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$\pi$  -  $\pi$  Bonding In Organosilicon Compounds

by

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A dissertation submitted to the University of Warwick for  
the degree of Doctor of Philosophy.

January, 1975.

#### ACKNOWLEDGEMENT

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This Thesis is the result of approximately two years work, between October, 1972 and December, 1974, and is the climax of my career as a student. It is all entirely original work, except where references are made.

I would like to thank Professor V. M. Clark for the use of the laboratory space and other facilities in the Department.

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## CHAPTER 1

### INTRODUCTION

#### (A) Theoretical Aspects of $p\pi$ - $p\pi$ Bonding in Organo silicon Compounds

Although chemists have known for a long time that compounds containing a carbon carbon double bond are stable, the situation is totally different on going from carbon to silicon. Up to the time of writing, there was no known isolable species containing a formal double or triple carbon-silicon bond.

Theoretical chemists have discussed  $2p\pi$  -  $3p\pi$  bonding in organosilicon compounds. In 1948, Pitzer<sup>1</sup> explained the preference of second row atoms for singly-bonded structures. The atoms of the second and subsequent rows all have inner electron shells which are larger (with respect to both size and number of electrons) than those of the first row. Consequently X-X single bond interatomic distances (Table (I)-1) are all larger for second-row atoms because of the increased repulsive forces between the inner shell electrons of one and the bonding orbital of the other. If a multiple bond is to be formed the  $p_y$  or  $p_z$  orbitals must approach sufficiently closely to form the  $\pi$ -component of the multiple bond by overlapping in a "sideways" fashion, and effective achievement of this is prevented by the repulsive effect of the large inner shells.

Mulliken<sup>3</sup> examined Pitzer's concepts quantitatively by evaluating the overlap integral  $S^*$ , which gives a measure of the electron density between the nuclei under consideration. Table (I)-2 gives calculated values of the overlap integral ( $S$ ) for  $2p$  -  $3p$  orbitals.

\*  $S = \int \psi_1 \cdot \psi_2 \cdot dv$ , where  $\psi_1$  and  $\psi_2$  are the atomic orbitals which overlap to form the bond considered, and  $dv$  is a small volume element.

Table (I)-1. Single-Bond Interatomic Distances, Å.

C - C 1.54	N - N 1.47	O - O 1.47	F - F 1.42
Si - Si 2.34	P - P 2.20	S - S 2.08	Cl - Cl 1.98
Ge - Ge 2.44	As - As 2.50	Se - Se 2.34	Br - Br 2.28
Sn - Sn 2.80	Sb - Sb 2.86	Te - Te 2.76	I - I 2.67

Data from Pauling<sup>2</sup>.

Table (I)-2. Calculated Overlap Integral at Appropriate Distances.

	C-C	C=C	Si-Si	Si=Si
Internuclear Distance (Å)	1.54	1.34	2.32	2.14
* $R/2r$	1.18	1.03	0.91	0.84
$S(2p\sigma-2p\sigma)$	0.33	0.32	-	-
$S(3p\sigma-3p\sigma)$	-	-	0.37	0.35
$S(2p\pi-2p\pi)$	-	0.27	-	-
$S(3p\pi-3p\pi)$	-	-	-	0.33

( $R$  = bond distance,  $r$  is the maximum in the radial probability curve,  $\xi = \frac{R}{r_1 + r_2}$ )

If an appropriate value of the parameter  $\xi$  was chosen, the value for  $S(2p_{\pi}-2p_{\pi})$  was found to be less than  $S(3p_{\pi}-3p_{\pi})$ . On repeating this calculation at constant  $\xi$ , one can obtain the expected results of low values of  $S(3p_{\pi}-3p_{\pi})$  compared to  $S(2p_{\pi}-2p_{\pi})$  as shown from Table (I)-3.

Table (I)-3. Calculated Overlap Integral at Constant ( $\xi$ ).

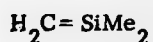
Bond	$\xi$		
	0.8	1.0	1.2
$S(2p_{\sigma}-2p_{\sigma})$	0.21	0.32	0.33
$S(3p_{\sigma}-3p_{\sigma})$	0.31	0.39	0.33
$S(2p_{\pi}-2p_{\pi})$	0.43	0.29	0.18
$S(3p_{\pi}-3p_{\pi})$	0.37	0.22	0.12

At  $\xi = 1.0$ , the C-C  $\pi$ -overlaps were found to be greater than Si-Si  $\pi$ -overlap (0.29 and 0.22 respectively). However, when the  $\sigma$ -overlaps were compared at  $\xi = 1.0$  the third-row overlap were found to be greater than the corresponding second-row overlaps. This led Mulliken to calculate that third-row elements form relatively stronger  $\sigma$ -bonds (as compared to  $\pi$ -bonds) than second-row elements. The reluctance for  $\pi$ -bonding in compounds of heavy elements is thus attributed to relatively stronger  $\sigma$ -bonds available on polymerisation.

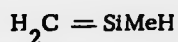
In another paper by Mulliken<sup>4</sup>, he pointed out that partial double bond character due to ( $d\pi-p\pi$ ) bonding in compounds of second row elements would improve their stability relative to a situation in which only  $p\pi-p\pi$  bonding were permitted.

In order to study the problem of  $p\pi-p\pi$  bonding in organosilicon compounds in more detail one must have an idea of the energetics of  $\pi$ -bonding. From the kinetic data of Flowers and Gusel'nikov<sup>5(a,b)</sup> on the pyrolysis of 1,1-dimethylsilacyclobutane<sup>(9)</sup> and from similar work by Davidson and Thomson<sup>6</sup> on trimethylsilane (see experimental part of the introduction), Walsh<sup>7</sup> estimated a value of  $138 \pm 22$  kJ/moles for both

1,1-dimethylsilaethylene (1) and 1-methylsilaethylene (2). The independence of the value for  $\pi$ -bonding energy on the substituent, is in agreement with the situation for olefins which also show little change in bond energy on changing substituent<sup>8</sup>. The value estimated by Walsh is not very different from a much lower estimate of 117 kJ/mol based on the dissociation energy of  $\text{Si}=\text{C}$ <sup>9</sup>. The estimated value for  $\pi$ -bonding in organosilicon compounds ( $\sim \frac{1}{2}$  the values for olefins) does not imply instability with respect to a unimolecular decomposition reaction but rather the very reactive behaviour of silaethylene in bimolecular reactions with other molecules.



(1)



(2)



(3)



(4)

The factors responsible for the instability of  $p\pi$ - $p\pi$  bonding in organosilicon compounds have been investigated thoroughly by Curtis<sup>10</sup>, using extended Huckel (EHMO) calculations on the molecules (3) and (4). The calculation showed that  $\text{C}=\text{Si}$  is exceedingly polar and behaves like a carbanion-siliconium ion combination. Energy mismatching between carbon and silicon p orbitals was suggested to be an important factor in the instability of silaethylene intermediates, the relatively high overlap integral of the  $\text{Si}=\text{Si}$   $\pi$ -bond (Table (I)-4) suggesting that compounds containing such bonds might be amenable to isolation.

Table (I)-4. Overlap Integrals  $p\pi$ - $p\pi$  and  $p\pi$ - $d\pi$   
Bonded atoms.

Orbitals	S	Orbitals	S
$2p\pi - 2p\pi$	0.270	$3p\pi - 3p\pi$	0.228
$2p\pi - 3p\pi$	0.182	$3p\pi - 3d\pi$	0.448
$2p\pi - 3d\pi$	0.362	$3d\pi - 3d\pi$	0.303



The high value of  $d\pi - p\pi$  suggests that its overall contribution to  $p\pi - p\pi$  bonding in silaethylene and disilaethylene can be substantial, in fact the result for silaethylene overlap population is 0.327 and is composed of  $p\pi - p\pi$  and  $p\pi - d\pi$  contributions. Fig. (I)-1.

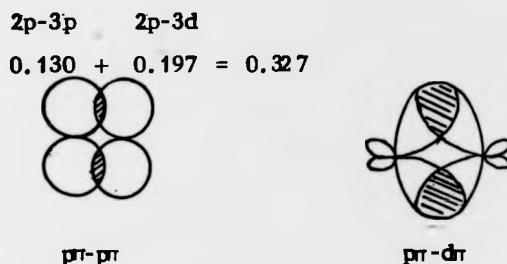


Fig. (I)-1 Contribution of  $p\pi - p\pi$  and  $p\pi - d\pi$  hybrid to the silaethylene overlap population.

The overlap population for disilaethylene was broken down into  $p\pi - p\pi$ ,  $p\pi - d\pi$  and  $d\pi - d\pi$  contributions<sup>10</sup>.

$p\pi - p\pi$	$p\pi - d\pi$	$d\pi - d\pi$
0.277	+0.348	+ 0.038 = 0.663

Fig. (I)-2 schematically shows the form of the molecular orbitals and their relative energies as calculated by the EHMO (Extended Hückel Molecular Orbital) method. The numbers over each energy level represent the overlap populations between the central atoms for each molecular orbital, positive numbers indicate bonding behaviour for that MO, while negative numbers indicate anti-bonding behaviour.

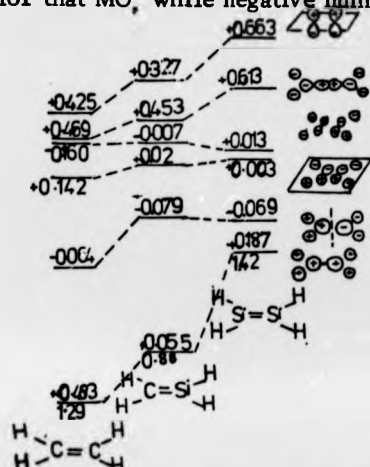


Fig. (I)-2 Relative energies and X-Y overlap populations for  $H_2XYH_2$  molecules ( $X, Y = C, Si$ ).

The head to tail dimerisation of silaethylenes which had been established earlier by Flowers and Gusel'nikov<sup>5(a,b)</sup>, and more recently by Barton<sup>11, 12</sup> was explained by Curtis<sup>10</sup>. From a molecular orbital standpoint, the LUMO's and HOMO's of  $\text{H}_2\text{C}=\text{SiH}_2$  are shown schematically in Fig. (I)-3. The relative sizes of the atomic orbitals represent the contribution of that atomic orbital to the MO. Thus in the  $\pi$ -bond the electrons are strongly localized on carbon, but the reverse is true in the  $\pi^*$ -LUMO. In a head-to-tail dimerization there is a net positive overlap (bonding) between the HOMO and LUMO - a situation that lowers the orbital symmetry restriction to dimerization<sup>13</sup>.

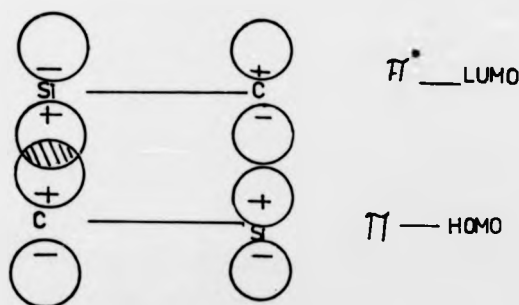
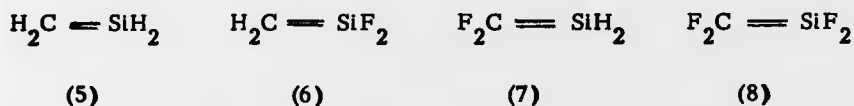


Fig. (I)-3. Orientation of HOMO and LUMO in head-to-tail dimerisation of  $\text{C}=\text{Si}$ .

The diradical species  $\text{H}_2\text{Si}-\text{SiH}_2$  was estimated to be less stable than the  $\pi$ -bonded disilaethylene by about 235 kcal/mole<sup>10</sup>. However, a suitable substituent, such as t-butyl, can stabilise the disilaethylene, and might make the compound amenable to isolation at low temperature.

Substituent effects on the stability of silaethylene intermediates have been calculated for a series of fluorinated species at the level of CNDO/2 (complete neglect of differential overlap)<sup>14</sup>. The following series of compounds were investigated.



According to Damrauer and Williams'<sup>14</sup> calculations, difference in reactivity among this series of compounds is attributed to a difference in the localised  $\pi$  electron density, as shown in Table (I) - 4.

Table (I)-4. Electron Densities of Compounds (5)-(8)

	Carbon	Silicon	Fluorine	Total
(5)	1.25	0.76		2.01
(6)	1.32	0.92	2 x 1.88	6.00
(7)	1.09	0.98	2 x 1.96	5.99
(8)	1.19	1.11	on carbon 2 x 1.97 on silicon 2 x 1.88	10.00

Assuming that the reactivity of these compounds is governed by electrostatic factors, (5), (6) and (7) were predicted to dimerise in head-to-tail fashion, giving the corresponding 1,3-disilacyclobutanes, whilst (8) was predicted to be unreactive towards dimerisation. These calculations again suggested a significant contribution from  $d\pi$  orbitals in (5)-(8) as shown in Table (I)-5.

Table (I)-5. Calculated charge densities of compounds (5)-(8).

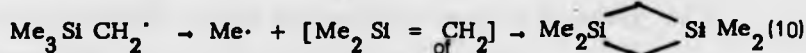
Compound	Charge Densities				$\pi$ Bond Orders			Total orbital charge densities.
	Si	C	Atoms on Si	Atoms on C	2p-3p	2p-3d <sub>xz</sub>	Total $\pi$ bond order	
(5) (H <sub>4</sub> )	0.40	-0.31	-0.12	0.07	0.74	0.63	1.37	0.76
(6) (F <sub>2</sub> H <sub>2</sub> )	0.76	-0.33	-0.31	0.10	0.70	0.64	1.34	1.02
(7) (H <sub>2</sub> F <sub>2</sub> )	0.31	0.17	-0.08	-0.17	0.80	0.54	1.34	0.64
(8) (F <sub>4</sub> )	0.73	0.12	-0.25	-0.15	0.75	0.59	1.34	0.98

An increase in charge density was observed especially if fluorine is attached to a silicon atom. In this situation fluorine withdraws electron density through the Si-F sigma bonds, allowing back-donation from fluorine sp<sup>3</sup> lone-pairs<sup>14</sup>.

(B) Experimental Evidence for  $\pi$ - $\pi$  Bonding in Organosilicon Compounds.

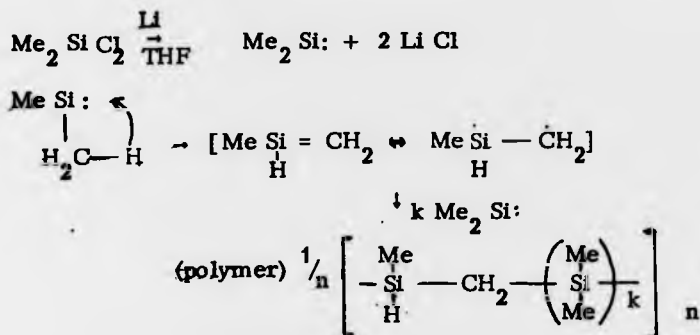
A review on  $\pi$ -bonding in organosilicon compounds has been made by Attridge<sup>15</sup>, covering the experimental work on silaethylene intermediates up to 1969.

In their work on the thermolysis of tetramethylsilane, Fritz and his coworkers<sup>16</sup> invoked a silaethylene intermediate. According to their mechanism tetramethylsilane dissociates thermally into free radicals Scheme (I-1).



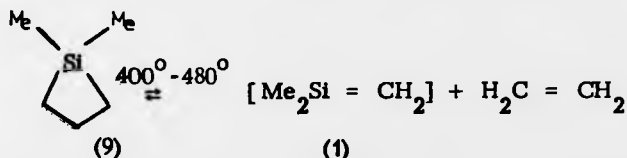
Scheme (I-1) A path-way for the thermolysis of Me<sub>4</sub>Si.

In the reaction of lithium metal with dihalosilane in THF<sup>17</sup>, the products obtained were explained by suggesting a mechanism which involved silaethylene intermediates according to scheme (I-2).

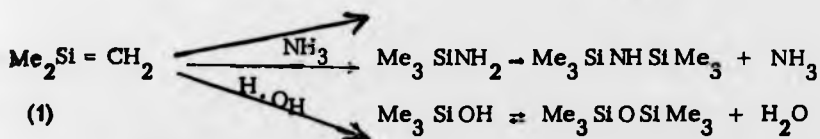
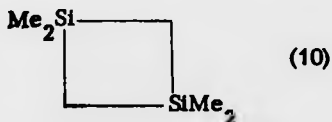


Scheme (I-2): Silaethylene as intermediates in the reaction between  $(\text{CH}_3)_2\text{SiCl}_2$  and Li.

In their kinetic studies of 1,1-dimethyl-1-silacyclobutane (9) thermolysis, Flowers and Guselnikov<sup>5(a,b)</sup> obtained excellent evidence that the thermolysis went through a silaethylene intermediate in a reversible rate-limiting step.



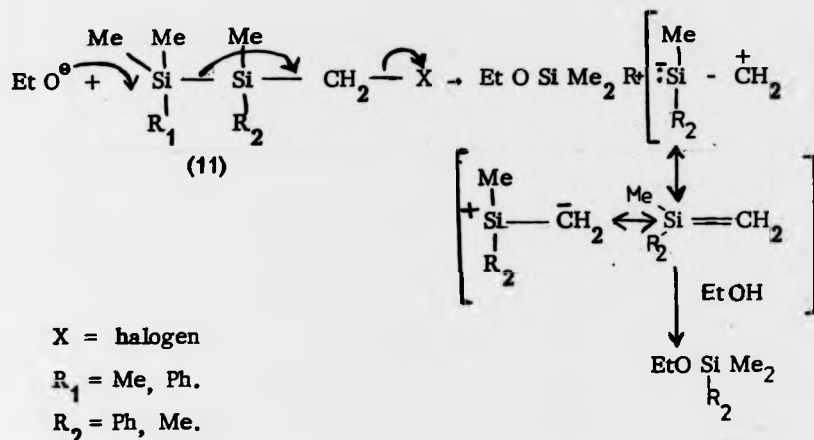
The 1,1-dimethylsilaethylene intermediates formed can undergo rapid dimerisation through head-to-tail fashion in vapour phase :



Scheme (I-3): Different reaction pathways for (1).

The reactive intermediate (1) may be trapped by water or ammonia, as indicated in Scheme (I-3).

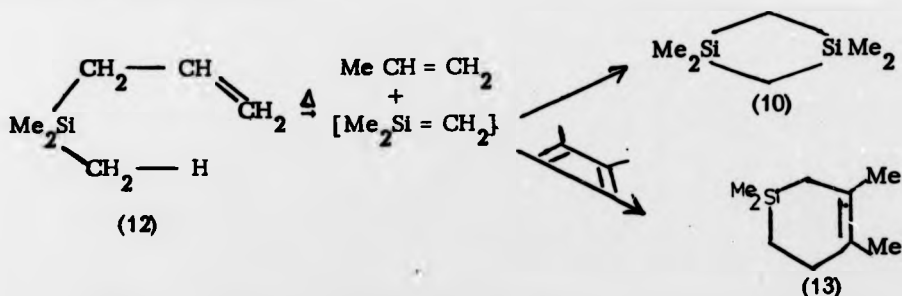
In the reaction of ethoxide with a disilane<sup>18</sup> dimethylphenylethoxysilane was obtained, a product which is most easily rationalised if reaction proceeds via an intermediate Scheme(I-4).



Scheme (I-4): Solvolysis mechanism for disilane derivatives (11).

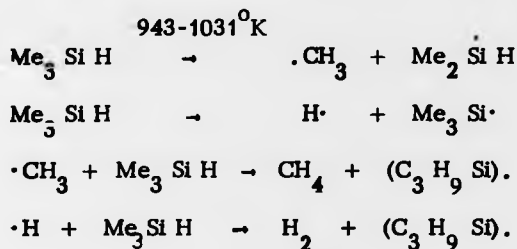
Strong evidence for the intermediacy of (1) has been acquired by Bailey and Kaufmann<sup>19</sup> in the pyrolysis of allyltrimethylsilane (12) the intermediate generated being intercepted in a Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene giving 1,1,3,4-tetramethyl-1-sila-3-cyclohexene (13). (Scheme (I-5)).

In absence of this reagent the intermediate dimerised to 1,1,3,3-tetramethyl-1,3-disilacyclobutane (10) in the normal manner. Presumably a six-electron concerted transition-state is involved in similar manner to the retro-ene reaction in organic chemistry.



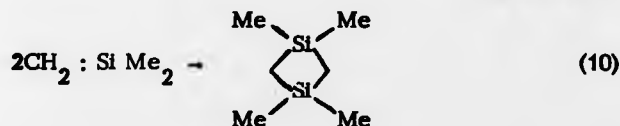
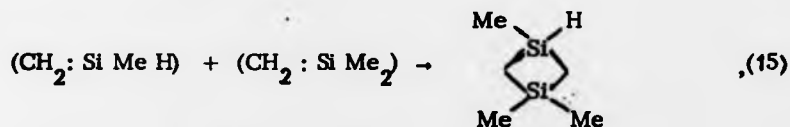
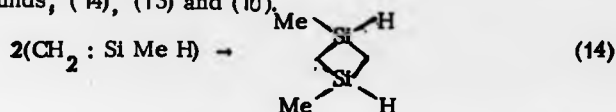
Scheme (I-5): Interception of (1) by using 2,3-dimethyl-1,3-butadiene.

From a rather complicated mechanistic sequence, Davidson and Lambert<sup>20</sup> suggested that on pyrolysis of trimethylsilane, a silaethylene derivative was generated as an intermediate, through a non-chain reaction path way, Scheme (I-6).

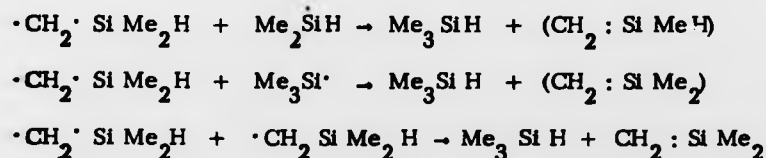


Scheme (I-6): Free radical mechanism for the pyrolysis of  $\text{Me}_3\text{SiH}$ .

and evidence for the formation of silaethylene intermediate had been suggested on the basis of isolation of three cyclic silicon compounds, (14), (15) and (10).

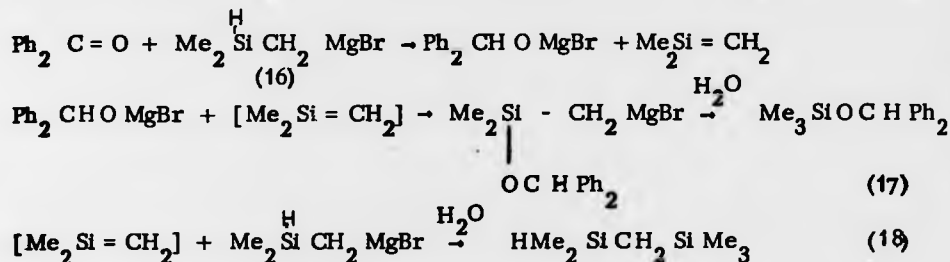


The most likely precursor to  $(\text{CH}_2 : \text{Si Me}_2)$  and  $(\text{CH}_2 : \text{Si Me H})$  is the radical  $\cdot\text{CH}_2\text{-Si Me}_2\text{H}$ , but since methane and hydrogen were both formed in non-chain sequences direct dissociation of  $\cdot\text{CH}_2\text{Si Me}_2\text{H}$  is excluded. The only possible rationalisation invoked is the disproportionation reaction:



Jarvie and Rowley<sup>22</sup> investigated the reaction between benzophenone and dimethylsilylmethylmagnesium bromide, isolating benzhydryloxytrimethylsilane (17) (89%) and three other minor products which were dimethylsilylmethyltrimethylsilane (18)

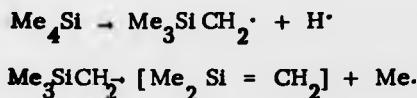
(12%), benzhydrol (8%) and 1,1-diphenylethylene (3%). This product distribution is rather abnormal, and indicative of a silaethylene intermediate formed via reductive hydride transfer as shown below in Scheme (I-7).



Scheme (I-7): A proposed mechanism for the reaction between  $\text{Ph}_2\text{CO}$  and  $\text{Me}_2\text{SiCH}_2\text{MgBr}$ .

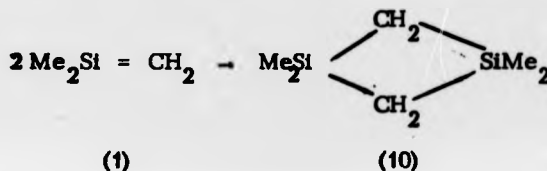
A silaethylene intermediate was suggested to explain the product obtained. The authors observed this abnormal behaviour only with benzophenone. On using acetone the reaction reverted to the normal condition giving the expected product of addition followed by  $\beta$ -elimination<sup>22</sup>.

The work on pyrolysis of tetramethylsilane<sup>16</sup> has been repeated under precise conditions<sup>21</sup>, 1,1,3,3-tetramethyl-1,3-disilacyclobutane(10) was isolated in low yield, a product which suggests the generation of 1,1-dimethylsilaethylene (1) as intermediate Scheme (I-8).



Scheme (I-8): (1) as intermediates in the pyrolysis of  $\text{Me}_4\text{Si}$ .

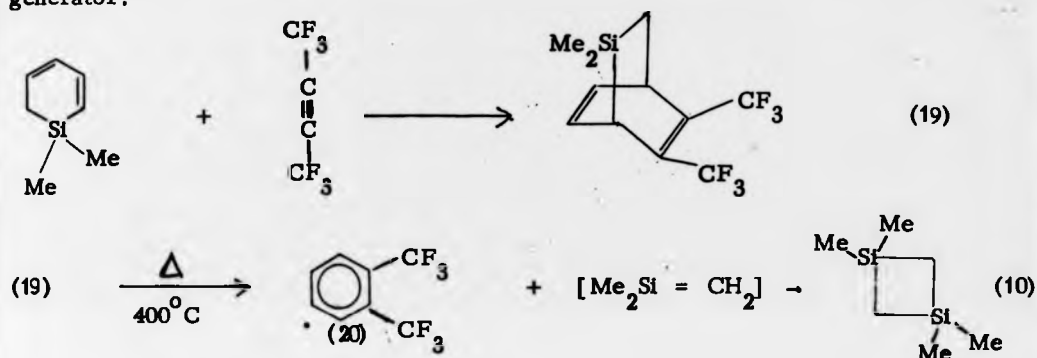
The production of this intermediate was proved by the formation of 1,1,3,3-tetramethyl 1,3-disilacyclobutane.





A value of 17 kcal mole<sup>-1</sup> was estimated to be the amount of energy available to stabilise the  $\pi$ -bond in Si = C which is a lower value than that derived by Walsh<sup>7</sup>.

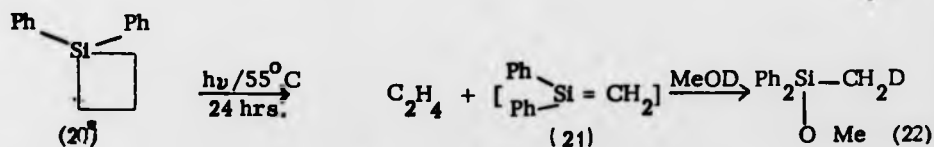
2,3-Bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo [2.2.2] octa-2,5-diene(19), has been prepared<sup>23</sup> by Diels-Alder reaction of 1,1-dimethyl-1-silacyclohexa2,4-diene and an excess of perfluoro-2-butyne,(19) has been used as a silaethylene generator.



Thermolysis of (19) is efficient at 400°, (20) and (10) being isolated in good yield.

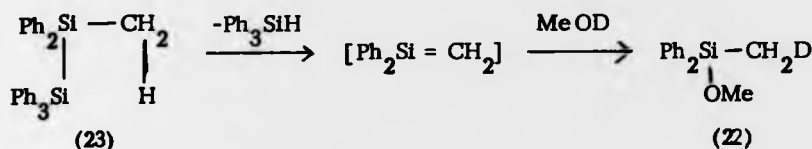
In a subsequent paper, Barton<sup>12</sup> was able to determine the i.r. spectra of  $\text{CH}_2=\text{SiMe}_2$  by depositing the pyrolysis product from 1,1-dimethyl-1-silacyclobutane on to a sodium chloride plate at -196°C. The sharp new adsorption which occurred at 1407 cm<sup>-1</sup> and which disappeared on warming the cell gently, was assigned to C=Si stretching.

A photochemical technique was used by Sommer<sup>24, 25</sup> and his co-workers, to generate a silaethylene intermediate. On photolysis of 1,1-diphenyl-1-silacyclobutane (20) at 55°C and 2537 Å, a novel intermediate (21) was obtained, which can add deuteriomethanol to give diphenyldeuteriomethylmethoxysilane (22) in high yield, (80%) (Scheme I-9).



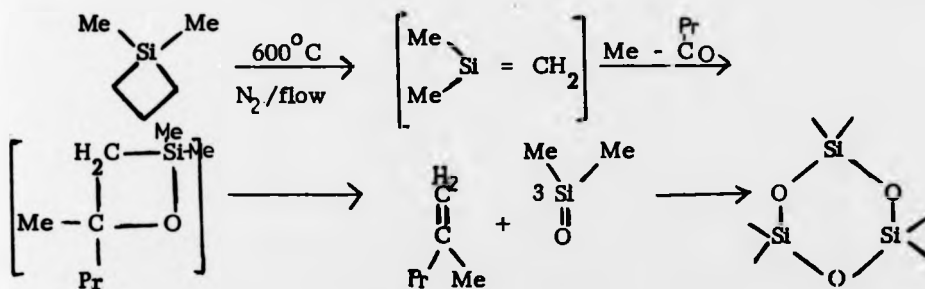
Scheme(I-9): Photolysis of (20) in presence of MeOD.

In a photochemical dehydrosilylation of pentamethylphenyldisilane<sup>25</sup> (23), a silaethylene intermediate was generated which formed (22) in the presence of deuteriomethanol as shown in Scheme (I-10)



Scheme (I-10) Dehydrosilylation of (23) in presence of MeOD.

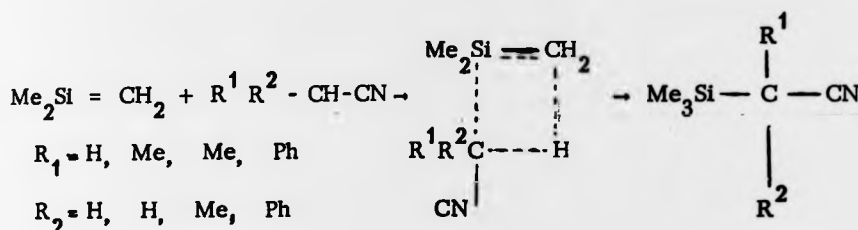
The silaethylene intermediates (1) which have previously been observed by Guselnikov and Flowers<sup>5(ab)</sup>, had been intercepted by adding methyl propyl ketone to the reaction mixture<sup>26</sup>. Scheme (I-11).



Scheme (I-11) Wittig type reaction, interception of (1) by ketone.

The highly polar nature of  $\text{Si} = \text{C}$  which has been suggested<sup>10</sup>, is the main driving force for this reaction which shows a similarity to the Wittig reaction in phosphorus chemistry, in which aldehyde or ketone is treated with a phosphorus ylide to give an olefin.

In a similar mechanism<sup>27</sup> dimethylsilaethylene (1) had been intercepted by acetonitrile or substituted acetonitrile via a four-centered transition state, (Scheme I-12), to give the corresponding  $\alpha$ -trimethylsilyl-substituted acetonitriles, 1, 1-dimethyl-1-silacyclobutane was used to generate silaethylene by heating at  $611^\circ\text{C}$ .

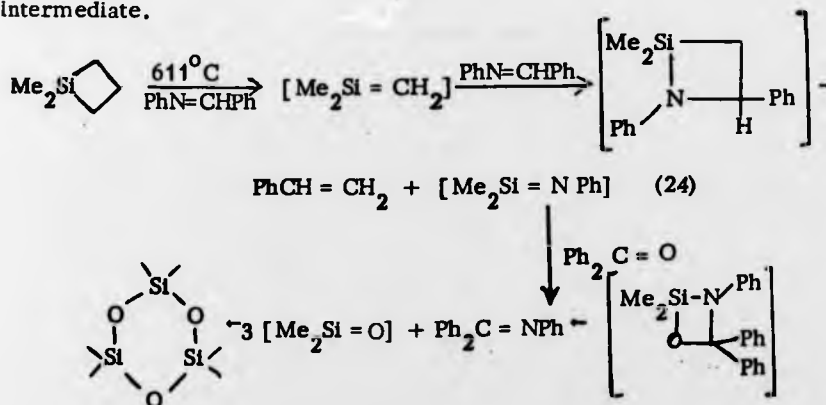


Scheme (I-12): A four-centered transition state in the reaction between silaethylene and acetonitrile or its derivatives.

Another probable complex multi-step mechanism, involving interaction between silicon and nitrogen, followed by 1, 3 shift of  $\text{Me}_3\text{Si}$  from nitrogen to the methylene in an allenic type system, can exist<sup>27</sup>.

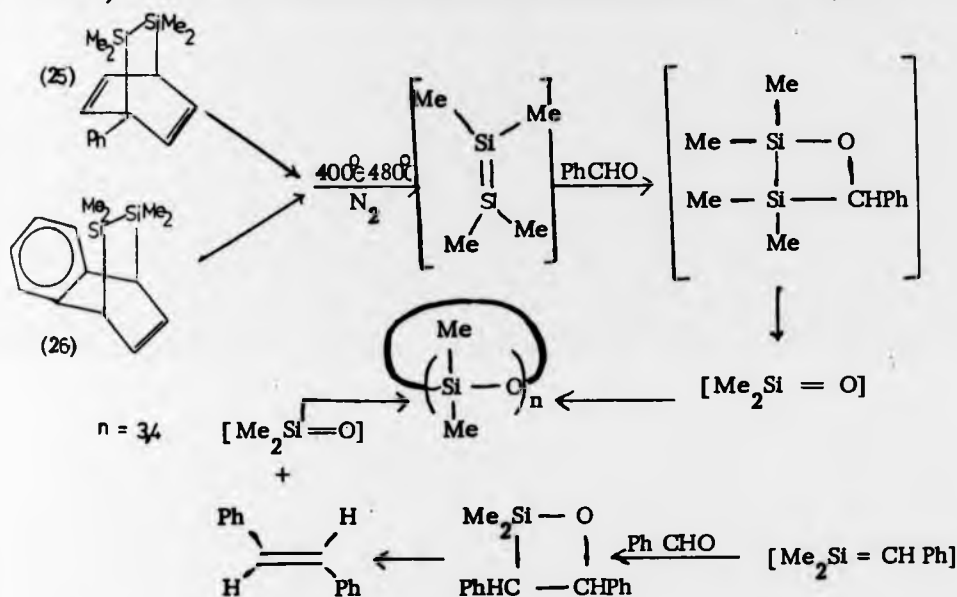
The above discussed reaction between  $\text{Si}=\text{C}$  and aldehydes or ketones<sup>24, 25, 26</sup> has been described again in a full paper<sup>28</sup> with a variety of ketones and aldehydes. In this work the silaethylene generator was a 11-disubstituted silacyclobutane using a thermolysis technique.

Sommer<sup>29</sup> was able to intercept  $\text{Si}=\text{C}$  with imines ( $-\text{N}=\text{C}$ ), and the products obtained were explained on the basis of a sillinene intermediate (24) according to Scheme (I-13). Benzophenone was used to intercept this unique intermediate.



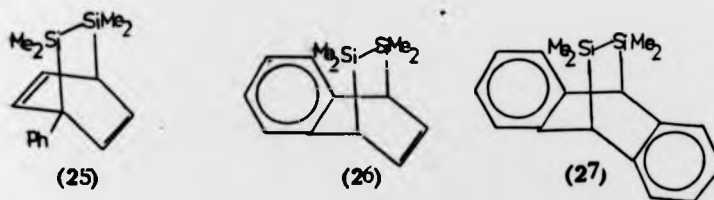
Scheme (I-13): Generation of  $\text{Si}=\text{N}$  via reaction of imines with  $\text{Si}=\text{C}$ .

In a one step reaction, Barton<sup>30</sup> was able to generate intermediates containing silicon-oxygen, silicon-silicon and silicon-carbon double bonds, by thermolysing 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2,2,2]octa-2,5-diene (25) or 5,6-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2,2,2]octa-2,5-diene (26) in presence of excess benzaldehyde at 480-500°C, Scheme (I-14).

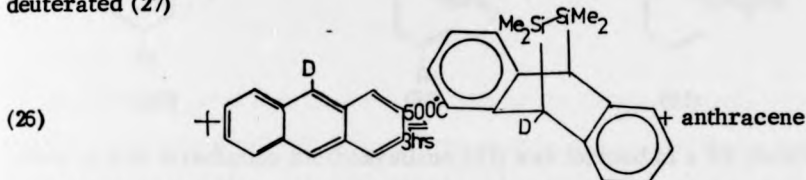


Scheme (I-14) Interception of silaethylenes resulting from pyrolysis of (25), (26) by using benzaldehyde.

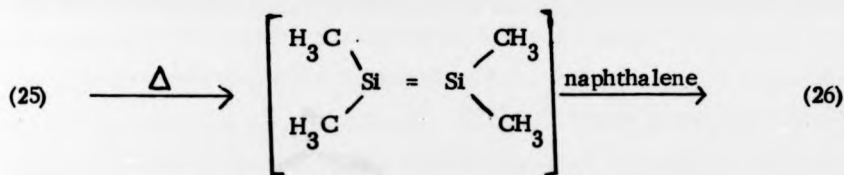
A similar approach was applied by Roark and Peddle<sup>31</sup> who succeeded in generating this intermediate, by pyrolysis of 7,8-disilabicyclo[2,2,2]octa-2,5-dienes derivatives (25), (26) and (27).



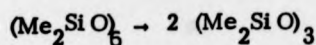
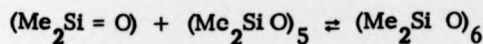
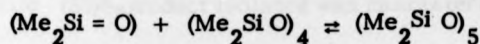
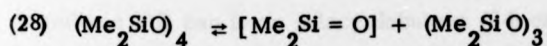
On heating these in a sealed tube at 500°C, 360°C and 260°C respectively, a white oily residue was obtained, which was thought to be a rearranged polymer of tetramethyldisilaethylene. To prove this, on heating (26) in presence of 9-deuterioanthracene, exchange of the tetramethyldisilene bridge occurred to give a statistical mixture of monodeuterated and undeuterated (27)



Compound (25) on pyrolysis in presence of excess naphthalene was found to give a quantitative yield of (26).



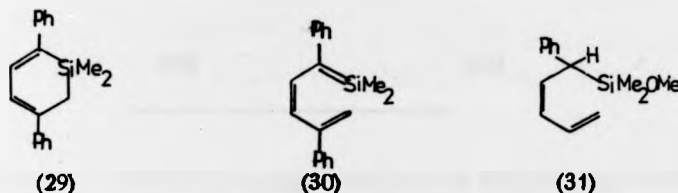
A dimethylsilanone ( $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{Si} = \text{O} \\ \diagup \\ \text{H}_3\text{C} \end{array}$ ) has been postulated as an intermediate<sup>32</sup>, in the pyrolysis of octamethylcyclotetrasiloxane (28) according to the following Scheme (I-15).



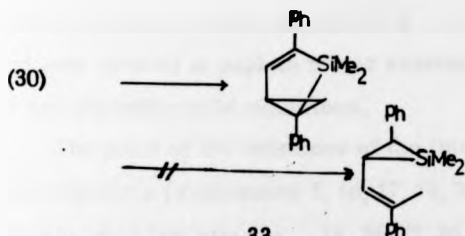
Scheme (I-15): Dimethyl silanone as intermediates in pyrolysis of (28).

A value of  $\geq 37.8 \text{ kcal mol}^{-1}$  was estimated for the  $\pi$ -bond energy in dimethyl silanone, which is quite consistent with the theoretical value  $40.4 \text{ K Cals mol}^{-1}$ <sup>32</sup>.

