1969

Part I. Electron impact formation of the phenalenium cation, Part II. Mass spectral rearrangements of organosilanes

Philip John Ihrig
Iowa State University

PART I: ELECTRON IMPACT FORMATION OF THE PHENALENIUM CATION

PART II: MASS SPECTRAL REARRANGEMENTS OF ORGANOSILANES

by

Philip John Ihrig

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1969

TABLE OF CONTENTS

PREFACE

The most urgent problems in organic mass spectrometry at its present stage of development center on the understanding of fragmentation mechanisms and the structure of the gaseous ions formed upon the energetic ionization of organic compounds. A knowledge of these processes is essential for the basic understanding of organic mass spectrometry which will lead to orderly advances in the field, including the immediate application to structure determination. This work is complicated by the fact that many of the ions which are observed in the mass spectra of organic compounds are not the result of simple bond cleavage processes but arise by structural rearrangement (1, 2, 3). As a result, any attempt to understand or to explain fragmentation processes requires a knowledge of ion structure and the pathway(s) by which these fragment ions are formed.

The studies presented here, although seemingly unrelated, are attempts to explain the fragmentation patterns observed in two broad types of organic compounds, to gain some insight into the structures of the gaseous ions which are observed, and as far as possible to determine the mechanism by which they are formed.

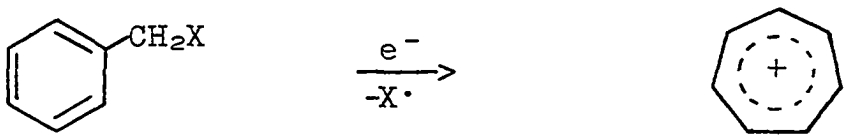
PART I: ELECTRON IMPACT

FORMATION OF THE PHENALENIUM CATION

HISTORICAL

Tropylium Ion Formation

The most thoroughly documented example of a ring expansion process occurring upon the electron bombardment of an organic molecule involves the formation of the symmetrical tropylium ion (1) from toluene and other substituted

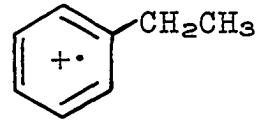


1

benzyl compounds. Much of the pertinent work relating to this problem has been reviewed (4, pp. 488-495).

Although this intense ion at m/e 91 ($C_7H_7^+$) in the mass spectrum of toluene was first thought to be the benzyl ion (5-10) a discrepancy of 16 kcal/mole (10) in the measured ionization potential of the benzyl free radical (11) and the calculated ionization potential of C_7H_7 using appearance potential data of the m/e 91 ion from toluene and bibenzyl led to the suggestion that the $C_7H_7^+$ ion in the mass spectrum of toluene was not the benzyl cation (12). Results from the study of the mass spectra of various deuterium labeled toluenes (13, 14) and ethylbenzenes (13) also suggested that this ion at m/e 91 was not the benzyl cation.

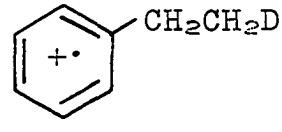
Ethylbenzene, upon electron impact (13), exhibits a metastable loss of $CH_3\cdot$ from the molecule ion. Deuterium



$\longrightarrow \quad C_7H_7^+ + CH_3\cdot$

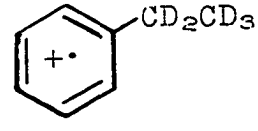
m/e 106 91

labeled ethylbenzenes (13) show that β cleavage occurs and that no deuterium-hydrogen exchange accompanies this process. Ethylbenzene-β-d_1 shows loss of only 16 corresponding to the loss of CH_2D, -α,β-d_5 shows only loss of 18 (CD_3), while the spectra of ethylbenzene-α-d_2 exhibits only the loss of 15 (CH_3). Ring substituted deuterio-ethylbenzenes also show



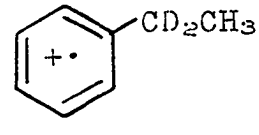
$\xrightarrow{*} \quad C_7H_7^+ + CH_2D\cdot$

m/e 107 91



$\xrightarrow{*} \quad C_7H_5D_2^+ + CD_3\cdot$

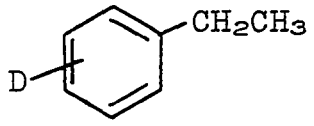
m/e 111 93



$\xrightarrow{*} \quad C_7H_5D_2^+ + CH_3\cdot$

m/e 108 93

retention of deuterium following initial β cleavage.



$$\xrightarrow{*} \quad C_7H_6D^+ \quad + \quad CH_3\cdot$$

m/e 107 92

A metastable peak (m/e = 46.4) in the spectrum of ethylbenzene shows that the $C_7H_7^+$ ion undergoes the loss of C_2H_2 to form $C_5H_5^+$ (m/e = 65). Corresponding metastables are also apparent for the deuterium labeled compounds. However, the loss of deuterium in this process is inconsistent with the benzyl structure for the $C_7H_7^+$ ions which undergo this process since all hydrogen and deuterium atoms become equivalent. Ethylbenzene-α-d_1, -o-d, m-d, and -p-d all have very nearly the same intensities at m/e = 65, 66, and 67. This suggests that hydrogen-deuterium exchange is occurring during the process leading to the formation of $C_5H_5^+$ ions or a much more symmetrical structure for the $C_7H_7^+$ ion than that of the benzyl cation (13).

Similarly, the mass spectra of toluene, deuterium labeled toluenes, and toluene-α-^{13}C show that the $C_7H_7^+$ ion cannot be interpreted as the benzyl cation (13-15).

The mass spectrum of toluene-α-d_3 shows that positional identity of the deuterium atoms is lost prior to or during

the formation of $C_7H_5D_2^+$ ion or $C_7H_4D_3^+$ ion since the loss of hydrogen or deuterium from the molecule ion is nearly in the ratio of 5:3. This random loss of deuterium is also exhibited by toluene-o-d, -m-d, and -p-d since 10% of the hydrogen atoms lost in forming $C_7H_7^+$ ions are deuterium which can come only from the ring. Furthermore, the spectra of these isomers are indistinguishable.

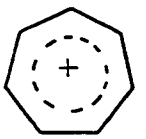
Analogous to this, o-, m-, and p-xylene all exhibit the same mass spectrum which indicates that the initial formation of a substituted $C_7H_7^+$ ion, $C_7H_6CH_3^+$, must undergo a process similar to the process leading to the formation of $C_7H_7^+$ ion from toluene (16).

As in the case of the ethylbenzenes the $C_7H_7^+$ ion from toluene exhibits the metastable loss of C_2H_2 to give the $C_5H_5^+$ ion. The intensities of the peaks at m/e = 65 and 66 in the mass spectrum of toluene-α-d_1, -o-d, -m-d, and -p-d can be interpreted only as nearly complete loss of positional identity of the hydrogen atoms.

That this is not an equilibration of only hydrogen and deuterium atoms can be seen from the mass spectrum of toluene-α-^{13}C. The loss of C_2H_2 from the $C_7H_7^+$ ion shows that the carbon atoms have also lost positional identity.

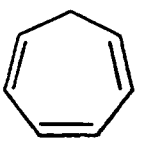
This loss of positional identity of both hydrogen and carbon atoms following the electron bombardment of these various alkylbenzenes led to the postulate that the $C_7H_7^+$ ion was the result of ring expansion to form the tropylium

ion (1) (13).



1

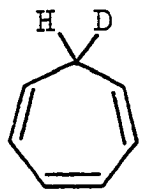
The suggestion that the $C_7H_7^+$ ion had the tropylium structure led to the examination of the mass spectrum of cycloheptatriene (2) (14, 17) which should lose a single hydrogen atom to form the tropylium ion. The spectra of



2

cycloheptatriene and of toluene are very nearly identical with the $C_7H_7^+$ ion the most prominent species in both spectra. Cycloheptatriene exhibits the same fragmentation as toluene with the same intensities for the fragments formed. This adds support to the idea that the $C_7H_7^+$ ion from toluene is the tropylium ion.

The mass spectrum of cycloheptatriene-7-d (3) (15) shows that loss of hydrogen to form $C_7H_7^+$ ions can only be accounted for on the basis of loss of positional identity of the hydrogen and deuterium atoms. The loss of C_2H_2 to form $C_5H_5^+$ ions or



3

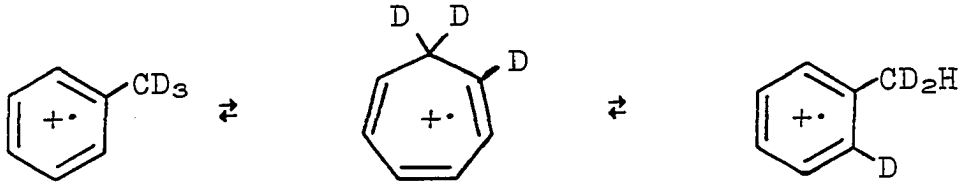
$C_5H_4D^+$ ions also shows randomization of the deuterium atom.

That the $C_7H_7^+$ ion has the tropylium ion structure is further supported by apparent heats of formation of the ion calculated from appearance potential measurements and thermal data. Cycloheptatriene gives a value of 233 kcal/mole for the heat of formation of the tropylium ion and values for heats of formation of this ion arising from toluene, ethylbenzene, propylbenzene, and bibenzyl are in agreement within 3 kcal (4, p. 495).

Although the evidence presented is quite indicative of a ring expansion process occurring, and the idea of the formation of the symmetrical tropylium ion being formed by electron impact has received wide acceptance, the mechanism of the rearrangement of the original benzyl portion of the molecule to the tropylium ion is still under active investigation. The simplest mechanism which can be invisioned--insertion of the α-carbon between carbon atoms 1 and 2 of the ring with the migration of an α-hydrogen atom to carbon 1--is ruled out by the results already discussed. This mechanism could not account

for the scrambling of hydrogen and deuterium atoms prior to the loss of C_2H_2 (C_2HD,C_2D_2) in the labeled compounds.

If the rearrangement of the benzyl portion of the molecule to the tropylium ion (irregardless of whether the loss of H· occurs prior to, concurrently with, or subsequent to the ring expansion) is a reversible process as has been suggested (4, p. 505) the randomization of hydrogen atoms

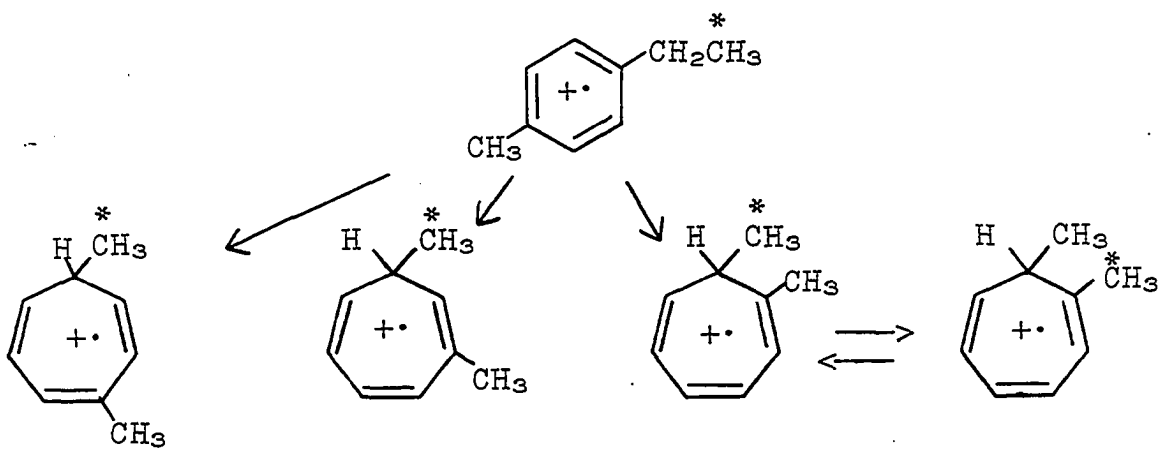


could be explained by this simple mechanism.

Recently Rinehart and co-workers have examined the mass spectrum of toluene-α-1-$^{13}C_2$ (18) and have shown that simple non-reversible insertion of the methyl carbon into the 1-2 bond of the ring is not occurring. The seven carbon atoms of the tropylium ion formed in this study lose all positional identity prior to the expulsion of acetylene. This would not be expected from a tropylium ion containing two adjacent ^{13}C atoms.

A study of the mass spectra of a series of deuterium labeled p-methylethylbenzenes and dimethylethylbenzenes (19) has shown that ring expansion precedes tropylium ion formation.

This is evident from the observation that the ratio of β-methyl to ring-methyl loss is 5:1 (independent of ionizing voltage) for either ring-methyl-d_3- or α-methyl-d_3-p-methylethylbenzenes, and that the loss of either methyl group is not accompanied by hydrogen scrambling. To account for this 5:1 ratio a mechanism involving initial formation of a dimethylcycloheptatriene ion has been proposed (19). Transfer of an α-hydrogen of the ethyl group to the ring carbon followed by the insertion of the α-carbon of the ethyl group between any two ring carbons (possibly through bridged intermediates) gives intermediates 4, 5 and 6. The third intermediate can then undergo a degenerate 7-α hydrogen shift which followed by the loss of a methyl group from only the 7 position will



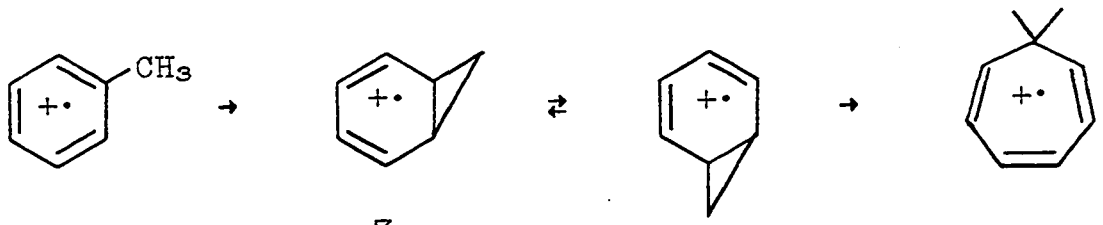
4 5 6

accommodate the observed ratio of 5:1 for the loss of β-methyl (denoted by *) or the α-methyl group. Whether or not scrambling of the remaining hydrogen and deuterium atoms occurred was not reported.

An analogous mechanism can also account for the slight preference of α-hydrogen loss in toluene (20) upon electron bombardment, as well as the fragmentation of labeled ethylbenzenes and cycloheptatriene (19).

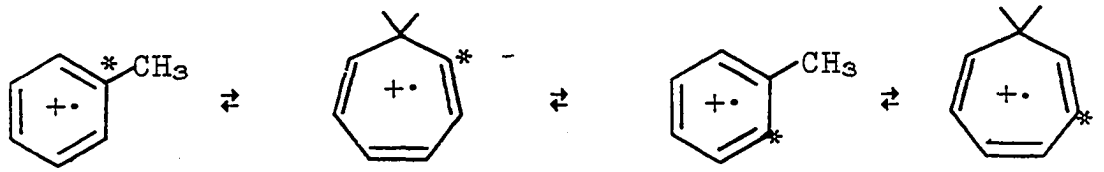
Additional information concerning the timing of tropylium ion formation is available from a kinetic study of the fragmentation of substituted toluenes (21). Utilizing an extension (22) of the method of McLafferty and Bursey (23, 24, 25) for analysing the effects of meta- and para-substituents on the mass spectral fragmentations of aromatic compounds, Brown (21) has shown that the initial step in tropylium ion formation from toluene does not involve the intermediacy of a benzyl cation. This suggests that a rearrangement to a cycloheptatriene ion is the initial step in tropylium ion formation from substituted toluenes. Exceptions to the above results were noted for meta- and para-methylanisole. These compounds retained the identity of substituent location in the loss of a hydrogen atom from the molecular ion. This initial rearrangement of the molecular ions of the substituted toluenes was also supported by identical metastable abundances for the loss of a hydrogen atom from each pair of substituted toluene molecular ions (21). An investigation of the effects of substituents on the formation of the ion at m/e 91 in the mass spectrum of bibenzyl also supports Brown's conclusions (26).

From the work of Brown with substituted toluenes (21) and the work of Harrison and Meyer with labeled methylethylbenzenes (19) it is reasonable to conclude that tropylium ion formation is preceded by the rearrangement to a cycloheptatriene ion. However, the process by which randomization of hydrogen and deuterium occurs and the mechanism by which randomization of carbon atoms occurs prior to fragmentation of the tropylium ion has not been determined. It is possible that insertion of the α-carbon occurs between any two ring carbon atoms as suggested by Harrison and Meyer (19). If the insertion is between carbons 1 and 2 of the ring, and if such a process would proceed via a norcaradiene intermediate (7), a series of 1,3 sigmatropic shifts could very readily account

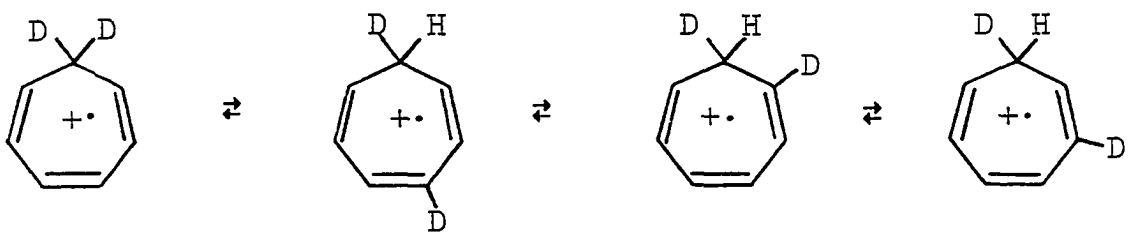


7

for the randomization of carbon atoms observed by Rinehart and co-workers (18). Such a rearrangement of 3,7,7-trimethylcycloheptatriene has been investigated and documented by Berson and Willcott (27). Reversibility of the insertion of the α-carbon between ring carbons 1 and 2 could also explain this observed randomization of carbon atoms.



The randomization of hydrogen atoms could also be explained by the reversible toluene-cycloheptatriene rearrangement. The possibility also exists that a series of 1,5-sigmatropic hydrogen shifts (28) in the cycloheptatriene ion (1,3 and 1,7 if the first excited state is involved; see discussion of Harrison and Meyer (19) for the suggestion that 1,7 shifts are involved) is responsible for the randomization



of hydrogen and deuterium in α-labeled ethylbenzenes and in labeled toluenes.

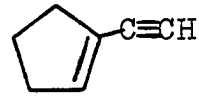
That randomization may be occurring in unrearranged molecular ions can be supported by the observation that randomization of hydrogen and deuterium occurs prior to the fragmentation of benzene (29, 30) and halo-benzenes (31). The suggestion that benzvalenes and/or prismanes (31) are

responsible for this randomization of hydrogen and deuterium atoms in halo-benzenes could also account for the randomization of carbon atoms in the mass spectrum of toluene (18).

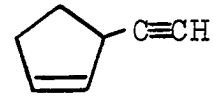
That major skeletal rearrangements can occur upon electron bombardment has been demonstrated by the investigation of other C_7H_8 hydrocarbons. The mass spectra of bicyclo[2.2.1]-heptadiene (8)(17, 32), spiro[2.4]heptadiene (9) (17, 33), 1-ethynylcyclopentane(10) (17), 3-ethynylcyclopentene(11) (34), methylfulvene (12) (35, 36), quadricyclane (13) (36), bicyclo-[3.2.0]heptadiene (14) (37), 1,5-heptadiyne (15) (38), propenylvinylacetylene (16) (39), allylvinylacetylene (17) (39), and isopropenylvinylacetylene (18) (39) all exhibit their most intense ion at m/e 91 ($C_7H_7^+$). Fragmentation of this ion suggests that it has the tropylium ion structure and labeling

8

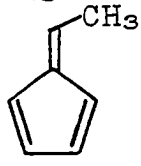
9



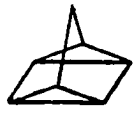
10



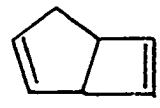
11



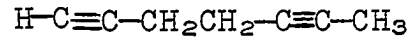
12



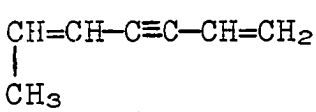
13



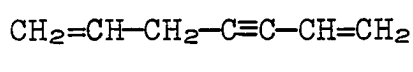
14



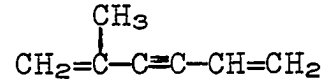
15



16



17



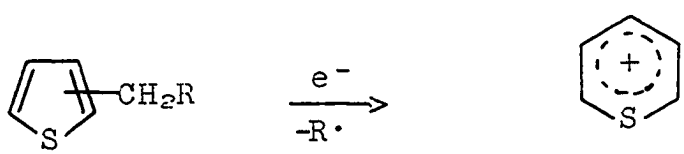
18

studies in 10 and 11 also support tropylium ion formation. The observation of an intense $C_7H_7Fe^+$ ion in the mass spectrum of divinylferrocene has been attributed to the formation of a complexed tropylium ion (40).

Ring Expansions in Other Cyclic Systems

Analogous rearrangements involving ring expansion have also been suggested to account for selected fragmentations in other hydrocarbon and heterocyclic ring systems. Methyl substituted cyclopentadienes show striking similarity in their mass spectra and this has been attributed to the formation of substituted benzenium ions (41).

The most intense ion in the mass spectra of 2- or 3-alkylthiophenes is the result of β-cleavage and it has been suggested that the resulting ion has the thiapyrylium structure (42, 43).



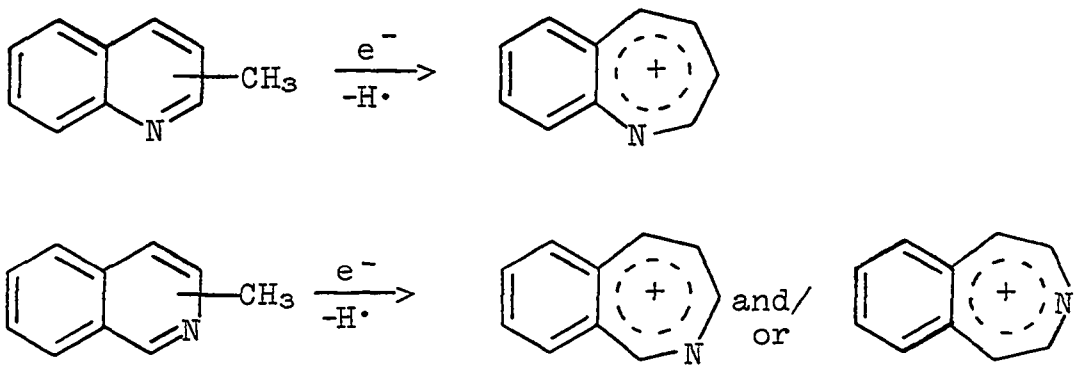
Analogously, benzothiophenes also undergo the same type of fragmentation with the formation of benzothiopyrylium ions (44).

The mass spectra of alkylsubstituted furans (45) and benzofurans (46) also exhibit intense ions which correspond to cleavage β to the heterocyclic ring and the stability of the ring expanded pyrylium ion has been postulated to account for this fragmentation.

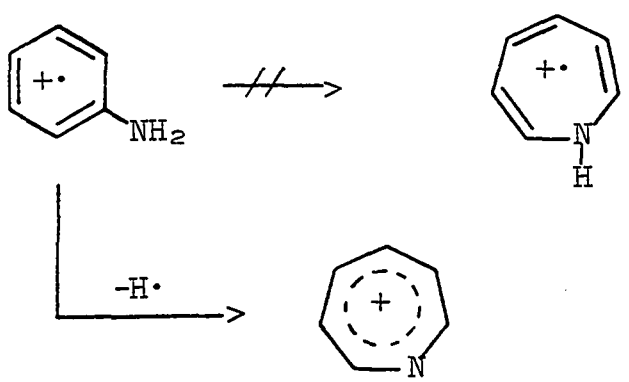
Although it has been postulated that ring expansion occurs in the mass spectra of C-alkylindoles (47, p. 397) and a study of ^{13}C labeled indoles lends support to this postulate (48), other investigators (49, 50) have discounted the formation of pyridinium ions in the mass spectra of C-alkylpyrroles. A more recent investigation of ^{13}C labeled N-alkylpyrolles and indoles indicates that ring expansion occurs upon electron bombardment with the formation of pyridinium and quinolinium ions (48).

A similar situation exists in the mass spectra of alkylpyridines, alkylquinolines, and alkylisoquinolines. Investigations of the decomposition of the m/e 92 ion ($C_5H_5NCH_3$) in the mass spectrum of 2- and 3-picolines has shown that ring expansion to the azatropylium ion is not occurring (51, 52). However, the investigation of the mass spectra of alkylquinolines and isoquinolines (53), including a study of the mass spectra of ^{13}C labeled compounds (48), has shown that the benzoazatropylium ion is involved in the fragmentation of the

quinolines investigated.

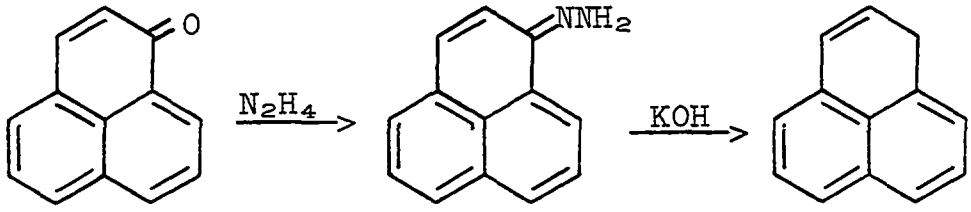


Recent investigations of the mass spectra of aniline-1-^{13}C (54, 55) have shown that the molecular ion does not rearrange to the azepinium ion but that at least partial ring expansion occurs in the $(M-1)^+$ ion with the formation of the azatropylium ion.



Chemical Evidence for the Phenalenium Cation

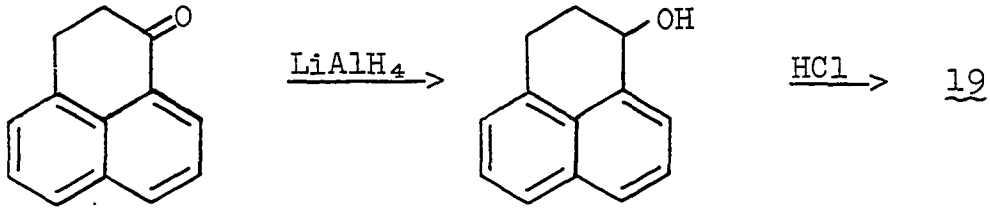
The isolation of phenalene (19) was first reported by Lock and Gergely in 1944 (56) when they obtained the hydrocarbon by reduction of phenalenonehydrazone with solid potassium hydroxide. These workers noted that the hydrocarbon was stable only



19

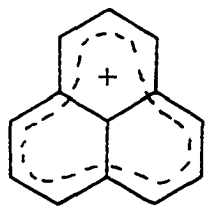
under vacuum and that it turned yellow upon contact with air.

Boekelheide and Larrabee later synthesized phenalene by hydride reduction of 1,2-dihydro-phenalenone (20) followed by dehydration of the alcohol with alcoholic hydrogen chloride (57). They also commented upon the instability of the hydrocarbon and were the first to suggest that phenalene may lose a

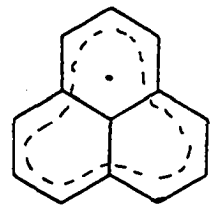


20 19

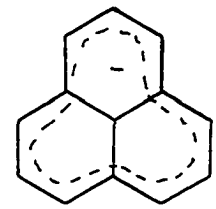
hydride ion, hydrogen atom, or a proton to form a stable phenalenium cation (21), radical (22), or anion (23). This idea was based upon the symmetry and the high degree of resonance stabilization available to the species formed.



21



22



23

Simple LCAO molecular orbital calculations support this idea and predict that the cation, radical, and anion should all have the small π-electron delocalization energy of 5.83β (β = 20 kcal) (58, 59) and that all should exhibit a gain of π electronic energy of 1.7β (34 kcal) (59).

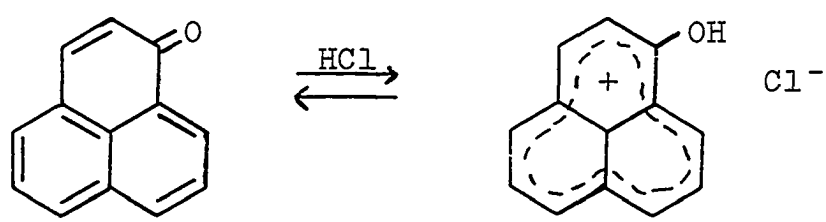
The phenalenium system is an odd-alternate hydrocarbon with 12, 13, or 14π electrons for the cation, radical, or anion, respectively, and that all three species possess the same π delocalization energy is apparent by HMO calculations since the extra one or two electrons of the radical or of the anion go into a molecular orbital of zero energy (with reference to the energy of an electron in the p_z orbital of an isolated sp^2 hybridized carbon atom) (59).

An excellent summary of the work related to the phenalenyl anion and radical is contained in a comprehensive review of phenalene chemistry by D. H. Reid (60), one of the foremost investigators in this area.

The possibility of a high degree of stability and symmetry in the phenalenium cation can be cited for many otherwise unusual chemical phenomena reported in the literature.

Boekelheide and Larrabee (61) have investigated a group of interesting reactions involving the acid catalysed dehydration of isomeric methylphenalenols which show that tautomerization of the phenalene nucleus occurs quite readily. This tautomerization has also been shown to occur by a study of isotopically labeled 1,2-dihydrophenalenol (62).

The high basicity of phenalenone (24) was first observed by Bamberger and Philips in 1877 (63). This basicity was also observed by Cook and Hewett in 1934 when they reported that phenalenone dissolved reversibly in concentrated hydrochloric acid to form the hydroxyphenalenium cation (64). This reaction is entirely analogous to the reaction of tropone with



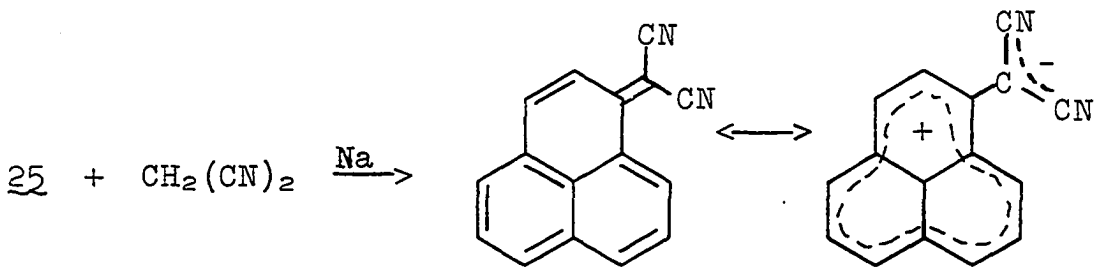
24

acid to form hydroxytropylium salts (65).

More recently the ketone has been shown to react with ethereal fluoroboric acid to form the 1-ethoxyphenalenium fluoroborate salt (25) (66). This salt

25

reacted with dicyanomethane to yield 25a, a compound which was reversibly soluble in acid and which existed in a dipolar form

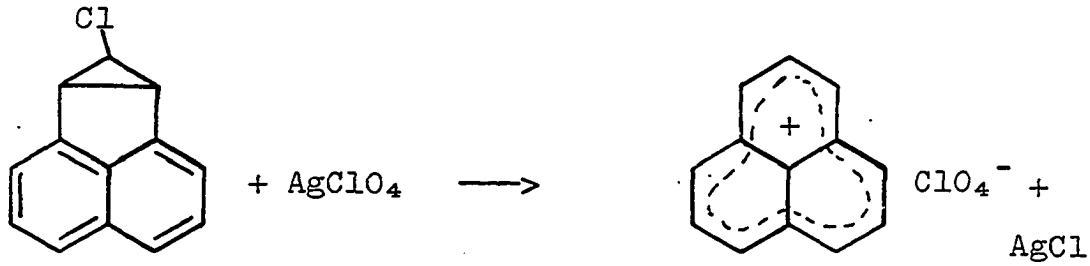


25a

as shown by nmr studies (66).

The low carbonyl stretching frequency of phenalenone (24) (1637 cm^{-1}) and high dipole moment (3.00 D) also suggest polarization of this ketone (67).

The first isolation of a phenalenium salt was accomplished by Pettit (59, 68). Phenalenium perchlorate was obtained by treatment of the covalent 7-chloro-6b,7a-dihydro-7H-cyclopropa[a]acenaphthylene (26) with silver perchlorate in dry nitromethane at 70°. After the addition of ether, the salt precipitated as a fine yellow solid in 84% yield.



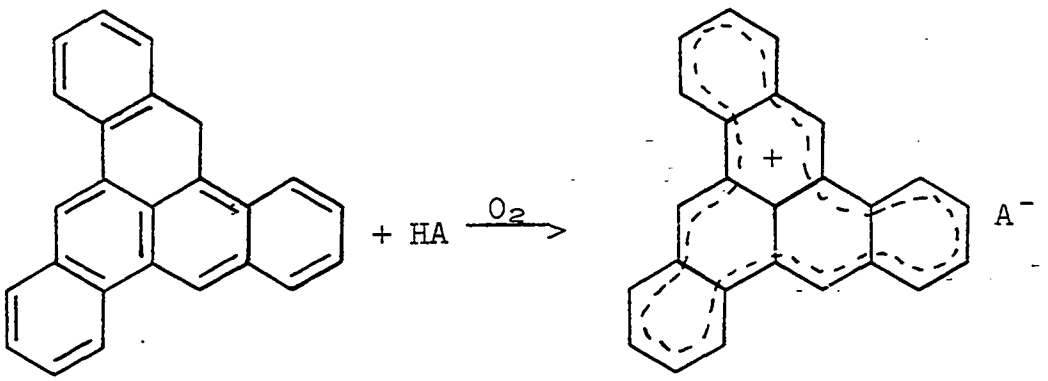
26

This yellow crystalline solid was insoluble in benzene, chloroform, ether, and other non-polar solvents. It was soluble in nitromethane, 35% hydrochloric acid, and 60% perchloric acid. The salt contained the perchlorate anion and was stable at room temperature under an atmosphere of nitrogen, but decomposed in moist air. When the salt was added to a solution of ethanol and water decomposition occurred and phenalene and phenalenone were isolated from the decomposition products.

Pettit also reports that the chloro compound, 26, when treated with aluminum chloride in nitrobenzene, or when treated with boron trifluoride in ether, gave the dark green color characteristic of the phenalenium cation but attempts to isolate these salts failed (59).

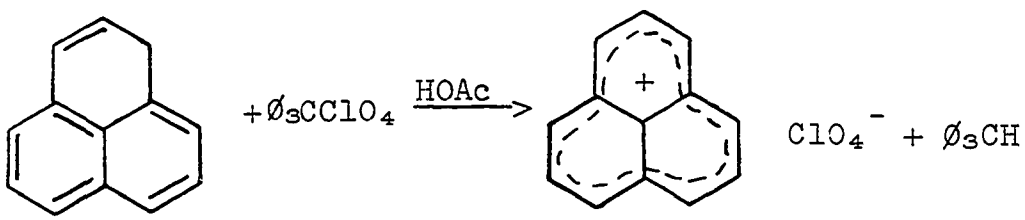
The isolation of salts of the 2:3-5:6-8:9-tribenzophenalenium cation was reported by Clar and Stewart (69). Treatment of 2:3-5:6-8:9-tribenzophenalene, 27, with molecular oxygen and acetic acid, perchloric acid, or hydrochloric acid

afforded the corresponding acetate, perchlorate, or chloride, respectively, which were stable salts with the exception of the acetate.



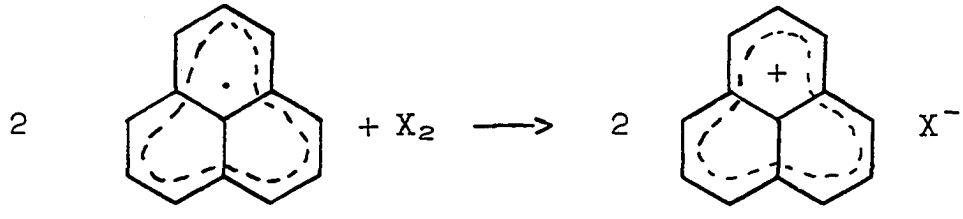
27

Bonthrone and Reid prepared phenalenium perchlorate by hydride transfer from phenalene by treatment of the hydrocarbon with triphenylmethyl perchlorate (70). The perchlorate

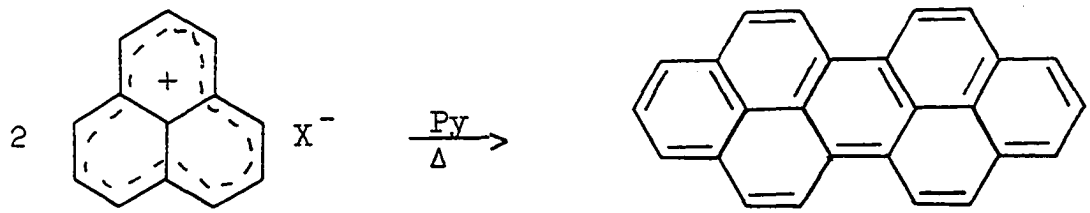


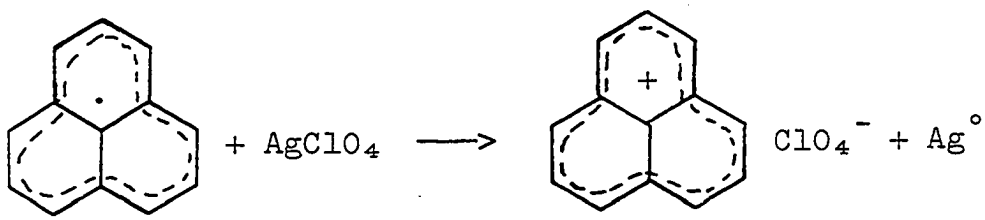
salt was again observed to be unstable in air and upon hydrolysis decomposed to give equal molar amounts of phenalene and phenalenone. Similarly, 3,6,9-trimethylphenalenium perchlorate was prepared. This salt was found to be stable in air and decomposed above 250°.

