J_{ab} = 0.9$ . "Skew" conformation model 91 has NMR parameters  $\delta H_a = 5.1$ ,  $\delta H_b = 4.7$  and  $J_{ab} = 1.5$  Hz [58].

Examination of these three parameters in other acyclic 2,3-dialkyl-1,3-butadienes gives information about these conformations. 52 (Table A.12) evidently prefers a planar transoid conformation. Compounds 53 (Table A.11) and 55 (Table A.8), with  $\beta$ -phenethyl and isobutyl groups, respectively, are only slightly hindered; their NMR parameters indicate only a small deviation from planarity. 2,3-Diisopropyl-1,3-butadiene (90) has NMR parameters  $\delta H_a = 4.91$ ,  $\delta H_b = 4.82$  and  $J_{ab} = 1.2$  Hz [57]; its isopropyl groups have increased steric bulk and 90 probably has a twisted transoid conformation as its NMR parameters are quite different from those of 51 or 91. However, unlike 91, compound 90 undergoes Diels-Alder reactions with dienophiles [57].

2,3-Dineopentyl-1,3-butadiene (57) has NMR parameters  $\delta H_a = 5.14$ ,  $\delta H_b = 4.73$  and  $J_{ab} = 2.5$  Hz; since these values are quite close to those of 91, based on NMR alone 57 has a "skew" conformation.

Compounds 57, 32, 59, 60 and 61 comprise an analogous series involving all the Group IV A elements from C to Pb, respectively. Because the heteroatom-carbon bond length increases down the column, the effective bulk of the substituents decreases, allowing the diene conformation to approach planar transoid. The NMR data of this series are interesting (Table A.5):  $\delta H_b$  remains virtually constant at 4.73 ppm throughout, while  $\delta H_a$  decreases steadily from 5.14 for C until the signals of  $H_a$  and  $H_b$  merge in the cases of Sn and Pb. Coupling constant  $J_{ab}$  decreases from 2.5 Hz for C to about 1.0 Hz for Si and Ge. UV data (as well as Diels-Alder reactivity of 32 [57]) indicate that 32, 59 and 60 have nearly planar transoid conformations, while NMR points to a "skew" conformation for 57. It is likely that the changes observed in  $\delta H_a$  (excepting the change from C to Si) are due to an increased inductive effect from progressively larger heteroatoms rather than a major conformation change.

The  $^1H$  NMR data for cyclic compounds 22,  $n=3-14,16$  are listed in Table A.1. The data for dimers 23,  $n=4,11-14,16$  and trimers 24,  $n=12-14,16$  are listed in Tables A.2 and A.3, respectively. A number of NMR parameters of monomers 22, dimers 23 and trimers 24 have been plotted as a function of ring size ( $\delta H_a$ , Fig. 3;  $\delta H_b$ , Fig. 4;  $\delta H_c$ , Fig. 5;  $\delta H_d$ , Fig. 6; and  $J_{cd}$ , Fig. 7).

The compounds with ring sizes 3-6 will be discussed first. As mentioned previously, dienes 22,  $n=3-5$  all have planar cisoid



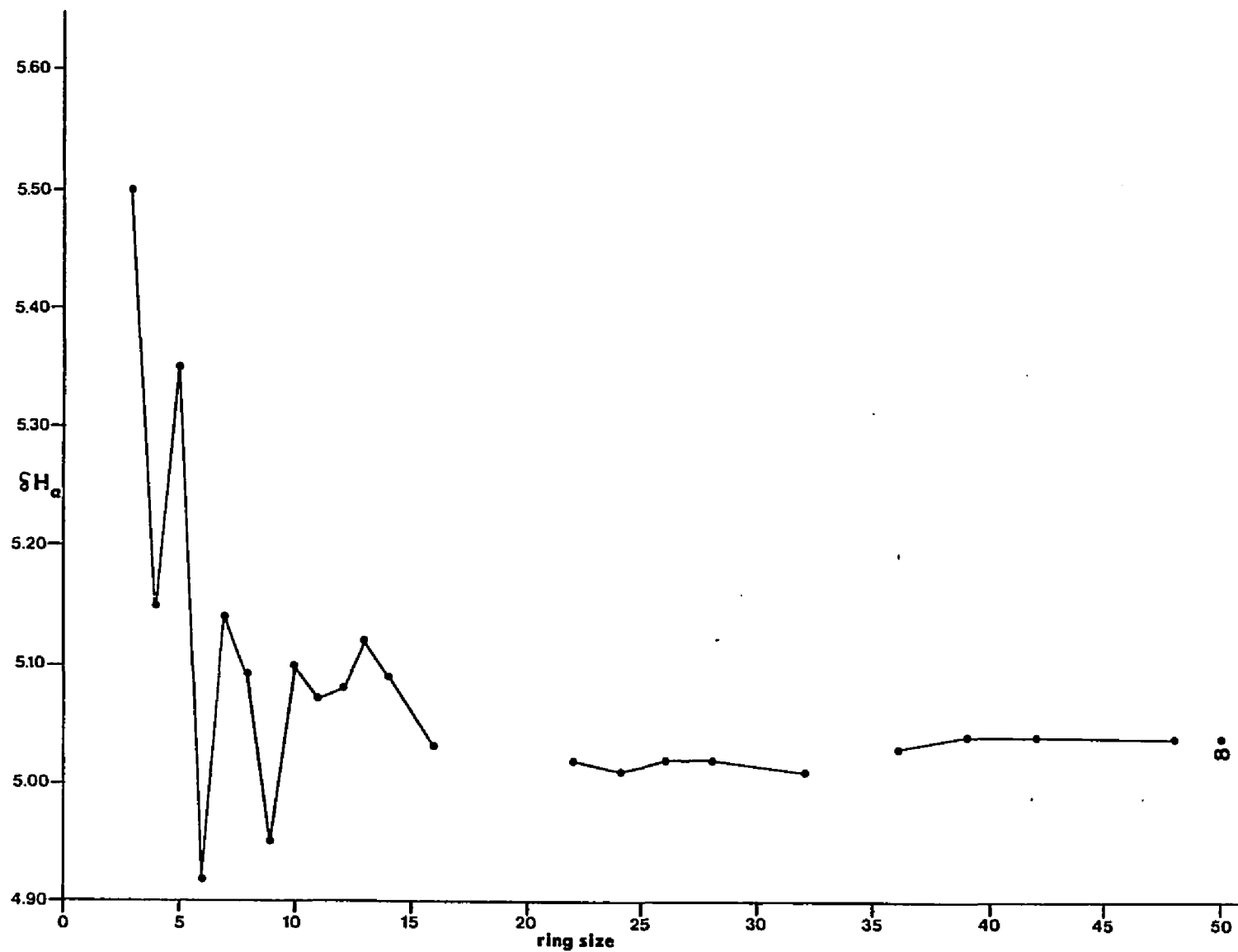


Fig. 3.  $\delta H_a$  as a function of ring size.

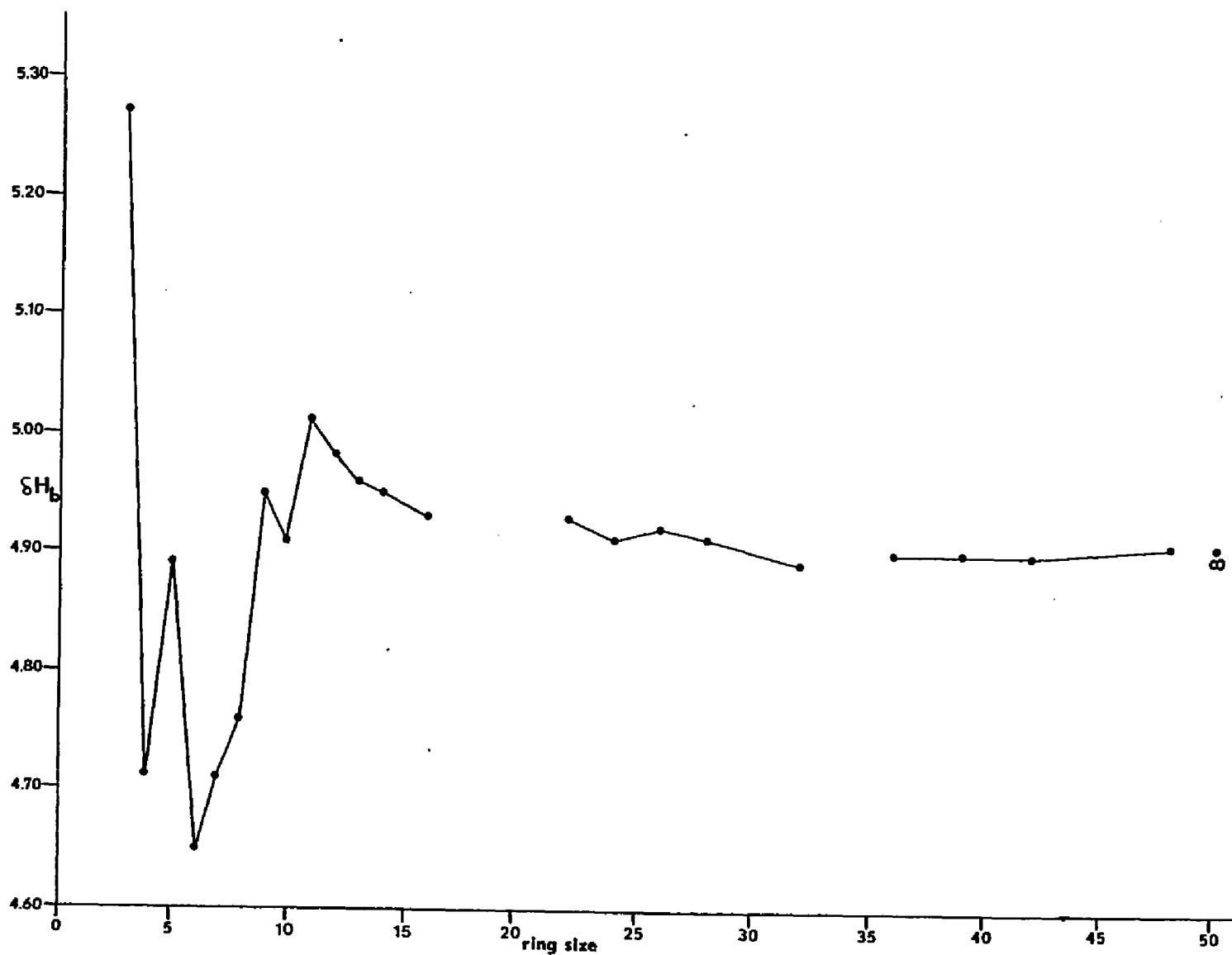


Fig. 4.  $\delta H_b$  as a function of ring size.

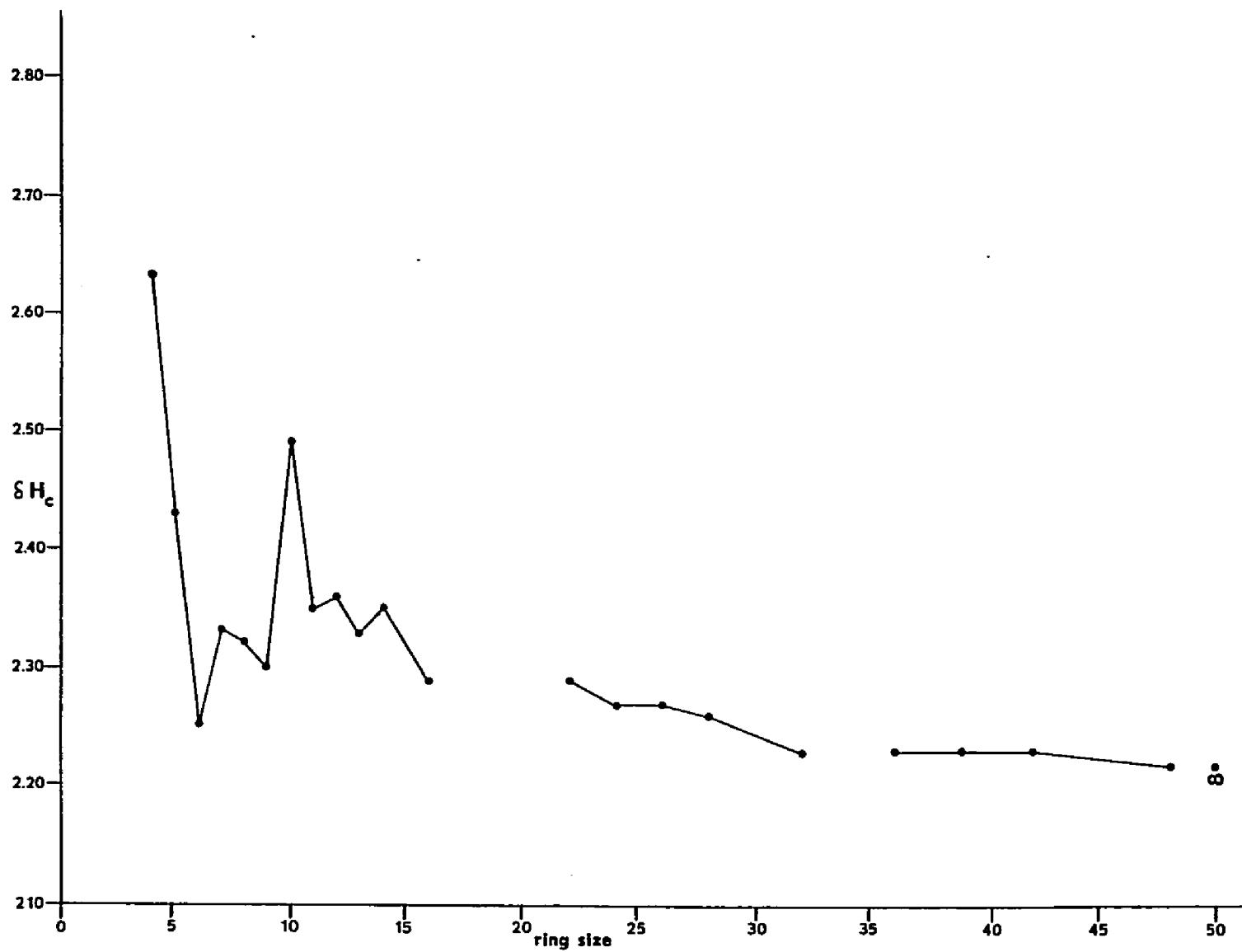


Fig. 5.  $\delta H_c$  as a function of ring size.

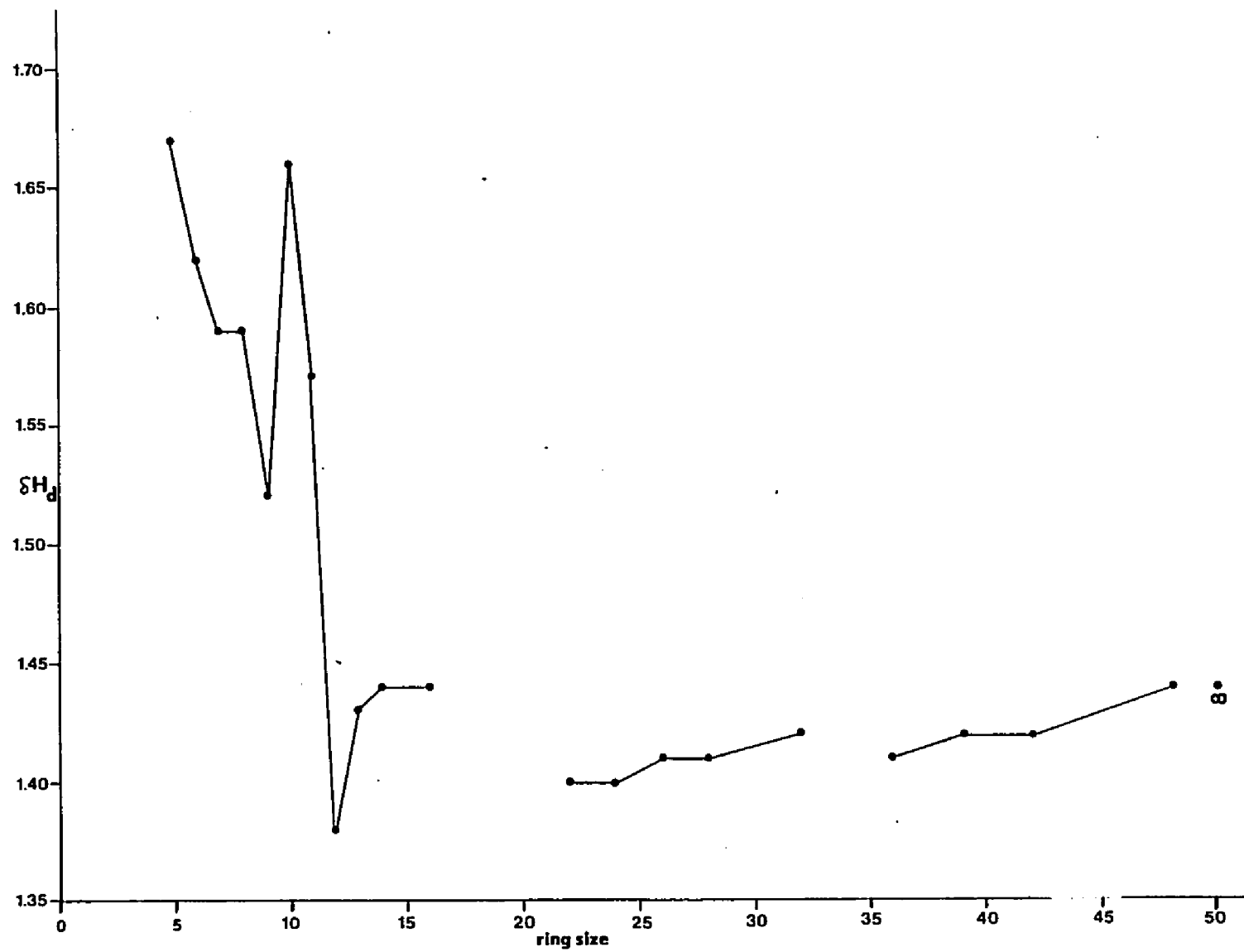


Fig. 6.  $\Delta H_d$  as a function of ring size.

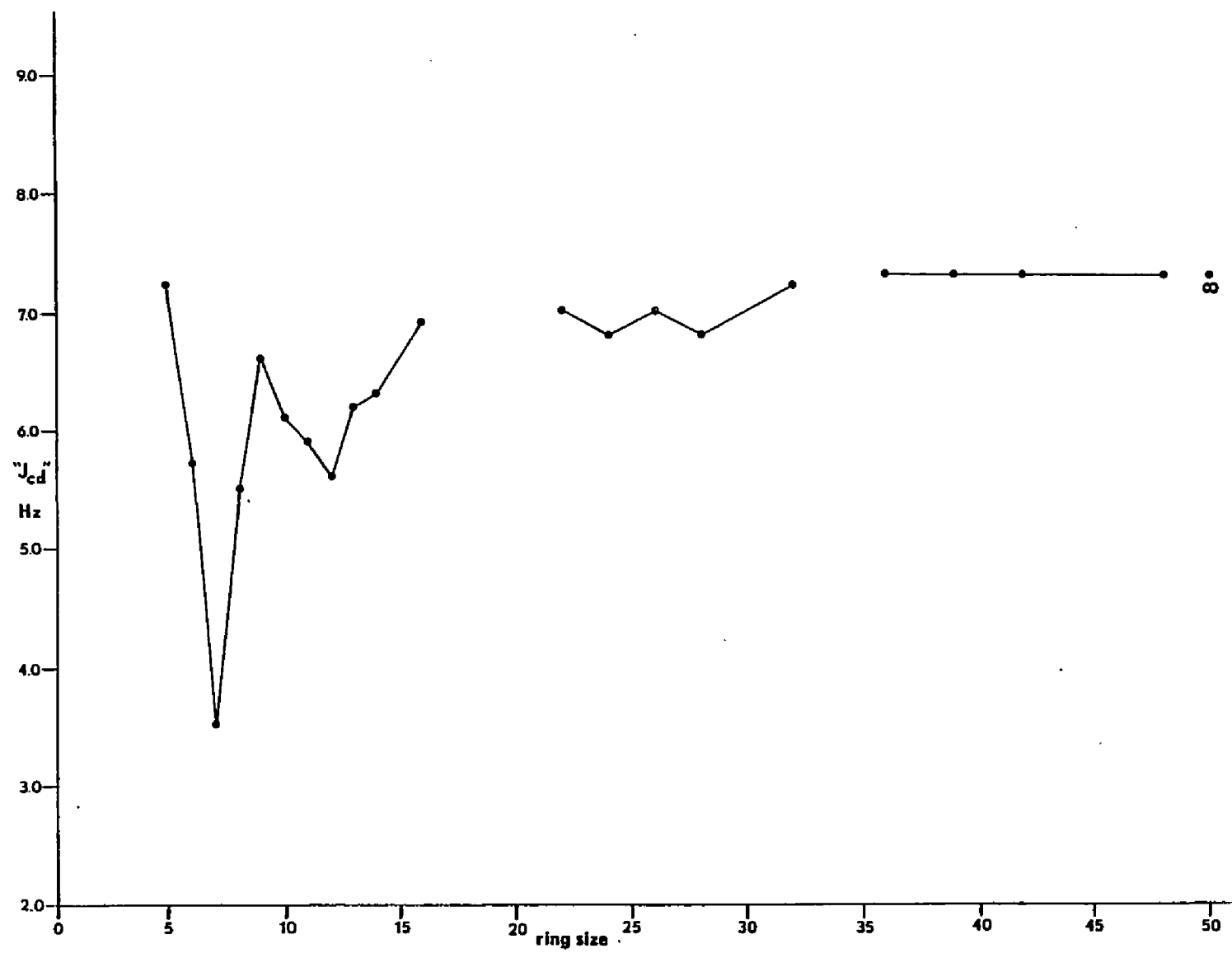


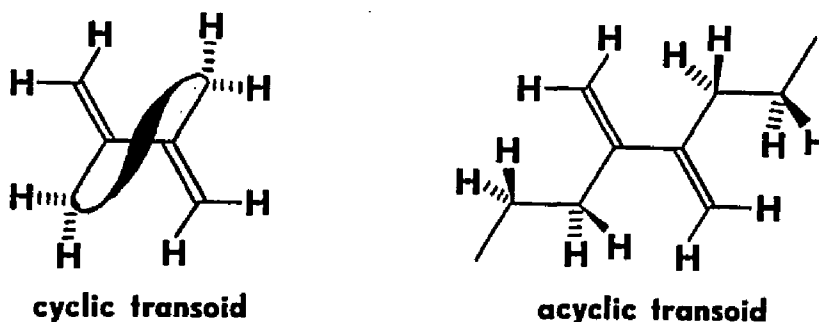
Fig. 7. " $J_{cd}$ " as a function of ring size.

conformations with varying degrees of ring strain. 22,n=5 has the least ring strain and will serve as a model for a planar cisoid conformation. 22,n=6 is twisted  $55^\circ$  from planarity and the chemical shift of the vinyl protons have been assigned in the literature as  $\delta H_a = 4.65$  and  $\delta H_b = 4.90$  [32]. Compounds 62, 63 and 64, with heteroatoms in the 5-membered ring (Table A.6), can be considered to provide intermediate geometries between that of 22,n=5 and that of 22,n=6. Examination of the chemical shifts of the vinyl protons in this series shows a steady decline in  $\delta H_a$ ,  $\delta H_b$  and the difference  $\delta H_a - \delta H_b$  ( $\Delta\delta H_{ab}$ ) from 22,n=5 with values  $\delta H_a = 5.37$ ,  $\delta H_b = 4.89$ ,  $\Delta\delta H_{ab} = 0.50$  to 64 with values  $\delta H_a = 4.90$ ,  $\delta H_b = 4.63$ ,  $\Delta\delta H_{ab} = 0.27$ . If three-dimensional models are examined, it can be seen that the effective size of the dimethyltin group in the ring is about the same as two methylenes, leading to the prediction that the diene moieties in 22,n=6 and in 64 should have similar conformations. Parameters  $\delta H_a$  and  $\delta H_b$  for these two compounds are virtually identical with the exception that the assignments for  $\delta H_a$  and  $\delta H_b$  are reversed. Obviously, the assignments for one of these two compounds are wrong. Because the assignments of  $\delta H_a$  and  $\delta H_b$  for all other compounds in this series (22) have  $\delta H_a$  larger than  $\delta H_b$ , it is assumed that it is the literature assignments which are incorrect.