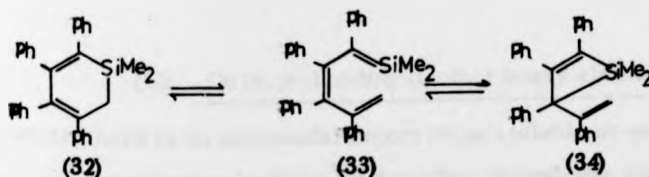
A recent paper by Sakurai<sup>33</sup> and his group concerns generation of an intermediate containing C=Si, in the photolysis of 1,1-dimethyl-2,3-diphenyl-1-sila-2,4-cyclohexadiene (29) in an nmr tube, using a 450 watt high-pressure mercury arc lamp in methanol/benzene:



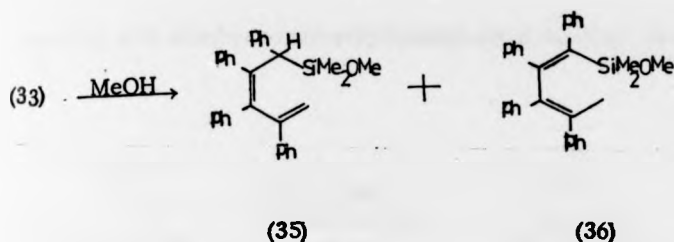
After 2.5 hr irradiation methoxysilane (31) was formed in a 5% yield but in the absence of methanol this intermediate rearranged intramolecularly through (2+4) cycloaddition. The alternative silacyclopentane is not formed in this reaction.



The same author<sup>33</sup> pointed out, that the tetraphenyl derivative of silacyclohexadiene (32) can form silacyclobutene (34) on irradiation, through the intermediate (33). The product isolated was characterised by nmr; intermediate



(33) was intercepted by adding MeOH to form (35) and (36).



In summary, there is no reported work in the literature up to the time of writing this thesis about isolable species containing a formal  $\pi$ - $\pi$  bond in organosilicon chemistry.

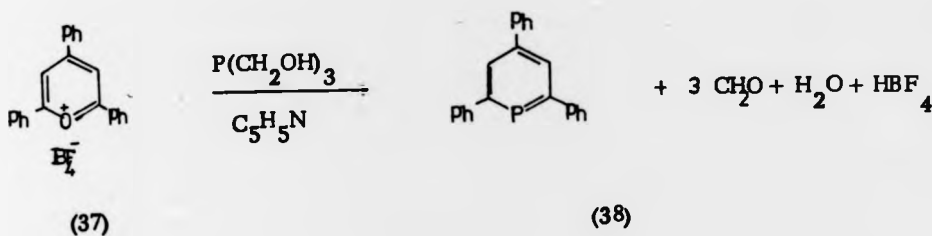
Thus, either thermolysis - [references 5, 6, 12, 16, 17, 19, 20, 21, 23, 27, 28, 29, 30, 31 and 32] or photolysis [references 24, 25, 26 and 33] has been applied to the generation of  $\pi$ -bonded organosilicon intermediates, the former technique having been used extensively by Barton and his co-workers, the latter technique used by Sommer and his co-workers. An intermediate containing  $\pi$ - $\pi$  bonding had been invoked to explain minor reaction pathways at room temperature [references 18 and 22] under mild conditions.

The proof of the existence of the intermediates, was based either on mechanistic investigations [references 5, 16, 17, 18, 20, 21, 22, 29, 30, 31 and 32], or trapping experiments [references 19, 24, 25, 26, 27, 28 and 33]. The nature of the trapping agent varied from an ordinary Diels-Alder reagent<sup>19</sup>, to aldehydes, ketones, alcohols and acetonitrile [15, 24, 25, 26, 28 and 33], in the latter cases the reaction resembles a conventional Wittig reaction, bearing in mind the high polarisability of  $\text{C}=\text{Si}$ <sup>10</sup>, which enables the intermediate to behave as a carbanion-siliconium ion.

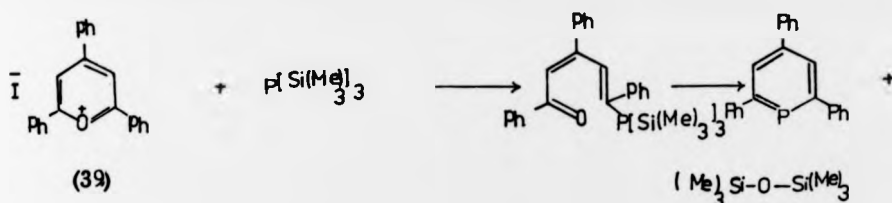
#### (C) . On $\pi$ - $\pi$ -bonding in other heavy elements.

Whilst there is no successful report on an isolable  $\pi$ - $\pi$  bonded organosilicon compound, the situation is different for other second-row elements. A series of Group(V) heteroaromatic compounds has been prepared and are reported in a series of papers by Märkl and his co-workers<sup>34</sup>. For example 2,4,6-triphenylphosphabenzene (38) has been prepared from the corresponding pyrylium tetrafluoroborate(37),

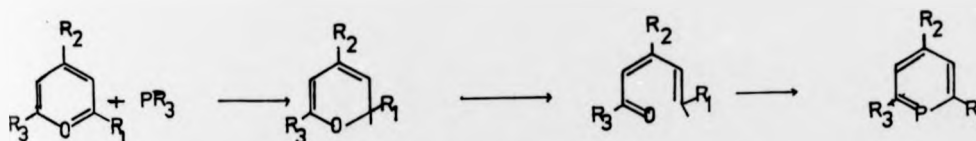
reacting with tris(hydroxymethyl)phosphine in boiling pyridine <sup>34(a)</sup>



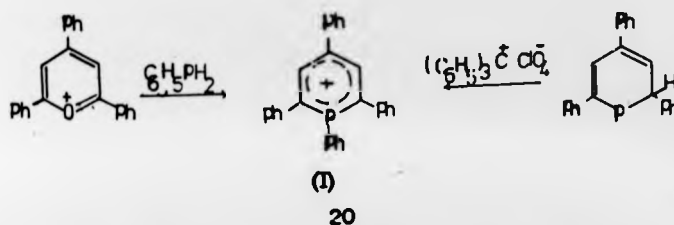
Similarly, a high yield of 2,4,6-Triphenylphosphabenzene (38) was obtained by refluxing 2,4,6-Triphenylpyrylium iodide (39) and tris(trimethylsilyl)phosphine in anhydrous acetonitrile <sup>34(b)</sup>



This method of preparation of alkylated phosphabenzenes can be extended to the preparation of alkyl derivatives, for example:

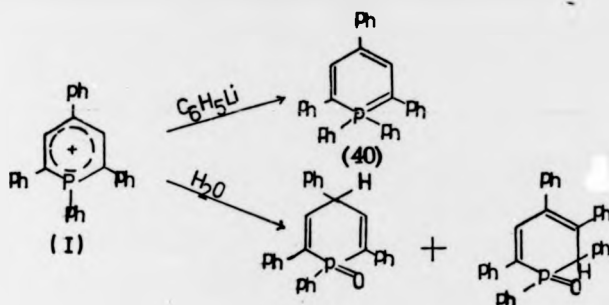


and a 1,1-diaryl-phosphabenzole (40) had been prepared <sup>34(c)</sup> (e.g.)

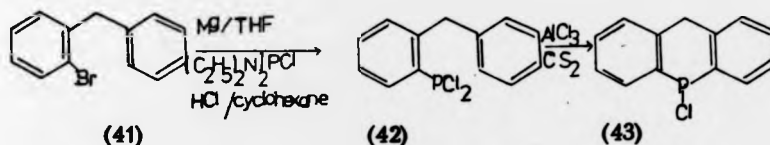




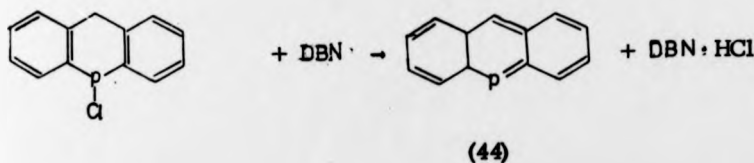
by reaction of phenyllithium on the phosphonium intermediate (I).



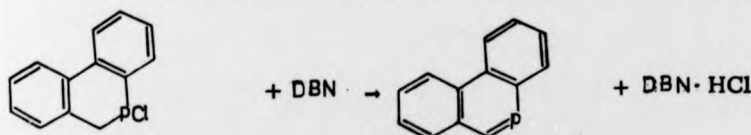
A dibenzo(b, e)phosphorine had been prepared by reaction of the Grignard compound from (o-bromophenyl)phenylmethane (41) and chloro bis(diethylamino)phosphine in tetrahydrofuran at  $-80^\circ\text{C}$ , to give o-benzylphenyldichlorophosphine (42), which



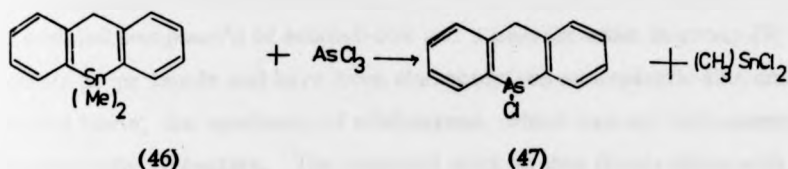
subsequently reacted with aluminium chloride in carbon disulphide and gave (43). On adding 1, 5-diazabicyclo[4, 3, 0]non-5-ene (DBN) to solution of (43) in toluene or dimethylformamide, dibenzophosphorine (44) was obtained.



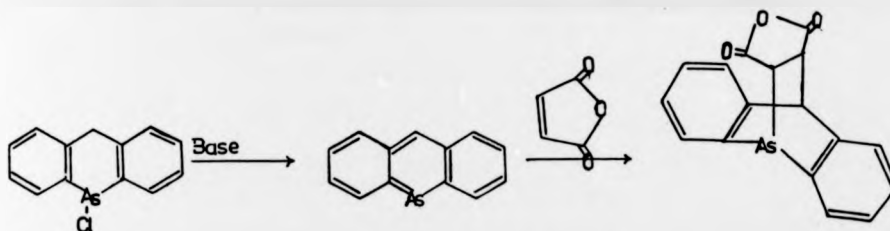
A similar route had been used for the synthesis of Dibenzob[d]phosphorine<sup>36</sup>



The preparation of 9-Arsaanthracene has been described by two groups.<sup>37, 38</sup> Jutzi prepared this compound in a two step reaction in which 9,9-dimethyl-9,10-dihydro-9-stannanthracene (46) was first condensed with arsenious chloride giving 9-chloro-9,10-dihydro-9-arsaanthracene (47).

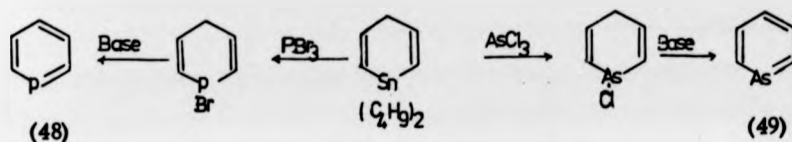


Subsequently the dihydroarsaanthracene was treated with base in THF at 0°. Arsaanthracene was found to add maleic anhydride to form a Diels-Alder adduct, similar to the reaction of anthracene itself but under much milder conditions.



The above method was used for preparation of phosphaaanthracene and stibaaanthracene<sup>39</sup>.

Recently Ashe<sup>40</sup> succeeded in preparing phosphabenzene (48) and arsabenzene (49) in a one-step reaction, treatment of 1,4-dihydro-1,1-dibutylstannabenzene with phosphorus tribromide or arsenic trichloride gave the dihydrobromide of phosphabenzene and arsabenzene. Alternatively, the products obtained on treatment with 1,5-diazobicyclo[4,3,0]non-5-ene (as a base) afforded phosphabenzene and arsabenzene. Nmr of these compounds shows a definite aromaticity.



(D) Object of the present investigations.

In the light of the above mentioned discussion, there is an accumulation of results concerning the generation of intermediate containing  $\pi-\pi$  bonds ((I)-B) in organosilicon chemistry. Section (I)-C has drawn together a variety of isolated compounds of second-row and a heavier atom in group (V) which contain  $\pi-\pi$  bonds and have been characterised as aromatic-like compounds<sup>40</sup>. On this basis, the synthesis of silabenzene, which has not been attempted before is potentially attractive. The reported work in this thesis deals with an attempt to isolate silabenzene or a derivative, via silanation of some cationic Ir(I) and Rh(I) organometallic species, and by attempted dehydrogenation of dihydro-silabenzene. In addition, a detailed investigation has been made of the mechanism of solvolytic rearrangement of chloromethyldimethylsilane in pyridine, using kinetic, spectroscopic and isotopic labelling techniques.

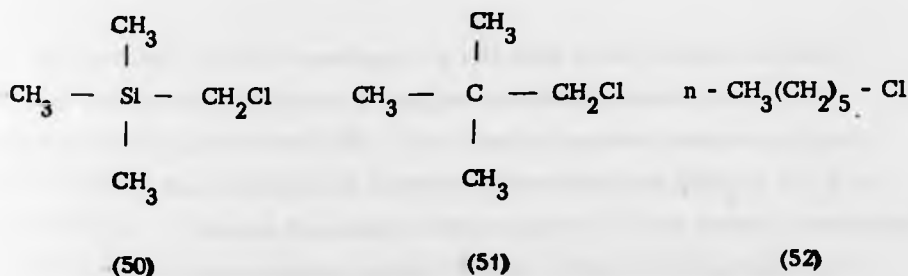
## CHAPTER 2

### Nucleophilic Reactions of $\alpha$ -Haloalkylsilanes.

In this Chapter the solvolysis of  $\alpha$ -haloalkylsilanes and trialkylsilanes (compounds with related structure to the substrate under investigation), will be reviewed in Sections A and B. Section C will cover the experimental details of the problem under investigation; Sections D and E discuss the possible reaction mechanisms, and finally Sections F and G will cover the experimental details concerning this work.

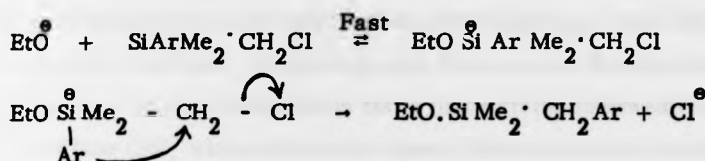
#### A. On the solvolysis of $\alpha$ -haloalkylsilanes.

An  $S_N2$  type mechanism has been observed earlier in the solvolysis of chloromethyltrimethylsilane (50) promoted by sodium ethoxide in dry ethanol.<sup>41</sup> Neopentyl chloride (51) was found to be less reactive; the reason for this was discussed on the basis of steric hindrance, which is less in (50) than in (51).



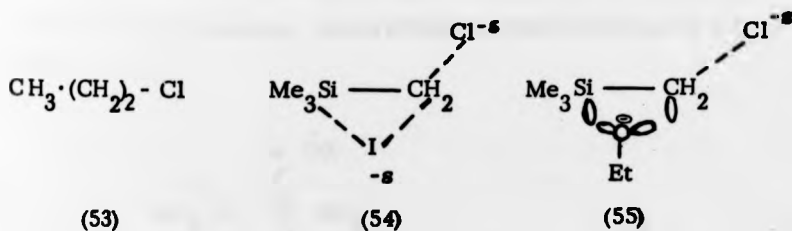
Compound (51) is also rather less reactive than n-hexyl chloride (52) towards nucleophilic reagents, and much less reactive towards electrophilic reagents, (e.g.  $\text{Ag}^+$ ). The lower reactivity which is observed in (50) under the influence of nucleophilic

attack can be attributed to the effect of  $\text{Me}_3\text{Si}$  as an electron releasing group. In agreement with this, the substitution reaction between substituted aryldimethyl halomethylsilanes ( $\text{XC}_6\text{H}_4\text{Me}_2\text{SiCH}_2\text{Cl}$ ) and sodium ethoxide in ethanol is slowed down by electron releasing substituents X(p-Me, p-MeO) and facilitated by electron withdrawing substituents.<sup>42</sup> Reaction takes place by a bimolecular mechanism, through a two-step process (Scheme II-1).<sup>42</sup>



Scheme (II-1): A bimolecular nucleophilic substitution reaction through a two step process.

The reaction between (50) and iodide ion in acetone solution has been investigated<sup>43, 44</sup>. The reactivity of (50) was estimated to be 16 times higher than n-butyl chloride (53). This observed high reactivity of the silicon compound was attributed to the ability of the vacant d-orbital on silicon to accommodate an electron from the donor  $\text{I}^\ominus$  to form an intermediate (54).



No intermediate corresponding to (54) can exist in the reaction between (50) and ethoxide ion because of the oxygen atom which cannot bind to Si-C bond in a comparable way (55). The situation becomes more complicated by the report<sup>45</sup> that solvolysis of iodomethyltrimethylsilane ( $\text{Me}_3\text{SiCH}_2\text{I}$ ) is several times slower than ethyl iodide in contrary to the earlier observation<sup>41</sup>.

In the case of the secondary halide 1-chloro-1-trimethylsilyl ethane (56) it has been observed<sup>46</sup> that (50) is 200 times more reactive than (56) towards iodide ion, a ratio similar to that found for primary and secondary alkyl halides.



(56)



(57)

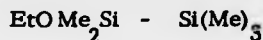


(58)

It has been pointed out<sup>47</sup> that the nature of nucleophile can change the selectivity in the nucleophilic substitution reaction of organosilicon compounds. Thus chloromethyldimethylpentamethyldisilane (57) undergoes three different types of nucleophilic reactions, depending upon the nature of the nucleophile used. With iodide ion in acetone, substitution takes place giving iodomethyldimethylpentamethyldisilane (58), with ethoxide in ethanol intramolecular rearrangement giving ethoxypentamethyldisilylmethane (59), while under the influence of nucleophilic attack of cyanide ion in ethanol cleavage of the carbon-silicon bond occurs to yield (60).

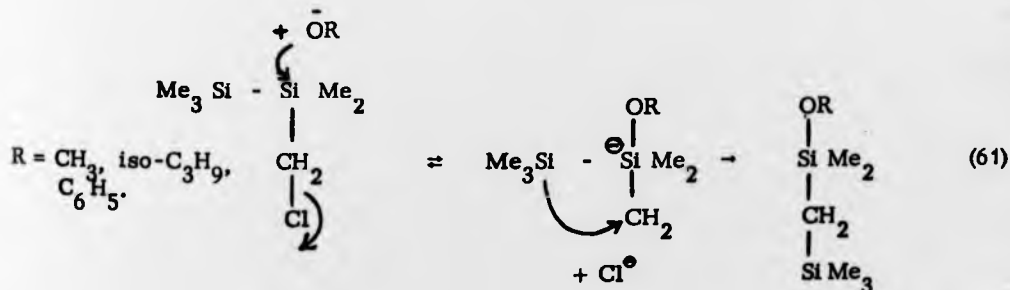


(59)



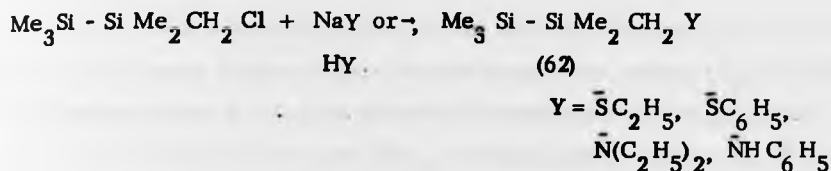
(60)

Kumuda in a subsequent paper<sup>48</sup> has shown that (57) underwent intramolecular rearrangement when treated with sodium methoxide, isopropoxide and phenoxide to give the corresponding, alkoxypentamethyldisilylmethanes (61) as shown in Scheme (II-2).



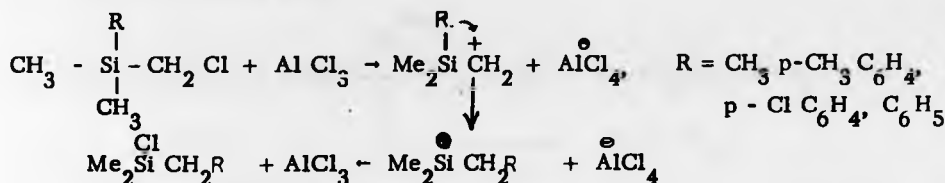
Scheme (II-2): Intramolecular rearrangement of disilane (57) with alkoxide ions.

Reaction of (57) with sodium ethylmercaptide and thiophenolate gives substitution products only (62); also substitution product was obtained on using diethylamine or aniline as nucleophile<sup>48</sup>, Scheme (II-3).

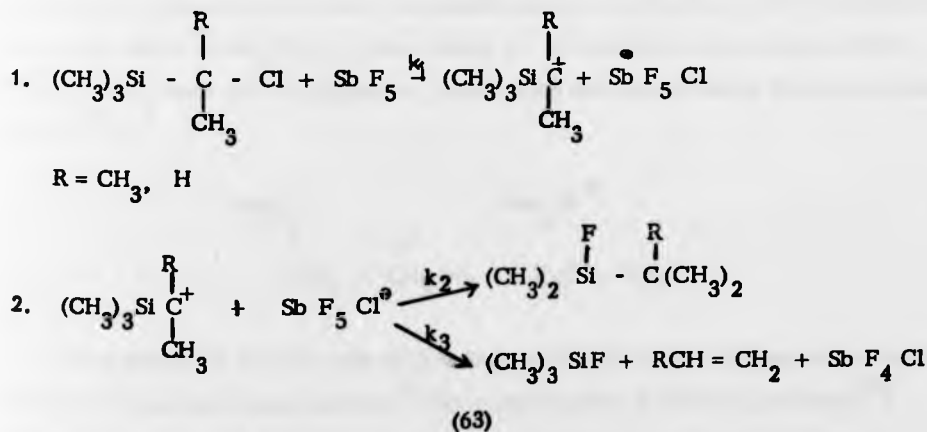


Scheme (II-3): Substitution product on the reaction of (62) with diethylamine, aniline, sodium ethylmercaptide and thiophenolate.

Similar rearrangement products to those previously reported<sup>48</sup> are found in the reaction of  $\alpha$ -halosilanes with aluminium chloride or antimony pentafluoride<sup>49, 50</sup> according to Scheme (II-4) and (II-5).



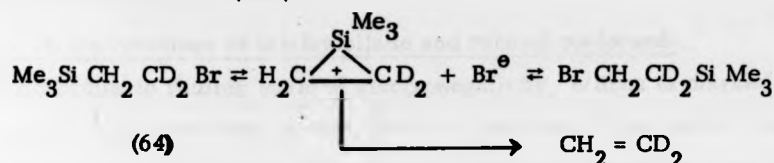
Scheme (II-4) : An intermolecular rearrangement of  $\alpha$ -halosilane in presence of aluminium chloride (used as a catalyst).



Scheme (II-5): A two step reaction between  $\alpha$ -halosilane and antimony pentafluoride.

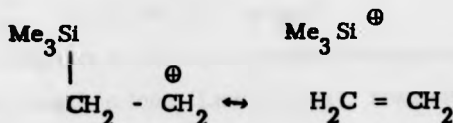
There are two possible pathways for the initial ion formed on step (1). Either this reacts further to give the rearrangement product ( $k_2$ ) or undergoes  $\alpha$ -elimination ( $k_3$ ) to give trimethylfluorosilane (63) and the olefin. Step (1) was first-order in both  $\text{SbF}_5$  and silane used, whilst step (2) occurred in a competitive second-order manner, first-order in both hexa-haloantimonate and the carbonium ion formed.<sup>50</sup>

Evidence has been obtained<sup>51</sup> for the migration of  $\text{Me}_3\text{Si}$  group during the solvolysis of (2-bromo-2,2-dideuteroethyl)trimethylsilane (64) in aqueous methanol. Solvolysis was allowed to proceed up to 50% completion and the recovered bromide was found to contain  $\text{Me}_3\text{SiCD}_2\text{-CH}_2\text{Br}$  and  $\text{Me}_3\text{SiCH}_2\text{CD}_2\text{Br}$  in 1:2 ratio via Scheme (II-6)



Scheme (II-6): A rearrangement of (64).

Additionally, the rates of solvolysis of the halides  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{X}$  (300 seconds for 50% completion) are substantially greater than would be expected. A possible explanation for this is the stabilisation of carbonium ion by the electron releasing effect of  $\text{Me}_3\text{SiCH}_2$  group which is involving hyperconjugation from  $\text{Me}_3\text{Si-CH}_2$  bond ( $\sigma$ - $\pi$  conjugation), associated with contribution from the following hybrid.<sup>51</sup>



The kinetics of the reaction of ( $\alpha$ -haloalkyl) silanes with antimony pentafluoride in nitromethane have been studied<sup>52</sup> (as a continuation to the original work<sup>50</sup>) using nmr to follow the reaction. The kinetic and thermodynamic data are consistent with a mechanism involving nucleophilic attack at the silicon atom before or during the rate-determining alkyl migration or alkene elimination. Reaction kinetics have been evaluated under pseudo-first order conditions for both reactants. A possible reaction pathway has been suggested which is



essentially the same as depicted in Scheme (II-5).

In the light of this discussion one can summarise the mechanisms of solvolysis of  $\alpha$ -haloalkylsilanes and related compounds as follows, depending on the substrate and the precise reaction conditions:

- (1) In most cases, reaction proceeds by overall second-order kinetics, but this may involve initial attack of nucleophile at silicon, and subsequent 1, 2-alkyl migration with loss of halide<sup>41, 42, 47, 48</sup> or simultaneous attack of the nucleophile at both silicon and carbon, again with subsequent rearrangement<sup>43, 44, 51</sup>.
- (2) In the presence of catalytic amounts of strong Lewis acids, halide ionisation followed by alkyl migration and halide return at silicon may occur<sup>49, 50</sup>.

#### B. On the reactions of trialkylsilane and related compounds.

According to Pauling scale of electronegativity, silicon is markedly more electropositive than carbon. The Si-C bond has 12 per cent of ionic character and is thus more polar than C-C bond which has 6 per cent of ionic character<sup>53</sup>; the electronegativity difference in the Si-H bond is 0.3 and it is polarised in the direction  $\overset{+}{\text{Si}}-\overset{-}{\text{H}}$ , while in the case of C-H the difference in electronegativity is 0.4 and the polarisation takes place in the opposite direction  $\overset{-}{\text{C}}-\overset{+}{\text{H}}$ . This dramatic difference in the electronegativity can be demonstrated in the reaction of triphenylsilane and triphenylmethane with methyl lithium<sup>53</sup>,



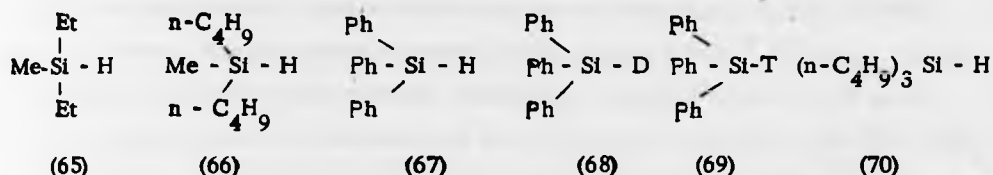
The silicon-hydrogen bond may be cleaved by nucleophiles or electrophiles (e.g. alkali, oxonium ions, Lewis acids), reaction proceeding with liberation of  $\text{H}_2$ <sup>54</sup>.



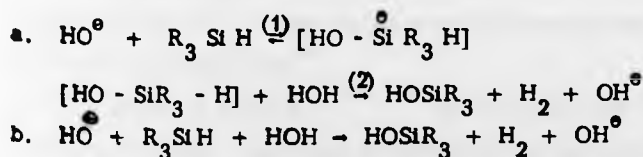
The solvolysis of trialkylsilanes has been studied extensively in the last twenty years, e.g. the solvolysis of methyldiethylsilane (65) and di-n-propylmethylsilane (66) catalysed by alkali has been examined under pseudo first-order

conditions<sup>55</sup>. The reaction was first order in both silane and hydroxide ion concentration, the rate constant showing a dependence on the amount of water present.

A kinetic isotope effect has been observed in the solvolysis of triphenylsilane (67), triphenyldeuterosilane (68) and triphenyltritiasilane (69) by hydroxide or ethoxide in ethanol which suggests a nucleophilic attack on silicon.



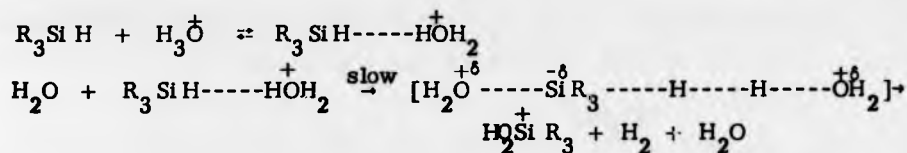
The reaction shows a small kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 1.15$ ) and ( $k_{\text{H}}/k_{\text{T}} = 1.3$ ). If this is a primary, rather than a secondary isotope effect then hydride ion is abstracted in the rate determining step<sup>56</sup>. The fact that a solvent isotope effect ( $k_{\text{EtOH}}/k_{\text{EtOD}} = 1.44$ ) occurs in the solvolysis of tri-n-propylsilane (70), indicates that the O-H bond breaking of solvent is also involved in the rate determining step<sup>56,57</sup>, and possibly the transition-state can be represented as  $[\text{OH} \cdots \overset{\text{R}_3}{\text{Si}} \cdots \text{H} \cdots \text{H} \cdots \text{OR}]^-$ . The smallness of the kinetic isotope effect will be discussed later in section (C-e). Two possible path-ways have been discussed (Scheme II-7, a, b),



Scheme (II-7): (a) a two step reaction, (1) fast step and (2) the slow step and rate determining step, (b) a concerted mechanism, involving Si-H bond breaking in the rate determining step.

Trialkylsilanes react with most anhydrous alcohols in the presence of alkali metal alkoxides<sup>58</sup>, the reactivity of the trialkylsilane falling with increasing size of the alkyl groups, while the reactivity of the alcohols falls in the order primary > secondary > tertiary. Steric effect are important, and thus reaction in iso-butanol is slower than in the other primary alcohols, though reaction in iso-amyl alcohol proceeds at a rate normal for primary alcohols<sup>58</sup>.

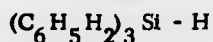
Eaborn<sup>59</sup> has examined the kinetics and the possible reaction mechanism, in the solvolysis of a series of trialkylsilanes  $R_3SiH$  ( $R = Et, n-Pr, n-Bu, i-Bu, i-Pr, Ph, (p-Cl C_6H_4)_3, (p-Cl C_6H_4)_2 Me, Ph Me_2, (p-Me C_6H_4)_2 Me_2$ ), in acidic ethanolic or 5 per cent aqueous ethanol solution. The main observations were as follows: (1) at low acid concentration, reaction shows a first-order dependence on the acid concentration. (2) Reaction is accelerated by electron-releasing groups and retardation is observed with electron-withdrawing groups (3). In 10% aqueous dioxan, reaction shows a solvent kinetic isotope effect ( $k_{H_2O}/k_{D_2O} = 2.25$ ). In the light of the above observations, Eaborn has suggested Scheme (II-8) as a possible reaction path-way. The nature of the postulated intermediate  $R_3Si-H---HOH_2^+$  is of interest, for it could involve a type of hydrogen bonding utilizing hydridic instead of protonic hydrogen.



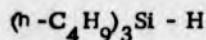
Scheme (II-8): A Possible reaction path-way in the solvolysis of trialkylsilane in acidic ethanol solution.

Reaction of organosilicon hydride with alcohol could also be catalysed by metals such as Cu<sup>58</sup>, again the ease of reaction decreases with increasing chain length of the alcohol used<sup>54</sup>.

In a series of papers<sup>60, 61, 62</sup>, the methanolysis of triphenylsilane (67) and related compounds catalysed by methoxide ion has been investigated thoroughly, in order to refine ideas about the nature of the transition state postulated earlier<sup>56</sup>. The following observations have been reported. (1) Reaction shows first-order dependence on both silane and methanol (2) Deuterated silanes like triphenylsilane (68), tribenzylsilane (71), tributylsilane (72), react more slowly by factors of  $1.2 \pm 0.08$ ,  $1.35 \pm 0.09$  and  $1.4 \pm 0.1$  respectively<sup>61</sup>. (3) In a mixture of  $CH_3OH$  and  $CH_3OD$ , methanolysis of (67) catalysed by methoxide shows a primary isotope effect for proton donation from solvent methanol  $k_H/k_D = 6 \pm 1$ <sup>55</sup>. From

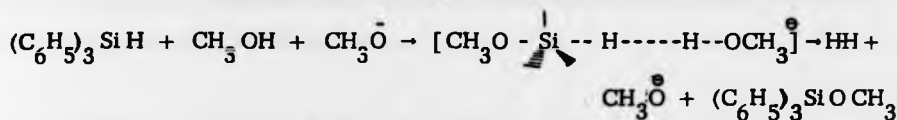


(71)



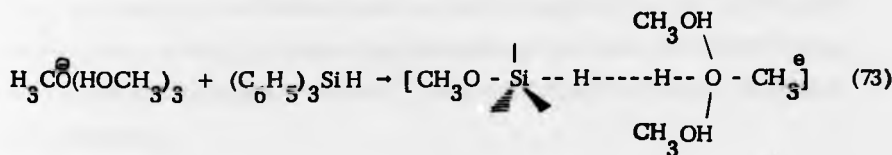
(72)

the above observation Schowen and his coworkers were able to formulate the following possible mechanism (Scheme II-9) for the expulsion of the very poor leaving group hydride ion ( $\text{H}^-$ ) from the silicon atom.



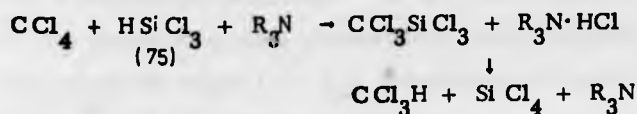
Scheme (II-9): Methanolysis of triphenylsilane catalysed by methoxide.

To explain the solvent primary kinetic isotope effect, it was suggested<sup>62</sup> that the attacking nucleophile is the solvated methoxide anion according to Scheme (II-10), in which the methanol of solvation is still co-ordinated in the transition state (73).



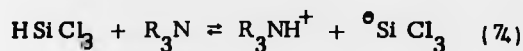
Scheme (II-10): Expulsion of weak hydride anion by solvated methoxide.

The above examples concerning solvolysis reactions of trialkylsilane under different conditions confirm the idea that Si-H bonds react with abstraction of hydride ion. Recently Benkeser<sup>63, 64</sup> in two subsequent papers has given evidence for the existence of trichlorosilyl anion (74) using tri-n-propylamine as an attacking base. The evidence was based on mechanistic investigation<sup>63</sup> and physical measurements<sup>64</sup>; according to the first report<sup>63</sup>, a series of polyhalo compounds are reduced cleanly and selectively by the trichlorosilane (75)-amine combination (e.g. Scheme (II-11)).



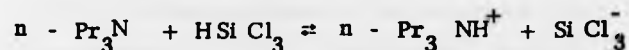
Scheme (II-11): Reduction of carbon tetrachloride using trichlorosilane-amine combination.

The conversion of hexachloroethane to tetrachloroethylene in presence of  $\text{Cl}_3\text{SiH} - \text{NR}_3$ , shows a striking similarity to phosphine halides<sup>65</sup>. The analogy with phosphorus chemistry is particularly enlightening in view of the isoelectronic relationship between phosphines and trichlorosilylanion; consequently Scheme (II-12) is more likely to occur in this reaction.



Scheme (II-12): Trichlorosilyl anion (74) as a product intermediate in the reaction of trichlorosilane and tri-n-butylamine.

In the second report a mixture of trichlorosilane and tri-n-propylamine was mixed together in acetonitrile solution. The nmr spectra of this compound shows a broad signal at 3.75 $\tau$  at 40°C which is attributed to  $n\text{-Pr}_3\text{N} \cdots \overset{\text{H}}{\text{SiCl}_3}$  species, on repeating the measurement at low temperature, (-40°C) the peak becomes a sharp singlet, a decoupling experiment has been performed using Forsen-Hoffman saturation technique<sup>64</sup>, has confirmed the idea of existence of the equilibrium.



No kinetic isotope effect was observed<sup>66</sup>, therefore, the Si-H bond may not break during or before the rate-determining step. There is ample evidence that tertiary amines react with trichlorosilane to form complexes containing nitrogen bound to silicon<sup>67</sup>. Complex formation is, then, most likely the first and slow step, concerted removal of the hydrogen by the amine from the silicon probably occurs next for the reasons stated. This evidence is consistent with Benkeser's mechanism (Scheme (II-12)), suggested earlier.<sup>63</sup>

On reviewing the above discussed work on the solvolysis of trialkylsilane or trihalosilanes, one can conclude the following points. (1) All reactions proceed with a bimolecular mechanism. (2) Si-H bond breaking is involved in the slow rate determining step. Consequently, reactions show a kinetic isotope effect within the range 1.1 - 1.5, according to the nature of the attached alkyl group<sup>56, 60</sup>. (3) Polarity and solvent compositions affect the reaction rate as shown from the solvent kinetic isotope effect<sup>56, 59 and 62</sup>. (4) Steric effects

play an important role in determining the reaction rate<sup>58</sup>, and catalysis by alkoxide or acid is essential for the reaction to proceed<sup>54, 55, 56, 58, 59, 60, 61 & 62.</sup>

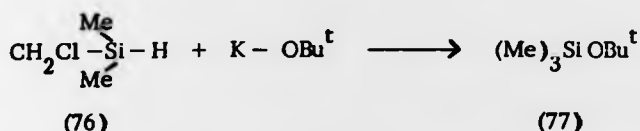
(5) In trihalosilanes reaction proceeds through a silanion<sup>63, 64</sup>. In this case no kinetic isotope effect was observed<sup>66</sup>, i.e. Si-H bond breaking does not occur before or during the rate determining step<sup>66</sup>.

#### C. Reactions of chloromethyldimethylsilane with Lithium t-Butoxide in Pyridine Medium.

In the last 5 years largely due to the efforts of Barton<sup>11, 12, 23 and 30</sup> and Sommer<sup>24, 25, 26, 27, 28 and 29</sup> an experimental basis has been established for silaethylene intermediates; pyrolysis and photolysis work were used extensively to generate these intermediates. In addition silaethylene intermediates were invoked as a transient in a variety of other reactions<sup>16, 17, 18, 19, 20, 21, 22, 32 and 33</sup>. However, there is no direct evidence for the existence of isolable species at room temperature containing ( $\text{X} = \text{Si} <$ ). Only Barton<sup>12</sup> was able to report the i.r. spectra of 1, 1-dimethylsilaethylene (1), resulting from the pyrolysis of 1, 1-dimethyl-1-silacyclobutane (9), using liquid nitrogen as a trapping matrix.

In this investigation we tried to generate dimethylsilaethylene at room temperature. On the basis of bond energies and speculation on the stability of Si-O bonds, one can expect reaction between a Si-H bond and an attacking base to proceed by base promoted proton abstraction (Section II-B). If the carbon atom next to silicon carries a halide (X), e.g.  $\alpha$ -halosilane, one might expect a simultaneous removal of the halide from the molecule (Section II-A). For this reason we chose chloromethyldimethylsilane (76) as a precursor and studied its reaction with lithium t-butoxide in pyridine solution.

In preliminary work, the reaction between (76) and potassium t-butoxide, was studied in pyridine solution, when t-butoxytrimethylsilane (77) was the only product observed.