Phenalenium iodide, bromide and chloride were prepared by the reaction of the phenylenyl radical and molecular halogen by a one electron transfer process (71). The order of



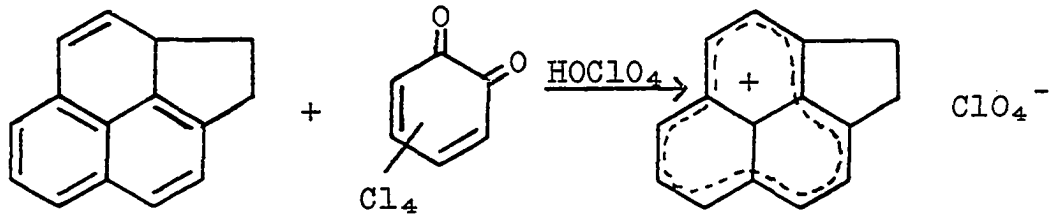
stability of these halide salts was found to be $I^- > Br^- > Cl^-$. The iodide was isolated and found to decompose upon heating. The bromide salt decomposed upon isolation and the chloride salt was not isolable. The iodide salt was insoluble in organic solvents but did dissolve in organic bases such as pyridine. When these solutions were heated the cation was reduced to the radical and peropyrene was formed. Reid also prepared phenalenium perchlorate by the oxidation of the radical with silver perchlorate (71).





The synthesis of various substituted phenalenium perchlorates was carried out by Bonthrone and Reid (70). This study of these salts has shown that the phenalenium perchlorates possess the following stability to heat, solvolysis, and air: 3-methoxy- ~3,6,9-trimethyl- ~3,6-dimethoxy- >>1,3-dimethyl- >2,3-dimethyl- >phenalenium > benzo[a]- >1,2-dihydrocyclopenta[cd]-phenalenium (28) >3-methylphenalenium perchlorate. These perchlorate salts were prepared by hydride abstraction with quinones in the presence of perchloric acid

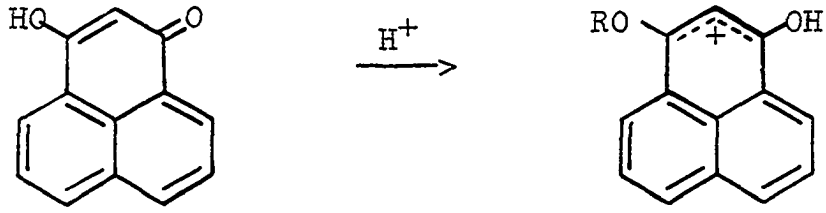
from the corresponding hydrocarbons. Various quinones were



28

used for hydride abstraction and tetrachloro-1,2-benzoquinone was found to be the most useful for these reactions (67).

A recent study of substituted phenalenium ions (72) has shown that as predicted by HMO calculations, 1,3-disubstituted phenalenium ions no longer possess the symmetrical ion structure but exist as a trimethine system condensed to a naphthalene ring. This is especially true for -OR or $-NR_2$ substituents.



The quantitative reduction of phenalenium perchlorate to phenalene has been done by Honnen (73) to show that the salt

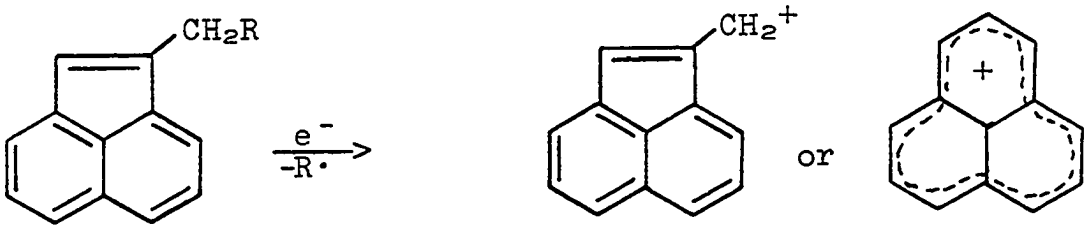
does have the phenalene structure. Honnen also states that the solid phenalenium salts which have been prepared are indefinitely stable only in the absence of other agents such as light, air, and water, and that the only stable solution of the cations are those of perchloric and sulfuric acids.

Physical evidence for the symmetrical phenalenium ion structure is available from the nmr spectra of phenalenium salts (74, p. 63, 75) and of 1,4,7-trimethylphenalenium perchlorate (76). The 100 MHz spectrum of phenalenium hexachloroantimonate (75) exhibits the expected A_2X pattern with ν_A at δ9.30 and ν_X at 8.58. The trimethylphenalenium perchlorate spectrum (60 MHz) exhibits an AB pattern (ν_A at δ9.30, 1H; ν_B at 8.18, 1H; J_{AB} = 8.3 Hz) and a methyl singlet at δ3.36 (9H).

RESULTS AND DISCUSSION

Mass Spectra

The possibility that ring expansion to a more stable ion may be a general phenomena in the mass spectra of various types of organic compounds led us to investigate a series of compounds which a priori might be expected to form the symmetrical phenalenium ion (21) upon electron bombardment. Specifically we undertook the investigation of 1-alkylacenaphthylenes (29) to determine whether they would exhibit fragmentation due to cleavage of the bond β to the 5 membered ring and if this process did occur to determine whether the ion formed had the benzyl type structure (30) or was the ring expanded phenalenium ion.



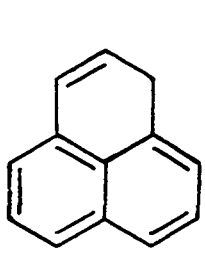
m/e 165 + R — 29

m/e 165 — 30

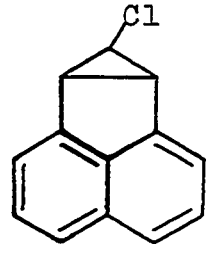
m/e 165 — 21

Of the possible compounds which might be expected to form the phenalenium ion upon electron impact we have investigated the mass spectra of phenalene (19), 7-chloro-6b, 7a-dihydro-7H-cycloprop[a]acenaphthylene (26), 6b, 7a-dihydro-7H-cycloprop[a]acenaphthylene (31), 1-methylacenaphthylene (32),

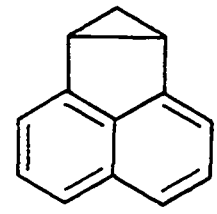
1-ethylacenaphthylene (33) and various isotopically labeled derivatives of 32 and 33. The 70 ev mass spectra of 19, 26,



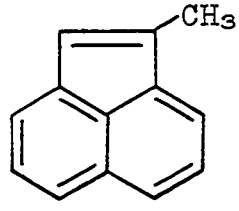
19



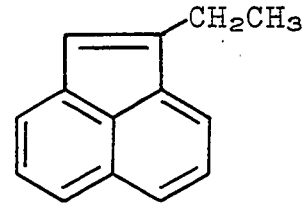
26



31



32



33

31, 32 and 33 are presented in Table 1 and in Figures 1 and 2.

The most striking feature of the mass spectrum of phenalene (19) (Table 1, Figure 1a) is the low abundance of fragment ions other than the ion at m/e 165 ($C_{13}H_9^+$). This ion must arise by the loss of a hydrogen atom from the molecular ion at m/e 166 ($C_{13}H_{10}^+$), and this process is accompanied by a metastable at m/e 164.0. This ion at m/e 165 ($C_{13}H_9^+$) corresponds in mass to the phenalenium ion and the small amount of fragmentation following its formation together with the observance of the ions at m/e 82.5 and 83, corresponding to the doubly charged

phenalenium ion and molecular ion respectively, point out the high degree of stability possessed by this hydrocarbon system.

Table 1. 70 ev mass spectra of 19, 26, 31, 32 and 33

m/e	Relative Intensity[a]			
	19	26	31	32
202		1.9		
201		1.8		
200		7.8		
199		2.8		
166	29.0	13.3	42.1	48.0
165	100.0	100.0	100.0	100.0
164	15.7	13.2	12.3	13.9
163	18.7	17.6	14.0	14.3
139	2.0	2.0	2.1	3.3
137	1.0	1.4	0.6	0.8
115	1.0	1.1	0.9	1.7
113	0.9	1.2	0.7	1.0
98	0.7	1.7	0.4	0.9
89	0.9	1.2	0.6	1.1
87	1.5	3.2	1.0	1.6
86	1.3	2.4	0.6	1.2
83 (166^{++})	4.9		8.2	6.8
82.5 (165^{++})	13.3	5.0	14.0	14.6
82.0 (164^{++})	9.8	6.6	12.1	14.3
81.5 (163^{++})	7.5	5.6	7.5	8.1
81	3.3	2.4	3.9	4.1
75	0.9	2.3	0.7	1.6
74	1.3	3.1	0.8	1.7
69.5 (139^{++})	4.7	1.6	4.8	5.2
63	3.1	4.3	1.6	2.9
62	1.4	3.1	0.7	1.3

[a]Uncorrected for naturally occurring ^{13}C.

Table 1 continued

m/e	Relative Intensity[a] 33	m/e	Relative Intensity[a] 33
181	4.3	126	1.0
180	33.7	115	1.2
179	25.6	113	0.7
178	9.2	98	1.0
177	3.3	90 (180^{++})	0.7
176	4.7	89.5 (179^{++})	1.8
166	13.7	89 (178^{++})	11.3
165	100.0	88.5 (177^{++})	0.8
164	8.4	81	1.0
163	9.3	76.5 (153^{++})	1.4
153	3.3	76 (152^{++})	9.3
152	8.4	75.5 (151^{++})	1.1
151	4.8	75 (150^{++})	3.9
150	3.3	74	1.9
139	2.4	69.5 (139^{++})	2.9
137	0.6	63	4.7
		62	1.4

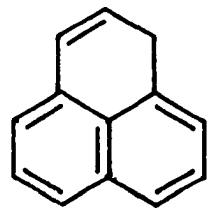
Support for the phenalenium ion formulation for m/e 165 is derived from the limited fragmentation which is observed. A metastable at m/e 117.1 shows that the ion at m/e 165 undergoes the loss of C_2H_2 to give the ion at m/e 139 ($C_{11}H_7^+$). A metastable at m/e 58.5 showing that the doubly charged ion at m/e 82.5 ($C_{13}H_9^{++}$) undergoes the loss of C_2H_2 to form the doubly charged ion at m/e 69.5 ($C_{11}H_7^{++}$) adds further support to the postulate that the ion at m/e 165 is the phenalenium

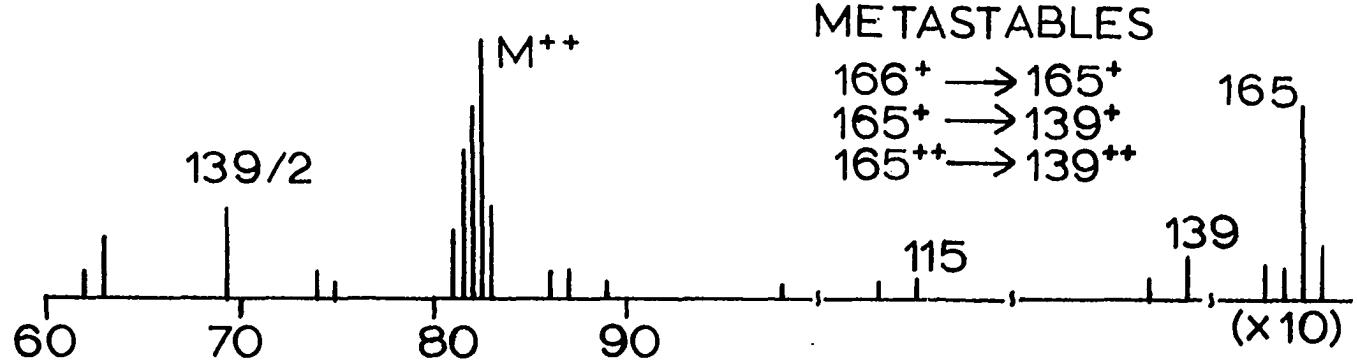
Figure 1. Mass spectra.

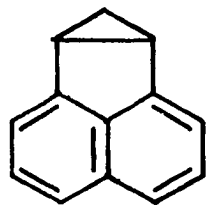
1a. Phenalene.

1b. 6b, 7a-Dihydro-7H-cycloprop[a]acenaphthylene.

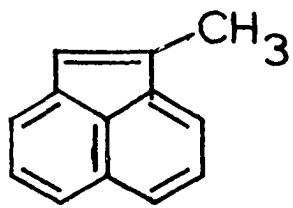
1c. 1-Methylacenaphthylene.




METASTABLES
166+ → 165+
165+ → 139+
165++ → 139++
M++
139/2
115
139
165
60
70
80
90
(x10)




(x10)


CH3

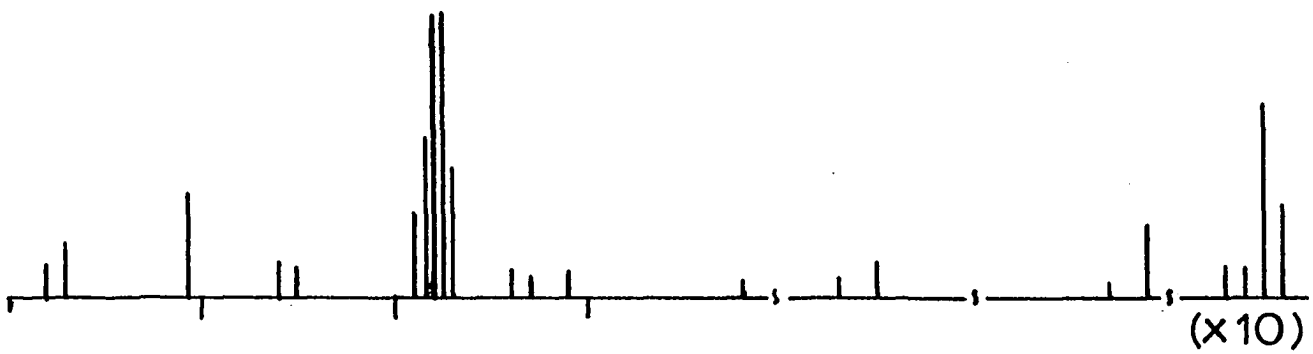
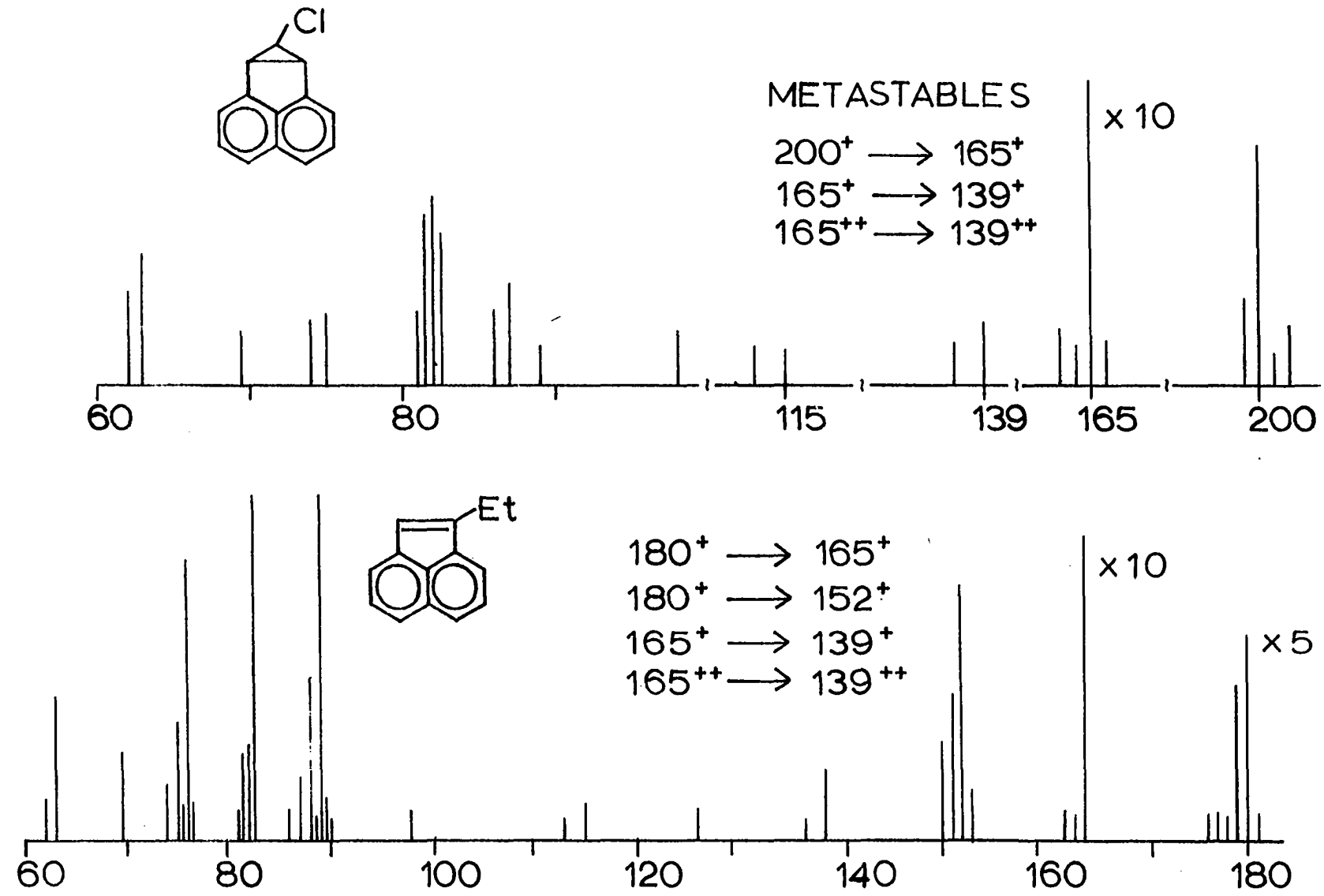

(x10)

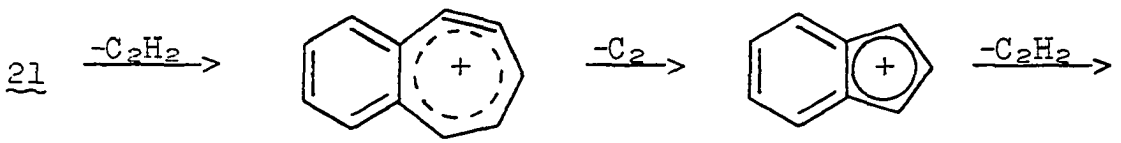
Figure 2. Mass spectra.

2a. 7-Chloro-6b, 7a-dihydro-7H-cycloprop[a]acenaphthylene.

2b. 1-Ethylacenaphthylene.


Cl
METASTABLES
200+ → 165+
165+ → 139+
165++ → 139++
x 10
60
80
115
139
165
200
Et
180+ → 165+
180+ → 152+
165+ → 139+
165++ → 139++
x 10
x 5
60
80
100
120
140
160
180

ion. This loss of the elements of acetylene is directly analogous to the metastable loss of C_2H_2 from the tropylium ion (4, p. 489). The structure of this ion at m/e 139 is not known although several structures can be suggested for $C_{11}H_7^+$. The presence of an ion at m/e 115, along with ions at m/e 89 and 63, is strongly suggestive (77) of the formation of the indenyl cation. If the indenyl cation is formed a possible sequence for the fragmentation of m/e 165 can be written.



m/e 89 $\xrightarrow{-C_2H_2}$ m/e 63

This loss of the C_2 fragment (139 → 115), however, is not accompanied by a readily discernible metastable.

Since there can be little doubt that the phenalenium ion is formed in the electron bombardment of phenalene, 26 was subjected to electron impact. The mass spectrum is summarized in Table 1 (Figure 2a). Again the base peak in the spectrum is the ion at m/e 165 which results from the metastable (m/e 136.2) loss of chlorine from the molecular ion. Although other structures can be postulated, and may even be involved as very short lived intermediates, the most likely structure for this

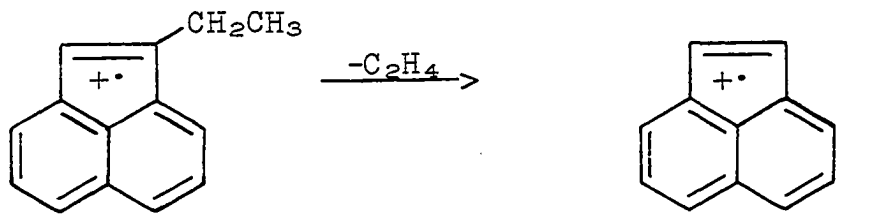
ion is the phenalenium ion. The limited fragmentation that is observed in the spectrum of this compound agrees closely both in mass and intensity with the fragment ions from phenalene. The somewhat lower relative intensity of the doubly charged ions at m/e 82.5 and 69.5 can be explained by the fact that the loss of the chlorine atom from the molecular ion occurs with release of excess kinetic energy to the chlorine atom.

A very similar mass spectrum is again observed for 31 (Table 1, Figure 1b). It should be pointed out that the ion at m/e 165 ($C_{13}H_9^+$) is the base peak in the spectrum and that a metastable (117.1) is present for the loss of C_2H_2 from this ion as is the metastable (58.5) for $165^{++} \rightarrow 139^{++}$. Furthermore, as was the case in the mass spectra of 19 and 26, fragment ions are observed at m/e 115, 89 and 63.

To test the possibility of a ring expansion process producing the phenalenium ion upon electron bombardment, 1-methylacenaphthylene (32) was synthesized and subjected to electron bombardment. The mass spectrum (Table 1, Figure 1c) of 32 is in close agreement with those of 19, 26 and 31. Comparison of the relative abundances of fragment ions from the four compounds shows only minor variations. Again metastable ions are observed for the loss of C_2H_2, not only from the ion at m/e 165, but also from the doubly charged ion at m/e 82.5.

1-Ethylacenaphthylene (33) (Table 1, Figure 2b) undergoes the metastable (151.1) loss of 15 mass units ($CH_3\cdot$) from its molecular ion at m/e 180 ($C_{14}H_{12}$) to give the base peak at m/e

165 ($C_{13}H_9^+$). A metastable at 117.0 shows that this m/e 165 ion loses C_2H_2, as in the previous compounds investigated, to form the ion at m/e 139. Other ions in the spectrum agree closely in mass and intensity with those associated with the decomposition of phenalenium ion. It should be noted that many of the ions in this spectrum are not present in the previous spectra but this is due to a separate fragmentation pathway initiated by the metastable (m/e 128.6) loss of ethylene from the molecular ion. Additional differences are



m/e 180 — 34, m/e 152

due to the doubly charged acenaphthylene (34) and molecular ions.

The great similarity below m/e 166 of the mass spectra of these compounds (Figures 1 and 2) is indicative of the same structure for the ions at m/e 165. Another criterion for ions which have the same structure and the same energy content is that they exhibit the same metastable decompositions and that the relative abundances of these metastables be the same (78). Inspection of Table 2 shows that the abundances of the metastables for the loss of C_2H_2 from the ion at m/e 165 (the only

metastable fragmentation observed) in the mass spectra of 19, 26, 31, 32 and 33 are nearly the same. The relative abundances of the metastables at m/e 58.5 ($165^{++} \rightarrow 139^{++}$) are also the same for these compounds (Table 2) showing that the same doubly charged species is being formed. Since it is unlikely that the

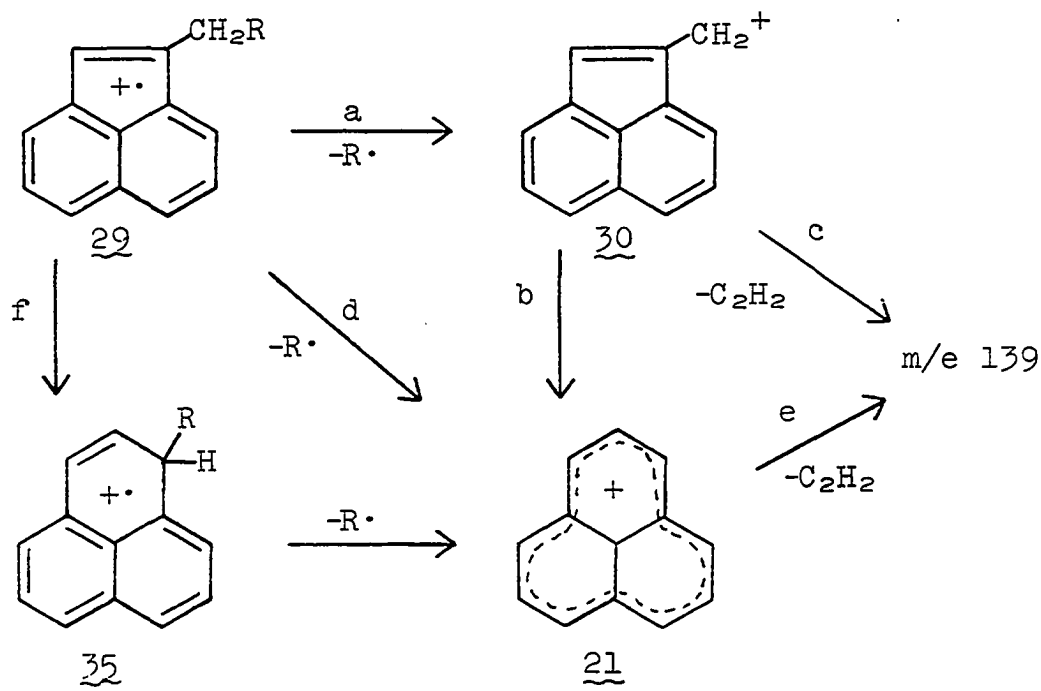
Table 2. Metastable abundances

Compound	$\frac{\text{m/e 117.1}}{\text{m/e 165}} \times 10^5$	$\frac{\text{m/e 58.5}}{\text{m/e 82.5}} \times 10^3$
19	7.0 ± 2.0	2.8 ± 0.2
26	8.9 ± 4.0	3.5 ± 0.9
31	8.8 ± 2.0	3.8 ± 0.1
32	8.5 ± 2.0	3.5 ± 0.5
33	9.7 ± 5.0	3.5 ± 0.6

ion at m/e 165 in the mass spectrum of phenalene has any structure other than the ring expanded phenalenium ion it is reasonable to conclude that the ions at m/e 165 in the mass spectra of 26, 31, 32 and 33 also have this symmetrical phenalenium structure.

The mass spectra of a series of isotopically labeled compounds was investigated in order to further substantiate the occurrence of this ring expansion in the alkylacenaphthylenes, 32 and 33, and if possible to gain some insight into the mechanism of this rearrangement. There are three likely pathways (Scheme 1) by which this rearrangement could occur.

Path a involves the loss of the R radical (R = H, Me) from the molecular ion of 29 to give the benzyl type ion, 30. This ion could then either rearrange to the symmetrical phenalenium ion (21) (path b) or could undergo the loss of acetylene to give the observed ion at m/e 139 (path c). Path d involves ring expansion of the molecular ion concurrent with the loss of the



Scheme 1. Possible pathways to the phenalenium ion.

R radical to give the phenalenium ion. This ion would then suffer the observed loss of acetylene to give the m/e 139 ion (path e). An alternate route (path f) involves initial ring expansion to a substituted phenalene molecular ion (35) which could then lose the R radical to give the phenalenium ion.

The mass spectrum of 1-ethylacenaphthylene-2-^{13}C (36, ^{13}C denoted by * (Table 3) containing 54% of the isotopic label) exhibits the loss of 15 mass units ($CH_3\cdot$) from the molecular ions to give ions at m/e 165 and 166 ($C_{13}H_9^+$) which retain all of the original carbon label. Measurement of label retention in the ions at m/e 139 and 140 ($C_{11}H_7^+$) formed by the loss of either labeled or unlabeled acetylene from the $C_{13}H_9^+$ ions shows that the $C_{11}H_7^+$ ions retain 45.4% of the carbon label. If the $C_{13}H_9^+$ ions have the benzyl type structure there are five possible C_2 units which could be lost as acetylene, none of which involves the labeled carbon atom. However, if the symmetrical phenalenium is formed, one of six possible acetylene losses would involve the labeled carbon and we would

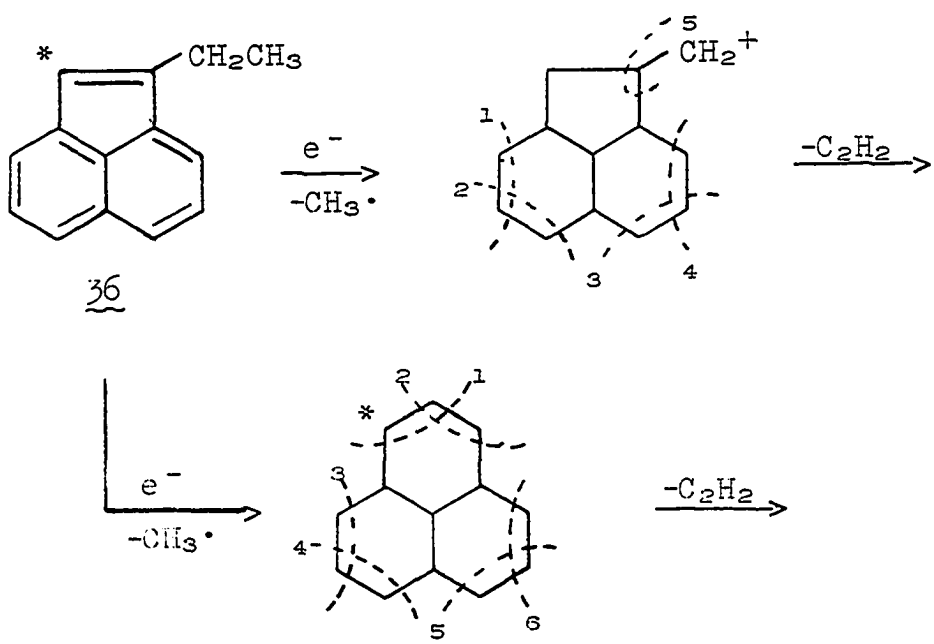


Table 3. Partial mass spectrum of 36

m/e	Intensity (30 ev)[a]	Intensity (18 ev)[a]
181	32.4	100.0
180	39.7	78.2
179	18.1	3.5
178	2.9	
166	100.0	27.0
165	83.5	20.9
164	7.8	
153	14.7	
152	13.7	
140	1.0	
139	1.1	

Label Incorporation and Retention in Major Ions[b]

$C_{14}H_{12}^+$ (14ev)	$C_{13}H_9^+$ (18ev)	$C_{11}H_7^+$ (30 ev)	
54.3	54.5	45.4	$\%^{13}C$
45.7	45.5	54.6	$\%^{12}C$

Predicted Label Retention for Symmetrical Phenalenium Ion[c]

$C_{11}H_7^+$	
45.4	$\%^{13}C$
54.6	$\%^{12}C$

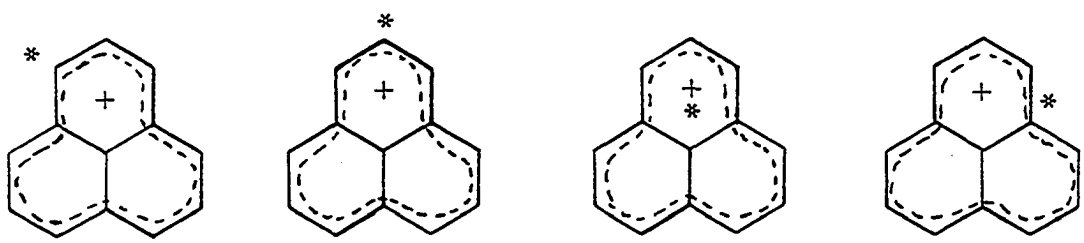
[a] Uncorrected for naturally occurring ^{13}C.

[b] See experimental section for method of calculation.

[c] See page 52.

expect 45.4% (p. 52) of the $C_{11}H_7^+$ ions to retain the carbon label. The excellent agreement of calculated and observed label retentions provide sound support for phenalenium ion formation.

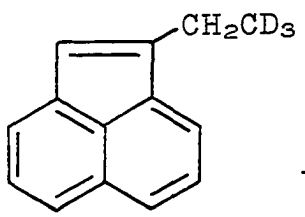
These results also suggest that the carbon atoms retain their positional integrity in the ring expanded phenalenium ion. If complete randomization of carbon atoms occurred during phenalenium ion formation, a loss of 8.3% of the carbon label would be expected (giving a retention of 46.1%). Such randomization would give structures 37, 38, 39 and 40 in relative amounts of 6:3:1:3. Although there has been a



37 38 39 40

report of complete randomization of a ^{14}C label in the naphthalene nucleus (79, 80) a recent reinvestigation has shown that such randomization does not occur (81). A mechanism for the ring expansion which results in partial randomization of carbon atoms, e.g., formation of only 37 and 38, would lead to a much higher predicted loss of carbon label than is observed in $C_{11}H_7^+$ ion formation.

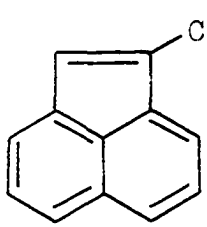
The mass spectrum of 1-ethylacenaphthylene-β-d_3 (41) (Table 4) shows that the loss of the methyl radical (m* at 148.6) occurs from the molecular ion at m/e 183 with very little prior scrambling of hydrogen and deuterium atoms. The fact that the $C_{13}H_9^+$ ion retains none of the deuterium found in the molecular ion shows that the loss of a methyl radical from 1-ethylacenaphthylene involves cleavage of the bond β to the 5 membered ring.



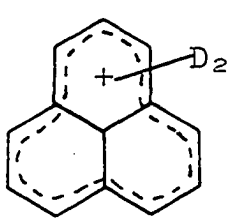
$\xrightarrow[-CD_3\cdot]{e^-}$ m/e 165 ⟶ m/e 139

41

The mass spectrum of 1-ethylacenaphthylene-α-d_2 (42) (Table 5) was then investigated. Again it is quite clear that loss of the β-methyl radical (m* at 153.3) involves only slight (less than 3%) hydrogen-deuterium scrambling since the label retention in the $C_{13}H_9^+$ ion (96.5% d_2) is nearly the same as the label incorporation in the molecular ion (98.8% d_2). The



$\xrightarrow[-CH_3\cdot]{e^-}$



⟶ m/e 141, 140, 139

42 m/e 167

Table 4. Partial mass spectrum of 41

m/e	Intensity (70 ev)[a]
184	8.3
183	52.8
182	28.6
181	8.3
180	5.3
166	16.2
165	100.0
164	8.1
163	8.6
139	2.0

[a]Uncorrected for 2.2% d_2 species and for naturally occurring ^{13}C.

label retention in the $C_{11}H_7^+$ ions is also quite informative. Although the data may be quantitatively inexact due to a trace impurity at m/e 142, it is evident that randomization of hydrogen and deuterium atoms is occurring prior to the loss of acetylene from the phenalenium ion at m/e 167. Complete loss of positional identity of all hydrogen and deuterium atoms in the $C_{13}H_9^+$ ion would predict that m/e 139, 140, and 141 would be found in the ratio of 3.3:40.4:56.2 (p. 52), the observed intensities of 7.5:31.0:61.4 agree quite well with the predicted values. This scrambling of hydrogen and deuterium atoms supports the ring expanded symmetrical phenalenium structure for the ion formed by the loss of a β-methyl radical

Table 5. Partial mass spectrum of 42

m/e	Intensity (30 ev)[a]	Intensity (18 ev)[a]
182	16.4	100.0
181	6.1	3.3
180	3.4	
168	13.7	3.3
167	100.0	24.3
166	8.7	.7
142	0.6	
141	1.7	
140	0.6	
139	0.2	

Label Incorporation and Retention[b] in Major Ions

$C_{14}H_{12}^+$ (14 ev)	$C_{13}H_9^+$ (18 ev)	$C_{11}H_7^+$ (30 ev)[c]	
	0.6	7.5	$\%d_0$
1.2	2.9	31.0	$\%d_1$
98.8	96.5	61.4	$\%d_2$

Predicted Label Retention for Symmetrical Phenalenium Ion[d]

$C_{11}H_7^+$	
3.3	$\%d_0$
40.4	$\%d_1$
56.2	$\%d_2$

[a]Uncorrected for natural ^{13}C and 1.2% d_1 species.

[b]See footnote b, Table 3.

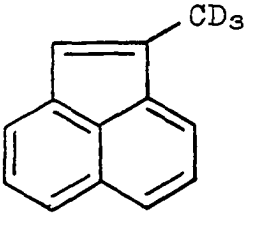
[c]Calculated on assumption that trace impurity at m/e 142 does not contribute to m/e 141.

[d]See footnote c, Table 3.

from 1-ethylacenaphthylene since the benzyl-type structure (Scheme 1) would not be expected to show this hydrogen-deuterium randomization.

The label retentions observed in the fragment ions formed from 41 and 42 are entirely analogous to the results observed in the mass spectral formation of tropylium ions from ethylbenzene-α-d_2 and -β-d_3 (4, p. 488).

The mass spectrum of 1-methylacenaphthylene-α-d_3 (43) (Table 6) shows that the molecular ion at m/e 169 undergoes the statistical loss of either a hydrogen or a deuterium atom to form $C_{13}H_9^+$ ions at m/e 168 and 169 in the ratio of 69:30. This observed intensity ratio agrees quite well with the predicted ratio of 66:32 (p. 52) if all hydrogen and deuterium atoms become equivalent prior to the formation of the phenalenium ion. Further support for complete randomization of hydrogen and deuterium atoms is evident upon inspection of the ions associated with the loss of C_2H_2, C_2HD, or C_2D_2 from the phenalenium ions formed. Using the corrected relative intensities of the ions at m/e 168 and 167 and



43

$$\xrightarrow[-H\cdot \text{ or } D\cdot]{e^-} \quad C_{13}H_6D_3^+ + C_{13}H_7D_2^+ \longrightarrow$$

$$C_{11}H_4D_3^+ + C_{11}H_5D_2^+ +$$

$$C_{11}H_6D^+ + C_{11}H_7^+$$

Table 6. Partial mass spectrum of 43

m/e	Intensity(70 ev)[a]	Intensity(30 ev)[a]	Intensity(25 ev)[a]
170	12.4	13.3	14.5
169	90.4	96.5	100.0
168	100.0	100.0	82.5
167	56.6	56.7	43.0
166	16.5	12.5	4.5
165	13.9	6.7	
164	5.4		
142	1.0	.5	
141	2.1	1.0	.09
140	1.5	.6	.04
139	0.7	.1	

Label Incorporation and Retention in Major Ions[b]

$C_{13}H_{10}^+$(12 ev)	$C_{13}H_9^+$ (18 ev)	$C_{11}H_7^+$ (25 ev)	
0.5		4.1	% d_0
1.0	1.5	28.2	% d_1
4.8	29.8	49.0	% d_2
93.6	68.7	18.7	% d_3

Predicted Label Retentions for Complete Randomization[c] Prior to Fragmentation[c]

$C_{13}H_9^+$	$C_{11}H_7^+$	
0.6	1.0	% d_0
1.9	18.3	% d_1
31.9	53.0	% d_2
65.5	27.6	% d_3

[a]Uncorrected for naturally occurring ^{13}C and 4.8% d_2, 1.0% d_2, and 0.5% d_0 species.