Examination of NMR parameters in Figs. 3-7 shows no definite trends with ring sizes 7-10. Interesting is the fact that  $\delta H_a$  and  $\delta H_b$  coalesce into a single signal for 22,n=9. Since examination of molecular models rules out transoid conformations for 22,n=7,8, these evidently have twisted cisoid conformations, while dienes 22,n=9,10 have either twisted cisoid or twisted transoid conformations. 22,n=9,10

likely exist in two or more major conformations, for which only an average is observed in the NMR.

From 22,n=11 to larger ring sizes there is a general trend in the NMR parameters toward values of "planar" transoid model 51. However, these model values are not attained by monomers 22,n $\geq$ 16, dimers 23,n $\geq$ 16 (ring sizes up to 32), on even trimers 24,n $\geq$ 14 (ring sizes up to 42). An exact match is finally obtained with trimer 24,n=16, which has a 48-membered ring. This can be attributed to a change from what might be termed the "cyclic transoid" conformations to the "acyclic transoid" conformation of an infinitely large ring:



The major factor contributing to the NMR differences between these conformations is probably the positions of allylic and homoallylic hydrogens relative to each other and to the vinyl hydrogens. In order for the NMR parameters involving the vinylic, allylic and homoallylic protons to match those of acyclic transoid model 51, ten consecutive ring carbons (centered about the quaternary carbons) must be coplanar. The diene moiety may achieve a transoid conformation with only four ring carbons being coplanar. Studies with space-filling models show that 22,n=10 has room to allow four coplanar carbon atoms, 22,n=14 is large enough to allow six coplanar carbon atoms, 22,n=18 is

big enough to accommodate eight coplanar carbons, and 22,n=22 will accommodate ten coplanar carbons. Although these molecules are large enough to allow these conformations, they are somewhat strained and it is thus not surprising that the NMR spectra indicated that these conformations predominate only in molecules somewhat larger than the minimum size necessary. Also, there are no sharp differences observed in the NMR spectra as these conformational changes occur as a function of ring size. Instead, a continuum is observed in the NMR parameters from the "cyclic transoid" conformations in smaller rings to the acyclic transoid conformations of larger rings. These changes are expected to occur in smaller rings for monomers (22) than for dimers (23) and trimers (24) which require coplanarity in two and three regions of the ring, respectively.

It is questionable whether even four ring carbons have become coplanar in the cases of 22,n=11,12. Their conformations are definitely closer to transoid than to cisoid, but with dihedral angles less than  $180^\circ$  (considerably less for 22,n=11).

Compounds 69-72 show characteristic NMR spectra. The spectra of these compounds all show multiplets for 5 methylenes centered at about  $\delta$  1.26, a methyl singlet between  $\delta$  0.91 and 0.96, a methyl triplet ( $J = 7.0-7.5$  Hz) between  $\delta$  0.85 and 0.87, and another methyl triplet ( $J = 6.8-7.0$  Hz) between  $\delta$  0.69 and 0.71. The methyl group of the ethyl group is more shielded by the double bond than the more distant methyl of the pentyl chain, hence its signal is upfield from that of the latter.



The mass spectra (MS) of a number of reaction products were obtained. Besides giving the molecular weight of the substance tested, MS yields additional information through fragmentation patterns. A discussion of the molecular ions of the compounds studied will be followed by longer discussion of their modes of fragmentation. Tables listing mass spectral data (fragment weights and intensities) are in Appendix B.

In all but one case (that of 61), a molecular ion was observed for the compounds tested. Determination of molecular weight in most cases merely confirmed a structure already elucidated using  $^1\text{H}$  NMR. However, the  $^1\text{H}$  NMR spectra of 22,  $n > 11$ , 23,  $n > 11$  and 24,  $n > 11$  are very similar, displaying only subtle differences.  $^1\text{H}$  NMR cannot distinguish these compounds because the increasing symmetry from 22 ( $\text{C}_{2v}$ ) to 23 ( $\text{D}_{2h}$ ) to 24 ( $\text{D}_{3h}$ ) results in no change in the number or relative areas of distinguishable signals. MS, however, gives the molecular weight of each and readily allows differentiation. Because the spectra taken are relatively low resolution, at high masses some of the values for the molecular ions (23,  $n=16$  and 24,  $n=12$ ) were one unit larger than they should have been (497 instead of 496 for the former and 577 instead of 576 for the latter).

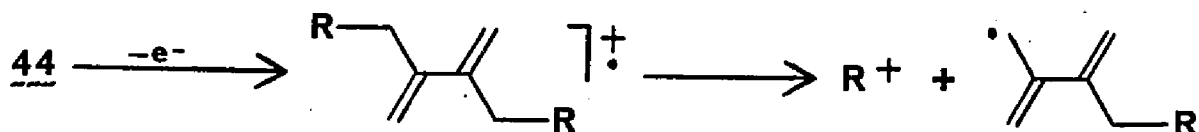
In the cases of germanium-, tin- and lead-containing compounds, a number of isotopes are present in significant proportions instead of just one. The molecular (and fragment) ions appear as a group of peaks with intensities proportional to their natural abundances. The natural abundances of the isotopes of germanium, tin and lead are listed in Table 9. When two heteroatoms are present, the patterns for

Table 9. % Isotopic Abundance

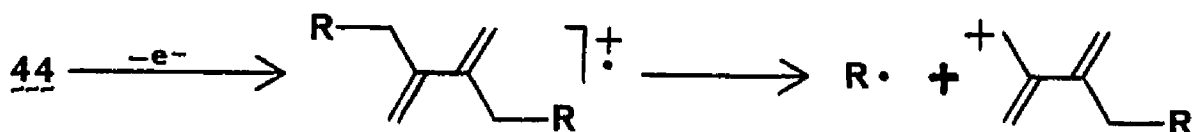
Isotope	% Abundance
<u>Germanium</u>	
70	20.52
72	27.43
73	7.76
74	36.54
76	7.76
<u>Tin</u>	
112	0.96
114	0.66
115	0.35
116	14.30
117	7.61
118	24.03
119	8.58
120	32.85
122	4.72
124	5.94
<u>Lead</u>	
204	1.5
206	23.6
207	22.6
208	52.3

the molecular ion become complex. The relative intensities for ions containing two germanium atoms or two tin atoms were calculated and are listed in Table 10 with the largest peak in each case being given the value of 100. The patterns observed in compounds 59, 60 and 73 for ions containing two heteroatoms matched the calculated patterns quite well. For compounds containing germanium, tin or lead, only the largest peaks in the patterns of isotopic peaks are listed in the tables in Appendix B.

2,3-Disubstituted-1,3-butadienes having the general formula 44 exhibit a number of distinctive fragmentation patterns. If the R-group in 44 is capable of stabilizing a positive charge, then cleavage to give  $R^+$  (see below) is the primary mode of fragmentation and  $R^+$  gives the base peak. The following compounds display this feature: 52 (R = allyl), 53 (R = benzyl), 57 (R = *t*-butyl), 32 (R = SiMe<sub>3</sub>), 59 (R = GeMe<sub>3</sub>), 60 (R = SnMe<sub>3</sub>) and 61 (R = PbMe<sub>3</sub>). Diene 55 (R = isopropyl) displays a strong peak for  $R^+$ , but it is not the base peak.



If  $R^+$  is not very stable, the R to allyl bond in 44 is still cleaved, but now to give  $R\cdot$  and a 2-vinylallyl cation as shown below:



Another favored mode of fragmentation involves a McLafferty-like rearrangement. This requires the presence of a proton  $\gamma$  to a double bond. This rearrangement leads to the loss of a neutral olefin

Table 10. Calculated Intensities for Ions Containing Two Ge or Sn Atoms

2 Ge		2 Sn	
Combined Mass	Relative Intensity	Combined Mass	Relative Intensity
140	17.67	224	$5.134 \times 10^{-2}$
142	47.23	226	$7.058 \times 10^{-2}$
143	13.36	227	$3.743 \times 10^{-2}$
144	94.49	228	1.554
145	17.86	229	0.8395
146	100.00	230	3.629
147	23.80	231	2.035
148	73.89	232	16.97
149	5.05	233	13.69
150	23.30	234	44.76
152	2.53	235	35.32
		236	92.76
		237	51.00
		238	100.00
		239	35.63
		240	82.21
		241	9.548
		242	33.18
		243	5.676
		244	22.98
		246	3.123
		248	1.965

molecule. Several examples are shown in Figs. 8 and 9 with the molecular weights (intensities in parentheses) of the fragment ions. In the case of 55, an allene radical cation may be obtained as shown in Fig. 10.

Turning to individual compounds, the MS of 52 shows a complex spectrum because of the large number of different rearrangements possible due to the number and position of double bonds. The MS of 53 is dominated by benzyl cation and peaks resulting from its fragmentation. Compounds 51, 55 and 57 exhibit straightforward fragmentation patterns which are outlined in Figs. 11, 12 and 13, respectively. The molecular weights are given with the relative intensities in parentheses in Figs. 12 and 13. Because the molecular ion of 57 may expel an isobutylene molecule to give a fragment ion which is equivalent to the molecular ion of 56, the features of the MS of 56 are contained within the MS of 57. The intensities of fragmentation peaks from 56 are marked with asterisks in Fig. 13.

Group IV element-containing compounds 32, 59, 60 and 61 display very similar MS. The molecular ion peak is moderately strong in 32 and an order of magnitude weaker in the cases of 59 and 60. The molecular ion for 61 was not observed. However, the fragmentation pattern for 61 was completely analogous to those of 32, 59 and 60.

As mentioned previously, the major fragment for this series of compounds is  $\text{Me}_3\text{M}^+$ . This fragment can expel methyl radicals leading to  $\text{Me}_2\text{M}^+$  and  $\text{MeM}^+$ . In the spectra of 60 and 61, the atomic cation radicals  $\text{Sn}^+$  and  $\text{Pb}^+$  were observed.

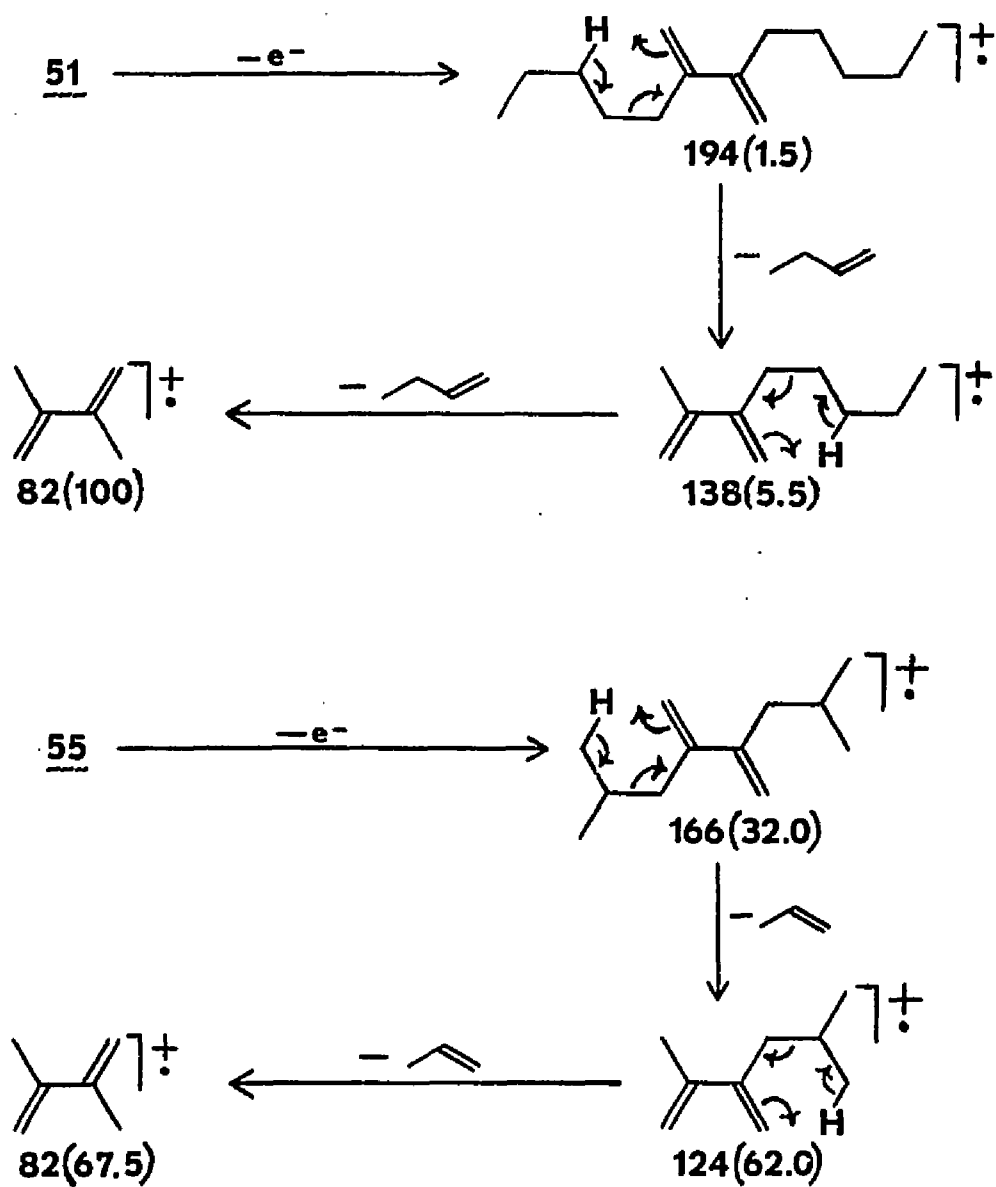


Fig. 8. McLafferty-like rearrangements in the MS of 51 and 55.

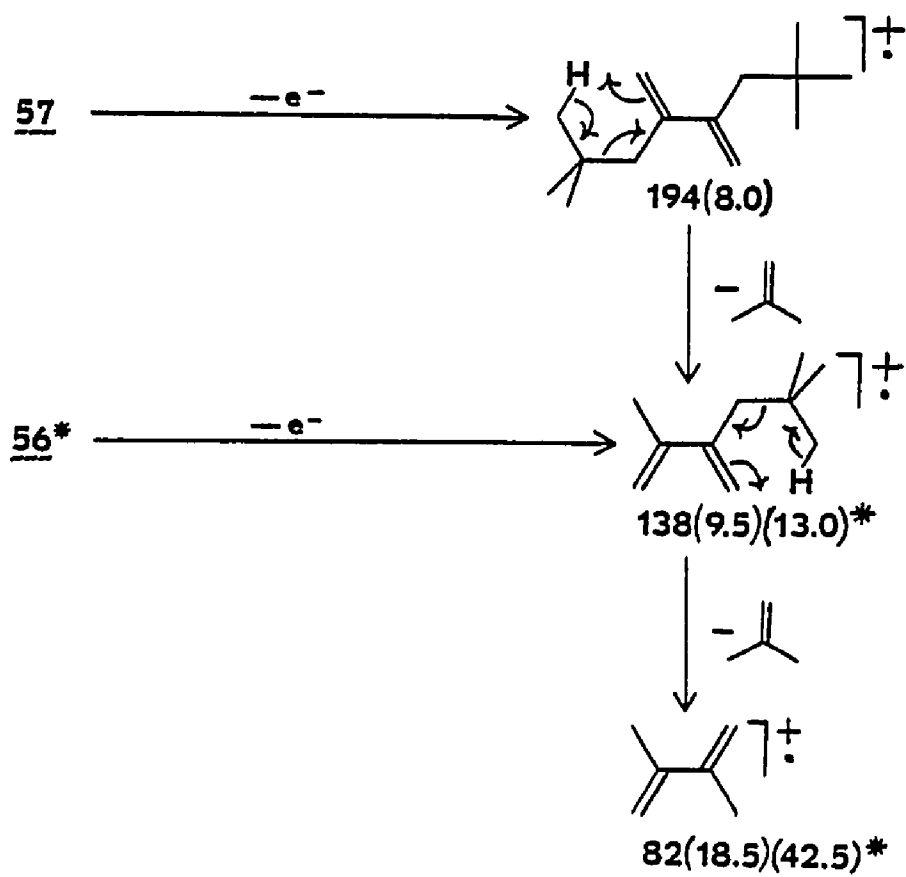


Fig. 9. McLafferty-like rearrangements in the MS of 56 and 57.

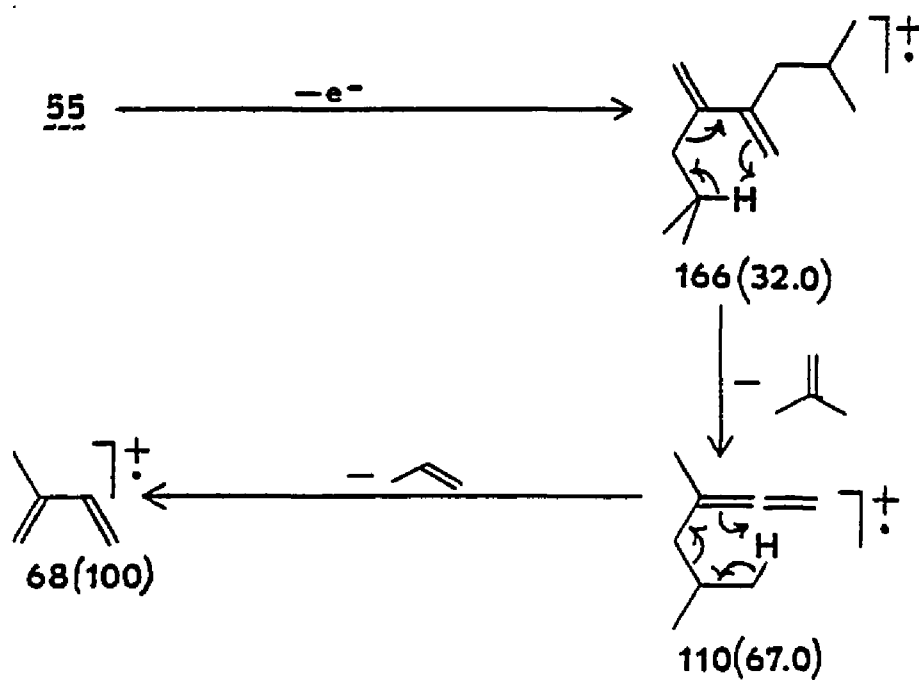


Fig. 10. McLafferty-like rearrangements involving an allene radical cation in the MS of 55.



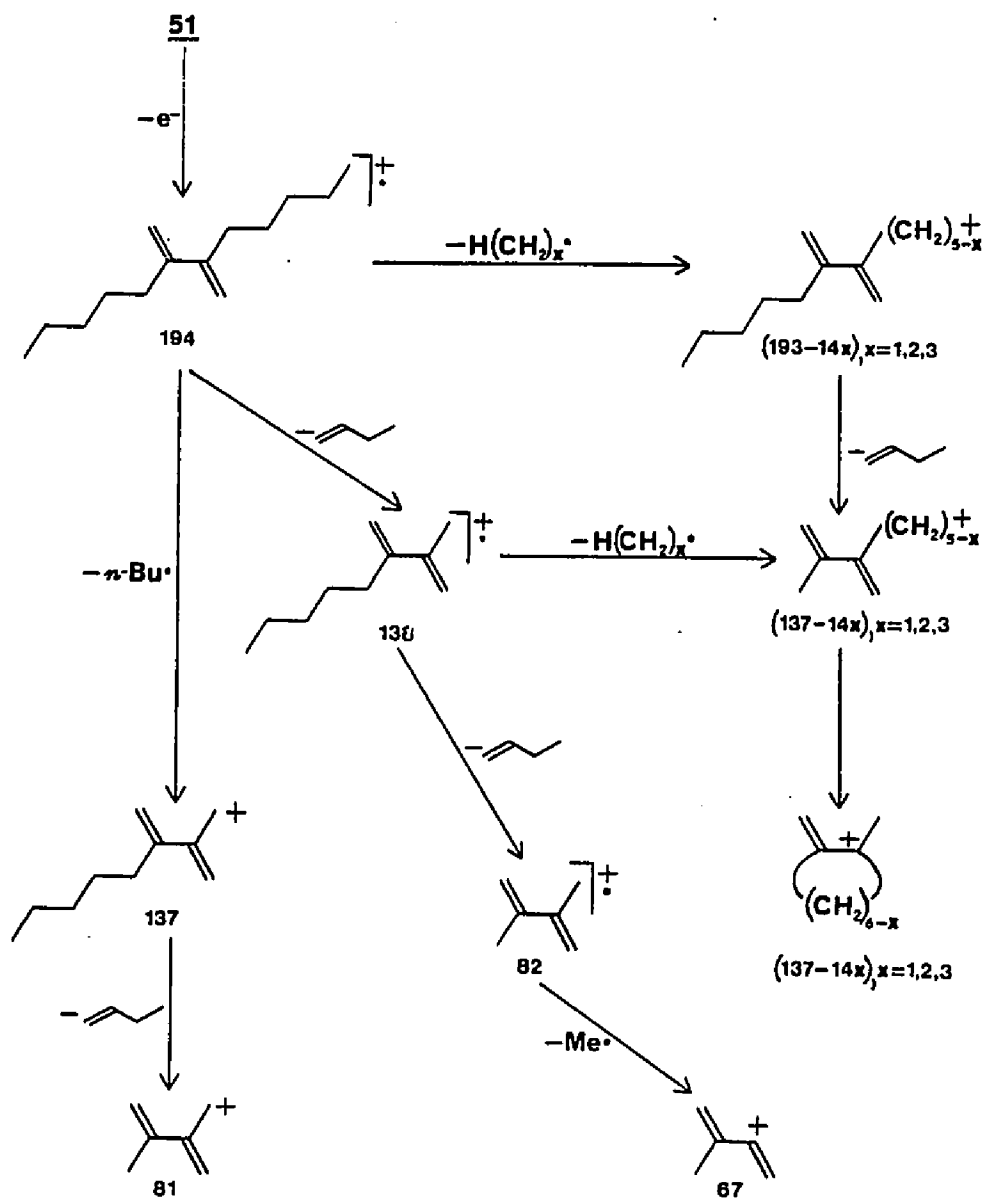


Fig. 11. MS fragmentation scheme for 51.