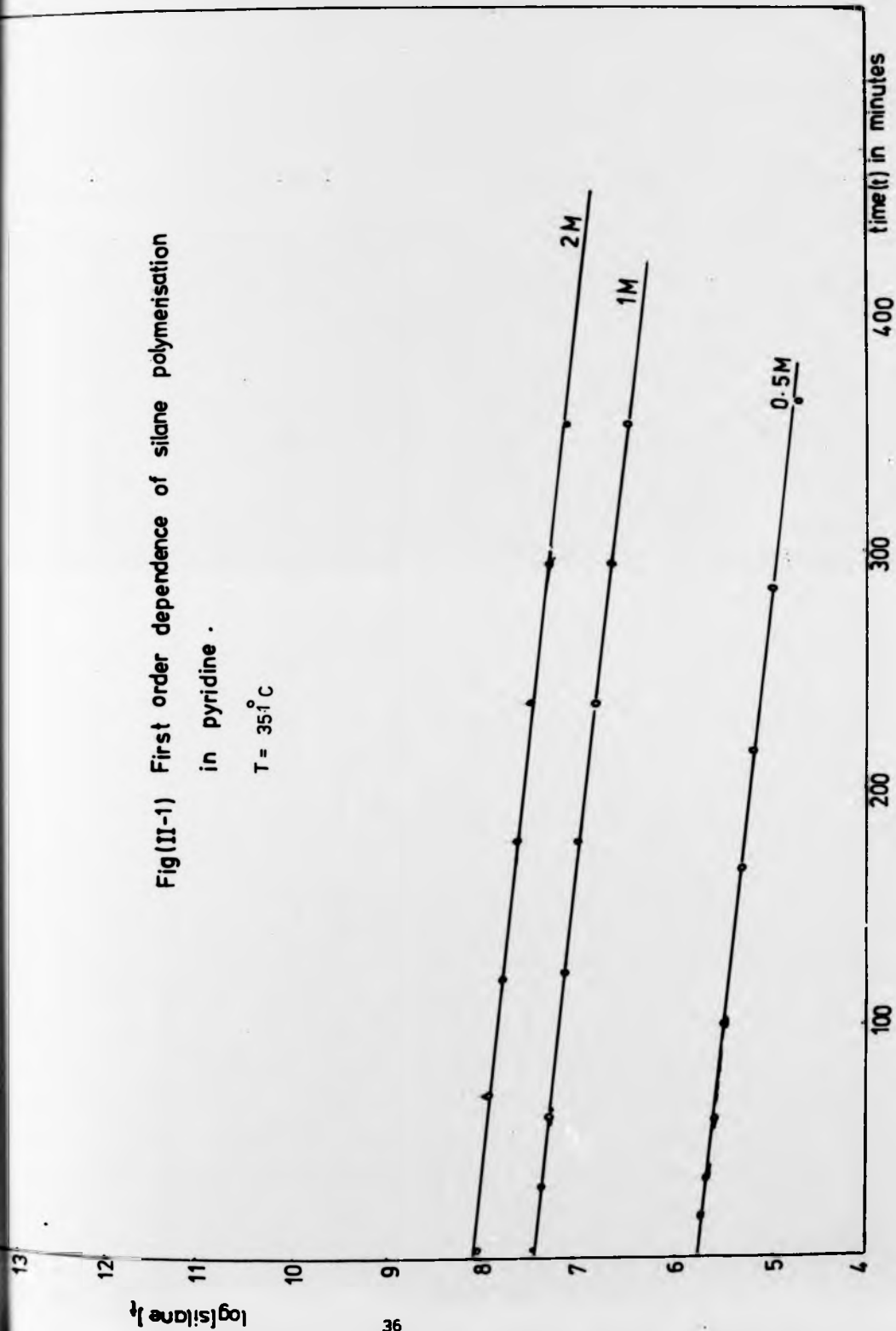
The reaction of (76) with strong base (KOH) has been studied earlier<sup>68</sup>; the comments on this work will be discussed in some detail with the possible mechanisms of this reaction later in this chapter. To evaluate a possible mechanism for this reaction, the reaction kinetics were studied over a wide range of concentration. Since potassium t-butoxide has limited solubility in pyridine, we chose lithium t-butoxide as a source for the t-butoxide anion.

In preliminary studies we observed that the reaction in pyridine was slow enough for convenient measurement by n.m.r. Pyridine proved to be a suitable solvent for mechanistic studies on other grounds, since it is quite transparent in the desired spectral region, and a good solvent for lithium t-butoxide. The reaction between (76) alone and pyridine was slow, but proceeded at a finite rate which was however much slower than the reaction of (76) with t-butoxide anion. Following the former process by n.m.r. at 35.1°C, diminution of all the signals due to (76) was observed, but no new resonances appeared and a brown solid, apparently polymeric material was deposited in the n.m.r. tube. The decay of Si-methyl signals followed first-order kinetics, and a rate constant of  $0.07 \times 10^{-5} \text{ sec}^{-1}$  was derived irrespective of silane concentrations. (Fig. II - 1).

In reactions with lithium t-butoxide, progress was followed by measuring the integral area of the base at 8.68 $\tau$  and of (77) at 8.76 $\tau$ . All measurements were carried out in duplicate and reproducible results were obtained ( $\pm 5\%$ ). Most reactions were followed to  $\geq 70\%$  completion, although some slower runs were only monitored for the first half-life to avoid complications arising from polymerisation.

Fig(II-1) First order dependence of silane polymerisation  
in pyridine .

$T = 35^{\circ}\text{C}$





(a) Dependence of reaction rate on the concentration of lithium t-butoxide  $[\text{Li-OBu}^t]$ .

In a series of measurements the effect of lithium t-butoxide concentration has been investigated within the range 0.05 M - 0.5 M under pseudo first-order conditions with silane (76),  $[\text{Si-H}] = 2.0 \text{ M}$ . The results obtained were plotted in Fig. (II - 2), and the rate constant calculated from the slope of these lines is presented in Table (II - 1) (a) and (b), from different batches of lithium t-butoxide.

Table (II - 1): Observed rate constant  $k$  under pseudo first order condition, with (76) present in excess.

(a)  $[\text{Si-H}] = 2.0 \text{ M}$ ,  $T = 35.1^\circ\text{C}$

$[\text{LiOBu}^t]_{\text{added}}$ in moles/litre	$10^{-4} \times k_{\text{SiH}}/\text{sec}^{-1}$ duplicate runs	$10^{-4} \times (\text{reaction rate})_{\text{initial}}/\text{sec}$	$\log(\text{rate})$	$\log[\text{LiOBu}^t]$
0.1	$3.816 \pm 0.031$ , $3.814 \pm 0.031$	0.38	-4.43	-1.00
0.2	$2.446 \pm 0.009$ , $2.496 \pm 0.013$	0.48	-4.32	-0.70
0.3	$1.705 \pm 0.013$ , $1.709 \pm 0.008$	0.51	-4.29	-0.52
0.4	$1.148 \pm 0.014$ , $1.172 \pm 0.001$	0.46	-4.34	-0.40
0.5	$0.727 \pm 0.03$ , $0.806 \pm 0.004$	0.36	-4.44	-0.30

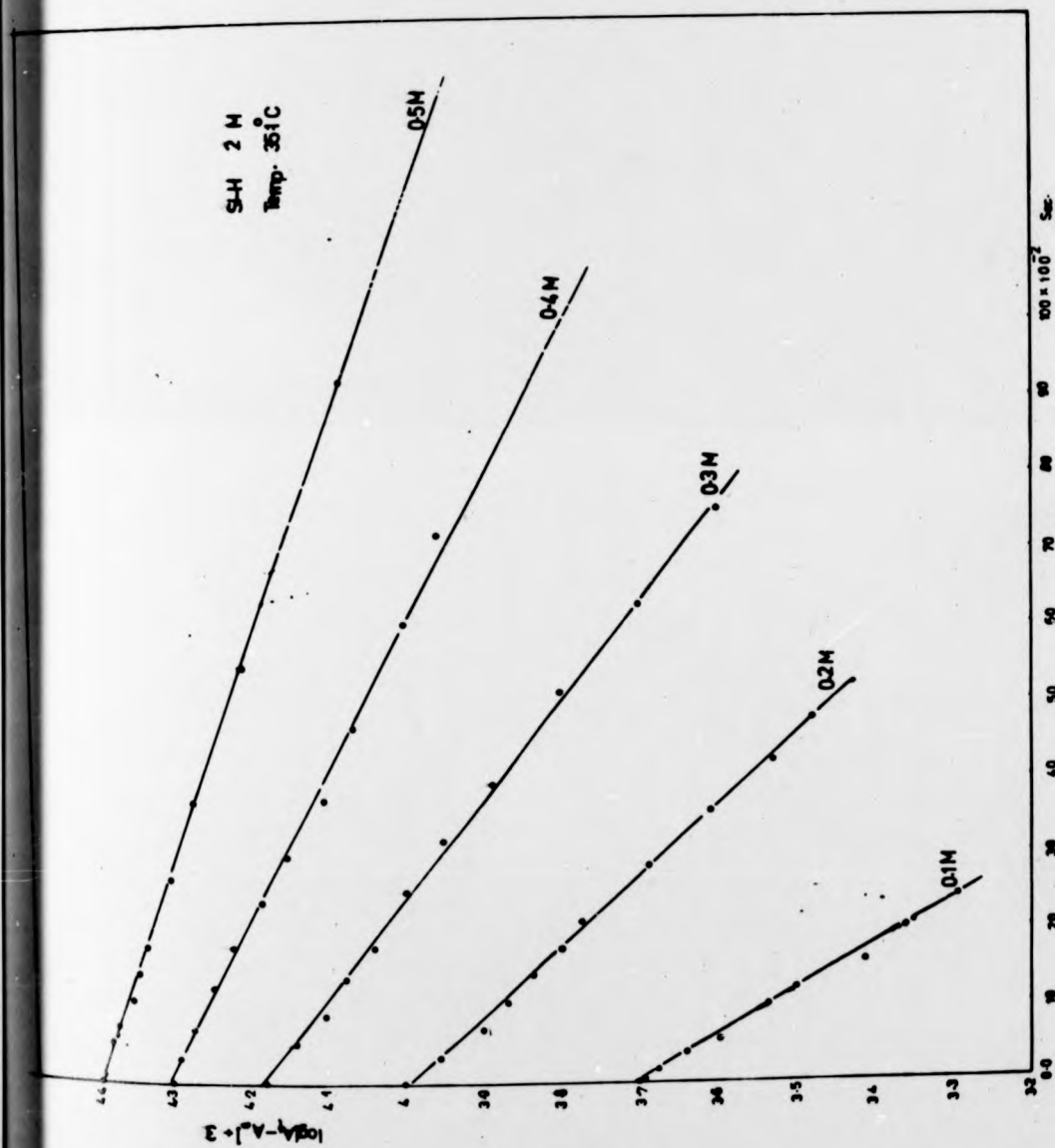
(b)  $[\text{Si-H}] = 2.0 \text{ M}$ ,  $T = 35.1^\circ\text{C}$

$[\text{LiOBu}^t]$ added in moles/litre	$10^{+4} \times k_{\text{SiH}} / \text{sec}^{-1}$	$10^{+4} \times (\text{reaction rate}) / \text{moles/l/sec}$	$\log(\text{rate})$	$\log[\text{LiOBu}^t]$
0.05	$5.636 \pm 0.021$	0.282	-4.55	-1.30
0.10	$3.447 \pm 0.004$	0.345	-4.46	-1.00
0.15	$2.640 \pm 0.012$	0.396	-4.40	-0.82
0.20	$2.640 \pm 0.003$	0.528	-4.28	-0.70
0.25	$2.165 \pm 0.004$	0.541	-4.26	-0.60
0.30	$1.870 \pm 0.001$	0.561	-4.25	-0.52
0.40	$1.470 \pm 0.002$	0.588	-4.23	-0.40
0.50	$0.840 \pm 0.003$	0.420	-4.37	-0.30

Although each individual run corresponds to first-order kinetics, the dependence of rate-constant on concentration clearly suggests that involvement of lithium t-butoxide is complex. The simplest interpretation is that lithium t-butoxide is aggregated in pyridine solution and predissociation to a monomer is required prior to reaction.



Consequently the concentration of the active entity  $\text{LiOBu}^t$  cannot be observed directly, and evaluation of the equilibrium constant  $K$  has not been attempted. Aggregation of organolithium compounds in organic media is common<sup>69</sup>. Lithium t-butoxide has been claimed to be hexameric in cyclohexane and tetrameric in benzene<sup>70</sup>, although independent studies<sup>71,72</sup> suggest that higher degrees of aggregation ( $N = 6; 9 \pm 0.9$ ) may exist in the latter solvent. This is similar to the solution behaviour of ethyl- and n-butyllithium<sup>69</sup> which are hexameric in non-polar solvents. Whilst the higher polarity of pyridine might lead to easier dissociation and the formation of smaller aggregates, complete dissociation would not be expected. There is evidence that potassium t-butoxide in dimethyl sulphoxide (a more polar base in a more polar solvent) is extensively aggregated<sup>72a</sup>.



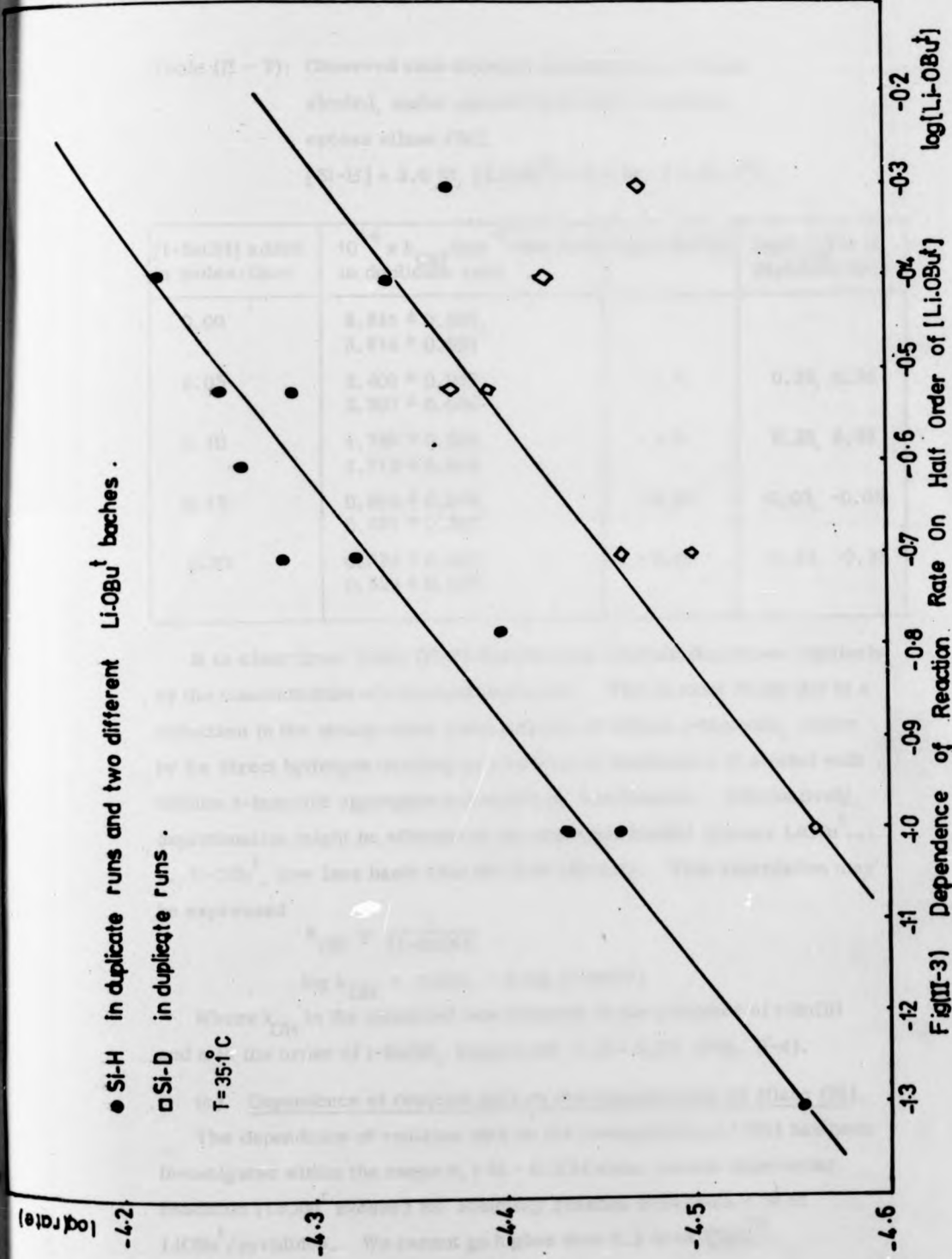
Fig(III-2) Dependence of reaction rate on Li-QBu concentration.

If the concentration of lithium t-butoxide monomer depended only on the concentration of aggregate at time  $t$ , then first-order kinetics would not have been observed. In the course of reaction lithium chloride is formed as lithium t-butoxide is consumed, and production of mixed aggregates would be expected. If the extent of aggregation were relatively unperturbed over the course of reaction, then the proportionality between monomeric and aggregated lithium t-butoxide would be maintained, so that first-order kinetics should persist under conditions where silane is present in large excess.

Plotting  $\log(\text{rate})$  versus  $\log(\text{LiOBu}^t)_{\text{init.}}$  for a series of runs, (Fig. II-3), and also for data derived from solvolysis of the deuterated silane (Table II-5a, b) suggest that the order dependence is not a simple function. At low concentrations of lithium t-butoxide ( $< 0.2$  M, least-squares slope on all data =  $0.45 \pm 0.015$ ) the variations suggest that the dominant aggregates are quite small, probably dimers. As the concentration increases, the gradient of the line tails off, which is what would be expected if the aggregation number was concentration dependent. At the highest concentrations of  $\text{LiOBu}^t$ , the rate is even inhibited. The limitation of n.m.r. as a kinetic tool preclude a more accurate assessment, but the observed trends are consistent and must be valid.

(b) Dependence of reaction rate on the t-butyl alcohol concentration [t-BuOH].

The basicity of lithium t-butoxide in pyridine might be expected to be reduced by added t-butyl alcohol, which will form strong hydrogen-bonds to the free base. The effect of added t-butanol in the range 0.05 M - 0.2 M with excess of silane (76) is presented in Table (II-2).



FigIII-3)

Table (II - 2): Observed rate constant in presence of t-butyl alcohol, under pseudo first order condition, excess silane (76).

[Si-H] = 2.0 M, [LiOBu<sup>t</sup>] = 0.1 M, T = 35.1°C

[t-BuOH] added in moles/litre	$10^4 \times k_{OH}/\text{sec}^{-1}$ observed in duplicate runs	log[t-BuOH]	log( $k_{OH}$ )-4 in duplicate runs
0.00	3.841 ± 0.031, 3.816 ± 0.031	-	-
0.05	2.400 ± 0.017, 2.307 ± 0.036	- 1.3	0.38, 0.36
0.10	1.789 ± 0.009, 1.712 ± 0.014	- 1.0	0.23, 0.23
0.15	0.895 ± 0.019, 0.891 ± 0.307	- 0.82	-0.05, -0.05
0.20	0.524 ± 0.007, 0.524 ± 0.075	- 0.69	-0.28, -0.28

It is clear from Table (II-2) that the rate constant decreases regularly as the concentration of t-butanol increases. This is most likely due to a reduction in the steady-state concentration of lithium t-butoxide, either by its direct hydrogen-bonding to t-butanol or interaction of alcohol with lithium t-butoxide aggregate and resulting stabilisation. Alternatively, deprotonation might be effected by the hydrogen bonded species LiOBu<sup>t</sup>...H-OBu<sup>t</sup>, now less basic than the free alkoxide. This retardation may be expressed

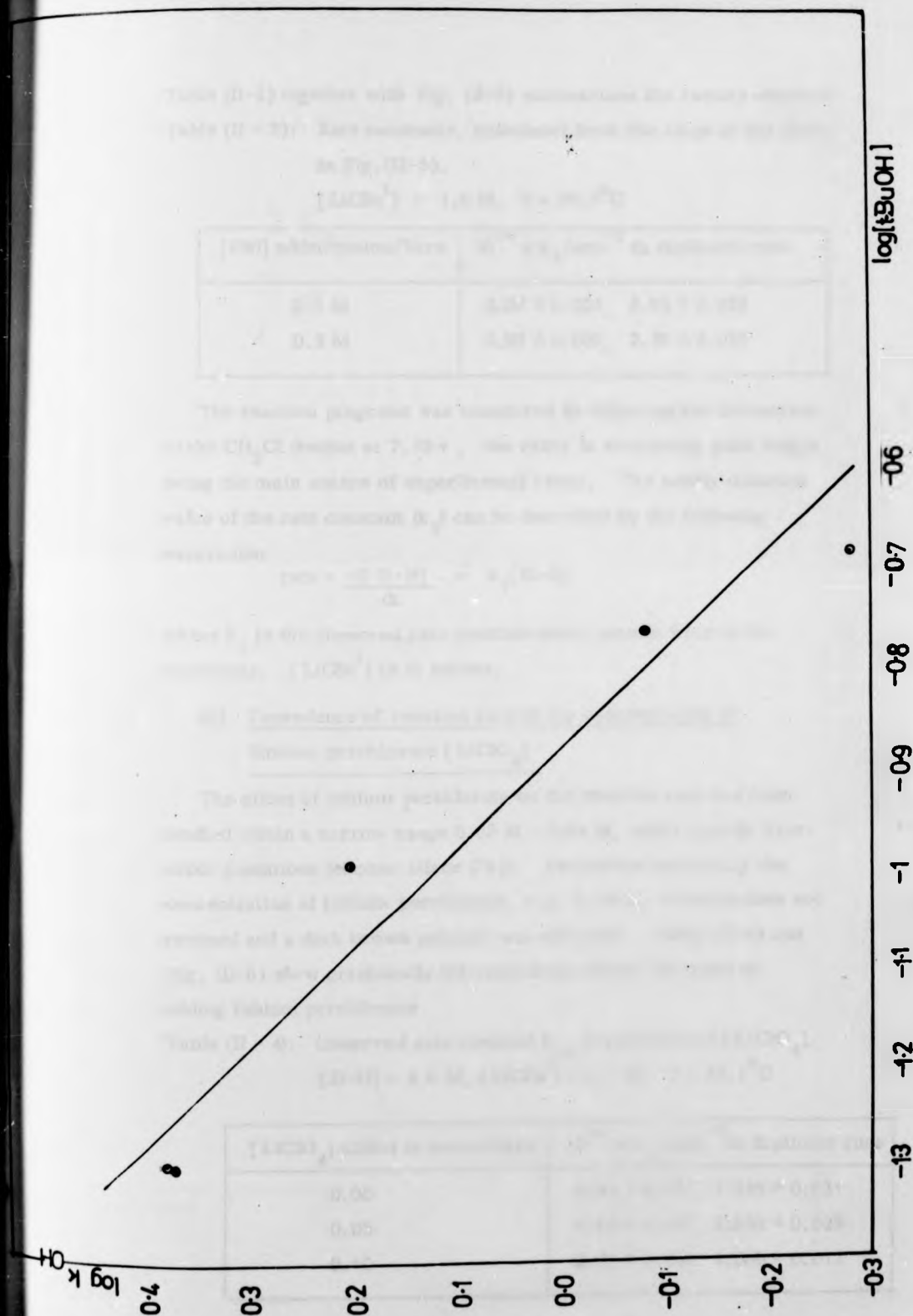
$$k_{OH} \propto \frac{1}{[t-BuOH]}$$

$$\log k_{OH} = \text{const.} - n \log [t-BuOH]$$

Where  $k_{OH}$  is the observed rate constant in the presence of t-BuOH and n is the order of t-BuOH, found to be  $-1.0 \pm 0.01$ , (Fig. II-4).

(c) Dependence of reaction rate on the concentration of silane (76).

The dependence of reaction rate on the concentration of (76) has been investigated within the range 0.1 M - 0.2 M under pseudo first-order condition (LiOBu<sup>t</sup> excess) for solubility reasons (maximum 1 M of LiOBu<sup>t</sup>/pyridine). We cannot go higher than 0.2 M of (76).



Fig(II-4): Participation of [t-BuOH] in the equation (II-b) with (-1)



Table (II-3) together with Fig. (II-5) summarises the results obtained.

Table (II - 3): Rate constants, calculated from the slope of the lines in Fig. (II-5).

$$[\text{LiOBu}^t] = 1.0 \text{ M}, T = 35.1^\circ\text{C}$$

[SH] added moles/litre	$10^{+4} \times k_1/\text{sec}^{-1}$ in duplicate runs
0.1 M	$4.07 \pm 0.021, 3.98 \pm 0.025$
0.2 M	$2.97 \pm 0.009, 2.89 \pm 0.011$

The reaction progress was monitored by following the diminution of the  $\text{CH}_2\text{Cl}$  doublet at  $7.15 \tau$ , the error in measuring peak height being the main source of experimental error. The nearly constant value of the rate constant ( $k_1$ ) can be described by the following expression

$$\text{rate} = \frac{-d[\text{Si-H}]}{dt} = k_1[\text{Si-H}]$$

where  $k_1$  is the observed rate constant under pseudo first-order conditions.  $[\text{LiOBu}^t]$  is in excess.

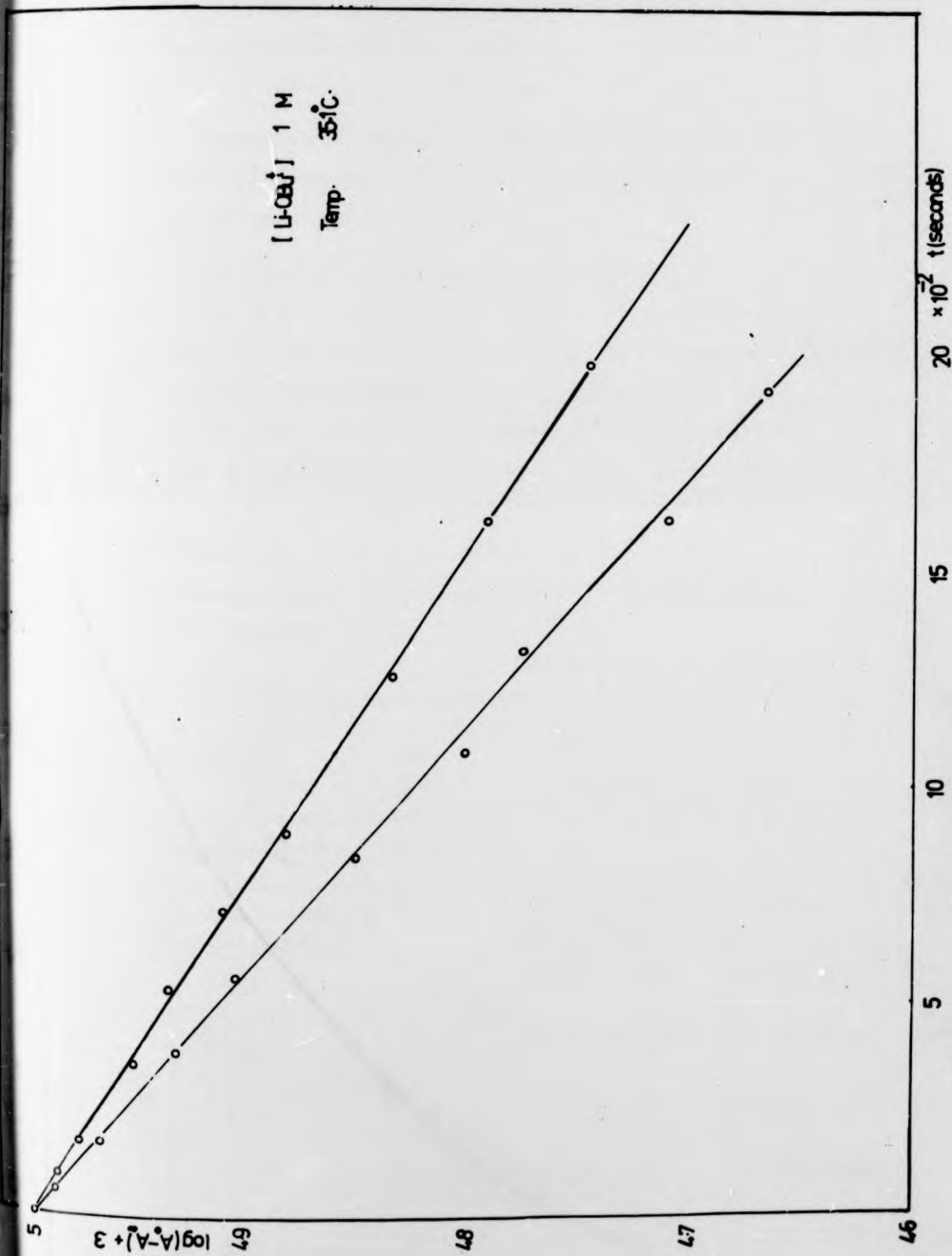
(d) Dependence of reaction rate on the concentration of lithium perchlorate  $[\text{LiClO}_4]$

The effect of lithium perchlorate on the reaction rate has been studied within a narrow range 0.05 M - 0.01 M, under pseudo first-order conditions (excess silane (76)). On further increasing the concentration of lithium perchlorate, e.g. 0.15 M, reaction does not proceed and a dark brown polymer was obtained. Table (II-4) and Fig. (II-6) show graphically the retardation effect observed by adding lithium perchlorate

Table (II - 4): Observed rate constant  $k_{\text{Li}}$  in presence of  $[\text{LiClO}_4]$ .  
 $[\text{Si-H}] = 2.0 \text{ M}, [\text{LiOBu}^t] = 0.1 \text{ M}, T = 35.1^\circ\text{C}$

$[\text{LiClO}_4]$ added in moles/litre	$10^{+4} \times k_{\text{Li}}/\text{sec}^{-1}$ in duplicate runs
0.00	$3.84 \pm 0.031, 3.816 \pm 0.031$
0.05	$1.98 \pm 0.017, 2.050 \pm 0.623$
0.10	$0.96 \pm 0.206, 1.060 \pm 0.012$





Fig(III-5) First order plot in sthne.

$k_{ij} \times 10^4 \text{ Sec}^{-1}$

4  
3.5  
3  
2.5  
2  
1.5  
1  
0.5  
0

00

005

01

$[\text{LiClO}_4] \text{ M.}$

Fig. (II-6) Effect Of  $[\text{LiClO}_4]$  On The Reaction Rate.

The observed reaction rate of  $[\text{LiClO}_4]$  can be explained as the rate of the following equilibrium:



Consequently, when the concentration of  $[\text{LiClO}_4]$  is increased, the concentration of  $[\text{Li}^+]$  and  $[\text{ClO}_4^-]$  will also increase, and the reaction rate will increase.

(a)  $[\text{LiClO}_4] = 0.1 \text{ M}$

As we pointed out in the previous section, the reaction rate must be affected by the concentration of  $[\text{LiClO}_4]$  involved in the reaction. The reaction between  $[\text{LiClO}_4]$  and  $[\text{H}_2\text{O}]$  has been investigated over a wide range of concentrations. The results are given in Table (II-5) and Table (II-6). The reaction rate is shown below in Table (II-6).

Table (II-5) shows the effect of  $[\text{LiClO}_4]$  on the reaction rate.

(b)  $[\text{LiClO}_4] = 0.1 \text{ M}$

$[\text{LiClO}_4] \text{ M.}$		$[\text{H}_2\text{O}] \text{ M.}$	
0.1	0.2	0.1	0.2
0.2	0.4	0.2	0.4
0.4	0.8	0.4	0.8
0.8	1.6	0.8	1.6

(c)  $[\text{LiClO}_4] = 0.1 \text{ M}$

$[\text{LiClO}_4] \text{ added}$ moles/l.	$k_{ij} \times 10^4 \text{ Sec}^{-1}$	$k_{ij} \times 10^4 \text{ Sec}^{-1}$ calculated from eq. (II-6)	$k_{ij} \times 10^4 \text{ Sec}^{-1}$ calculated from eq. (II-6)	$k_{ij} \times 10^4 \text{ Sec}^{-1}$ calculated from eq. (II-6)
0.1	$2.77 \pm 0.004$ $2.72 \pm 0.004$	0.277, 0.275	-4.36, -4.38	-4.37
0.2	$1.74 \pm 0.007$ $1.64 \pm 0.023$	0.346, 0.306	-4.36, -4.51	-4.43
0.3	$1.36 \pm 0.005$ $1.41 \pm 0.019$	0.406, 0.435	-4.37, -4.37	-4.37
0.4	$0.95 \pm 0.007$ $0.94 \pm 0.055$	0.280, 0.279	-4.42, -4.42	-4.42
0.5	$0.73 \pm 0.003$ $0.72 \pm 0.069$	0.365, 0.365	-4.43, -4.43	-4.43

The observed retardation effect by  $[\text{LiClO}_4]$  can be explained on the basis of the following equilibrium



Consequently addition of  $\text{LiClO}_4$  will reduce the concentration of  $\text{OBu}^t$  by the common ion effect, or co-aggregation of lithium perchlorate and lithium t-butoxide may occur.

(e) Evaluation of the kinetic isotope effect.

As we pointed out, chapter (II -A, B), a primary kinetic isotope effect must be observed if the Si-H bond breaking is involved before or during rate determining step. For this reason, the reaction between chloromethyldimethyldeuterosilane (78) has been investigated over a wide range of  $[\text{LiOBu}^t]$ , under pseudo first-order conditions of both (78) and  $\text{LiOBu}^t$ , the results being tabulated below in Table (II-5a, b) and illustrated in Fig. (II-7a, b).

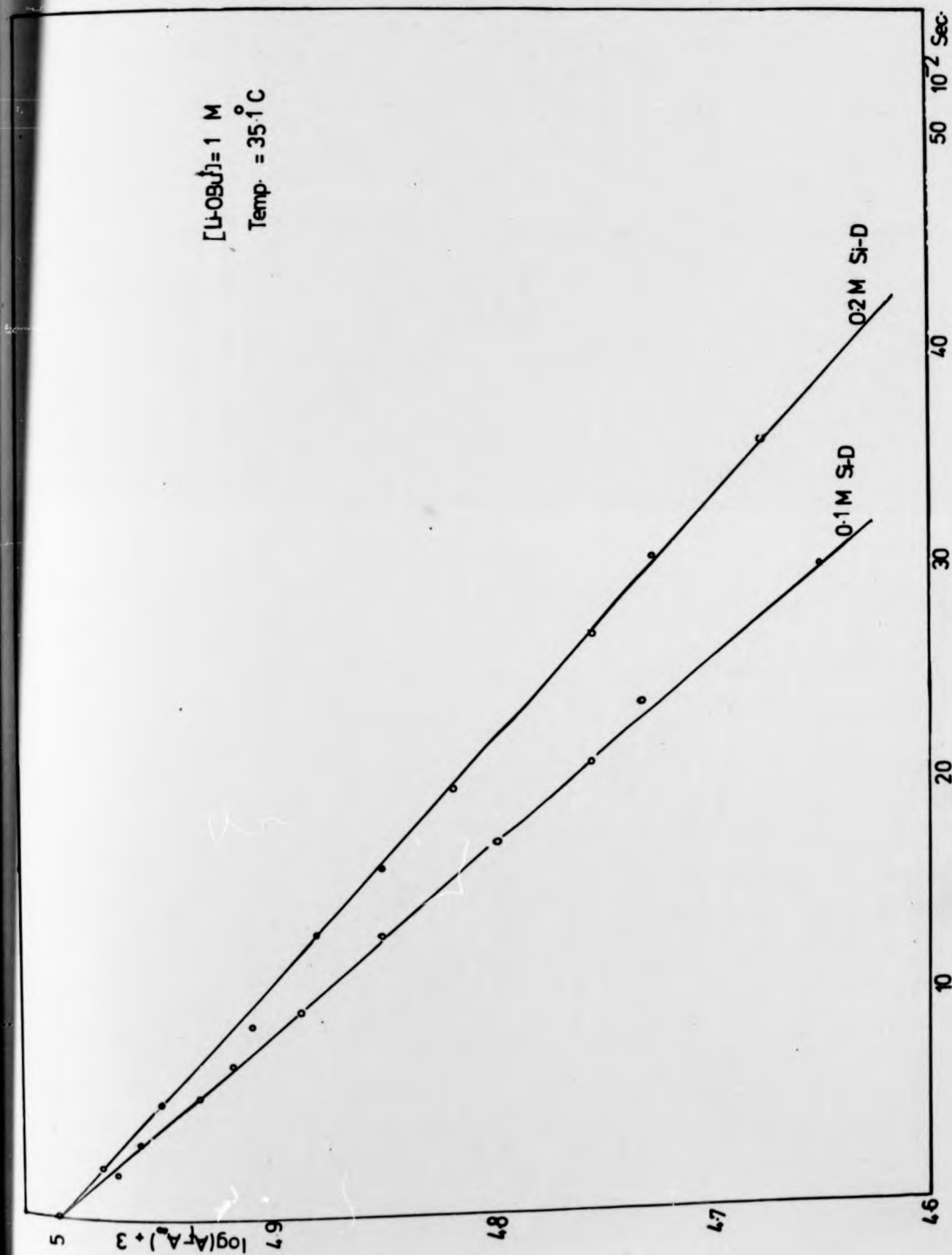
Table (II - 5): Kinetic isotope effect on the rate constant.

(a)  $[\text{LiOBu}^t] = 1.0 \text{ M}$ ,  $T = 35.1^\circ\text{C}$

[Si-D] added moles/litre	$10^{+4} \times k_{\text{Si-D}}/\text{sec}^{-1}$ in duplicate runs
0.1	$2.59 \pm 0.015$ , $2.65 \pm 0.019$
0.2	$2.05 \pm 0.008$ , $2.01 \pm 0.017$

(b)  $[\text{Si-D}] = 2 \text{ M}$ ,  $T = 35.1^\circ\text{C}$

$[\text{LiOBu}^t]$ added moles/litre.	$10^{+4} \times k/\text{sec}^{-1}$	$10^{+4} \times \text{reaction rate moles/l/sec}$	$\log[\text{rate}]$	$\log \text{LiOBu}^t$
0.1	$2.77 \pm 0.024$ , $2.75 \pm 0.034$	0.277, 0.275	-4.56, -4.56	-1.0
0.2	$1.74 \pm 0.008$ , $1.53 \pm 0.033$	0.348, 0.306	-4.46, -4.51	-0.7
0.3	$1.36 \pm 0.005$ , $1.41 \pm 0.009$	0.408, 0.423	-4.39, -4.37	-0.52
0.4	$0.95 \pm 0.007$ , $0.94 \pm 0.054$	0.380, 0.376	-4.42, -4.42	-0.40
0.5	$0.73 \pm 0.003$ , $0.72 \pm 0.069$	0.365, 0.360	-4.45, -4.45	-0.30



Fig(III-2b) First order plot in Si-D

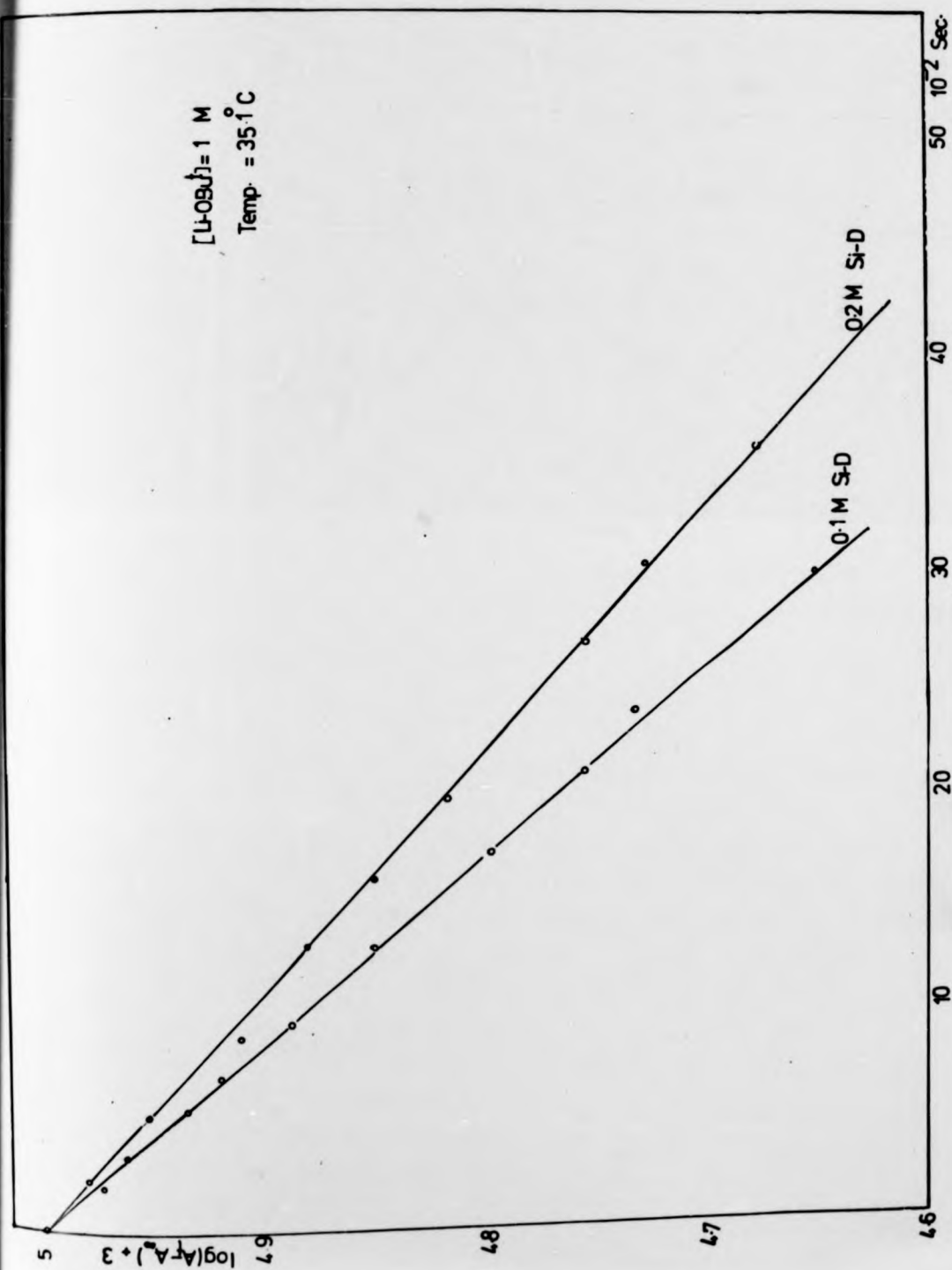
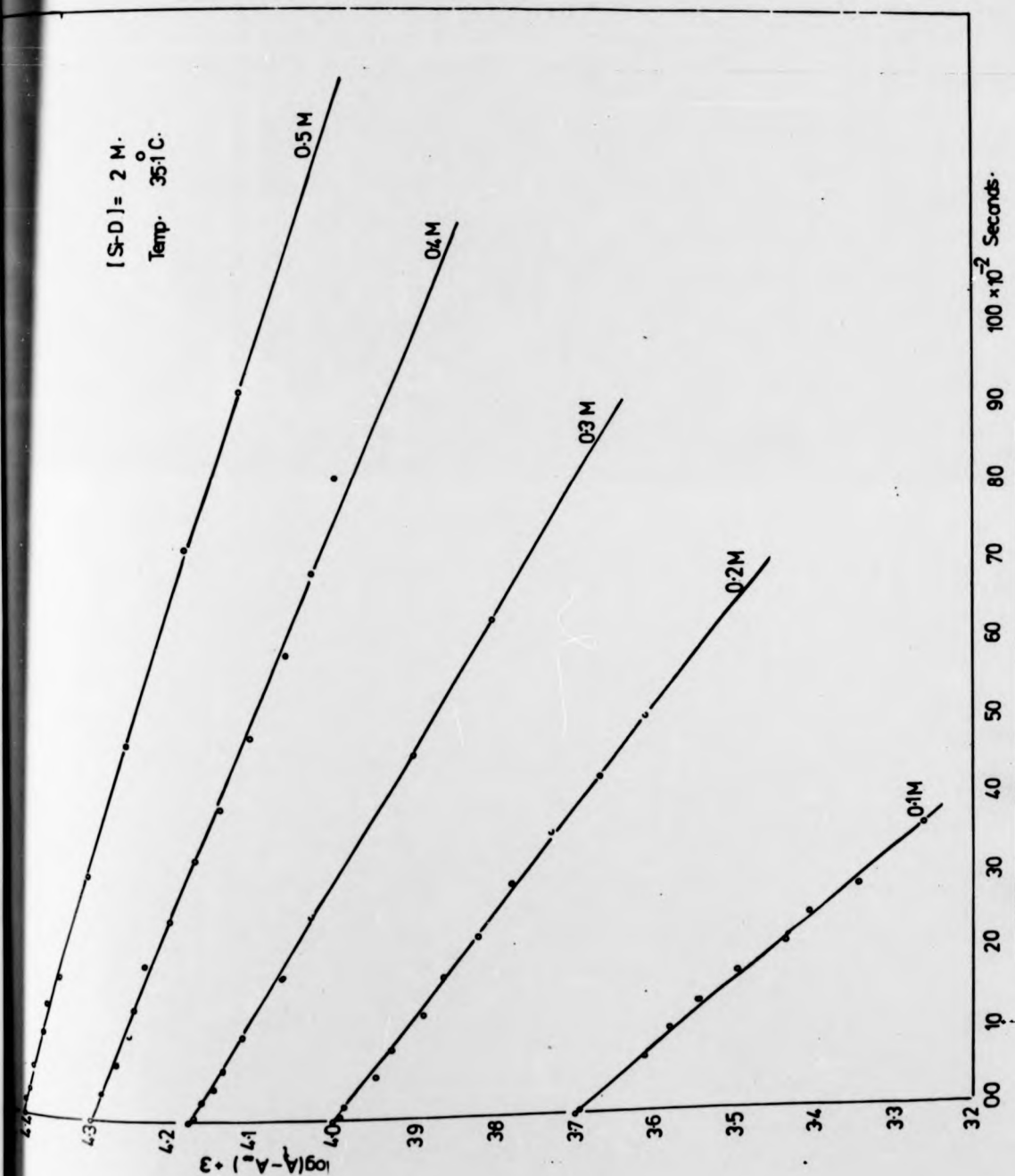


Fig (I-2a) First order plot in Si-D



Fig(II-76) Stoness Of Reaction Rate On Increasing [U-OB]

The regular decrease on the rate constant on increasing the concentration of  $\text{LiOBu}^t$  was discussed earlier under the effect of  $[\text{LiOBu}^t]$  on the reaction rate (Section (II-a)), and is shown in Fig. (II-3).