[b]See footnote b, Table 3.

[c]See footnote c, Table 3.

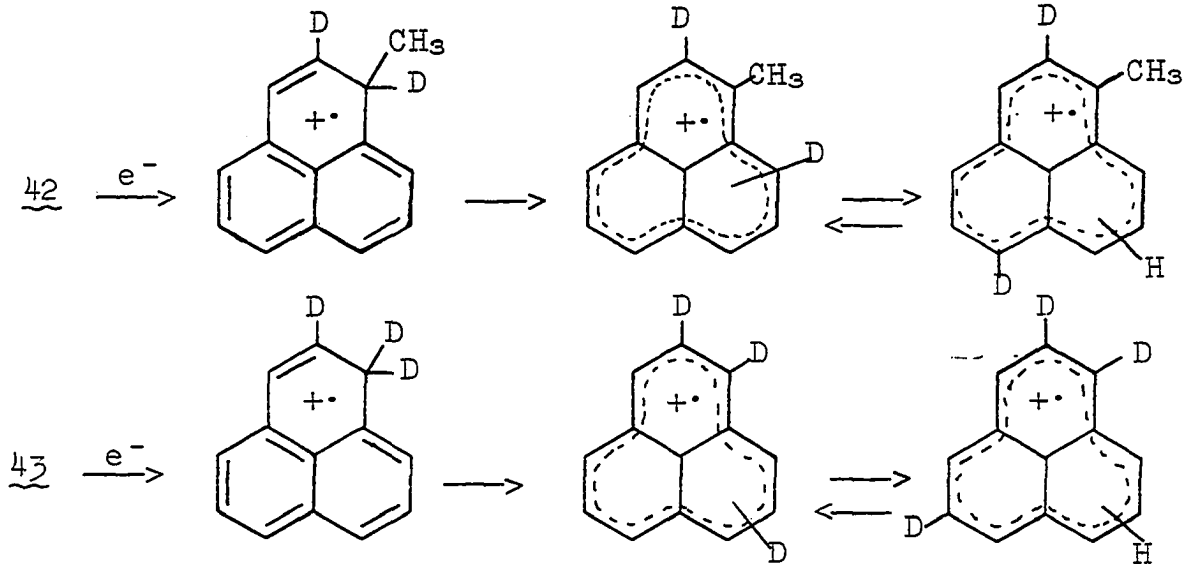
assuming that all hydrogens and deuteriums undergo loss of positional identity upon electron impact, one can calculate that the loss of a C_2H_2, C_2HD, or of a C_2D_2 fragment should produce an intensity pattern of 2:18:54:26 (p. 52) for the ions at m/e 139, 140, 141, and 142. The ion intensities obtained from the 25 ev spectrum of 43, in which hydrogen stripping from all major ions is practically eliminated, are 4:28:49:19, in good agreement with the expected intensities. This loss of positional identity of hydrogen and deuterium atoms in the molecular ion adds further support to the symmetrical phenalenium ion structure for the $C_{13}H_9^+$ ions observed at m/e 165 in the mass spectra of alkylacenaphthylenes and is again analogous to the results obtained in the investigation of tropylium ion formation from toluene-α-d_3 (4, p. 490). From the results obtained with the labeled compounds as well as the great similarity of the mass spectra of phenalene and the alkylacenaphthylenes, it is clear that the symmetrical phenalenium ion is being formed upon electron bombardment of alkylacenaphthylenes.

The exact mechanism of this ring expansion process, just as in the alkylbenzene → tropylium ion rearrangement, is very difficult to visualize. The results with the labeled ethylacenaphthylenes, 41, 42 and 43, point out that the benzyl-type structure cannot be responsible for the fragmentation of the $C_{13}H_9^+$ ion (path c, Scheme 1) although it could be suggested that it is the immediate precursor to the phenalenium ion

(path b). However, making the assumption that both methyl- and ethylacenaphthylenes rearrange to the phenalenium ion by a similar mechanism excludes all possibility of benzyl-type ion involvement. This assumption also excludes the possibility that ring expansion and the loss of either an α-hydrogen atom or the α-methyl radical occur simultaneously (path d). Both mechanisms (paths a and d) would predict that only a deuterium would be lost from the trideuteriomethylacenaphthylene, quite contrary to the observed random loss of hydrogen and deuterium leading to the formation of the $C_{13}H_9^+$ ions.

The most plausible mechanism for electron impact phenalenium ion formation from alkylacenaphthylenes involves initial ring expansion followed by the loss of the hydrogen atom or of the methyl radical (path f). This is in agreement with the results obtained in the investigation of the mass spectra of alkylbenzenes (4, p. 492, 19) which show that ring expansion is the initial step in tropylium ion formation. This mechanism would lead to the formation of a protonated phenalenyl system from 1-methylacenaphthylene or to a protonated methylphenalenyl system from 1-ethylacenaphthylene. Alternatively, the ethylacenaphthylene could ring expand with the formation of a methylated phenalenyl system. This mechanism can readily account for the observed randomization of hydrogen and deuterium in the mass spectra of 1-ethylacenapthylene-α-d_2 (42) and 1-methylacenaphthylene-α-d_3 (43) by fast

exchange of hydrogen for deuterium, as seen below. This rationalization of the hydrogen-deuterium scrambling would



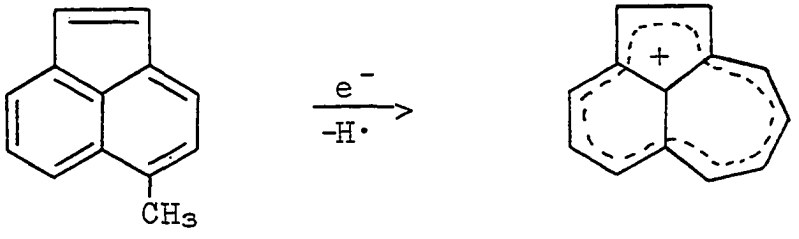
require that the rate of exchange of the hydrogen atoms is much faster than the rate of the loss of either a hydrogen (deuterium) atom from 43 or of a methyl radical from 42. The observation that the $(M-1)^+$ ion in ethylacenaphthylene (Table 1) is 25% as intense as the $(M-15)^+$ ion indicates that the loss of a methyl radical is somewhat faster than the loss of a hydrogen atom. Similar arguments concerning the rates of hydrogen exchange compared to the loss of a hydrogen atom or of a methyl group from other radical cations formed by electron bombardment have been suggested (82, 19).

The alternate mechanism for 1-ethylacenaphthylene, formation of a methylated phenalenyl system followed by exchange of methyl for hydrogen, should be energy dependent and one would expect that the label retention in the $C_{11}H_7^+$ ions from

1-ethylacenaphthylene-α-d_2 would vary with the energy of the bombarding electrons. However, the excess energy necessary to cause fragmentation of the phenalenium cation (fragmentation is absent below ca. 25 ev) is greater than the energy required for this methyl-hydrogen exchange and therefore this energy dependence cannot be ascertained. However, migrations of alkyl groups are relatively rare in organic mass spectrometry (1).

Finally, the determination of the energetics of phenalenium ion formation has been attempted. Due to limitations in instrumentation exact appearance potential measurements for this ion have not been determined. However, from measurements undertaken for its formation from 1-methylacenaphthylene, the appearance potential of the m/e 165 ion is 12.1 ev (obtained by linear extrapolation of the ionization efficiency curve). This value is comparable to the appearance potential of the tropylium ion from toluene which has been found to be 11.8 ev (83, 84).

Some indication of the stability of a gas phase phenalenium ion is obtained by comparing the relative ease of the hydrogen loss-ring expansion process in hydrocarbons of similar structure. It would be expected that 5-methylacenaphthylene (44) would undergo ring expansion upon electron bombardment to form the 2H-benz[cd]azulene carbonium ion (45) (85). The relative amounts of this ion formed from the molecular ion ($(M-1)^+/M^+$) as well as the relative amounts of hydrogen loss



44 45

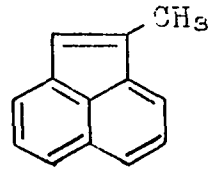
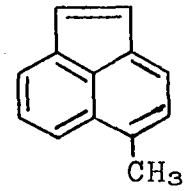
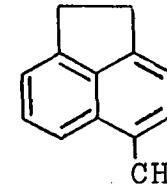
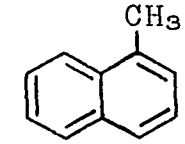
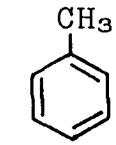
from other methyl aromatics is summarized in Table 7. An attempt to correlate these ratios with Hückel delocalization energies in a linear fashion was unsuccessful although a similar trend is observed (see Table 7). The ratios do indicate that the gas phase phenalenium ion is formed more readily than the other ring expanded hydrocarbon ions which is in accord with ion stabilities predicted from observations in solution and with theoretical predictions.

Calculated Label Retentions

Label retention in the ions at m/e 139 and 140 formed by the loss of C_2H_2 or $^{13}CCH_2$ from the carbon labeled phenalenium ion (54.5% ^{13}C) is predicted to be 45.4% ^{13}C. This is based on consideration of the loss of label in only one of the six possible C_2H_2 fragmentations, or conversely, retention of the label in five of the six losses.

$$54.5 \times 5/6 = 45.4\%\ ^{13}C$$

Table 7. Ratios of $(M-1)^+/M^+$

					
Electron Energy (ev)			$(M-1)^+/M^+$		
70	2.06	1.30	0.38	0.80	1.49
25	1.78	1.10	0.31	0.67	1.19
22	1.43	0.86	0.26	0.55	0.97
20	1.15	0.66	0.21	0.43	0.77
18	0.78	0.41	0.15	0.30	0.53
16	0.45	0.19	0.06	0.16	0.32
15	0.30	0.11	0.05	0.10	0.20
14	0.15	0.05	0.03	0.04	0.11
13	0.07		0.01		0.04
12	0.03				
Hückel Delocalization Energy for Corresponding Ring Expanded Ion					
	5.83β[a]	5.57β[b]		4.70β[c]	2.99β[c]

[a]Source (58, 59).

[b]Source: (85).

[c]Source: (86).

There are eight isomeric dideuterio phenalenium ions, each capable of losing six C_2H_2 (D) fragments. Of the forty-eight possible fragmentations only one involves the loss of both deuteriums (C_2D_2), nineteen involve the loss of one deuterium (C_2HD), and twenty-eight involve only hydrogen (C_2H_2). Of the two isomeric phenalenium ions containing one deuterium only three of the twelve possible C_2H_2(D) losses include the deuterium atom. Since the phenalenium ion formed by electron bombardment of 1-ethylacenaphthylene-α-d_2 was 96.5% d_2, 2.9% d_1, and 0.6 d_0, the predicted label retentions for fragmentation of a phenalenium ion in which complete randomization of hydrogen and deuterium has occurred can be arrived at as shown below.

To retain 2 deuterium

$$96.5 \times 28/48 = 56.2\%\ d_2$$

To retain 1 deuterium

$$96.5 \times 19/48 = 38.3$$
$$+\ 2.9 \times 9/12 = 2.2$$
$$40.4\%\ d_1$$

To retain no deuterium

$$96.5 \times 1/48 = 2.0$$
$$+\ 2.9 \times 3/12 = .7$$
$$+\ 0.6 \times 1.0 = .6$$
$$3.3\%\ d_0$$

The predicted label retention in the phenalenium ion formed from 1-methylacenaphthylene-α-d_3, assuming complete

randomization of hydrogen and deuterium occurs prior to phenalenium ion formation, is calculated by correcting the hydrogen-deuterium ratio of 7:3 for the actual label incorporation in the molecule (93.6% d_3, 4.8% d_2, 1.0% d_1, 0.5% d_0).

To retain 3 deuterium

$$93.6 \times 0.7 = 65.5\%\ d_3$$

To retain 2 deuterium

$$93.6 \times 0.3 = 28.1$$
$$+\ 4.8 \times 0.8 = \underline{3.8}$$
$$31.9\%\ d_2$$

To retain 1 deuterium

$$4.8 \times 0.2 = 1.0$$
$$+\ 1.0 \times 0.9 = \underline{.9}$$
$$1.9\%\ d_1$$

To retain no deuterium

$$1.0 \times 0.1 = 0.1$$
$$0.5 \times 1.0 = \underline{0.5}$$
$$0.6\%\ d_0$$

The calculation of predicted label retention in the ions formed by loss of C_2H_2, C_2HD, or C_2D_2 from the deuterated phenalenium ions is analogous to the calculation for 1-ethyl-acenaphthylene-α-d_2. In the seventeen possible trideuterated isomers, eight losses involve C_2D_2, fifty-three involve C_2HD, and forty-one involve C_2H_2. Consideration of these values as well as those for di- and mono-deuterated species and knowing the label retention in the phenalenium ions (86.7% d_3, 29.8%

d_2, 1.5% d_1) allows one to calculate the expected label retentions.

To retain 3 deuterium

$$68.7 \times 41/102 = 27.6\% \; d_3$$

To retain 2 deuterium

$$68.7 \times 53/102 = 35.6$$
$$+ \; 29.8 \times 28/48 = \underline{17.4}$$
$$53.0\% \; d_2$$

To retain 1 deuterium

$$68.7 \times 8/102 = 5.4$$
$$+ \; 29.8 \times 19/48 = 11.8$$
$$+ \; 1.5 \times 9/12 = \underline{1.1}$$
$$18.3\% \; d_1$$

To retain no deuterium

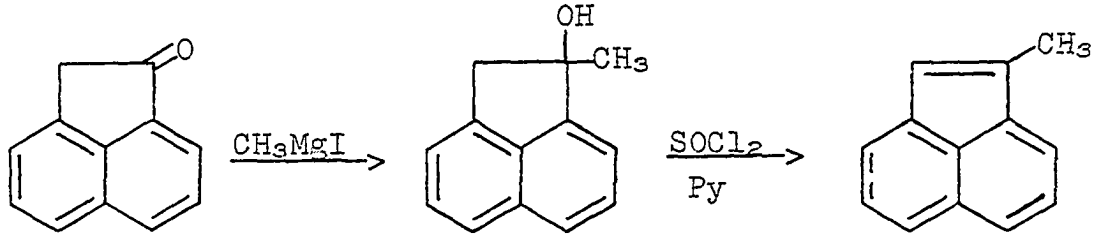
$$29.8 \times 1/48 = 0.6$$
$$+ \; 1.5 \times 3/12 = \underline{0.4}$$
$$1.0\% \; d_0$$

Synthesis of Compounds for Investigation

The syntheses of phenalene (19) (57) and 6b,7a-dihydro-7H-cycloprop[a]acenaphthylene (31) (87) have been described. The sample of 7-chloro-6b,7a-dihydro-7H-cycloprop[a]acenaphthylene (26) (59, 68) was generously donated by Professor R. Pettit of the University of Texas.

1-Methylacenaphthylene (32) was prepared by the thionyl chloride-pyridine dehydration of 1-methyl-1-acenaphthenol.

The alcohol, 47, was prepared by the reaction of the methyl Grignard reagent with acenaphthenone (46) (88). Hydrocarbon 32 can also be prepared by sulfuric acid catalysed dehydration

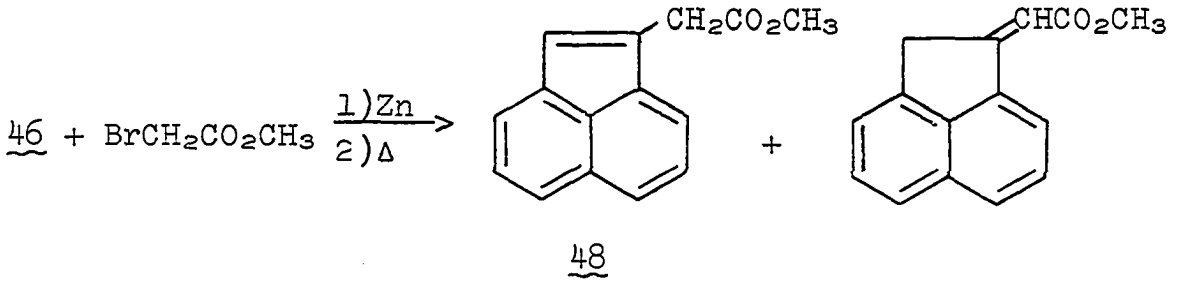


46 47 32

of the alcohol, 47, but this method was found to be unsatisfactory for the analogous preparation of the methyl-d_3 derivative 43 due to loss of deuterium label. This loss of deuterium is presumably due to methyl-methylene isomerism, a process which was also found to occur thermally, particularly on glpc columns.

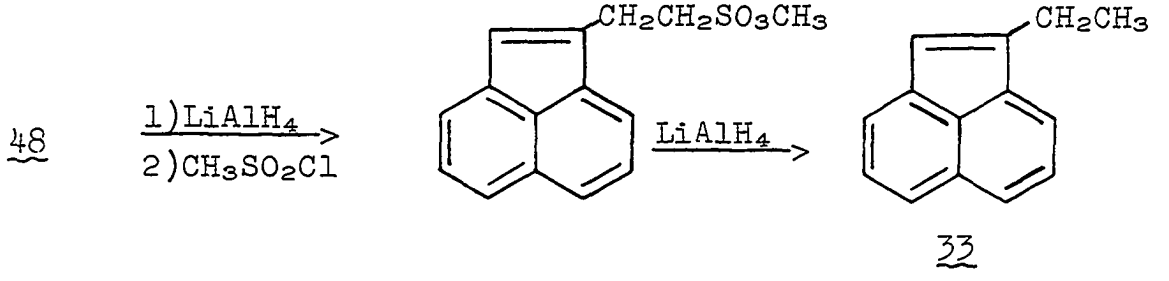
The synthesis of 1-ethylacenaphthylene (33) was also attempted by the dehydration of the alcohol formed from acenaphthenone and ethylmagnesium iodide. However, this resulted in an inseparable mixture of the ethyl and ethylidene isomers. Methyl 1-acenaphthenylacetate (48) was successfully prepared by the Reformatsky reaction of methylbromoacetate and acenaphthenone. Dehydration occurred during distillation

to produce the isomeric esters which were easily separated by



48

column chromatography. Subsequent hydride reduction of 48, conversion of the alcohol to the methanesulfonate ester, and treatment with lithium aluminum hydride gave 1-ethylacenaphthylene. The use of lithium aluminum deuteride instead of

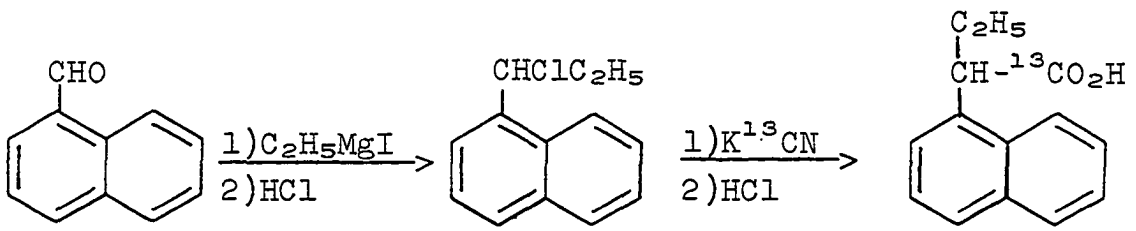


33

lithium aluminum hydride in this sequence of reactions resulted in the formation of 1-ethylacenaphthylene-β-d_3 (41).

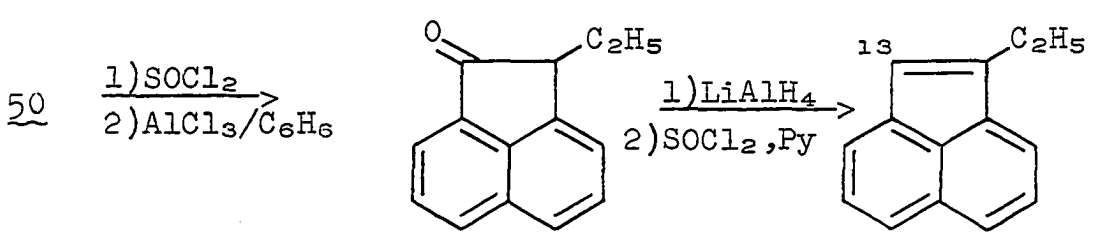
The synthesis of 1-ethylacenaphthylene-2-^{13}C (35) was accomplished by the sequence of reactions shown below. Reaction of α-naphthaldehyde with ethylmagnesium iodide gave an alcohol which was converted to chloride 49 by reaction with

anhydrous hydrogen chloride in pentane. Treatment of 49 with



49 50

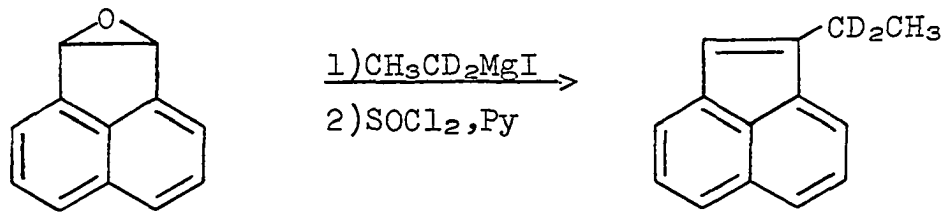
labeled potassium cyanide in dimethylformamide followed by hydrolysis gave the acid 50. Following conversion of 50 to the acid chloride with thionyl chloride, Friedel-Crafts ring closure with aluminum chloride in benzene gave 2-ethylacenaphthenone-1-^{13}C (51). Hydride reduction of 51 followed by thionyl chloride-pyridine dehydration gave 1-ethylacenaphthylene-2-^{13}C.



51 35

Because of the observed ethyl-ethylidene isomerization in attempts to dehydrate 1-ethyl-1-acenaphthenol an alternate

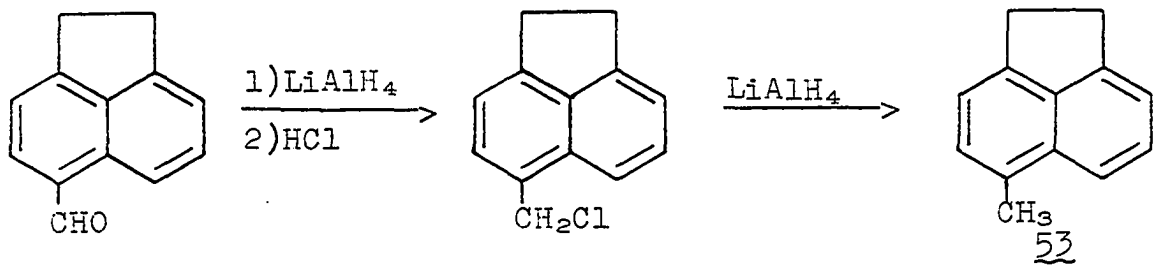
route became necessary for the synthesis of 1-ethylacenaphthylene-α-d_2 (42). Preparation of epoxyacenaphthene (52) by treatment of acenaphthylene with m-chloroperbenzoic acid followed by reaction with the appropriately labeled Grignard



52 42

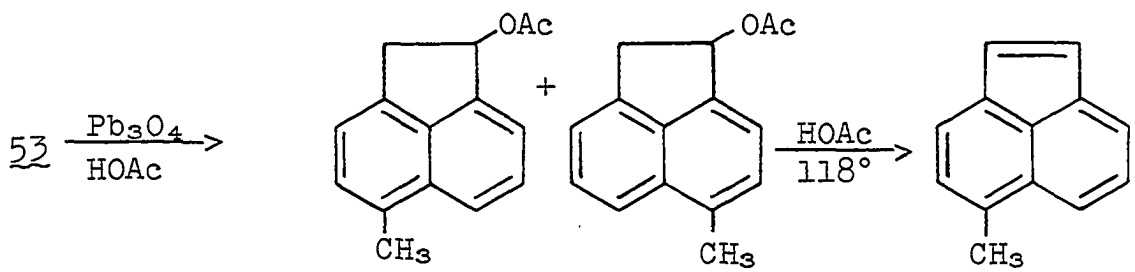
reagent and subsequent dehydration resulted in the preparation of 42.

Synthesis of 5-methylacenaphthylene (44) was accomplished by the sequence of reactions outlined below. 5-Acenaphthenecarboxaldehyde, prepared by the Vilsmeyer reaction with acenaphthene (89) was reduced to alcohol with lithium aluminum hydride. Treatment of this alcohol with concentrated



53

hydrochloric acid containing zinc chloride yielded the corresponding chloro derivative which was converted to 5-methylacenaphthene (53) by reaction with lithium aluminum hydride. Oxidation of 53 with lead tetraacetate resulted in a mixture of 5- and 6-methyl-1-acetoxyacenaphthene, which upon heating with glacial acetic acid yielded 5-methylacenaphthylene.



Suggestions for Further Research

Phenalenium Ion Formation

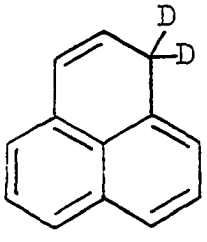
The most conclusive evidence for phenalenium ion formation from alkylacenaphthylenes upon electron bombardment would be the determination of the gas phase heats of formation of the ion at m/e 165 from these compounds and comparison of the values obtained to the heats of formation of the m/e 165 ion from phenalene and 6b,7a-dihydro-7H-cycloprop[a]acenaphthylene. The values obtained should be in very good agreement if the ring expanded phenalenium ion is being formed (83, 84).

The heats of formation may be calculated from the expression (90, p. 163)

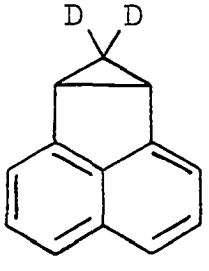
$$AP(F^+) = \Delta H_f(F^+) + \Delta H_f(N) - \Delta H_f(M)$$

where F^+ is the phenalenium ion, M is the molecule under investigation, and N is the neutral fragment. It is obvious that two problems are involved in determining these heats of formation for the phenalenium ion. The accurate determination of the appearance potential of the ion must be obtained and secondly the accurate estimation or the determination of the heats of formation of the hydrocarbons must be undertaken.

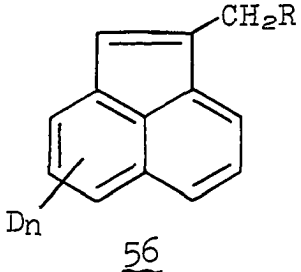
An investigation of additional labeled compounds could be invaluable as tests of the postulated mechanism of the ring expansion process. Investigation of the mass spectra of 1,1-dideuteriophenalene (54), 1',1'-dideuteriocyclopropylacenaphthylene (55), and a ring-deuterio alkylacenaphthylene (56) could be quite informative in regard to scrambling of hydrogen and deuterium in the formation of the phenalenium ion and its subsequent fragmentation.



54



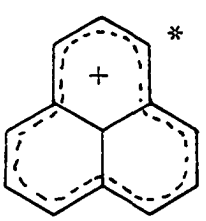
55



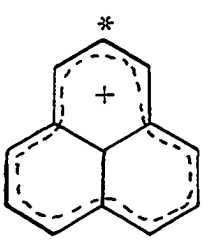
56

At present no straightforward synthetic route to 54 is available and whether or not it would retain positional integrity of the label once synthesized is not known since the possibility exists that scrambling of the label could occur by a series of 1,5-sigmatropic shifts. The utilization of diazomethane-d_2 would result in the preparation of 55.

It would also be very interesting to explore the mass spectra of 1-ethylacenaphthylene-1-α-$^{13}C_2$ and 1-ethylacenaphthylene-1-^{13}C. The di-labeled compound would serve as an excellent test of the postulate that positional integrity of the carbon atoms is maintained in this ring expansion. The mono-labeled compound would indicate whether or not the insertion of the α-carbon into the 5-membered acenaphthylene ring occurred in a specific manner or if it occurred by alternate routes giving ions 37 and 38.



37

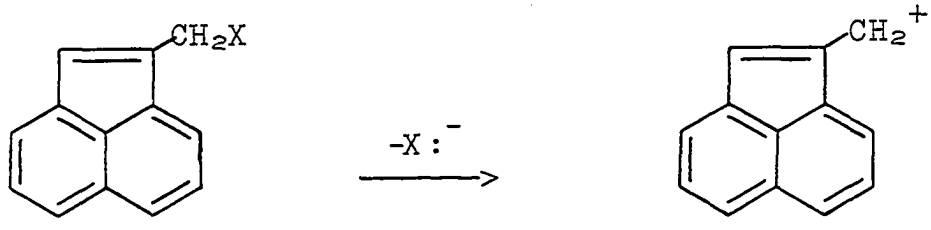


38

As added evidence of the stability of the gas phase phenalenyl system, it would be interesting to explore the negative ion mass spectra of the compounds investigated. It

has been stated (59) that the phenalenyl anion has the same delocalization energy as the cation since the two extra electrons of the anion would be in an orbital of zero energy. Furthermore, the stability of the anion is well documented (60). Although there are severe limitations on obtaining negative ion mass spectra, perhaps the stability of the ion involved would partially compensate for these inherent difficulties.

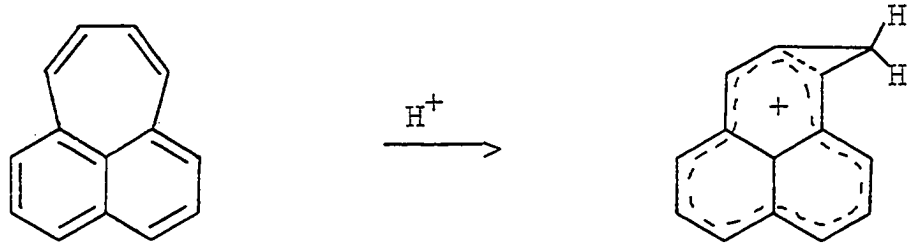
As an extension of phenalenium ion formation by electron impact of alkylacenaphthylenes, it would be quite interesting to study the behavior of the benzyl type ion (30) in solution. Although the analogous ring expansion of the benzyl



30

cation to tropylium ion in solution is not known, it is possible that 30 could rearrange to the phenalenium ion. Synthetic routes to halomethylacenaphthylenes are known and modification of these procedures could result in the formation of other derivatives of acenaphthylene-1-methanol. Another possible route to the desired material would be from acenaphthylene-1-carboxylic acid.

Another aspect of phenalenium ion chemistry which would be quite interesting would be a study of the preparation and observance of the homophenalenium ion (57). This ion could easily result from the protonation of cyclohepta(d.e)naphthalene (58).

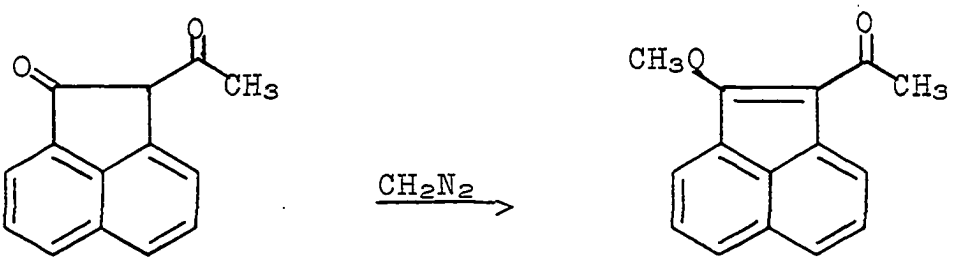


58 57

Synthetic Acenaphthene Chemistry

Epoxyacenaphthene (a previously unknown α-aryl epoxide (91)) has been isolated in 30% yield by treatment of acenaphthylene with m-chloroperbenzoic acid. However, the conversion of olefin to epoxide is closer to 75-80% and a better means of separation from the small amount of acenaphthenone formed and the elimination of its formation during the separation could substantially increase the yield.

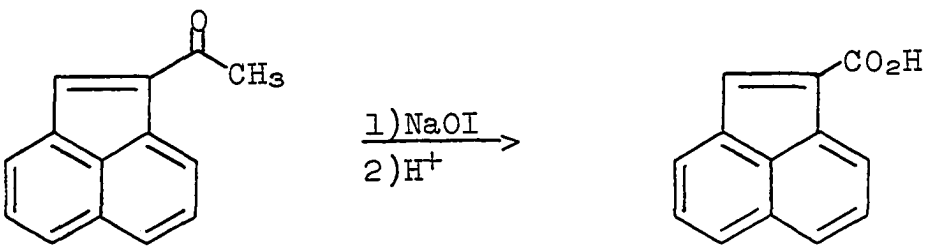
The preparation of 2-acetylacenaphthenone (59) was accomplished in 43% yield by the method of Ramirez, Ramanathan, and Desai (92). These authors report that 59 upon treatment with diazomethane affords the enol ether 60 although their



59 60

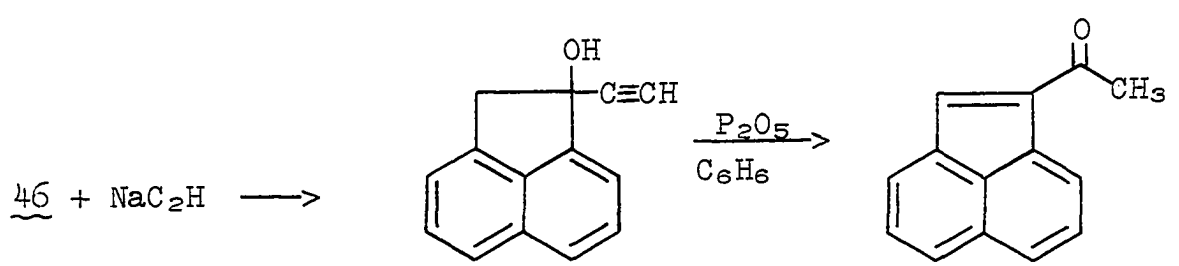
evidence for this particular enol ether is rather meager. Attempts to reproduce this work led to a mixture of enol ethers upon treatment of 59 with diazomethane using boron trifluoride-etherate as catalyst. The isolation of these enol ethers is of interest since reduction with lithium aluminum hydride is a possible route to 1-acetylacenaphthylene (61). Reduction of other enol ethers of β-diketones has given α,β-unsaturated ketones (93, 94).

1-Acetylacenaphthylene is interesting as a possible precursor to acenaphthylene-1-carboxylic acid (62). Various attempts at the preparation of 62, carbonation of the Grignard or oxidation of acenaphthylene-7-carboxaldehyde, have not been successful. However, treatment of 1-acetylacenaphthylene with sodium hydroxide and iodine could form the acid under very mild oxidative conditions.



61 62

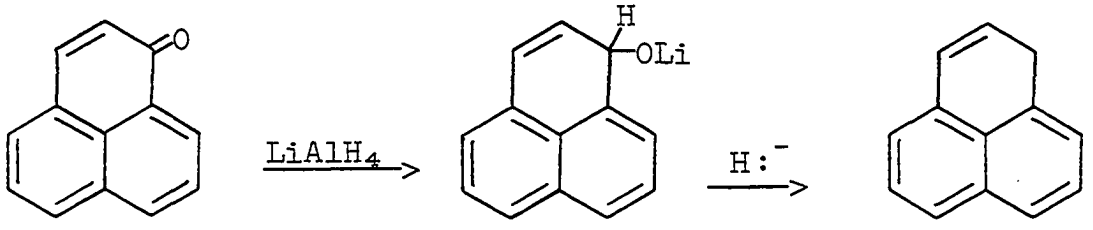
An alternate route to the preparation of 61 is also available. This synthesis would involve treatment of acenaphthenone with sodium acetylide to form 1-ethynylacenaphthenol (63). This alcohol might then be both dehydrated and hydrated in the same reaction following a similar procedure for the preparation of 1-acetylcyclohexene (95).



63

Boekelheide and Larrabee reported that phenalenone upon reduction by lithium aluminum hydride gave a small yield (14%)

of phenalene (19) (57). The postulated mechanism for this reaction involves the displacement of the LiO^- moeity from



19

the intermediate alkoxide. This reaction was repeated using lithium aluminum deuteride and phenalene was isolated in 23% yield (2 runs). However, the formation of a red color during the reaction and the small amount of deuterium incorporation (78.6% d_0, 20.1% d_1, and 1.3% d_2) indicates that the postulated mechanism cannot account for the observed results. Furthermore, the nmr spectrum of the phenalene isolated from this reaction shows that the deuterium is randomly distributed throughout the molecule. The preparation of 3-methylphenalenone (96) would introduce a substituent label which could be informative in regard to mechanism of this reduction. Other anomolous hydride reductions have been reported, those of most interest being reductions of tropones and tropolone methyl ethers (97, 98).

EXPERIMENTAL

Instruments and Methods

All mass spectra were obtained using an Atlas MAT model CH4 single focusing mass spectrometer. An ionizing potential of 70 electron volts was normally used. However, most samples were run at various electron energies as reported in the discussion of the individual compounds. An accelerating potential of 3000 volts and an electron current of 5-10 μA were employed.

All hydrocarbon samples were prepared for mass spectral measurement by developing (pentane) a sample of the compound on an alumina thin layer chromatogram followed by selective removal of the alumina. Direct insertion of the absorbed sample into the ion source was then employed. This technique was necessary due to the relatively high vapor pressure of the hydrocarbons and allowed the measurement of their mass spectra without using the heated inlet, a method which in certain cases produces pronounced thermal reactions.

The calculation of isotopic label retention in fragment ions and label incorporation in molecular ions follows the method outlined by Biemann (99, p. 223). As nearly as possible all of the labeled compounds and the unlabeled standards were run under identical instrument conditions.

All nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60 spectrometer at

60 MHz. The chemical shift values are reported in parts per million (ppm), δ units, relative to the internal standard, tetramethylsilane.

Infrared spectra (ir) were obtained using a Perkin-Elmer Model 21 spectrometer.

All gas liquid partition chromatography (glpc) was carried out on an Aerograph 200 dual column instrument. Unless noted otherwise, a 5′ x 1/4″ SE 30 column was used for all separations.