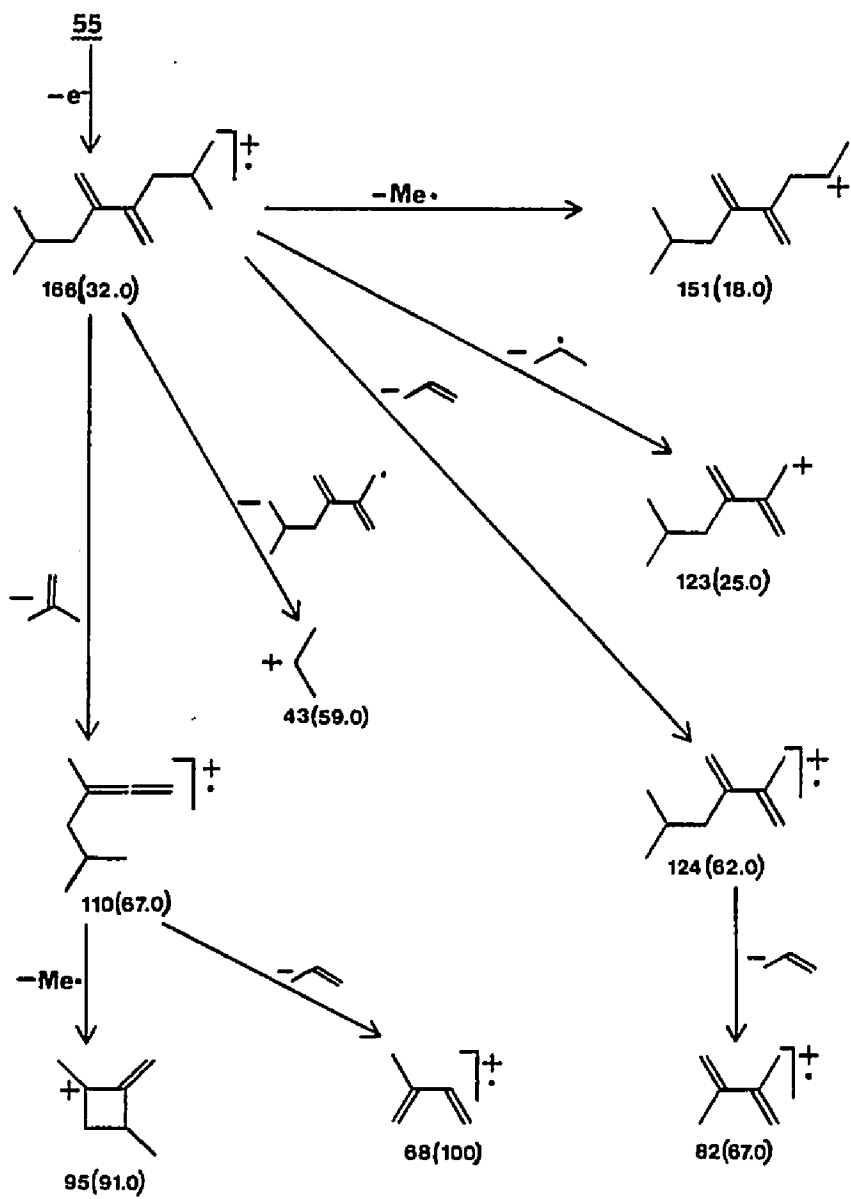


Fig. 12. MS fragmentation scheme for 55.

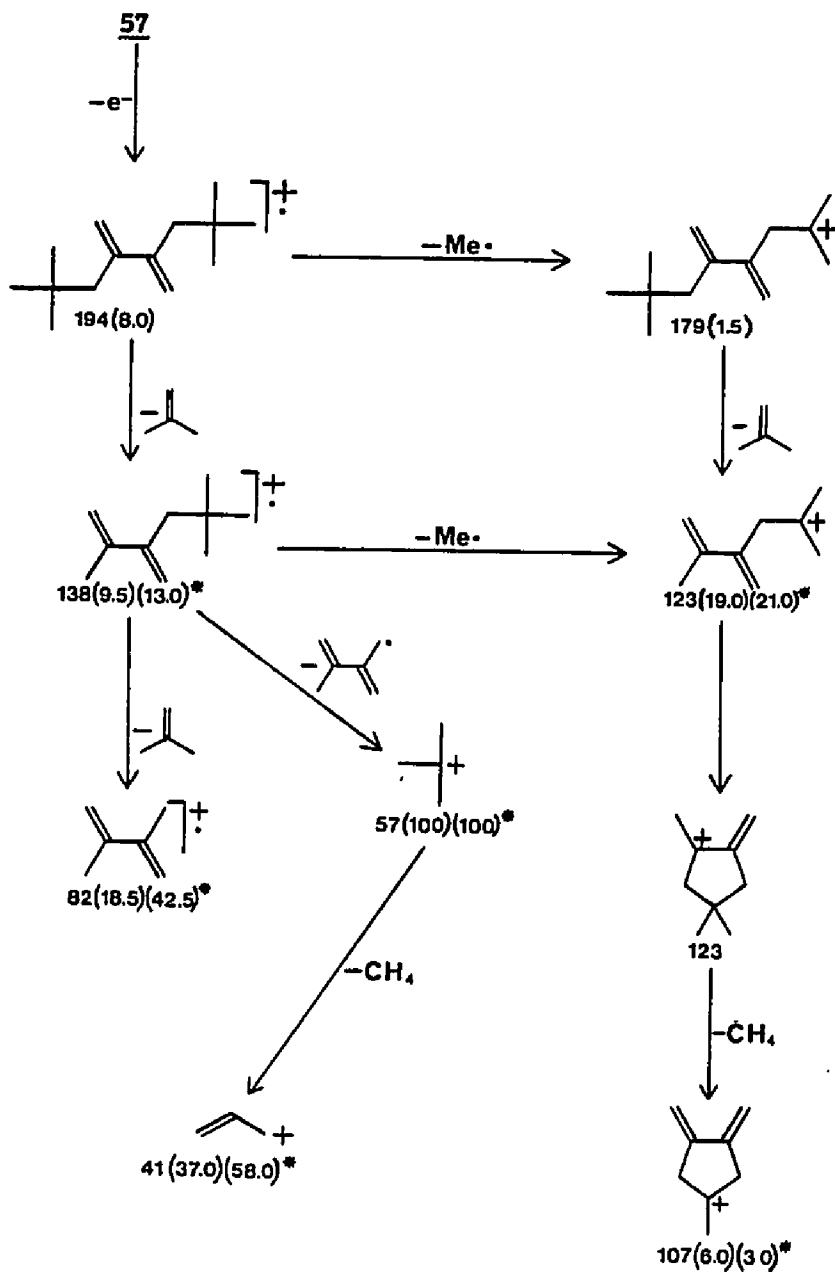


Fig. 13. MS fragmentation scheme for 56, 57.

The other major mode of fragmentation in these compounds involves first the expulsion of a methyl radical from the molecular ion. This fragment can expel a  $\text{Me}_3\text{M}^+$  cation, leaving neutral molecules 62 (M = Si), 63 (M = Ge), 64 (M = Sn) and the analogous lead compound. These molecules are subsequently ionized to their molecular ions which are of relatively strong intensity. These ions readily expel methyl radicals to give very stable cations (base peak in the MS of 62 and 63). Further fragmentation leads to  $\text{MeM}^+$ .

The general fragmentation scheme for compounds 32, 59, 60 and 61 is given in Fig. 14. Because these compounds fragment to 62, 63, 64 and the analogous lead compound, their fragmentation is observed in the MS of the former compounds. The portion of the fragmentation common to both groups of compounds has been blocked off.

1,2-Bis(methylene)cycloalkanes 22,n=11,16 fragment in a straightforward manner. These compounds display molecular ions of moderately strong intensity. Two McLafferty-like rearrangements result in the expulsion of an  $\alpha,\omega$ -diene to form the cation radical of 4. One of these rearrangements followed by cleavage of the remaining allyl-carbon bond leads to a large peak at  $m/e$  81. Cleaving one of the initial allyl-carbon bonds leads to a species which contains an allyl cation and a radical at the end of an alkyl chain. This radical may "back-bite" onto the chain, abstracting a hydrogen atom from virtually anywhere along the chain, leaving a secondary radical. This radical may disproportionate to a primary radical and an alkene. Either the radical or the double bond may stay with the charge-bearing fragment. This leads to two series of fragments, with molecular weights (M-1-14n)

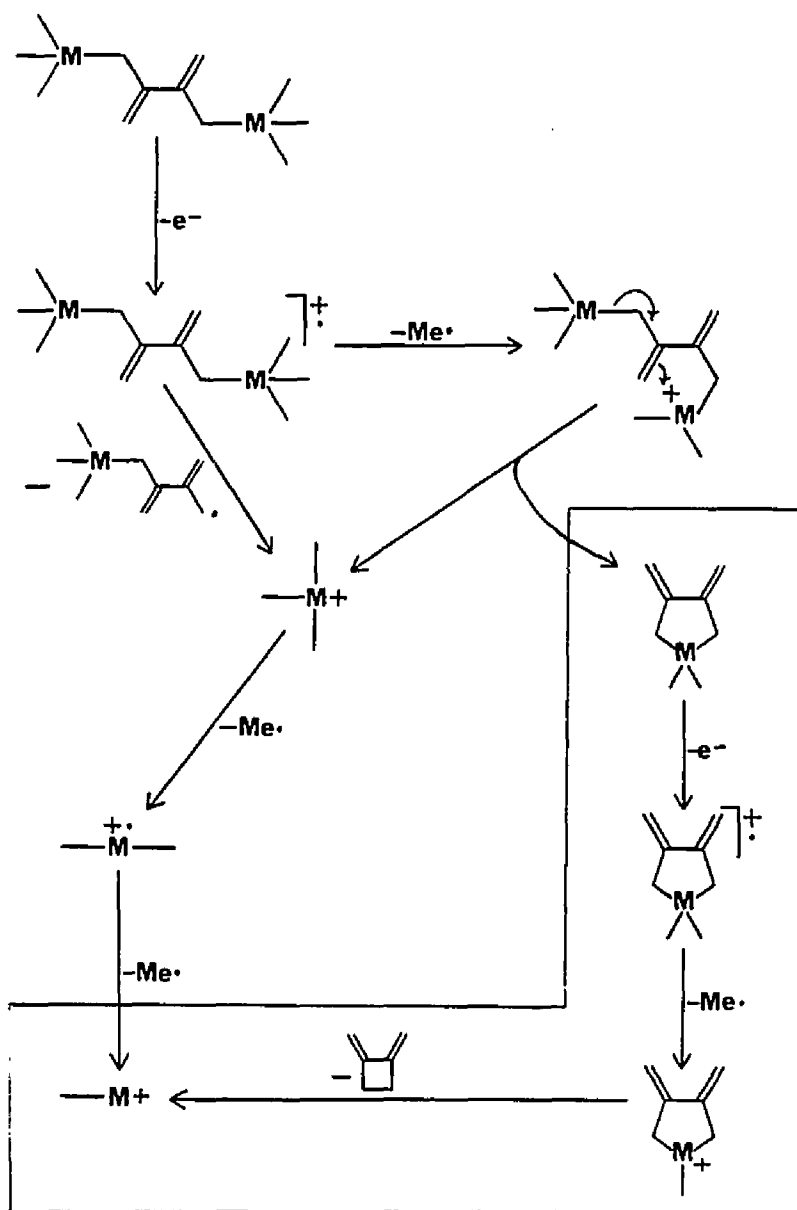
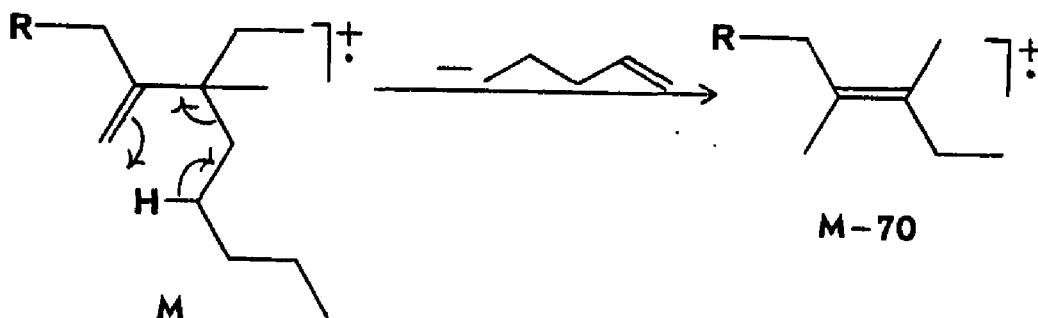


Fig. 14. MS fragmentation scheme for 32, 59, 60 and 61.

and (M-14n) where  $n = 1, 2, 3 \dots$ . The M-14n fragments may recyclize to the molecular ions of 22 with ring sizes smaller than the parent; this is favored only in smaller rings (22,n=5-7). The modes of fragmentation of 22,n=11,16 are shown in Figs. 15 and 16 respectively.

Dimeric products 23,n=11,12,14,16 display very similar MS to each other. The molecular ions of these compounds are moderately strong. Fragments observed in the MS of 22,n=11,16 were observed in the MS of the dimers as well. The most prominent feature in the MS of these compounds is the large number of groups of three peaks spaced 14 units apart; this is not observed in the MS of monomers 22,n=11,16. The MS of trimer 24,n=12 is very similar to those of the dimers 23, with the exception that the spectrum is nearly devoid of peaks between the molecular ion and the first of a series of three peak groups centered at  $m/e$  189.

The MS of 69-72 are quite similar to one another. The molecular ions of these molecules are weak. A major mode of fragmentation in all of these compounds involves a McLafferty-like rearrangement resulting in the loss of a neutral 1-pentene molecule. This rearrangement is shown below:



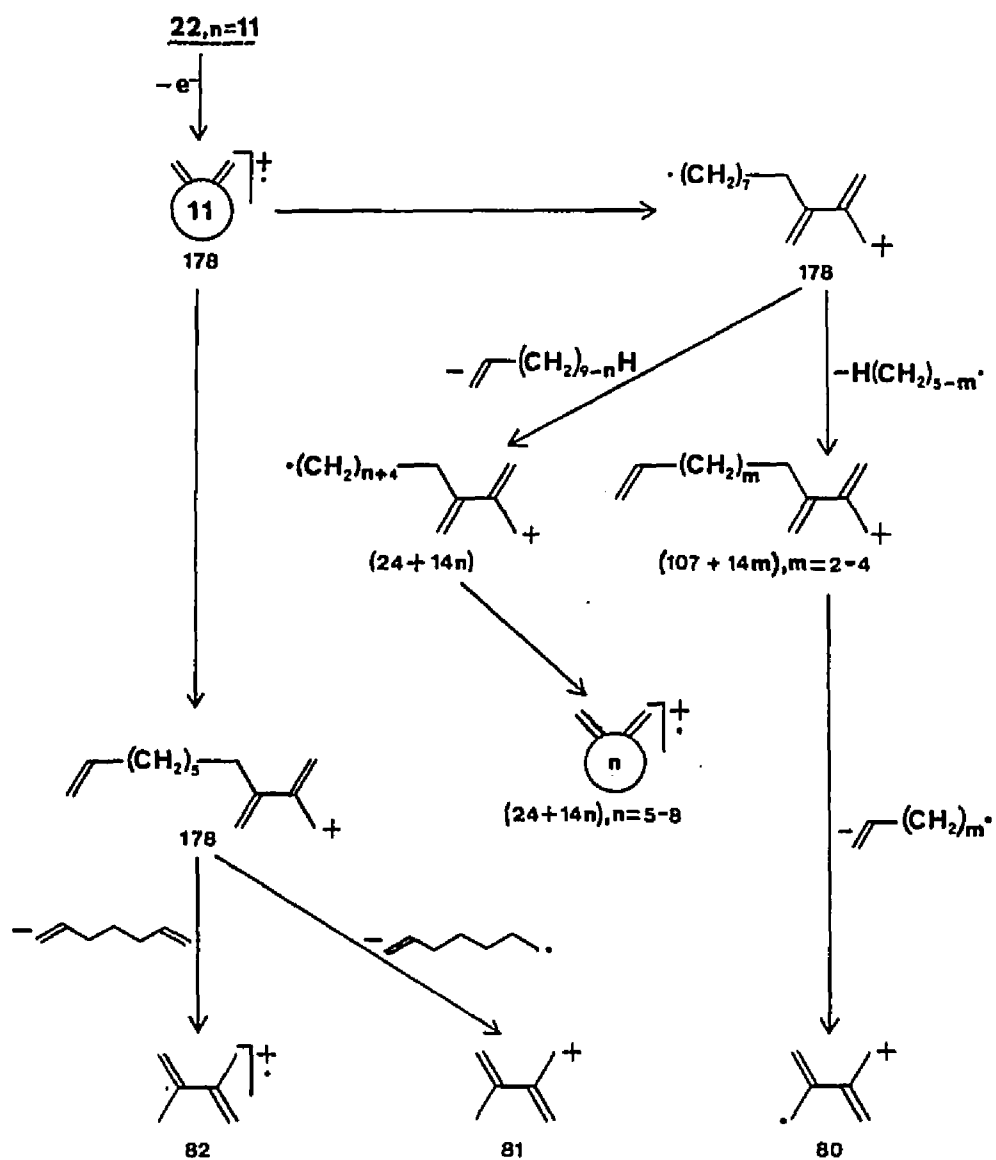
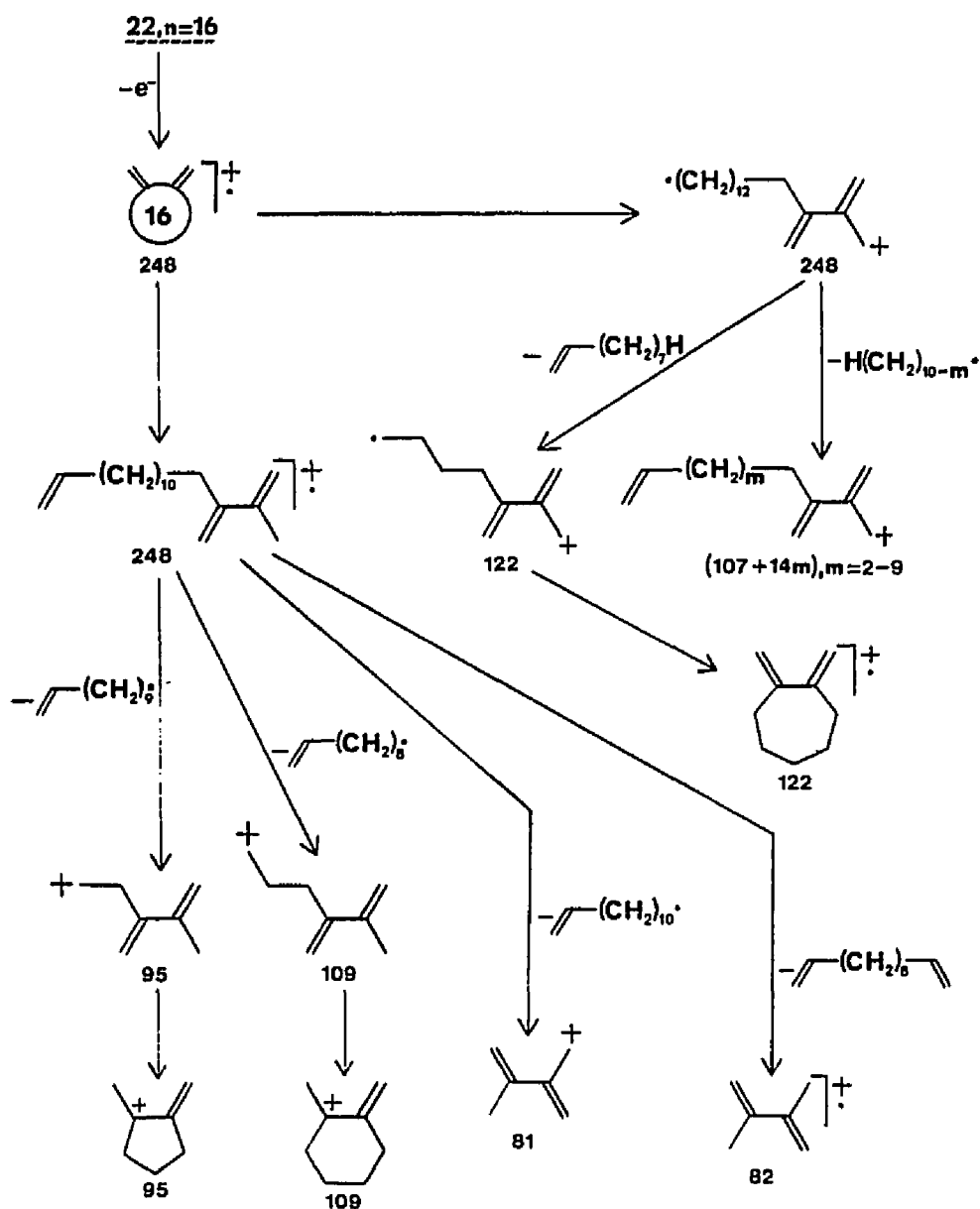
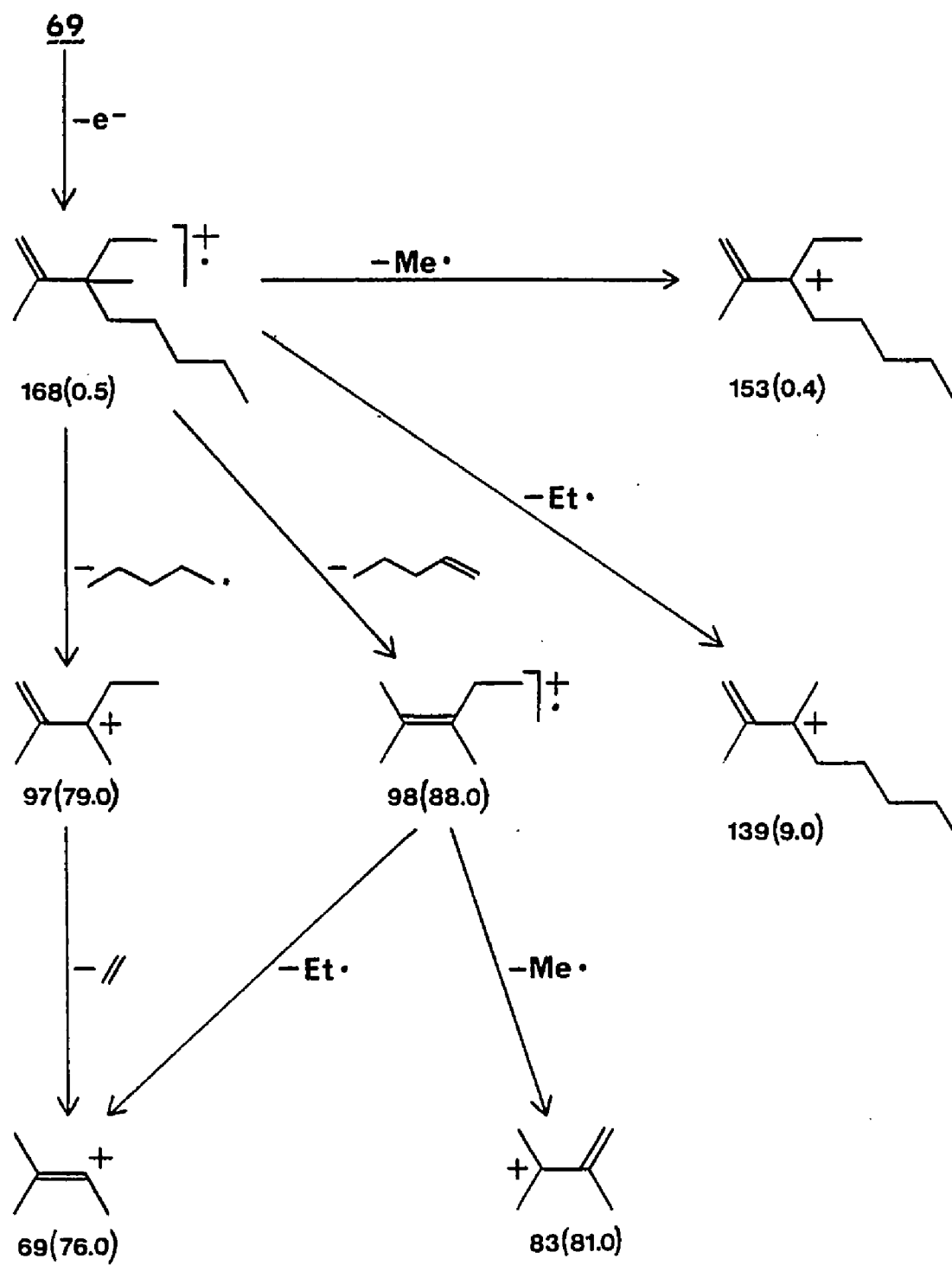