From the data reported in Tables (II-1) and (II-5b) an estimated value average to  $1.33 \pm 0.1$  for  $k_{\text{Si-H}}/k_{\text{Si-D}}$  under pseudo first-order condition (excess silane), also from Tables (II-3) and (II-5a) an average value for  $k_{\text{Si-H}}/k_{\text{Si-D}}$  average to  $1.5 \pm 0.1$  was obtained, these results being consistent with earlier observations<sup>56</sup> for bond breaking of Si-H in the rate determining step under the influence of the attacking base, with reservation to be discussed in more detail later in this chapter.

#### D. A Possible Mechanisms for the Reaction between Chloromethyldimethylsilane (76) and $\text{LiOBu}^t$ in Pyridine.

The various pathways connecting (76) and (77) are summarised in scheme (II-13). These vary in the nature of the reactive intermediate, and the timing of steps prior to and subsequent to its formation.

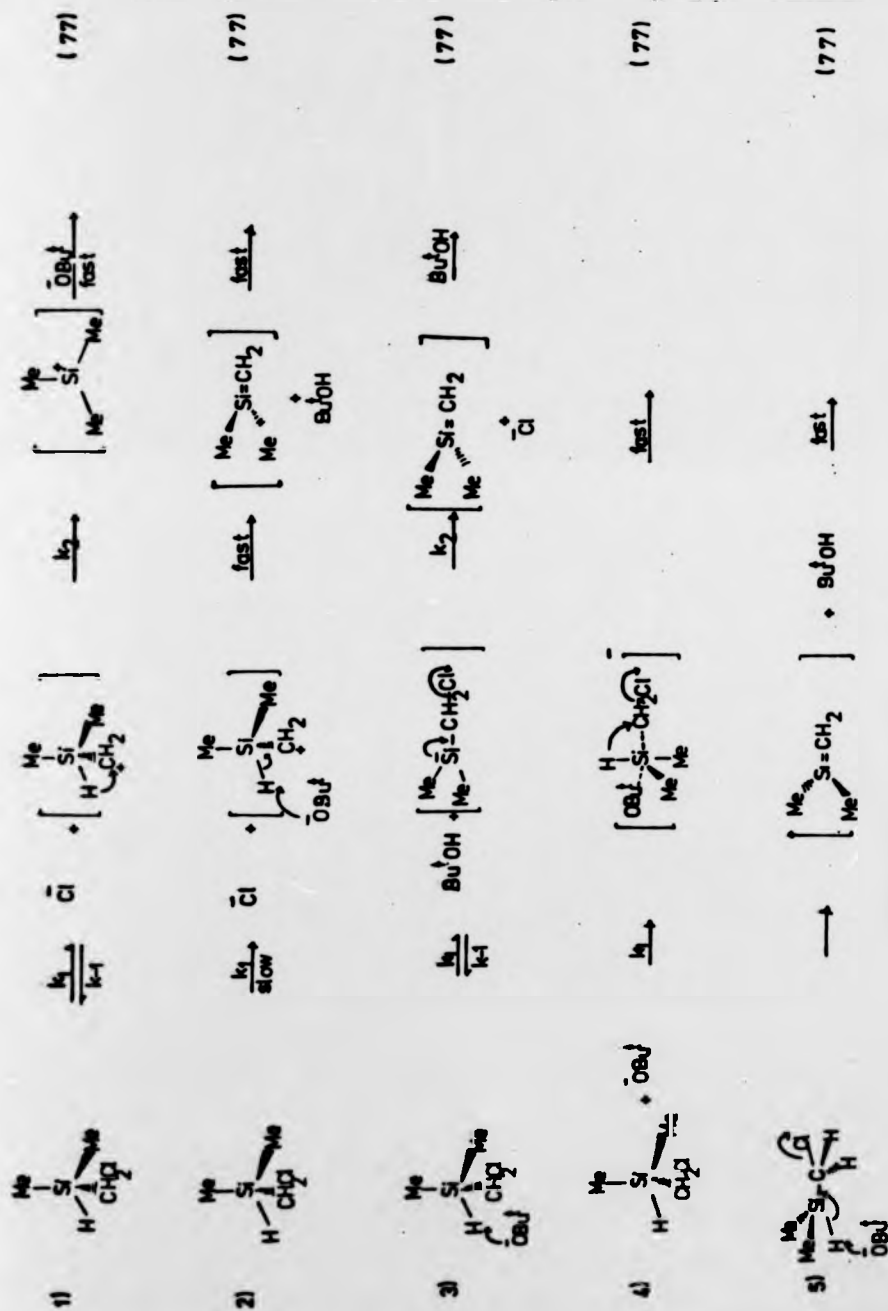
Discussing these in turn:-

Path (1) is essentially an  $\text{S}_{\text{N}}1$  reaction with rearrangement occurring at the carbonium ion stage. This mechanism is inconsistent with several experimental features of the reaction. The deuterium kinetic isotope might be expected to be close to 1.0 unless Si-H hyperconjugation were involved, but more importantly this mechanism would predict first-order dependence on silane and zero order dependence on base. Furthermore none of the substitution product  $\text{BuO-SiHMe}_2$  can be detected under our reaction conditions.

Mechanism (2) is an  $\text{E1}$  reaction, and again this is incompatible with the observed kinetic dependence on lithium t-butoxide.

In the case of mechanism (3) there is precedent for the formation of silanions and thus trimethylsilyl lithium can be prepared in aprotic media. Additionally the trichlorosilyl anion (74) has been claimed to be an intermediate in the reaction of (75) with amines<sup>63,64,66</sup> and these results encouraged us to consider an  $\text{E1cB}$  type mechanism. The difference





Scheme (II-3): A general scheme for all possible reaction mechanisms leading to (77)



between this and a conventional E2 reaction can be quite subtle, and kinetics alone are not valuable.<sup>72b</sup> If a carbanion or silanion intermediate in an E1cB reaction has sufficient lifetime, then elimination should be accompanied by hydrogen isotope exchange of the starting material in a deuterated medium. (An E1cB reaction with  $k_2 \gg k_{-1}$  may be operationally indistinguishable from an E2 reaction). In order to test this possibility, the following experiment was conducted:-

Lithium t-butoxide (0.1 M) in pyridine (200  $\mu$ L) was mixed with a solution of t-butanol-O-d (200  $\mu$ L, 0.5 M) in pyridine and silane (76) (200  $\mu$ L) added to this mixture. Before reaction commenced, the n.m.r. spectrum was recorded and the doublet signal of  $\text{CH}_2\text{Cl}$  (7.15 $\tau$ ) observed. As reaction proceeded with formation of (77), this signal was monitored and did not change in shape. In particular, there was no evidence for a new signal corresponding to the proton of  $\text{CHDCl}$  which might be expected to appear as a broadened singlet in the vicinity of the mid-point of the original  $\text{CH}_2\text{Cl}$  resonance. This absence of deuterium exchange, shown in Fig. (II-8), was checked by isotope reversal experiment, using deuterated silane and unlabelled t-butanol, with the same results.

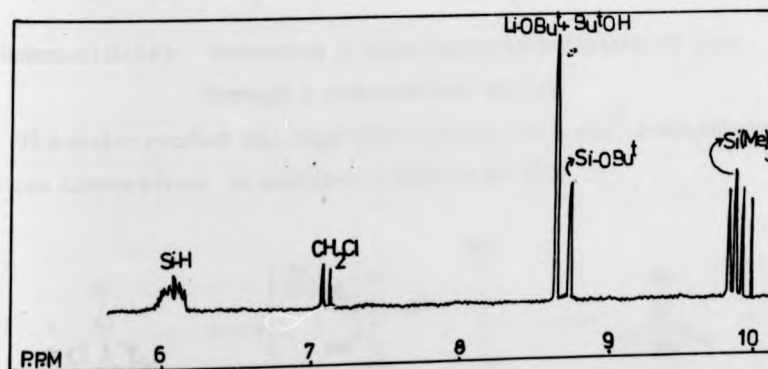
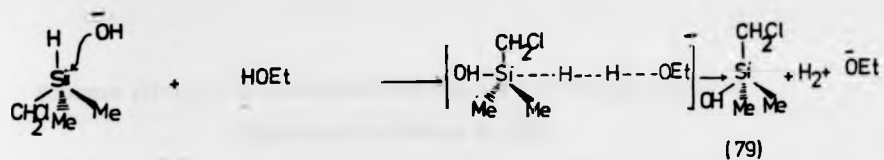


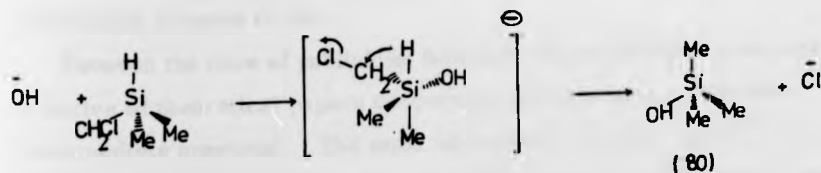
Fig. (II-8): No exchange between  $\text{Si-H}$  and  $\text{Bu}^t\text{OD}$  to form  $\text{Si-D}$  at 50% of reaction completion.

As has been pointed out in section (II-A) a pentacovalent silanion intermediate (path 4) is quite feasible. This could then rearrange to the observed product with simultaneous release of chloride ion. In fact, Sommer<sup>68</sup> has employed this mechanism to explain the solvolysis of (76). Thus treatment of a solution of (76) in 95% ethanol with dilute aqueous KOH gave rise to two products, chloromethyldimethylsilanol (79) 31% and trimethylsilanol (80) 69%. Reaction was extremely rapid, being complete in 15 seconds at room temperature, and the formation of (79) was accompanied by an equivalent quantity of hydrogen. The reaction pathway was rationalised by the mechanism outlined in Scheme (II-14).



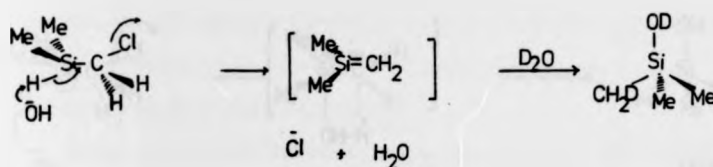
Scheme (II-14): Formation of chloromethyldimethylsilanol (79) through a pentacovalent silicon.

The major product was suggested to occur via a  $dsp^3$  5-coordinate silicon intermediate, as outlined in Scheme (II-15).



Scheme (II-15): An intramolecular rearrangement through a  $dsp^3$  silicon intermediate giving (80).

On repeating the reaction in deuterated solvent (70% dioxane, 30% D<sub>2</sub>O) the rearranged product (80) was obtained in 77% yield entirely lacking any evidence of C-D stretch in the infra-red spectrum<sup>68</sup>. This experiment was judged to rule out the possibility that a silaethylene intermediate is involved in the reaction according to Scheme (II-16).

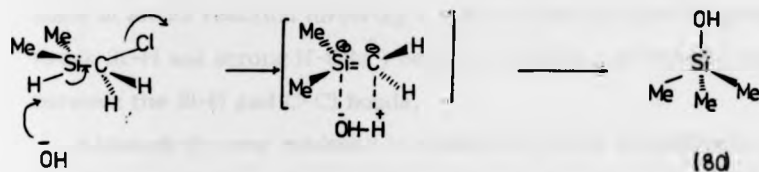


Scheme (II-16): An excluded mechanism for the formation of deuterated analogue to (80).

The rigorous interpretation of this result is more restrictive; however, a sounder mechanism is that in the event of there being a silaethylene intermediate according to Scheme (II-16), then hydration of this species must involve the molecule of water which initiates reaction as hydroxide ion, and H-D interchange does not occur intra- or intermolecularly. This could be the case if H-OD were strongly hydrogen-bonded to the polar silaethylene intermediate, and its lifetime were little more than a rotation about the H-O bond, followed by immediate collapse to (80).

Between the time of publishing Sommer's work (1959) and this year, a series of theoretical papers concerning silaethylene as a reactive intermediate appeared. The most important is Curtis' paper<sup>10</sup>, in which he pointed out the high polarisability of a C=Si double bond. In fact, it can behave as a carbanion-siliconium ion<sup>10</sup>; Gusel'nikov's<sup>5</sup> work is also extremely important as he succeeded in intercepting the

silaethylene intermediate very efficiently by adding water, giving trimethylsilanol, Scheme (I-3). There is now a degree of precedent for explaining the rearranged product obtained by Sommer as proceeding through silethylene as an intermediate, which is hydrogen bonded to the water formed by expulsion of proton by the base added in a fast step, e.g. Scheme (II-17).



Scheme (II-17): A 1,1-dimethylsilaethylene as an intermediate for the formation of (80).

The present work involves the same substrate, but lithium *t*-butoxide in pyridine as reagent. Under these conditions the chance of deprotonation is increased because of the higher basicity of alkali metal *t*-butoxides in aprotic solvents<sup>73</sup> when compared to alkalimetal hydroxides in water. In addition the nucleophilicity of lithium *t*-butoxide is tempered by its high steric requirements, and the greater steric sensitivity of nucleophilic reactions when compared to proton transfer processes may again favour the silaethylene route.

Mechanism (5) is the silicon equivalent of an E2 reaction. For this to occur, (a) reaction must obey second-order kinetics (when considered in terms of monomeric lithium *t*-butoxide) and (b) there should be an observable kinetic isotope effect on substitution at silicon  $\left(\frac{k_H}{k_D} \sim 4\right)^{61}$ .

This is much greater than the experimental value of 1.3 - 1.5, which is barely outside the range of secondary isotope effects. It is particularly

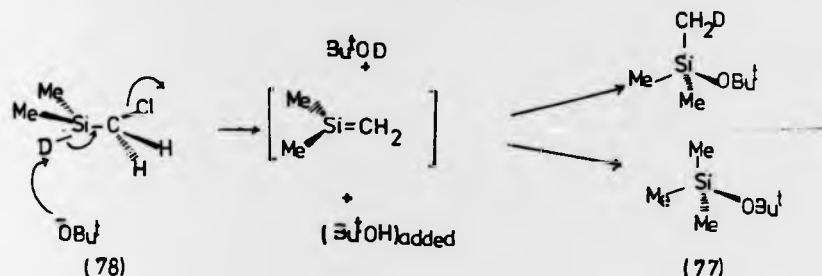
relevant that low isotope effects in the solvolysis of silicon hydrides have been observed earlier<sup>56</sup>, and more recently by Schowen's group<sup>60,62</sup> who have studied the solvolysis of triarylsilanes catalysed by methoxide or ethoxide ion in the corresponding alcohol. The value of kinetic isotope effect observed on replacement of Si-H by Si-D in the reaction varied from 1.15 to 1.7 depending on the nature of the aryl substituents<sup>60,62</sup>. This led us to presume that the transition-state in an E2 reaction involving a silicon hydride might be product-like (weak Si-H and strong H-OBu<sup>t</sup>) because of attenuated orbital coupling between the Si-H and C-Cl bonds.

Although the new evidence is consistent with a silaethylene intermediate (mechanism 5) it could also be considered as evidence for a penta-coordinated silanion intermediate (mechanism 4) with a rather high secondary isotope effect. Further experiments were desirable and in the first we attempted to trap any silaethylene by its known<sup>19</sup> Diels-Alder reaction. Thus lithium *t*-butoxide in pyridine (200  $\mu$ L, 0.1 M) was placed in an n.m.r. tube together with 2,3-dimethylbutadiene (200  $\mu$ L). There was added silane (76) by injection under nitrogen, but after completion of reaction the only product observed was *t*-butoxytrimethylsilane (77). Reaction was repeated with 1,3-butadiene and with furane, but in all cases (77) was the only product obtained, although the yield was reduced from 95% to around 90%, as evidenced by comparison with standard spectra.

#### B Product Analysis by Mass Spectrometry.

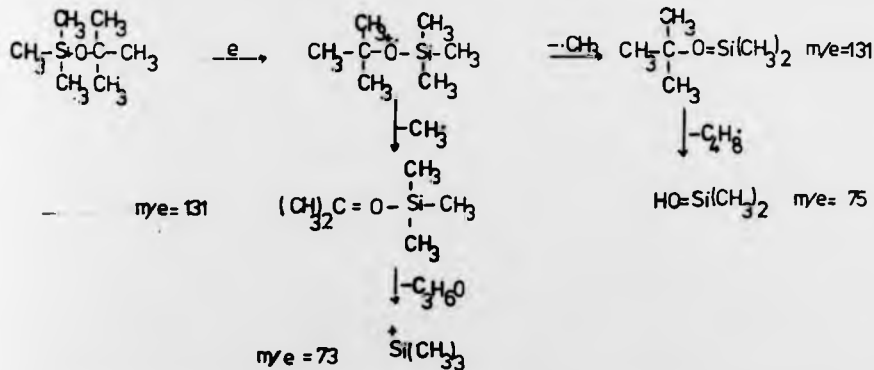
Although deuterated chloromethyldimethylsilane (78) does not undergo exchange with *t*-butanol in the course of solvolytic rearrangement, it is possible that irreversible formation of a silaethylene might lead to product in which some exchange had occurred (Scheme (II-18)). Reaction of the deuterated compound (78) was therefore conducted with lithium *t*-butoxide in pyridine containing varying quantities of *t*-butanol, and (77) isolated from the reaction mixture and purified by low-temperature

fractional distillation. An authentic sample of (77) was prepared by reaction between lithium t-butoxide and chlorotrimethylsilane. The mass spectral fragmentation pattern is shown in Fig. (II-9).



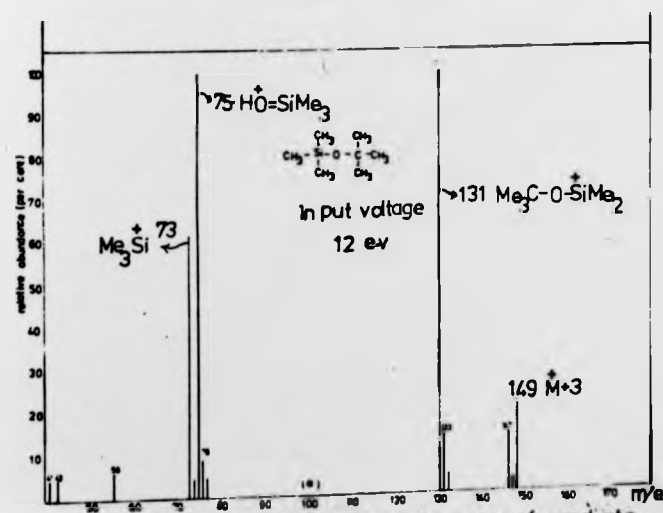
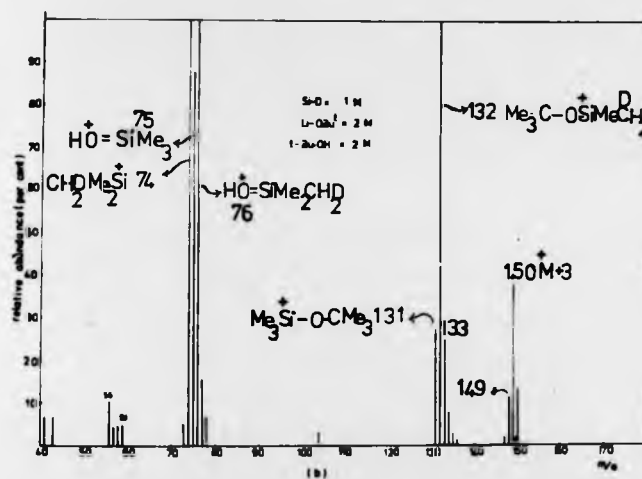
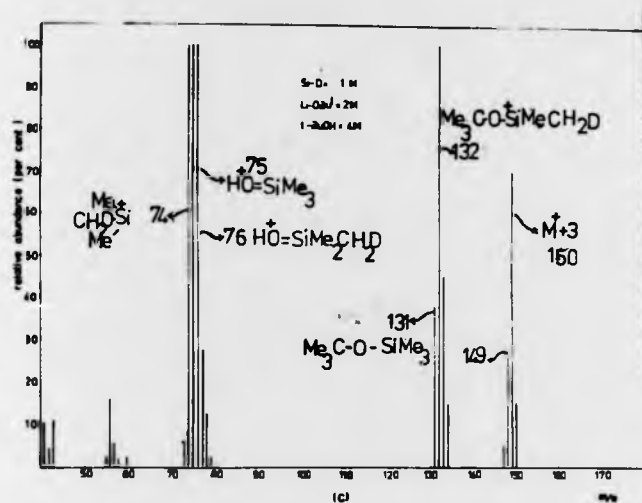
Scheme (II-18): Possible mechanism for the reaction of (Si-D) with  $\text{LiOBu}^t$  in presence of t-BuOH.

The mass spectra of trimethylsilyl ethers<sup>74</sup> can either proceed by  $\alpha$ -fission at silicon or carbon, giving two different daughter ions which undergo further fragmentation as shown in Scheme (II-19).



Scheme (II-19): Possible fragmentation of t-butoxytrimethylsilane.

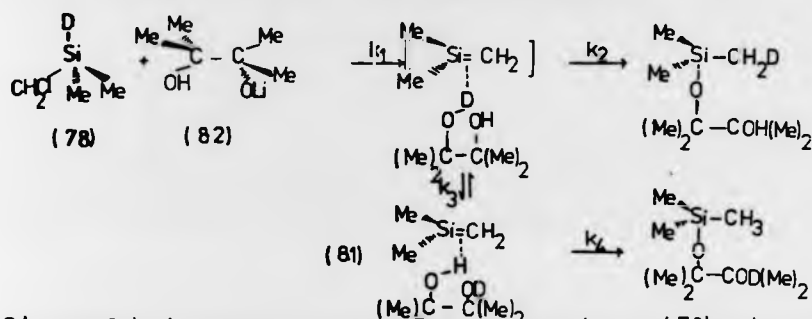
This mechanism of fragmentation has been confirmed by deuterium labelling experiment<sup>75</sup>. The mass spectrum of (77) indeed shown these features, and analysis of the deuterium content of the sample may be carried out from the  $m/e$  131/132 ratio ( $M^+ - 15$ ) or the  $m/e$  73/74 ratio ( $\text{SiMe}_3$ ). Even at very low input voltages, the parent peak is very weak. The spectrum are complicated by overloading of sample



Fig(II-9) Electron impact mass spectrometry of products isolated according to scheme(II-18) and standard (77)

and therefore unsuitable for rigorous quantitative analysis. Additionally, the relative contributions of  $\alpha$ -silicon cleavage and  $\alpha$ -carbon cleavage to the  $(M^+ - 15)$  fragment cannot be established. Nevertheless, it is obvious from the 73/74 ratios that little isotope exchange has occurred.

In an attempt to provide a more intimate test for the intermediacy of a silaethylene, reaction with an ambident base was examined. The monolithium salt of pinacol was particularly suitable in this regard, and the substance of the experiment is explained by Scheme (II-20).

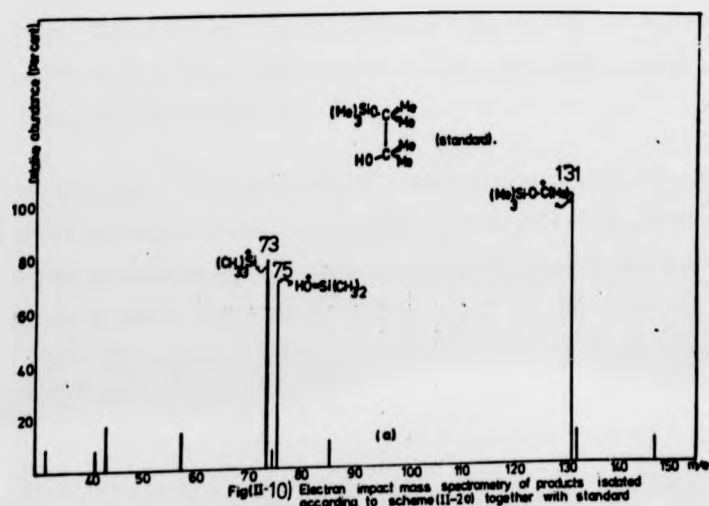
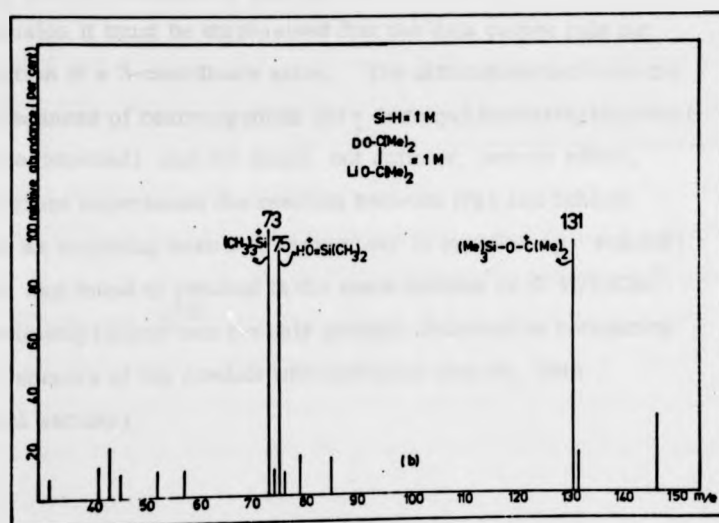
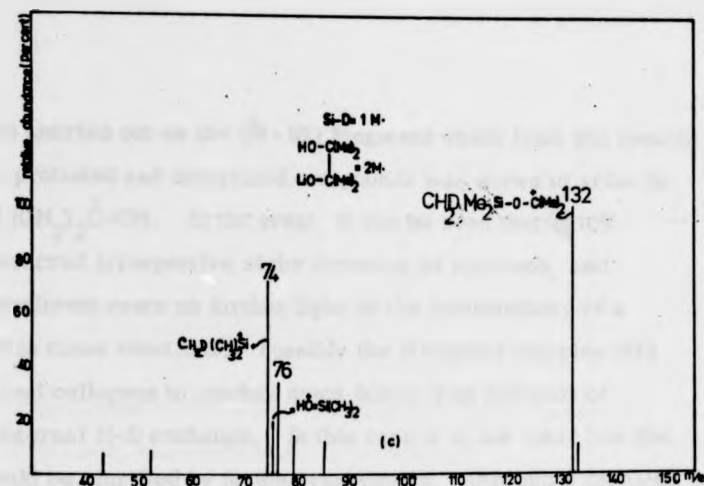


Scheme (II-20) A suggested mechanism<sup>2</sup> for the reaction between (78) and (mono) lithio pinacoxide (82)

If a silaethylene intermediate is formed which is strongly hydrogen-bonded to the attaching base moiety, then isotope exchange merely requires an H-bond rearrangement. The rate of this process  $k_3$  would be expected to be high since the barrier to reorganisation should be quite small. Of course  $k_2$  may also reflect an exceedingly rapid process. Experiments to generate authentic samples of deuterated and undeuterated mono-O-trimethylsilyl-2,3-dimethylbutane-2,3-diol were carried out as before, the mono-deuterated base being prepared by reaction of 2,3-dimethylbutane-2,3-diol-O, O-d<sub>2</sub><sup>(83)</sup> with one equivalent of butyl lithium. Reaction between (76) and this deuterated base<sup>(84)</sup> was carried out in pyridine at 40° with aqueous work-up and fractional distillation. Particular care was taken at this stage to wash out oxygen-bound deuterium to avoid interference in the analysis. Conversely, reaction was carried out between deuterated (76) and protiated base (82).

If the condition  $k_3 \gg k_2$  is observed, then product should show substantial isotope exchange depending in part on the isotope effect  $k_4/k_2$ . Representative mass spectra are shown in Figure (II-10) and





Fig(II-10) Electron impact mass spectrometry of products isolated according to scheme(II-2a) together with standard

analysis was carried out on the ( $\overset{+}{M}$  - 59) fragment which from the spectra of authentic protiated and deuterated compounds was shown to arise by cleavage of  $(CH_3)_2\overset{+}{C}$ -OH. In the event, it can be seen that  $\leq 10\%$  exchange occurred irrespective of the direction of approach, and thus the experiment casts no further light on the intermediacy of a silaethylene in these reactions. Possibly the H-bonded complex (81) is formed, and collapses to product much faster than diffusion of alcohol or internal H-D exchange. In this case it is not clear how the situation could be clarified by further experiment, although a resolved asymmetric chloromethylsilane might prove effective.

In conclusion it must be emphasised that the data cannot rule out the intervention of a 5-coordinate anion. The difficulties here are the observed cleanness of rearrangement (no *t*-butoxychloromethyldimethylsilane can be detected) and the small, but definite, isotope effect.

In a separate experiment the reaction between (76) and lithium *p*-cresoxide as attacking base was carried out in pyridine as solvent; the reaction was found to proceed in the same fashion as Si-H/LiOBu<sup>t</sup>. *p*-Cresoxytrimethylsilane<sup>(85)</sup> was the only product observed by comparing the n.m.r. spectra of the product with authentic sample, (see experimental section).

F.

## EXPERIMENTAL

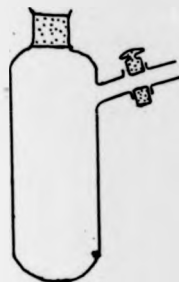
The techniques used in this work, together with the preparation of the compounds used, are described in this section.

### (a) Techniques Used for the Handling of Air-sensitive Compounds.

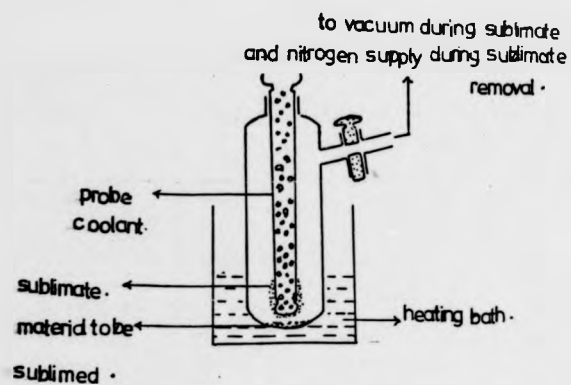
Since in this investigation we are dealing mainly with oxygen and moisture sensitive compounds, handling of materials was carried out in a nitrogen atmosphere. Laboratory nitrogen was deoxygenated by passing through chromous-chloride solution mixed with zinc amalgam, and dried by passing through Dreschel tubes filled with silica gel and potassium hydroxide. Custom-made glassware was used (Fig. II-11), to perform any chemical operation under inert atmosphere of nitrogen. Greaseless joints were used wherever possible to avoid contamination of compound with grease. Throughout this work, the reaction vessels were evacuated and refilled again with nitrogen, on a vacuum line interconnected with a purified nitrogen line, in such a way that this process is carried out easily and efficiently, Fig. (II-12).

Reaction Vessels. Three-necked flasks fitted with vacuum-tap, or Schlenck tubes were used throughout this work, to carry out the preparation under nitrogen atmosphere, easily and efficiently.

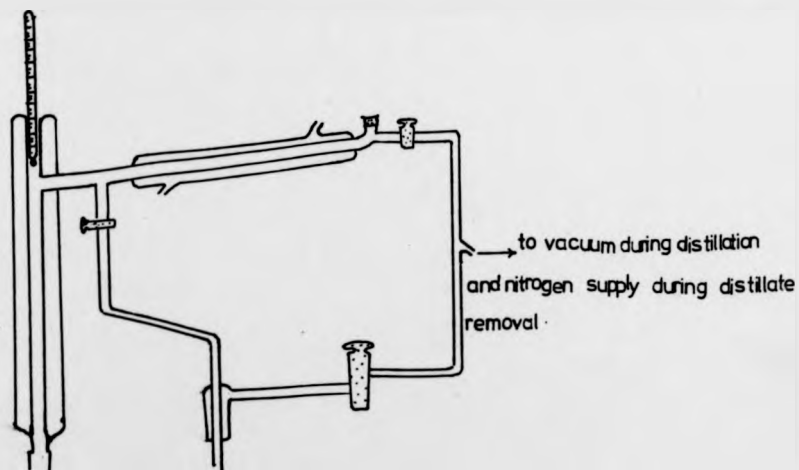
Filtration under nitrogen. Filtration of air-sensitive compounds was carried out by using a positive nitrogen pressure applied into the solution to be filtered. The filtrate was forced to move through the filter paper which was attached firmly by a nichrome wire, as shown in Fig. (II-13)<sup>76</sup>.



Schlenk tube



Vacuum sublimation apparatus



Modification of Perkin triangle used for fractionation  
under reduced pressure.

Figure (II- 11 ) : Apparatus used for handling and preparing  
air-sensitive compounds.

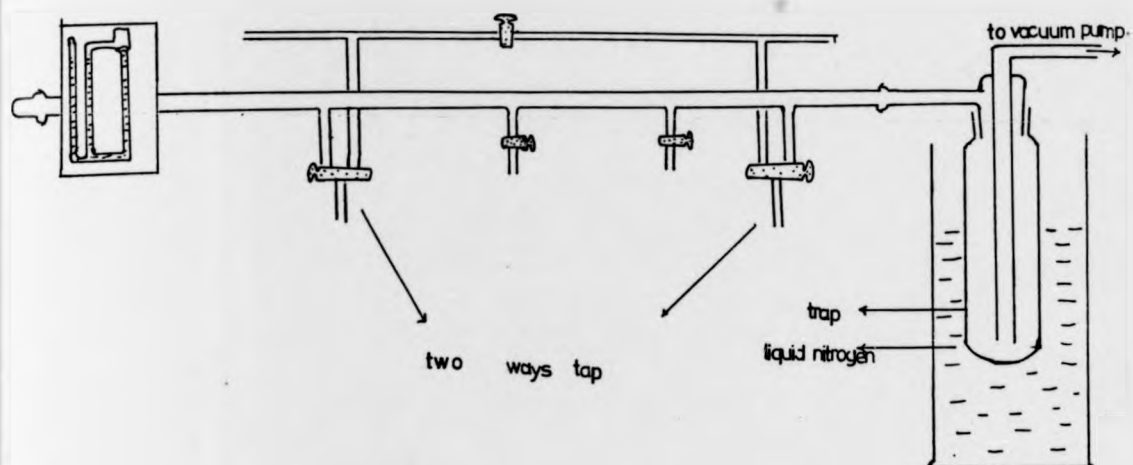


Figure (II-12 ) : Nitrogen line interconnected with high vacuum system.

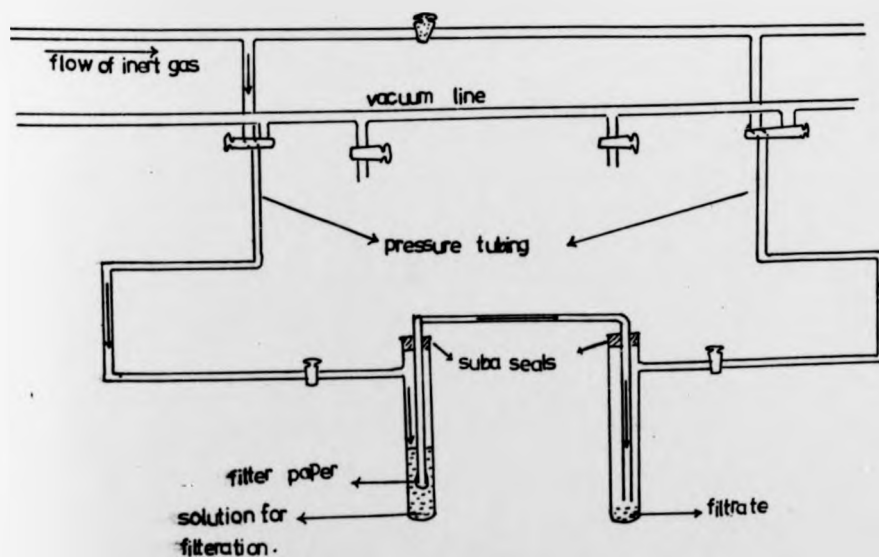


Figure (II-13): Diagram representing the filtration of an air-sensitive compound under flow of inert gas.

Molecular Distillation Apparatus. A different shape with a different size apparatus was used to distil the product from the crude material. Fig(II-14) shows the different apparatuses used for distillation.