All melting points were determined with a Thomas-Hoover capillary melting point apparatus. All melting points and boiling points are uncorrected and are reported in degrees centigrade. All pressures are given in millimeters of mercury.

Micro analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of Compounds

The sample of 7-chloro-6b, 7a-dihydro-7H-cycloprop[a]acenaphthylene (26) was generously sent to us by Professor R. Pettit of the University of Texas, Austin, Texas.

Phenalene (19)

The title compound was prepared by the dehydration of 2,3-dihydrophenalene-1-ol following the procedure of Boekelheide and Larrabee, (57) mp 84-85° (lit. (57), mp 85-86°).

2,3-Dihydrophenalene

This compound was prepared by catalytic hydrogenation of phenalene following the procedure of Boekelheide and Larrabee (57), mp 62-65° (lit.(57) mp 65°).

6b, 7a-Dihydro-7H-Cycloprop[a]acenaphthylene (31)

The title compound was prepared by a modification of the method of Wittig and Schwarzenbach (87).

An ethereal solution of diazomethane was prepared and standardized by the method of Arndt (100) after storing for 1 hr over water soluble starch to remove methylamine (87). Three hundred ml of this solution (144 mmole) was added via a siphon tube (under nitrogen) to a solution of zinc iodide (7.1 g, 63 mmole, dried for 24 hr at 110° over P_2O_5) and 200 ml of dioxane (distilled from calcium hydride). The addition of the diazomethane solution was accompanied by the rapid evolution of gas. The zinc iodide solution had been prepared in a 500-ml round bottom flask equipped with a nitrogen inlet, a magnetic stirrer, and a reflux condenser. The entire assembly had been flame dried under nitrogen. After completing the addition of the diazomethane solution, acenaphthylene (7.1 g, 50 mmole) was added during 5 min and the resulting solution heated at reflux for 72 hr. The mixture was then cooled and filtered through a sintered glass funnel. The ethereal solution was washed twice with 50 ml of 5% hydrochloric acid, twice with 30 ml of water, and once with 30 ml of saturated sodium chloride solution. The ethereal

solution was dried ($MgSO_4$) and the solvent removed at reduced pressure. The yellow solid remaining (a mixture of the desired product and acenaphthylene by nmr analysis) was dissolved in 100 ml of Skellysolve B and a solution of bromine (10 g) in 15 ml of pentane was added dropwise with stirring. After stirring at room temperature for 0.5 hr, the entire solution was chromatographed on a neutral alumina column. Elution with pentane afforded 4.54 g (54%) of the desired hydrocarbon. Four recrystallizations from ethanol gave colorless plates, mp 116° (lit. (87) mp 116°). The nmr spectrum of this material was identical to the published spectrum (101).

1-Acenaphthenol

The title compound was prepared by the procedure of Cason (102), mp 144-145° (lit.(102) mp 144.5-145.5°), by the lead tetraacetate oxidation of acenaphthene followed by basic hydrolysis of the acetate.

1-Acenaphthenone (46)

This compound was prepared by the chromic acid oxidation of the alcohol following the procedure of Fieser and Cason (103), mp 118-121° (lit. (103) mp 121-121.5).

1-Methylacenaphthene-1-ol (47)

This compound was prepared by the reaction of methylmagnesium iodide and acenaphthenone following the procedure of Brown and Hammick (104), mp 102-104° (lit. (88) mp 103-104°).

1-Methylacenaphthylene (32)

1-Methylacenaphthene-1-ol (0.19 g, 1 mmole) was dissolved in 3 ml of pyridine and cooled to 5°. Thionylchloride (0.12 g, 1 mmole) was added to the stirred solution over 5 min and the mixture was stirred at 5° for 1.5 hr. The resulting solution was poured into 15 ml of 5% hydrochloric acid and extracted twice with 15 ml of ether. The ether extracts were combined and washed with 10 ml of water. After drying ($MgSO_4$) the solvent was removed at reduced pressure. The orange oil which remained was chromatographed on 10 g of neutral alumina and elution with pentane afforded 0.08 g (50%) of 1-methylacenaphthylene. The compound was identified by glpc and nmr comparison with a sample of 1-methylacenaphthylene prepared by a modification of the procedure of O'Brien and Smith (88), bp 89-92° (0.2 mm) (lit. (88) bp 84-94° (0.1 mm)). The nmr spectrum consisted of resonances at δ2.38 (d, J = 1.5 Hz, 3H, $-C\underline{H}_3$), 6.56 (q, J = 1.5 Hz, 1H, $\underline{H}-C=C-CH_3$), and 7.22-7.73 (m, 6H, aromatic protons).

1-Methylacenaphthylene-α-d_3 (43)

This compound was prepared from acenaphthenone by the method described above for the preparation of 1-methylacenaphthylene using methylbromide-d_3 (Merck, Sharpe and Dohme of Canada). Mass spectral analysis at 11 ev showed the sample to be 93.6% d_3, 4.8% d_2, 1.0% d_1, and 0.5% d_0.

The nmr spectrum of the material was consistent with the title compound and differed from the nmr spectrum of

1-methylacenaphthylene in that the methyl singlet at δ2.38 was absent and the olefinic quartet at δ6.56 appeared as a slightly broadened singlet.

5-Chloromethylacenaphthene

5-Hydroxymethylacenaphthene (0.73 g, 4 mmole) mp 157-158° (lit. (105) mp 156-157°)), prepared by the hydride reduction of 5-acenaphthenecarboxaldehyde (106), was stirred with 15 ml of concentrated hydrochloric acid containing zinc chloride (0.5 g) for 5 hr. The resulting gray mixture was poured into 25 g of crushed ice and extracted twice with 30 ml of ether. The ether extracts were combined and washed with 15 ml of water. After drying ($MgSO_4$) the ether was removed at reduced pressure leaving 0.76 g of 5-chloromethylacenaphthene, identified by nmr and mass spectral analysis and by subsequent reaction. After recrystallization from ethanol-water the colorless plates melted at 95-96°.

The nmr spectrum exhibited resonances at δ3.32 (s, 4H, $-CH_2-CH_2-$), 4.96 (s, 2H, $-CH_2Cl$), and 7.0-7.9 (m, 5H, aromatic protons). In its mass spectrum the compound exhibited molecular ions at m/e 202 and m/e 204 with intensities characteristic for the chlorine isotopes. The compound was sensitive to both light and air and turned brown upon standing.

5-Methylacenaphthene (53)

5-Chloromethylacenaphthene (0.75 g, 4 mmole) in 20 ml of anhydrous ether was added dropwise to a solution of lithium aluminum hydride (0.20 g, 5 mmole) in 5 ml of ether over a

0.5 hr period. This mixture was heated at reflux for 11 hr and the excess hydride destroyed by the slow addition of water. The mixture was poured into 20 ml of 5% hydrochloric acid and ether workup gave 0.58 g of a tan solid. Chromatography on neutral alumina and elution with pentane gave 0.36 g of 5-methylacenaphthene as colorless needles, mp 94-95° (lit. (89) mp 95.6-95.9°).

5 (and 6)-Methyl-1-acenaphthenyl Acetate

This compound was prepared by the lead tetraacetate oxidation of 5-methylacenaphthene as described for the preparation of 1-acenaphthenylacetate (102). The orange oil obtained was approximately an equal molar mixture of isomers as shown by the two aromatic methyl resonances in its nmr spectrum at δ2.57 and 2.64. The ir spectrum (capillary film) showed strong absorbances at 5.77μ (C=O) and 8.10μ (-C-O-C).

5-Methylacenaphthylene (44)

The title compound was prepared by treatment of the acetate mixture obtained above with refluxing acetic acid, an extension of the procedure developed by Richter and coworkers (107). The compound, a characteristic yellow oil, was purified by column chromatography on alumina (hexane eluent). The nmr spectrum was consistent with 5-methylacenaphthylene and exhibited resonances at δ2.57 (d, J = 1.0 Hz, 3H, Ar-C$\underline{H}_3$)$_3$, 6.83 (s, 2H, $\underline{H}$-C=C-$\underline{H}$), and 6.95-7.78

(m, 5H, aromatic protons).

Methyl 1-Acenaphthylenylacetate (48)

Powdered zinc (8.23 g, 126 mmole), which had been previously washed with sodium hydroxide, water, dilute acetic acid, ethanol, acetone, and ether and had been dried at 90° for 3 hr, was placed in a three neck flask equipped with a mechanical stirrer, reflux condenser with drying tube, and an addition funnel. The entire assembly was then dried with a soft flame. After cooling 10 ml of a solution of acenaphthenone (7.12 g, 42 mmole), methylbromoacetate (19.28 g, 126 mmole), ether (10 ml) and benzene (35 ml) was added. Stirring and heating on the steam bath initiated the reaction. The remainder of the solution was then added dropwise over 45 min with stirring and occasional heating. After the addition was completed the mixture was refluxed for an additional 45 min. The mixture was allowed to cool and was poured into 100 ml of 5% hydrochloric acid. The aqueous phase was withdrawn and extracted with 30 ml of ether. The organic phases were combined and washed successively with two 25 ml portions of 5% sodium hydroxide and with four 25 ml portions of water. The ethereal solution was dried ($MgSO_4$) and the solvent removed at reduced pressure. The remaining red oil was distilled and two fractions of a yellow semi-solid were collected. The first fraction (A) (bp ca. 150°, 0.1 mm Hg, 2.46 g), and the second fraction (B) (bp ca. 160°, 0.1 mm Hg, 1.85 g) were analysed by glpc and by nuclear magnetic

resonance. Fraction A was shown to be a mixture of acenaphthenone, methyl-1-acenaphthylenylacetate, and the isomeric α,β-unsaturated ester with the desired methyl-1-acenaphthylenylacetate comprising ca. 1 g of fraction A. Chromatography on a silica gel column of fraction A using a 1:1 (v/v) mixture of Skellysolve B and benzene as eluent gave an ester mixture as a yellow solid free of the starting ketone. The nmr spectrum of this material showed that the desired methyl-1-acenaphthylenylacetate (resonances at δ 3.48 (s, 3H, -O-C$\underline{H}_3$), 3.59 (d, J = 1.5 Hz, 2H, -C$\underline{H}_2$-CO_2CH_3), 6.71 (t, J = 1.5 Hz, 1H, $\underline{H}$-C=C-CH_2-)$_3$ and 7.04-7.67 (m, 6H, aromatic protons)) comprised 90% of the ester mixture. The ir spectrum (CCl_4) showed strong absorbance at 5.73μ (C=O) and at 8.55μ (C-O-C).

2-(1-Acenaphthylenyl)ethanol

A solution of methyl-1-acenaphthylenylacetate from above (0.49 g, 22 mmole) in 10 ml of anhydrous ether was added dropwise with stirring to a slurry of lithium aluminum hydride (0.05 g, 1.3 mmole) in 5 ml of ether. The 50-ml round bottom flask, equipped with a reflux condenser with drying tube, addition funnel, and a magnetic stirrer had been dried with a strong nitrogen flow using a soft flame. The addition of the ester was accomplished in 20 min and the orange colored mixture was stirred at room temperature for an additional 30 min. The excess hydride was destroyed by the dropwise addition of water and the resulting yellow

mixture was transferred to a separatory funnel with 10 ml each of water and ether. The mixture was then washed with 15 ml of 5% hydrochloric acid and the aqueous phase separated and extracted with 10 ml of ether. The ethereal solutions were combined and washed with 10 ml each of saturated sodium bicarbonate, water, and saturated sodium chloride solution. After drying ($MgSO_4$), the solvent was removed at reduced pressure leaving 0.44 g of a light yellow oil. The nmr spectrum of the crude product was consistent with the desired alcohol and showed resonances at δ2.76 (triplet of doublets, J = 7, 1.5 Hz, 2H, $-C\underline{H}_2CH_2OH$), 3.70 (t, J = 7 Hz, 2H, $C\underline{H}_2-OH$), 3.50 (broad singlet, 1H, $-O\underline{H}$), 6.48 (t, J = 1.5 Hz, 1H, $\underline{H}-C=C-$), and 6.95-7.65 (m, 6H, aromatic protons). A very weak resonance at δ6.10 showed that the allylic alcohol was present in only trace amounts.

2-(1-Acenaphthylenyl)ethyl Methanesulfonate (48)

The crude alcohol from above was dissolved in 10 ml of anhydrous pyridine and after cooling to 0° methanesulfonyl-chloride (0.29 g, 2.5 mmole) was added dropwise with stirring. The mixture was then placed in the refrigerator for 15 hr. The yellow mixture, with solid pyridinehydrochloride present, was poured into 15 ml of water and extracted twice with 15 ml portions of ether. The ether extracts were combined and washed with four 15 ml portions of 5% hydrochloric acid and once with 15 ml each of water and saturated sodium chloride. The ether solution was dried ($MgSO_4$) and the solvent removed

at reduced pressure leaving 0.54 g of an orange liquid. The nmr spectrum of the sulfonate ester exhibited resonances at δ2.70 (s, 3H, $SO_3C\underline{H}_3$), 3.06 (triplet of doublets, J = 7, 1.5 Hz, 2H, $-C\underline{H}_2-CH_2-SO_3-$), 4.38 (t, J = 7 Hz, 2H, $-C\underline{H}_2-SO_3-$), 6.68 (t, J = 1.5 Hz, 1H, $\underline{H}-C=C-$), and 7.16-7.77 (m, 6H, aromatic protons). There was no evidence for any of the isomeric allylic ester.

1-Ethylacenaphthylene (33)

A solution of the mesylate ester from above (0.54 g, 2 mmole) in 12 ml of anhydrous ether was added dropwise with stirring to a slurry of lithium aluminum hydride (0.04 g, 1 mmole) in 5 ml of anhydrous ether. The 50-ml round bottom flask, equipped with a magnetic stirrer, reflux condenser with drying tube, and an addition funnel, had been flame dried under a steady flow of nitrogen. The resulting green mixture was heated under reflux for 9 hr and the excess hydride destroyed by the dropwise addition of water. The resulting yellow mixture was poured into 15 ml of 5% hydrochloric acid and the aqueous phase was separated and extracted with 15 ml of ether. The ether extracts were combined and washed with 15 ml each of saturated sodium bicarbonate solution, water, and saturated sodium chloride solution. The organic phase was dried ($MgSO_4$) and the ether removed at reduced pressure. The remaining yellow oil (0.35 g) was chromatographed on neutral alumina and elution with pentane afforded three fractions. Glpc analysis of these fractions on a silicone gum rubber

column showed the first fraction to be a mixture of 1-ethylacenaphthene and 1-ethylacenaphthylene. The last two fractions (0.21 g) contained only the desired product as shown by comparison of glpc retention time and nmr spectrum with a sample of 1-ethylacenaphthylene prepared by the method of Morel and Mollier (108) by the reaction of ethylmagnesiumiodide and acenaphthenone followed by acid catalysed dehydration of the alcohol. The nmr spectrum of this bright yellow oil exhibited resonances at δ1.32 (5, J = 7 Hz, 3H, $-CH_2C\underline{H}_3$), 2.75 (quartet of doublets, J = 7 Hz, 1.5 Hz, 2H, $-C\underline{H}_2CH_3$), 6.55 (t, J = 1.5 Hz, 1H, $\underline{H}$-C=C-), and 7.10-7.72 (m, 6H, aromatic protons) and was identical to the nmr spectra of 1-ethylacenaphthylene obtained by other independent routes (vide infra).

1-Ethyl-β-d_3-Acenaphthylene (41)

The deuterated analog of 1-ethylacenaphthylene was prepared from methyl-1-acenaphthylenylacetate by the same sequence of reactions described above using lithium aluminum deuteride in place of lithium aluminum hydride. The same amount of starting ester was used and the yield of hydrocarbon following chromatography was 0.28 g (62%). The nmr spectra of the intermediates were consistent with the incorporation of deuterium as expected and the spectrum of the deuterated hydrocarbon exhibited the same aromatic multiplet and olefinic triplet as 1-ethylacenaphthylene. The methylene protons appeared as a broadened singlet at δ2.70. There was

no nmr or glpc evidence for either 1-ethylacenaphthene or the ethylidene isomer. Mass spectral analysis showed that the compound was 94.21% d_3, 3.42% d_2, and 2.36% d_0.

α-Ethyl-1-naphthalenemethanol

This compound was prepared by the reaction of ethyl Grignard reagent with α-naphthaldehyde (Aldrich Chemical Co.) following the procedure of Kon and Spickett (109).

α-Ethyl-1-naphthylchloromethane (49)

Following the procedure of Best[a] for the preparation of secondary benzylic chlorides, a solution of α-ethyl-1-naphthalenemethanol (9.3 g, 0.05 mmole) and 150 ml of pentane containing calcium chloride (5.0 g) was cooled to 0° and hydrogen chloride gas was bubbled through this stirred solution for 0.5 hr. The mixture was then poured into 100 g of crushed ice and the aqueous phase was separated and extracted twice with 50 ml of pentane. The organic phases were then combined and washed successively with water, saturated sodium bicarbonate solution, and water. After drying ($MgSO_4$), the solvent was removed at reduced pressure to give 10.0 g (95%) of the crude chloride which was purified by elution chromatography on silica gel (hexane).

---

[a] D. C. Best, Ames, Iowa. Private communication. 1967.

2-Ethyl-2-(1-Naphthyl)acetonitrile

A mixture of α-ethyl-1-naphthylchloromethane (0.51 g, 2.5 mmole), potassium cyanide (0.26 g, 4 mmole) and 15 ml of dimethylformamide was stirred and heated at 55° for 24 hr. The reaction was accompanied by the gradual appearance of a gelatinous white precipitate. After cooling, the mixture was poured into 30 ml of water and extracted three times with 20 ml of ether. The ethereal solutions were combined and washed twice with 20 ml of water. After drying ($MgSO_4$) the solvent was removed at reduced pressure leaving ca. 0.5 g of a colorless oil. The ir spectrum showed absorbance at 4.46μ (C≡N) among others and the nmr spectrum was consistent with the desired nitrile.

2-Ethyl-2-(1-naphthyl)acetic acid (50)

Following the procedure of Robson and co-workers (110) for the hydrolysis of nitriles the crude nitrile from above was dissolved in 20 ml of anhydrous methanol and dry hydrogen chloride gas was bubbled through for 3.5 hr. The methanol was then removed at reduced pressure and 21 ml of concd. hydrochloric acid was added. The resulting mixture was stirred and heated at 100° for 10 hr. After cooling, the mixture was poured into 30 ml of water and extracted twice with 25 ml of ether. The ether extracts were then combined and washed twice with 20 ml of 10% sodium bicarbonate solution and with 15 ml of water. The three aqueous washings were combined, acidified to Congo Red paper with 50%

hydrochloric acid, and extracted three times with 20 ml of ether. The ether extracts were combined, dried ($MgSO_4$), and the solvent removed at reduced pressure leaving 0.38 g of oil which solidified to colorless plates, mp 86-87° (lit. (111) mp 86-87°).

2-Ethylacenaphthenone (51)

Employing the procedure of Bachmann and Sheehan (112) for the preparation of 8-ethylacenaphthenone, the acid from above was dissolved in 2 ml of thionyl chloride and allowed to stand at room temperature for 1 hr. The excess thionyl chloride was then removed at reduced pressure and 5 ml of benzene (sodium dried) was added and removed at reduced pressure. Benzene (15 ml) was then added at room temperature and anhydrous aluminum chloride (0.80 g, 6 mmole) was added with stirring. After 2 hr at room temperature, the mixture was a very dark color and was poured into a mixture of 30 g of crushed ice and 22 ml of concd. hydrochloric acid. The aqueous phase was separated and extracted twice with 20 ml of ether. The ether extracts and the original benzene solution were combined and washed twice with 20 ml of 10% sodium bicarbonate solution and twice with 20 ml of water. After drying ($MgSO_4$) and treating with charcoal, the solvent was removed at reduced pressure leaving a dark oil which was chromatographed on silica gel. Elution with 10% benzene in hexane gave 0.21 g of colorless oil. The ir spectrum showed a strong absorbance at 5.83μ (C=O, acenaphthenone exhibits

carbonyl stretching at 5.81μ.) The nmr spectrum was consistent with 2-ethylacenaphthenone and exhibited resonances at δ0.97 (t, J = 7 Hz, 3H, $-CH_2\underline{CH_3}$), 1.87-2.33 (m, 2H, $-CH_2CH_3$), 3.58 (t, J = 7 Hz, 1H, $-\underline{CH}-CH_2CH_3$), and 7.28-8.04 (m, 6H, aromatic protons).

1-Ethylacenaphthylene (33)

The 2-ethylacenaphthenone from above was reduced to the corresponding alcohol with lithium aluminum hydride and the crude alcohol was dissolved in 10 ml of anhydrous pyridine and cooled to 0°. Thionyl chloride (0.3 ml) was added and the mixture allowed to stir at 0° for 2 hr. The mixture was diluted with 20 ml of ether, 2 g of crushed ice was added, and the entire mixture poured into 30 ml of 5% hydrochloric acid. The aqueous phase was separated and extracted twice with 15 ml of ether. The ethereal solutions were combined and washed three times with 5% hydrochloric acid and twice with 10 ml of water. The organic phase was dried ($MgSO_4$) and the solvent removed at reduced pressure to give a characteristic yellow oil which was purified by chromatography on alumina. Elution with hexane gave a small amount of 1-ethylacenaphthylene, identified by glpc retention time and comparison of its nmr spectrum to that of 1-ethylacenaphthylene synthesized by alternate routes.

1-Ethylacenaphthylene-2-^{13}C (35)

The title compound was synthesized by the reactions described above using potassium cyanide-^{13}C (Bio-Rad

Laboratories) for the substitution of chlorine in α-ethyl-1-naphthylchloromethane.

1,2-Epoxyacenaphthene (52)

Acenaphthylene (6.08 g, 0.04 mole) was added over 5 minutes to a solution of m-chloroperbenzoic acid (10.32 g, 0.06 mmole) in 100 ml of chloroform previously cooled to 0°C. The mixture was then allowed to stand in the refrigerator for 24 hrs. During this time there was the gradual disappearance of the yellow coloration of acenaphthylene. The mixture, with a white precipitate of m-chlorobenzoic acid, was poured into 50 ml of saturated sodium bicarbonate solution. The aqueous phase was separated and extracted with 25 ml of chloroform. The organic phases were combined and washed successively with 30 ml of 5% sodium thiosulfate solution, 30 ml of saturated sodium bicarbonate, and 30 ml of water. The chloroform solution was dried ($MgSO_4$) and the solvent removed on a rotary evaporator leaving 8.1 g of a yellow oil which slowly crystallized. Three recrystallizations from carbontetrachloride afforded 1.44 g (30%) of colorless plates, mp 83-84°C. Mass spectral examination showed a strong molecular ion at m/e 168 ($C_{12}H_8O$) which lost, with the corresponding metastable, the elements of carbon-monoxide, presumably by the rearrangement to acenaphthenone, a previously observed electron impact induced rearrangement of epoxides (113). The ir spectrum (Nujol mull) showed no absorbtion characteristic of acenaphthenone and showed absorbance characteristic of

epoxides at 12.34 and 12.84μ. The nmr spectrum consisted of resonances at δ4.77 (s, 2H, H-C(O)-C-H) and 7.13-7.75 (m, 6H, aromatic protons).

Anal. Calcd. for $C_{12}H_8O$: C, 85.69; H, 4.79. Found: C, 85.73; H, 4.83.

Ethanol-1,1-d_2

The title compound was prepared by the lithium aluminum deuteride reduction of phenylacetate following the procedure of Letsinger and Pollart (114).

Ethyliodide-1,1-d_2

The deuterated ethanol was converted into the iodide by the procedure of Leffek, Llewellyn, and Robertson (115). Mass spectral analysis showed that the compound was 98.5% d_2, 1.2% d_1, and 0.3% d_0.

1-Ethyl-α-d_2-Acenaphthylene (42)

A solution of 1,2-epoxyacenaphthene (0.51 g, 3 mmole) in 12 ml of ether was added dropwise, with stirring, to the Grignard reagent prepared from ethyliodide-1-1-d_2 (0.93 g, 6.0 mmole) and magnesium (0.16 g, 0.006 g atom) in 5 ml of ether. The addition was completed in 0.5 hr and after stirring for an additional 0.5 hr water was added dropwise to destroy excess Grignard reagent and 20 ml of 5% ammonium chloride solution was added. After the addition of 15 ml of ether the aqueous phase was separated and extracted twice with 15 ml of ether. The ether phases were combined, washed three times with 20 ml of water, and dried ($MgSO_4$). After removal

of the solvent at reduced pressure, the crude alcohol was dehydrated, and the product purified by the same procedure as described for the preparation of 1-ethylacenaphthylene-2-^{13}C. The compound thus obtained had the same glpc retention time as 1-ethylacenaphthylene prepared by an alternate route (vide supra) and its nmr spectrum was identical to that previously described except that the triplet at δ1.32 appeared as a broadened singlet ($-CD_2-C\underline{H}_3$), the olefinic triplet at δ6.55 appeared as a singlet ($\underline{H}-C=C-CD_2$), and the methylene proton resonance at δ2.75 was absent. Low voltage mass spectral analysis showed that the material was 98.7% d_2, and 1.3% d_1.

PART II: MASS SPECTRAL REARRANGEMENTS OF ORGANOSILANES

HISTORICAL

Although various groups have investigated the mass spectra of Group IVB organometallic compounds most of the work has been concerned with the energetics of the processes involved and the general fragmentation patterns of these compounds. Interesting rearrangement processes are observed although very little labeling work has been done and the mechanisms of these rearrangements are not known. Much of this work has been reviewed (2, p. 654, 116, 117). In addition, the use of gas chromatography in conjunction with mass spectrometry has added much impetus to the investigation of the mass spectra of volatile trimethylsilyl derivatives of organic compounds. The mass spectra of these compounds show interesting rearrangements involving the trimethylsilyl group and considerable effort has been extended in the interpretation of the mass spectra of these derivatives (118, and references contained therein).

Several authors have compared the mass spectra of various series of tetraorgano Group IVB compounds (119-129). The most prominent feature of the mass spectra of these simple organometallics is the observation that most of the ion current is carried by even electron ions (mono- or trisubstituted metal atom) and that very little fragmentation of the groups attached to the metal atom occurs. The primary process observed for tetraorganosilanes, -germanes, -stannanes, and

-plumbanes is the initial loss of an alkyl radical from the weak or non-existent molecular ion to give the even electron R_3M^+ ion. When R = Me this ion is the base peak in the mass spectrum and this ion then fragments by the metastable loss of ethylene to give the even electron $MeMH_2^+$ ion (35.8% for C, 11.9% for Si, 5.2% for Ge, absent for Sn and Pb (119)) or fragments by the successive loss of two methyl radicals to

$$Me_4M^{+\cdot} \xrightarrow{-Me\cdot} Me_3M^+ \xrightarrow{-C_2H_4} MeMH_2^+$$

give the MeM^+ ion. Other hydride ions (Me_2MH^+, MH_3^+) have been observed but the fragmentation routes mentioned are of major importance.

When the alkyl groups are larger than methyl an alternate route is responsible for the formation of the fragment ions of the type RMH_2^+ and R_2MH^+. This process involves the loss of an olefin from the initially formed R_3M^+ ions. The mass spectrum of tetraethylsilane (124) serves as a typical example (the relative intensity of the ion is shown below the ion; a * denotes a metastable process). The intensities of the ions formed by this process vary with the central metal atom and

$$\underset{(8)}{Et_4Si^{+\cdot}} \xrightarrow[*]{-29} \underset{(82)}{Et_3Si^+} \xrightarrow[*]{-28} \underset{(100)}{Et_2SiH^+} \xrightarrow[*]{-28}$$

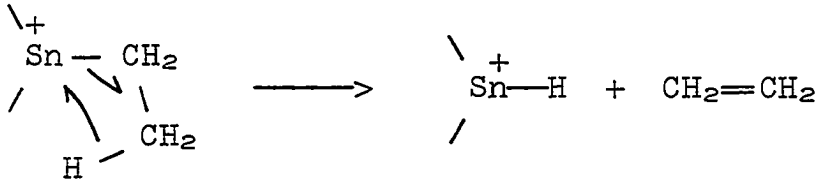
$$\underset{(35)}{EtSiH_2^+} \xrightarrow[*]{-28} \underset{(6)}{SiH_3^+}$$

with the size of the alkyl groups. Again the even electron ions comprise most of the ion current (in the example above the ions shown are 81% of the total ion current) and very little fragmentation of the alkyl groups is observed.

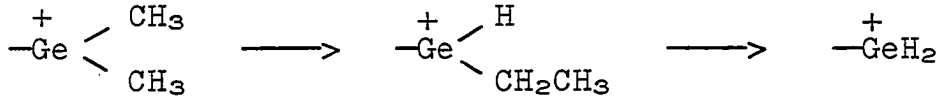
As expected, both of the above processes are observed in the mass spectra of Group IVB organometallics in which varied alkyl groups are attached to the metal. The ion intensities for a particular process are dependent upon the size and branching of the alkyl groups and upon the metal atom. Again ethylene elimination from even electron ions with at least two methyl groups is common as is olefin elimination when larger alkyl groups are present. The substitution of aryl groups for some or all of the alkyl groups makes the molecular ions more intense but even electron ions still dominate the spectra. A limited amount of fragmentation involving the aromatic portion of the molecule is observed (either the loss of H· or C_2H_2) and in mixed arylalkyl compounds the alkyl groups are lost much more readily from the molecular ions. Similarly, the substitution of an unsaturated acyclic group for one of the alkyl groups does not affect the basic fragmentation pattern and does not become involved in separate fragmentation processes (130).

Possible mechanisms for olefin elimination from the even electron ions observed in the mass spectra of Group IVB organometallics have been suggested, although no labeling

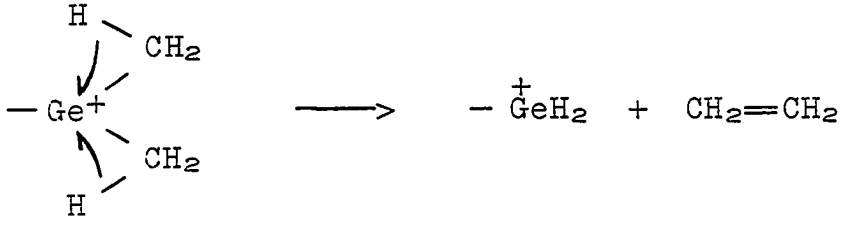
studies have been conducted to determine the origin of the transferred hydrogen atoms. The loss of ethylene from ethyl substituted stannanes has been postulated to occur by transfer of a β-hydrogen atom back to the metal atom with concurrent formation of the olefin (128). The loss of ethylene



from dimethylalkylgermyl ions has been postulated to occur by initial rearrangement to an alkyl-ethyl-hydrogen substituted metal atom followed by the elimination of the olefin or to



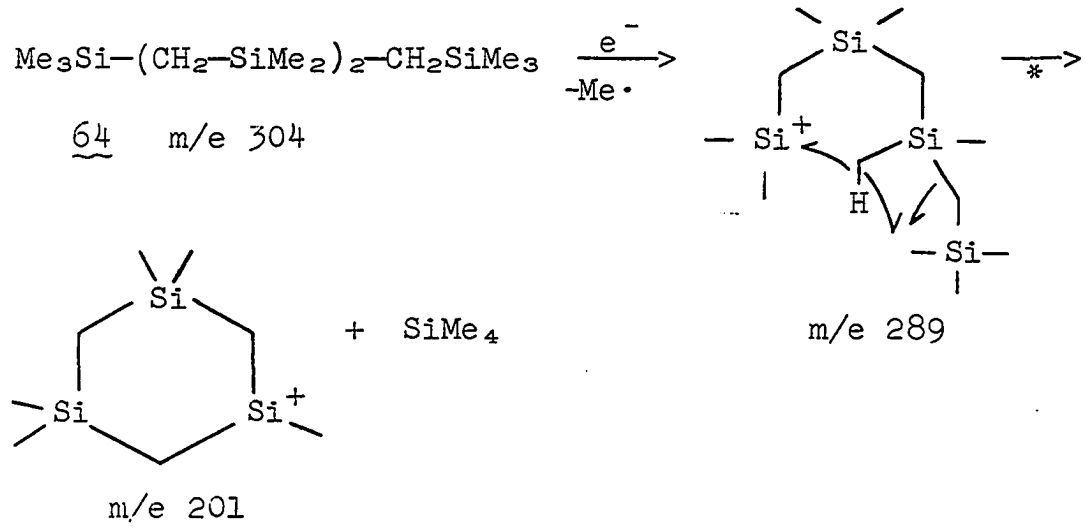
involve the transfer of one hydrogen atom from each methyl group back to the metal atom (129).



In addition to cleavage and olefin elimination processes which are observed in the mass spectra of simple organometallic compounds, more complex fragmentations which result from

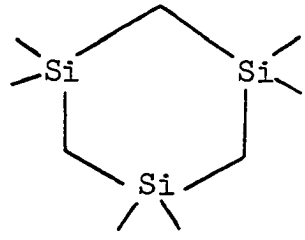
skeletal rearrangements have been observed in cyclic organometallic compounds and in compounds containing more than one metal atom.

A mass spectral study of both linear and cyclic compounds which contain alternating methylated silicon atoms and methylene units has been conducted (131-133). Again typical C-Si bond cleavage processes are evident. The loss of a methyl radical is responsible for the base peak in the cyclic compounds but in the linear compounds this initial loss of a methyl radical is followed by the metastable loss of 88 mass units (Me_4Si) to give the base peak. Although no labeling studies have been conducted and alternate rearrangement processes could account for the observed fragmentations, Beynon (3, p. 420) has suggested the following mechanism for this rearrangement in octamethylsilanonane (64). The metastable



loss of Me_4Si is also observed from the ion at m/e 217 (M-87)

in the mass spectrum of 64 and can also be formulated as having a cyclic structure (3, p. 420). The above mechanism would be in agreement with the observation that the cyclic compounds, e.g., 65, have somewhat more intense molecular ions and that the base peak in their mass spectra corresponds to the loss of



65

a methyl radical from the odd electron molecular ion. The second most intense ion in the mass spectra of these cyclic compounds arise by the loss of Me_4Si from the $(M-15)^+$ ion.

The involvement of the methylene units in this unusual loss of Me_4Si from the alternating Si-C compounds is not required and alternate rearrangement mechanisms may be operative. An investigation of cyclicpolysilanes of the type $(R_2Si)_n$ (R = Ph, n = 4, 5, 6; R = Me, n = 5, 6, 7)[a] in which there are no methylene units showed similar fragmentation processes occurred in these compounds. These compounds give surprisingly intense molecular ions, particularly the permethylated

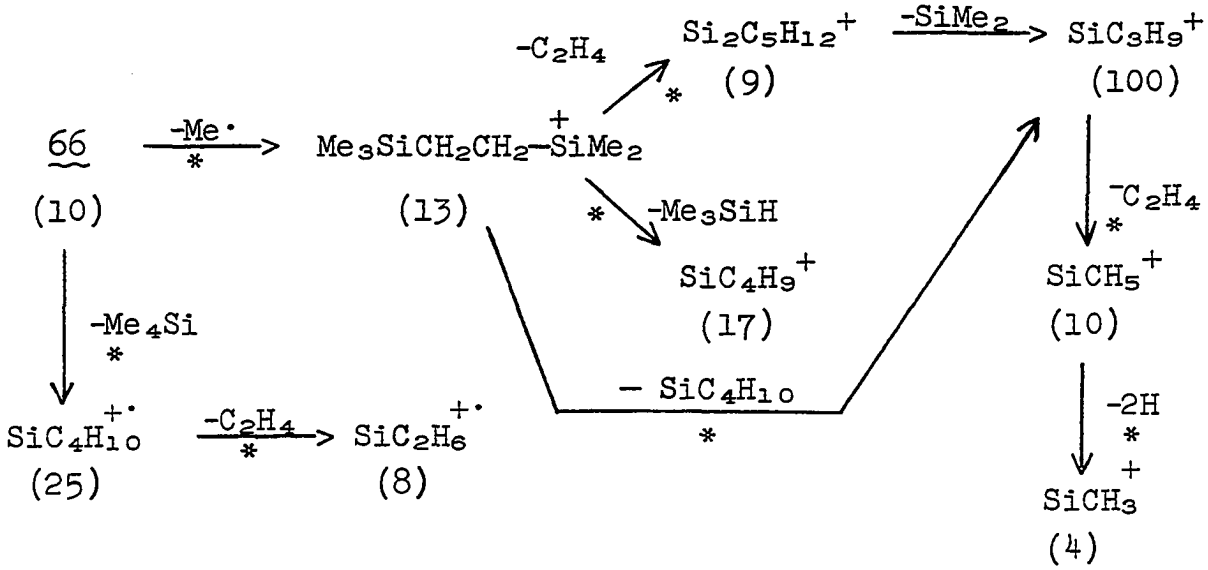
---

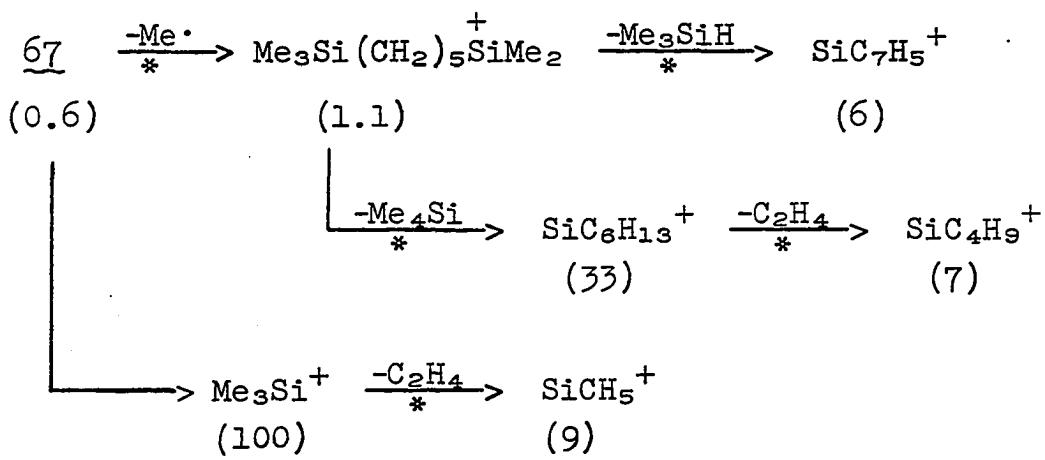
[a]T. H. Kinstle, Ames, Iowa. Private communication. 1968.

derivatives (53% for Si_5, 55% for Si_6, 31% for Si_7), and this may indicate an unusually high stability of these odd electron ions. The base peak in the mass spectra of all of the cyclic polysilanes studied is the rearrangement ion, R_3Si^+. The most interesting process observed, however, is the loss of tetra-substituted silanes from the ions formed by the loss of Me_3Si from molecular ions of the permethyl polysilanes. Depending upon the number of silicon atoms in the ring the $(M-SiMe_3)^+$ ions undergo the metastable loss of either $MeSiH_3$ (n = 5), Me_2SiH_2 (n = 5,6), or Me_3SiH (n = 6,7). These fragmentations must involve rearrangement and it is also interesting to note that they are not limited to even electron ions since the metastable loss of Me_3SiH (n = 5) or Me_4Si (n = 6) is observed from the appropriate molecular ion. The molecular ion of the heptasilane undergoes the metastable loss of Si_2Me_5 which is followed by the loss of either Me_2SiH_2 or Me_3SiH. Another interesting aspect of the mass spectra of these cyclic polysilanes is the loss of Ph_2Si units from the molecular ions as well as even electron fragment ions in the mass spectra of the perphenyl compounds.