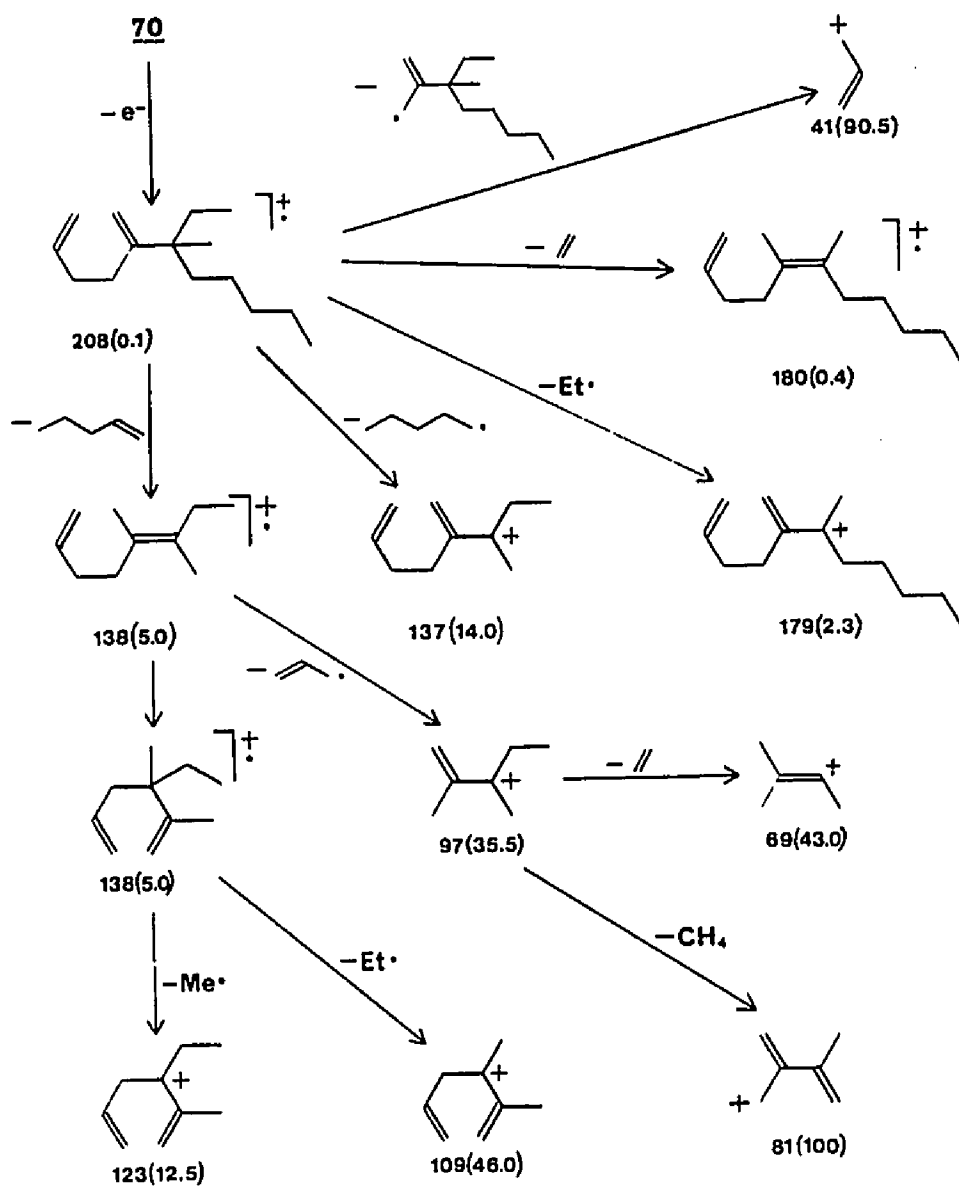
Fig. 15. MS fragmentation scheme for  $\underline{22, n=11}$ .





Fragmentation of  $R^+$  is important in the MS of 70 and 71. In general, these compounds exhibit fragmentation patterns typified by the MS of 69. The modes of fragmentation of 69 are given in Fig. 17. The MS of 70 is somewhat more complex than those of 69, 71, 72 as Cope rearrangements may accompany the McLafferty-like rearrangements mentioned previously. The fragmentation pattern of 70 is given in Fig. 18. Molecular weights of fragments are given with intensities in parentheses for both Fig. 17 and Fig. 18. A strong to very strong peak with  $m/e = 55$  ( $C_4H_7^+$ ) is unexplained but present in all of these compounds.

Fig. 17. MS fragmentation scheme for 69.

Fig. 18. MS fragmentation scheme for 70.

## EXPERIMENTAL

Nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker WM-250 spectrophotometer. All samples were run with  $\text{CDCl}_3$  as the solvent. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). Mass spectra (MS) were recorded using a Finnigan 3300 Quadrupole GC/MS coupled to an INCOS data system equipped with a 6 ft x 2 mm column packed with 3% OV-17 on 100/120 Chromosorb W-HP. Mass spectra of some compounds with high molecular weights were obtained using a solid probe coupled with MS. Ultraviolet spectra were recorded using a Varian Cary 219 UV/Vis spectrophotometer. All samples were run with hexane as the solvent. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia or the University Analytical Center, Tucson, Arizona. Melting points were uncorrected.

Volatile products were isolated and purified by gas chromatography with a Varian Aerograph, Model 700 equipped with 10% SE-30 on Chromosorb W-HP. Non-volatile products were isolated and purified using medium pressure (~ 65 psi) liquid chromatography with a 4 ft x 2 in column packed with LiChroprep Si60 and pentane as the solvent.

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Pentane was washed with sulfuric acid, fractionally distilled from NaOH and stored over NaOH. *n*-Butyllithium was used as received from Aldrich Chemical Co. or Alfa Division, Ventron Corp.

Potassium t-butoxide was used as received from Aldrich Chemical Co. All other reagents were used as received or purified by standard methods. Drying of organic solutions was done using anhydrous magnesium sulfate. Pentane was removed using a rotary evaporator. Crude products, separated using GC, were bulb to bulb distilled using a Kugelrohr distillation apparatus prior to separation. Distillation was not performed prior to LC separations. All glassware used in anion preparations and reactions was dried for several h at 120° before use. All preparations and reactions of anions were done under positive argon pressure. All transfers of anions were done via syringe or cannula.

<sup>1</sup>H NMR and MS data are compiled in tables at the end of the Experimental section. Reported yields are based on the parent hydrocarbon, 2,3-dimethyl-1,3-butadiene (4). Yields were determined using NMR by adding known amounts of benzene, dichloromethane or p-dioxane to the sample and measuring the areas of pertinent signals. Peak areas from GC traces were also used in determining yields when appropriate. All products were liquids at room temperature except those for which melting points are listed.

#### Dianion 1

2,3-Bis(methylene)butadiene dianion 1 was prepared by adding 2.0 mL (17.7 mmol) of 2,3-dimethyl-1,3-butadiene (4) in 25 mL of pentane dropwise via an addition funnel over 15 min to a stirred mixture of 4.0 g (35.6 mmol) potassium t-butoxide, 60 mL pentane and 2.47 mL (35.6 mmol) 1.44 M n-butyllithium in a 250 mL round bottom flask. After 30 min continued stirring, the orange dianion salt was

filtered using a Schlenk filter and repeatedly washed with pentane to remove lithium t-butoxide, any excess *n*-butyllithium and hexane. The resulting solid was blown dry with argon. The dianion salt was suspended with stirring in THF (60 mL) at 0° for reactions. The yield of dianion 1 is known to be 73% based on D<sub>2</sub>O quench [6, 10].

#### Reaction of Dianion 1 with Methyl Iodide

Methyl iodide (2.25 mL, 35.4 mmol) in pentane (25 mL) was added dropwise via an addition funnel to the stirring suspension of dianion 1 in THF at 0°. The solution was stirred while warming to room temperature. After addition of 100 mL pentane, the solution was extracted repeatedly with water to remove iodides and THF. The resulting organic phase was dried and filtered. After removal of pentane, the remaining crude product was distilled and purified using GC, giving a 43% yield of 3,4-bis(methylene)hexane (27) [13], identified by NMR (Table A.4, Fig. A.5) and UV ( $\lambda_{\text{max}} = 228$ ,  $\epsilon = 12800$ ).

#### Reaction of Dianion 1 with Dimethyl Sulfate

Dimethyl sulfate was reacted similarly with dianion 1. After addition of pentane, the solution was extracted twice with equal volumes of 0.10 M NaOH solution then extracted repeatedly with water. A 61% yield of 3,4-bis(methylene)hexane 27 [13] was obtained.

#### Reaction of Dianion 1 with Ethyl Bromide

Ethyl bromide was reacted with dianion 1 using the procedure described above for methyl iodide, giving a 43% yield of

4,5-bis(methylene)octane (50) [6, 10] identified by NMR (Table A.4) and UV ( $\lambda_{\text{max}} = 228$ ,  $\epsilon = 12600$ ).

Reaction of Dianion 1 with 1-Bromopropane

Similar reaction of 1 with 1-bromopropane gave a 34% yield of 5,6-bis(methylene)decane (30) [14], identified by NMR (Table A.4) and UV ( $\lambda_{\text{max}} = 229$ ,  $\epsilon = 12000$ ).

Reaction of Dianion 1 with 1-Bromobutane

Dianion 1 was reacted similarly with 1-bromobutane and gave a 30% yield of 6,7-bis(methylene)dodecane (51), identified by NMR (Table A.4, Fig. A.6), MS (Table B.1) and elemental analysis (calculated for  $C_{14}H_{26}$ : C, 86.52; H, 13.48; found: C, 86.54; H, 13.46).

Reaction of Dianion 1 with 2-Bromopropane

A suspension of dianion 1 in THF was added via syringe to a stirring solution of 2-bromopropane (3.32 mL, 35.4 mmol) in THF (200 mL). The solution was stirred while warming to room temperature. After addition of 200 mL pentane, the solution was extracted repeatedly with water, dried and filtered. After removal of pentane, the crude products were distilled. The products were separated and purified by GC and identified by spectral data and/or elemental analysis. Three products were identified: 2,7-Dimethyl-4,5-bis(methylene)octane (55), 41% yield,  $^1\text{H}$  NMR (Table A.8, Fig. A.8), MS: (Table B.4), UV: ( $\lambda_{\text{max}} = 231$ ,  $\epsilon = 11700$ ), elemental analysis (calculated for  $C_{12}H_{22}$ : C, 86.7; H, 13.3; found: C, 86.8; H, 13.2); 2,5-dimethyl-3-methylene-1-hexene (56), 2% yield, identified by  $^1\text{H}$  NMR

(Table A.9); 3-ethyl-2,3-dimethyl-1-octene (69), 1% yield, identified by  $^1\text{H}$  NMR (Table A.13, Fig. A.15) and MS (Table B.15).

#### Reaction of Dianion 1 with Allyl Chloride

Dianion 1 was reacted in a similar manner with allyl chloride to generate two products: 5,6-Bismethylene-19-decadiene (52), 70% yield,  $^1\text{H}$  NMR (Table A.12, Fig. A.7), MS (Table B.2), elemental analysis (calculated for  $\text{C}_{12}\text{H}_{18}$ : C, 88.82; H, 11.18; found: C, 88.79; H, 11.20); and 6-ethyl-6-methyl-5-methylene-1-undecene (70), 10% yield,  $^1\text{H}$  NMR (Table A.14, Fig. A.16), MS (Table B.16).

#### Reaction of Dianion 1 with Benzyl Chloride

Benzyl chloride was reacted similarly with 1, and the residue was separated using LC. 1,6-Diphenyl-3,4-bis(methylene)hexane (53) was obtained in 53% yield and identified by NMR (Table A.11) and MS (Table B.3). 1,2-Diphenylethane (54) was obtained in 22% yield and identified by NMR and MS comparisons with authentic material.

#### Reaction of Dianion 1 with Benzyl Bromide

Benzyl bromide was reacted similarly with 1 except that diethylamine (75 mL) was added to the washed pentane solution and it was allowed to stand for two h to remove excess benzyl bromide. The solution was then extracted repeatedly with water, filtered and evaporated, and separated using LC, giving 54 (30%) and 53 (21%).



#### Reaction of Dianion 1 with t-Butyl Bromide

In the same manner, 1 was reacted with t-butyl bromide to give a variety of products. Obtained in 15% yield was 2,2,7,7-tetramethyl-4,5-bis(methylene)octane (57), identified by NMR (Table A.5, Fig. A.9) and MS (Table B.6). 2,7,7-Trimethyl-3-methylene-1-hexene (58) was generated in 15% yield and identified by NMR (Table A.10) and MS (Table B.5). 1,2,5,6-Tetrakis(methylene)cyclooctane (23,n=4) [31] was also obtained in 15% yield and identified by NMR (Table A.2, Fig. A.3) and MS (Table B.23). A 12% yield of 3-ethyl-2,3-dimethyl-1-octene (69), identified by NMR (Table A.13, Fig. A.15) and MS (Table B.15), was also found.

#### Reaction of Dianion 1 with Trimethylsilyl Chloride

Similar reaction of 1 with trimethylsilyl chloride gave, after purification by GC, a 47% yield of 2,3-bis(trimethylsilylmethyl)-1,3-butadiene (32) [15], identified by elemental analysis (calculated for  $C_{12}H_{26}Si_2$ : C, 66.63; H, 11.57; found: C, 66.65; H, 11.58), NMR (Table A.5, Fig. A.10), MS (Table B.7) and UV ( $\lambda_{max} = 240$ ,  $\epsilon = 11700$ ).

#### Reaction of Dianion 1 with Trimethylgermyl Bromide

Trimethylgermyl bromide was reacted in the same manner with 1. Three products were identified: 2,3-Bis(trimethylgermylmethyl)-1,3-butadiene (59) was obtained in 54% yield and identified by elemental analysis (calculated for  $C_{12}H_{26}Ge_2$ : C, 45.68; H, 8.31; found: C, 45.76; H, 8.35), NMR (Table A.5, Fig. A.11), MS (Table B.8) and UV ( $\lambda_{max} = 241$ ,  $\epsilon = 13800$ ). 3-Ethyl-3-methyl-2-(trimethylgermylmethyl)-1-octene (71) was obtained in 5% yield and identified by NMR (Table A.15, Fig. A.17)

and MS (Table B.17). 2,3-Bismethylene-1-trimethylgermyl-5-trimethylgermyloxyhexane (73) was obtained in 4% yield and identified by NMR (Table A.19) and MS (Table B.19).

#### Reaction of Dianion 1 with Trimethyltin Chloride

A similar reaction of 1 with trimethyltin chloride gave two products. Obtained in 32% yield was 2,3-bis(trimethylstannylmethyl)-1,3-butadiene (60) mp  $-9$  to  $-7^{\circ}$ , identified by elemental analysis (calculated for  $C_{12}H_{26}Sn_2$ : C, 35.35; H, 6.43; found: C, 35.53; H, 6.45), NMR (Table A.5, Fig. A.12), MS (Table B.9) and UV ( $\lambda_{max} = 247$ ,  $\epsilon = 12700$ ). 3-Ethyl-3-methyl-2-(trimethylstannylmethyl)-1-octene (72) was generated in 6% yield and identified by NMR (Table A.16) and MS (Table B.18).

#### Reaction of Dianion 1 with Trimethyllead Chloride

A suspension of dianion 1 in THF (prepared on a 7.0 mmol scale) was added dropwise via syringe to a stirring solution of trimethyllead chloride (2.00 g, 6.95 mmol) in THF (150 mL) at  $0^{\circ}$ . The solution was allowed to stir while warming to room temperature. Pentane was added and the solution was washed twice with 1 M NaCl solution (350 mL) followed by multiple washings with water to remove inorganic salts and THF. The remaining pentane solution was dried and filtered. After removal of pentane, the crude product, 2,3-bis(trimethylplumbylmethyl)-1,3-butadiene (61) was identified by NMR (Table A.5). The compound decomposed slowly in the presence of air and rapidly when distillation under reduced pressure was attempted. Attempts to isolate the compound using LC failed as it decomposed on

silica gel or alumina (the tin analog 60 decomposed on silica and alumina as well). The yield of 61 was about 30%; GC/MS data are given in Table B.10.

#### Reaction of Dianion 1 with Dichlorodimethylsilane

A suspension of dianion 1 in THF was added dropwise via syringe to a stirring solution of dichlorodimethylsilane (2.15 mL, 17.7 mmol) in THF (200 mL) at 0°. The solution was stirred while warming to room temperature. After pentane (150 mL) was added, the mixture was extracted twice with 1 M NaCl solution (350 mL) to remove the bulk of chlorides and THF. The mixture was then filtered over Celite to remove polymer. The resulting pentane solution was washed repeatedly with water to remove residual chlorides and THF. The solution was dried and filtered. The crude product was distilled prior to purification by GC. The reaction generated 1,1-dimethyl-3,4-bismethylene-1-silacyclopentane (62) in 30% yield as identified by NMR (Table A.6, Fig. A.13) and MS (Table B.11) and elemental analysis (calculated for C<sub>18</sub>H<sub>14</sub>Si: C, 69.49; H, 10.20; found: C, 69.26; H, 10.21). This reaction was run once with the only change being that a 30% excess of potassium t-butoxide was used in the preparation of dianion 1. The products were separated and purified by GC. 62 was obtained in 22% yield. The other compounds were isolated from this reaction: (t-Butoxydimethylsiloxy)ethene (74) was produced in 25% yield and identified by NMR (Table A.18) and MS (Table B.20); 4-(t-butoxydimethylsiloxy)-1-butene (75) was found in 4% yield as identified by NMR (Table A.17).

#### Reaction of Dianion 1 with Dichlorodimethylgermane

A suspension of dianion 1 (25 mmol) in THF was added via cannula to a stirring solution of dichlorodimethylgermane (5.0 g, 28.8 mmol) in 200 mL THF at 0°. The solution was stirred while warming to room temperature. After addition of pentane (200 mL), the solution was extracted twice with equal volumes of 1.0 M NaI solution and then repeatedly extracted with water to remove salts and THF. The resulting pentane solution was dried and filtered. After pentane was evaporated, the remaining liquid was distilled and the products separated and purified by GC. 1,1-Dimethyl-3,4-bismethylene-1-germacyclopentane (63) was obtained in 32% yield and identified by elemental analysis (calculated for C<sub>18</sub>H<sub>14</sub>Ge: C, 52.57; H, 7.72; found: C, 52.72; H, 7.74), <sup>1</sup>H NMR (Table A.6, Fig. A.14), MS (Table B.12) and UV ( $\lambda_{\text{max}} = 227$ ,  $\epsilon = 6400$ ). 3-Ethyl-2,3-dimethyl-1-octene (69), identified by <sup>1</sup>H NMR (Table A.13, Fig. A.15) and MS (Table B.15), was found in 3% yield.