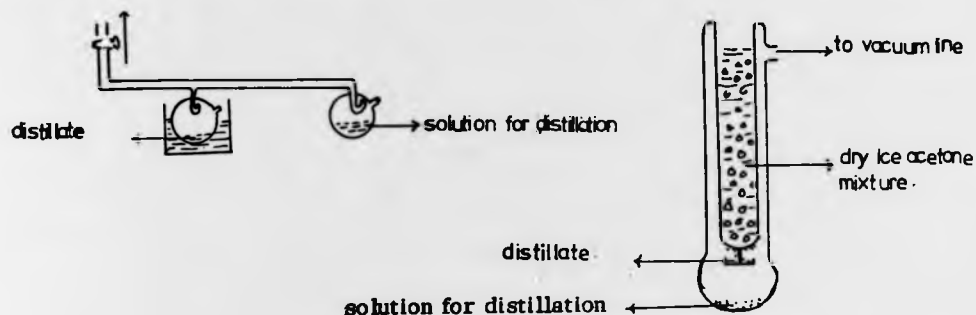


Figure (II-14): Apparatus used for molecular distillation.

Preparation of n.m.r. Samples. Fig. (II-15) shows the simple device used to prepare a solution for nmr measurements in some cases an nmr tube sealed to the reaction system was used, Fig(II-16).

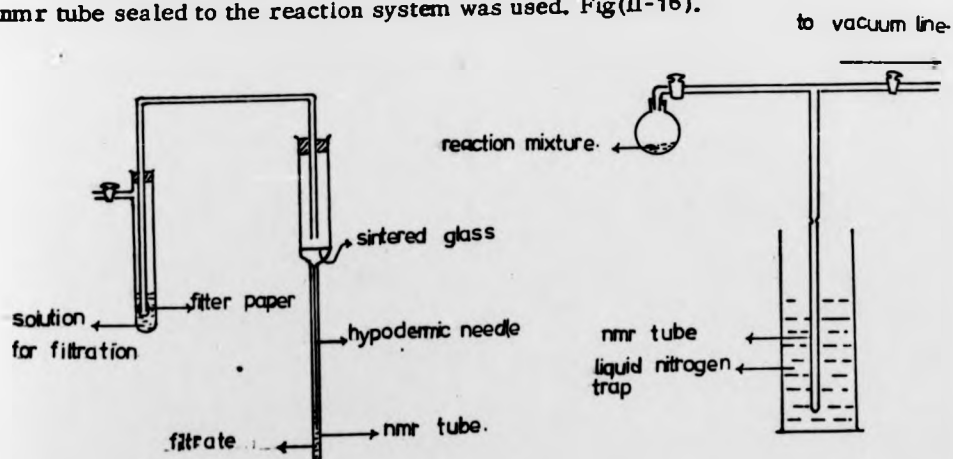


Figure (II-15): Preparation of solution for nmr measurement under nitrogen

Figure (II-16): Nmr tube used as a receiver to condense the product.

**Fractionations.** Fractionation of liquids was carried out by using N. F. 1300 spinning band distillation apparatus for separation of narrow-range (b. p) mixtures. For wide range b. p fractions a modified Perkin triangle apparatus was used (Fig. (II-11)). Special apparatus had been made for low temperature fractionation, which was used for separation of very small fractions up to 100  $\mu$ l. Fig. (II-17).

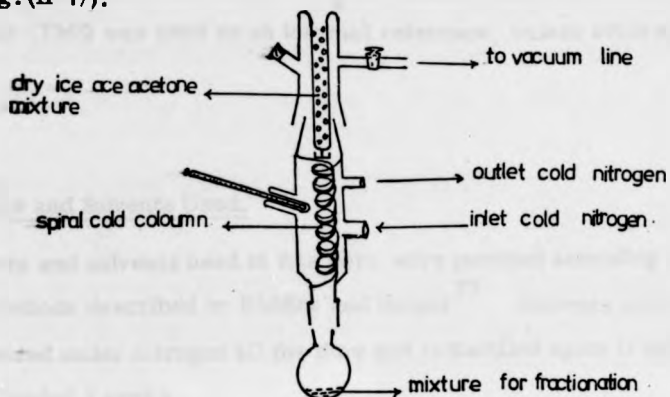


Figure (II-17): Low temperature apparatus for fractionation.

**(b) Instruments Used.**

**Ultra-Violet Spectra.** U. V. spectra were recorded on a Unicam SP800, calibrated on the 341 m $\mu$  peak of holmium glass.

**Infra-red Spectra.** I. R. spectra were recorded on a Perkin-Elmer 257 or P. E. 621 grating machine calibrated on the 1601 cm<sup>-1</sup> peak of polystyrene. Spectra were taken as liquid film between 5mm thick sodium chloride plates or in the case of solids, spectra were recorded as a mull by using a suitable mulling agent (normally nujol). Maxima are designated as w(weak), m(medium), s(strong) or mw(medium weak), ms(medium strong), b(broad), according to the strongest peak height.

**Mass Spectra.** A high resolution Micromass 12 (V.G. Micromass Ltd.), was employed for recording mass spectra. Chemical ionisation mass spectra were recorded on an A. E. I. MS 50.

Nuclear Magnetic Resonance Spectra. Proton magnetic resonance ( $^1\text{H}$ ) spectra were recorded by using a Perkin Elmer R12 nmr spectrometer for recording spectra at constant temperature, and 60 M Hz. Carbon magnetic resonance spectra ( $^{13}\text{C}$ ) and ( $^1\text{H}$ ) spectra were recorded at 90 M Hz on a Bruker WH 90 employing Pulse Fourier Transform (F. T.). In all measurements tetramethylsilane (TMS) was used as an internal reference, unless otherwise stated.

(c) Reagents and Solvents Used.

Reagents and solvents used in this work were purified according to the standard methods described by Riddick and Bunger<sup>77</sup>. Solvents were deoxygenated and stored under nitrogen all the time and redistilled again if the time of storage exceeded 3 weeks.

(d) Preparation of Starting Materials.

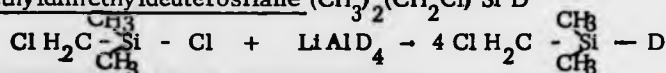
Chloromethyldimethylsilane  $\text{ClH}_2\text{C}(\text{CH}_3)_2\text{SiH}$  was prepared from Trimethylchlorosilane in two-steps according to Kaesz and Stone<sup>78</sup>: 150 ml (1.618 moles) of trimethylchlorosilane was placed in a three necked flask, fitted with a dry-ice acetone condenser and chlorine gas inlet, provided with magnetic stirrer and kept at  $0^\circ\text{C}$ . The flask was exposed to an ordinary spot light lamp, and chlorine gas (purified by passing over 10% potassium permanganate solution, and finally dried by passing through concentrated sulphuric acid) was allowed to pass into the flask at a slow rate, with the lamp switched on. Progress of the reaction was monitored by taking the  $^1\text{H}$  spectrum every 30 minutes. After about 4 hours passage of chlorine was stopped and using Perkin triangle distilling apparatus, unreacted material was recovered (40 ml), and the fraction collected at  $114^\circ\text{C}$  (760 mm Hg). (75 ml) (0.81 moles) was identified by its nmr  $\tau$  ( $\text{CCl}_4$ ), 7.09 (2H, s,  $\text{CH}_2\text{Cl}$ ),  $\tau$  9.42 (6H, s,  $(\text{CH}_3)_2$ ) as chloromethyldimethylchlorosilane.

A solution of 50 gms (0.35 moles) of chloromethyldimethylchlorosilane in 50 ml dry ether was placed in 250 ml flask, fitted with a water condenser, and equalised pressure dropping funnel, and maintained at  $0^\circ\text{C}$ . A suspension



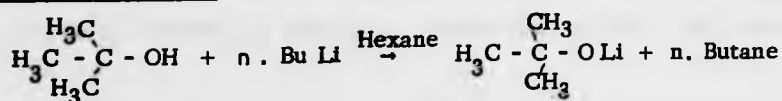
of 3.40 gms of Lithium aluminium hydride in 50 ml of dry ether was added gradually from the dropping funnel over 60 minutes. The mixture was stirred for another 60 minutes at room temperature. Volatile material was removed from suspended solids by distillation in vacuo. The distillate was fractionated by using a Perkin triangle apparatus to remove the ether under nitrogen and product was collected. b.p. (51°C, 760 mm Hg). (20 gms) (0.18 moles), 70% yield of pure chloromethyldimethylsilane was obtained. nmr  $\tau(\text{CCl}_4)$  5.9 (1H, m, Si-H), 7.15 (2H, d,  $\text{ClCH}_2$ ;  $J_{1,2} = 2.5$  Hz), 9.79 (6H, d,  $(\text{CH}_3)_2\text{Si}$ ;  $J_{1,3} = 6$  Hz).

Chloromethyldimethyldeuterosilane  $(\text{CH}_3)_2(\text{CH}_2\text{Cl})\text{Si D}$



20 gms (0.14 moles) of chloromethyldimethylchlorosilane was reduced in similar manner by using 1.4 gms of lithium aluminium deuteride. There was thus obtained 10 gms (0.09 moles) of chloromethyldimethyldeuterosilane (65% yield), nmr  $\tau(\text{CCl}_4)$  7.23 (2H, s,  $\text{Cl} - \overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ ) and 9.77 (6H, s,  $\text{C} - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}$ ) and showing no trace of Si-H resonances.

Lithium t-Butoxide  $(\text{Li O Bu}^t)$



100 ml of 2.1 M dry tert-butyl alcohol in dry ether was placed in 500 ml two-necked flask fitted with nitrogen gas inlet and pressure equalised dropping funnel, 100 ml of 2.1 M n.Bu Li (previously standardised according to <sup>79</sup>) was added slowly at 0°C and the resulting solution stirred for a further 30 minutes at room temperature. The solvent was removed by vacuum distillation and solid white lithium t-butoxide was obtained and used without any further purification. An attempt to recrystallise the product from different solvents tetrahydrofuran, n-Hexane, and cyclohexane failed, also Lithium t-butoxide was found to decompose on attempted sublimation, nmr  $\tau(\text{pyridine})$  8.71 (9H, s,  $\text{C}(\text{CH}_3)_3$ ) with no observable hydroxy resonances.

t-Butanol-O-d<sub>3</sub>-C(CH<sub>3</sub>)<sub>3</sub>

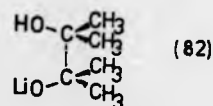
Prepared according to reference 80. Thus 50 gm (0.2 moles) of aluminium t-butoxide was placed in a 100 ml round-bottom flask fitted with a water condenser

the nitrogen gas inlet, 10 gms (0.2 moles) of deuterium oxide was added to the aluminium t-butoxide. The flask was kept in an oil bath at 100°C and left to reflux for 2 hours. Product was distilled using a fractionating column equipped with Perkin triangle. The nmr spectra of the compound isolated at this stage showed that the alcohol was still wet. By trying different drying agents we found that residual water was best removed by refluxing the product with sodium (0.5 gm), with a little loss of product yield. 10 gms (80%) of dry 2-Deuteroxy-2-methylpropane was obtained. Nmr  $\tau$  (pyridine) 8.61 (9H, S, C(CH<sub>3</sub>)<sub>3</sub>), showing no trace of O-H resonances.

#### Trimethylbutoxysilane (H<sub>3</sub>C)<sub>3</sub>-C-O-Si-(CH<sub>3</sub>)<sub>3</sub>

8.1 gms (0.1 moles) Lithium-tert-butoxide was mixed with 5 gms (0.046 moles) of trimethylchlorosilane in a two-necked flask fitted with a nitrogen gas inlet. The mixture was shaken vigorously using a mechanical shaker for about 15 minutes. The resulting trimethylbutoxysilane was distilled under vacuum, crude product was fractionated by using spinning band distillation apparatus and the fraction (b.p. 103.5° 76 mm)<sup>81</sup> obtained was analysed by nmr, CCl<sub>4</sub> $\tau$ : 8.77 (9H, S, OBut), 9.92 (9H, S, Si(CH<sub>3</sub>)<sub>3</sub>). Yield 3.5 gms (52%). Fig. (II-18).

#### (Mono) Litho-2, 3-Dimethylbutane-2, 3-diol.



12.41 gms of anhydrous pinacol (dried by azeotropic distillation with benzene) was dissolved in 50 ml dry ether and transferred to a Schlenk tube fitted with pressure equalised dropping funnel and nitrogen inlet. The solution was kept at 0° whilst 50 ml of 2.1 M n-Butyllithium was added slowly from the funnel with continuous stirring. After 1½ hours stirring the solvent was removed under vacuum and the residue dissolved in warm tetrahydrofuran (THF), and filtered under nitrogen pressure. The filtrate was cooled by using a dry-ice acetone mixture, when white solid crystalline material was obtained. After further filtration by the same technique the residual crystals were washed with cold THF at -30°C, and dried under vacuum.

Monolithium pinacoxide solid (Mol. Wt = 123.94), was analysed for lithium as follows: 0.54 gms of the salt was dissolved in 50 ml of distilled water using volumetric flask, 10 ml of 0.1M HCl was added to 5 ml of lithium pinacoxide, the

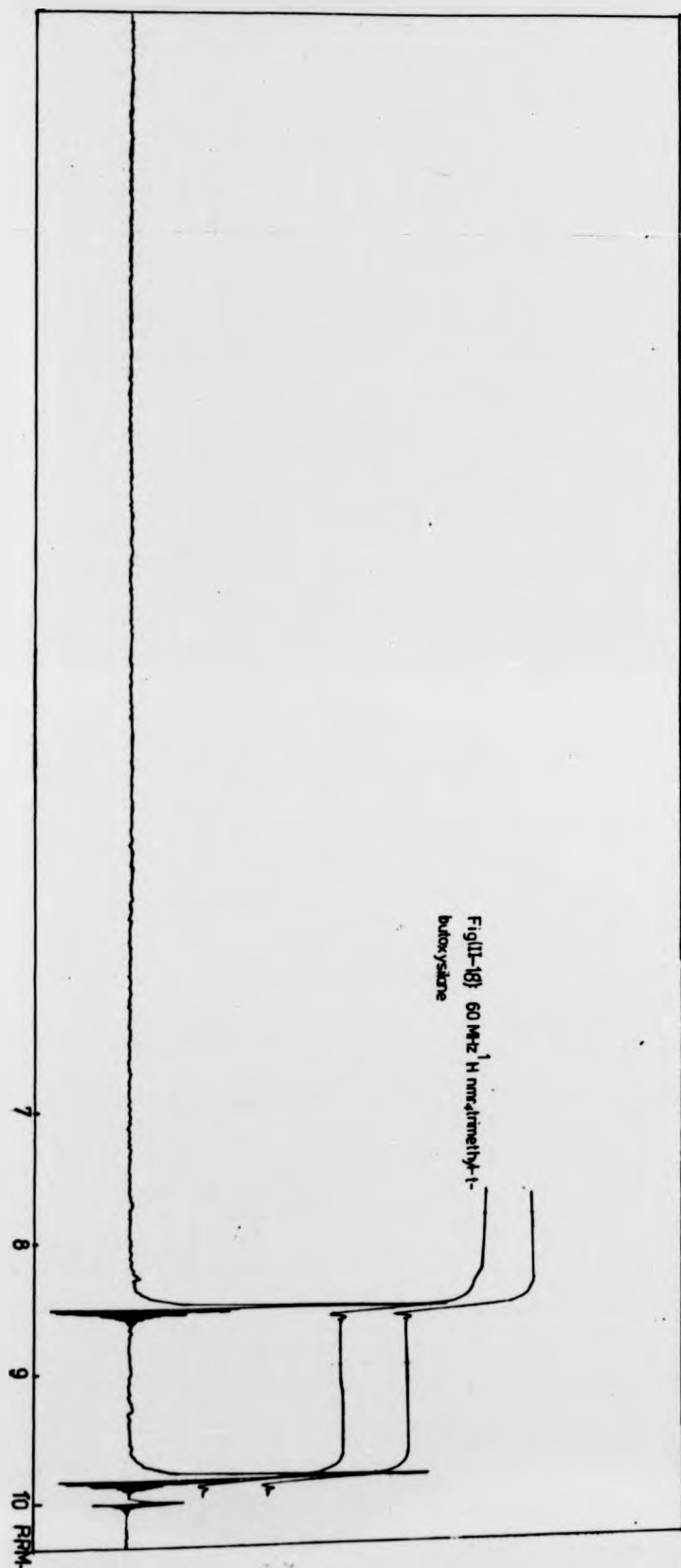


FIGURE 18. 60 MHz  $^1\text{H}$  NMR spectrum of 1-butoxysilane

excess acid was back-titrated using 0.1M NaOH, below is the result of this titration:

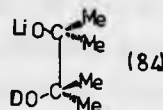
(HCl)  $5.3 \times 0.1 = V \times 0.1$  (NaOH) (using Ph.Ph as indicator)

$\therefore V_{\text{NaOH}} = 5.3 \text{ ml}$

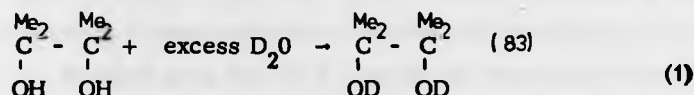
Volume of HCl consumed in neutralisation of lithium-pinacoxide =  $10 - 5.3 = 4.7 \text{ ml}$

$\therefore M$  of lithium-pinacoxide = 0.09M which is consistent with the expected value for monolithium-pinacoxide concentration (0.087 M)

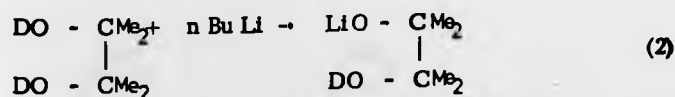
(Mono) Lithio-2,3-Dimethylbutane-2,3-diol-O-d.



This was prepared by a two-stage sequence:

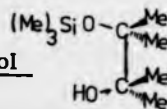


11.8 gms (0.1 moles) of anhydrous pinacol was placed in Schlenck tube, 15 gms (0.75 moles) of deuterium oxide was added to the pinacol at room temperature and the resulting solution was magnetically stirred for 20 minutes. Excess  $\text{D}_2\text{O}$  was removed under vacuum. Another 15 gms of  $\text{D}_2\text{O}$  was added to the solid residue and the same process repeated again, so that hydrated dideuteropinacol was obtained. The water of hydration was removed by azeotropic distillation with benzene giving white solid nmr  $\text{CCl}_4$   $\tau$  8.85(12H) 8 gms (80%) yield.

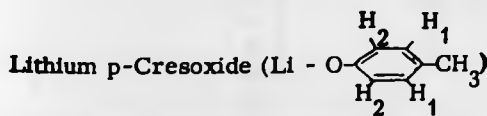


6.18 gms of dideuteropinacol<sup>(83)</sup> dissolved in 50 ml of dry ether was introduced into a Schlenck tube fitted with pressure equalised dropping funnel and nitrogen gas inlet. 50 ml of 1.71M n-Butyllithium was added gradually to the stirred solution at  $0^\circ\text{C}$ . After 30 minutes stirring, solvent was removed under vacuum and the solid residue was recrystallised from warm THF. A white crystalline solid was obtained nmr  $\text{CDCl}_3$   $\tau$  8.8(12H, S,  $\text{C}_1^{\text{D}}$ ,  $\text{C}_2^{\text{D}}$ ), yield 4.5 gm (59%).

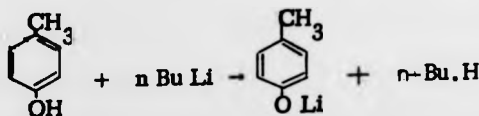
2-Trimethylsilyloxy-2,3-dimethylbutan-3-ol



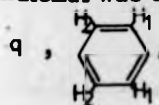
1.24 gms (0.011 moles) of (82) was dissolved in 30 ml anhydrous pyridine (A.R pyridine was employed, traces of water being removed by refluxing 250 ml pyridine over  $\frac{1}{2}$  gm Lithium aluminium hydride and subsequent distillation) was placed in a 50 ml two-necked flask fitted with a water condenser and nitrogen gas inlet, 0.544 gms (0.005 moles) of trimethylchlorosilane was added from a weighed syringe to the stirred solution, at 40°C. After 2.5 hours the solution was transferred to a separatory funnel, 30 ml of dry pentane was added to extract the product and pyridine was removed efficiently by washing with cold water several times, until there was no detectable amount of pyridine present in the aqueous layer. The pentane solution was transferred to Perkin triangle fractionating column and pentane removed by distillation. The residue was trap to trap distilled as in Fig. (II-14) and finally fractionated very efficiently using a low-temperature distillation apparatus, Fig. (II-7). Nmr  $\tau$  (C Cl<sub>4</sub>) 8.0 (1H, S, OH), 8.78 (6H, S, O - C), 8.93 (6H, S, C), 9.88 (9H, S, Si). Fig. (II-19), yield 0.60 gm (66%). Found (C 56.7% H 11.4%) C<sub>9</sub>H<sub>22</sub>O<sub>2</sub>Si require (C 56.8% H 11.5%)



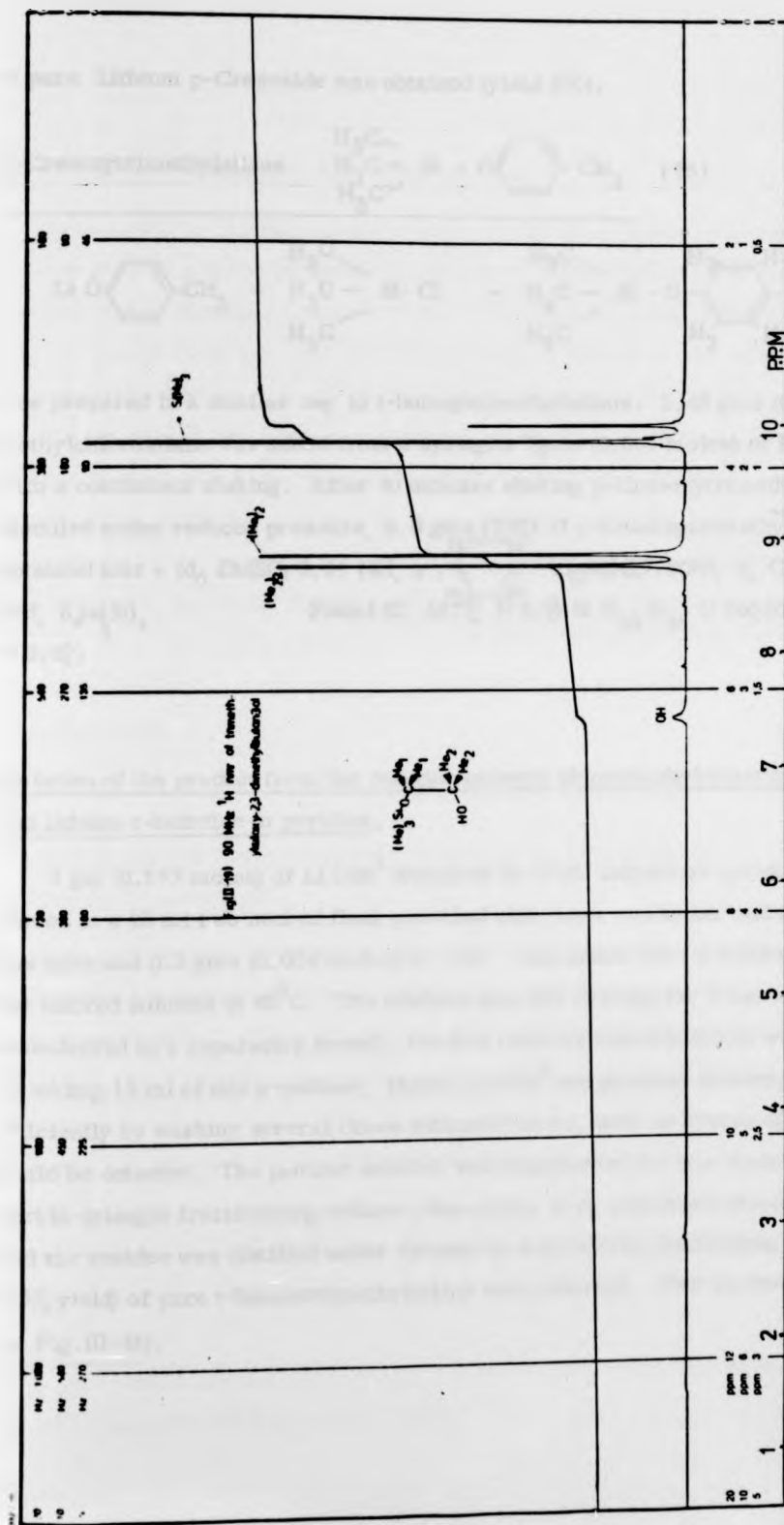
Prepared in a similar way to LiOBu<sup>t</sup>



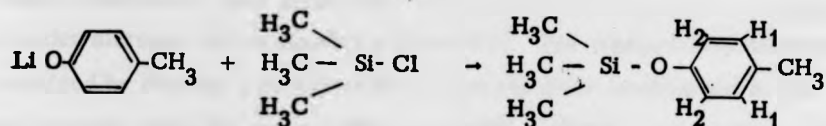
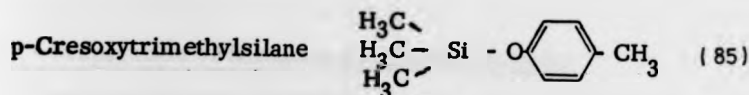
10.818 gms of p-Cresol (purified by double distillation and purity checked by nmr) was dissolved in 50 ml dry ether and placed in three-necked flask fitted with nitrogen gas inlet, pressure equalised dropping funnel, 50 ml of 2.0M n-Bu Li was added gradually from the funnel to the stirred solution at room temperature. After 30 minutes stirring, solvent was removed by vacuum distillation and the solid washed with n-Hexane, and filtered under nitrogen atmosphere. A white solid crystalline material was obtained, which was dried under vacuum, nmr  $\tau$  (d<sub>6</sub>-DMSO): 3.52(4H,




10 Hz), 7.91 (3H, S, CH<sub>3</sub>) nmr  $\tau$  (pyridine) 7.31(3H, S, CH<sub>3</sub>), 10 gms



of pure Lithium p-Cresoxide was obtained (yield 87%).



was prepared in a similar way to t-butoxytrimethylsilane. 5.43 gms (0.05 moles) of trimethylchlorosilane was added from a syringe to 7gms (0.061 moles) of lithium p-cresoxide with a continuous shaking. After 10 minutes shaking p-Cresoxytrimethylsilane was distilled under reduced pressure, 6.5 gms (73%) of p-Cresoxytrimethylsilane was obtained nmr  $\tau$  ( $d_6$  DMSO) 3.31 (4H, q, ,  $J_{\text{H}_1\text{H}_2} = 10\text{ Hz}$ ), 7.8 (3H, s,  $\text{CH}_3$ ), 9.8 (9H, s,  $\text{M}_3\text{Si}$ ). Found (C, 66.7% H 8.9%) Si  $\text{C}_{10}\text{H}_{16}\text{O}$  require (C 66.3% H 8.8%)

Isolation of the product from the reaction between chloromethyldimethylsilane and lithium t-butoxide in pyridine.

1 gm (0.012 moles) of  $\text{Li OBu}^t$  dissolved in 15 ml anhydrous pyridine was placed in a 25 ml two necked flask provided with water condenser and nitrogen gas inlet and 0.5 gms (0.004 moles) of (76) was added from a microsyringe to the stirred solution at  $40^\circ\text{C}$ . The mixture was left stirring for 2 hours, then transferred to a separatory funnel. Product t-butoxytrimethylsilane was extracted by adding 15 ml of dry n-pentane, excess  $\text{Li OBu}^t$  and pyridine solvent was removed efficiently by washing several times with cold water, until no traces of pyridine could be detected. The pentane solution was transferred for fractionation using a Perkin-triangle fractionating column after drying over anhydrous calcium chloride and the residue was distilled under vacuum by trap to trap distillation; 0.5 gms (75% yield) of pure t-butoxytrimethylsilane was collected. Nmr is exactly the same as in Fig. (II-18).



### G. Preparation of Solutions for Kinetic Analyses.

Stock solutions of clear colourless 1M LiOBu<sup>t</sup> were prepared in a volumetric flask under nitrogen and stoppered by suba-seal. The required concentration was obtained by diluting a certain volume from the stock solution and to the desired volume using the same solvent (normally pyridine) in nmr tube. The required concentration of SiH<sub>4</sub><sup>D</sup> was calculated according to their molecular weight (108.64 and 109.64 respectively) and silane was added neat from a previously weighed microsyringe to the reaction mixture. Spectra were recorded immediately on the Perkin-Elmer R12 nmr machine at 35.1°C and the peak of Si-OBu<sup>t</sup> increase or OBu<sup>t</sup> decrease was measured at suitable time intervals, (normally 3 quick peak area measurements are recorded for each point, the time between the 3 readings being not more than 20 seconds). Data thus obtained was subjected to analysis by standard techniques as described later.

### . Essentials and Theoretical Basis of the Kinetic Measurements Required for the Present Work.

(a) Rate of Reaction: is defined as the rate of change of concentration, it can be expressed in terms of increase in product concentration, in this case it can be expressed as  $(+ \frac{dC_C}{dt} \text{ or } \frac{dC_D}{dt})$ . It can also be expressed in concentration decrease of reactants as  $(- \frac{dC_A}{dt} \text{ or } - \frac{dC_B}{dt})$ , where A, B and C, D are the reactants and products of the following equation.



the units of the reaction rate are moles/litre/sec for reaction in solution, and partial pressure/sec for gas phase reaction<sup>82</sup>.



(b) Order of Reaction (n): is defined as the sum of all the components of the concentration e.g. in the above example  $A^{n_1} + B^{n_2} + \dots \rightarrow C + B + \dots$  the overall order being given by  $n = n_1 + n_2$ ,  $n_1$  and  $n_2, \dots$  are the individual orders for each component.<sup>83</sup>

There are a number of methods which are normally used for determination of individual order discussed in many texts. The integrated form of the rate equation combined with isolation methods has been used in this work, where all components are kept in excess except one which is kept at low concentration if the data obtained from the kinetic measurement fitting kinetic equation of  $n^{\text{th}}$  order, this means that this component participates with  $n^{\text{th}}$  order. This process can be repeated for other components<sup>83, p. 81</sup>.

(c) Rate Constant (k): it is numerically equal to the reaction rate when the reactants are at unit concentration, and in general is the constant appearing in the kinetic equation<sup>83</sup>

$$-\frac{dA}{dt} = k [A]^{n_1} [B]^{n_2}$$

for the equation  $A^{n_1} + B^{n_2} + \dots \rightarrow C + D$

the units for the rate constant depend on the order of reaction under consideration and in general has the unit moles<sup>1-n</sup> litres<sup>n-1</sup> sec<sup>-1</sup>, where  $n$  is the overall order of the reaction. Pseudo- $n^{\text{th}}$  order of reaction in some catalytic reaction in which the catalyst concentration is unchanged or one of the components are in large excess over another; under these conditions the order determined for the component existing with low concentration are estimated under pseudo- $n^{\text{th}}$  order condition, if the kinetic data are fitting  $n^{\text{th}}$  order kinetic equation. The latter method has been used in this investigation.

(d) First-order reactions:<sup>82, p. 14</sup> are defined as those reactions in which the rate of reaction is proportional to one of the component concentration with  $n = 1$ ,

Algebraically

$$\frac{dC_A}{dt} = -k_A C_A$$

the integral form of this equation is  $\log \frac{C_A}{C_{A0}} = -0.434 k_A t$  or  $\log C_A = \log C_{A0} - 0.434 k_A t$  where  $k_A$  is the constant,  $C_{A0}$  is the  $[A]$  at zero time.

In case of pseudo first order reactions we got  $\frac{dC_A}{dt} = -k_A' C_A$ , where  $k_A' = k_A [B]$ ,  $[B]$  are kept in large excess compared to  $[A]$ , the integrated form of the pseudo first order equation is

$$\log C_A = \log C_{A0} - 0.434 k_A' t$$

this is the equation used for this work.

(e) Kinetic Isotope Effect on Reaction Rates. <sup>84</sup>, 85

The difference in rate between the breaking of an A-B bond and an A-B<sup>1</sup> bond (perhaps by the attack of some reagent to form a new bond to one of the two atoms), where B and B<sup>1</sup> are isotopes, can be rationalized in terms of the loss of A-B stretching frequency in the transition state. Most bonds in an ordinary molecule at ordinary reaction temperatures are in their lowest vibrational quantum state, but even at this level they contain zero-point vibrational energy, equal to  $\frac{1}{2}h\nu$ . Equation (1) is a fairly good approximation for the ratio between  $\nu^*(A-B)$  stretching frequency) and  $\nu(A-B)$ ,

$$\frac{\nu^*}{\nu} = \sqrt{\frac{m_B(m_A + m_B)}{m_B^1(m_A + m_B^1)}} \quad (1)$$

if B and B<sup>1</sup> are two different atoms, therefore one can expect a difference in the zero-point energy which can be expressed as in (2), substitution in (1) using Planck's equation.

$$E_{AB} - E_{AB^1} = \frac{1}{2} h\nu \left[ 1 - \sqrt{\frac{m_B(m_A + m_B)}{m_B^1(m_A + m_B^1)}} \right] \quad (2)$$

This difference in the zero-point energies of the reactants may be compensated by a difference in the zero-point energies of the transition states. Equation (2) combined with Arrhenius equation, and neglecting other sources of differences in zero-point energies, the following relation can be obtained:

$$\frac{k_{AB}}{k_{AB^1}} = e^{\frac{h\nu/2kT}{\mu_{AB} - \mu_{AB^1}}} \left[ 1 - \frac{\mu_{AB}}{\mu_{AB^1}} \right]$$

where  $\mu_{AB}$  and  $\mu_{AB^1}$  are the reduced masses of AB and AB<sup>1</sup> respectively.

If the bond-making or bond-breaking in the transition state involves an isotopically substituted atom, this is called "primary" isotope effects. Isotope effects which are not primary are termed "secondary" isotope effect, in the former case  $\frac{k_H}{k_D} \sim 7$  and in the latter case  $\frac{k_H}{k_D} \sim 1-2$  and some - times  $< 1$  <sup>84 p, 208</sup>.

Kinetic isotope effect can be studied with any heavy isotope ( $^{13}\text{C}$ ,  $\text{D}$ ,  $^{34}\text{S}$ ,  $^{37}\text{Cl}$ , -----). Fig. (II-20) represents graphically the relative position of (C-H) and (C-D) energy. <sup>86</sup>

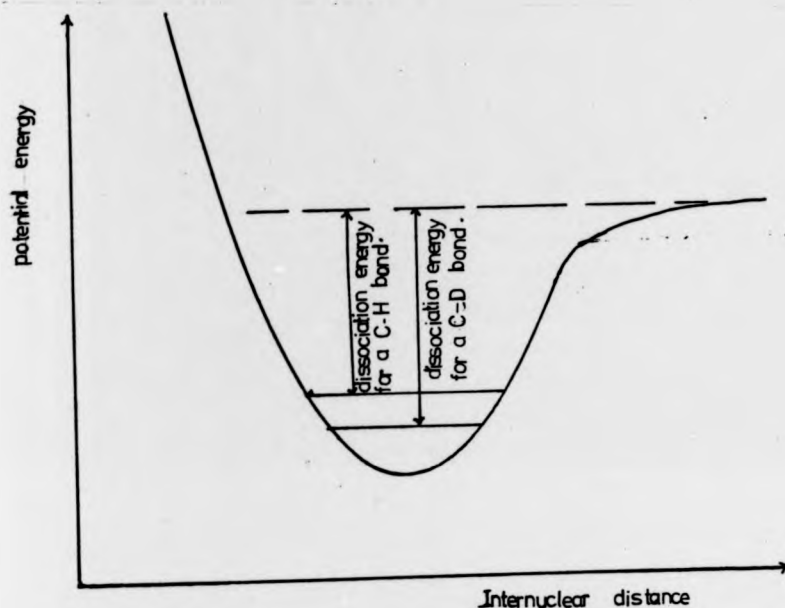


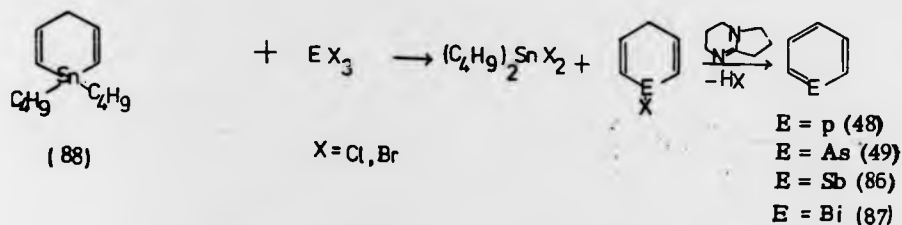
Fig. (II-20): A C-D bond vibration at a lower energy than does a corresponding C-H bond, thus the dissociation energy is higher.

### CHAPTER 3.

#### An Attempt to Synthesise Silabenzene.

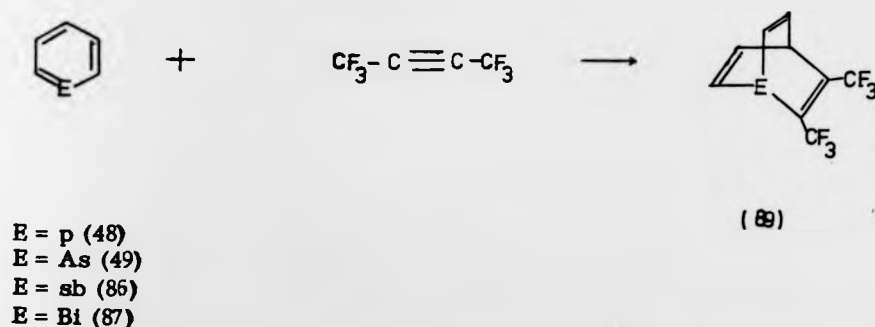
There is an accumulation of results concerning species containing  $\pi$ - $\pi$  bonding in organosilicon (Chapter I-B) as intermediates resulting from the pyrolysis or photolysis of strained cyclic compounds containing silicon atoms, or in the pyrolysis of alkyl silanes. Up to now, however, there is no published work concerning such an isolable species. Only Barton<sup>12</sup> has reported the i. r. spectra of 1,1-dimethylsilaethylene at  $(-196^{\circ}\text{C})$ .

There is an increase in interest in the synthesis of aromatic compounds containing heavy atoms from group (V). A series of compounds with a heavy substituent attached to the aromatic ring have been prepared by Märkl and his coworkers<sup>34</sup> (Chapter I-C). Ashe<sup>40</sup>, succeeded in synthesising phosphabenzene (48) and arsabenzene (49) in a one step reaction (Chapter I-C), and more recently stibabenzene (86)<sup>87</sup>, and the unstable bismabenzene (87). They were obtained by the route shown in Scheme (III-1). Treatment of 1,4-dihydro-1,1-dibutylstanbenzene (88) with the appropriate metal chloride or bromide in THF, afforded 1,4-dihydro-1-halometalbenzene, which can undergo  $\beta$ -elimination using 1,5-diazobicyclo [4,3,0]non-5-ene (DBN), as base, giving the corresponding heteroaromatic compound. (Scheme III-1).



**Scheme (III-1):** General scheme for the synthesis of heterocyclic compounds, containing group (V) elements as a heavy atom.

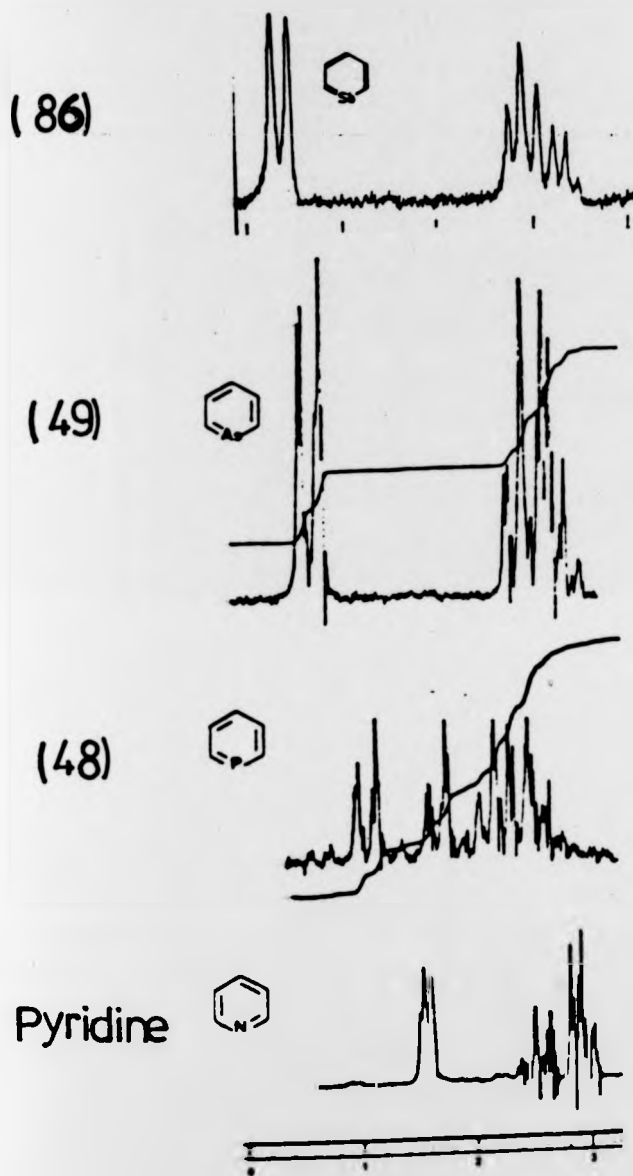
An attempt to isolate bismabenzene (87) by the same route failed, since the product polymerise immediately on adding (DBN) to 1,4-dihydro-1-chlorobis-mabenzene. On the other hand, addition of hexafluorobutyne after precipitation of the hydrochloride of the base gave a 1:1 adduct (89). This behaviour towards hexafluorobutyne was observed with other heterocyclic compounds<sup>88</sup> (Scheme III-2).