Similar rearrangement processes were also observed in a mass spectral investigation of a series of α,ω-bis-trimethylsilylalkanes ($Me_3Si(CH_2)_nSiMe_3$, n = 1-6) (134). The authors made no attempt to assign structures to the fragment ions or to define the mechanisms of the rearrangement processes. The

fragmentation schemes of 1,2-bis-trimethylsilylethane (66) and 1,5-bis-trimethylsilylpentane (67) are outlined below. The

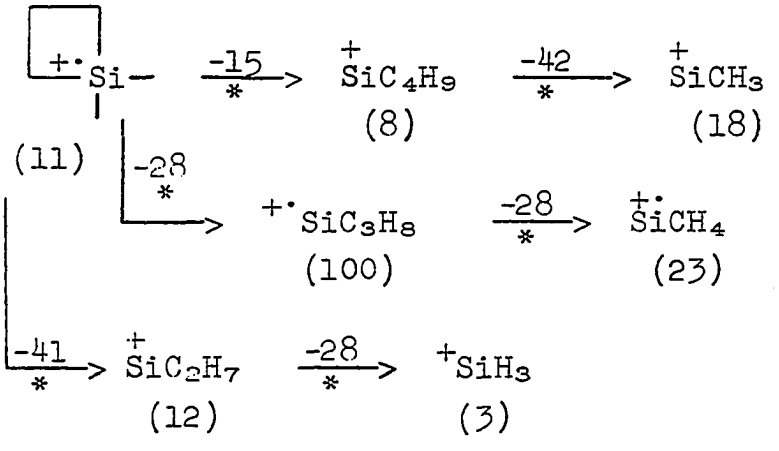


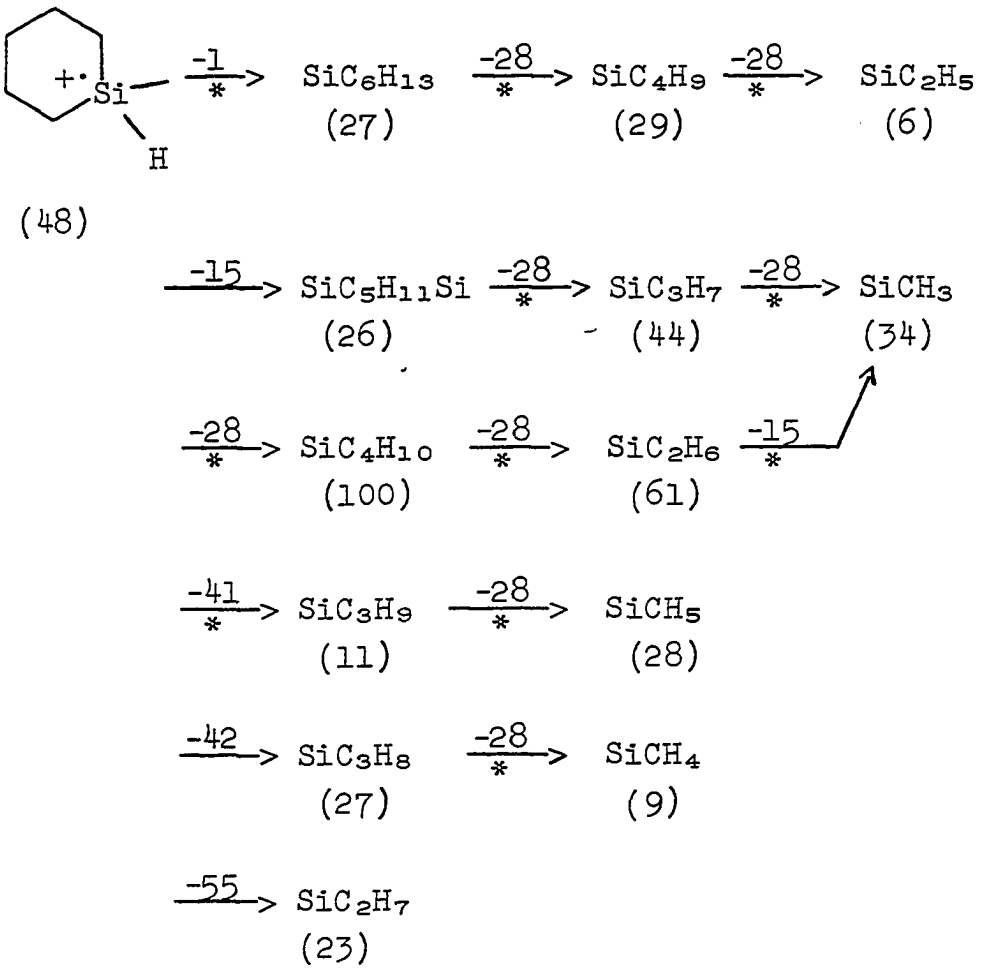


other compounds are quite analogous with a gradual change noticed going from the shorter to the longer chain compounds. The structures of many of the ions are unknown and reasonable cyclic and/or acyclic structures might be proposed. An investigation of selectively labeled compounds in this series

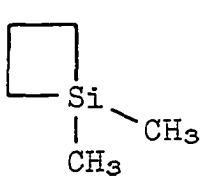
would be very informative as to the origin of the transferred methyl groups and/or hydrogen atoms but such an investigation has not been carried out. It is interesting to note that the loss of Me_4Si and Me_3SiH is again observed from both odd and even electron ions, and these fragmentation processes are quite similar to those discussed previously. It should also be pointed out that in the compounds with 2 or 3 methylene units reasonably intense odd electron ions are formed by the sequence $M^{+\cdot} \longrightarrow (M - 88)^{+\cdot} \longrightarrow (M - 88 - 28)^{+\cdot}$.

The mass spectra of a series of silacycloalkanes ($(CH_2)_nSiRR'$, n = 3, 4, 5 R = R' = Me; n = 4, 5, R = Me, R' = H) has also been investigated (135). These compounds again show typical C-Si bond cleavage processes but the most remarkable feature of their mass spectra is that the base peak is an odd electron formed by the metastable loss of ethylene

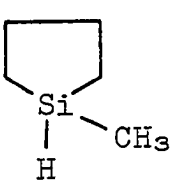




from the molecular ions. Again no labeling work was conducted and the structure of the fragment ions is open to speculation. The authors point out that the mass spectra of 68 and 69 are practically identical and suggest that a ring



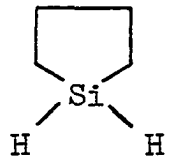
68



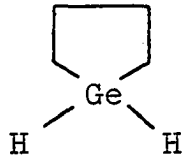
69

expansion rearrangement may be occurring in the molecular ion of 68 to give the same ion as is formed from 69 upon electron impact.

An earlier study of the effect of different heteroatoms upon the fragmentation of five-membered heterocycles (136) had shown that the base peak in the mass spectrum of silacyclopentane (70) was also the odd electron ion formed by the

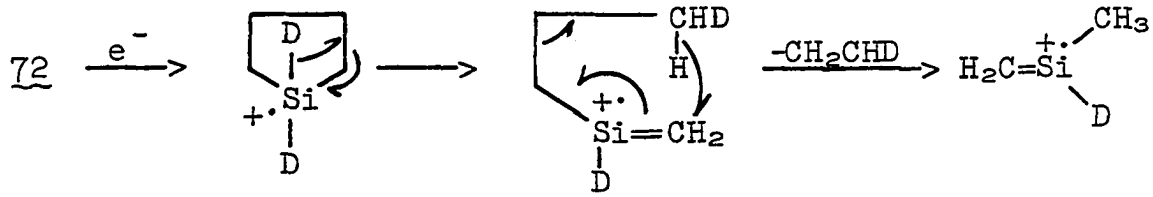


70

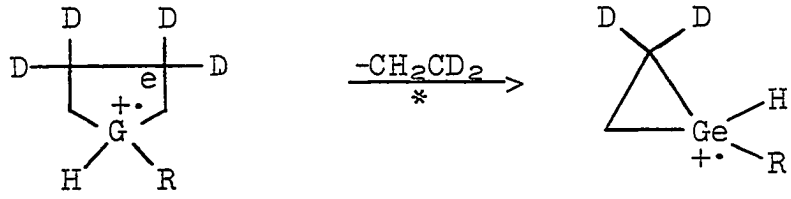


71

metastable loss of ethylene from the molecular ion. A similar loss of 28 mass units from the molecular ion was observed in the mass spectrum of germacyclopentane (71) although it was not the base peak in the spectrum. The observation that 1/3 of the ethylene units lost from silacyclopentane-1,1-d_2 (72) included one deuterium atom led Djerassi and his co-workers to suggest the mechanism shown below (136).



A recent reinvestigation of the mass spectra of germacyclopentanes and germacyclopentenes by Djerassi and co-workers (137) led to the postulation of an alternate mechanism for the observed loss of ethylene from 1-alkyl- or 1,1-dialkyl germacyclopentanes. The mass spectra of a series of alkylgermacyclopentanes-3,3,4,4-d_4 shows that only C_2 and C_3 are involved in this fragmentation and these authors suggest that the ions formed by this process have a germacyclopropane structure, 73. They do not comment on the discrepancy



73

between this mechanism and that previously suggested for the fragmentation of silacyclopentane although it seems very reasonable to this author that the two compounds undergo the loss of ethylene by the same mechanism. The observed deuterium incorporation in the loss of ethylene from silacyclopentanes as well as the results with the deuterated germacyclopentanes would both be compatible with a mechanism in which the hydrogen atom on the metal and the hydrogen atoms on either C_2 or C_5 undergo partial scrambling. Additional labeling experiments would again be very informative.

Another interesting rearrangement process in the mass spectra of Group IVB organometallics has recently been reported (138). The investigation of a series of compounds of the type $A_3MM'B_3$, where A and B are alkyl or aryl groups and M and M' are Si, Ge, or Sn, has revealed that these compounds produce ions which result from the transfer of groups A and B from one metal atom to the other, e.g., $A_3MM'B_3 \rightarrow A_2MB^+$, AMB_2^+, MB_3^+, $B_2M'A^+$, $BM'A_2^+$, $M'A_3^+$. These ions are not very intense and typical cleavage processes comprise most of the ion current. These authors also report that a similar scrambling of groups does not occur in compounds in which the metal is replaced by carbon. A similar scrambling of ligands is observed in other organometallic compounds of the type $\emptyset_3SnFe(CO_2)\pi\text{-}C_5H_5$ (139, 140).

RESULTS AND DISCUSSION

This investigation of mass spectral rearrangements of organosilanes has two objectives. We wanted to determine whether or not organosilanes would undergo a typical McLafferty rearrangement upon electron bombardment and of more importance to gain some preliminary knowledge of the mechanisms by which gaseous organosilyl ions lose ethylene and other olefins.

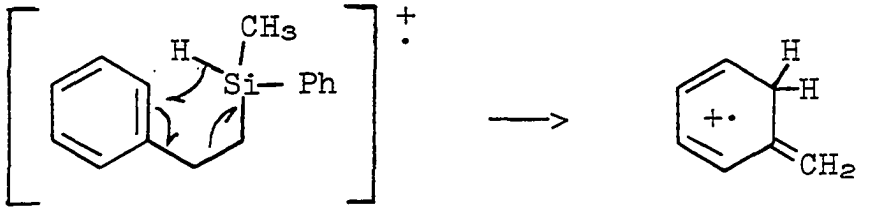
McLafferty Rearrangement

A very common and well documented rearrangement in organic mass spectrometry is the fragmentation of odd electron ions by the transfer of a γ-hydrogen atom to the radical-cation center followed by, or concurrent with, the cleavage of the β-bond. This process is commonly called the McLafferty rearrangement and a typical example is the formation of the m/e 92 ion in the mass spectrum n-butylbenzene (4, p. 508, 99, p. 122).

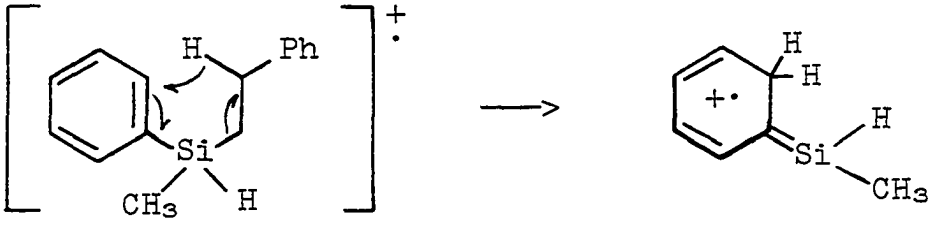
m/e 92

In an attempt to determine whether or not a silicon atom would participate in this rearrangement, we investigated the

mass spectra of a series of compounds related to methylphenyl-2-phenylethylsilane (74). As shown below, this



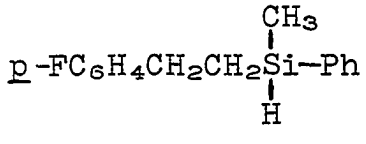
74 m/e 226 m/e 92



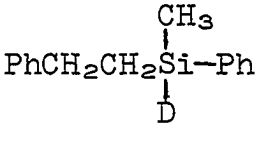
74 m/e 226 m/e 122

compound is a priori capable of undergoing the McLafferty rearrangement by transfer of hydrogen from silicon or by cleavage of a Si-C bond.

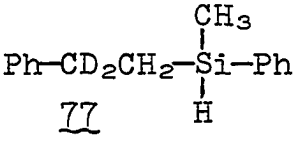
Investigation of the mass spectra of 74, 2-(4-fluorophenyl)-ethylmethylphenylsilane (75), methylphenyl-2-phenylethylsilane-d (76), and methylphenyl-2-phenylethyl(2,2-d_2)-silane (77) was inconclusive with regard to the occurrence of



75



76

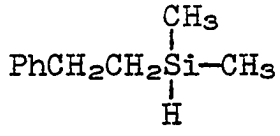


77

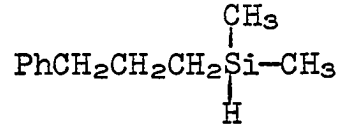
the McLafferty rearrangement in these compounds and will not be discussed further.

A very surprising observation was noticed in the mass spectrum of 74. The molecular ion underwent the metastable loss of the elements of benzene to give the base peak in the spectrum at m/e 148, an odd electron ion. Investigation of the mass spectrum of 75, in which the p-fluoro substituent should have no effect (141) showed that the phenyl group involved in this fragmentation was that originally attached to the silicon.

Attempts to explain this unusual formation of the odd electron ion formed by the loss of benzene from the molecular ions of 74 and 75 was greatly complicated by the observation that dimethyl-2-phenylethylsilane (78) and dimethyl-3-phenylpropylsilane (79) also undergo the metastable loss of benzene to give intense peaks in their mass spectra. The mechanism



78



79

by which these rearrangements occur and the structures of the odd electron ions formed by these processes must await more extensive labeling studies.

Olefin Elimination

One of the most interesting rearrangements observed in the mass spectra of Group IVB organometallics is the facile loss of 28 mass units ($CH_2{=}{=}CH_2$) from dimethylalkylmetal fragment ions. In an attempt to explore the mechanism of this process we decided to investigate in some detail the mass spectrum of phenyltrimethylsilane (80). The phenyl substituted silane was chosen for study since the aromatic nucleus would help stabilize the molecular ion as well as other ions in the spectrum and the aromatic ring would not be expected to undergo any fragmentation processes other than the loss of acetylene units. The silicon compound was selected for study rather than the germanium or tin analog because of its availability and because the preparation of various labeled silanes appeared to be more feasible than the other Group IVB organometallics. The complications in interpretation of mass spectra caused by the presence of the various isotopes of Ge and Sn were also considered in selecting the silicon compound. In addition, the tendency for rearrangement ions to be formed in the mass spectra of germanes and stananes is somewhat less (vide infra).

The mass spectrum of 80 is given in Table 8. The base peak in the spectrum is the even electron ion at m/e 135 which may be formulated as 81. This ion, 81, is formed by the loss of a methyl radical from the odd electron molecular ion and is the only metastable fragmentation (Table 9) of the molecular

Table 8. Partial mass spectrum of phenyltrimethylsilane[a,b,c]

m/e	Intensity %	m/e	Intensity %	m/e	Intensity %
150	7.0	91	2.2	57	1.3
135	100.0	83	0.9	55	1.6
133	0.6	81	1.0	53	4.4
131	0.5	79	1.8	51	1.2
121	1.2	77	1.1	50	0.5
119	2.5	74	1.3	45	2.3
117	0.6	73	2.0	43	10.0
109	1.0	69	0.9	42	0.5
107	4.4	67.5	4.3	39	0.9
105	6.4	67	1.6		
103	0.6	66	0.9		
95	0.7	65	1.0		
93	2.0	59	1.0		

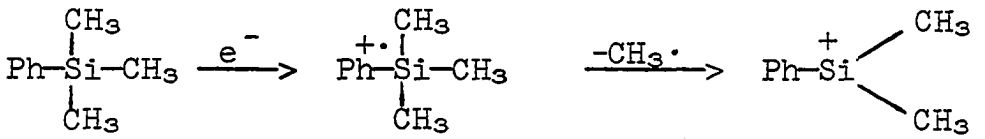
[a]All ions >0.5% relative intensity with m/e >30 at 70 ev and employing the heated inlet (source temperature 200°).

[b]The spectrum exhibits only minor variations when measured at a source temperature of ca. 80°.

[c]The reported spectrum agrees very well with that previously reported (131).

ion. This loss of a methyl radical is not unexpected since in the mass spectra of organosilanes the even electron ions comprise a very large part of the ion current (119, 3, p. 418)

(116), p. 313)[a]. That this ion at m/e 135 is formed in an energetically favored process is evident since its intensity



80 m/e 150 (7.0) 81, m/e 135 (100.0)

equals that of the molecular ion at 10 ev.

The m/e 135 ion undergoes five metastable fragmentations: (1) the loss of hydrogen to give the m/e 133 ion; (2) the loss of a second methyl radical to give the odd electron ion at m/e 120 (0.4%), which then loses the third methyl radical to give the $C_6H_5Si^+$ ion at m/e 105; (3) the loss of acetylene to give the m/e 109 ion; (4) the loss of methane to give the ion at m/e 119; and (5) the loss of ethylene to give the m/e 107 ion.

Although the structure of the ion at m/e 119 is not known, comparison of its intensity with the intensity of the corresponding ion in the mass spectra of phenyltrimethylgermane, phenyltrimethylstannane, and t-butylbenzene (Table 10) shows that the intensity of this ion parallels the expected stability

---

[a]Note (Table 8) that the molecular ion is one of the few odd electron ions observed in the mass spectrum of 80.

Table 9. Observed metastable ions in the spectrum of 80

Transition	Metastable
150 → 135	121.3
135 → 133	131.1
135 → 120	106.7
135 → 119	105.0
135 → 109	88.0
135 → 107	84.8
135 → 91	61.3[a]
133 → 131	129.1
121 → 119	117.1
120 → 105	91.9
119 → 93	72.7
109 → 83	63.2
107 → 105	103.1
107 → 81	61.3[a]
105 → 103	101.1
105 → 79	59.4
91 → 65	46.4
93 → 67	48.3

[a]Results with labeled compounds indicate that the 107 → 81 transition is primarily responsible for the metastable ion at m/e 61.3.

Table 10. Partial mass spectra of $PhM(CH_3)_3$[a,b]

m/e	Relative Intensity			
M =	C	Si	Ge[c]	Sn[d,e]
P^+	20.4	6.0	5.6	1.6
P-15	100.0	100.0	100.0	100.0
P-30	1.4	0.3	0.3	1.2
P-31	5.0	2.2	2.2	0.7
P-43	59.8	3.9	---	---
P-45	1.0	5.3	17.3	33.0

[a]All ions with intensity >1% of the base peak with m/e >P-46.

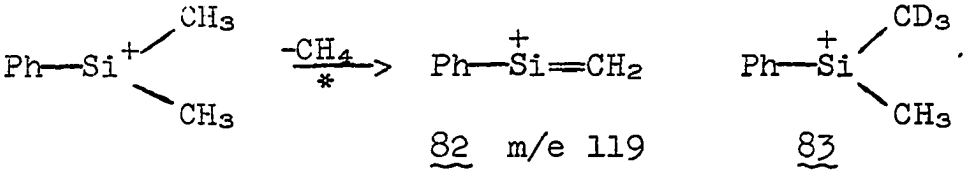
[b]All spectra were recorded at 70 ev and the same instrumental conditions were employed.

[c]Normalized to ^{74}Ge.

[d]Normalized to ^{120}Sn.

[e]The reported spectrum is in agreement with that previously reported (126).

of an elusive (142, 143) doubly bonded species 82. Furthermore, label retentions in the m/e 119 ion from 83 (vide infra)



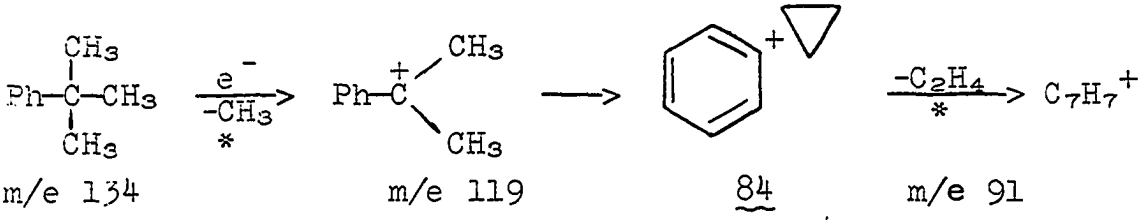
would lend support for the loss of methane involving only the

two methyl groups in 83.

It is also interesting to note the continual decrease of molecular ion relative stability and the increase of the P-45 relative intensity with increasing size of the metal atom. This trend has also been observed in tetraalkylorganometallics and has been attributed to increase of polarizability and the resulting decrease of stability of the metal-carbon bond (124).

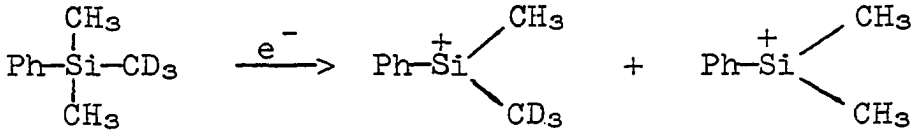
The most interesting feature of the mass spectrum of 80 is the last mentioned fragmentation of the m/e 135 ion, the loss of ethylene to give the m/e 107 ion whose formation is accompanied by an intense metastable (Table 9). This fragmentation is also important at low electron energies and is 1.2% of m/e 135 at 18 ev.

A mass spectral investigation of the carbon analog of 80, t-butylbenzene, has led to the postulate that a symmetrical phenylated cyclopropane 84 is an intermediate in the metastable formation of the $C_7H_7^+$ ion by the loss of ethylene from the M-15 ion (144, 4, p. 511). A similar intermediate, a phenylated silacyclopropane, could also be invoked to explain this interesting loss of ethylene from the m/e 135 ion in the mass spectrum of 80.



m/e 134 m/e 119 84 m/e 91

The possibility that such an intermediate was involved was first tested by isotopic labeling. The trideuterio derivative 85 was prepared and its mass spectrum showed that



85 m/e 138 m/e 135

following the loss of either $CD_3\cdot$ or $CH_3\cdot$ (to give ions at m/e 135 and 138 in the ratio of 1:2) ethylene with varying amounts of deuterium was lost to produce ions at m/e 107, 108, and 109. Due to superimposition of ions formed by different routes, it was not possible to interpret these results in an unambiguous manner. It was clear, however, that hydrogen rearrangements were not occurring prior to the loss of the first methyl group since no ions (other than expected isotopic species) were observed at m/e 136 and 137 and that the aromatic ring hydrogens were not involved in these processes ($M^+ \rightarrow 135 \rightarrow 107$) since no ion at m/e 110 ($138-C_2H_4$) was observed. This is in direct contrast to the mass spectrum of pentafluorophenyltrimethylsilane (145) in which various fragments with fluorine attached to silicon are observed.

In order to circumvent the problems associated with the calculation of label retention in the ions at m/e 107, 108, and 109 from 85, the disilane 86 and its deuterated analog 87 were prepared and their mass spectra were measured (Table 11).

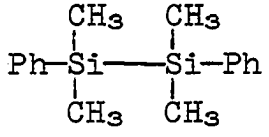
Table 11. Mass spectra[a] of 86 and 87

m/e	Relative Intensity	
	86	87[b]
276		7.2
270	9.2	
261		1.5
258		1.0
255	3.1	
200		7.2
197	15.0	7.2
195	1.0	1.5
141		1.5
138		100.0
135	100.0	1.5
123		0.6
122		0.7
121		0.7
120	1.1	0.8
119	2.3	1.1
112		0.6
111		0.3
110		0.6
109	0.9	1.4
108		2.3
107	4.4	1.5
106		1.2
105	5.9	5.7

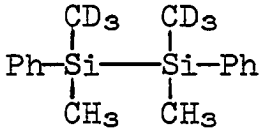
[a]All ions >m/e 100 at 70 ev.

[b]Ion intensities at m/e 105-123 uncorrected for ^{29}Si, ^{30}Si, ^{13}C, and 3.9% d_5 species due to presence of isobaric ions.

The base peak in the spectrum of 86 is the result of cleavage of the silicon-silicon bond to give the ion at m/e 135. This

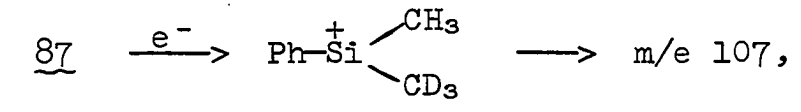


86



87

ion then undergoes the same fragmentations as the m/e 135 ion from phenyltrimethylsilane. In the mass spectrum of the deuterated compound, 87, the base peak is shifted cleanly to m/e 138 and this ion then loses C_2H_3D, $C_2H_2D_2$, and C_2H_3D[a] in relative amounts of 24.1:50.0:25.9[b] to give ions at m/e 109, 108 and 107, respectively. Two facts follow from the



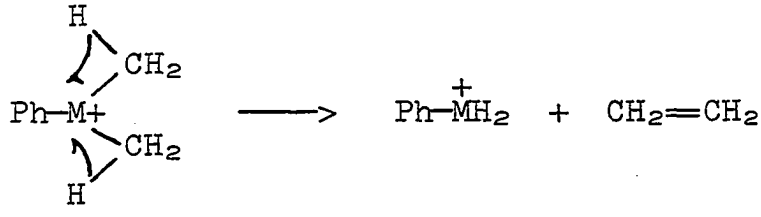
---

[a]Metastables at 86.1, 84.5 and 83.0

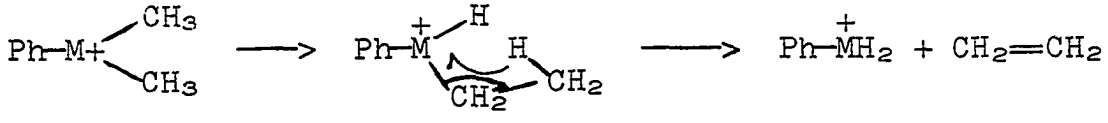
[b]Calculated from the 26 ev spectrum. The ion at m/e 109 in the unlabeled compound is the result (metastable at 88.1) of the loss of acetylene and is assumed to involve only the aromatic ring. This ion is shifted to m/e 112 (138→112, m* at 90.9) in the spectrum of 87 and does not effect the calculated ratio. Similarly the ion at m/e 105 must be $PhSi^+$ and since the hydrogen atoms of the aromatic ring do not become involved in the randomization the intensity of the ion at m/e 107 can be readily corrected for the isotopic contribution of the ion at m/e 105.

observation that this ratio of label retentions is not skewed. The equality of the label retention in the d_0 and d_2 species points out that a significant isotope effect is not operative in this randomization, although small (0.5-1.0) deuterium isotope effects have been observed in mass spectrometry (146). This symmetrical ratio also points out that the aromatic ring protons are not involved in this randomization since an equal number of hydrogen and deuterium atoms must be involved.

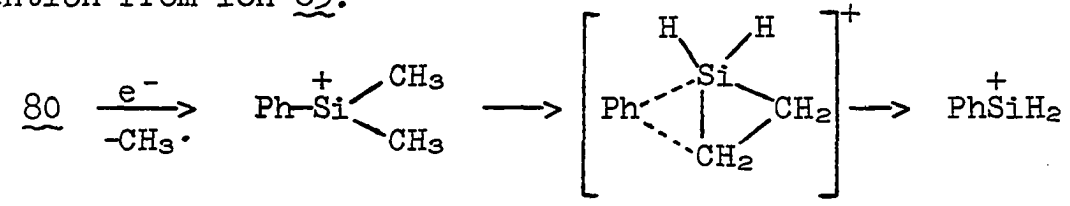
The mechanisms which have been postulated to be responsible for this loss of ethylene from dimethylalkyl or dimethylaryl ions in the mass spectra of Group IVB organometallic compounds will not account for the observed randomization. Transfer of a hydrogen atom to the metal atom from each methyl group with the concurrent loss of ethylene (129) would predict that the



trideuterio ion should fragment by the loss of $CD_2{=}CH_2$ to give only the d_1 species. Similarly, a simple rearrangement to an ethylphenylsilane ion followed by the loss of ethylene, a rearrangement which has also been suggested (129), would predict that only d_1 species would be formed.

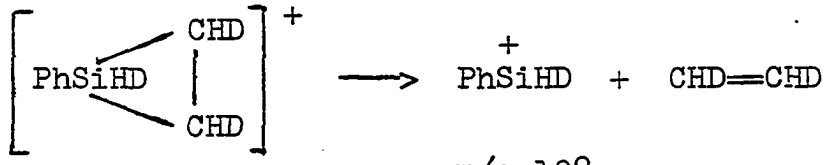


The intermediacy of a phenylated silacyclopropane (88) was at first thought to be responsible for the observed label retention from ion 83.

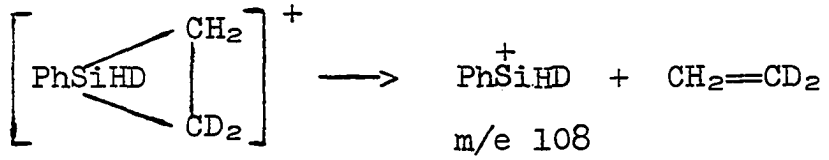


88

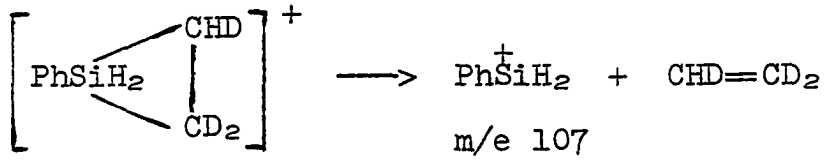
Consideration of the various labeled isomers (disregarding stereoisomerism and assuming that the 2 carbon atoms involved are indistinguishable) would predict that the label retention would be in the ratio of 1:2:1.



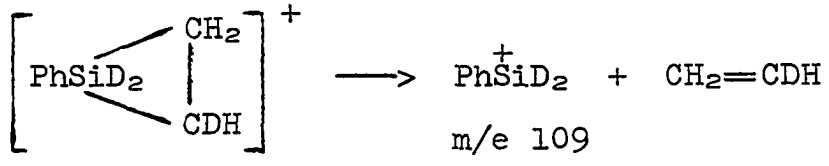
m/e 108



m/e 108



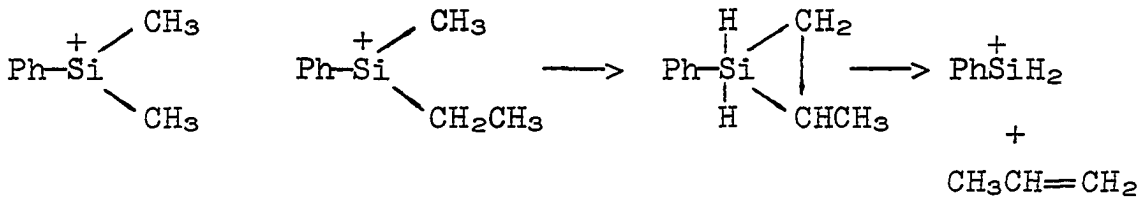
m/e 107



m/e 109

In an attempt to substantiate the intermediacy of the phenylated silacyclopropane in the loss of ethylene from 81, we investigated the mass spectra of silanes which would readily

form the ethylmethylphenylsilyl ion, 89. If a phenylated silacyclopropane intermediate is involved in this rearrangement, it would be expected that 89 would undergo the



81 89 m/e 149

metastable loss of propene to give the same m/e 107 ion as is observed in the mass spectrum of phenyltrimethylsilane. This would be analogous to the formation of $C_8H_9^+$ and $C_7H_7^+$ from 3-ethyl-3-phenylpentane (4, p. 513).

The mass spectrum of diethylmethylphenylsilane (Table 12) exhibits an intense ion at m/e 149 (89) and a reasonably intense ion at m/e 107. However, there is no metastable at 76.9 for the process 149 → 107 and there is a metastable supported pathway (M^+ → 163 → 135 → 107) for the formation of the ion at m/e 107 from the ion formed by the initial loss of a methyl radical from the molecular ion (Scheme 2).

In an attempt to overcome the difficulty presented by this alternate route to m/e 107, 1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane (90) was prepared. The mass spectrum of 90 (Table 13) exhibits an intense ion at m/e 149, but again no metastable is apparent for m/e 149 → m/e 107 and the same alternate route to 107 is available as a result of the

Table 12. Mass spectrum of diethylmethylphenylsilane[a]

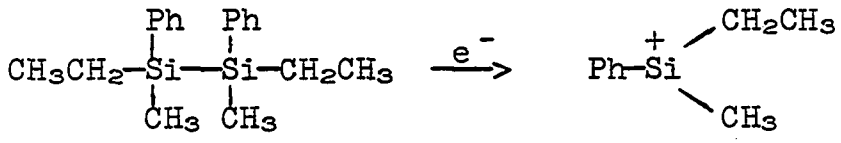
m/e	Relative Intensity	m/e	Relative Intensity
178	1	121	100
163	1	120	2
149	53	119	3
137	3	107	10
135	5	105	11

[a]All ions with m/e >100 and relative intensity of at least 1% of the base peak at 70 ev.

Table 13. Mass spectrum of 1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane[a]

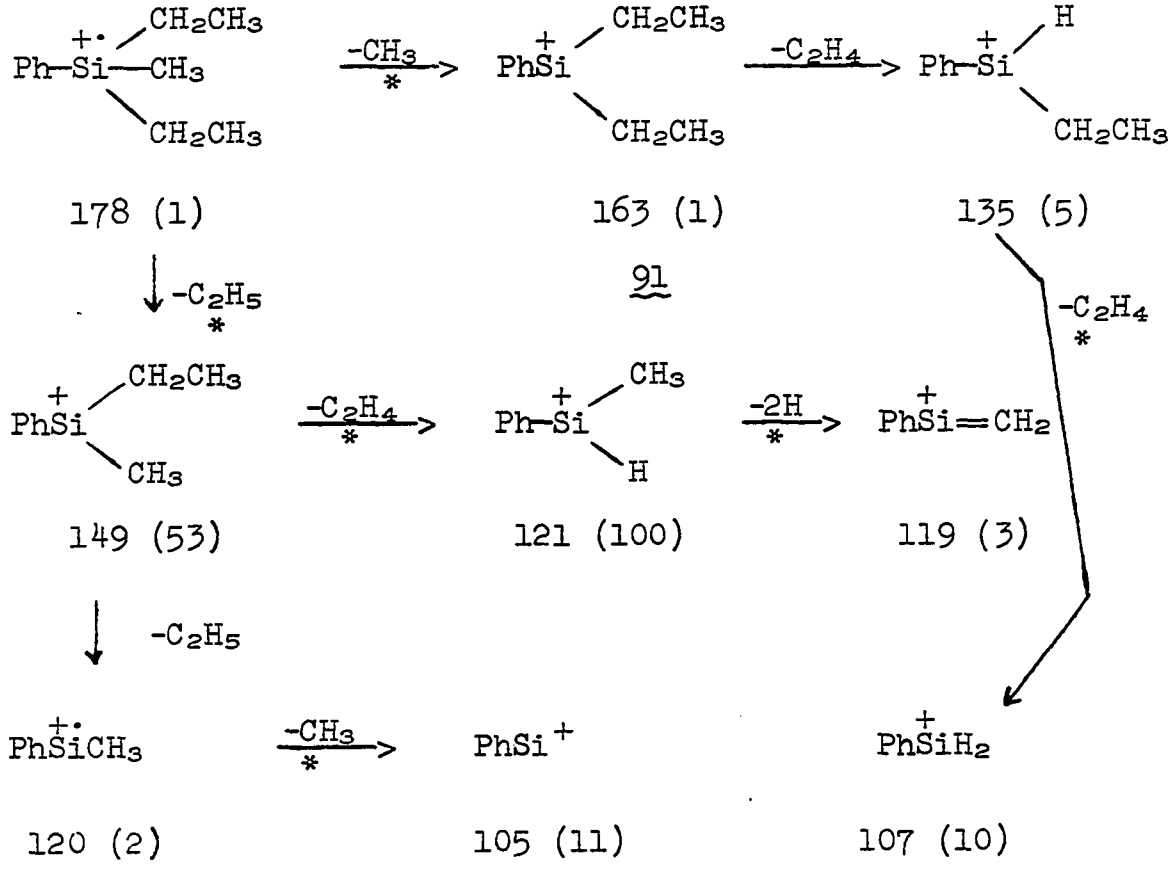
m/e	Relative Intensity	m/e	Relative Intensity
298	9	149	51
269	6	148	3
241	15	135	6
227	2	121	100
211	6	120	3
197	8	119	3
183	3	107	3
163	2	105	16

[a]All ions with relative intensity >2% and m/e >100 at 70 ev.