#### Reaction of Dianion 1 with Dimethyltin Dichloride

A suspension of dianion 1 in THF was added dropwise via syringe to a stirring solution of dimethyltin dichloride (3.9 g, 17.8 mmol) in THF (200 mL). The solution was stirred while warming to room temperature. After addition of pentane (200 mL), the mixture was extracted several times with water to remove salts and THF and then filtered over Celite to remove polymer. The solution was repeatedly washed with water and filtered over Celite as the solution continued to steadily precipitate a fluffy white solid. The resulting solution

was dried and filtered. After removal of pentane, the residue was distilled. The distillate continued to steadily precipitate a white solid. The product was isolated using GC, but continued to polymerize steadily to the white solid homopolymer 64. The  $^1\text{H}$  NMR spectrum of the solution shows the presence of 1,1-dimethyl-3,4-bismethylene-1-stannacyclopentane (64) (Table A.6) and its homopolymer 65 (Table A.7).

#### Reaction of Dianion 1 with Dibromomethane

A suspension of dianion 1 in THF was added dropwise via syringe to stirring THF (200 mL) while a solution of dibromomethane (1.25 mL, 17.8 mmol) in THF (50 mL) was added simultaneously at  $0^\circ$  via an addition funnel. After completion of the additions, the solution was stirred while warming to room temperature. Pentane (150 mL) was added and the mixture was extracted 2 x 350 mL 1 M  $\text{NH}_4\text{Cl}$  to remove the bulk of the bromides and THF while minimizing emulsions. The mixture was then filtered over Celite to remove polymers. The resulting pentane solution was repeatedly extracted with water to remove any remaining bromides and THF. The solution was dried and filtered. After evaporation of pentane, the remaining liquid was distilled and the products separated using GC. 1,2-Bis(methylene)cyclopentane (22,n=5) [22] was obtained in 5% yield and identified by NMR (Table A.1, Fig. A.1). 1,2,5,6-Tetrakis(methylene)cyclooctane (23,n=4) [31] was generated in 11% yield and identified by NMR (Table A.2).

#### Reaction of Dianion 1 with Dichloromethane

Dianion 1 was reacted with dichloromethane using the 2-bromopropane procedure above. 1,2-Bis(methylene)cyclopentane (22,n=5)

[22] was obtained in 12% yield and identified by NMR (Table A.1, Fig. A.1).

#### Reaction of Dianion 1 with 1,1-Dichloroethane

1,1-Dichloroethane reacted similarly with 1, giving 1,2-bis-(methylene)-4-methylcyclopentane (66) in 6.0% yield ( $^1\text{H}$  NMR, Table A.20; MS, Table B.13). trans-4-Methylene-5-methyl-2,5-hexadiene (67a), its cis isomer 67b and 4-methylene-5-methyl-1,5-hexadiene (68) were obtained as a mixture in 6.5, 1.4 and 2.2%, respectively, based on GC peak areas and  $^1\text{H}$  NMR (Tables A.21, A.22, A.23); MS, Table B.14.

#### Reaction of Dianion 1 with 1,2-Dichloroethane

In a similar reaction, 1 was reacted with 1,2-dichloroethane to generate in 19% yield 1,2-bis(methylene)cyclohexane (22,n=6) [24, 25, 27], which was identified by NMR (Table A.1).

#### Reaction of Dianion 1 with 1,2-Dibromoethane

Dianion 1 was reacted similarly with 1,2-dibromoethane. However, neither disubstitution nor oxidative dimerization of 1 was observed. A 12% yield of 3-ethyl-2,3-dimethyl-1-octene (69) (NMR: Table A.13, Fig. A.15; MS: Table B.15) and a 7% yield of 6,7-bis(methylene)dodecane (51) (NMR: Table A.4, Fig. A.6; MS: Table B.1) were obtained. A GC/MS analysis of the crude product showed a series of unidentified compounds with molecular weights corresponding to 1 condensing with two molecules of THF anion and a varying number of ethylene molecules.

Reaction of Dianion 1 with Hexachloroethane

Hexachloroethane was reacted similarly with 1. Oxidative dimer 23,n=4, the only product identified ( $^1\text{H}$  NMR, Table A.1, Fig. A.3), was obtained in 11% yield.

Reaction of Dianion 1 with 1,3-Dibromopropane,  
1,4-Dibromobutane and 1,5-Dibromopentane

Similar reactions of dianion 1 with 1,3-dibromopropane, 1,4-dibromobutane, and 1,5-dibromopentane generated 22,n=7-9 [10, 26, 27] in 18%, 18%, and 15% yields, respectively. With 1,3-dibromopropane, elimination product 52 (6% yield;  $^1\text{H}$  NMR, Table A.12, Fig. A.7) and a trace of oxidative dimer 23,n=4 [31] were also found. With 1,4-dibromobutane, 69 ( $^1\text{H}$  NMR, Table A.13, Fig. A.15) was found in 2% yield.

Reaction of Dianion 1 with 1,6-Dibromohexane

Using the simultaneous addition procedure described above for dibromomethane, 1 was reacted with 1,6-dibromohexane to give 1,2-bis(methylene)cyclodecane (22,n=10;  $^1\text{H}$  NMR, Table A.1, Fig. A.2) [10] in 20% yield.

Reaction of Dianion 1 with 1,8-Dibromooctane

Dianion 1 was reacted with 1,8-dibromooctane several times by the above procedure. Best results were obtained when the addition of the dibromide was kept slightly ahead of the addition of dianion (a yellow color rather than an orange color). The mixture was extracted with 1 M NaI solution to minimize emulsions, and then filtered over Celite to remove polymers. The residue was separated using LC. The

products were identified by retention times and spectral data. 1,2-Bis(methylene)cyclododecane (22,n=12) [27, 29, 30] was obtained in 2% yield ( $^1\text{H}$  NMR, Table A.1). 1,2,13,14-Tetrakis(methylene)cyclotetracosane (23,n=12) (mp 60-61°) was found in 7% yield ( $^1\text{H}$  NMR, Table A.2, Fig. A.4; MS, Table B.25). 1,2,13,14,25,26-Hexakis(methylene)cyclohexatriacontane (24,n=12) was generated in 3% yield ( $^1\text{H}$  NMR, Table A.3; MS, Table B.28).

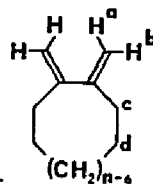
Reaction of Dianion 1 with 1,7-Dibromoheptane,  
1,9-Dibromononane, 1,10-Dibromodecane and  
1,12-Dibromododecane

These reactions were done analogously. Monomers 22, dimers 23 and trimers 24 were separated by LC and identified by their retention times and by NMR (Tables A.1, A.2, A.3) and MS (Tables B.21, B.22, B.24, B.26, B.27). The reaction of dianion 1 with 1,7-dibromoheptane yielded monomer 22,n=11 in 2% yield and dimer 23,n=11 in 2% yield. The reaction of dianion 1 with 1,9-dibromononane produced monomer 22,n=13 in 4% yield and dimer 23, n=13 in 2% yield and trimer 24,n=13 in 1% yield. The reaction of dianion 1 with 1,10-dibromodecane generated monomer 22,n=14 in 5% yield, dimer 23,n=14 (mp 60-61°) in 3% yield and trimer 24,n=14 in 1% yield. The reaction of dianion 1 with 1,12-dibromododecane resulted in an 8% yield of monomer 22,n=16, a 4% yield of dimer 23,n=16 (mp 60-64°) and a 2% yield of trimer 24,n=18.



APPENDIX A

<sup>1</sup>H NMR DATA AND SPECTRA

Table A.1. NMR assignments for 22.

n	$\delta H_a$	$\delta H_a$ (Lit.)	$\delta H_b$	$\delta H_b$ (Lit.)	$\Delta\delta H_{ab}$	$\Delta\delta H_{ab}$ (Lit.)	$\delta H_c$	$\delta H_c$ (Lit.)	$\delta H_d$	$\delta H_d$ (Lit.)	Other $\delta H$	Other $\delta H$ (Lit.)	$J_{ab}$	" $J_{cd}$ "	Other J's	Reference
3		5.50		5.27		0.23		1.56	--	--	--	--	0.85	--	$J_{bc} = 1.7$ $J_{ac} = 2.6$	17
4	5.15	5.17	4.71	4.70	0.44	0.47	2.63	2.64	--	--	--	--	0	--		19
5	5.35	5.37	4.89	4.87	0.46	0.50	2.43	2.40	1.67	1.65	--	--	0	7.2	$J_{ac} = 2.1$ $J_{bc} = 2.1$	32
6	4.92	4.65	4.63	4.90	0.29	-0.25	2.25	2.25	1.62	1.62	--	--	2.6	5.7	$J_{ac} = 1.3$ $J_{bc} = 1.1$	27
7	5.14	5.11	4.71	4.71	0.43	0.40	2.33	2.25	1.59	1.50	$H_e = 1.57$	$H_e = 1.50$	2.6	3.5	$J_{bc} = 1.1$	27
8	5.09	5.12	4.76	4.78	0.33	0.34	2.32	2.33	1.50	1.55	$H_e = 1.56$	$H_e = 1.55$	2.4	5.5	$J_{bc} = 0.7$	27
9	4.95		4.95		0.00		2.30		1.52		$H_e = 1.44$ $H_f = 1.34$		0	6.6	$J_{bc} = 0.7$	
10	5.10		4.91		0.19		2.49		1.66		$H_e = 1.45$ $H_f = 1.36$		1.5	6.1	$J_{ab} = 0.9$	
11	5.07		5.01		0.06		2.35		1.57		$H_{e,f,g}$ 1.27-1.31		0.9	5.9		
12	5.08	5.11	4.98	5.02	0.10	0.09	2.36	2.36	1.38	1.30	$H_{e,f,g}$ 1.23-1.34	$H_{e,f,g}$ 1.30	1.1	5.6	$J_{ab} = 1.1$	27
13	5.12		4.96		0.16		2.33		1.43		$H_{e,f,g,h}$ 1.28		1.0	6.2	$J_{ab} = 1.0$	
14	5.09		4.95		0.14		2.35		1.44		$H_{e,f,g,h}$ 1.27-1.31 m 12H 1.20hs 4H		1.1	6.3	$J_{ab} = 1.1$	
16	5.03		4.93		0.10		2.29		1.44		$J_{e,f,g,h,i}$ 1.26		1.0	6.9		

Table A.2<sup>a</sup> NMR assignments for 23.

n	$\delta H_a$	$\delta H_b$	$\Delta\delta H_{ab}$	$\delta H_c$	$\delta H_d$	Other $\delta H$	$J_{ab}$	" $J_{cd}$ "
4	4.89	4.81	0.08	2.39	--	--	2.2	--
4 <sup>b</sup>	4.90	4.80	0.10	2.40	--	--	2	--
11	5.02	4.93	0.09	2.29	1.40	$\delta H_{e,f,g}$ 1.21-1.31	1.0	7.0
12	5.01	4.91	0.10	2.27	1.40	$\delta H_e=1.27$ $\delta H_{f,g}=1.21$	1.0 ( $J_{ab}$ )	6.8
13	5.02	4.92	0.10	2.27	1.41	$\delta H_{e,f,g,h}$ = 1.23		7.0
14	5.02	4.91	0.11	2.26	1.41	$\delta H_{e,f,g,h}$ = 1.24	1.3 ( $J_{ab}$ )	6.8
16	5.01	4.89	0.12	2.23	1.42	$\delta H_{e,f,g,h,i}$ = 1.23		7.2

<sup>a</sup>Labeling analogous to that in Table A.1.

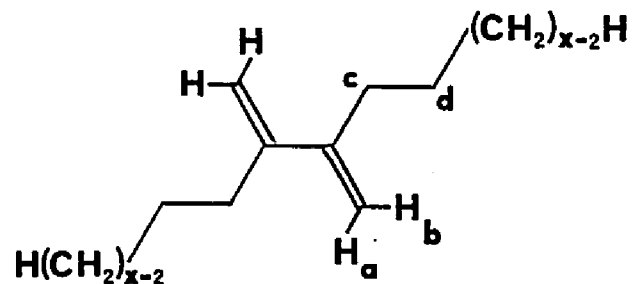
<sup>b</sup>Literature values [31].

Table A.3.<sup>a</sup> NMR assignments for 24.

n	$\delta H_a$	$\delta H_b$	$\Delta\delta H_{ab}$	$\delta H_c$	$\delta H_d$	Other $\delta H$	"J <sub>cd</sub> "
12	5.03	4.90	0.13	2.23	1.41	$\delta H_{e,f,g} = 1.26$	7.3
13	5.04	4.90	0.14	2.23	1.42	$\delta H_{e,f,g,h} = 1.26$	7.3
14	5.04	4.90	0.14	2.23	1.42	$\delta H_{e,f,g,h} = 1.26$	7.3
16	5.04	4.91	0.13	2.22	1.44	$\delta H_{e,f,g,h,i} = 1.26$	7.3

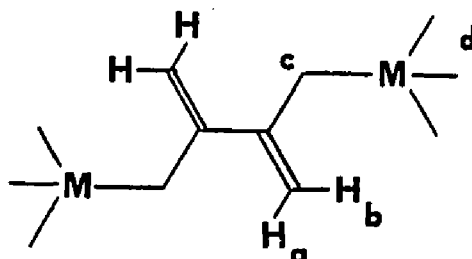
<sup>a</sup>Labeling analogous to that in Table A.1.

Table A.4. NMR assignments for 4(x=1), 27(x=2), 50(x=3), 30(x=4) and 51(x=5)



$x$	$\delta\text{H}_a$	$\delta\text{H}_a$ (Lit.)	$\delta\text{H}_b$	$\delta\text{H}_b$ (Lit.)	$\Delta\delta\text{H}_{ab}$	$\Delta\delta\text{H}_{ab}$ (Lit.)	$\delta\text{H}_c$	$\delta\text{H}_c$ (Lit.)	$\delta\text{H}_d$	$\delta\text{H}_d$ (Lit.)	Other $\delta\text{H}$	Other $\delta\text{H}$ (Lit.)	$J_{ab}$	$J_{cd}$	$J_{yz}$	Reference
1	5.05	5.10	4.96	5.02	0.09	0.08	1.91	2.00	--	--	--	--	--	--	--	61
2	5.07	5.07	4.94	4.93	0.13	0.14	2.27	2.28	1.07	1.07	--	--	$1.0(J_{ab})$	7.4	$J_{cd}=7.4$	13
3	5.95		4.90		0.15		2.21		1.46		$\delta\text{H}_e=0.90$		$1.0(J_{ab})$	7.2	$J_{de}=7.3$	6
4	5.95	4.95	4.91	4.85	0.14	0.10	2.23		1.43		$\delta\text{H}_e=1.33$ $\delta\text{H}_f=0.91$		$1.1(J_{ab})$	7.3	$J_{ef}=7.2$	14
5	5.04		4.91		0.13		2.22		1.44		$\delta\text{H}_e=1.30$ $\delta\text{H}_f=1.29$ $\delta\text{H}_g=0.89$		0.9	7.5	$J_{fg}=6.8$	--

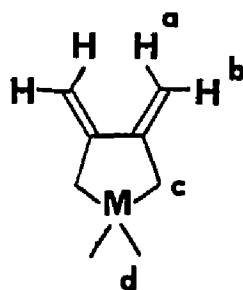
Table A.5. NMR assignments for 57(M=C), 32(M=Si), 59(M=Ge), 60(M=Sn) and 61(M=Pb).



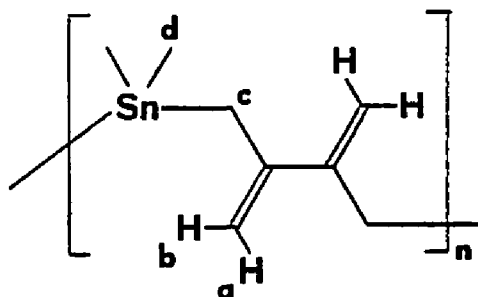
M	$\delta H_a$	$\delta H_b$	$\delta H_c$	$\delta H_d$	$\Delta\delta H_{ab}$	$J_{ab}$ (Hz)
C	5.14	4.73	2.15	0.89	0.41	2.5
Si						
Exp	4.91	4.72	1.74	-0.01	0.19	1.1( $J_{ab}$ )
Lit. <sup>a</sup>	4.92	4.73	1.75	0.0	0.19	
Ge	4.85	4.74	1.88	0.12	0.11	1.0( $J_{ab}$ )
Sn <sup>b</sup>	4.75	4.75	1.95	0.05	0.00	
Pb	4.71	4.71	2.48	0.72	0.00	

<sup>a</sup>[15]

<sup>b</sup> $J(^{117}\text{Sn}-^1\text{H}_d) = 52.9$  Hz  
 $J(^{119}\text{Sn}-^1\text{H}_d) = 51.2$  Hz  
 $J(^{117,119}\text{Sn}-\text{H}_c) = 63.5$  Hz  
 $J(^{117,119}\text{Sn}-\text{H}_{ab}) = 19.0$  Hz

Table A.6. NMR assignments for 62(M=Si), 63(M=Ge) and 64(M=Sn).

M	$\delta H_a$	$\delta H_b$	$\Delta\delta H_{ab}$	$\delta H_c$	$\delta H_d$	$J_{ab}$	$J_{ac}$	$J_{bc}$
Si	5.21	4.73	0.48	1.61	0.14	1.8	1.8	1.6
Ge	5.12	4.70	0.42	1.74	0.32	2.1	1.8	1.8
Sn	4.90	4.63	0.27	1.80	0.30	1.6	1.3	1.9

Table A.7. NMR assignments for 65.

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Chemical shifts (ppm)

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$$\delta H_a = 4.75$$

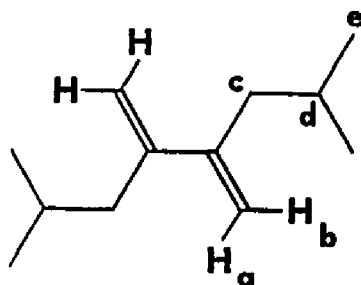
$$\delta H_b = 4.75$$

$$\delta H_c = 1.96$$

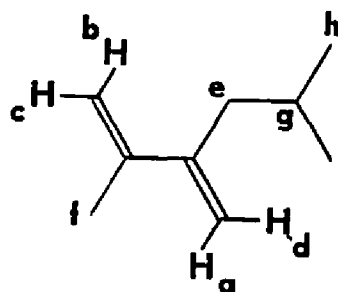
$$\delta H_d = 0.02$$

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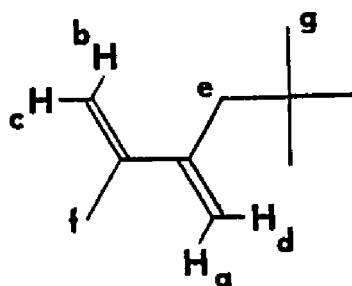


Table A.8. NMR assignments for 55.

Chemical shifts (ppm)	Coupling constants (Hz)
$\delta H_a = 5.04$	$J_{ab} = J_{ab'} = 0.9$
$\delta H_b = 4.86$	$J_{ac} = 0.5$
$\delta H_c = 2.09$	$J_{cd} = 6.7$
$\delta H_d = 1.74$	$J_{de} = 6.6$
$\delta H_e = 0.86$	

Table A.9. NMR assignments for 56.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.09$	$J_{ab} = 1.1$
$\delta H_b = 5.04$	$J_{ae} = 0.6$
$\delta H_c = 4.96$	$J_{eg} = 6.8$
$\delta H_d = 4.90$	$J_{gh} = 6.6$
$\delta H_e = 2.13$	
$\delta H_f = 1.90$	
$\delta H_g = 1.78$	
$\delta H_h = 0.87$	

Table A.10. NMR assignments for 58.

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Chemical shift (ppm)

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$$\delta H_a = 5.19$$

$$\delta H_b = 5.08$$

$$\delta H_c = 4.94$$

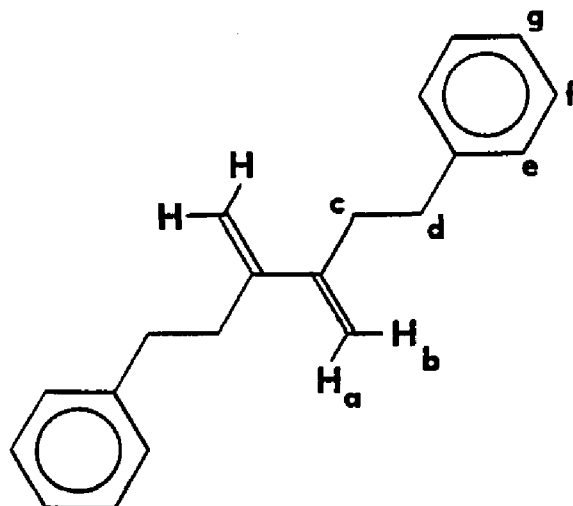
$$\delta H_d = 4.85$$

$$\delta H_e = 2.21$$

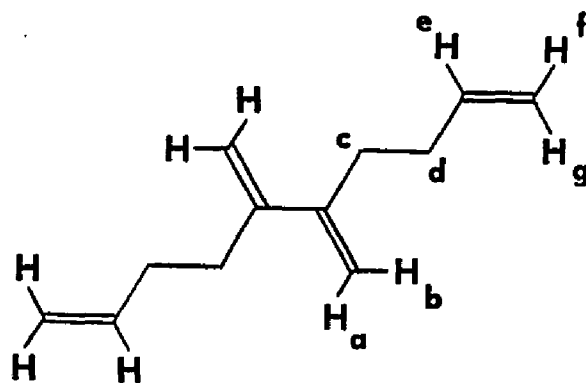
$$\delta H_f = 1.91$$

$$\delta H_g = 0.89$$

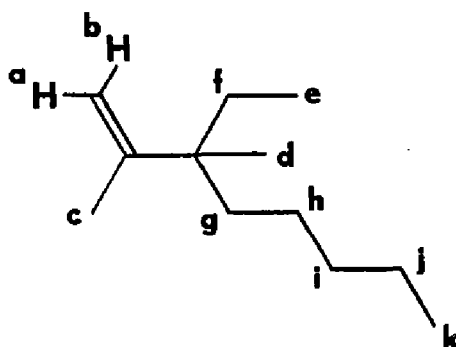
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Table A.11. NMR assignments for 53.