**Scheme (III-2):** Diels-Alder reaction of substituted E-benzene with hexafluorobutyne.

Pyridine itself does not react with dienophiles. This led Ashe to conclude that the heavier heterocycles react more rapidly with hexafluorobutyne, probably because of the increase in reactivity as a result of  $\pi$ -bonding contributions.

The proton spectra of the three compounds isolated are shown in Fig. (III-1) together with the  $^1H$  nmr spectra of pyridine.



Fig(III-1) 60 MHz  $^1\text{H}$  nmr of (48),(49),(86)  
and pyridine

The  $\alpha$  protons of (48), (49) and (86) appeared at very low field as a doublet with  $J_{H_\alpha H_\beta} = 10$  Hz, 11 Hz and 11 Hz respectively compared to 5.5 Hz in the case of pyridine. The chemical shift of the  $\alpha$  protons is  $\tau$  1.4 for phosphabenzene, 0.7 for arsabenzene and -0.7 for stibabenzene. This progressive shift to lower field can probably be associated with the magnetic anisotropy of the increasing large heteroatom. These low-field chemical shifts values are consistent with an appreciable ring current of the three compounds, corroborated by the fact that the  $\beta$  and  $\gamma$  protons appear in the normal position of the aromatic compounds  $2\tau$ ; phosphabenzene has a more complex pattern because of the coupling between  $H_\alpha$  and  $^{31}\text{P}$ ,  $J = 38$  Hz<sup>40</sup>.

This reported work on heterocyclic aromatic compounds with heavy atoms of group (V) encouraged us to think about silabenzene as a potentially aromatic compound. In this context we had been guided by the earlier work of Benkeser<sup>89</sup> on the synthesis of 1,1-dichloro-1-sila-2,4-cyclohexadiene (90).

Three main different approaches to generate silabenzene or its derivatives were attempted:

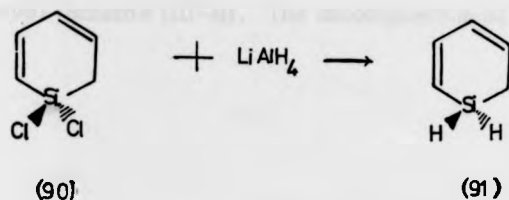
- (A)  $\beta$ -elimination of (90);
- (B) hydrosilylation of Ir(I) and Rh(I) complexes using (91) as hydrosilylating agent;
- (C) catalytic dehydrogenation of 1,6-dihydrosilabenzene (91).

(A)  $\beta$ -elimination of 1,1-dichloro-1-sila-2,4-cyclohexadiene (90).

Since (90) was synthesised nine years ago<sup>89</sup> we expect that considerable emphasis has been placed on attempts to generate silabenenes by base-promoted eliminations. Since nothing has appeared in the published literature this approach may be fruitless and little time was spent on it. A brief study was made of the reaction between (90) and DBN as a base, (a reagent which has been used successfully by Ashe<sup>40</sup>). In a typical run, 165 mg (1 mmole) of (90) mixed with 400  $\mu$ l dry THF was placed in nmr tube, 248 mg (1.5 mmole) of DBN was added from a previously weighed microsyringe. At room temperature, (90) was completely decomposed with a formation of dark brown polymer. Repeating the same experiment with a less powerful base, pyridine, the same results were observed.

(B) Reactions of 1-sila-2,4-cyclohexadiene (91) with Ir(I) and Rh(I) complexes.

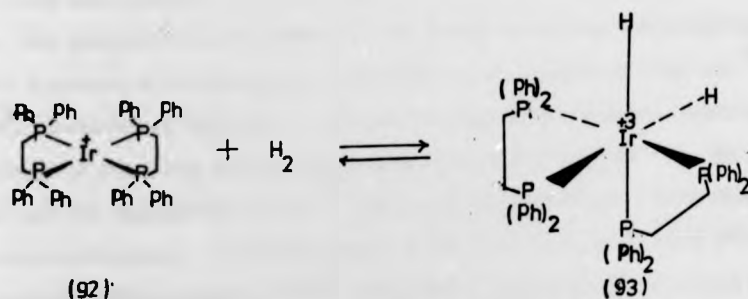
This was the second approach towards the generation of silabenzene. Reduction of (90) using  $\text{Al Li H}_4$  (excess) in triethyleneglycoldimethylether, afforded 1-sila-2,4-cyclohexadiene (91), (see experimental section).



(91) has been used in a series of reactions with Ir(I), and Rh(I) complexes.

(I) Reaction of 1-sila-2,4-cyclohexadiene with Iridium(I)bis(bis-1,2-diphenylphosphinoethane) hexafluorophosphate.

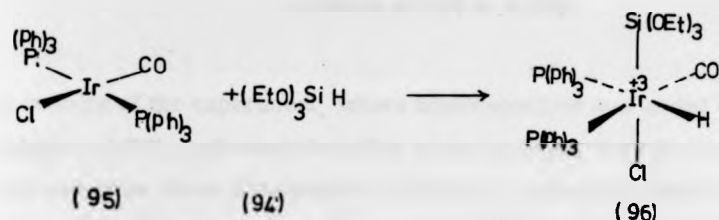
One of the most striking properties of Ir(I) square planar  $d^8$  complexes is their ability to undergo oxidative addition reactions<sup>90</sup>, being converted into octahedral complexes by adding another ligand such as oxygen or hydrogen. The adducts formed have been characterised by i.r and nmr spectra, and it has shown that these products usually have the cis-configuration (ref. 90 p. 59). For example, di-1,2-bis-diphenylphosphinoethaneiridium(I)hexafluorophosphate (92) a complex with  $d^8$  electronic configuration), reversibly adds hydrogen at atmospheric pressure<sup>91</sup>, according to Scheme (III-3).



Scheme (III-3): A reversible oxidation-addition, process of  $\text{Ir}^8$  and  $\text{Ir}^6$  cationic species.



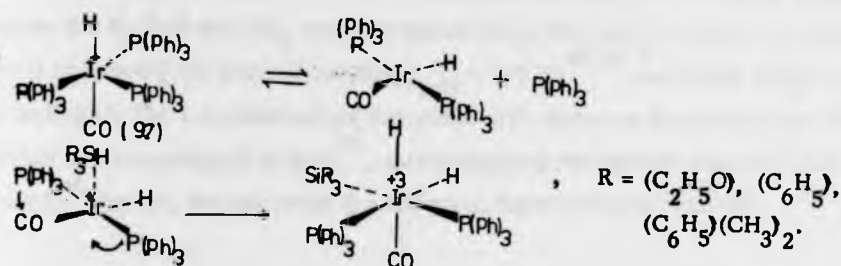
Oxidative-addition reactions of this type have been used to form Iridium-silicon  $\sigma$ -bonds by intervention of a silicon hydride addend. Harrod and his group<sup>92</sup>, have investigated the addition of silicon hydrides to Ir(I) complexes in the hope that a detailed understanding of their oxidative addition reactions would help to solve a problem in homogeneous catalysis, namely the activation of saturated hydrocarbons. Thus, the addition of triethoxysilane (94) to Vaska's compound (95), at room temperature<sup>92</sup>, occurs in 1:1 ratio to give the corresponding Ir(III) adduct (96) (Scheme (III-4)). The decomposition of (96) was observed by heating



Scheme (III-4): hydrosilylation of Ir(I) to give Ir(III) adduct.

in vacuo, giving back the two reactants (95) and (94). A further investigation has been carried out on a similar system<sup>93</sup>, namely the addition of (R)<sub>3</sub>SiH. (R = C<sub>6</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>O, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>) to hydridocarbonyltris (triphenylphosphine)-iridium(I) (97). The adducts formed show considerable stability. The similarity of i.r and nmr spectra of all the adducts leaves little doubt that they were isostructural. Thus, the symmetric and antisymmetric (Ir-H) stretching vibration was demonstrated by the appearance of strong and weak bands in the region of 2100 cm<sup>-1</sup>. The 16-line pattern observed at high field in the proton magnetic resonance spectrum has been explained on the basis of coupling between the metal hydride (in the cis-configuration) and the phosphorus nuclei.<sup>93</sup> The products formed have been discussed in terms of a two step mechanism. Predissociation of the five co-ordinate Ir(I) (97), to a square planar intermediate occurs, first, followed by approach of the silane along the axis perpendicular to the plane of the molecule, accompanied by simultaneous migration

of phosphine ligand in a direction away from the approaching silane, to give the cis isomer, Scheme (III-5). A serious objection to such a simple Scheme is that



Scheme (III-5): A two step reaction for the oxidative addition of Ir(I) to Ir(III).

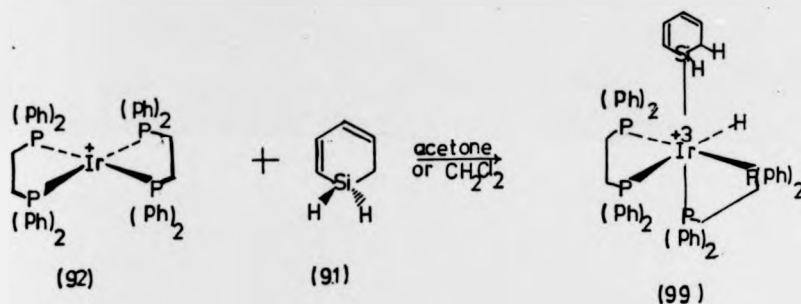
the results of the experiment, where triethoxysilane was added to the deuterido analogue of (97), indicated that either of the hydrogen ligands in the product may originate from the silicon hydride. However, a possible explanation for this contradiction, is an exchange between hydridodeuteridotriethoxysilylcarbonylbis-(triphenylphosphine)iridium(III), and excess silane<sup>93</sup>. A similar result has been observed by Chalk<sup>94</sup>.

The hydrosilylation of the bi(bis-1, 2-diphenylphosphinoethane) iridium(I) cation (92) by different alkylsilanes has been examined kinetically<sup>95</sup>. From the calculated heat of reaction and entropy of activation, the author was led to conclude that the tendency of silicon hydrides to yield oxidative products increases with increasing electronegative substitution on the silicon, as observed earlier<sup>92, 93</sup>; again hydrosilylation is stereospecifically (cis).

The fact that (92) can form stable dihydride adducts<sup>91</sup>, combined with the fact that Ir(I) can undergo hydrosilylation<sup>92, 93, 94</sup> with different alkylsilanes bearing in mind that the rate of addition of the addend is increased by increasing the electronegativity of substituent, encouraged us to think about the possibility of a reaction between (91) and Ir(I) complexes.

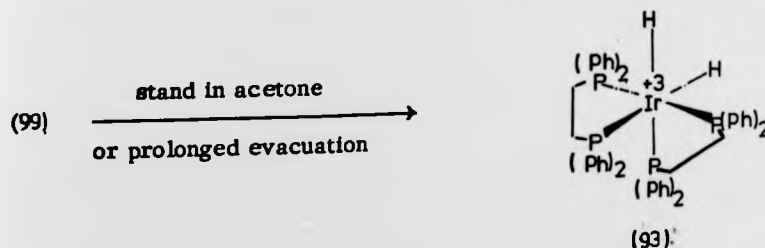
An instantaneous reaction has been observed between (91) as hydrosilylating reagent and (92) by decolourisation of (92) in acetone solution on mixing equimolar quantities of the reactants. (To avoid any trouble which might result from the high nucleophilicity of chloride ion, we exchanged  $\text{Cl}^-$  for  $\text{PF}_6^-$  in the initial adduct (which

additionally gives a product more soluble in acetone). In a typical run, equimolar quantities of (91) and (92) were mixed together in a Schlenk tube under nitrogen, when instantaneous decolourisation was observed in a few seconds. The nmr spectra of the resulting solution has been recorded immediately (Fig. (III-2)) at room temperature. The olefinic resonances are at  $3.8\tau$  (2H) and  $5\tau$  (2H), and those due to Si-H and  $\text{CH}_2$  are part obscured by  $\text{PCH}_2\text{CH}_2\text{P}$  in the  $7.3\tau$  region. Ir-H is broad [1 H trans P coupling,  $J_{\text{P-H}} = 110 \text{ Hz}$ <sup>96,97</sup> and three different cis couplings]. The i.r spectrum of the adduct (99) shows an intense band at  $2080 \text{ cm}^{-1}$  which can be assigned to Ir-H<sup>97</sup>, and comparing the earlier results of hydrosilylation of (92)<sup>95</sup> hence, we can write the following equation (Scheme (III-6)).

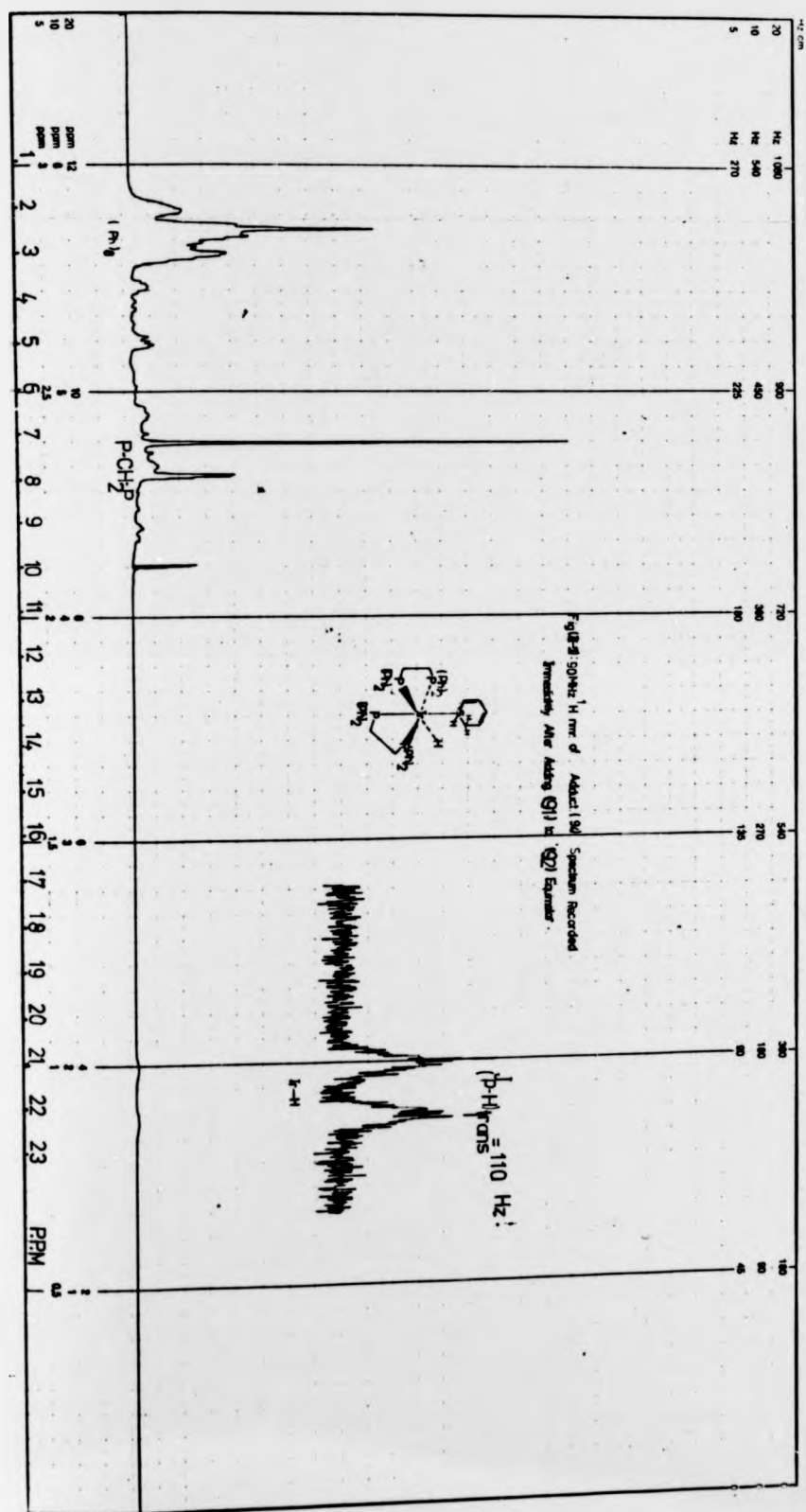


Scheme (III-6): Oxidation-addition of Ir(I) by (86).

The adduct formed (99), on standing in acetone for 12 hours, or prolonged evacuation was found to undergo the following rearrangement, (Scheme (III-7)).

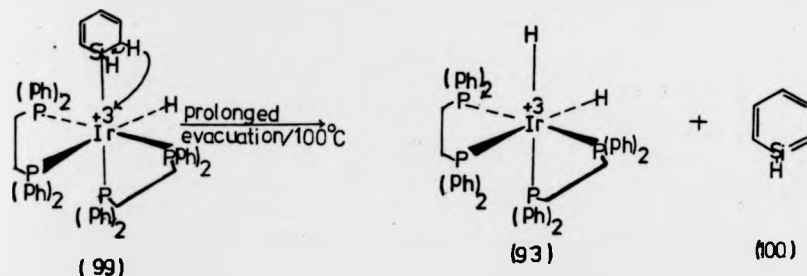


Scheme (III-7): Formation of Ir(III)dihydridodiphos from intermediate (99) by heating under vacuum.



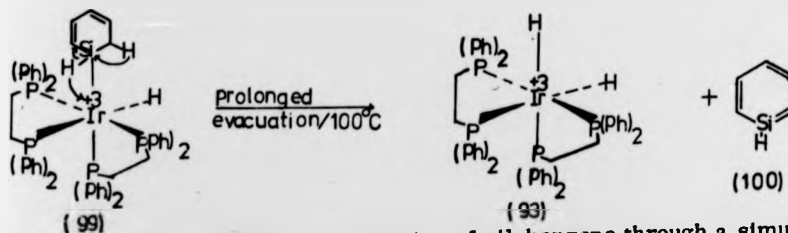
The resulting dihydridobi(bis-1, 2-diphenylphosphinoethane)-Iridium(III) (93) has been characterised by nmr and i.r. The fact there are two quartets demonstrates a strong trans-phosphine coupling ( $J_{H-P} = 110$  Hz) and three cis-phosphine couplings two of which are equivalent ( $J_{H-P} = 15$  Hz) and the third near-equivalent Fig. (III-3). The infra-red spectrum shows a closely spaced doublet at 2045 and 2065  $\text{cm}^{-1}$  due to symmetric and antisymmetric Ir-H stretching. An authentic sample of this cis-dihydride was prepared by passing hydrogen into a solution of (92).

According to Scheme (III-7), one can conclude that the silicon containing part of the molecule must be generated irreversibly, the fact the Ir(III)dihydrido complex (93) was obtained and since there is no other source for hydrogen abstraction, one can think about the possibility of  $\beta$ -elimination of hydrogen, Scheme (III-8), giving the dihydride (93), and silabenzene (100), the latter being rapidly consumed under the conditions of reaction.

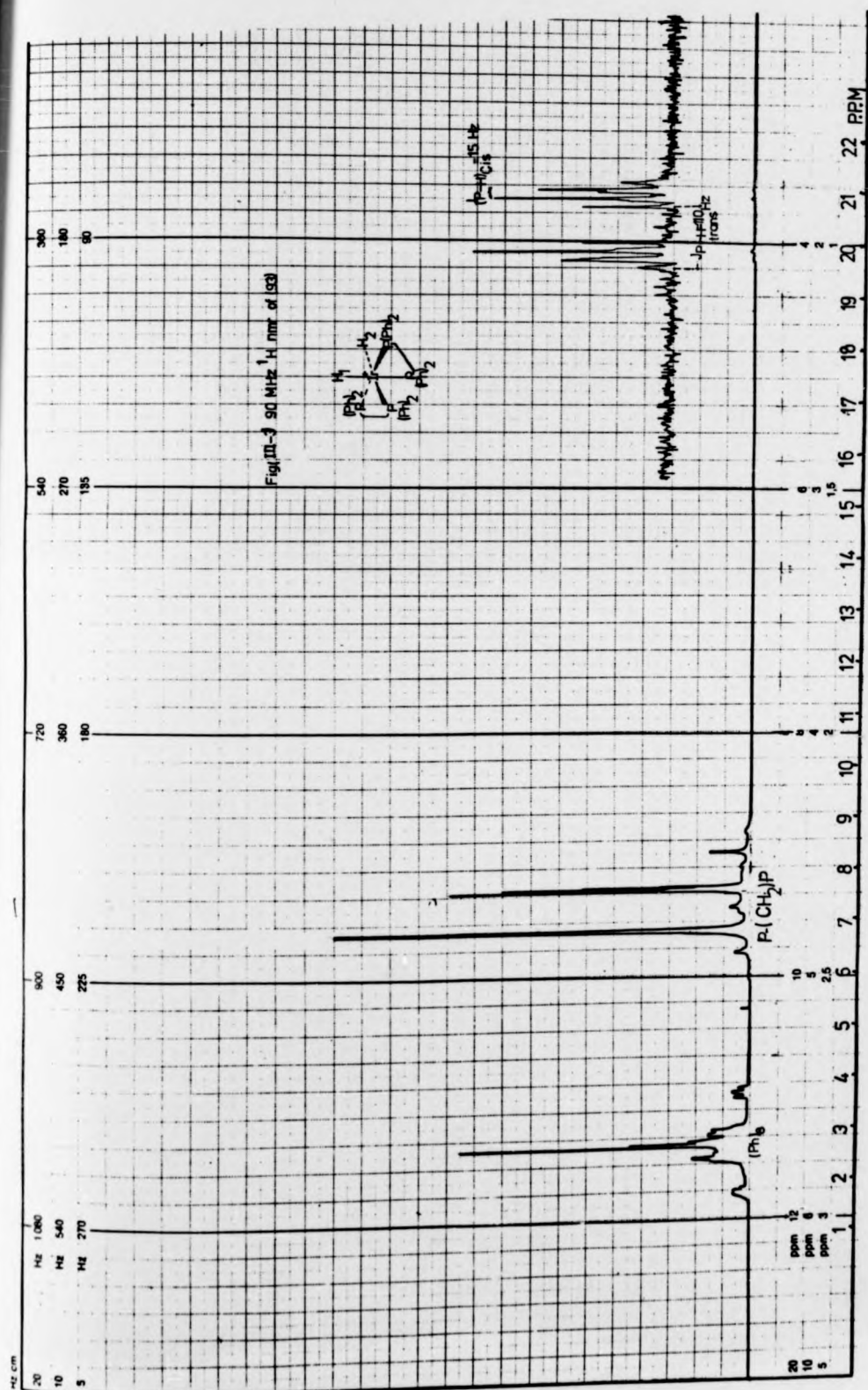


Scheme (III-8): Generation of silabenzene by  $\beta$ -elimination of hydrogen next to silicon.

The second possible mechanism to explain the formation of the dihydride (93) is a direct transfer of the hydrogen bonded to silicon to the iridium, followed by a new Si-H bond formation through 1, 2-hydride transfer from the  $\text{CH}_2$  next to silicon, Scheme (III-9).

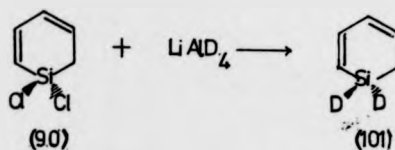


Scheme (III-9): Generation of silabenzene through a simultaneous Si-H bond breaking and formation.

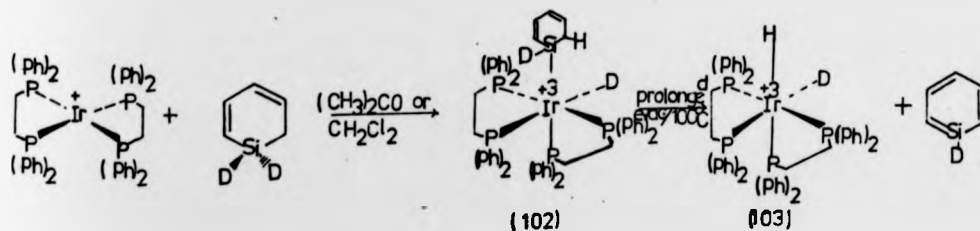




To our knowledge there is no reported work on a similar system, and the only way to discriminate between these two possible path-ways (Scheme (III-8) and (III-9)) is to investigate the reaction between 1, 1-dideutero-1-sila-2, 4-cyclohexadiene (101) and (92). (101) has been prepared by the reduction of (90) using  $\text{LiAlD}_4$ , (see experimental section).

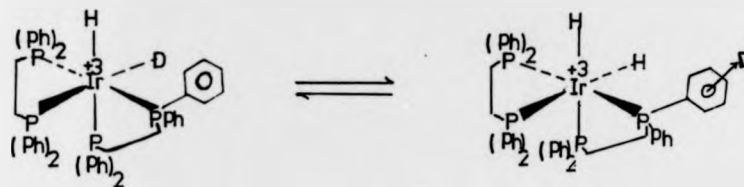


The reaction of (101) with (92) has been used to discriminate between the mechanisms of Scheme (III-8) and (III-9). Equimolar quantities of (101) and (92) were mixed together in dichloromethane solution in a small Schlenk tube. Solvent was removed under vacuum and the product was recrystallised from acetone. On heating under vacuum, (see experimental details), the i.r spectra of the white solid residue showed a fairly broad band (centered at  $2065 \text{ cm}^{-1}$ ) with a new band at  $1560 \text{ cm}^{-1}$ . Furthermore the region characteristic of the diphos which shows a sharp line at  $730, 655 \text{ cm}^{-1}$ , was completely replaced by a new broad band centered at  $690 \text{ cm}^{-1}$ . In addition the spectra shows a very clear double quartet centered at  $\tau 23.57$  showing the similarity between  $^1\text{H}$  nmr of (93) and the adduct formed on adding (101) to (92), Scheme (III-10) is a possible reaction path way, proceeding through the adduct (102)



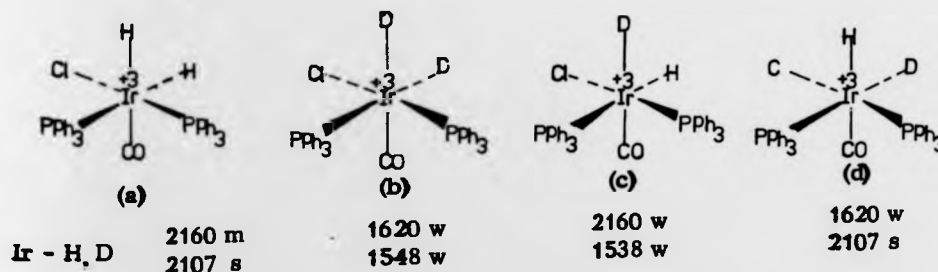
Scheme (III-10): A possible mechanism for the hydrosilylation of  $\text{Ir(I)}$  bis diphos.

Since the adduct formed after heating in vacuo at 100°C (103) shows spectral similarity with (93) for the Ir-H bond, one can explain this on the basis of H/D exchange between Ir-D and the aromatic ring of the  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  eg. Scheme (III-11), this may not be 100% exchange since there is a new band at  $1560\text{ cm}^{-1}$  which can be assigned for Ir-D bond<sup>98</sup>.



Scheme (III-11): A H/D exchange between Ir-D and  $\text{H-C}_6\text{H}_5$ .

Vaska<sup>98</sup> was able to isolate an Ir(I) complex containing  $\text{Ir}^{\text{D}}\text{-H}$  bond in the reaction involving the addition of HD to (95), four different isomers a, b, c and d were isolated and identified by comparing the i.r. spectra of an authentic sample.



The results obtained have been interpreted on terms of exchange  $\text{H}_2 \rightleftharpoons \text{HD} \rightleftharpoons \text{D}_2$  which is catalysed by the Ir(I) complex. Comparing i.r. spectra of (103) which shows Ir-D bond  $1560\text{ cm}^{-1}$  and  $2065\text{ cm}^{-1}$  assigned for Ir-H and the isolated compound (c) or (d), one can observe a spectral similarity which may confirm the structure of compound (103).

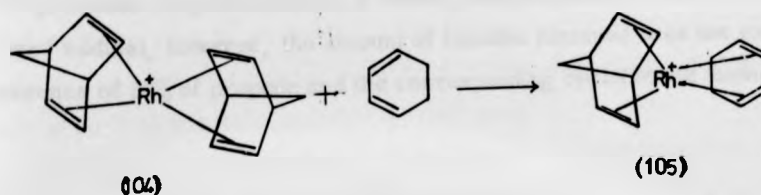


A serious objection to Scheme (III-8) is that (99) can possibly be hydrolysed by traces of water present giving the Ir(I) dihydrido (93) or alternatively Ir-D can be exchanged with the  $H_2O$  giving Ir-H, however, although we were using dry solvents and made all precautions to avoid any moisture which can give doubtful results (dry purified  $N_2$  has been employed as an inert atmosphere throughout the work), this possibility cannot be entirely eliminated.

According to Scheme (III-9), silabenzene must be generated by heating under vacuum, since one of the reactants involved in this Scheme has a relatively high molecular weight ( $M Ir(p-p)_2 pF_6 = 1133.2$ ) and the second reactant has a relatively small molecular weight ( $M(91) = 96$ ) we found that conventional glassware for organometallic preparation is useless to obtain silabenzene on a very small scale. Therefore, special apparatus has been designed in such a way that solvent and product resulting from heating under vacuum can be distilled directly into an nmr tube (the description of the apparatus will be described in the experimental part). An equimolar quantity of (92) and (91) was mixed together in a small two necked flask connected directly to an nmr tube through a greaseless tap, using dry  $CD_2Cl_2$  as a solvent. The solution was stirred for 60 minutes at  $40^\circ C$  and solvent was removed by distillation directly into the nmr tube, then the residue was heated up at  $100^\circ C$  with continuous pumping. The product separated on pumping was collected into the nmr tube and the nmr spectrum recorded at 90 MHz at room temperature. A complex pattern was observed but apart from about 5% of starting material no bands which could credibly be assigned to silabenzene or decomposition and polymerisation products were observed.

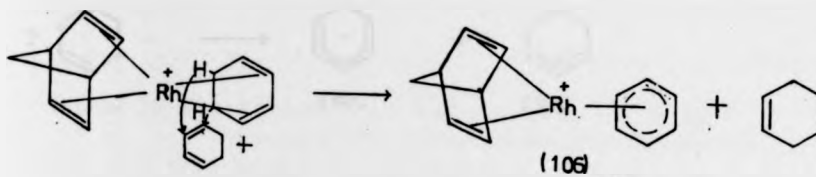
(II) Reaction of bis bicyclo[2.2.1]heptadiene rhodium(I)tetrafluoroborate with (91).

Green<sup>99</sup> succeeded in reacting 1,3-cyclohexadiene with (104) in  $CH_2Cl_2$  at room temperature, giving Rh(I)(norbornadienecyclohexadiene)tetrafluoroborate (105).



Scheme (III-12): Formation of (105).

(105) was found to catalyse, the disproportionation of 1,3-cyclohexadiene giving norbornadiene benzene Rh(I) <sup>cation</sup> (106) and cyclohexene, Scheme (III-13).



Scheme (III-13): Disproportionation of cyclohexene and (106).

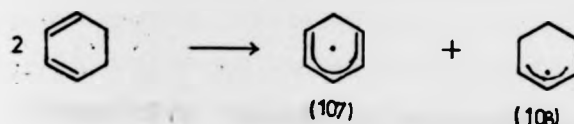
This reported mechanism in Scheme (III-13) may explain the inability of 1,4-cyclohexadiene to undergo ready disproportionation.<sup>99</sup>

Since (91) potentially contains the two double bonds required for co-ordination to Rh(I) complex, this encouraged us to try the reaction between (91) and (104) under similar conditions. An excess of (91) was added to a solution of (104) in  $\text{CH}_2\text{Cl}_2$  with continuous stirring at room temperature. A gradual change in colour to yellow-orange was obtained, adding cold dry ether at  $-80^\circ\text{C}$  precipitated yellow crystalline material. Removal of the solvent under vacuum by distillation gave an oil with the odour of norbornadiene. There is no reported  $^1\text{H}$  nmr spectral for the yellow crystals obtained because of its very low solubility in all solvents available. The i.r spectrum shows a broad band centred at  $1080\text{ cm}^{-1}$  due to  $\text{BF}_4^-$  in (104), and another broad band at about  $1650\text{ cm}^{-1}$  carbon hydrogen analysis shows consistency with the formula  $\text{C}_{12}\text{H}_{14}\text{BF}_4\text{RhSi}$ ; although the physical properties of the product do not encourage its formulation as a monomeric silabenzene complex.

### C) Catalytic dehydrogenation of 1-sila-2,4-cyclohexadiene.

It has been reported<sup>100</sup> that 1,3-cyclohexadiene can isomerise at  $440.2^\circ\text{C}$  into cyclohexene and benzene, the amount of benzene produced can increase by adding propene<sup>100</sup> which suggests that the reaction occurs by a radical-chain mechanism. The presence of cyclohexene as a product suggests that intermediacy of cyclohexenyl radical, however, the amount of benzene obtained does not exceed 34.9% in presence of 50% of propene and the corresponding cyclohexene formed is 4.2%.

Benson and Shaw<sup>101</sup> on their investigation on the kinetics and mechanism of the pyrolysis of 1,4-cyclohexadiene and related compounds including 1,3-cyclohexadiene show that the initiation step is going through an intermediate (107), Scheme (III-14).



Scheme (III-14): The initiation step in the pyrolysis of 1,3-cyclohexadiene and (108) intermediate.

This step (Scheme (III-14)) was suggested to be the initiation step in the chain decomposition of 1,3-cyclohexadiene, which leads to benzene and cyclohexene<sup>101</sup>.

Recently chloroanil has been used for catalytic dehydrogenation of 1,3-cyclohexadiene at 150°C giving benzene (35%)<sup>102</sup>, after 60 minutes the yield dropped to 12%, but rose again by oxidising the catalyst with air. A fused salt of Ag-KCl was used as an active catalyst for dehydrogenation of iso-Pr OH but was less active for 1,3-cyclohexadiene<sup>103</sup>.

The fact that 1,3-cyclohexadiene can be disproportionated into benzene and cyclohexene<sup>100-103</sup>, was potentially attractive as a new synthetic route for silabenzene from catalytic dehydrogenation of (91), since benzene itself has been obtained in a moderately low yield ~35% from pyrolysis of 1,3-cyclohexadiene. We felt that improvement of the yield was important and at the same time we could be guided by the results obtained for generation of benzene from 1,3-cyclohexadiene. For this purpose small scale pyrolysis has been employed (30  $\mu$ l for each run was used), and new apparatus has been developed (see experimental details), in such a way that the pyrolysate can be condensed into an nmr tube. Handling of the material at all times is carried out under a dry nitrogen atmosphere. It has been known<sup>104</sup> that six-membered alicyclic rings may be aromatized in a number of ways, but that aromatization is accomplished most easily if there are already one or two double bonds in the ring. A catalyst is normally used which may be Pd, Pt or Ni. S and Se also can be used and give rise to H<sub>2</sub>S or H<sub>2</sub>Se<sup>104</sup>. Since the pyrolysis is carried out at high temperature under dynamic vacuum, a catalyst such as Pd/C is therefore suitable for this work<sup>105</sup>.

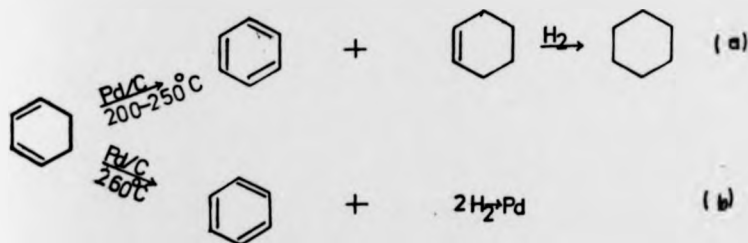
In a series of experiments, 1,3-cyclohexadiene was pyrolysed at varying temperatures, Table (III-1) summarises the results obtained. The product isolated was

characterised by its nmr spectrum (benzene appeared at 2.7 $\tau$ ). The integrated area was used as a quantitative tool to determine the quantity of each component produced in the reaction.

Table (III-1): Pyrolysis of 1,3-cyclohexadiene at variable temperature. Volume of starting materials is 50  $\mu$ l.

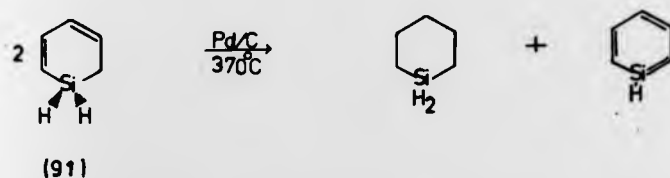
Temperature in $^{\circ}$ C	% of cyclohexane	% of Benzene
200	46%	54%
230	38%	62%
250	13%	87%
255	5%	95%
260	0.5%	99.5%

It is clear from Table (III-1) that (1) at relatively low temperature (200 $^{\circ}$ C - 250 $^{\circ}$ C) there are two competitive pathways: (1) disproportionation leading to cyclohexane and benzene Scheme (III-15a); (2) catalytic or stoichiometric dehydrogenation. The latter is the predominant pathway at high temperatures, Scheme (III-15b).



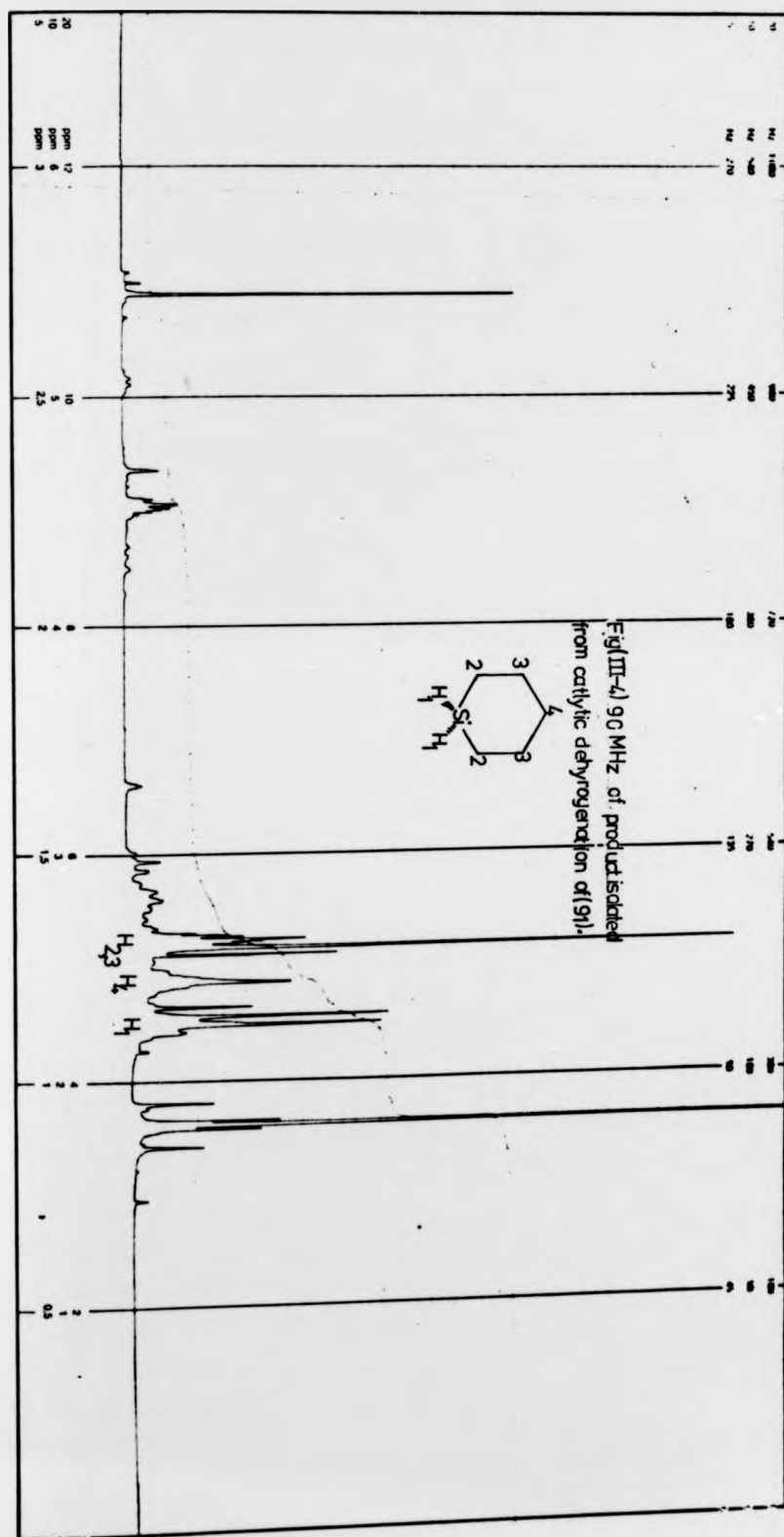
Scheme (III-15): Vapour phase pyrolysis of 1,3-cyclohexadiene.