90

rearrangement of the alkyl and aryl groups in the molecular ion (*vide infra*).



Scheme 2. Fragmentation of diethylmethylphenylsilane.

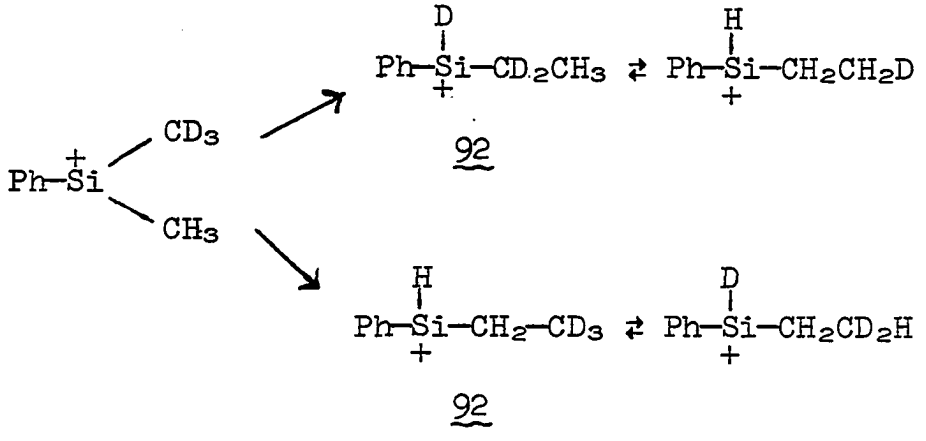
The absence of the metastable for the m/e 149 → m/e 107 fragmentation, although not surprising since the alternate pathway for the formation of m/e 107 by the successive loss of ethylene units from the diethylphenylsilane ion (91) would be expected from previous mass spectral studies of organosilanes, would indicate that the phenylated silacyclopropane is not involved in the loss of ethylene from the dimethylphenylsilyl ion in the mass spectrum of phenyltrimethylsilane.

It also became apparent that the formation of a phenylated silacyclopropane intermediate in this fragmentation should either result in complete randomization of the three hydrogens and three deuteriums in the mass spectrum of 87, or that only one deuterium should be retained in the $PhSiH_2^+$ ion. Complete randomization of hydrogen and deuterium prior to the loss of ethylene from the symmetrical phenylated silacyclopropane would predict a ratio of 1:3:1 for the label retentions in the ions at m/e 107, 108 and 109. Similarly, any other mechanism which would result in complete randomization of hydrogen and deuterium prior to the loss of ethylene, irregardless of the intermediates involved, should give d_0, d_1, and d_2 species in the ratio of 1:3:1.

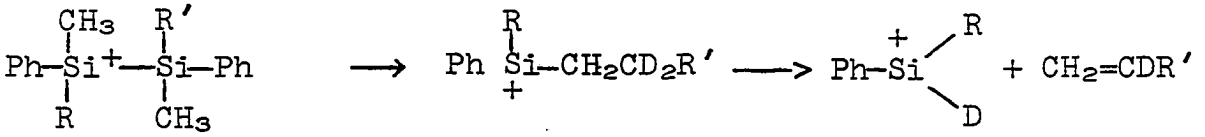
Although various mechanisms can be written for the loss of ethylene from the dimethylphenylsilyl ion, it is very difficult to arrive at a mechanism which will give the observed 1:2:1 ratio. The possibility that two or more mechanisms may be

operating simultaneously was considered as a possibility, but the observation that the 1:2:1 ratio was independent of electron energies from near the appearance potential of the m/e 107 ion (22 ev) to 31 ev tends to indicate that a single mechanism is operative. The extent of label retention should be energy dependent near the appearance potential of the ion if a dual mechanism were responsible for this randomization. The ratio of 1:2:1 is also the same with source temperatures of 80° and 200° indicating that a thermal process is not responsible for the randomization.

Consideration of the 20 permutations for 3 hydrogen atoms and 3 deuterium atoms attached to 1 silicon atom and 2 carbon atoms pointed out that one mechanism which could account for the observed randomization of hydrogen and deuterium prior to the loss of ethylene would involve initial rearrangement to an ethylphenylsilane ion (92) followed by or concurrent with the complete randomization of the hydrogen (deuterium) attached to silicon and the three β hydrogens (deuterium). Fragmentation of these ions would then give ions at m/e 107, 108 and 109 in the ratio of 1:2:1 by the transfer of a β hydrogen (deuterium) back to the silicon atom with the simultaneous loss of ethylene. The specificity of this β hydrogen transfer has been documented (vide infra) for dialkylphenylsilyl ions but was not known for ions in which a hydrogen was attached to silicon.



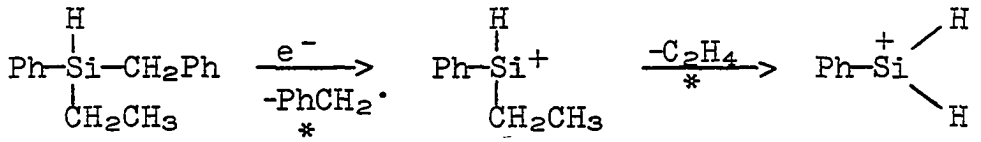
92



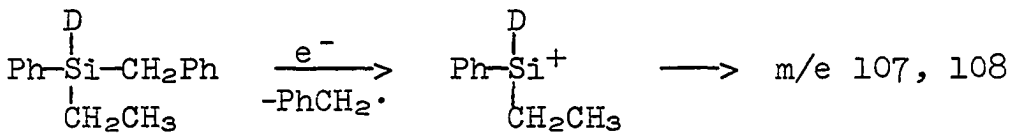
$R = R' = CH_2CD_3$ $R = CH_3, R' = D$ $R' = D$

$R = R' = CH_2CD_2CH_2CH_3$ $R = CH_3, R' = CH_2CH_3$ $R' = CH_2CH_3$

In an attempt to determine whether or not the randomization of hydrogen and deuterium was occurring in the ethylphenylsilane ion, compounds 93 and its deuterated analog 94 were prepared. Complete randomization of the deuterium and the three β-hydrogens in 95 would predict that the ions at m/e 107 and 108 in the mass spectrum of 94 would be of equal intensity. The results from the mass spectrum of 94 are summarized in Table 14. It is obvious that the postulated randomization is not operative since at electron energies above 30 ev the label retention in the ions corresponding to $PhSiH_2^+$ is identical to the label retention in the $PhSiHC_2H_5^+$

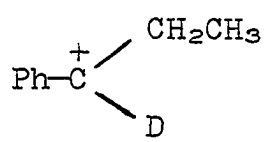


93 135 (88) 107 (100)



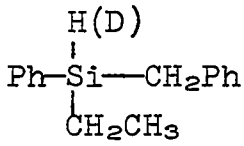
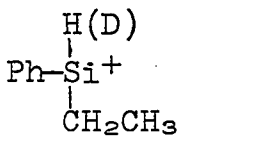
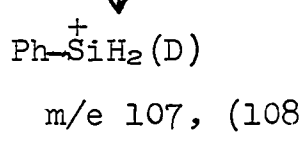
94 95

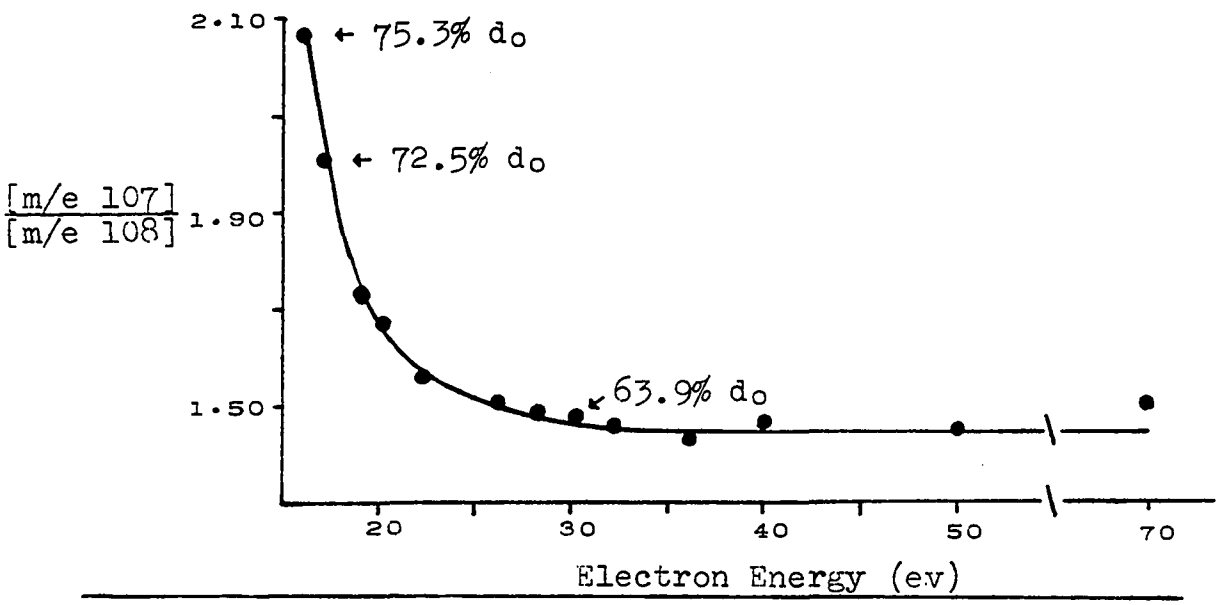
ions. The energy dependence of this label retention below 30 ev implies that at least two mechanisms are operative for the formation of m/e 107 in the mass spectrum of 94. It is interesting to note that the label retention in the ion formed by the loss of ethylene from the analogous carbon ion, 96, is also energy dependent (147).



96

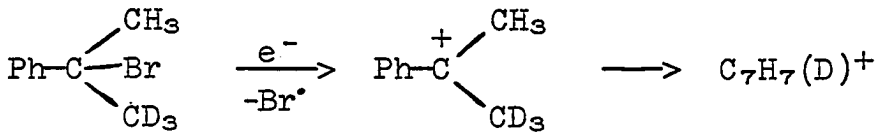
Table 14. Mass spectral label retentions in 94

	53.5% d_0 46.5% d_1	(18 ev)
m/e 226, (227)		
	63.7% d_0 36.3% d_1	(18 ev)
m/e 135, (136)	62.3% d_0 37.7% d_1	(25 ev)
	75.3% d_0 24.7% d_1	(16 ev)
m/e 107, (108)	72.5% d_0 27.5% d_1	(17 ev)
	63.9% d_0 36.1% d_1	(30 ev)



In an attempt to gain further insight into the mechanism of this loss of ethylene from the phenyldimethylsilyl ion a series of substituted phenyltrimethylsilanes was prepared and compared to the results obtained with a series of substituted t-butylbenzenes. By studying the effects of substituents on these mass spectral fragmentations it was hoped that we could apply kinetic arguments for such processes which had been documented by McLafferty and Bursey (23, 24, 25). The results with these substituted compounds are presented in Table 15. Again we are left with anomolous results. The Z/Z_o values do not correlate with Hammet σ or σ^+ values, making the determination of a ρ value for this reaction unobtainable. Although the Z/Z_o values for the meta-para pairs of isomers are nearly the same, they are not in good enough agreement to allow us to conclude that the carbon bound to silicon undergoes loss of positional identity. The variations in the values of Z/Z_o for these compounds could be the result of numerous complications in substituent effect determinations recently discussed by McLafferty (148).

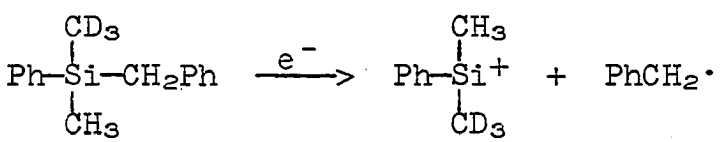
Although this 1:2:1 ratio remains unexplained, it is obvious that no simple mechanism is responsible for the fragmentation of the gaseous dimethylphenylsilyl ion. It is unfortunate that similar deuterium labeling studies have not been carried out for the carbon analog. The synthesis of 97 and a mass spectral study of label retention in the $C_7H_7^+$ ions



97 m/e 122 m/e 91, 92

formed from 97 could be very interesting and informative with regard to the silane work and as a test of the intermediacy of the phenylated cyclopropane in the mass spectra of t-butylbenzene.

It would also be very interesting to explore the mass spectra of other compounds which would give the dimethylphenylsilyl ion. Investigation of alternate precursors to this ion would help determine whether or not this ratio of 1:2:1 is of a general nature or is specific for 87. An excellent silane to investigate would be benzylmethyltrideuteriomethylphenylsilane (98) since the benzyl group would fragment as the radical leaving the charge localized on silicon, and should give 83 with a different energy content.



98 83

Table 15. Substituent effects on the abundance of $(M-15)^+$ and $(M-15-28)^+$ in the mass spectra of substituted phenyltrimethyl silanes and t-butylbenzenes

$$Z_1 = \frac{[YC_6H_4Si(CH_3)_2^+]}{[YC_6H_4Si(CH_3)_3^{+\cdot}]} \qquad Z_2 = \frac{[YC_6H_4SiH_2^+]}{[{}_6C_6H_4SiMe_2^+]}$$

Y	Z_1/Z_o [a]	Z_2/Z_o [b]
H	1.00	1.00
p-NMe_2	0.02	0.20
m-NMe_2	0.01	0.20
p-CH_3	0.60	0.70
m-CH_3	0.55	1.66
p-F	1.02	0.82
m-F	0.84	1.26
p-Cl	0.72	0.35
m-Cl	0.60	0.56
p-Br	0.55	0.26
m-Br	0.62	0.59
p-NO_2	3.98	0.41
m-NO_2	4.55	0.46

[a]Measured at 3.0 ev above the electron energy at which the molecular ion is 1% as intense as at 70 ev (referred to as T). This method has also been used to determine appearance potentials (90, p. 172).

[b]Measured at T + 7.0 ev.

Table 15 continued

$$Z_1 = \frac{[YC_6H_4C(CH_3)_2^+)}{[YC_6H_4C(CH_3)_3^{+\cdot}} \qquad Z_2 \frac{[YC_6H_4CH_2^+]}{[YC_6H_4C(CH_3)_2^+}$$

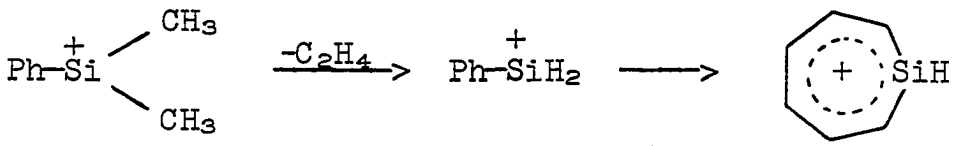
Y	Z_1/Z_o[c]	Z_2Z_o[d]
H	1.00	1.00
p-NH_2	0.22	0.03
m-NH_2	0.04	1.93
p-OH	0.53	0.21
m-OH	0.21	0.83
p-CH_3	0.63	0.32
p-F	1.10	0.60
m-F	0.78	1.33
p-Cl	0.73	0.59
m-Cl	0.64	0.98
p-Br	0.75	0.49
m-Br	0.66	0.83
p-CN	1.40	1.52
m-CN	2.16	1.57
p-NO_2	3.91	0.71
m-NO_2	4.19	1.13

[c]Measured at T + 3.0 ev.

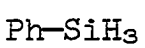
[d]Measured at T + 5.0 ev.

One final aspect of this problem concerns the nature of the ion formed by the loss of ethylene from the phenyldimethylsilyl ion. The loss of ethylene from the analogous carbon ion gives the $C_7H_7^+$ ion at m/e 91, presumably the tropylium ion. An analogous silicon containing ion, a silatropylium,

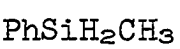
could well be the ion observed at m/e 107 in the mass spectra



of the various silanes investigated. Unfortunately, the only metastable fragmentation of this m/e 107 ion is the loss of C_2H_2. The other ions observed below m/e 90 in the mass spectrum of phenyltrimethylsilane could arise by several pathways and/or from several precursors. Cursory attempts to resolve the structure of this ion, investigation of the mass spectra of phenylsilane (99) and methylphenylsilane (100),

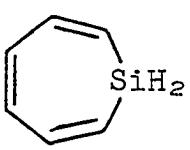


99



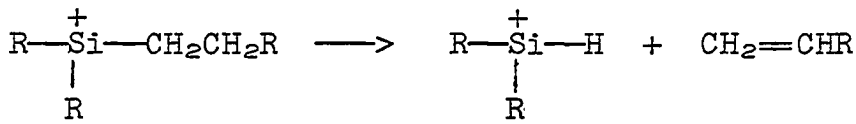
100

were not successful. The synthesis and investigation of the mass spectra of silatropilidene (101) would be very imformative in this regard.

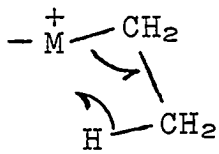


101

Another interesting aspect of the mass spectra of organosilanes is the elimination of neutral olefins from various trisubstituted silyl ions with alkyl groups larger than methyl. It has been postulated that this process involves

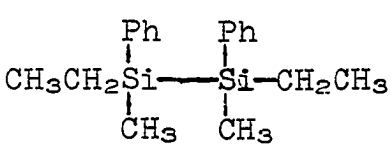


transfer of a β-hydrogen back to the central metal atom (128)

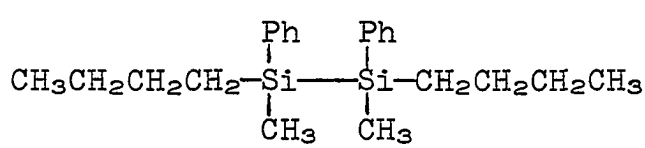


and we decided to explore the site-selectivity of this transfer using appropriately labeled substrates.

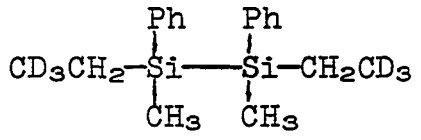
The mechanism of this process was studied by investigating the mass spectra of 1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane (90), 1,2-di-n-butyl-1,2-dimethyl-1,2-diphenyldisilane (102), and their specifically deuterated analogs 103 and 104. The mass spectra of 90 and 103 are given in



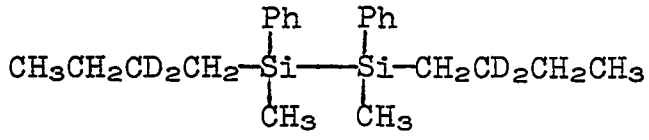
90



102



103



104

Table 16 and are illustrated in Scheme 3. It is readily apparent that the transferred hydrogen atoms in this olefin elimination process have their origin on the carbon β to the silicon atom. The high degree of site-selectivity is evident from inspection of the m/e 120-122 region of the mass spectrum of 103 at 20 ev which shows the selectivity to be 98%. The question then arose, however, whether or not the site-selectivity of this hydrogen transfer was the result of specific β-hydrogen transfer or was instead due to the terminal position of the deuterium atoms in 103.

The mass spectra of 102 and 104 (Table 17, Scheme 4) show that the transfer of hydrogen back to silicon in these even electron ions involves only the β-hydrogen atoms and is independent of the length of the alkyl group involved. Again the degree of site-selectivity is very high, e.g., in the fragmentation of the m/e 177 [179] → m/e 121 [122] the selectivity is >95% (calculated from the 20 ev spectrum).

It should also be pointed out that the site-selectivity of this β-hydrogen transfer is also very high in silyl ions which contain one hydrogen atom attached to silicon (Table 14).

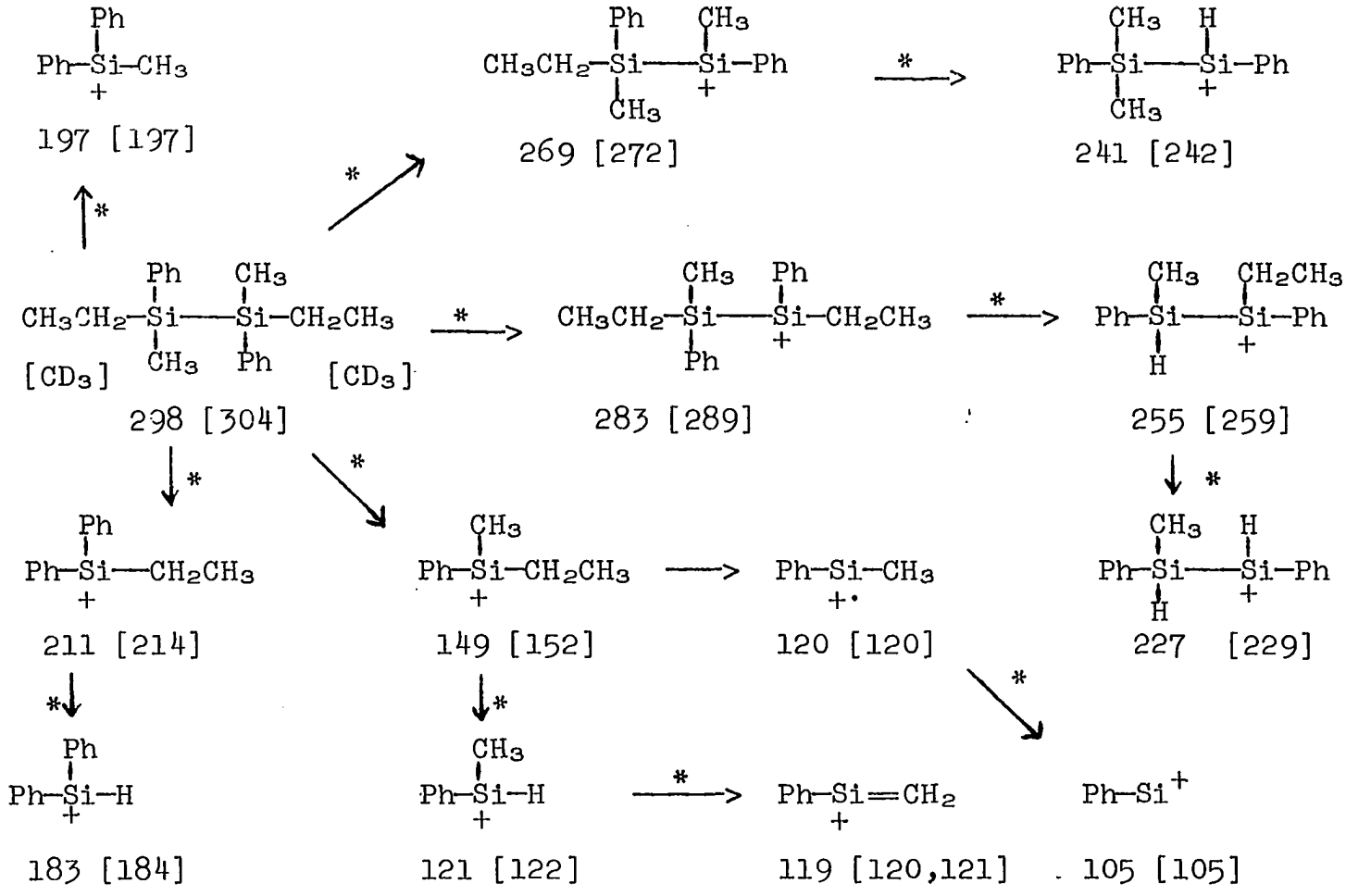
Table 16. Mass spectra[a] of 90 and 103

m/e	Relative Intensity		m/e	Relative Intensity	
	90	103		90	103
304		12.5	163	1.8	
298	9.1		152		67.8
272		7.2	151		5.4
269	6.1		149	51.4	
242		14.7	148	3.5	
241	15.1		135	6.0	5.8
229		1.3	122		100.0
227	1.7		121	100.0	10.3
214		7.1	120	3.5	4.0
211	6.2		119	3.0	
197	8.3	8.9	109		2.2
184		3.1	108		1.3
183	3.3		107	3.1	3.1
165		1.3	106		4.6
164		0.9	105	16.6	16.0

[a]All ions with m/e >100 and relative intensity >1%.

This site-selectivity in the elimination of an olefin from even electron ions in the mass spectra of organosilanes is quite remarkable since similar hydrogen transfer-olefin elimination processes in other even electron gaseous ions have been shown to occur randomly from the alkyl chain eventually lost (149, 150).

The mass spectra of these disilanes exhibit several rearrangement ions other than those formed by the loss of an olefin. These rearrangement ions, e.g., the ions at m/e 197



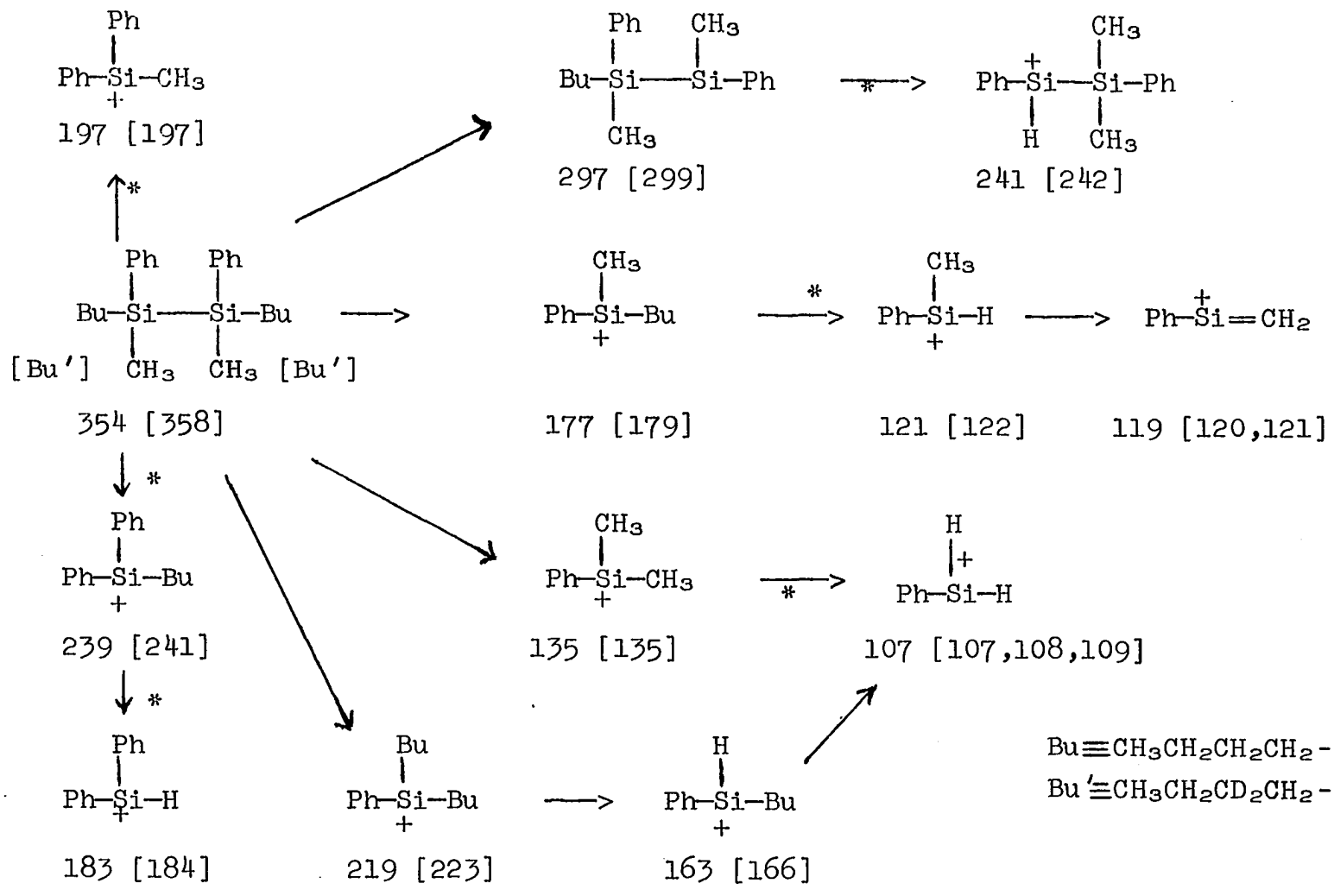
Scheme 3. Fragmentation of 1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane. Numbers in [ ] indicate mass of corresponding ion from 103.

Table 17. Mass spectra[a] of 102 and 104

m/e	Relative Intensity		m/e	Relative Intensity	
	102	104		102	104
358		9.1	165		1.0
354	11.1		164		1.0
299		1.7	163	1.9	1.0
297	2.6		149		1.5
242		12.2	147	2.1	
241	20.5	6.1	135	7.3	5.1
239	5.3		122		100.0
229		1.0	121	100.0	28.2
227	1.9		119	3.0	
197	10.9	8.1	108		1.0
184		2.7	107	2.8	1.7
183	4.7		106		2.5
179		41.7	105	17.1	12.2
177	68.0				

[a]All ions with m/e >100 and relative intensity >1%.

and 211 in the mass spectrum of 90 (Scheme 3) and the ions at m/e 239, 219, 197 and 135 in the mass spectrum of 102 (Scheme 4), are the result of a rearrangement of the groups attached to silicon in the molecular ions. Rearrangements of this type have been observed previously (138, 139, 140).



Scheme 4. Fragmentation of 1,2-di-n-butyl-1,2-dimethyl-1,2-diphenyldisilane. (Bu=$CH_3CH_2CH_2CH_2$-, Bu'=$CH_3CH_2CD_2CH_2$-)

EXPERIMENTAL

Instruments and Methods

All mass spectra were obtained using an Atlas MAT model CH4 single focusing mass spectrometer. The 2-phenylethylsilanes were first absorbed on a small sample of neutral alumina and inserted into the ion source via the vacuum lock. The remainder of the samples investigated were run by vaporization into the stainless steel inlet system maintained at 120-140°. The source temperature was maintained at 200-220° for these volatile samples. An ionizing current of 3-8μA and an accelerating potential of 3000 volts were employed. The electron energies reported are nominal values.

The calculation of deuterium retention in fragment ions and deuterium incorporation in molecular ions follows the method outlined by Biemann (99, p. 223). As near as possible all of the labeled compounds were run under the same instrument conditions as the unlabeled standards.

All nuclear magnetic resonance (nmr) spectra were obtained using a Varian Associates A-60 spectrometer at 60 MHz. Unless otherwise noted, all nmr spectra were obtained as solutions in carbontetrachloride with tetramethylsilane as the internal standard. The chemical shift values are reported in parts per million (ppm), δ units, relative to the internal standard.

Infrared spectra (ir) were obtained using a Perkin-Elmer Model 21 spectrometer and were obtained as solutions in

carbontetrachloride unless noted otherwise.

All gas liquid partition chromatography (glpc) analyses and purifications were carried out on an Aerograph 200 dual column instrument. Unless noted otherwise, all analyses and purifications were accomplished using 1/4 in. aluminum columns packed with 20% SE 30 on Chromasorb P. Carrier gas (helium) flow rates of 50-60 ml/min were used, and the thermal conductivity detector block and injection port were maintained at 50-100° above the column oven temperature. Individual analyses are reported in the following manner: (column length, liquid phase, oven temperature). The purity of samples collected by preparative glpc was verified by glpc analysis. Similarly all commercial samples and those obtained from Professor Gilman whose mass spectra are reported were checked for purity by glpc and if necessary were purified by preparative glpc or by recrystallization.

All melting points were determined with a Thomas-Hoover capillary melting point apparatus. All melting points and boiling points are uncorrected and are reported in degrees centigrade. All pressures are reported in millimeters of mercury.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Compounds for Investigation

The following compounds were donated by Professor Henry Gilman:

Phenyltrimethylsilane

m-Dimethylaminophenyltrimethylsilane

p-Dimethylaminophenyltrimethylsilane

Phenylsilane

1,1,2,2-Tetramethyl-1,2-diphenyldisilane

Methylphenyl-2-phenylethylsilane

Methylphenyl-3-phenylpropylsilane

General

All reactions were carried out in an atmosphere of nitrogen in flame dried apparatus unless noted otherwise. All reaction solvents employed were anhydrous. Unless noted otherwise, reactions were carried out at room temperature. Each compound whose preparation is described gave a consistent nmr spectrum and exhibited the correct molecular ion(s) in its mass spectrum.

Phenyltrimethyltin

This compound was prepared by the method of Bullard and Robinson (151) utilizing bromotrimethyltin and phenylmagnesium bromide. Purification was accomplished by preparative glpc (7'SE 30, 167°).

Phenyltrichlorogermane

This compound was prepared in low yield by the procedure

of Rijkens and Van Der Kerk (152,p.123) utilizing tetrachlorogermanium and tetraphenylgermane in the presence of aluminum chloride, bp 104-105° (13 mm) (lit. (153) bp 100-102° (12 mm).

Phenyltrimethylgermane

This compound was prepared in high yield from phenyltrichlorogermane and methylmagnesium iodide following the procedure of Bauer and Burschkies (154). Purification was not necessary as shown by glpc (7'SE 30, 150°)

Dimethylphenyltrideuteriomethylsilane

A solution of dimethylphenylchlorosilane (1.70 g, 0.010 mole) in 6 ml of ether was added dropwise to a solution of trideuteriomethyl Grignard reagent prepared from methyl-bromide-d_3 (0.86 g, 8.7 mmoles) and magnesium (0.125 g, 0.01 g atom) in 6 ml of ether. The addition was carried out at 0°C. After completion of the addition the mixture was allowed to warm to room temperature and stirred for 3 hr. During this time a white precipitate slowly formed. Water (5 ml) was then added and the ether phase was separated and washed with 10 ml of water. After drying ($MgSO_4$) the major portion of the ether was removed by distillation and final traces were removed at reduced pressure leaving 1.22 g of a light yellow oil. Glpc analysis of this oil (7'SE 30, 147°) showed it to contain 85-90% one component with the same retention time as an authentic sample of phenyltrimethylsilane. A sample for mass spectral analysis was purified by glpc (7'SE 30, 147°). Low voltage mass spectrometry showed the sample to be 0.5% d_0,

1.5% d_2, and 98.0% d_3.

Dimethylphenylsilane-d

Following the procedure of Russell (155) for the preparation of phenyldimethylsilane a solution of phenyldimethylchlorosilane (0.68 g, 4 mmole) in 7 ml of ether was added dropwise to a stirred slurry of lithium aluminum deuteride (0.04 g, 1 mmole) and 9 ml of ether. The resulting mixture was stirred at room temperature for 5 hr and 5 ml of 5% hydrochloric acid was added in one portion. The entire mixture was then poured into 20 ml of water and the organic phase was separated. The aqueous phase was extracted twice with 10 ml of ether and all ethereal solutions were combined and dried ($MgSO_4$). The major portion of the ether was removed by distillation. Analysis of the colorless liquid remaining (0.67 g) by glpc (7'SE 30, 140°) showed only one component in addition to ether. A sample was purified by preparative glpc (7'SE 30, 140°). Low voltage mass spectrometry showed the material to be >98% deuterated.

1,2-Dimethyl-1,2-diphenyldisilane

Following the procedure of Steudel and Gilman (156) a mixture of phenylmethylchlorosilane (46.8 g, 0.3 mmole, Dow Corning, redistilled) magnesium turnings (7.30 g, 0.3 g atom), 6 drops of ethyliodide, and 150 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was heated at reflux with stirring for 30 hr. The reaction turned a dark gray-brown upon heating and after 6-10 hr copius amounts of a

precipitate had formed. The mixture was cooled, 150 ml of pentane was added and the excess magnesium and precipitated magnesium chloride removed by filtration. The solid was washed with an additional 50 ml of pentane and the filtrate was fractionated. The disilane was collected at 86-89° (0.05 mm) (lit. (156)bp 88°, 0.003 mm affording 17.80 g, 49%). A sample for mass spectral analysis was further purified by preparative glpc (7'SE 30, 205°).

1,2-Dimethyl-1,2-diphenyl-1,2-bis-trideuteriomethyldisilane

Methyliodide-d_3 (0.44 g, 3 mmole, Merck, Sharpe, and Dohme of Canada) was added to a mixture of 1/8" pieces of clean lithium wire (0.06 g, 0.009 g atom) and 3 ml of ether. The metallation was then allowed to proceed with stirring for three hr. The methyllithium-ether solution was then filtered under nitrogen into a second flask and 1,2-dimethyl-1,2-diphenyldisilane (0.15 g, 0.6 mmole) was added with a syringe. Immediate formation of a white precipitate was noted and after stirring for 1 hr at room temperature 3 ml of 5% hydrochloric acid was added in one portion. The aqueous phase was separated and extracted with 5 ml of ether. The ethereal solutions were combined and washed three times with 5 ml of water. The organic phase was then dried ($MgSO_4$) and the ether removed by distillation. The yellow liquid remaining (0.2 g) was analysed by glpc (7'SE 30, 220°) and contained only one component other than ether. A sample was purified by preparative glpc (7'SE 30, 220°) and the collected sample shown

to have the same retention time as an authentic sample of 1,1,2,2-tetramethyl-1,2-diphenyldisilane. The purified material slowly solidified (ca. 3 months); mp 32-33° (lit. (157) mp 34-35°). Low voltage mass spectrometry showed the material to be 96.1% d_6 and 3.9% d_5.

1,2-Diethyl-1,2-dimethyl-1,2-diphenyldisilane

A solution of 1,2-dimethyl-1,2-diphenyldisilane (0.48 g, 2.0 mmole) in 8 ml of anhydrous ether was added dropwise to a stirred solution of ethyllithium (10.0 mmole, 8 ml of 1.34 M ethyl lithium in benzene, Alpha Inorganics, Inc.) and 10 ml of ether. After stirring for 27 hr, 5 ml of 5% hydrochloric acid was added in one portion and the organic phase was separated. After washing twice with 5 ml of water, the ethereal solution was dried ($MgSO_4$). The ether and benzene were removed at reduced pressure leaving 0.61 g of crude product as a colorless oil. A sample was purified by preparative glpc (7'SE 30, 215°). The nmr spectrum (Figure 3) of the purified material exhibited resonances at δ0.29, (s, 3, -SI-C$\underline{H}_3$), 0.88 (t, J = 1.5 Hz, 5, -SiC$\underline{H}_2$C$\underline{H}_3$) and 7.21 (broadened singlet, 5, Si-C$_6\underline{H}_5$).