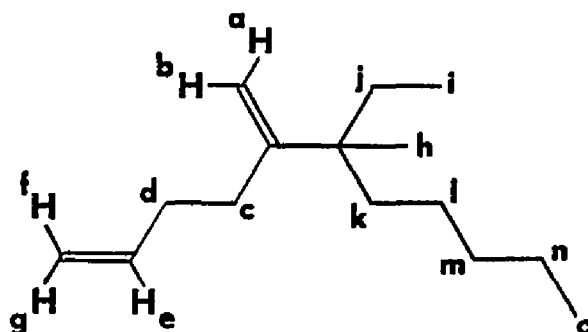
Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.16$	$J_{cd} = 8.0$
$\delta H_b = 4.99$	
$\delta H_c = 2.78$	
$\delta H_d = 2.56$	
$\delta H_{e,f,g} = 7.18-7.34$	

Table A.12. NMR assignments for 52.

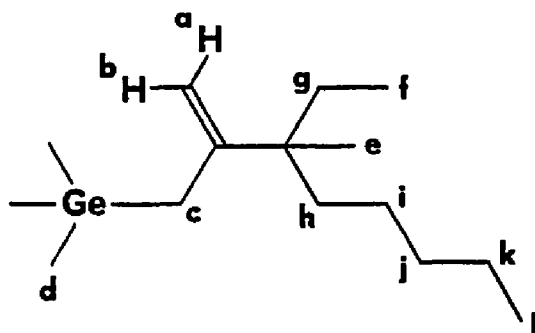
Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.09$	$J_{ab} = J_{ab'} = 0.7$
$\delta H_b = 4.95$	$J_{cd} = 7.7$
$\delta H_c = 2.34$	$J_{de} = 6.5$
$\delta H_d = 2.21$	$J_{ef} = 10.3$
$\delta H_e = 5.83$	$J_{eg} = 17.3$
$\delta H_f = 5.02$	$J_{df} = 1.6$
$\delta H_g = 4.96$	$J_{dg} = 1.2$
	$J_{fg} = 2.0$

Table A.13. NMR assignments for 69.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 4.81$	$J_{ab} = 1.6$
$\delta H_b = 4.63$	$J_{ac} = 0.9$
$\delta H_c = 1.63$	$J_{ef} = 6.9$
$\delta H_d = 0.95$	$J_{jk} = 7.5$
$\delta H_e = 0.71$	
$\delta H_{f,g,h,i,j} = 1.18-1.31$	
$\delta H_k = 0.87$	

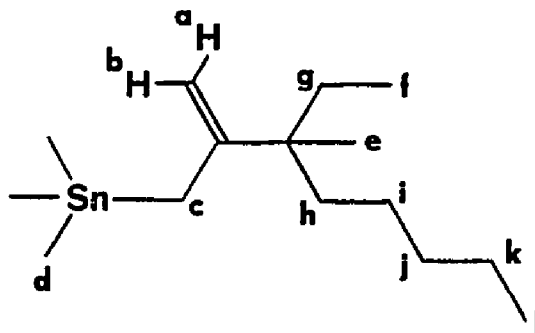
Table A.14. NMR assignments for 70.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 4.79$	$J_{ab} = 0.7$
$\delta H_b = 4.88$	$J_{bc} = 1.3$
$\delta H_c = 1.97$	$J_{cd} = 7.5$
$\delta H_d = 2.22$	$J_{de} = 6.5$
$\delta H_e = 5.87$	$J_{df} = 1.6$
$\delta H_f = 4.99$	$J_{dg} = 1.1$
$\delta H_g = 4.96$	$J_{ef} = 17.2$
$\delta H_h = 0.96$	$J_{eg} = 10.1$
$\delta H_i = 0.70$	$J_{fg} = 2.0$
$\delta H_{j,k,l,m,n} = 1.11-1.50$	$J_{ij} = 6.9$
$\delta H_o = 0.87$	$J_{no} = 7.0$

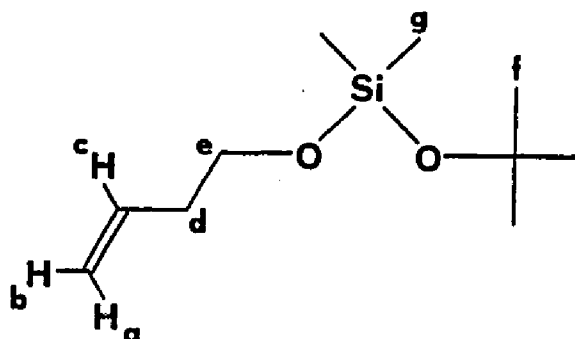
Table A.15. NMR assignments for 71.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 4.64$	$J_{fg} = 6.9$
$\delta H_b = 4.64$	$J_{kl} = 7.5$
$\delta H_c = 1.54$	
$\delta H_d = 0.15$	
$\delta H_e = 0.91$	
$\delta H_f = 0.69$	
$\delta H_{g,h,i,j,k} = 1.14-1.34$	
$\delta H_l = 0.85$	

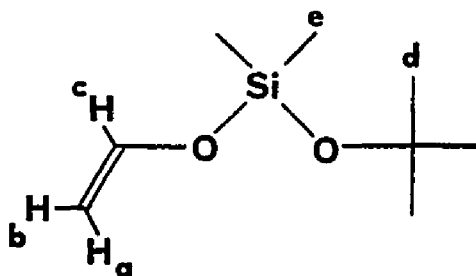


Table A.16. NMR assignments for 72.

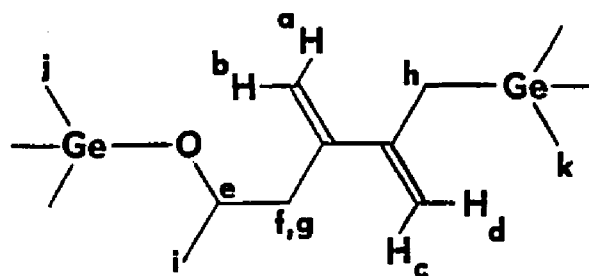
Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 4.57$	$J_{fg} = 6.8$
$\delta H_b = 4.57$	$J_{kl} = 7.5$
$\delta H_c = 1.67$	$J_{(117\text{Sn}-H_d)} = 53.0$
$\delta H_d = 0.08$	$J_{(119\text{Sn}-H_a)} = 51.2$
$\delta H_e = 0.92$	$J_{(117,119\text{Sn}-H_c)} = 70.0$
$\delta H_f = 0.70$	$J_{(117,119\text{Sn}-H_{ab})} = 20.0$
$\delta H_{g,h,i,j,k} = 1.12-1.38$	
$\delta H_l = 0.85$	

Table A.17. NMR assignments for 75.

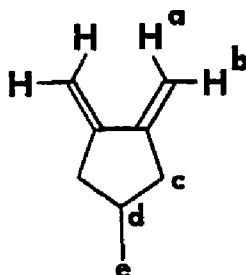
Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.06$	$J_{ab} = 1.3$
$\delta H_b = 5.01$	$J_{ac} = 17.5$
$\delta H_c = 5.81$	$J_{ad} = 1.5$
$\delta H_d = 2.30$	$J_{bc} = 9.6$
$\delta H_e = 3.69$	$J_{bd} = 1.1$
$\delta H_f = 1.27$	$J_{cd} = 6.9$
$\delta H_g = 0.10$	$J_{de} = 6.9$

Table A.18. NMR assignments for 74.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 4.46$	$J_{ab} = 0.7$
$\delta H_b = 4.14$	$J_{ac} = 13.6$
$\delta H_c = 6.45$	$J_{bc} = 5.9$
$\delta H_d = 1.28$	
$\delta H_e = 0.18$	

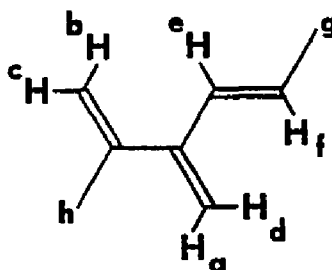
Table A.19. NMR assignments for 73.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.12$	$J_{ef} = 2.9$
$\delta H_b = 5.01$	$J_{eg} = 9.2$
$\delta H_c = 4.94$	$J_{fg} = 13.8$
$\delta H_d = 4.78$	
$\delta H_e = 3.86$	
(cis to e) $\delta H_f = 2.57$	
(trans to e) $\delta H_g = 2.21$	
$\delta H_h = 1.88$	
$\delta H_i = 1.60$	
$\delta H_j = 0.16$	
$\delta H_k = 0.11$	

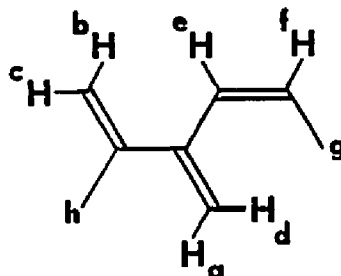
Table A.20. NMR assignments for 66.

Chemical shift (ppm)	Coupling constant (Hz)
$\delta H_a = 5.34$	$J_{de} = 5.9$
$\delta H_b = 4.86$	
$\delta H_{c,c'} = 2.04,^a 2.56^a$	
$\delta H_d = 1.06^a$	
$\delta H_e = 0.99$	

<sup>a</sup>Multiplets.

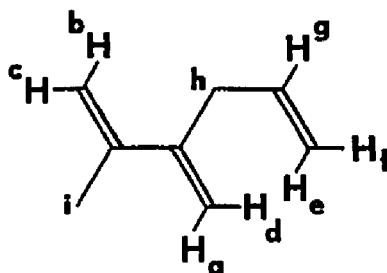
Table A.21. NMR assignments for 67a

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.04$	$J_{ef} = 15.4$
$\delta H_b = 5.02$	$J_{eg} = 1.6$
$\delta H_c = 4.99$	$J_{fg} = 6.6$
$\delta H_d = 4.96$	
$\delta H_e = 6.14$	
$\delta H_f = 5.82$	
$\delta H_g = 1.78$	
$\delta H_h = 1.91$	

Table A.22. NMR assignments for 67b

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a, \delta H_b, \delta H_c, \delta H_d, \delta H_e, \delta H_f^a$	$J_{eg} = 1.8$
$\delta H_g = 1.70$	$J_{fg} = 6.9$
$\delta H_h = 1.94$	

<sup>a</sup>Absorptions of vinyl hydrogens  $H_a-H_f$  are obscured by those of compounds 67a and 68.

Table A.23. NMR assignments for 68.

Chemical shift (ppm)	Coupling constants (Hz)
$\delta H_a = 5.15$	$J_{ad} = 0.5$
$\delta H_b = 5.10$	$J_{ah} = 1.3$
$\delta H_c = 5.00$	$J_{eg} = 17.3$
$\delta H_d = 5.00$	$J_{fg} = 10.4$
$\delta H_e = 5.07$	$J_{gh} = 6.6$
$\delta H_f = 5.05$	
$\delta H_g = 5.90$	
$\delta H_h = 3.03$	
$\delta H_i = 1.92$	



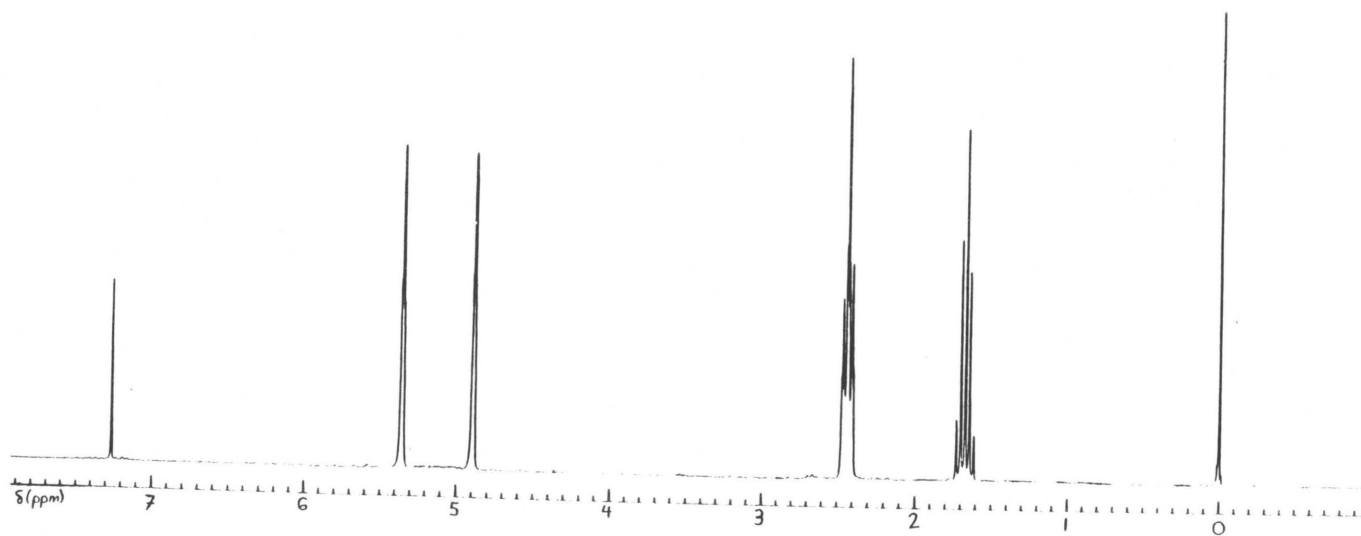


Figure A.1. NMR spectrum of 22,n=5.

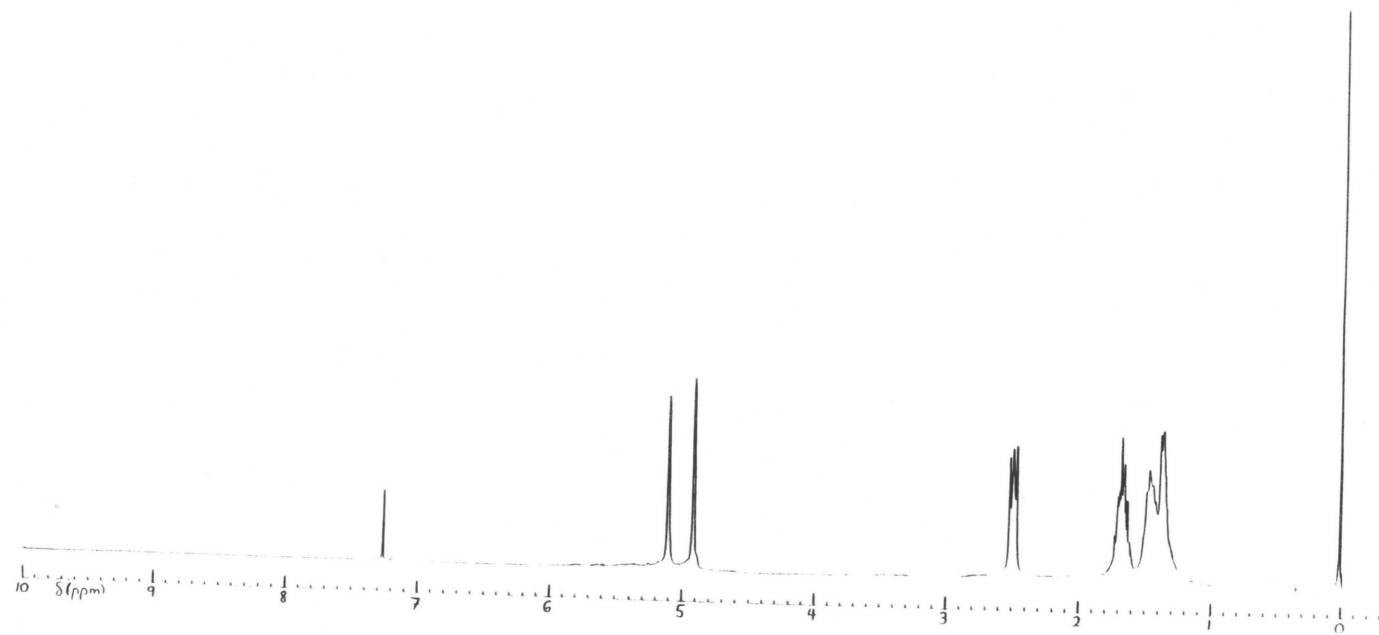


Figure A.2. NMR spectrum of 22,n=10.

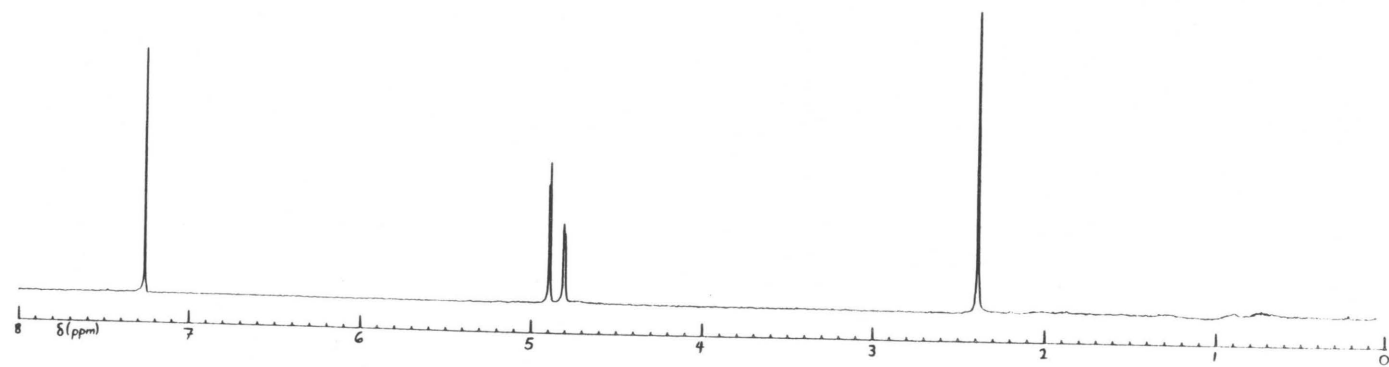


Figure A.3. NMR spectrum of 23,n=4.

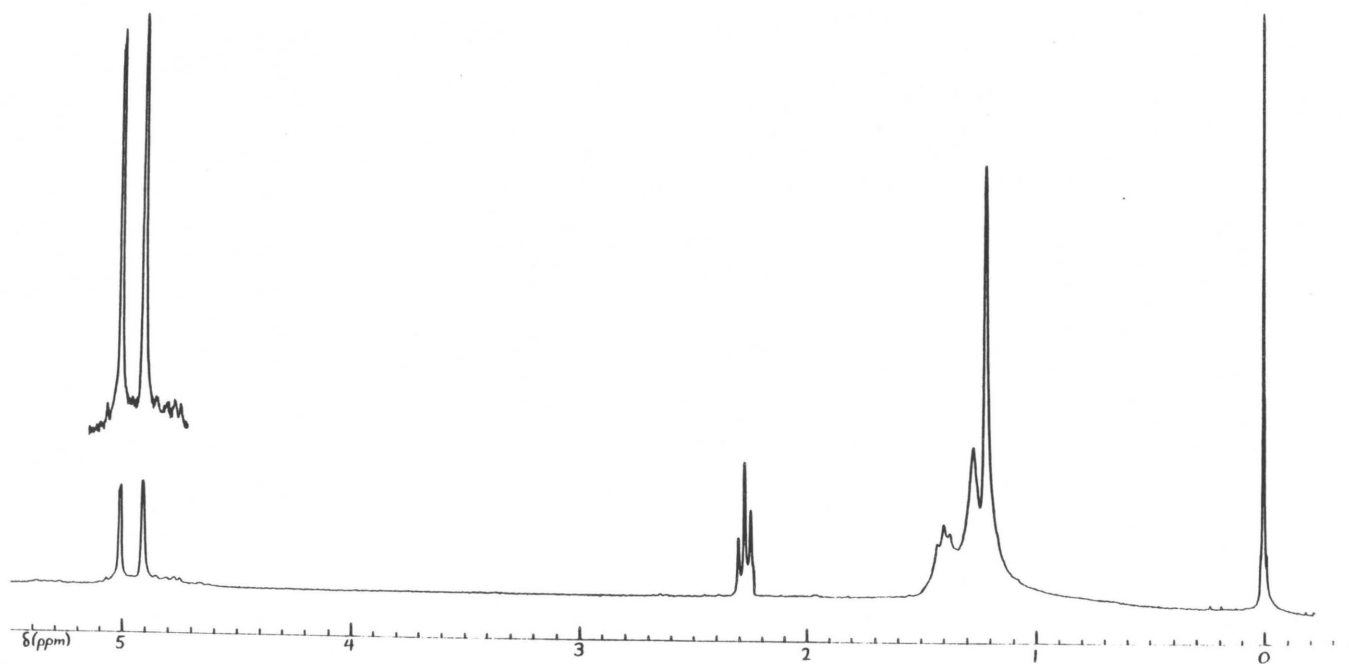


Figure A.4. NMR spectrum of 23,n=12.

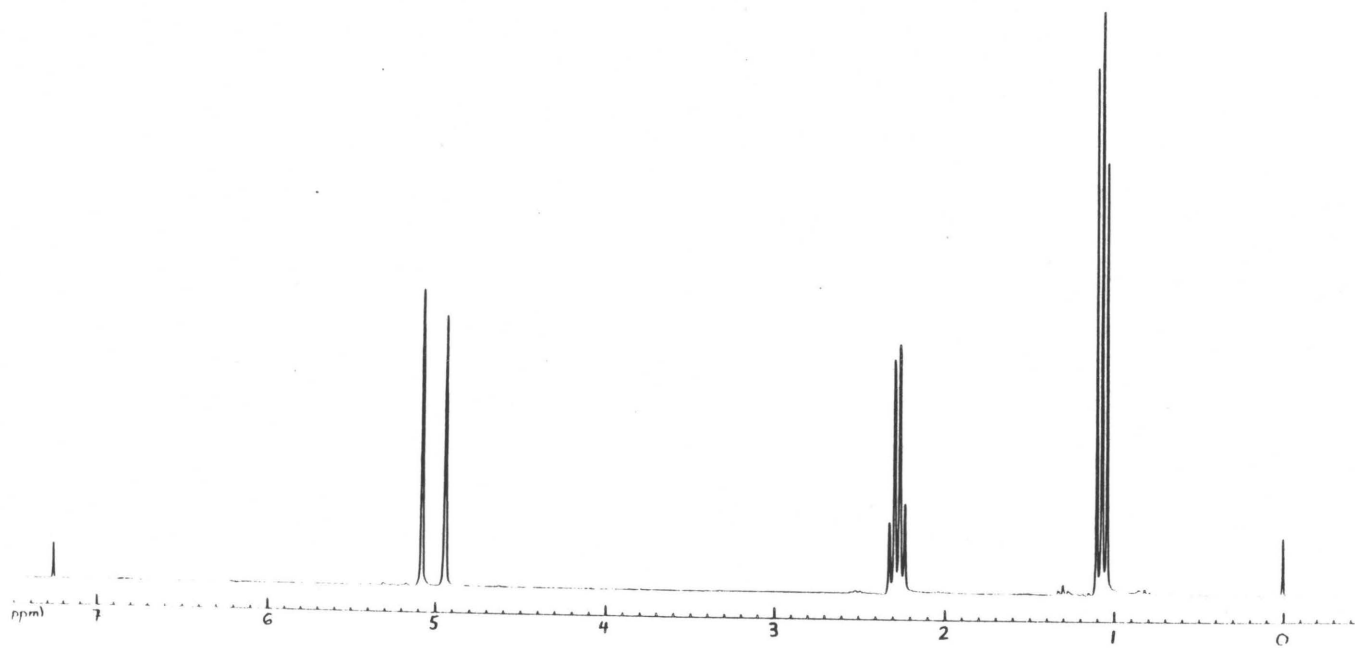


Figure A.5. NMR spectrum of 27.