In the attempts at dehydrogenating silacyclohexadiene, 30-40  $\mu$ l was used for each run, pyrolysis was started at 180°C and was increased by 10°C for each run, up to 260°C. A considerable recovery of the starting material was observed, as shown from the nmr spectrum of the isolated compound which shows similarity with the nmr spectrum of the starting material in the range between 260°C-380°C. Products isolated had a different nmr spectrum to the starting material. The spectrum shape does not change on changing the temperature within the range -40°C - room temperature, indicating the existence of thermally stable species. Most of the signal patterns appeared at high field within the region 8.45 $\tau$  - 9.12 $\tau$  a low intense signal appeared at 4.59 $\tau$  as a quartet which is the normal position for an olefinic double bond.<sup>106</sup> The ratio between the high field signal and low field signal was 14:1 in addition there was a considerable intense signal at 2.75 which is the normal position for benzene<sup>106</sup>, (Fig. (III-4)) shows the nmr spectrum of the isolated product at 90 MHz; furthermore the i.r spectrum of the isolated product in a chloroform solution shows an intense peak at 2250  $\text{cm}^{-1}$  which is the same position as Si H<sub>2</sub> in silacyclohexane i.r. spectrum<sup>107</sup>. In addition to this observation, a white polymer was observed as a condensate on the area between the heating column and the receiver, indicating the formation of a thermally unstable species. This could be an intermediate containing C=Si bond which tends to polymerise as a result of strong  $\sigma$  bond formation<sup>3</sup> by considering these results and the disproportionation observed by 1,3-cyclohexadiene, Scheme (III-15), one can write the following Scheme (III-16).



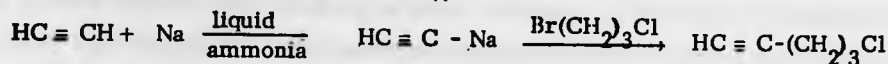
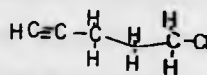
Scheme (III-16): Disproportionation of (91) to sila—cyclohexane and silabenzene.

Again the invoked mechanism Scheme (III-16) is not an absolute explanation for the results obtained.



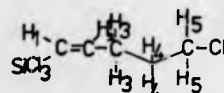
(D) EXPERIMENTAL

5-chloro-1-pentyne

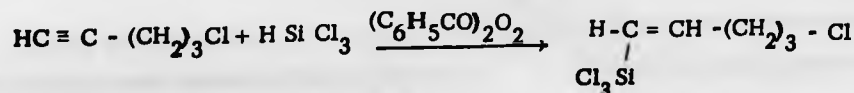


The method described in this work is a modification of reference (108). A 5 litre flange flask was fitted with mechanical stirrer mounted through Hershberg stirrer, dry ice acetone condenser and two long needles as gas inlets for both ammonia gas and acetylene. The flask was kept in dry ice acetone bath at  $-80^\circ\text{C}$ , and charged with about two litres of liquid ammonia, by condensing ammonia gas (obtained from an ammonia cylinder and purified by passing over potassium hydroxide pellets). A rapid stream of acetylene gas was passed into the ammonia and after a few minutes, 69 gms (3 moles) of sodium metal cut into small pieces, was added to the solution, with a continuation of acetylene passage at such a rate that the entire solution did not turn blue. If it did, the addition of sodium was stopped, and the solution stirred for a few minutes until the colour was discharged. 472 gms (3 moles) of 1-bromo-3-chloropropane diluted with 300 ml of dry pentane was added very slowly from a dropping funnel. After complete addition, the solution was further stirred for another two hours. Distilled water was added very slowly from the dropping funnel, until the solution warmed up to room temperature. The contents were transferred to a separatory funnel and the aqueous layer removed. The organic layer was washed several times with a 10% solution of aqueous hydrochloric acid, until no detectable amount of ammonia remained. The produce was fractionated using Perkin-triangle distilling apparatus and the fraction collected at  $116^\circ\text{C} - 117^\circ\text{C}$  (760 mm Hg), giving 130 gms (45%) of 5-chloro-pent-1-yne, nmr:  $\tau 6.36(2\text{H}, \text{t}, \text{H}_2\text{C Cl}, J_{1,2}=7.5 \text{ Hz})$ ,  $7.6 - 8.2 (5\text{H}, \text{m}, \text{HC}=\text{C}-(\text{CH}_2)_2-)$ ,  $\nu_{\text{max}}(\text{liquid film})$ , ( $\nu$  3580), ( $\nu$  3300), ( $\nu$  2900-3000), ( $\nu$  2120), ( $\nu$  1600), ( $\nu$  1480), ( $\nu$  1300).

5-chloro-1-(trichlorosilyl)-1-pentene

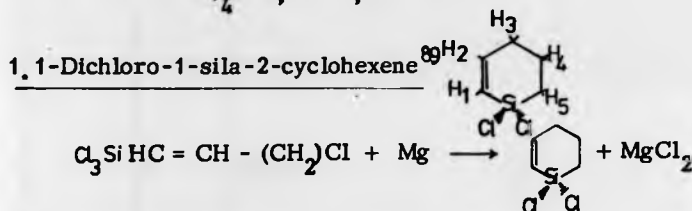


was prepared by addition of trichlorosilane to 5-chloro-1-pentyne, in the presence of benzoyl peroxide 89

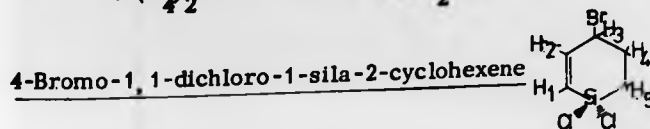




70 gms (0.68 moles) of 5-chloro-1-pentyne mixed with 600 ml cyclohexane was introduced into 1 litre flask fitted with a double surface water condenser and a mechanical stirrer mounted with Hersberg stirrer. 201 gms (1.48 moles) of trichlorosilane together with 14 gms of benzoyl peroxide was added to the mixture which was brought to reflux. Reaction progress was monitored by taking the nmr at intervals. After 85 hours, reflux was stopped and excess solvent was removed using a rotary evaporator. Paraffin oil was added to the residue to decompose any excess of benzoyl peroxide present and product was distilled under reduced pressure (1 mm Hg) and collected at 60°C - 64°C. Two isomers were obtained and no attempt was made to separate them. 73 gms (45%) nmr  $\tau$  ( $\text{CCl}_4$ ), the signals appeared at low field between 3-4.3 due to (cis) and (trans) olefinic protons which overlap<sup>89</sup>, 6.49 (2H, t,  $\text{CH}_2\text{Cl}$ ,  $J_{45} = 6\text{Hz}$ ), 8.00 (2H, q,  $-\text{C}-\text{H}_3$ ,  $J_{3,4} = J_{4,5} = 6.5\text{ Hz}$ ).

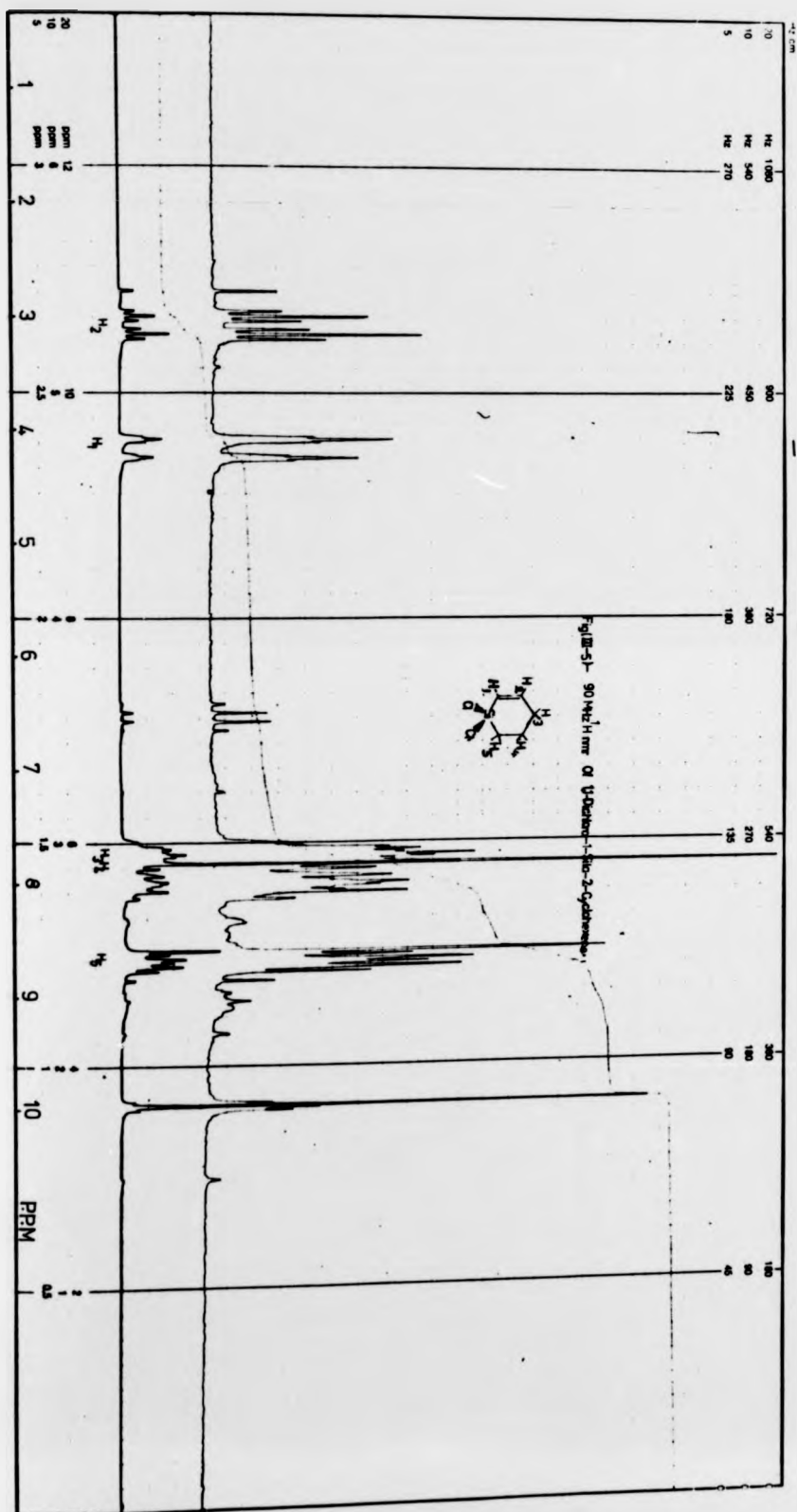


60 gms (2.47 moles) of powdered magnesium mixed with 1250 ml of dry ether, was introduced into a two litre flange flask fitted with double surface water condenser, pressure equalized dropping funnel, and a mechanical stirrer mounted with Hersberg stirrer. Methyl iodide (0.5 ml) was added to initiate the reaction and 61.55 gms (0.26 moles) 5-chloro-1-trichlorosilyl-1-pentene, diluted with 300 ml dry ether was added dropwise and mixture was brought into reflux. Reaction progress was monitored by taking nmr spectra every 2 hours. After 20 hours reaction was stopped, excess magnesium and magnesium chloride produced in the reaction was removed by filtration, ether was removed on a rotary evaporator. The solution was filtered again, and then fractionated under reduced pressure. 1,1-Dichloro-1-silacyclohex-2-ene was collected (25.9 gms, 61%) at 58-60°C 15mm. nmr  $\tau$   $\text{CCl}_4$ , 3.09 (1H, 2t,  $\text{H}^2\text{C} =$ ,  $J_{2,3} = 4\text{ Hz}$ ), 4.13 (1H, 2t,  $-\text{C}-\text{SiH}_2$ ,  $J_{1,2} = 2\text{Hz}$ ), 7.48 - 8.23 (4H, m,  $\text{C}(\text{H}_3)_2$ ), 8.69 (2H, m,  $\text{C}(\text{H}_3)_2$ ,  $\text{SiCl}_2$ ), Fig. (III-5).

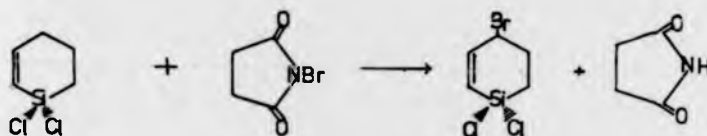


Allylic bromination of 1,1-dichloro-1-sila-2-cyclohexene with N-Bromosuccinimide was carried out to obtain the Bromo derivative. Excess silacyclohexene was used

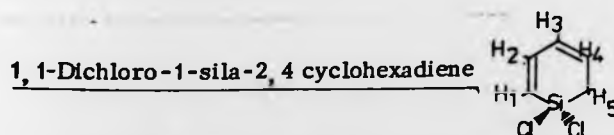




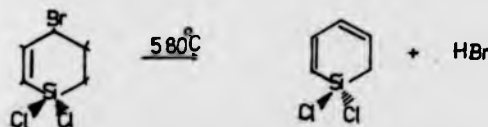
to avoid side reactions producing higher brominated species



51.8 gms (0.31 moles) of 1,1-dichloro-1-silacyclohexene dissolved in 600 ml of carbon tetrachloride together with 23.95 gms (0.134 moles) of N-bromosuccinimide was placed in a one litre one-necked flask, fitted with a water condenser. The mixture was brought to reflux, after 4 hours reaction was stopped. Succinimide was filtered washed 3 times with 30 ml of carbon tetrachloride and solvent was removed under aspirator vacuum. The unreacted material was recovered by distillation at  $20^{\circ}\text{C}$  (0.1 mm Hg), (20 gms). Product was collected at  $42^{\circ}\text{C}$  -  $50^{\circ}\text{C}$  (0.1 mm Hg), yield 20 gms of pure material (44%). Nmr  $\tau(\text{CCl}_4)$ , 3.05 (1H, 2d,  $\text{H}_2 = \text{Br}$ ,  $J_{2,3} = 5\text{Hz}$ ) 4.11 (1H, d,  $\text{H}_1 - \text{Si}$ ,  $J_{1,2} = 14\text{Hz}$ ), 5.22 (1H, q,  $\text{H}_3 - \text{Br}$ ,  $J_{3,4} = 5\text{Hz}$ ), 7.4 - 7.7 (2H, m,  $\text{H}_4 - \text{SiCl}_2$ ), 8.05 - 8.80 (2H, m,  $\text{H}_5 - \text{SiCl}_2$ ) Fig. (III-6). Recovered starting material was recycled under similar conditions.



Dehydrobromination of 4-Bromo-1,1-dichloro-1-sila-2-cyclohexene was carried out in the vapour phase at  $580^{\circ}\text{C}$  under high vacuum



A thermolysis apparatus was specially designed Fig. (III-8) to condense the product whilst allowing the hydrogen bromide produced to enter the vacuum line, and be condensed separately at  $-196^{\circ}$



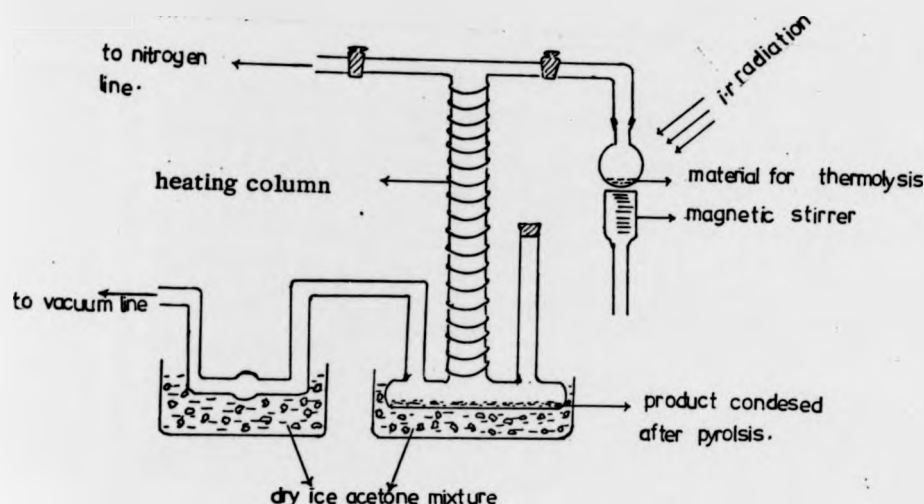
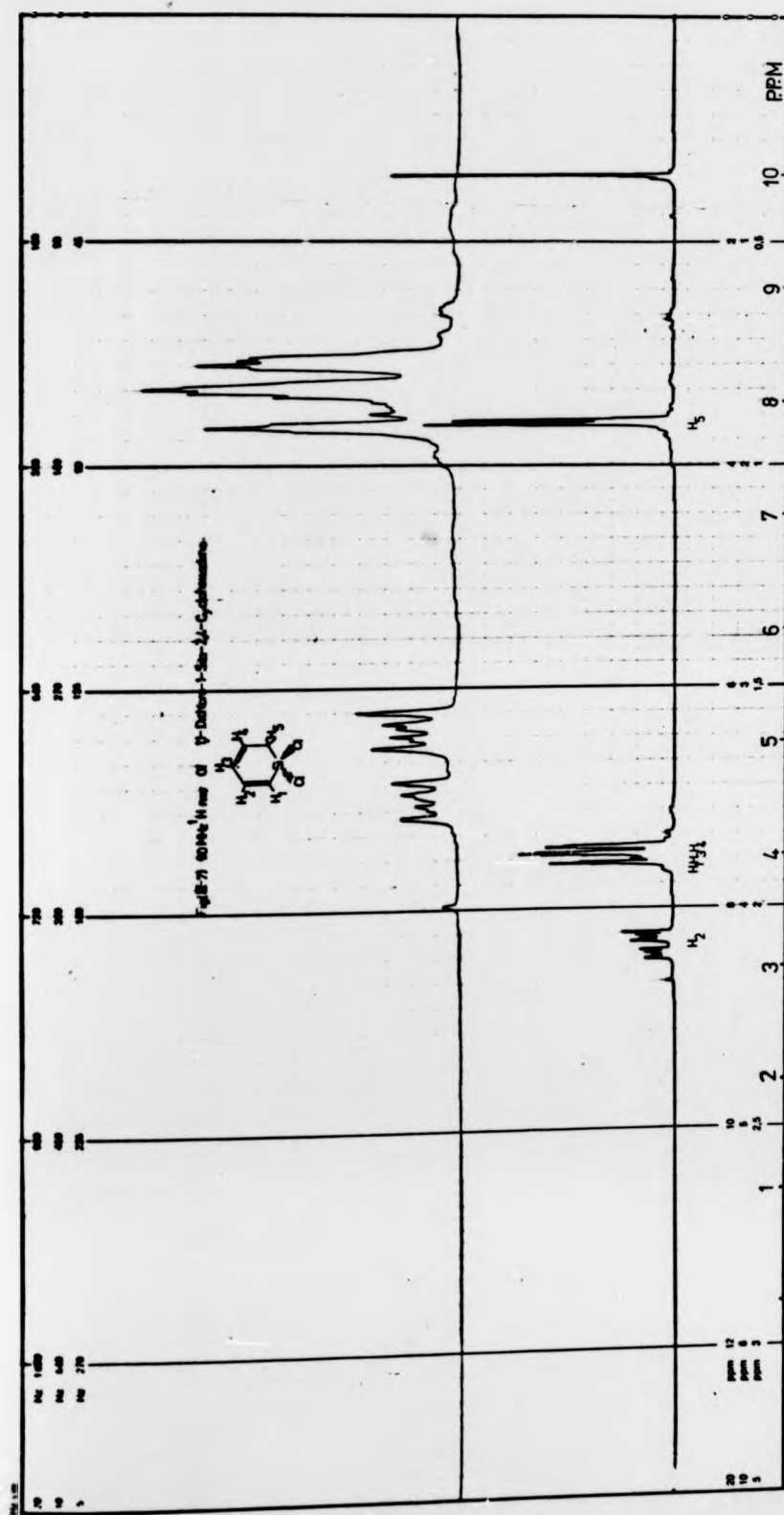
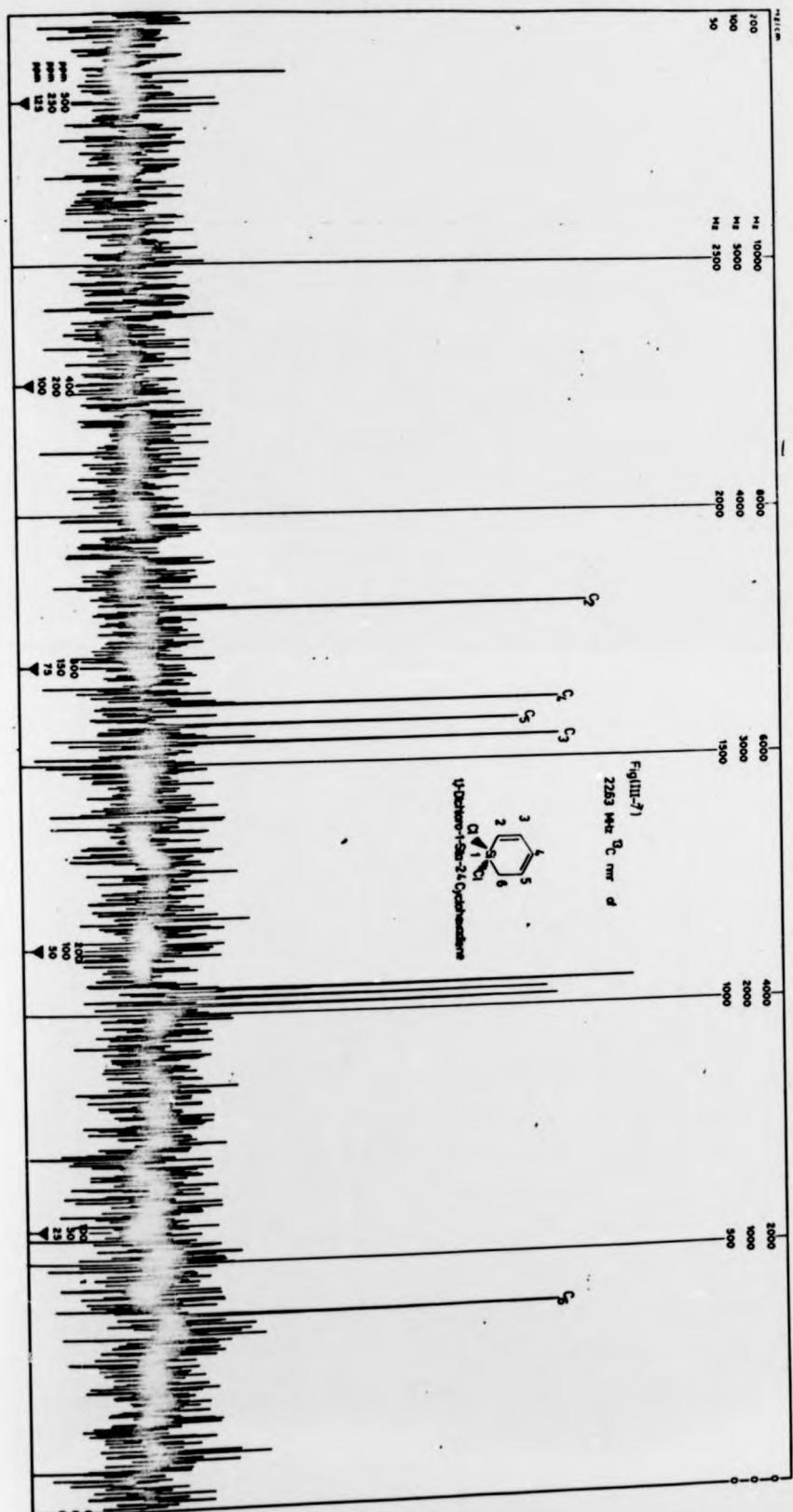


Figure (III-8): Thermolysis apparatus used under dynamic vacuum.

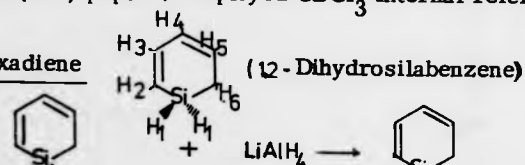
20.5 gms (0.083 moles) of the bromosilacyclohexene derivative was placed in 25 ml round bottom flask which was connected to the thermolysis apparatus. The temperature was adjusted at  $580^{\circ}\text{C}$ , and the trap was kept at  $-80^{\circ}\text{C}$  by using dry ice acetone mixture. The vacuum line was opened (0.001 mm Hg) and starting material vaporised by heating with an i.r. lamp (the slower the distillation the better the yield). At the end of the distillation the vacuum line was disconnected, nitrogen was admitted into the apparatus after cooling the heating column by switching off the applied voltage. Product was purified by trap to trap distillation, and final fractionation was achieved by spinning band distillation  $52^{\circ}\text{C}$ , (18 mm Hg). 6.5 gms pure compound was obtained (53.4% yield), nmr  $\tau$  3.06 (1H, 2q,  $\text{HC}=\text{C}^{\text{SiO}_2}$ ,  $J_{1,2} = 3$  Hz), 3.90 (3H, m,  $\text{H}_3$ ,  $\text{SiCH}_2$ ), 7.89 (2H, d,  $\text{H}_2\text{C}-\text{SiO}_2$ ,  $J_{1,2} = 3$  Hz) Fig. (III-7). The method of preparation described here is essentially the same as ref. 8, but the technique used was found to give a better yield, v<sub>max</sub> i.r (liquid film), (m 3035), (m 3005), (s 1620), (s 1540), (m 1380), (s 1360), (m 1260), (m 1150), (s 870), (s 790), (s 700), (s 640), (s 550). In this manner a total of 65gms of 1,1-dichlorosilacyclohexadiene was obtained by accumulating the product from several runs.  $^{13}\text{C}$  nmr, ( $\text{CDCl}_3$  22.63 MHz), 20.67 (C-6), 122.51 (C-3), 125.70 (C-5)





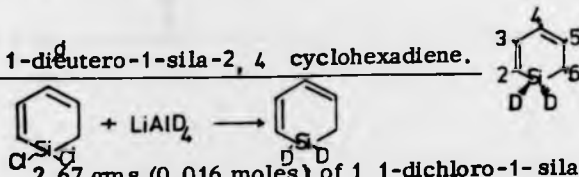
129.15(C-4), 146.37 (C-2) p.p.m. employed  $\text{CDCl}_3$  internal reference, Fig. (III-7).

1-sila-2, 4-cyclohexadiene



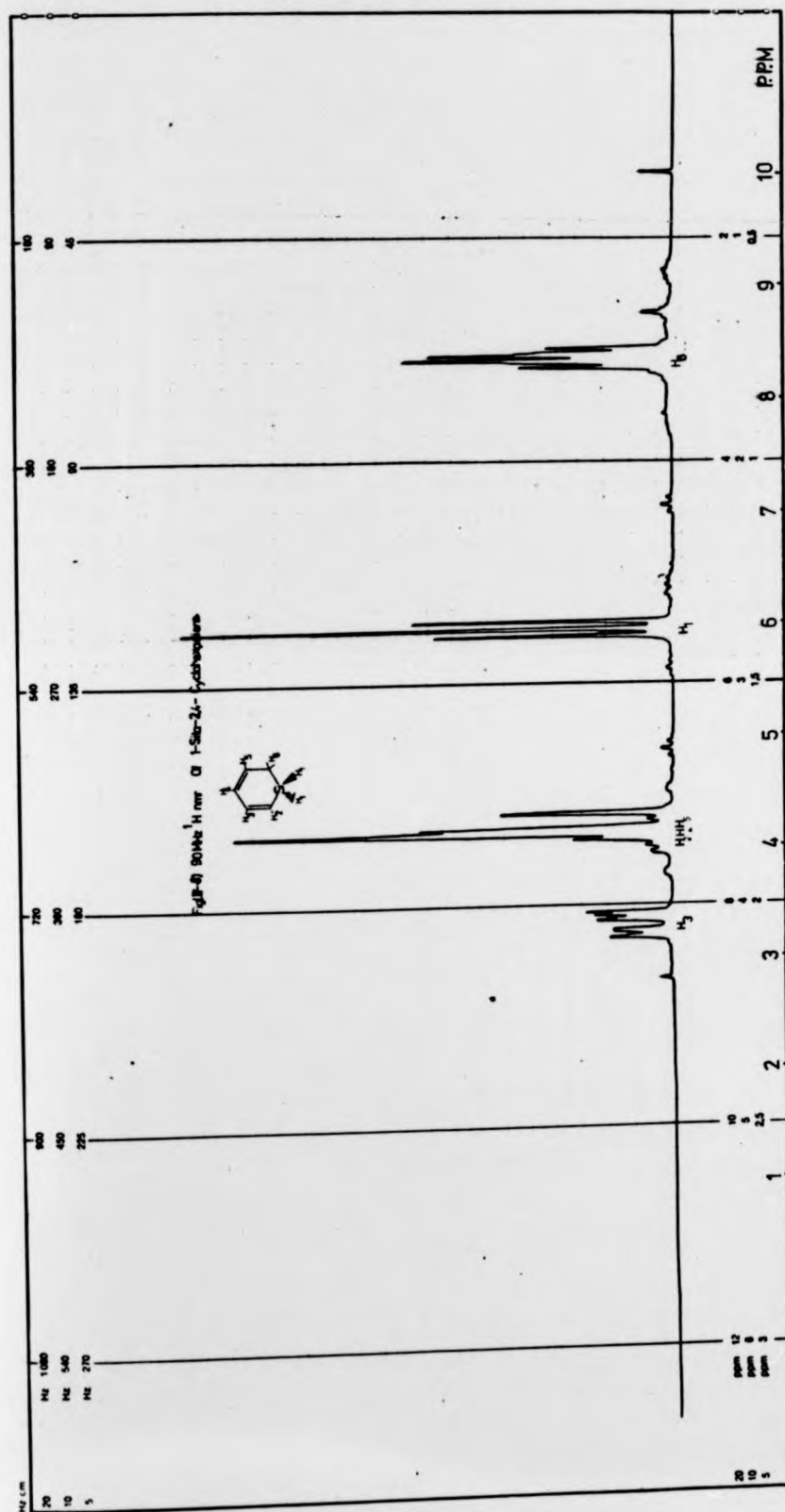
1.213 gms (0.032 moles) of lithium aluminium hydride suspended in 30 ml of triethyleneglycoldimethyl ether, was placed in a 100 ml 2 necked flask, fitted with a double surface water condenser and dropping funnel pressure equalized. 5.28 gms (0.032 moles) of 1,1-dichloro-1-sila-2,4-cyclohexadiene diluted with 10 ml of the same ether was added gradually from the dropping funnel to the stirred solution at  $0^\circ\text{C}$ . After complete addition, solution was stirred further for another  $\frac{1}{2}$  hour, product was distilled directly from the reaction mixture at  $0^\circ\text{C}$  and 0.1 mm Hg. Nmr spectra are consistent with the structure of the compound. Yield 2.4 gms (51%) of pure 1-sila-2,4-cyclohexadiene. Nmr  $\tau$  ( $\text{CCl}_4$ ), 3.19 (1H, q,  $J_{1,2} = 6\text{ Hz}$ ), 4.11 (3H, C,  $J_{1,2} = 6\text{ Hz}$ ), 5.90 (2H, t,  $J_{5,6} = 6\text{ Hz}$ ), 8.31 (2H, m,  $J_{1,2} = 6\text{ Hz}$ ) Fig. (III-8). i.r.  $\nu_{\text{max}}$  (liquid film) (m, 3060), (m 3010), (s 2150), (m 1650), (w 1600), (w 1390), (vw 1360), (w 1250), (w 1180), (w 1130), (s 960), (m 900), (m 875), (m 856), (b 710), (s 630), Fig. (III-8).  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ; 22.63 MHz), 5.59 (C-6), 117.51 (C-3), 126.35 (C-5), 127.58 (C-4), 143.90 (C-2) p.p.m. Fig. (III-8).  $\lambda_{\text{max}}$  (Cyclohexane) 270 nm ( $\epsilon$  5600).

1,1-dideutero-1-sila-2, 4 cyclohexadiene.

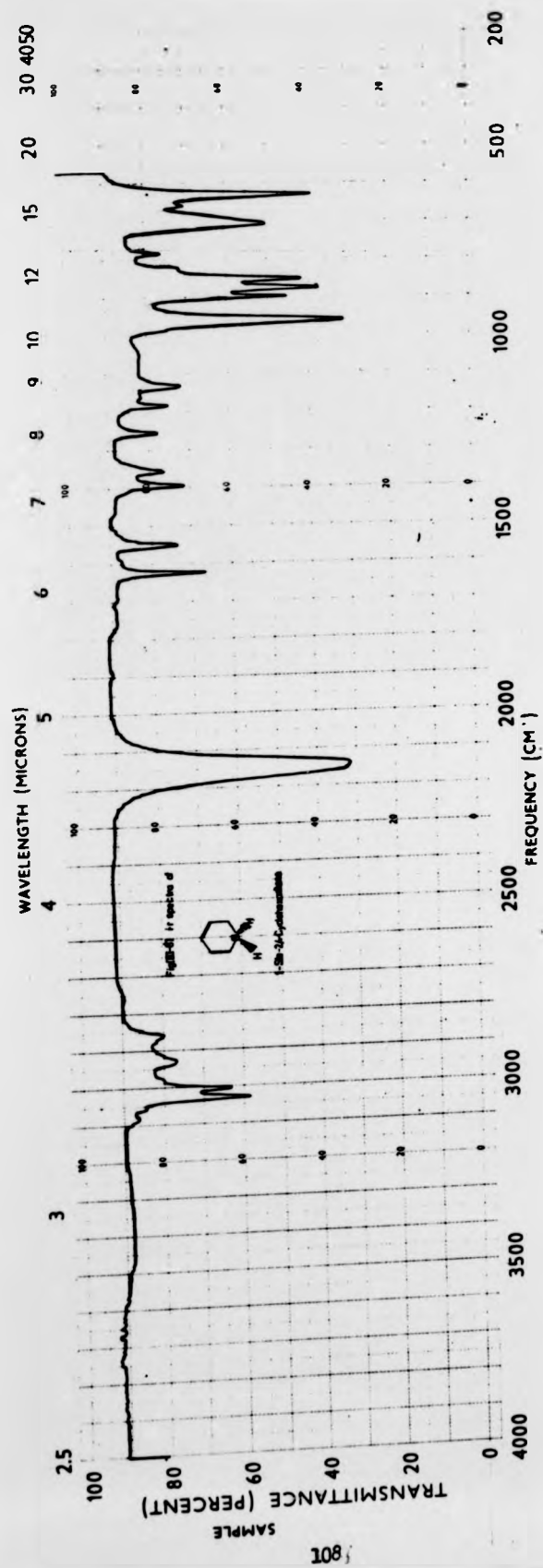


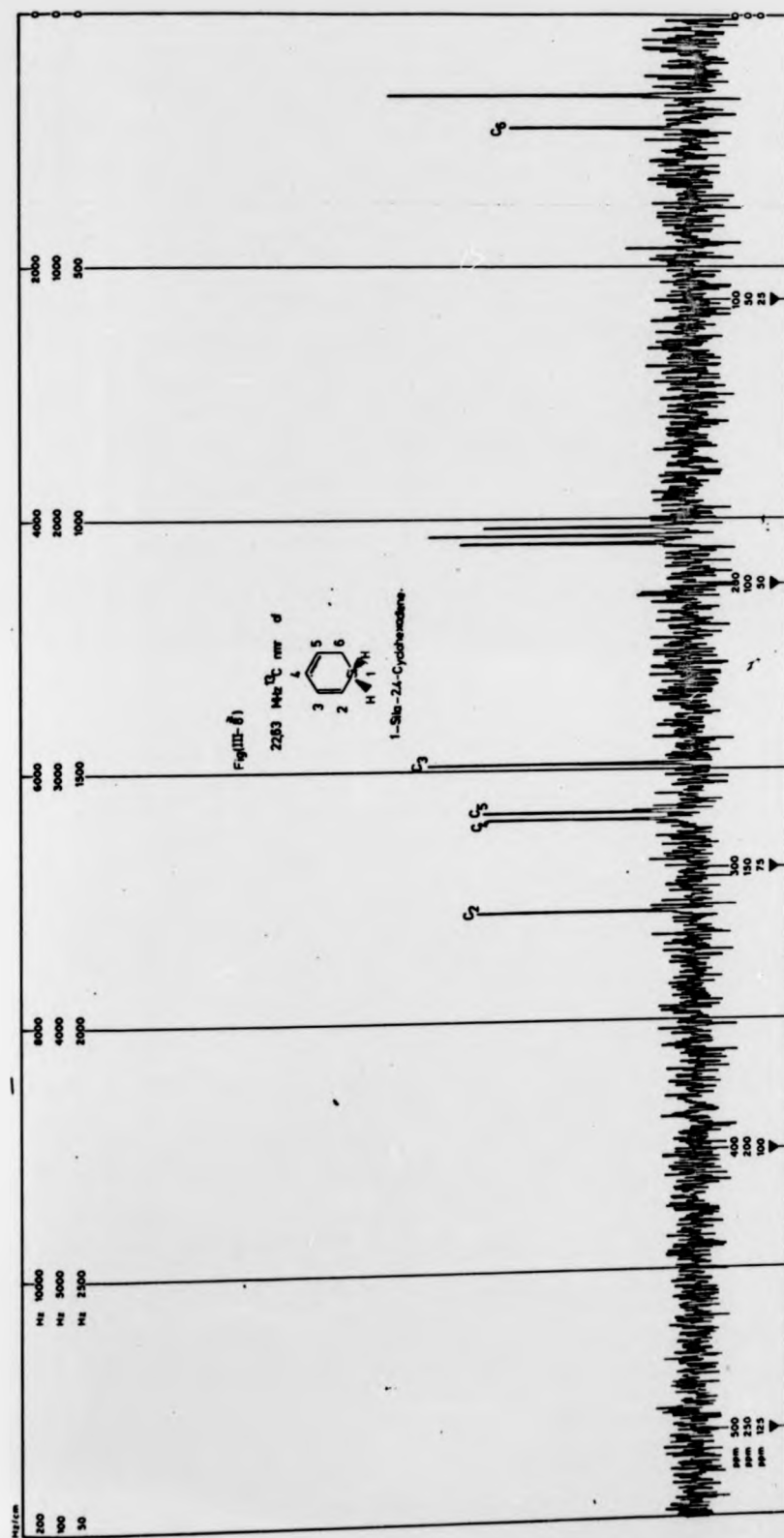
2.67 gms (0.016 moles) of 1,1-dichloro-1-sila-2,4-cyclohexadiene was reduced by 0.679 gms (0.016 moles) of lithium aluminium deuteride in the same fashion as is described for the reduction of 1,1-dichloro-1-sila-2,4 cyclohexadiene, and product was distilled at room temperature (0.005 mm Hg). 1.2 gms (76% yield) of pure compound was collected and product was characterised by nmr and i.r spectra. Nmr  $\tau$  3.14 (1H, t,  $J_{1,2} = 4\text{ Hz}$ ), 4.11 (3H, C,  $J_{1,2} = 4\text{ Hz}$ ), 8.36 (2H, s,  $J_{1,2} = 4\text{ Hz}$ ) Fig. (III-9). i.r.  $\nu_{\text{max}}$  (liquid film), (m 3020), (m 3000), (b 2920), (b 2825), (m 1640), (s 1550), (m 1380), (m 1345), (w 1245), (w 1170), (b 1120), (s 910), (s 715), (s 695), (s 635), Fig. (III-9).  $\lambda_{\text{max}}$  (cyclohexane) 265 nm ( $\epsilon$  5000).