Anal. Calcd. for $C_{18}H_{26}Si_2$: C, 72.40; H, 8.78. Found: C, 72.21; H, 8.89.

Diethylmethylphenylsilane

A solution of phenylmethylchlorosilane (0.47 g, 3 mmole) in 10 ml of anhydrous ether was added dropwise to a stirred solution of ethyllithium (13 mmole, 10 ml of 1.34 M ethyllithium in benzene, Alpha Inorganics, Inc.) and 5 ml of ether.

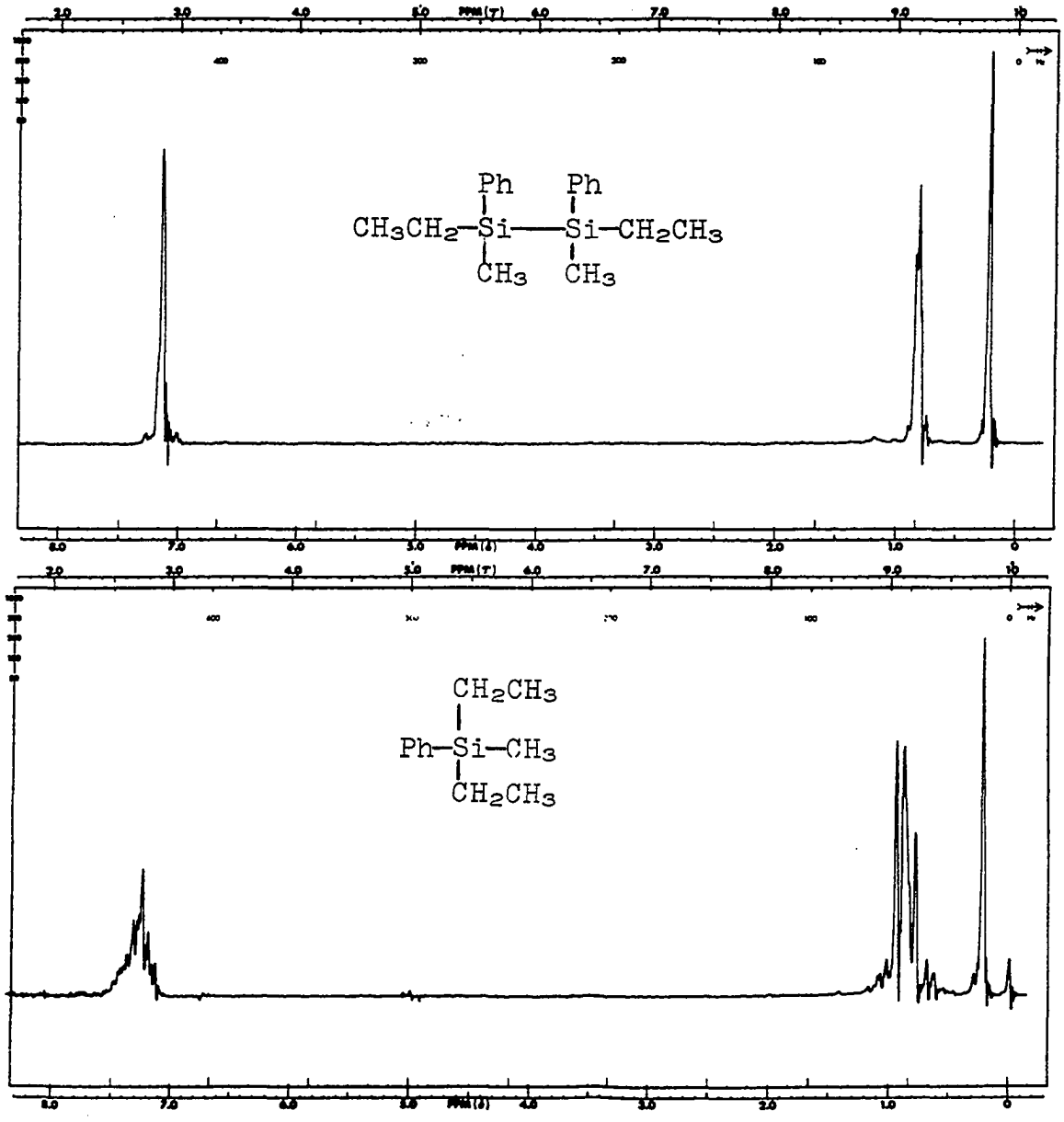


Figure 3. Nmr spectra of 1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane (top) and diethylmethylphenylsilane (bottom).

The reaction was then stirred at room temperature for 20 hr and worked up as described for the disilane above. A sample of the colorless oil (0.68 g) was purified by preparative glpc (8'SE 30, 170°). The mass spectrum showed a molecular ion at m/e 178 and the nmr spectrum (Figure 3) consisted of resonances at δ0.18 (s, 3, Si-C$\underline{H}_3$), 0.58-1.16 (m, 10, Si-C$\underline{H}_2$C$\underline{H}_3$), and at δ7.07-7.56 (m, 5, Si-C$_6\underline{H}_5$).

Anal. Calcd. for $C_{11}H_{18}Si$: C, 74.05; H, 10.17. Found: C, 74.07; H, 10.14.

Ethyliodide-2,2,2-d_3

Following the procedure of Shiner and Smith (158) acetic acid-d_4 (6.4 g, 0.1 mmole, Merck, Sharpe and Dohme) in 25 ml of anhydrous ether was added to a magnetically stirred slurry of lithium aluminum hydride (3.8 g, 0.1 mole) and 30 ml of ether. The mixture was then heated at reflux for 18 hr and cooled to 15°. Sulfuric acid (100 ml, 25%) was added slowly through the condenser and thoroughly stirred. The mixture was distilled through a 10" column packed with glass beads and the azeotrope boiling from 70-100° was collected and added to 30 ml of 47% hydroiodic acid in a 50 ml conical flask equipped with an efficient reflux condenser. The mixture was heated in an oil bath at 85° for 3 hr, cooled, and the ethyliodide removed with a capillary. Further periods of heating (3, 5, 6 and 5 hr) followed by cooling and removal of product afforded 8.21 g (56%, based on acetic acid) of ethyliodide

which was dried with calcium chloride and molecular sieves. Mass spectral analysis at 15 ev showed the product to contain 0.8% unlabeled material, 1.2% dideuterated material, and 98.0% trideuterated ethyliodide.

1,2-(2',2',2',2",2",2"-Hexadeuterio)-diethyl-1,2-dimethyl-1,2-diphenyldisilane

A flame dried 50-ml three necked flask equipped with an argon inlet, condenser, and a rubber septum was charged with 20 ml of pentane (washed with potassium permanganate solution and concentrated sulfuric acid and distilled from Drierite). Ethyl-2,2,2-d_3 iodide (1.0 g, 6 mmole) was added and the solution was cooled to 0°C. A solution of t-butyllithium (6.7 mmole) in pentane (5.7 ml) (Lithium Corporation of America, Inc.) was then added. The mixture was stirred magnetically for 0.5 hr and 1,2-dimethyl-1,2-diphenyldisilane (0.30 g, 1.2 mmole) was added. After stirring at 0° for 3 hr, the mixture was allowed to warm to room temperature and stirring continued for 20 hr. The mixture was hydrolyzed by the addition of 10 ml of 5% hydrochloric acid. The organic phase was separated, washed twice with water, dried ($MgSO_4$) and concentrated by distillation to afford 0.35 g of colorless liquid which was analysed by glpc (7'SE 30, 215°). Comparison of retention times with an authentic sample of 1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane showed that ca. 80% of the reaction mixture was the desired product. A sample for mass

spectral analysis was obtained by preparative glpc (6'SE 30, 206°). Low voltage mass spectrometry showed the compound to be 95.4% d_6, 2.8% d_5, 0.2% d_4, and 1.6% d_3.

Methylphenylsilane

Employing a modification of the procedure of Brooks (159) methylphenylchlorosilane (Dow-Corning, 1.55 g, 0.01 mmole) was added dropwise over 10 min to a stirred slurry of lithium aluminum hydride (0.2 g, 0.005 mmole) and 15 ml of anhydrous ether. After stirring at room temperature for 1 hr, 10 ml of 5% hydrochloric acid was added in two portions. The organic layer was then separated and the aqueous phase was extracted with 10 ml of ether. The ether phases were combined, washed three times with 10 ml of water, and dried ($MgSO_4$). The ether was removed at reduced pressure leaving 1.12 g of colorless liquid. Purification by preparative glpc (7'SE 30, 125°) gave a pure sample of methylphenylsilane. The nmr spectrum of this sample exhibited resonances at δ0.28 (t, J = 4.5 Hz, 3, -Si-C$\underline{H}_3$), 4.27 (q, J = 4.5 Hz, 2, -Si$\underline{H}_2$), and 7.05-7.50 (m, 5, Si-C$_6\underline{H}_5$).

1,2-di-n-Butyl-1,2-dimethyl-1,2-diphenyldisilane

Following the procedure of Jones and Gilman (160) a three neck 50-ml flask equipped with a nitrogen inlet, magnetic stirrer, and an addition funnel was charged with 10 ml of ether (dried over sodium) and 1/8" pieces of clean lithium wire (0.43 g, 0.06 mmole). Five drops of a solution of n-butylbromide (3.42 g, 0.025 mole) in 5 ml of anhydrous ether

was added and the mixture stirred for five min. The mixture was then cooled to -10° and the remainder of the n-butyl-bromide solution added over 30 min with stirring. The mixture was stirred at -10° for an additional 30 min and warmed to 0°. Stirring was continued for 2.5 hr while warming slowly to room temperature. The butyllithium solution was filtered through glass wool (under nitrogen) into a second 50 ml flask and 1,2-dimethyl-1,2-diphenyldisilane (2.42 g, 0.01 mole) was added dropwise over 10 min. The exothermic reaction was accompanied by the immediate formation of a white precipitate. After stirring for 15 hr, glpc analysis (8'SE 30, 235°) of the reaction mixture showed no remaining starting material and only one other component which had the same retention time as the product formed by the reaction of 1,2-dimethyl-1,2-diphenyldisilane with commercial n-butyllithium. The reaction mixture was then cooled to 0° and 10 ml of 5% hydrochloric acid was added. The aqueous phase was separated and extracted twice with ether. The ethereal solutions were combined and dried ($MgSO_4$). Removal of most of the ether by distillation with final traces being removed at reduced pressure afforded 3.02 g of a colorless oil. A sample was purified by preparative glpc (6'SE 30, 220°). The nmr spectrum (Figure 4) consisted of resonances at δ0.30 (s, 3, Si-CH_3), 0.56-1.48 (m, 9, Si-$CH_2CH_2CH_2CH_3$), and 7.18 (s, 5, Si-C_6H_5). The nmr spectrum (Figure 4) of phenyltri-n-butylsilane is shown for comparison.

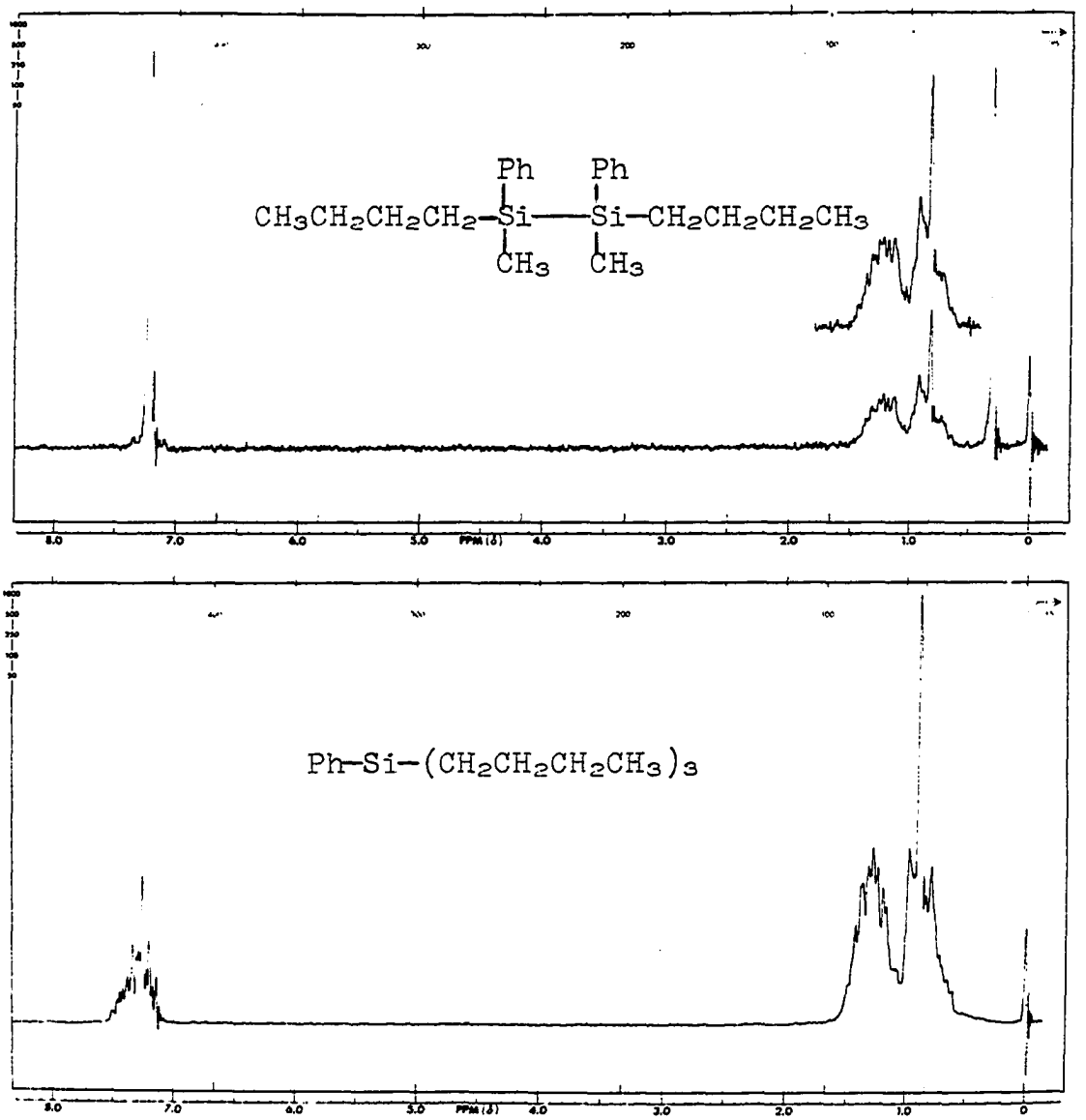


Figure 4. Nmr spectra of 1,2-di-n-butyl-1,2-dimethyl-1,2-diphenyldisilane (top) and phenyltri-n-butylsilane (bottom).

Anal. Calcd. for $C_{22}H_{34}Si_2$: C, 74.49; H, 9.66. Found: C, 74.34; H, 9.75.

Diethylethylmalonate

The title compound was prepared by alkylation of malonic ester with sodium ethoxide and ethyliodide, bp 103-108° (21 mm) (lit. (161) bp 100-103 (14 mm)).

Butanoic acid-2-2-d_2

The sodium salt of diethylethylmalonate (prepared from 0.2 mole of the ester by the procedure of Krapco (162)) was dissolved in 50 ml of deuterium oxide and cooled to 0°. Sodium metal (6.0 g, 0.25 mole) was then added cautiously and the resulting solution was heated at reflux for 12 hr. The solution was then cooled and acidified by the dropwise addition of phosphorus tribromide (27 g, 0.1 mole). The resulting mixture was distilled (20 mm) and the volatile components (bp <45°) were combined and extracted with ether in a liquid-liquid extraction apparatus for 40 hr. The ethereal solution was dried ($MgSO_4$) and the ether and ethanol removed by distillation leaving 9.0 g of crude butanoic acid by glpc analysis (6′ Carbowax 20 M, 190°).

1-Butanol-2-2-d_2

The crude butanoic acid from above was dissolved in 15 ml of tetrahydrofuran (THF) (distilled from lithium aluminum hydride) and added dropwise over 2 hr to a stirred slurry of lithium aluminum hydride (3.04 g, 0.08 mole) and 30 ml of THF. The resulting mixture was heated at 50° for 20 hr and water

was added dropwise to destroy excess hydride. After the addition of 50 ml of water, the mixture was extracted with ether using a liquid-liquid extraction apparatus for 72 hr. The ethereal solution was dried ($MgSO_4$) and concentrated by distillation. Analysis of the crude product by glpc (6' Carbowax 20M) showed that 1-butanol was the major component.

1-Bromobutane-2,2-d_2

The crude alcohol from above was treated with 16 ml of a 4:1 mixture (v/v) of 48% hydrobromic acid (14 ml) and 98% sulfuric acid (3.5 ml). The resulting mixture was heated on a steam bath for 5 hours and cooled. The mixture was then extracted three times with 20 ml of ether. The ether phases were combined, washed twice with water, dried ($MgSO_4$) and concentrated. Distillation of the product afforded 4.86 g (13% based on diethylethylmalonate) of 1-bromobutane-2-2-d_2, bp 100-103° (lit. (163) bp 100.4°). Low voltage mass spectrometry showed that the material was 81.0% d_2, 6.0% d_1, and 13.0% d_0.

1,2-(2',2',2",2"-Tetradeuterio)-di-n-butyl-1,2-dimethyl-1,2-diphenyldisilane

This compound was prepared and purified by the method described for the preparation of 1,2-di-n-butyl-1-2-dimethyl-1,2-diphenyldisilane using the deuterated bromobutane from above.

Low voltage mass spectrometry showed that the compound was 71.1% d_4, 5.9% d_3, 19.9% d_2, 0.8% d_1, and 2.40% d_0. The

intense ion corresponding to m/e 177 in the unlabeled silane (formed by cleavage of the Si-Si bond) was 80.5% d_2, 6.6% d_1, and 12.9% d_0.

Methylphenyl-2-phenylethylsilane

The Grignard reagent prepared from 2-phenylbromoethane (1.85 g, 0.010 mole) and magnesium (0.26 g, 0.011 g atom) in 13 ml of ether was filtered through glass wool under argon and added dropwise to a magnetically stirred solution of methylphenylchlorosilane (1.56 g, 0.010 mole) and 10 ml of ether. The addition was completed in 20 min. After stirring for 1.5 hr voluminous amounts of white precipitate had formed and 10 ml of 5% hydrochloric acid was added in one portion. The ether layer was separated and the aqueous phase was extracted with 10 ml of ether. The ethereal solutions were combined and dried ($MgSO_4$). The major portion of the ether was removed by distillation and final traces were removed at reduced pressure. Analysis by glpc (7'SE 30, 194°) showed only one major component with the same retention time as a sample of the title compound obtained from the Gilman group which had been synthesized by an alternate method (159). The nmr spectrum (Figure 5) consisted of resonances at δ0.30 (d, J = 3.5 Hz, 3, Si-C$\underline{H}_3$), 0.94-1.32 (m, 2, Si-C$\underline{H}_2$), 2.52-2.80 (m, 2, Ø-C$\underline{H}_2$-), 4.38 (sextet, 1, Si-$\underline{H}$), 7.08 (s, 5, -CH_2-$C_6\underline{H}_5$), and 7.05-7.60 (m, 5, Si-$C_6\underline{H}_5$). The nmr spectrum of the compound obtained from the Gilman Group was identical to that described.

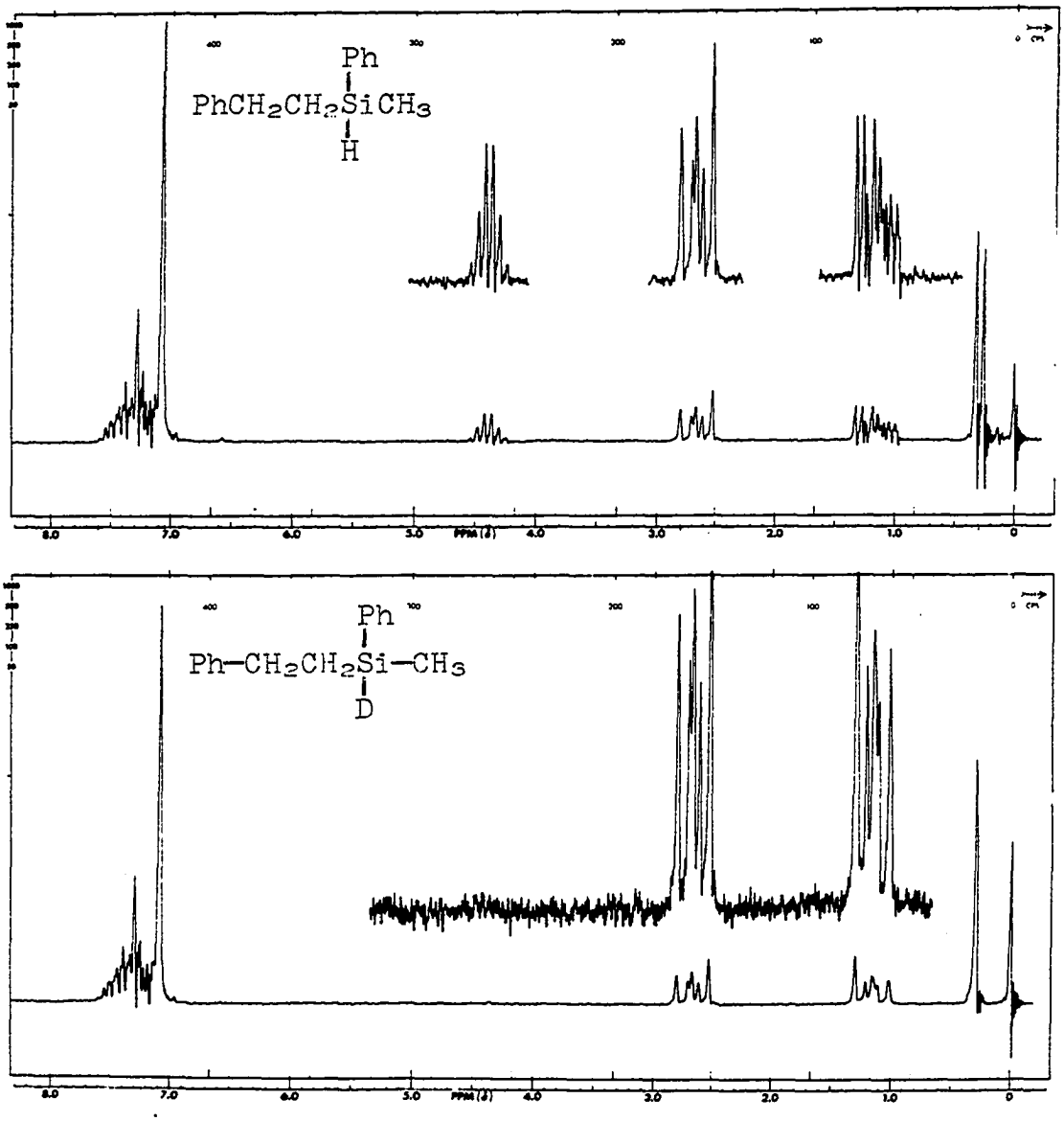


Figure 5. Nmr spectra of methylphenyl-2-phenylethylsilane (top) and methylphenyl-2-phenylethylsilane-d (bottom).

Methylphenyl-2-phenylethylsilane-d

A mixture of methylphenyl-2-phenylethylsilane (0.226 g, 1 mmole), lithium aluminum deuteride (0.21 g, 5 mmole), and 5 ml of anhydrous tetrahydrofuran was heated at 55°C for 24 hr. After cooling, 10 ml of 5% hydrochloric acid was added dropwise with stirring and the mixture was extracted twice with 30 ml of ether. The ether extracts were combined, washed with water, and dried ($MgSO_4$). The ether was removed by distillation and the product analysed by glpc (7'SE 30, 200°). The material had the same retention time as the starting material and no other components were present. The nmr spectrum (Figure 5) of the material was in agreement with essentially complete deuterium incorporation at silicon and low volatage mass spectrometry showed the material to be 93.8% d, and 6.2% d_o. The sample for mass spectral analysis was purified by preparative glpc (6'SE 30, 195°).

Dimethyl-2-phenylethylsilane

Employing a modification of the procedure of Steward and Pierce (164) for the preparation of the title compound, the Grignard reagent prepared from 2-phenylethylbromide (1.85 g, 0.01 mole) and magnesium turnings (0.26 g, 0.011 g atom) in 10 ml of anhydrous ether was filtered through glass wool (under nitrogen) and added dropwise to a stirred solution of dimethyldichlorosilane (Pierce Chemical Co.) (0.01 mole, 0.94 g) and 10 ml of anhydrous ether. After stirring at room temperature for 14 hr, voluminous amounts of white precipitate

had formed. Ten ml of 5% hydrochloric acid was added in one portion. The aqueous phase was separated and extracted with 15 ml of ether. The ethereal solutions were combined, dried ($MgSO_4$), and the ether removed by distillation leaving 1.80 g of crude product as a colorless liquid. A sample was purified by preparative glpc (7'SE 30, 168°). The nmr spectrum (Figure 6) of the purified material exhibited resonances at δ0.08 (d, J = 3.5 Hz, 6, Si-$C\underline{H}_3$), 0.80-1.13 (m, 2, Si-$C\underline{H}_2$-), 2.53-2.81 (5 line multiplet, 2, Ø-$C\underline{H}_2$-), 3.95 (nine lines, J = 3.5 Hz, 1, Si-$\underline{H}$), and 7.12 (s, 5, $C_6\underline{H}_5$-).

2-(4-Fluorophenyl)-ethanol

A solution of 4-fluorophenylacetic acid (12.32 g, 0.08 mole) in 35 ml of anhydrous THF was added dropwise over 1 hr to a stirred slurry of lithium aluminum hydride (3.04 g, 0.08 mole) in 30 ml of THF. A green color accompanied the addition of the acid. The resulting mixture was stirred and heated at 50° for 36 hr. After cooling, 3 ml of ethyl-acetate was added dropwise and the mixture was concentrated to 20 ml at reduced pressure. The residue was poured slowly into 15 ml of water and extracted with 30 ml of ether. The aqueous phase was separated and acidified with 10% hydrochloric acid and extracted twice with 30 ml of ether. The ether phases were combined and washed with 30 ml of 5% hydrochloric acid and with water. After drying ($MgSO_4$) the solvent was removed at reduced pressure affording 11.66 g of

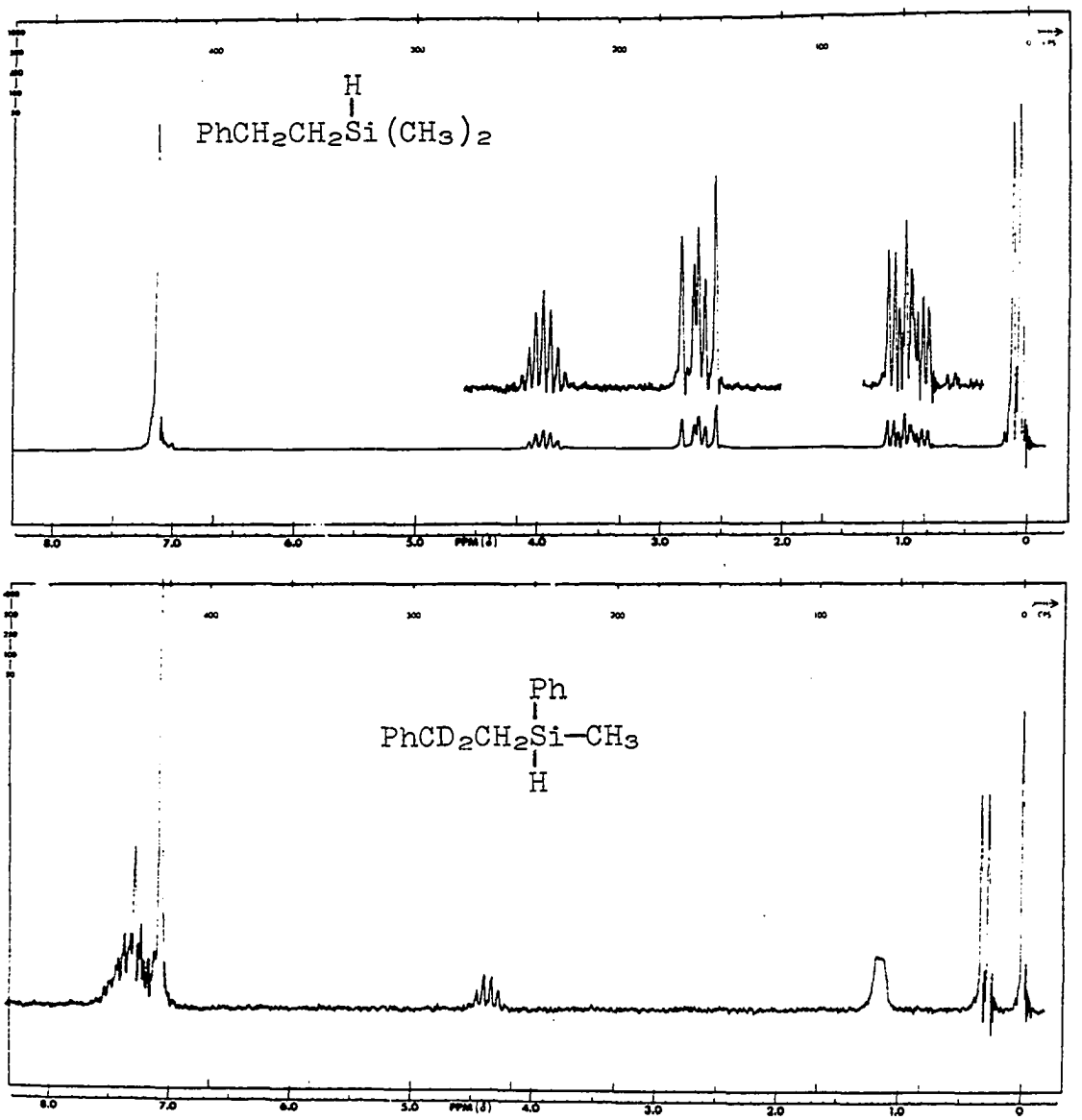


Figure 6. Nmr spectra of dimethyl-2-phenylethylsilane (top) and methylphenyl-2-phenylethyl(2,2-d_2)-silane (bottom).

a light yellow liquid. The nmr spectrum was consistent with the title compound and exhibited resonances at δ2.70 (t, J = Hz, 2, F-C_6H_5-$C\underline{H}_2$-), 3.65 (t, J = 7 Hz, 2, -$C\underline{H}_2$OH), 4.28 (s, 1, -O$\underline{H}$), and 6.73-7.27 (m, 4, p-F-$C_6\underline{H}_4$-).

2-(4-Fluorophenyl)-bromoethane

This compound was prepared in 65% yield (bp 103-110° (13 mm)) (lit. (165) bp 101-102° (17 mm)) from the corresponding alcohol by the procedure of Smith and Anderson (166) for the preparation of 2-phenylbromoethane.

2-(4-Fluorophenyl)-ethylmethylphenylsilane

This compound was prepared by the method described for the preparation of methylphenyl-2-phenylethylsilane (p. 150)(74) starting with 2-(4-fluorophenyl)bromoethane. The nmr spectrum was identical to that of 74 except for the aromatic protons at δ6.68-7.58 (m, 9H). Purification was accomplished by preparative glpc (8'SE 30, 190°). The collected material had nearly the same retention time at various temperatures as 74.

Ethylphenylacetate-2,2-d_2

This compound was prepared by the method of Saunders and Edison (167) in 31% yield (bp 35-38°, 0.08 mm). Low voltage mass spectrometry showed that the material was 95.8% d_2 and 4.2% d_1.

2-Phenylethanol-2,2-d_2

A 250 ml three neck flask equipped with a magnetic stirrer, condenser, nitrogen inlet, and an addition funnel

was flame dried under nitrogen and charged with lithium aluminum hydride (1.14 g, 0.03 mole) and 100 ml of anhydrous ether. A solution of ethylphenylacetate-2,2-d_2 (9.10 g, 0.055 mole) in 20 ml of anhydrous ether was added dropwise with stirring over 45 min and the mixture stirred at room temperature for an additional 30 min. Water was added dropwise until excess hydride was destroyed and the lithium salts had hydrolyzed to a granular white precipitate. The ether solution was removed by decanting and the remaining salts were rinsed twice with 25 ml of ether. The ethereal solutions were then combined and dried ($MgSO_4$). Removal of the ether at reduced pressure afforded 6.6 g of 2-phenylethanol-2,2-d_2. The nmr spectrum consisted of signals at δ3.06 (s, 1, -O<u>H</u>), 3.62 (s, 2, -C<u>H</u>$_2$-O), and 7.10 (s, 5, -CD_2-C_6<u>H</u>$_5$).

<u>2-Phenylbromoethane-2,2-d_2</u>

This compound was prepared in 73% yield (bp 98-99° (15 mm)) (lit. (166) bp 95-96° (13 mm)) by treatment of the alcohol with phosphorus tribromide following the procedure of Smith and Anderson (166), a procedure which has been shown (166) to result in formation of the bromide with very little (1.46%) randomization of label. Low voltage mass spectral analysis showed the compound to be 95.9% d_2 and 4.10% d_1. Deuterium incorporation in the ion at m/e 91 (formed by cleavage of the benzyl C-C bond) was found to be 95.1% d_2, 4.2% d_1, and 0.7% d_0.

Methylphenyl-2-phenylethyl(2,2-d_2)silane

This compound was prepared in good yield from 2-phenylbromoethane-2,2-d_2 and methylphenylchlorosilane by the procedure used for the preparation of methylphenyl-2-phenylethylsilane (74). Purification (a small impurity, ca. 2%, could not be removed) of the crude product was accomplished by preparative glpc (8'SE 30, 185°). The purified material had the same retention time (6' Carbowax 20M, 8'SE 30) as an authentic sample of 74. The nmr spectrum (Figure 6) of the purified sample consisted of resonances at δ0.30 (d, J = 3.5 Hz, 3, Si-C$\underline{H}_3$), 1.06-1.24 (m, 2, Si-C$\underline{H}_2$-), 4.39 (septet, J = 3.5 Hz, 1, Si-H), 7.08 (s, 5,-CD_2-$C_6\underline{H}_5$), and 7.12-7.67 (m, 5, Si-$C_6\underline{H}_5$).

4-t-Butylacetanilide

The title compound was prepared by alkylation of acetanilide following the procedure of Carpenter, Easter, and Wood, (168) mp 170.5-171.5° (lit. (168) mp 170-171°).

2-Nitro-4-t-butylacetanilide

The title compound was prepared by nitration of 4-t-butylacetanilide following the procedure of Carpenter, et al. (168), mp 105-106° (lit. (168) mp 104-105°).

2-Nitro-4-t-butylaniline

This compound was prepared by basic hydrolysis of the acetanilide by the method of Carpenter, et al. (168), mp 103.5-105.5 (lit. (168) mp 102.5-105.5).

3-t-Butylnitrobenzene

The title compound was prepared by diazotization of 2-nitro-4-t-butylaniline following the procedure of Biekart, et al., (169) bp 132-133° (12 mm) (lit. (169) bp 136-137° (16 mm)).

4-t-Butylaniline

Following the procedure of Vogel (170,p.580) for the hydrolysis of 4-bromoacetanilide, 4-t-butylacetanilide (10.0 g,0.053 mole) was dissolved in 35 ml of boiling ethanol and 22 ml of conc. hydrochloric acid was added slowly. The mixture was heated at reflux for 2 hrs and diluted with 100 ml of water. After cooling the mixture was extracted twice with 20 ml of ether (discarded). The aqueous phase was made basic with 20% sodium hydroxide and extracted twice with 30 ml of ether. These ether extracts were combined, dried ($MgSO_4$), and solvent removed at reduced pressure affording 5.48 g (70%) of a light orange oil identified by its nmr spectrum as 4-t-butylaniline (δ1.21 (s, 9, $-C(C\underline{H}_3)_3$), 3.24-3.64 (broad singlet, 2, $-N\underline{H}_2$), and 6.38 and 7.03 (A_2B_2, J = 8.5 Hz, 4, $-C_6\underline{H}_4-$)). A small sample for mass spectral analysis was purified by preparative glpc (7'SE 30, 175°). The free amine decomposes upon standing in air and is best stored as the hydrochloride salt.

4-t-Butylphenyldiazonium chloride

A slurry of 4-t-butylaniline hydrochloride was prepared from 4-t-butylaniline (5.0 g, 0.033 mole) and 20 ml of 20% hydrochloric acid. This slurry was cooled in an ice-salt bath

and a solution of sodium nitrite (2.5 g, 0.04 mole) in 5 ml of water was added over 10 min with constant swirling. After an additional 5 min a positive test for nitrous acid was obtained with potassium iodide-starch paper. This solution of the diazonium chloride was divided into three portions and each reacted as described below.

4-t-Butylbenzonitrile

A solution of 4-t-butylphenyldiazonium chloride from above was added slowly to 3 ml of the warm (60°) copper(I) cyanide solution (170, p. 607) with shaking and heated on the steam bath for 20 min. After cooling, the mixture was diluted with 15 ml of water and extracted three times with 15 ml of ether. The ether extracts were combined and washed three times with 15 ml of 5% sodium hydroxide, twice with 15 ml of water, and finally with saturated sodium chloride solution. After drying ($MgSO_4$), the ether was removed at reduced pressure and the crude product analysed by glpc (7'SE 30, 175°). Four components were apparent and by comparison of retention time one was identified as t-butylbenzene, one as 4-t-butylphenol, and one as 4-chloro-t-butylbenzene (see preparation and characterization below). A sample of the fourth component was purified by preparative glpc (7'SE 30, 165°). The ir spectra of the collected material exhibited a strong band at 4.49μ (among others). The mass spectrum showed a strong molecular ion at m/e 159 (expected from $C_{11}H_{13}N$) and the nmr spectrum showed resonances at δ1.31 (s, 9, C-($C\underline{H}_3$)$_3$), and 7.48

(collapsed AA'BB' with 2 small side peaks with J = 9 Hz, p-NC-C_6H_4-C).