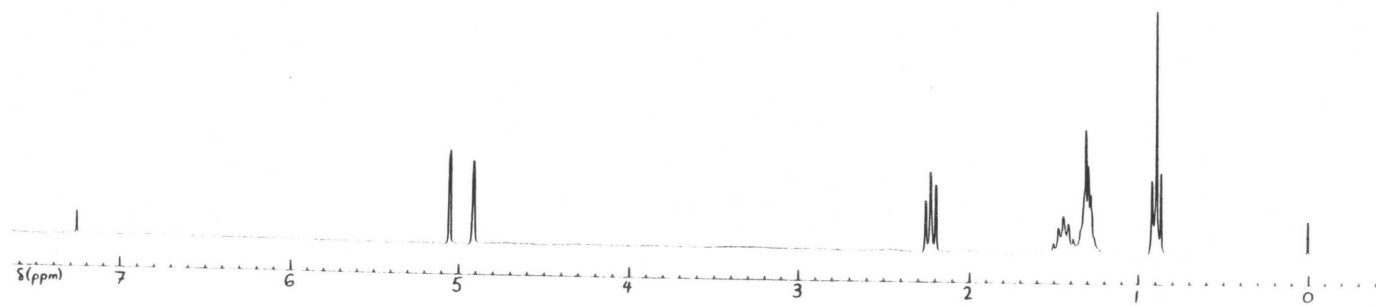


Figure A.6. NMR spectrum of 51.

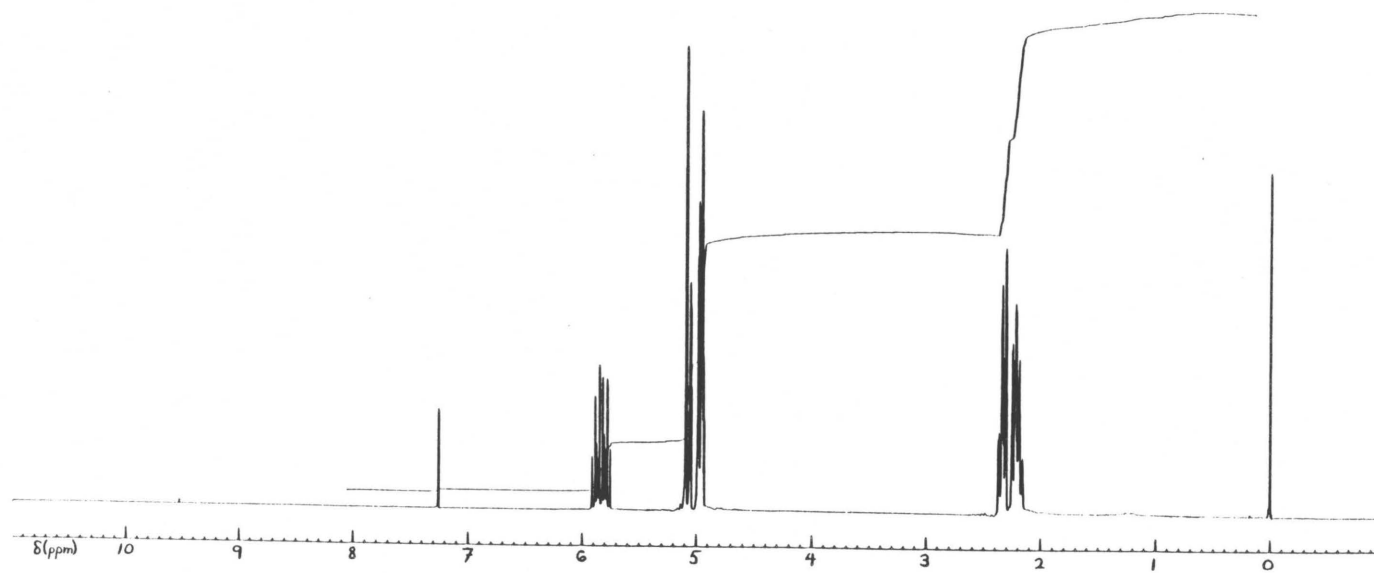


Figure A.7. NMR spectrum of 52.

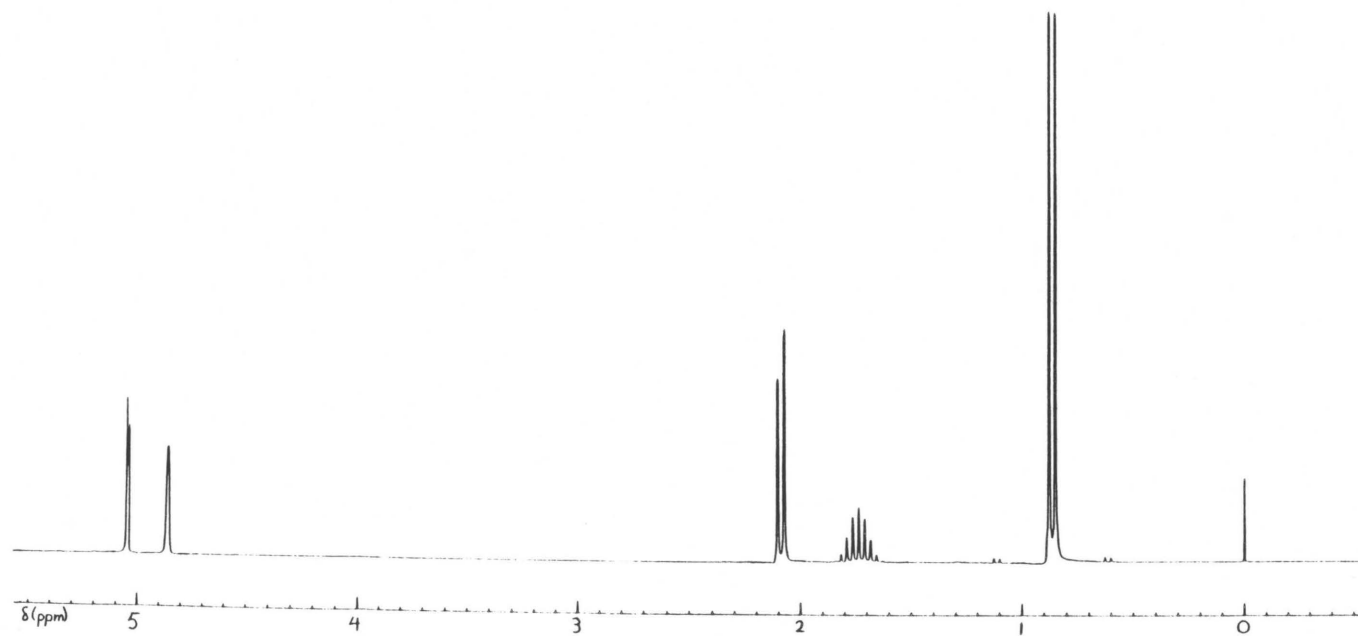


Figure A.8. NMR spectrum of 55.



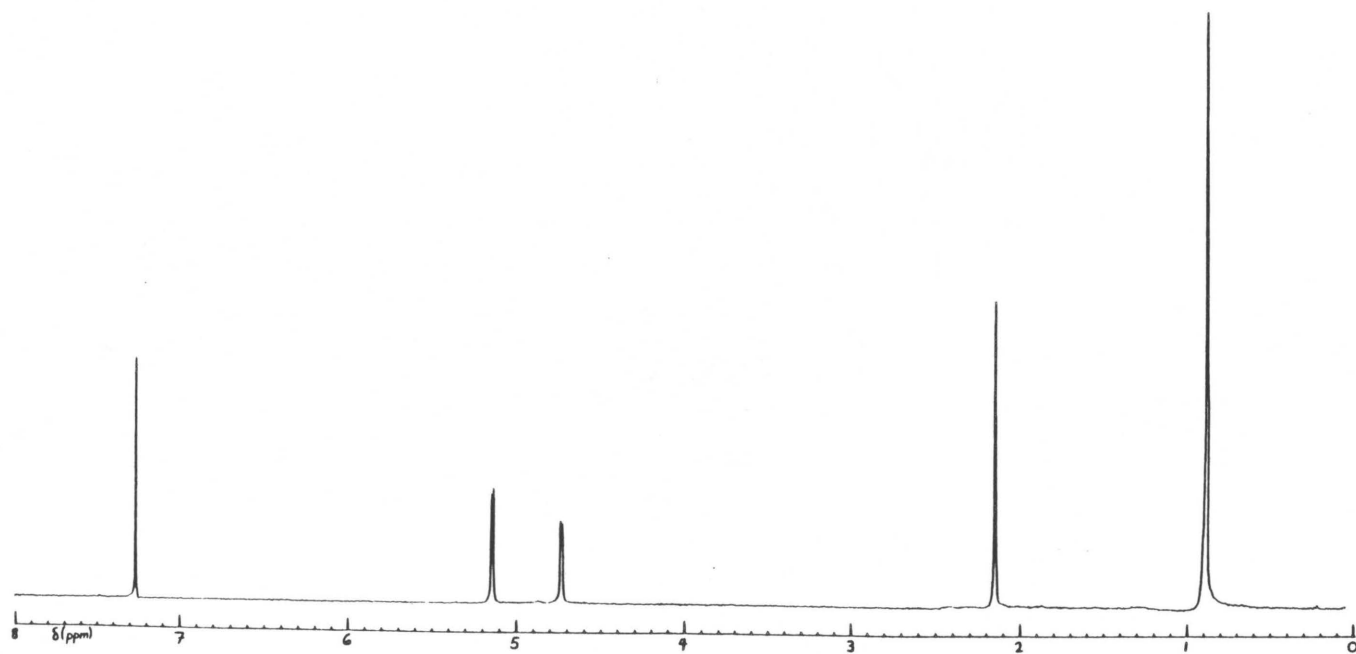


Figure A.9. NMR spectrum of 57.

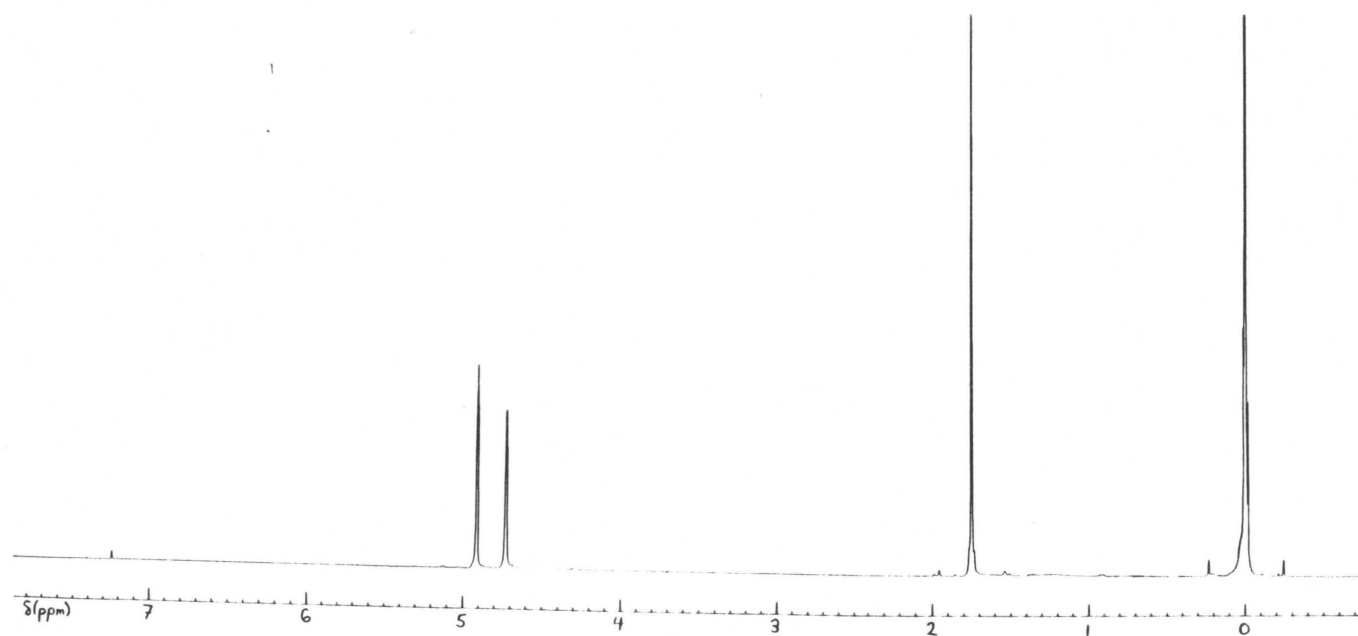


Figure A.10. NMR spectrum of 32.

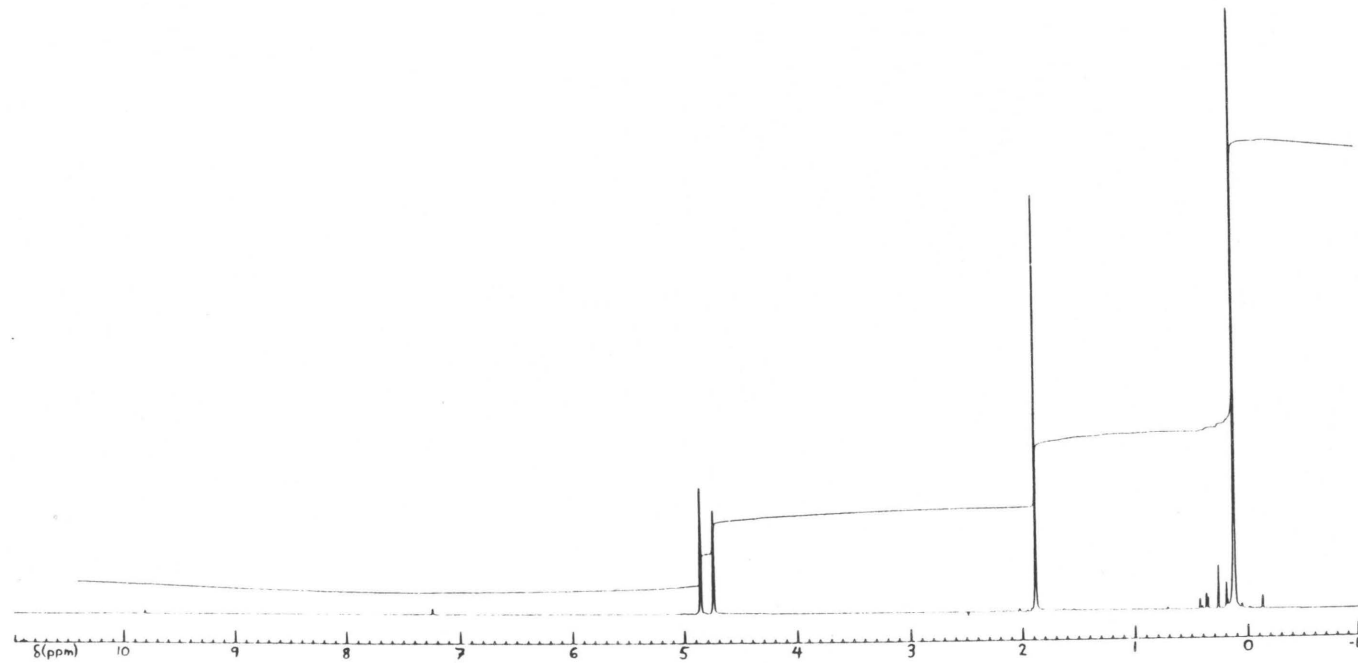


Figure A.11. NMR spectrum of 59.

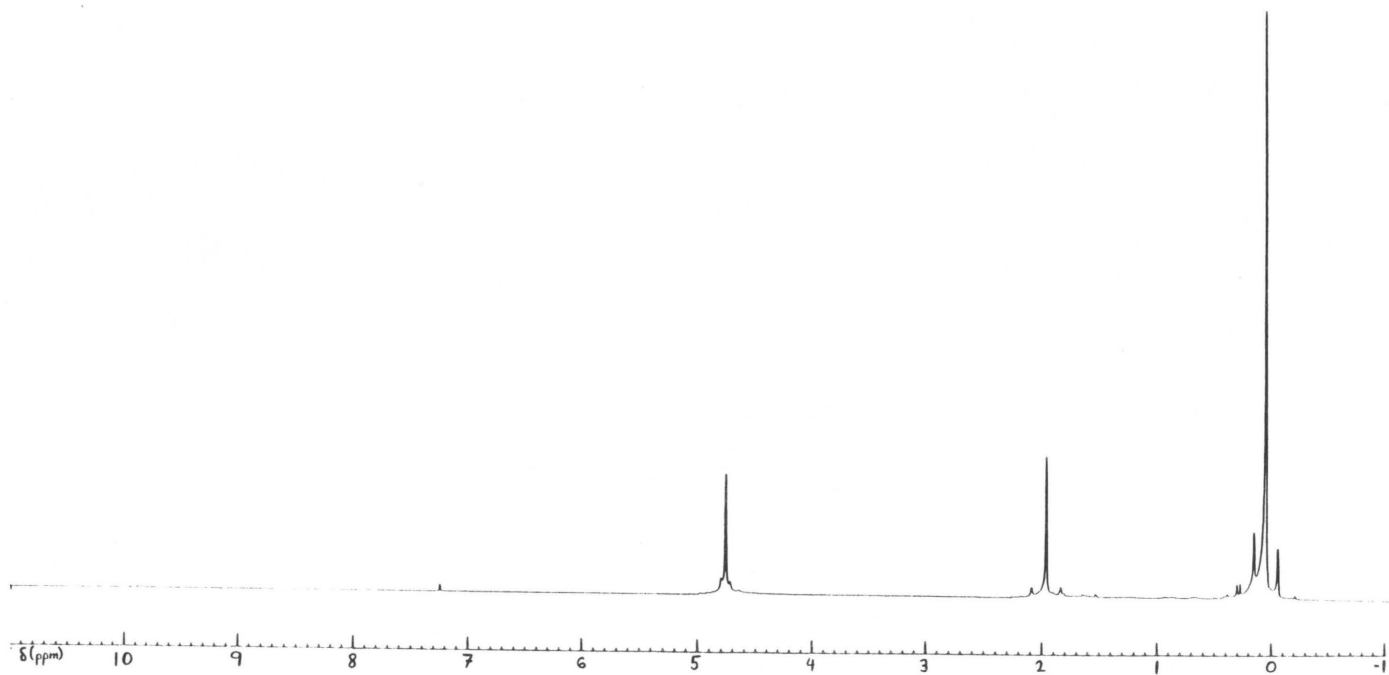


Figure A.12. NMR spectrum of 60.

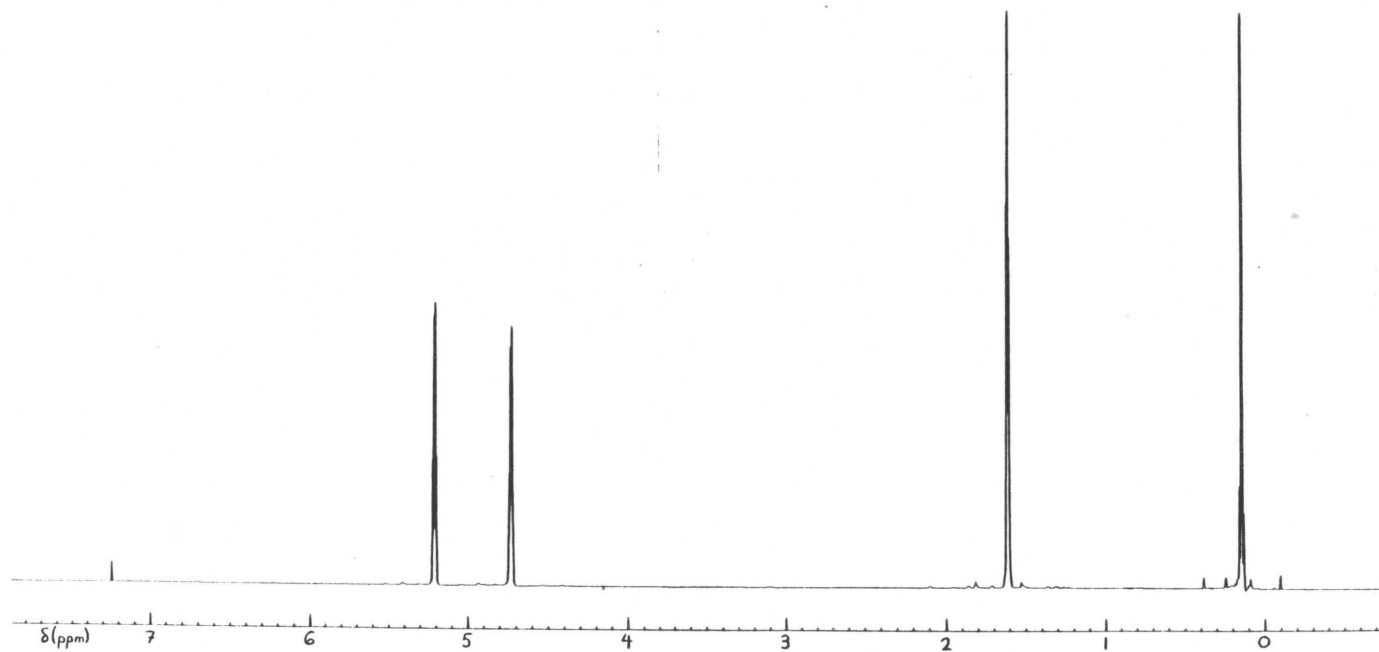


Figure A.13. NMR spectrum of 62.