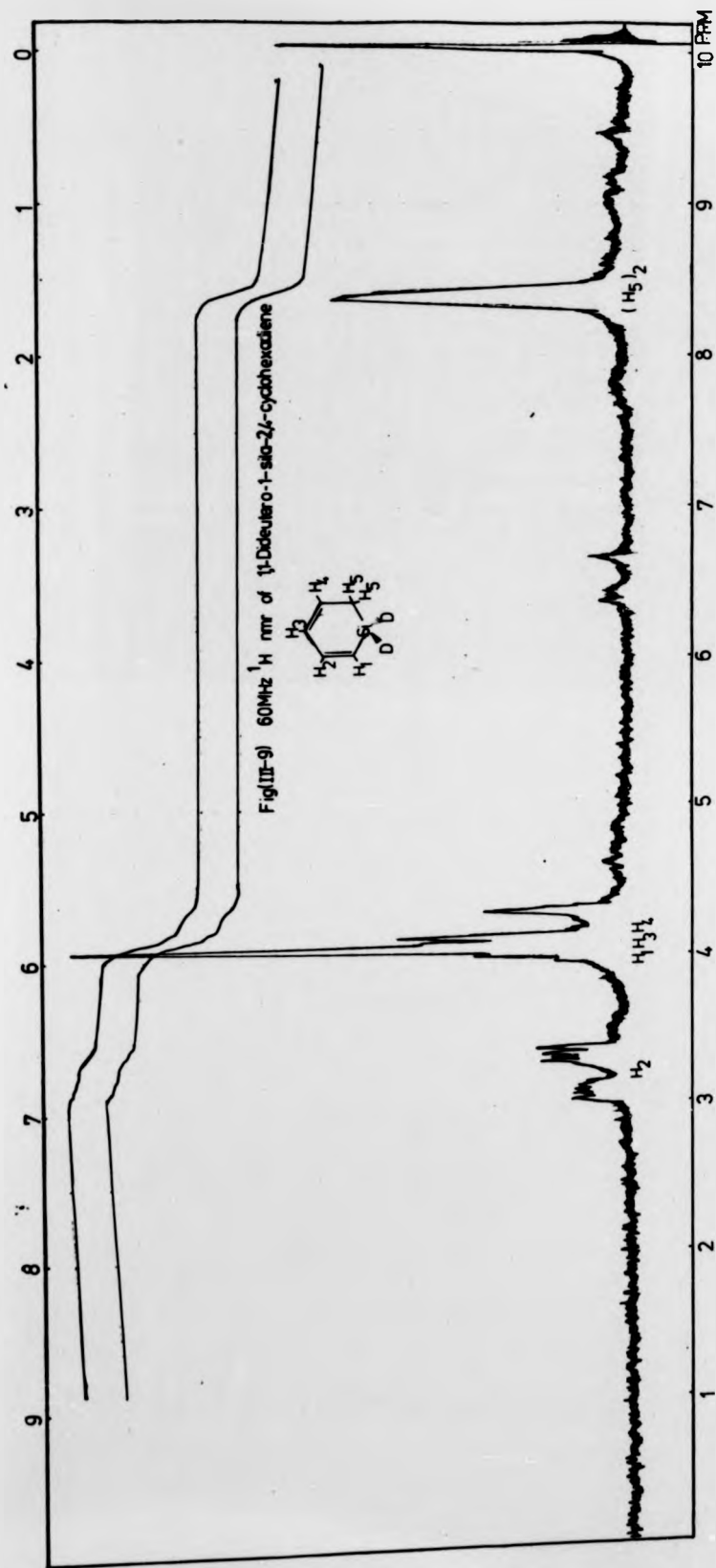


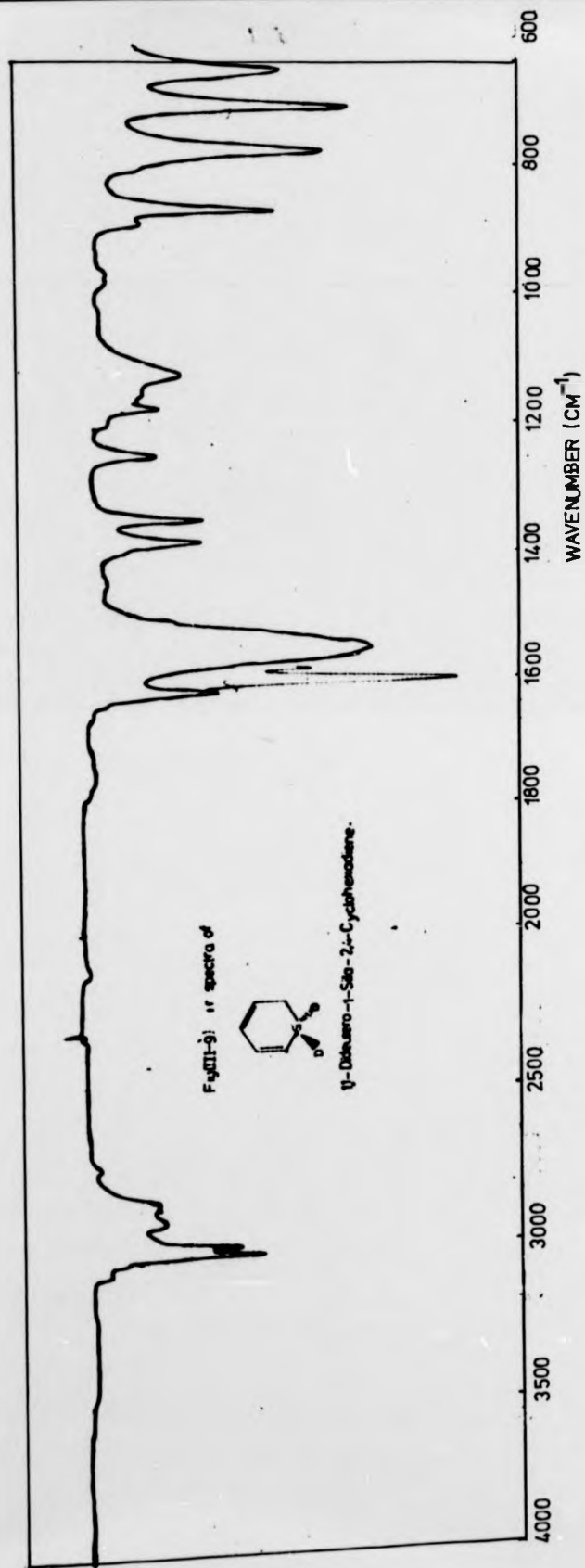












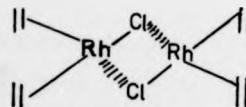
trans-chlorocarbonylbis(triphenylphosphine)Iridium(I) (Vaska's compound),  
was prepared according to ref .109

7.54 gms (0.025 moles) of Iridium(III) chloride 3-hydrate mixed with 26.20 gms (0.1 moles) of triphenylphosphine in 300 ml of dimethylformamide, was placed in 500 ml round-bottomed flask fitted with a water condenser. The mixture was brought to vigorous reflux and after 12 hours the solution was filtered while hot, and 600 ml of warm methanol was added to the filtrate. The solution kept cold when a yellow crystalline product was obtained. This was filtered and washed with 50 ml of cold methanol. Contamination by oxygen adduct was removed by heating under vacuum at 100°C for 12 hours. Thus 12 gms of pure compound (85% yield) was obtained. I.r  $\nu_{\max}$  (Nujol mull) (s 1961) (s 1445), (s 1385), (s 1100), (m 1030), (m 1000), (s 750), (s 710), (s 700).

bis[1, 2-diphenylphosphinoethane]iridium(I) hexafluorophosphate (92)  
was prepared by a similar method described in <sup>91</sup>. To a solution of bis-triphenylphosphine carbonylchloroiridium(I) (3.9 gms, 0.005 moles) in benzene (20 mls) under dry nitrogen, there was added bis 1, 1-diphenylphosphinoethane (4.2 gms 0.01 moles) in benzene (40 mls); a white crystalline precipitate was formed. Toluene (50 mls) was added and the suspension refluxed for 30 hours. The orange crystalline product was filtered under nitrogen and heated under vacuum at 100°C for 24 hours, to remove any possible contamination by O<sub>2</sub> adduct or CO adduct. I.r shows the absence of O<sub>2</sub> adduct stretching at (1810 cm<sup>-1</sup>) and CO stretching at (1930 cm<sup>-1</sup>). 4.4 gms (86% yield) of pure compound was obtained. I.r  $\nu_{\max}$  (nujol mull): (s 1435), (m 1310), (s 1100), (w 1070), (w 1020), (w 1000), (m 880), (w 850), (m 810), (s 746), (m 665), (s 650).

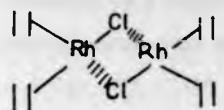
To the product (1.021 gms, 0.0013 moles) in dichloromethane (10 ml) there was added potassium hexafluorophosphate (0.4 gms excess) in distilled water, (10 ml). After shaking in separatory funnel, solvent was removed from the organic layer by vacuum distillation, and solid residue was recrystallised from acetone. 1 gm (88% yield) of pure compound, bis(1, 2-diphenylphosphinoethane)iridium(I) hexafluorophosphate was obtained. I.r.  $\nu_{\max}$  (nujol mill), (s 1430), (m 1380), (w 1310), (s 1100), (w 1030), (w 1000), (b 840), (s 745), (b 700), (m 670).

Tetraethylene chloro( $\psi$ -chloro)dirhodium

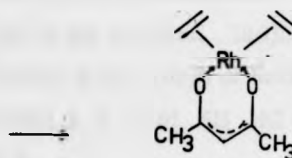


This was prepared according to <sup>110</sup> 5 gms (0.019 moles) of rhodium trichloride trihydrated were dissolved in a mixture of 12.5 ml methanol and 7.5 ml water. A slow stream of ethylene gas was bubbled through the stirred solution in a Schlenck tube at room temperature. After 7 hours passage of ethylene gas was stopped, and the orange-brown crystals collected by filtration. The solid was washed with dry ether, and dried by suction. Collected material 2.4 gms in 6 hours, of tetraethylene chloro( $\psi$ -chloro)dirhodium. Obtained yield (85%).

Rhodium(I) bisethylene acetylacetonate

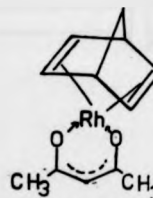
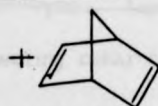
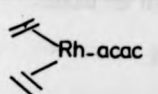


+ 2 Na acac



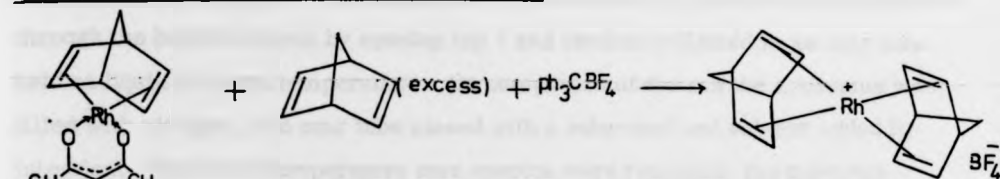
1.5 gms (0.012 moles) of sodium acetylacetonate was added to a mixture of 1.63 gms (0.004 moles) of Rh(I) bisethylene acac in 50 ml dry ether. The mixture was stirred and after 4 hours the solution was filtered, and solid residue recrystallised from dry ether. 2.1 gms (90%) of complex m.p 144° a yellow crystalline material was collected.

Rhodium(I) norbornadiene acetylacetonate:



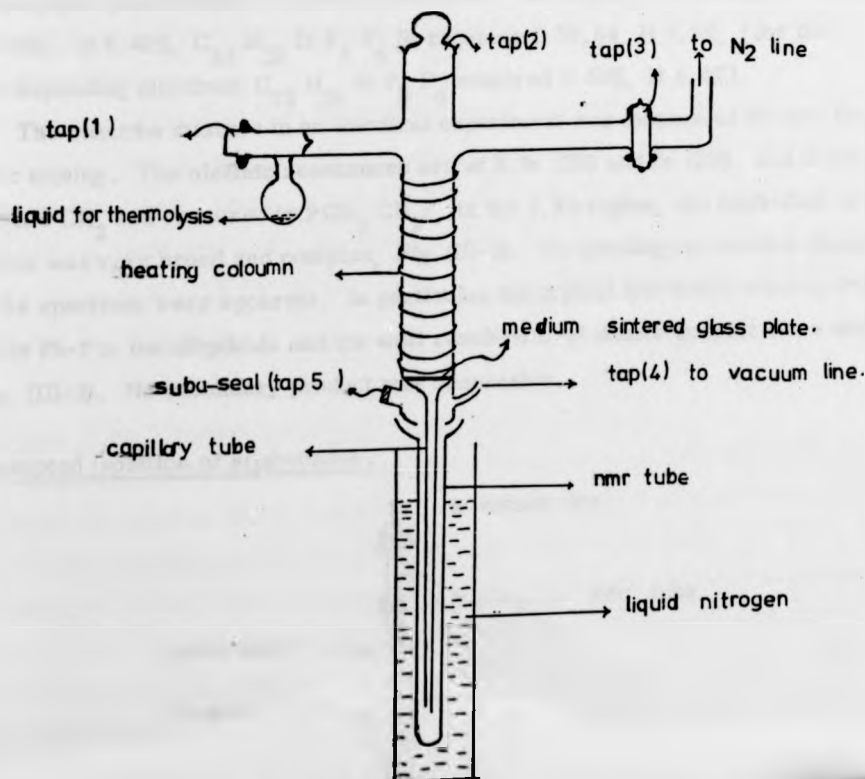
2.2 gms (0.0085 moles) of Rh(I)-bisethyleneacetylacetonate dissolved in 15 ml of dry dichloromethane was placed in a Schlenck tube provided with nitrogen gas inlet and magnetic stirrer. 0.867 (0.008 moles) norbornadiene was added to the stirred solution under nitrogen and an instantaneous evolution of ethylene gas was observed. After 20 hours reaction was stopped, solvent was removed under vacuum distillation when a pale -yellow crystalline solid was obtained. No further purification was attempted, 2.3 gms of Rh(I) norbornadieneacetylacetonate were obtained, m.p 122°C (yield 92%).

### Rhodium(I) bisnorbornadiene tetrafluoroborate



was prepared according to <sup>111</sup>. 2.3 gms of (6.9 m moles) triphenylmethyl-tetrafluoroborate dissolved in 15 ml of dry dichloromethane was added slowly to a mixture of Rh(I) norbornadiene acac (2.3gm, 6.9 mmoles) and 5 ml of norbornadiene(excess). An immediate formation of very deep intense red solution was observed. Cooling in dry ice, and addition of 50 ml of NBD was found necessary to bring the crystals out of the solution. Rh(I)bis (NBD)  $\text{BF}_4$  was obtained as a bright red crystalline material 2 gms (85%) of Rh(I) bisnorbornadiene tetrafluoroborate mp  $157^\circ\text{C}$ . Nmr  $\tau$  ( $\text{CDCl}_3$ ), 4.47 (d, 8H,  $\text{HC}=\text{CH}$ ,  $J=2\text{Hz}$ ), 5.81 (s, 4H, C-H) and 8.43 (s, 4H,  $\text{CH}_2$ ).

### Thermolysis of 1-sila-2,4-cyclohexadiene (91).





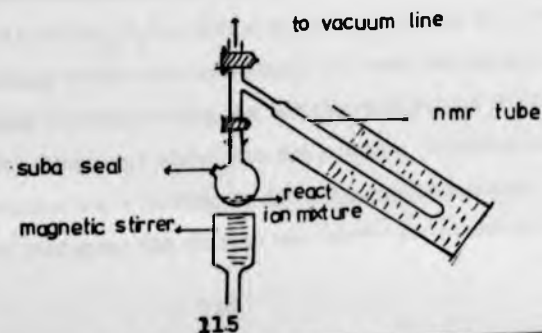
Palladium on charcoal (10% 3 gms) was heated in the thermolysis tube for 2 hours at  $250^{\circ}$  in vacuo. 1-Silacyclohexa-2,4-diene ( $30\ \mu\text{l}$ ) was slowly vapourised through the heated column by opening tap 1 and product collected in an nmr tube held at liquid nitrogen temperature. On completion of the run the apparatus was filled with nitrogen, the nmr tube closed with a suba-seal and solvent added by injection. When low-temperature nmr spectra were recorded, the tube was maintained at low temperature and rapidly transferred to a pre-cooled probe.

Reaction of bi(bis-1,2-diphenylphosphinoethane)iridium(I)hexafluorophosphate with (91).

To a solution of bi(bis-1,2-diphenylphosphinoethane)iridium(I) hexafluorophosphate (0.295 gms, 25 m-moles), in acetone -  $d_6$  ( $800\ \mu\text{l}$ ), there was added 0.0247 gms (25 m-moles) of silacyclohexadiene at room temperature, solvent was removed in vacuo and the residue held at  $35^{\circ}\text{C}$  and sampled until infra-red monitoring showed complete absence of acetone at  $1710\ \text{cm}^{-1}$ . (30 hours pumping under vacuo is the time required to remove all acetone). There was thus obtained 1-silacyclohexadienyl (bis-1,2-diphenylphosphinoethane)-iridium(III) hydride. (0.25 gms, 86% yield). Found C, 56.00%, H 4.40%,  $\text{C}_{52}\text{H}_{50}\text{IrP}_5\text{F}_6$  Si requires C 55.64, H 4.8%, [for the corresponding dihydride  $\text{C}_{75}\text{H}_{59}\text{IrP}_5\text{F}_6$  required C 55%, H 4.4%].

The reaction mixture in an identical experiment was monitored by nmr immediately after mixing. The olefinic resonances are at  $3.8\tau$  (2H) and  $5\tau$  (2H), and these due to SiH and  $\text{CH}_2$  are obscured by  $\text{PCH}_2\text{-CH}_2\text{P}$ , in the  $7.3\tau$  region; the high-field Ir-H region was very broad and complex, Fig. (III-2). On standing in solution changes in the spectrum were apparent. In particular the typical low-field ortho-hydrogen of the Ph-P in the dihydride and the well resolved Ir-H double quartet were observed, Fig. (III-3). No secondary product was observable.

Attempted isolation of silabenzene.





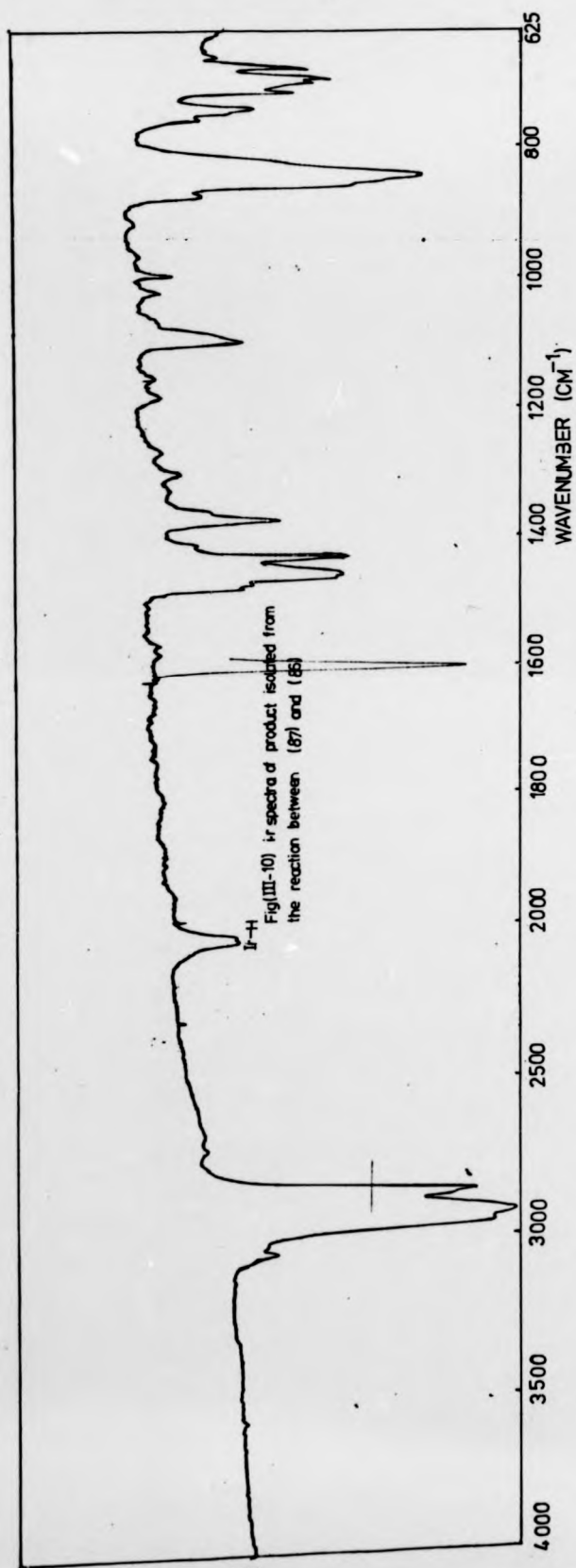
0.113 gms (1 m-moles) of (92) was introduced into the reaction flask shown. 800  $\mu$ l of dichloromethane was added from the side arm. The resulting solution was stirred under a nitrogen atmosphere. The flask was isolated from the vacuum line and 10 mg (1 m-moles) of (91) was added to the stirred solution. After 2 hours stirring at 40°C, the system was frozen and evacuated. The nmr tube was maintained at liquid nitrogen temperature and solvent transferred from the reaction flask by distillation in vacuo. The residue was gradually heated to 100°C and product collected in the nmr tube. After 60 mins heating at 100°C and pumping, the tube was sealed off under a nitrogen atmosphere, and transferred to the probe of the nmr machine. The residue was recrystallised from acetone. After 30 hours pumping to remove excess solvent, there was obtained 0.1 gms (88% yield), i.r and nmr spectrum are identical with bis(diphenylphosphinoethane)-iridium(III) dihydride hexafluorophosphate (93).  $\nu_{\max}$  i.r (nujol mull), (m 2065), (m 2045), (s 1460), (s 1100), (w 1000), (s 840), (m 740), Fig. (III-10), nmr  $\tau$  (acetone  $d_6$ ) 20.07 (2H, 2q,  $\overset{\text{H}}{\text{Ir}}-\overset{\text{H}}{\text{H}}$ ,  $J_{(\text{H}-\text{P})_{\text{cis}}} = 15 \text{ Hz}$ ,  $J_{(\text{H}-\text{P})_{\text{trans}}} = 110 \text{ Hz}$ ) 7.09 (4H, m,  $\text{P}(\text{CH}_2)_2\text{P}$ ), 2.7 (40H, m, 8  $\text{C}_6\text{H}_5$ ), Fig. (III-3).

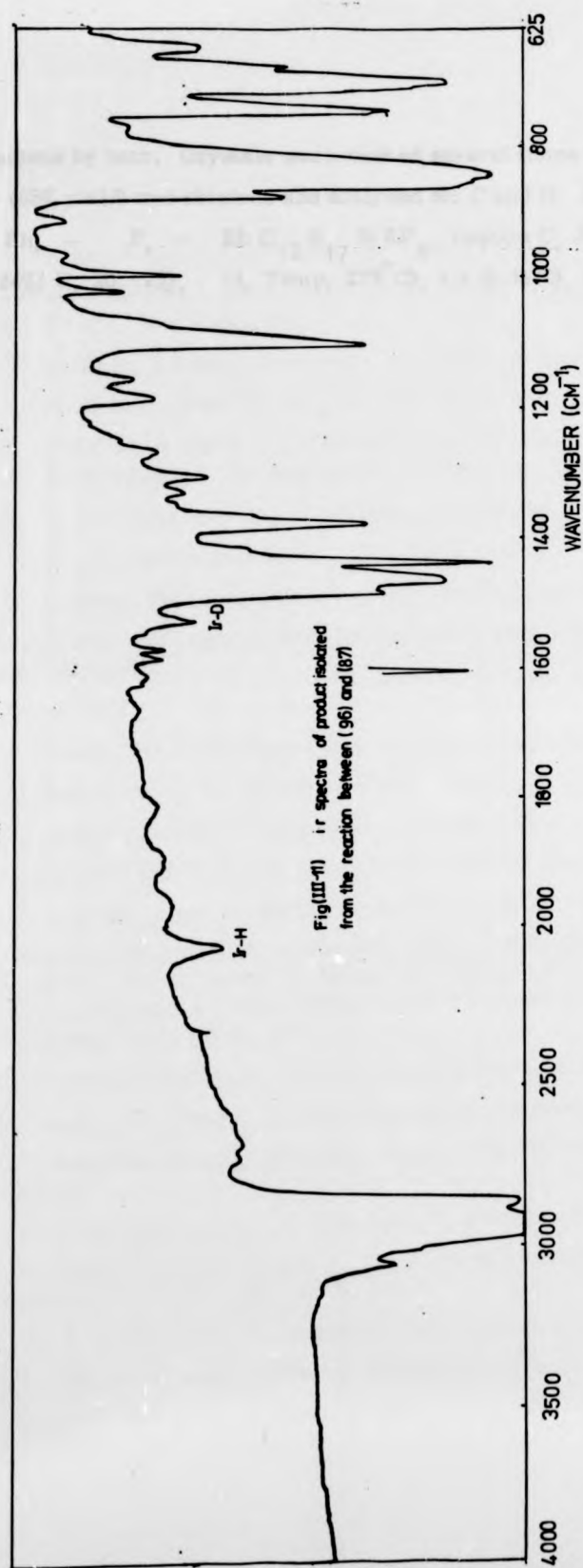
Reaction Ir(I) bis(bis-1, 2-diphenylphosphinoethane) with 1, 1-dideutero-1-sila-cyclohexadiene

The same apparatus used for the reaction of (92) with (91) was used in this experiment. The steps and method of preparation of this experiment were the same as described above.  $\nu_{\max}$  i.r (nujol mull), (b 2065), (w 1500), (s 1435), (w 1310), (w 1190), (s 1100), (m 1025), (m 1000), (s 835), (s 740), (s 700), Fig. (III-11), nmr  $\tau$  (acetone  $d_6$ ), 22.07 (2H, 2q,  $\overset{\text{H}}{\text{Ir}}-\overset{\text{H}}{\text{H}}$ ,  $J_{(\text{P}-\text{H})_{\text{cis}}} = 15 \text{ Hz}$ ), 7.091 (4H, m,  $\text{PCH}_2-\text{CH}_2\text{P}$ ) 2.7 (40H, m, 8  $\text{C}_6\text{H}_5$ ).

Reaction of Rh(I)bisnorboradiene tetrafluoroborate with (91)

0.109 gms (0.29 m-moles) of Rh(I) bisnorbornadiene tetrafluoroborate was dissolved in 10 ml of  $\text{CH}_2\text{Cl}_2$  in a Schlenk tube. 0.5 gms (5.2 m moles) of (91) were added gradually to the stirred solution at room temperature, under a nitrogen atmosphere. After 1 hour stirring the solution had turned dark yellow-orange. 5 ml of cooled dry ether was added into the solution, a yellow crystalline material was obtained after cooling in dry ice/acetone mixture. The solution was filtered under nitrogen, the filtrate was tested for presence of the displaced





Fig(III-11) i r spectra of product isolated from the reaction between (96) and (87)

norbornadiene by nmr. Crystals were washed several times with dry ether,  
0.1 gms (85% yield) was obtained and analysed for C and H. (Found: C, 37.93%  
H, 4.63% Rh, — F, — Rh C<sub>12</sub> H<sub>17</sub> Si BF<sub>4</sub>, require C, 38.12%; H, 4.24%;  
Rh, 27.24%; F, 20.12%), (d, Temp. 275°C), i.r (b 1650), (b 1040).

## REFERENCES

1. K. S. Pitzer, *J. Amer. Chem. Soc.*, **70**, (1948), 2140.
2. L. Pauling, *Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, 1960.
3. R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, (1950), 4493.
4. R. S. Mulliken, *J. Amer. Chem. Soc.*, **77**, (1955), 884.
5. a) L. E. Gusel'nikov and M. C. Flowers, *Chem. Comm.*, (1967), 864.  
b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, (1968), 419.
6. I. M. T. Davidson and J. M. Thompson, *J. Chem. Soc., D*, (1971), 251.
7. R. Walsh, *J. Organometal. Chem.*, **38**, (1972), 245.
8. S. W. Benson, *Thermochemical Kinetics*, Wiley, (1968), p. 50.
9. R. A. Jackson in *Essays on Free Radical Chemistry*, *Chem. Soc. Spec. Publ.*, **24**, (1970), p. 295.
10. M. David Curtis, *J. Organometal Chem.*, **60**, (1973), 63.
11. T. J. Barton, 3rd International Organosilicon Symposium, Madison, Wis., (1972).
12. T. J. Barton and C. L. McIntosh, *Chem. Comm.*, (1972), 861.
13. R. G. Pearson, *Accounts Chem. Res.*, **4**, (1971), 152.
14. R. Damrauer and D. R. Williams, *J. Organometal Chem.*, **66**, (1974), 241.
15. C. J. Attridge, *Organometal Chem. Rev. A*, **5**, (1970), 323.
16. G. Fritz and B. Rabbe, *Z. Anorg. Allg. Chem.*, **286**, (1956), 149;  
**299**, (1959), 232; G. Fritz, D. Habel, D. Kummer and G. Teichmann,  
*Z. Anorg. Allg. Chem.*, **302**, (1959), 60; G. Fritz and J. Grobe, *Z. Anorg. Allg. Chem.*, **315**, (1962), 157.
17. O. M. Nefedov and M. N. Manakov, *Angew. Chem. Inter. Ed.*, **5**, (1966), 1021.
18. M. Kumada, K. Tamao, M. Ishikawa and M. Matsumo, *Chem. Comm.*, (1968), 614.
19. W. J. Bailey and M. S. Kaufmann, *Abstr. 157th Meeting Amer. Chem. Soc.*, (1969), p. Org. 55.
20. I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, (1971), 882.
21. R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson and J. Stevenson, *J. Organometal Chem.*, **34**, (1972), 53.
22. A. W. P. Jarvie and R. J. Rowley, *J. Organometal. Chem.*, **36**, (1972), C7.
23. T. J. Barton and Eugene Kline, *J. Organometal Chem.*, **42**, (1972), C21.
24. P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Comm.*, (1973), 54.

25. P. Boudjouk, J. R. Roberts, C. M. Golline and L.H.Sommer, *J. Amer. Chem. Soc.*, 94, (1972), 7926.
26. D. N. Roark and L.H.Sommer, *Chem. Comm.*, (1973), 167.
27. R. D. Bush, C. M. Golino, D. N. Roark and L. H. Sommer, *J. Organometal Chem.*, 59 (1973), C17.
28. C.M. Golino, R. D. Bush, D. N. Roark and L. H. Sommer, *J. Organometal Chem.*, 66 (1974), 29.
29. C. M. Golino, R. D. Bush and L.H.Sommer, *J. Amer. Chem. Soc.*, 96, (1974), 615.
30. T. J. Barton and J.A.Kilgour, *J. Amer. Chem. Soc.*, 96, (1974), 2278.
31. D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 94, (1972), 5837.
32. I. M. T. Davidson and J. F. Thompson, *Chem. Comm.*, (1971), 251.
33. Y. Nakadaiva, S. Kanouch and H.Sakurai, *J. Amer. Chem. Soc.*, 96, (1974), 5621.
34. (a) G. Märkl, *Angew. Chem. Int. Ed. Engl.*, 5, (1966), 846.  
 (b) G. Märkl, F. Lieb, and A. Mertz, *ibid.*, 6, (1967), 458, 944.  
 (c) G. Märkl, and A. Mertz, *Tetrahedron Lett.*, (1969), 1231.
35. P. deKoe and F. Bickelhaupt, *Angew. Chem.*, *Int. Ed. Engl.*, 6, (1967), 567.
36. P. deKoe, R. Van Veen, and F. Bickelhaupt, *Angew. Chem.*, *Int. Ed. Engl.* 7, (1968), 465.
37. P. Jutzi and Deucherr, *Angew. Chem.*, *Int. Ed. Engl.*, 8, (1969), 991.
38. H. Vermeer and F. Bickelhaupt, *ibid.*, 8, (1969), 992.
39. P. Jutzi, *J. Organometal Chem.*, 19, (1969), P1.
40. A. J. Ashe (III), *J. Amer. Chem. Soc.*, 93, (1971), 3295.
41. C. F. Whitmore and L. H. Sommer, *J. Amer. Chem. Soc.*, 68, (1946), 481.
42. C. Eaborn and J. C. Jeffery, *J. Chem. Soc.*, (1957), 137,
43. G. D. Cooper and M. Proper, *J. Amer. Chem. Soc.*, 76, (1954), 3943.
44. R. W. Bott, C. Eaborn and T. W. Swaddle, *J. Organometal. Chem.*, 5, (1966), 233.
45. V. B. Miller, M. B. Nelmann, A. V. Savitskii and V. F. Mironov, *Dokl. Akad. Nauk S.S.S.R.*, 101, (1955), 495; *Chem. Abstr.* 50, (1956), 3217.
46. J. C. Jeffery, Ph.D. Thesis, University of London, 1957.
47. M. Kumuda and M. Ishikawa, *J. Organometal Chem.*, 1, (1964), 411.
48. M. Kumuda, M. Ishikawa and K. Tamo, *J. Organometal. Chem.*, 5, (1966), 226.
49. R. W. Bott, C. Eaborn and B. M. Rushton, *J. Organometal Chem.*, 3, (1965), 455.
50. T. J. Halrston and D. H. O'Brien, *J. Organometal. Chem.*, 23, (1970), C41.
51. M. A. Cook, C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, 24, (1970), 301.

52. T.J. Hariston and D.H. O'Brien, *J. Organometal. Chem.*, 29, (1971) 79.
53. C. Eaborn, *Organosilicon Compounds*, Butterworth Scientific Publication, London 1960, pp 88.
54. W.S. Miller, J.S. Peake and W.H. Nebergall, *J. Amer. Chem. Soc.*, 79 (1957), 5604.
55. F.P. Price, *J. Amer. Chem. Soc.*, 69, (1947), 2600.
56. L. Kaplan and K.E. Wilzbach, *J. Amer. Chem. Soc.*, 74 (1952) 6152; 77 (1955), 1297.
57. C. Eaborn, *Organosilicon Compounds*, Butterworth Scientific Publication, London, 1960, pp 200.
58. B.N. Dolgov, N.P. Karitonov and M.G. Moronkov, *J. Gen. Chem.*, Moscow, 24 (1954), 1178; *Chem. Abstr.*, 49, (1955), 12275.
59. J.E. Baines and C. Eaborn, *J. Chem. Soc.*, (1956) 1436.
60. R.L. Schowen and R. Bacon, *Tetrahedron Lett.*, (1970), 4177.
61. K. O'Donnell, R. Bacon, K.L. Chellapa, R.L. Schowen and J.K. Lee, *J. Amer. Chem. Soc.*, 94 (1972), 2500.
62. C.R. Howie, J.K. Lee and R.L. Schowen, *J. Amer. Chem. Soc.*, 95, (1973), 5286.
63. R.A. Benkeser and W.E. Smith, *J. Amer. Chem. Soc.*, 90, (1968), 5307.
64. R.A. Benkeser, K.M. Foley, J.M. Grutzner and W.E. Smith, *J. Amer. Chem. Soc.*, 92, (1970), 697.
65. I.J. Borowitz, K.C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, 31, (1966), 4031.
66. S.C. Bernstein, *J. Amer. Chem. Soc.*, 92, (1970), 699.
67. H.J. Chambell-Ferguson and F.A.V. Ebsworth, *J. Chem. Soc., A*, (1966), 1508.
68. L.H. Sommer, W.P. Parle, Jr., D.R. Weyenberg, *J. Amer. Chem. Soc.*, 81, (1959), 251.
69. J.B. Smart, R. Hagon, P.A. Scherr, L. Ferrier and J.P. Oliver, *J. Amer. Chem. Soc.*, 94, (1972), 8371.
70. M.S. Bains, *Can. J. Chem.*, 42, (1964), 945.
71. J.B. Golovanov, A.K. Pariskunov, T.V. Talalaeva, G.W. Tsareva and K.A. Kocheshkov, *Dokl. Akad. Nauk., U.S.S.R.*, 149, (1963), 835.
72. G.E. Hartwell and T.L. Brown, *J. Inorg. Chem.*, 5, (1966), 1257.
- 72a. D.E. Pearson and C.A. Buehler, *Chem. Rev.*, (1974), 45.
- 72b. R. Breslow, *Tetrahedron Lett.*, (1964), 399.
73. I. Dostrovsky and E.D. Hughes, *J. Chem. Soc.*, (1946), 157, 161, 164, 166, 169 and 171.
74. H. Budzikiewicz, C. Djerassi, D.H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day Inc., London, 1967, pp 227.
75. Reference 74, pp 471.
76. Martin J. Smith, Ph.D. Thesis, Oxford University, 1971.



77. J. A. Riddick and W. B. Bunger, Organic Solvents, Technique of Chemistry, Volume I, J. Wiley Interscience, 1970.
78. H. D. Kaesz and F. G. A. Stone, J. Chem.Soc., (1957), 1433.
79. Organic Reactions, J. Wiley Interscience (VI), (1964), 353.
80. M. Morton, J. A. Caland and I. Plirma, J.Amer.Chem.Soc., 78, (1956), 5395.
81. B. Nahlovsky and V. Chvalovsky, Collection Czechoslov.Chem.Comm., 33, (1968), 4422.
82. S. W. Benson, Foundation of Chemical Kinetics, McGraw Hill Series, in Advanced Chemistry, 1960, p10.
83. K. J. Laidler, Chemical Kinetics, McGraw-Hill Book, (1965), p5.
84. E. R. Thornton, Solvolysis Mechanism, Ronald Press, (1964), p194.
85. C. J. Collins, and N. S. Bowman, Isotope Effect in Chemical Reactions, J.A.C.S. special publication, 1970, pp 37.
86. J. March, Advanced Organic Chemistry and Structure, McGraw-Hill, London, 1968, pp 214.
87. A. J. Ashe(III), J.Amer.Chem.Soc., 93, (1971), 6690.
88. A. J. Ashe(III), J.Amer.Chem.Soc., 94, (1972), 7596.
89. R. Benkeser and R.Cunico, J. Organometal.Chem., 4, (1965), 284.
90. J. P. Collman and W. R. Roper, Advances in Organometallic Chemistry, Academic Press, 7, (1968), 53.
91. L. Vaska, and L. D. Catone, J.Amer.Chem.Soc., 88, (1966), 5324.
92. A. J. Chalk and J. F. Harrod, J.Amer.Chem.Soc., 87, (1965), 16.
93. J. F. Harrod, D. F. R. Gilson and R. Charles, Can.J.Chem., 47, (1969), 2205.
94. A. J. Chalk, J.Chem.Comm., 1969, (1207).
95. J. F. Harrod and C. A. Smith, J.Amer.Chem.Soc., 92, (1970), 2699,
96. A. P. Ginsberg, "Transition Metal Chemistry," Marcel Dekker, New York, 1965, Vol.(I), pp 111.
97. R. C. Taylor, J. F. Young and G. Wilkinson, Inorg.Chem., 5, (1966), 20.
98. L. Vaska, J.Chem.Comm., 614, (1966).
99. M. Green and T. A. Kue, J.Chem.Soc.Dalton, 1972, 832.
100. R. J. Ellis and H. M. Frey, J.Chem.Soc., (1966), 553.
101. S. W. Benson and R. Shaw, Trans.Faraday Soc., 63, (1967), 985.
102. Yeda Research and Development Co. Ltd., Fr. 1,562, 322 (C1.BO1J), 04 Apr. 1969, Israeli Appl. 13 Mar. 1967; pp 4.
103. O. G. Mardashev, Yu. S. Tsvetkova, G. K. Erofeev and B. V. Vetsl, Akad. Belarus, S.S.R., Ser.Khim.Navak, 4, (1973), 14-18.
- 104.<sup>P.A</sup> Plattner "Newer Methods of preparative Organic Chemistry", Interscience Publishers, Inc., New York, Vol(I), (1948), 21-59.



105. Shulkin and Naryschkina, <sup>Prace.</sup> J. Chem. [4] 13, (1961), 183.
106. D. W. Mathieson, Nuclear Magnetic Resonance, Academic Press, London, (1967), pp 183.
107. G. D. Oshesky and F. Bentley, J. Amer. Chem. Soc., 79, (1957), 2057.
108. K. N. Campbell and B. K. Campbell, Org. Syn. Coll., 4, (1963), 117.
109. Inorganic Synthesis, McGraw-Hill book, London, (1968), pp 103.
110. R. Cramer, J. Amer. Chem. Soc., 86, (1964), 217.
111. M. Green, T. A. Kuc and S. H. Taylor, J. Chem. Soc. (A), (1971), 2334.