4-t-Butylchlorobenzene

A solution of copper(I) chloride (6 ml) (170, p. 190) was cooled to 0° and added to a solution of 4-t-butylphenyldiazonium chloride at 0°. The mixture was allowed to warm to room temperature with occasional shaking and finally heated on the steam bath for 15 min. The reaction was worked up as described for 4-t-butylbenzonitrile. Analysis of the reaction product by glpc (7'SE 30, 175°) showed one major component and two smaller components identified as t-butylbenzene and 4-t-butylphenol by comparison of retention times with authentic samples. The major component was purified by preparative glpc (7'SE 30, 165°). The mass spectrum of the liquid obtained showed a strong molecular ion containing chlorine at m/e 158 and 160 ($C_{10}H_{13}Cl$). The nmr spectrum showed resonances at δ1.26 (s, 9, $-C(CH_3)_3$) and 7.18 (s, 4, p-Cl-C_6H_4).

4-t-Butylphenyldiazonium fluoroborate

A solution of recrystallized sodium fluoroborate (1.52 g) in 3 ml of water was added over 5 min to a solution of 4-t-butylphenyldiazonium chloride from above with shaking at 0°. After standing at 0° for 10 min the diazonium fluoroborate salt was filtered and washed twice with 2 ml of water, once with 2 ml of methanol, and twice with 3 ml of ether. The salt was then dried in air for 1 day.

4-t-Butylfluorobenzene

The diazonium fluoroborate from above was placed in a small round bottom flask equipped with an efficient reflux condenser and heated cautiously with a small flame until decomposition had started. The flask was then heated intermittently until decomposition was complete. The residue was diluted with 15 ml of water and extracted twice with 10 ml of ether. The ether extracts were combined, washed twice with water and once with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated at reduced pressure. The only major product by glpc analysis (7'SE 30, 154°) was purified by preparative glpc. The purified colorless liquid showed a strong molecular ion at m/e 152 ($C_{10}H_{13}F$) in its mass spectrum and its nmr spectrum exhibited resonances at δ1.28 (s, 9, C-($C\underline{H}_3$)$_3$) and 6.71-7.38 (m, 4, $\underline{p}$-F-$C_6\underline{H}_4$).

3-t-Butylaniline

The title compound was prepared by the reduction of 3-$\underline{t}$-butylnitrobenzene with tin and hydrochloric acid following the procedure of Vogel (170, p. 563) for the reduction of nitrobenzene. The nmr spectrum of the purified product exhibited resonances at δ1.22 (s, 9, -C-($C\underline{H}_3$)$_3$), 3.41 (broad singlet, 2, -$N\underline{H}_2$), and 6.12-7.09 (m, 4, $\underline{m}$-NH_2-$C_6\underline{H}_4$-). A sample for mass spectral analysis was purified by preparative glpc (7'SE 30, 175°). The amine was converted into its hydrochloride salt for storage.

3-t-Butylphenyldiazonium chloride

3-t-Butylaniline hydrochloride (6.10 g, 0.33 mole) was dissolved in 50 ml of 20% hydrochloric acid by heating on the steam bath. After cooling to room temperature the solution was placed in an ice-salt bath. The amine hydrochloride precipitated upon cooling. A solution of sodium nitride (2.5 g, 0.04 mole) in 5 ml of water was added dropwise during 10 min with constant stirring. The mixture became homogeneous and after stirring for an additional 10 min at -5°, a positive test for nitrous acid was obtained with potassium iodide-starch paper. This solution of the diazonium chloride was then divided into 3 portions, each kept at < 0°, and reacted as described below.

3-t-Butylbenzonitrile

A solution of 3-t-butylphenyldiazonium chloride from above was added slowly, with stirring, to 5 ml of warm (60°) copper-(I) cyanide solution (170, p. 607) and heated on the steam bath for 20 min. After cooling the mixture was diluted with 45 ml of water and extracted three times with 25 ml of ether. The ether extracts were combined and washed four times with 20 ml of 5% sodium hydroxide, twice with 20 ml of water, and once with 20 ml of saturated sodium chloride. The ethereal solution was then dried ($MgSO_4$) and treated with decolorizing charcoal. After filtering the solvent was removed at reduced pressure and the crude product analysed by glpc (7'SE 30, 175°). Four components were apparent and by comparison of

retention time one was identified as t-butylbenzene (ca. 5%), one as 3-t-butylchlorobenzene (ca. 40%, see preparation and characterization below), and one as 3-t-butylphenol (ca. 20%). A small sample of the fourth component (ca. 30%) could not be separated cleanly from the 3-t-butylphenol by preparative glpc so the entire reaction product was chromatographed on neutral alumina. Elution with pentane afforded a mixture of t-butylbenzene and 3-chloro-t-butylbenzene, and elution with pentane-benzene (10:3) afforded 3-t-butylbenzonitrile. The mass spectrum exhibited a strong molecular ion at m/e 159 ($C_{11}H_{13}N$) and the ir spectrum showed a strong band at 4.48μ (among others). The nmr spectrum consisted of resonances at δ1.32 (s, 9, C-$(CH_3)_3$) and 7.28-7.65 (m, 4, m-NC-C_6H_4-).

3-t-Butylchlorobenzene

A solution of copper(I) chloride (10 ml) (170, p. 190) was cooled to 0° and added to a solution of 3-t-butylphenyldiazonium chloride at 0°. The mixture was allowed to warm to room temperature with occasional shaking and finally heated on the steam bath for 15 min. The reaction was worked up as described for 3-t-butylbenzonitrile. The crude product was then chromatographed on neutral alumina and elution with hexane afforded a mixture of t-butylbenzene and 3-chloro-t-butylbenzene which was combined with the 3-t-butylchlorobenzene obtained from the 3-t-butylbenzonitrile preparation. A sample of 3-chloro-t-butylbenzene was purified by preparative glpc (7′ SE 30, 165°). The colorless liquid obtained

showed strong molecular ions containing chlorine at m/e 158 and 160 ($C_{10}H_{13}Cl$) and the nmr spectrum showed resonances at δ1.30 (s, 9, -C-$(CH_3)_3$) and at 6.98-7.33 (m, 4, m-Cl-C_6H_4-).

3-t-Butylphenyldiazonium fluoroborate and 3-t-butylfluorobenzene

A solution of recrystallized sodium fluoroborate (1.8 g) in 3.5 ml of water was added over 5 min to a stirred, cold (0°), solution of 3-t-butylphenyldiazonium chloride. After standing at 0° for 10 min the diazonium fluoroborate was filtered and washed twice with 2 ml of ice water, once with 2 ml of ice-cold methanol, and twice with 2 ml of cold ether. The salt was dried in air for 2 hr at which time it was noted that slow decomposition was occurring. The pasty mass was transferred to a small flask and decomposed and worked up as described for the preparation of 4-t-butylfluorobenzene. A sample of the only major component by glpc analysis was purified by preparative glpc (7'SE 30, 150°). The nmr spectrum exhibited resonances at δ1.30 (9, s, C-$(CH_3)_3$) and 6.57-7.27 (m, 4, m-F-C_6H_4-). The mass spectrum showed a strong molecular ion at m/e 152 ($C_{10}H_{13}F$).

2-Bromo-4-t-butylacetanilide

Following the procedure of Vogel (170, p.605) for the preparation of 3-bromo-4-acetaminotoluene, 4-t-butylacetanilide (16.0 g,0.83 mole) was dissolved in 45 ml of glacial acetic acid by heating in a hot water bath at 60°. Bromine (19.5 g,0.12 ml) was then added dropwise over 10 min and the stirred solution was heated in the water bath at 65° for 2 hr. The reaction

mixture was then poured onto 200 g of crushed ice and water containing sodium bisulfite. The product was collected by filtration and washed well with cold water to afford 23.5 g (>100%) of crude 2-bromo-4-t-butylacetanilide. A small sample was recrystallized from cyclohexane, mp 154-156° (lit. (171) mp 156.6-157.6°).

2-Bromo-4-t-butylaniline

The crude 2-bromo-4-t-butylacetanilide from above was dissolved in 50 ml of 95% ethanol by heating on the steam bath and 30 ml of conc hydrochloric acid was added. Heating was continued for 3 hrs and the reaction mixture cooled to room temperature. The mixture was then cooled in an ice bath and sodium hydroxide was added until pH 10 was reached. The mixture was extracted three times with 50 ml of ether. The ether extracts were combined and washed four times with 50 ml portions of water. After drying ($MgSO_4$) the ether was removed at reduced pressure leaving 17.8 g of a yellow oil. The nmr spectrum was consistent with the title compound.

3-t-Butylbromobenzene

Employing a modification of the procedure of Vogel (170, p. 605) for the preparation of 3-bromotoluene the crude 2-bromo-t-butylaniline from above was dissolved in a cold (5°) solution of 45 ml of ethanol and 11 ml of concd. sulfuric acid. A solution of sodium nitrite (8.2 g) in 15 ml of water was then added to the stirred solution of the amine sulfate at a rate such that the temperature did not rise above 10°. After

stirring for an additional 10 min a positive test for nitrous acid was obtained with potassium iodide-starch paper. Copper powder (1.93 g) was added and the mixture warmed cautiously in a hot water bath until evolution of nitrogen commenced and then cooled in ice to moderate the decomposition. Final decomposition was accomplished by heating in a boiling water bath for 20 min. The resulting mixture was poured into 200 g of a mixture of crushed ice and water and then extracted twice with 50 ml of ether. The ether extracts were combined and washed three times with water and once with saturated sodium chloride solution. The ethereal solution was dried ($MgSO_4$) and distilled at reduced pressure. 3-Bromo-t-butylbenzene (10.4 g, 59% based on 4-t-butylacetanilide was collected at 103-104° (15 mm) (lit. (171) bp 71-72° (4 mm)). A sample for mass spectral analysis was purified by preparative glpc (6'SE 30, 175°).

Nitration of t-butylbenzene

Following the procedure of Craig (172) a cooled (20°) mixture of concd. sulfuric acid (32.4 ml) and concd. nitric acid (27.0 g, 0.3 mole, d = 1.42, 70%) was added, with stirring, over 1 hr to t-butylbenzene (0.3 mole, 41.2 g). The mixture was then stirred at 40° for 1 hr and cooled. The organic phase was extracted twice with 100 ml of ether, washed twice with 50 ml of water, twice with 50 ml of 5% sodium hydroxide solution, twice with water and dried ($MgSO_4$). The ether was removed at reduced pressure and the yellow oil

distilled affording three fractions of a mixture of 2- and 4-nitro-t-butylbenzene. Redistillation through a 60 cm Podbielniak column at reduced pressure afforded 17.5 g of 4-nitro-t-butylbenzene, bp 170-175° (55 mm) (lit. (172) bp 155-158° (30 mm)), containing <5% of the ortho isomer by glpc analysis.

3-Chlorophenyltrimethylsilane

This compound was prepared by the method of Clark and co-workers (173) using 3-chlorophenylmagnesium bromide and chlorotrimethylsilane, bp 111-112° (37 mm) (lit. (174) bp 105° (24.5 mm)). A sample for mass spectral analysis was purified by preparative glpc (7'SE 30, 150°).

4-Fluorophenyltrimethylsilane

4-Fluorobromobenzene (3.50 g, 0.02 mole) was dissolved in 30 ml of anhydrous THF and cooled in an acetone-Dry Ice bath. A solution of n-butyllithium in hexane (13 ml, 1.6 M, 0.022 mole) was added with a syringe and the mixture stirred at -50° for 1.5 hr. Trimethylchlorosilane (2.16 g, 0.02 mole) was added and stirring continued for 1 hr. (The yellow color which had formed upon the addition of the alkyllithium was discharged by the addition of the chlorosilane). The mixture was then allowed to warm to room temperature and most of the THF was removed at reduced pressure. The remaining mixture was treated with 20 ml of pentane, washed with water, and dried ($MgSO_4$). The pentane was removed by distillation to give 2.88 g of a light yellow oil. A sample of the product

was purified by preparative glpc (6' Carbowax 20M, 115°). The nmr spectrum of the purified sample exhibited resonances at δ0.24 (s, 9, Si-($C\underline{H}_3$)$_3$) and 6.79-7.52 (m, 4, $\underline{p}$-F-$C_6\underline{H}_4$-Si-).

3-Fluorophenyltrimethylsilane

This compound was prepared in the manner described above for the preparation of 4-fluorophenyltrimethylsilane starting with 3-fluorobromobenzene. Purification was accomplished by glpc at the same conditions described for the 4-fluoro isomer. The nmr spectrum consisted of resonances at δ0.27 (s, 9, -Si($C\underline{H}_3$)$_3$) and 6.71-7.41 (m, 4, $\underline{m}$-F-$C_6\underline{H}_5$-).

3-Bromophenyltrimethylsilane

Using the procedure described for the preparation of 4-fluorophenyltrimethylsilane this compound was prepared from $\underline{m}$-dibromobenzene. Purification was accomplished by preparative glpc (8'SE 30, 170°). The nmr spectrum of the purified material consisted of resonances at δ0.25 (s, 9, -Si-($C\underline{H}_3$)$_3$) and 6.98-7.53 (m, 4, $\underline{m}$-Br-$C_6\underline{H}_4$-).

4-Chlorophenyltrimethylsilane

Using the procedure described for the preparation of 4-fluorophenyltrimethylsilane, the compound was prepared from 4-chlorobromobenzene. Purification was accomplished by preparative glpc (7'SE 30, 143°). The nmr spectrum of the purified material consisted of resonances at δ0.23 (s, 9, -Si-($C\underline{H}_3$)$_3$) and at 7.11-7.45 (m, 4, $\underline{p}$-Cl-$C_6\underline{H}_4$-).

3-Tolyltrimethylsilane

m-Bromotoluene was converted to 3-tolyltrimethylsilane by the procedure described for the preparation of 4-fluorophenyltrimethylphenylsilane. A sample of the crude product was purified by preparative glpc (7'SE 30, 138°). The nmr spectrum of the purified material consisted of resonances at δ0.24 (s, 9, Si-($C\underline{H}_3$)$_3$), 2.33 (s, 3, $C\underline{H}_3$-Ø), and 6.98-7.28 (m, 4, m-CH_3-$C_6\underline{H}_4$-).

4-Tolyltrimethylsilane

This compound was prepared and purified in the manner described for the 3-tolyl isomer. The nmr spectrum of the purified material consisted of resonances at δ0.22 (s, 9, Si-($C\underline{H}_3$)$_3$), 2.40 (s, 3, $C\underline{H}_3$-Ø-), and 7.16 (distorted quartet, J = 8 Hz, 4, CH_3-$C_6\underline{H}_4$-).

4-Nitrophenyltrimethylsilane

Following the procedure of Deans and Eaborn (175) a solution of fuming nitric acid (95 wt %, 6 ml) and acetic anhydride (10 ml) was prepared at 0° and added dropwise during 2.5 hr to a boiling solution of 1,4-bis-trimethylsilylbenzene (5.0 g, 22.4 mmole) in acetic anhydride (14 ml). The mixture was cooled and poured into 100 ml of a mixture of crushed ice and water. The resulting mixture was extracted three times with 25 ml of ether and the organic extracts combined and washed with 5% sodium hydroxide until the basic washings became pale yellow. All aqueous washings were then combined and extracted with 50 ml of ether. All ether extracts were combined and

washed twice with 5% sodium hydroxide solution, twice with water, and dried ($MgSO_4$). The ether was removed at reduced pressure and the crude product chromatographed on alumina. Elution with hexane gave 3.01 g (70%) of 4-nitrophenyltrimethylsilane. The sample for mass spectral analysis, purified by glpc (6'SE 30, 165°), crystallized upon cooling, mp 35-36° (lit. (175) mp 37°).

1,3-bis-Trimethylsilylbenzene

This compound was prepared in 55% yield by the method of Clark and co-workers (173) bp 106-109° (15 mm) (lit. (173) bp 112 (22 mm).

3-Nitrophenyltrimethylsilane

The title compound was prepared by the method of Deans and Eaborn (175) for the preparation of 4-nitrophenyltrimethylsilane (described above). Purification for mass spectral analysis was accomplished by glpc (7'SE 30, 165°). The nmr spectrum exhibited resonances at δ0.34 (s, 9, Si-($C\underline{H}_3$)$_3$) and 7.33-8.30 (m, 4, $\underline{m}$-NO_2-$C_6\underline{H}_4$-).

Benzylethylphenylsilane

An ethereal solution of ethyllithium, prepared from bromoethane (0.545 g, 5.0 mmole) and finely chopped lithium wire (0.08 g, 12.0 mmole) in 5 ml of ether, was filtered (under nitrogen) through glass wool and added dropwise to a solution of benzylphenylsilane (176) (0.98 g, 5.0 mmole) in 10 ml of ether. The addition was completed in 0.5 hr and the mixture was stirred for 1 hr. The reaction mixture was poured into

25 ml of 5% hydrochloric acid and the ether layer was separated. After washing with water and drying ($MgSO_4$) the solvent was removed at reduced pressure. Analysis of the crude oil by glpc (8' SE 30, 194°) showed only one component other than bibenzyl (impurity in benzylphenylsilane). A sample was purified by preparative glpc (8'SE 30, 200°). The nmr spectrum of the purified material exhibited resonances at δ0.63-1.16 (m, 5, Si-$C\underline{H}_2C\underline{H}_3$), 2.34 (d, J = 3.5 Hz, 2, Si-$C\underline{H}_2\emptyset$), 4.31 (m, 1, Si-$\underline{H}$), and 6.75-7.45 (m, 10, aromatic protons).

Anal. Calc. for $C_{15}H_{18}Si$: C, 79.57; H, 8.01. Found: C, 80.17; H, 8.76. C, 80.32; H, 8.71.

Benzylethylphenylsilane-d

Benzylethylphenylsilane (0.22 g, 1.0 mmole) was added dropwise to a stirred slurry of lithium aluminum deuteride (0.21 g, 5 mmole) in 5 ml of tetrahydrofuran (distilled from lithium aluminum hydride). The resulting mixture was heated at reflux for 30 hr. After cooling, 5 ml of 5% hydrochloride acid was added and the mixture was extracted twice with 30 ml of ether. After washing with water, the ethereal solution was dried ($MgSO_4$) and the solvent removed at reduced pressure. Glpc analysis (8'SE 30, 200°) showed the same mixture, bibenzyl and silane, as in the starting material. A sample was purified by preparative glpc (8'SE 30, 200°). The nmr spectrum of the purified material was consistent with partial deuteration (45.5% by nmr integration) at silicon and was very

similar to that of the undeuterated compound except that the doublet of the benzyl protons was superimposed over a slightly broadened singlet. Low voltage mass spectra analysis showed that the compound was 46.5% d_1 and 53.5% d_0.

BIBLIOGRAPHY

1. P. Brown and C. Djerassi, Angew. Chem., 79, 481 (1967).

2. H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif. 1967.

3. J. H. Beynon, R. A. Saunders and A. E. Williams, "The Mass Spectra of Organic Molecules", Elsevier Publishing Co., Amsterdam, Holland. 1968.

4. H. M. Grubb and S. Meyerson in F. W. McLafferty, ed., "Mass Spectrometry of Organic Ions", p. 453, Academic Press, Inc., New York, N.Y. 1963.

5. I. W. Kinney and G. L. Cook, Anal. Chem., 24, 1991 (1952).

6. F. W. McLafferty, Anal. Chem., 28, 306 (1956).

7. F. H. Field and J. L. Franklin, J. Chem. Phys., 22, 1895 (1954).

8. M. J. O'Neal and T. P. Wier, Anal. Chem., 23, 830 (1951).

9. H. E. Lumpkin and B. H. Johnson, Anal. Chem., 26, 1719 (1954).

10. D. O. Schissler and D. P. Stevenson, J. Chem. Phys., 22, 151 (1954).

11. F. P. Lossing, K. U. Ingold and I. H. S. Henderson, J. Chem. Phys., 22, 621 (1954).

12. J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, J. Chem. Phys., 22, 1948 (1954).

13. P. N. Rylander, S. Meyerson and H. M. Grubb, J. Am. Chem. Soc., 79, 842 (1957).

14. S. Meyerson and P. N. Rylander, J. Chem. Phys., 27, 901 (1957).

15. S. Meyerson, J. Am. Chem. Soc., 85, 3340 (1963).

16. S. Meyerson and P. N. Rylander, J. Phys. Chem., 62, 2 (1958).

17. V. Hanuš and Z. Dolejšek, Kernenergie, 3, 836 (1960).

18. K. L. Rinehart, Jr., Allan C. Buchholz, G. E. Van Lear and H. L. Cantrill, J. Am. Chem. Soc., 90, 2983 (1968).

19. A. G. Harrison and F. Meyer, J. Am. Chem. Soc., 86, 4757 (1964).

20. J. G. Burr and R. A. Meyer, J. Chem. Phys., 40, 2046 (1964).

21. P. Brown, J. Am. Chem. Soc., 90, 4461 (1968).

22. P. Brown, J. Am. Chem. Soc., 90, 4459 (1968).

23. F. W. McLafferty and M. M. Bursey, J. Am. Chem. Soc., 88, 529 (1966).

24. F. W. McLafferty and M. M. Bursey, J. Am. Chem. Soc., 89, 1 (1967).

25. M. M. Bursey, Org. Mass Spectrom., 1, 31 (1968).

26. F. W. McLafferty and M. M. Bursey, J. Am. Chem. Soc., 90, 5299 (1968).

27. J. A. Berson and M. R. Willcott, J. Am. Chem. Soc., 88, 2494 (1966).

28. A. P. ter Borg, H. Kloosterziel and N. Van Meurs, Rec. Trav. Chim. Pays-Bas, 82, 717 (1963).

29. G. G. MacDonald and J. S. Shannon, Aust. J. Chem., 15, 771 (1962).

30. K. R. Jennings, Z. Naturforsch., 22A, 454 (1967).

31. D. H. Williams, S. W. Tam and R. G. Cooks, J. Am. Chem. Soc., 90, 2150 (1968).

32. S. Meyerson, J. D. McCollum and P. N. Rylander, J. Am. Chem. Soc., 83, 1401 (1961).

33. V. Hanuš, Nature, 184, 1796 (1954).

34. V. Hanuš and Z. Dolejšek, Jaderná energie, 6, 350 (1960).

35. V. Hanuš and Z. Dolejšek, Collection Czech. Chem. Commun., 28, 652 (1963).

36. Z. Dolejšek, V. Hanuš and H. Prinzbach, Angew. Chem., 74, 902 (1962).

37. C. Lifshitz and S. Bauer, J. Phys. Chem., 67, 1629 (1963).

38. A. A. Polyakova, R. A. Khmel'nitskii and A. A. Petrov, Zh. Obshch. Khim., 34, 3296 (1964); J. Gen. Chem. U.S.S.R., 34, 3336 (1964).

39. A. A. Polyakova and A. A. Petrov, Zh. Obshch. Khim., 31, 3515 (1961); J. Gen. Chem. U.S.S.R., 31, 3278 (1961).

40. D. T. Roberts, W. F. Little and M. M. Bursey, J. Am. Chem. Soc., 90, 973 (1968).

41. A. G. Harrison, P. Haynes, S. McLean and F. Meyer, J. Am. Chem. Soc., 87, 5099 (1965).

42. V. Hanuš and V. Čermák, Collect. Czech. Chem. Commun., 24, 1602 (1959).

43. N. G. Foster and R. W. Higgins, Org. Mass Spectrom., 1, 191 (1968).

44. Q. N. Porter, Aust. J. Chem., 20, 103 (1967).

45. J. Collin, Bull. Soc. Chim. Belges, 69, 575 (1960).

46. B. Willhalm, A. F. Thomas and F. Gautschi, Tetrahedron, 20, 1185 (1964).

47. J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry", Elsevier Publishing Co., Amsterdam, Holland. 1960.

48. M. Marx and C. Djerassi, J. Am. Chem. Soc., 90, 678 (1968).

49. H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenney, D. J. Newman and J. M. Wilson, J. Chem. Soc., 1949 (1964).

50. A. M. Duffield, R. Beugelmanns, H. Budzikiewicz, D. A. Lightner, D. H. Williams and C. Djerassi, J. Am. Chem. Soc., 87, 805 (1965).

51. P. N. Rylander, S. Meyerson, E. L. Eliel and J. D. McCollum, J. Am. Chem. Soc., 85, 2723 (1963).

52. K. R. Jennings and J. H. Futrell, J. Chem. Phys., 44, 4315 (1966).

53. S. D. Sample, D. A. Lightner, O. Buchardt and C. Djerassi, J. Org. Chem., 32, 997 (1967).

54. A. V. Robertson, M. Marx and C. Djerassi, Chem. Commun., 414 (1968).

55. K. L. Rinehart, Jr., A. C. Bucholz and G. E. Van Lear, J. Am. Chem. Soc., 90, 1073 (1968).

56. G. Lock and G. Gergely, Chem. Ber., 77, 461 (1944).

57. V. Boekelheide and C. E. Larrabee, J. Am. Chem. Soc., 72, 1245 (1950).

58. V. Gold and F. L. Tye, J. Chem. Soc., 2184 (1952).

59. R. Pettit, J. Am. Chem. Soc., 82, 1972 (1960).

60. D. H. Reid, Quart. Rev. (London), 19, 274 (1965).

61. V. Boekelheide and C. E. Larrabee, J. Am. Chem. Soc., 72, 1240 (1950).

62. M. Nakazaki, U. S. Atomic Energy Commission Reports, UCRL-3700, [California University, Berkeley, Lawrence Radiation Lab.]. 1957.

63. E. Bamberger and M. Philips, Ann. Chem., 240, 147 (1877).

64. J. W. Cook and C. L. Hewett, J. Chem. Soc., 365 (1934).

65. W. v. E. Doering and L. H. Knox, J. Am. Chem. Soc., 76, 3203 (1954).

66. H. Prinzbach and V. Freudenberger, Angew. Chem., 77, 346 (1965).

67. D. H. Reid and R. G. Sutherland, J. Chem. Soc., 3295 (1963).

68. R. Pettit, Chem. Ind. (London), 1306 (1956).

69. E. Clar and D. G. Stewart, J. Chem. Soc., 23 (1958).

70. W. Bonthrone and D. H. Reid, J. Chem. Soc., 2773 (1959).

71. D. H. Reid, Tetrahedron, 3, 339 (1958).

72. S. Hünig and E. Wolff, Chimia, 22, 33 (1968).

73. L. R. Honnen, Diss. Abs., 24 (3), 972 (1963).

74. W. G. Schneider, in B. Pesce, ed., "Nuclear Magnetic Resonance in Chemistry", p. 63, Academic Press, New York. 1965.

75. H. Prinzbach, V. Freudenberger and U. Schiedegger, Helv. Chim. Acta, 50, 1087 (1967).

76. W. Bonthrone and D. H. Reid, J. Chem. Soc., B, 91 (1966).

77. "Catalog of Mass Spectral Data", American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburg, Pennsylvania, spectrum No. 1102.

78. T. W. Shannon and F. W. McLafferty, J. Am. Chem. Soc., 88, 5021 (1966).

79. A. T. Balaban and D. Fărcasiu, J. Am. Chem. Soc., 89, 1958 (1967).

80. A. T. Balaban and D. Fărcasiu, Tetrahedron Lett., 1273 (1968).

81. H. A. Staab and M. Haenel, Angew. Chem. Internat. Edit., 7, 548 (1968).

82. N. M. M. Nibbering and Th. J. deBoer, Org. Mass Spectrom., 1, 365 (1968).

83. D. O. Schissler and D. P. Stevenson, J. Chem. Phys., 22, 151 (1954).

84. S. Meyerson, J. D. McCollum and P. N. Rylander, J. Am. Chem. Soc., 83, 1401 (1961).

85. V. Boekelheide and C. D. Smith, J. Am. Chem. Soc., 88, 3950 (1966).

86. G. Naville, H. Strauss and E. Heilbronner, Helv. Chim. Acta, 43, 1243 (1960).

87. G. Wittig and K. Schwarzenbach, Ann. Chem., 651, 1 (1961).

88. S. O'Brien and D. C. C. Smith, J. Chem. Soc., 2905 (1963).

89. L. F. Fieser and J. E. Jones, J. Am. Chem. Soc., 64, 1666 (1942).

90. R. W. Kiser, "Mass Spectrometry", Prentice-Hall, Inc., Englewood Cliffs, N.J. 1965.

91. H. J. Richter and S. F. Silver, J. Org. Chem., 33, 3283 (1968).

92. F. Ramirez, N. Ramanathan and N. B. Desai, J. Am. Chem. Soc., 84, 1317 (1962).

93. M. Stiles and A. Langroy, Tetrahedron Lett., 337 (1961).

94. G. Stortz and F. H. Clark, Jr., J. Am. Chem. Soc., 83, 3114 (1961).

95. J. H. Saunders, Organic Syntheses, Coll. Vol. 3, 22 (1955).

96. D. F. Tavares and J. P. Borger, Can. J. Chem., 44, 1323 (1966).

97. O. L. Chapman, D. J. Pasto and A. A. Griswold, J. Am. Chem. Soc., 84, 1213 (1962).

98. D. I. Schuster, J. Org. Chem., 31, 4287 (1966).

99. K. Biemann, "Mass Spectrometry", McGraw-Hill Book Co., New York, N.Y. 1962.

100. F. Arndt, Organic Syntheses, Coll. Vol. 2, 65 (1943).

101. V. Rautenstrauch and F. Wingler, Tetrahedron Lett., 4703 (1965).

102. J. Cason, Organic Syntheses, Coll. Vol. 3, 3 (1955).

103. L. Fieser and J. Casin, J. Am. Chem. Soc., 62, 432 (1940).

104. B. R. Brown and D. L. Hammick, J. Chem. Soc., 1395 (1948).

105. H. J. Richter, J. Am. Chem. Soc., 75, 2774 (1953).

106. D. C. Morrison, J. Org. Chem., 23, 33 (1958).

107. H. J. Richter, R. L. Dressler and S. F. Silver, J. Org. Chem., 30, 4078 (1965).

108. J. Morel and Y. Mollier, C. R. Acad. Sci., Paris, 260, 5300 (1965).

109. G. A. R. Kon and R. G. W. Spickett, J. Chem. Soc., 2725 (1949).

110. R. Robson, P. W. Grubb and J. A. Barltrop, J. Chem. Soc., 2153 (1964).

111. S. Casadio, G. Pala, T. Bruzzese and E. Marassa Uberti, Farmaco, eds., Sci., 117, 797 (1962).

112. W. E. Bachman and J. C. Sheehan, J. Am. Chem. Soc., 63, 2598 (1941).

113. R. E. Stark, "Electron Induced Fragmentation of Selected Oxiranes and Olefins", Unpublished M.S. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology. 1966.

114. R. L. Letsinger and D. F. Pollart, J. Am. Chem. Soc., 78, 6079 (1956).

115. K. T. Leffek, J. A. Llewellyn and R. E. Robertson, Can. J. Chem., 38, 1505 (1960).

116. M. I. Bruce, in F. G. A. Stone and R. West, eds., "Advances in Organometallic Chemistry", vol. 6, p. 313, Academic Press, Inc., New York. 1968.

117. F. Glocking, Quart. Rev. (London), 22, 317 (1968).

118. J. Diekman, J. B. Thomson and C. Djerassi, J. Org. Chem., 32, 3904 (1967).

119. V. H. Diebeler, J. Res. Nat. Bur. Stand., 49, 235 (1952).

120. D. B. Chambers, F. Glocking, J. R. C. Light and M. Weston, Chem. Commun., 281 (1966).

121. E. Heldt, K. Hoppner and K. H. Krebs, Z. Anorg. Allg. Chem., 347, 95 (1966).

122. N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, and V. M. Vdovin, Zh. Obshch. Khim., 36, 89 (1966); J. Gen. Chem. U.S.S.R., 36, 93 (1966).

123. J. L. Occolowitz, Tetrahedron Lett., 529 (1966).

124. J. J. de Ridder and G. Dijkstra, Rec. Trav. Chim. Pays-Bas, 86, 737 (1967).

125. J. J. de Ridder, G. van Koten and G. Dijkstra, Rec. Trav. Chim. Pays-Bas, 86, 1325 (1967).

126. M. Gielen and J. Nasielski, Bull. Soc. Chim. Belges, 77, 5 (1968).

127. S. Boué, M. Gielen and J. Nasielski, Bull. Soc. Chim. Belges, 77, 43 (1968).

128. D. B. Chambers, F. Glocking and M. Weston, J. Chem. Soc. A, 1759 (1967).

129. F. Glocking and J. R. C. Light, J. Chem. Soc., A, 717 (1968).

130. R. A. Khmel'nitskii, A. A. Polyakova, A. A. Petrov, F. A. Medvedev and M. D. Stadnichuk, Zh. Obshch. Khim., 35, 773 (1965); J. Gen. Chem. U.S.S.R., 35, 778 (1965).

131. G. Fritz, H. Buhl, J. Grobe and F. Aulinger, Z. Anorg. Allg. Chem., 312, 201 (1961).

132. F. Aulinger and W. Reering, Fresenius' Z. Anal. Chem., 197, 24 (1963).

133. G. Fritz, H. Buhl and D. Kummer, Z. Anorg. Allg. Chem., 327, 165 (1964).

134. N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, K. S. Pushchevaya and V. M. Vdovin, Zh. Obshch. Khim., 37, 917 (1967); J. Gen. Chem. U.S.S.R., 37, 867 (1967).

135. N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, V. M. Vdovin and T. N. Arkhipova, Zh. Obshch. Khim., 36, 96 (1966); J. Gen. Chem. U.S.S.R., 36, 99 (1966).

136. A. M. Duffield, H. Budzikiewicz and C. Djerassi, J. Am. Chem. Soc., 87, 2920 (1965).

137. A. M. Duffield, C. Djerassi, P. Mazerolles, J. Dubac and G. Manual, J. Organometal. Chem., 12, 123 (1968).

138. D. B. Chambers and F. Glocking, J. Chem. Soc., A, 735 (1968).

139. H. Svec and J. A. Junk, J. Am. Chem. Soc., 89, 2836 (1967).

140. J. H. Smith, K. Mehner and H. D. Kaesz, J. Am. Chem. Soc., 89, 1759 (1967).

141. M. M. Bursey, R. D. Rieke, T. A. Elwood and L. R. Dusold, J. Am. Chem. Soc., 90, 1557 (1968).

142. L. E. Guselnikov and M. C. Flowers, Chem. Commun., 864 (1967).

143. M. D. Curtis, J. Am. Chem. Soc., 89, 4241 (1967).

144. P. N. Rylander and S. Meyerson, J. Am. Chem. Soc., 78, 5799 (1956).

145. J. Miller, J. Chem. Soc., A, 828 (1967).

146. J. MacLeod and C. Djerassi, J. Am. Chem. Soc., 89, (1967).

147. S. Meyerson and H. Hart, J. Am. Chem. Soc., 85, 2358 (1963).

148. F. W. McLafferty, Chem. Commun., 956 (1968).

149. C. Djerassi and C. Fenslau, J. Am. Chem. Soc., 87, 5747 (1965).

150. M. Y. Sheikh, A. M. Duffield and C. Djerassi, Organ. Mass Spectrom., 1, 251 (1968).

151. R. H. Bullard and W. B. Robinson, J. Am. Chem. Soc., 49, 1368 (1927).

152. F. Rijkens and G. J. M. Van Der Kerk, "Organogermanium Chemistry", Schotanus and Jens Utrecht N. V., Utrecht. 1964.

153. W. M. Metlesics and H. Zeiss, J. Am. Chem. Soc., 82, 3321 (1960).

154. H. Bauer and K. Burschkies, Chem. Ber., 66B, 1156 (1933).

155. G. A. Russell, J. Org. Chem., 21, 1190 (1960).

156. W. Steudel and H. Gilman, J. Am. Chem. Soc., 82, 6129 (1960).

157. H. Gilman, R. K. Ingham, A. G. Smith, J. Org. Chem., 18, 1743 (1953).

158. V. J. Shiner and M. L. Smith, J. Am. Chem. Soc., 80, 4095 (1958).

159. H. G. Brooks, "Syntheses and Reactions of Some Organosilicon Hydrides", Unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

160. R. G. Jones and H. Gilman, Organic Reactions, 6, 352 (1951).

161. C. D. Hurd, R. N. Jones and F. H. Blunck, J. Am. Chem. Soc., 57, 2033 (1935).

162. A. P. Krapco, J. Org. Chem., 27, 2375 (1962).

163. A. Lieben and A. Rossi, Ann. Chem., 158, 161 (1871).

164. O. W. Steward and O. R. Pierce, J. Am. Chem. Soc., 83, 1916 (1961).

165. C. M. Suter and A. W. Weston, J. Am. Chem. Soc., 63, 602 (1941).

166. W. B. Smith and J. D. Anderson, J. Am. Chem. Soc., 82, 656 (1960).

167. W. H. Saunders and D. H. Edison, J. Am. Chem. Soc., 82, 138 (1960).

168. M. S. Carpenter, W. M. Easter and T. F. Wood, J. Org. Chem., 16, 586 (1951).

169. H. J. B. Biekart, H. B. Dessens, P. E. Verkade and B. M. Webster, Rec. Trav. Chim. Pays-Bas, 71, 321 (1952).

170. A. I. Vogel, "Practical Organic Chemistry", third edition, John Wiley and Sons, Inc., New York, N.Y. 1962.

171. E. Berliner and M. M. Chen, J. Am. Chem. Soc., 80, 343 (1958).

172. D. Craig, J. Am. Chem. Soc., 57, 195 (1935).

173. H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, J. Am. Chem. Soc., 73, 3798 (1951).

174. H. Freiser, M. V. Eagle, J. L. Speier, J. Am. Chem. Soc., 75, 2821 (1953).

175. F. B. Deans and C. Eaborn, J. Chem. Soc., 498 (1957).

176. H. Gilman and E. Zeuch, J. Am. Chem. Soc., 81, 5925 (1959).

ACKNOWLEDGEMENTS

The author would like to thank Dr. Thomas H. Kinstle for his excellent guidance during the course of this research. Without his encouragement, interest, and patience, this work could not have been completed.

The author also acknowledges the many staff members and graduate students who have been willing to discuss various aspects of this work and who have helped to make the past four years a very enjoyable experience.

Financial support from the National Science Foundation, the Department of Health, Education and Welfare, and Eli Lilly and Company is gratefully acknowledged.

The author is also deeply indebted to his wife for encouragement during his graduate education and during the completion of this thesis.