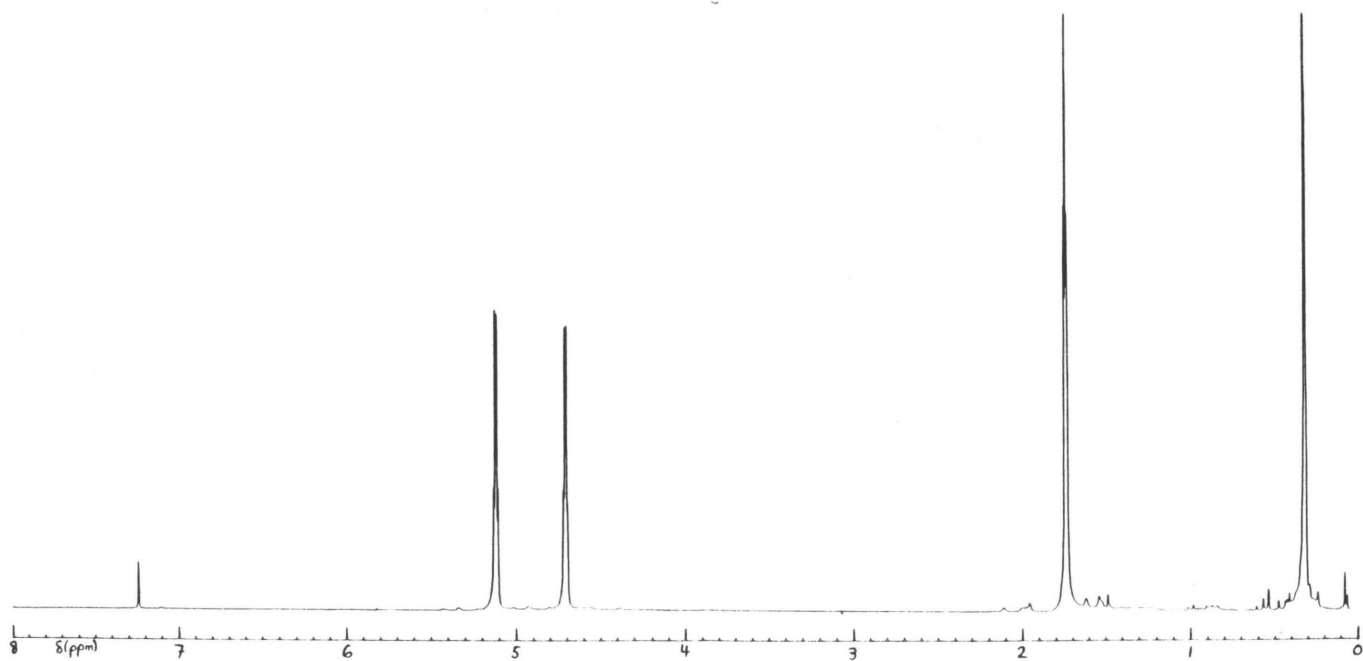


Figure A.14. NMR spectrum of 63.

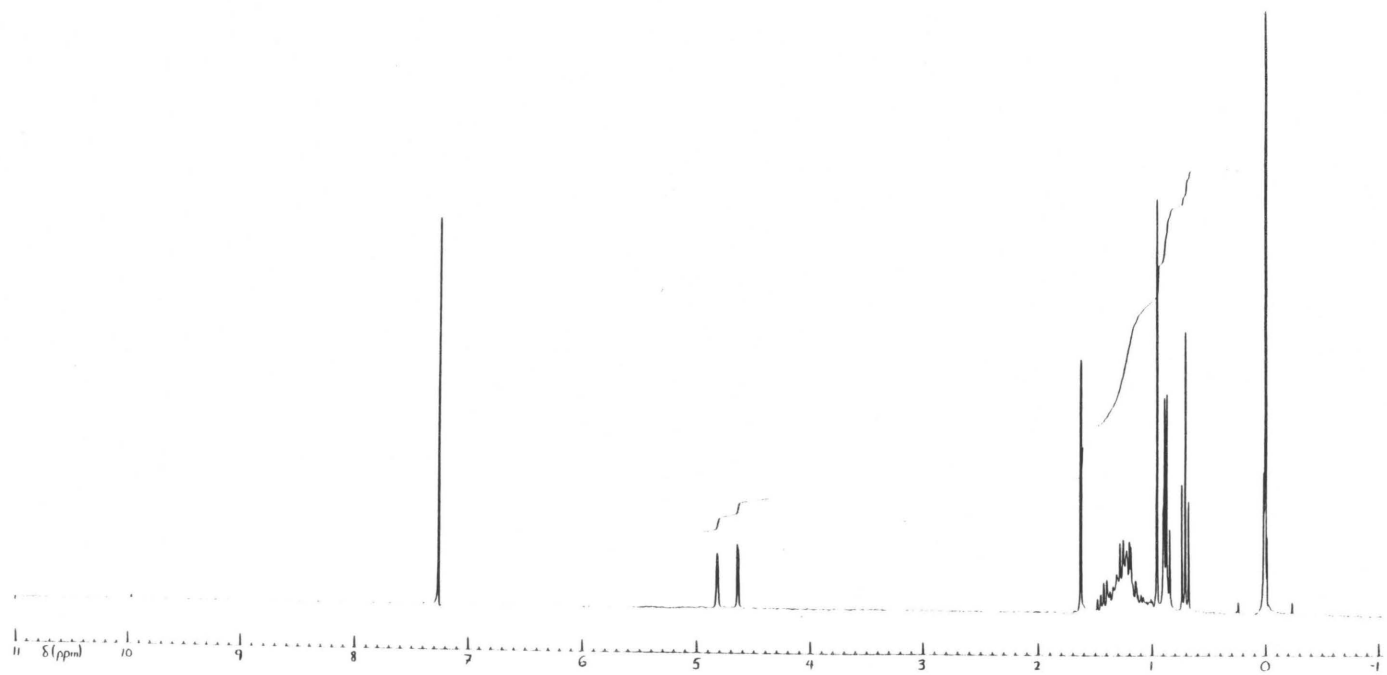


Figure A.15. NMR spectrum of 69.

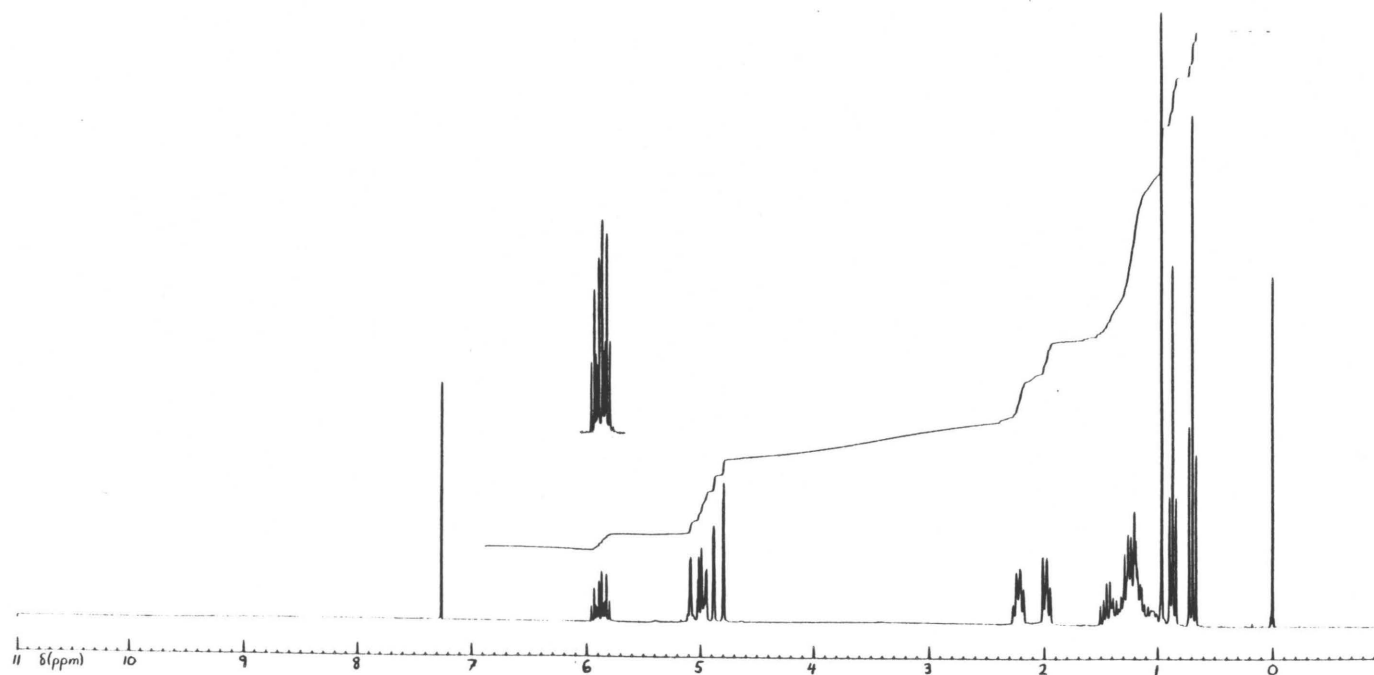


Figure A.16. NMR spectrum of 70.



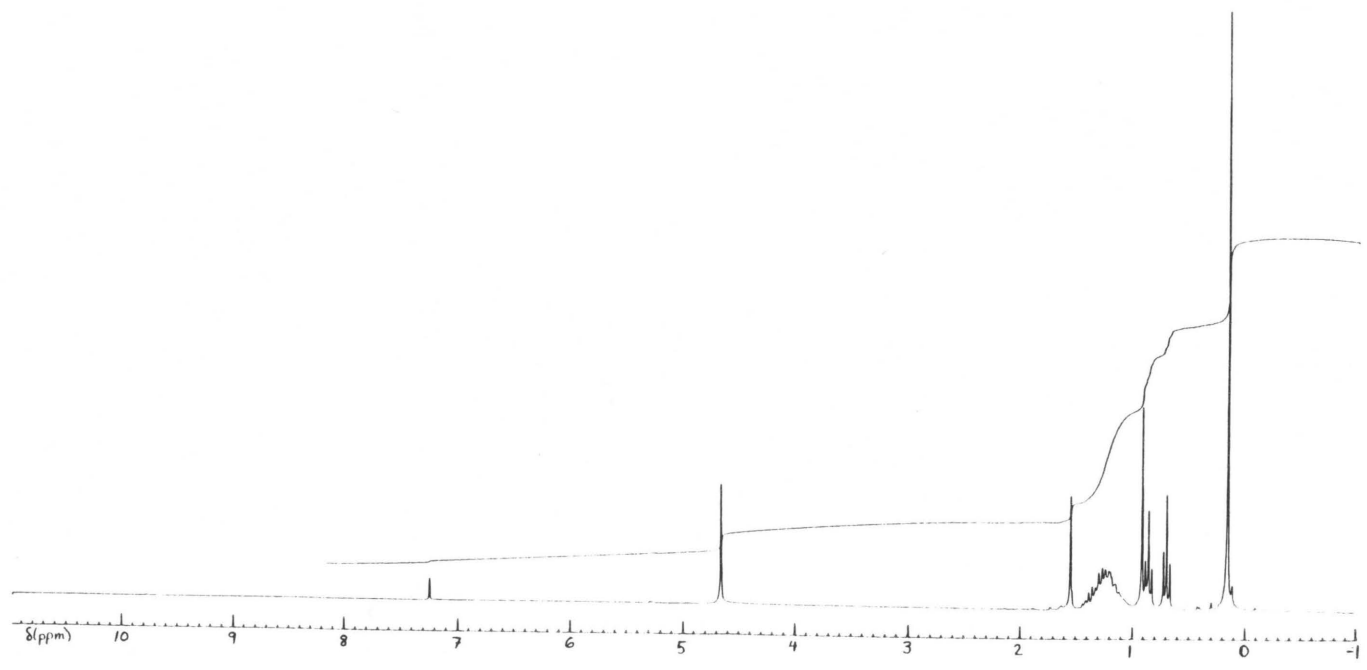


Figure A.17. NMR spectrum of 71.

APPENDIX B

MASS SPECTRAL DATA

Table B.1. MS data for 51.

Peak	Intensity
194	1.5
179	0.2
165	1.6
151	0.6
138	5.5
137	4.0
123	23
109	50
95	55
82	100
81	55
79	37.5
67	67
55	47.5
53	34
43	26
41	63
39	33

Table B.2. MS data for 52.

Peak	Intensity
162	0.5
161	4.0
147	8.0
133	26
119	39
107	44
105	54
93	75
92	83
80	43
79	96
77	88
67	48
65	42
55	46
53	46
41	100
39	85

Table B.3. MS data for 53.

Peak	Intensity
262	0.2
171	0.4
157	5.0
143	15.5
129	37.5
115	10.0
104	7.0
91	100
77	10.5
65	30
55	3.0
51	6.5
41	6.5
39	9.0

Table B.4. MS data for 55.

Peak	Intensity
166	32
151	18
124	62
123	25
110	67
95	91
93	28
91	35.5
82	67.5
79	45
77	39
68	100
65	29.5
55	30
53	30.5
43	59
41	65
39	41

Table B.5. MS data for 58.

Peak	Intensity
138	13
123	21
107	3.0
91	11
82	42.5
79	23.5
77	15.5
67	20
65	14.5
57	100
53	15
41	58
39	36

Table B.6. MS data for 57.

Peak	Intensity
194	8.0
179	1.5
138	9.5
123	19
107	6.0
91	17
82	18.5
78	13
57	100
41	37

Table B.7. MS data for 32.

Peak	Intensity
226	11
211	8.0
152	9.0
138	16
123	34
110	8.0
95	11
83	6.0
73	100
59	17
58	5.0
45	48
43	17
39	10

Table B.8. MS data for 59.

Peak	Intensity
316 <sup>a</sup>	0.8
301 <sup>a</sup>	0.4
198 <sup>b</sup>	0.7
184 <sup>b</sup>	12
169 <sup>b</sup>	18
119 <sup>b</sup>	100
104 <sup>b</sup>	16
89 <sup>b</sup>	38
43	12
39	4

<sup>a</sup>Contains two Ge atoms.

<sup>b</sup>Contains Ge atom.

Table B.9. MS data for 60.

Peak	Intensity
408 <sup>a</sup>	1.1
393 <sup>a</sup>	3.5
292 <sup>b</sup>	1.2
277 <sup>b</sup>	4.7
262 <sup>b</sup>	1.4
247 <sup>b</sup>	2.0
230 <sup>b</sup>	19
215 <sup>b</sup>	17
185 <sup>b</sup>	10
165 <sup>b</sup>	100
150 <sup>b</sup>	22
135 <sup>b</sup>	77
120 <sup>b</sup>	28
39	10

<sup>a</sup>Contains two Sn atoms.

<sup>b</sup>Contains Sn atom.

Table B.10. MS data for 61.

Peak	Intensity
318 <sup>a</sup>	22
303 <sup>a</sup>	13
288 <sup>a</sup>	3.0
253 <sup>a</sup>	93
238 <sup>a</sup>	15
223 <sup>a</sup>	95
208 <sup>a</sup>	60
97	25
83	23
71	26
57	29.5
55	30.5
42	100
39	16

<sup>a</sup>Contains Pb atom.

Table B.11. MS data for 62.

Peak	Intensity
138	50
123	100
110	14
97	19
95	69
83	18
79	21
73	7.0
69	13
67	17
58	16
55	15
43	40
39	31

Table B.12. MS data for 63.

Peak	Intensity
184 <sup>a</sup>	37
169 <sup>a</sup>	100
155 <sup>a</sup>	5
141 <sup>a</sup>	14
129 <sup>a</sup>	13
115 <sup>a</sup>	21
103 <sup>a</sup>	25
91	27
89 <sup>a</sup>	77
79	37
65	13
52	32
39	49

<sup>a</sup>Contains Ge atom.

Table B.13. MS data for 66.

Peak	Intensity
108	26
93	100
91	82.5
79	29
77	67.5
67	10
65	24
63	14.5
53	15.5
52	11.5
51	29.5
41	36
40	18
39	83
38	11.5



Table B.14. MS data for 67a, 67b, 68.

Peak	Intensity
108	66
93	100
91	72.5
79	42
77	59.5
67	8.0
65	29
63	14.5
53	13
52	14
51	25
41	28.5
40	20.5
39	73
38	12

Table B.15. MS data for 69.

Peak	Intensity
168	0.5
153	0.4
139	9.0
98	88
97	79
83	81
69	76
67	38
55	100
43	24.5
41	67
39	25.5

Table B.16. MS data for 70.

Peak	Intensity
208	0.1
180	0.4
179	2.3
151	5.0
138	5.0
137	14
123	12.5
109	46
97	35.5
95	92
81	100
79	28
69	43
67	76
55	87.5
43	46
41	90.5
39	27

Table B.17. MS data for 71.

Peak	Intensity
286 <sup>a</sup>	0.5
216 <sup>a</sup>	23
173 <sup>a</sup>	19
159 <sup>a</sup>	7.0
127	8.0
119 <sup>a</sup>	100
105 <sup>a</sup>	12
104 <sup>a</sup>	7.0
89 <sup>a</sup>	13
67	8.0
55	21
43	15
41	25

<sup>a</sup>Contains Ge atom.

Table B.18. MS data for 72.

Peak	Intensity
332 <sup>a</sup>	6.0
317 <sup>a</sup>	52
304 <sup>a</sup>	0.5
262 <sup>a</sup>	100
111	6.0
98	15
97	16
83	12
69	8.0
55	11

<sup>a</sup>Contains Sn atom.

Table B.19. MS data for 73.

Peak	Intensity
360 <sup>a</sup>	0.08
345 <sup>a</sup>	0.33
279 <sup>a</sup>	0.66
253 <sup>a</sup>	0.64
237 <sup>a</sup>	2.6
211 <sup>b</sup>	3.2
195 <sup>b</sup>	1.1
183 <sup>b</sup>	1.3
161 <sup>b</sup>	2.0
143 <sup>b</sup>	1.1
119 <sup>b</sup>	100
105 <sup>b</sup>	30
89 <sup>b</sup>	48
77	11.0
65	7.5
53	5.0
41	10.5
39	13.5

<sup>a</sup>Contains two Ge atoms.

<sup>b</sup>Contains Ge atom.

Table B.20. MS data for 74.

Peak	Intensity
174	5.0
159	99.5
131	2.0
115	48
103	75
101	100
87	4.5
77	32.5
75	80
71	6.0
61	27
59	35
45	27
43	34

Table B.21. MS data for 22,n=11.

Peak	Intensity
178	11.5
163	15
149	12
136	22
135	14
122	45.5
108	79.5
95	75
94	15.5
91	38
82	29
81	34
80	63
68	100
55	67
41	72.5

Table B.22. MS data for 22,n=16.

Peak	Intensity
248	20.5
233	7.0
219	1.5
205	2.5
191	0.5
177	1.5
163	4.5
149	11.5
135	18
122	36
109	79.5
95	100
91	26
82	45.5
81	95.5
77	26
69	75
55	52
41	51

Table B.23. MS data for 23,n=4.

Peak	Intensity
160	1.0
147	4.5
132	100
117	46
115	17.5
105	14.5
104	21
91	49
79	28.5
77	28.5
65	15
51	15.5
41	15.5
39	30

Table B.24. MS data for 23,n=11.

Peak	Intensity
356	11
341	1.0
327	0.2
313	0.2
299	0.5
285	0.5
271	0.2
259	2.0
257	1.5
245	6.0
243	3.0
229	3.5
217	3.5
215	3.5
203	3.5
201	4.0
189	4.0
187	3.0
175	7.5
173	6.0
163	9.0
161	11.5
159	10
149	9.0
147	28.5
145	14.5
135	47
132	24
121	71
117	10
108	74
94	93
80	100
68	77.5
55	60
41	68

Table B.25. MS data for 23,n=12.

Peak	Intensity
384	10.0
369	0.9
356	0.6
355	0.5
341	0.5
327	0.3
313	0.4
301	0.3
299	0.4
287	0.4
285	0.4
273	1.3
271	1.0
259	2.8
257	1.8
245	1.5
243	2.3
231	2.7
229	2.3
219	1.4
217	2.1
215	1.5
205	0.7
203	1.5
201	0.9
191	1.0
189	2.5
187	1.7
177	2.3
175	3.8
173	2.5
163	3.0
161	6.5
159	5.0
149	8.0
147	12
145	12
135	16
133	16
131	15
121	31
119	32
109	37.5
108	36
107	50
105	38

Table B.25.--Continued

Peak	Intensity
95	60
94	28
93	46.5
91	27
82	58.5
81	80
79	53
69	49
67	100
55	68
41	43



Table B.26. MS data for 23,n=14.

Peak	Intensity
440	2.0
313	0.4
301	0.6
299	0.6
287	1.0
285	1.0
273	0.9
271	1.3
259	1.3
257	1.4
247	0.7
245	1.1
243	0.7
233	0.5
231	0.7
219	0.5
217	0.5
215	0.4
205	0.6
203	0.7
201	0.5
191	0.5
189	0.8
187	0.9
177	1.1
175	1.5
173	1.7
163	2.0
161	3.5
159	5.0
149	5.0
147	7.5
145	13.5
135	9.5
133	12
131	20
121	20.5
119	25
109	30
108	29
107	35
105	32.5
95	60.5
94	28
93	36

Table B.26.--Continued

Peak	Intensity
82	49.5
81	73.5
79	38.5
69	53
67	99
55	100
43	38
41	80

Table B.27. MS data for 23,n=16.

Peak	Intensity
497	5.8
327	0.2
315	1.6
313	2.1
301	0.8
299	2.3
287	1.9
285	1.9
274	1.9
273	2.0
259	0.6
177	0.5
175	1.0
173	1.9
163	1.5
161	3.5
159	7.0
149	5.0
147	10
145	17.5
135	12
133	15.5
131	22.5
121	22
119	23.5
109	28.5
108	39.5
105	25.5
96	24
95	22
93	29
82	100
79	28
69	33
68	29
67	27
55	40
41	37.5

Table B.28. MS data for 24,n=12.

Peak	Intensity
577	3.3
562	0.2
549	0.3
548	0.3
191	1.0
189	2.0
187	3.0
177	1.0
175	3.0
173	6.0
163	4.0
161	8.0
159	14
149	10
147	7.0
145	17
135	13
133	11
131	15
121	19
119	22
117	10
108	100
105	22
95	81
91	17
82	79
80	44
68	91
55	26
41	28

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