A STUDY OF ELIMINATION AND ADDITION REACTIONS OF SOME ORGANOSILANES

BY

JACQUES THOMPSON

A Thesis presented for the
degree of Doctor of Philosophy
in the
University of Aston in Birmingham.

November, 1968.

SUMMARY

Although the solvolytic elimination reaction of beta-halogenoalkyltrialkylsilanes has been the subject of many investigations, and several mechanisms have been proposed for the elimination reaction, some aspects of the work had not been covered. In an attempt to acquire more information concerning the nature of the intermediate, a study of the stereochemistry of the reaction was undertaken.

In order to elucidate the stereochemical path of the reaction, erythro-1,2-dibromopropyltrimethylsilane was prepared and the products of solvolysis in aqueous ethanol were examined. Product analysis indicated that a stereospecific, predominantly trans, elimination was taking place. This result suggested that the trimethylsilyl group could be interacting with the positive charge developing on the beta-carbon atom.

Further evidence in support of this supposition was provided by a study of the effect of deuterium substitution on the rate of solvolysis of these silanes. Deuterium was substituted for hydrogen on the alpha and beta-carbon atoms, and in the trialkyl group attached to the silicon atom. The secondary isotope effects, recorded as a difference in rate constant in comparison with the non-deuterated molecule, strengthened the result of the stereochemical study, and contributed further evidence to the indication that the rate-determining step involved the cleavage of the carbon-bromine bond.

The observation that the trimethylsilyl group migrated during a related reaction, supplied additional evidence that the trimethylsilyl group may interact with the positive charge on the beta-carbon atom.

It was concluded therefore, that the rate-determining step in the neutral solvolysis of beta-halogenoalkyltrialkylsilanes, is the cleavage of the carbon-halogen bond, which may be assisted by the trialkylsilyl group interacting with the positive charge developing on the beta-carbon atom.

--o--

This work was carried out between 1965 and 1968 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

J. Thompson

J. Thompson

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr. A. W. P. Jarvie and Dr. A. Holt for their supervision and encouragement of this work, and to Dr. A. Whittingham for several helpful discussions; to Dr. J. Homer for his assistance in the interpretation of the nmr spectra, and to Mrs. V. Shearsby, Miss M. Sparkes and Mr. E. Hartland for the various spectra they prepared.

The author is also indebted to the Science Research Council for the provision of a grant.

To my wife Elizabeth

"On a huge hill,
Cragged and steep, Truth stands, and he that will
Reach her about must, and about must go."

John Donne (1573 - 1631)
Dean of St. Paul's

ERRATA

Page 5, line 13 - For "beta-halogenoethyltrialkylsilane", read "beta-halogenoethyltrialkylsilanes"

Page 30, lines 20 and 22; page 31, line 3 - For "beta-halogenoethyltrialkylsilanes", read "beta-halogenoalkyltrialkylsilanes"

Page 31, line 2 - For "beta-halogenoethyltrichlorosilanes", read "beta-halogenoalkyltrichlorosilanes"

Page 44, line 18 - For "cyclopropenium", read "silacyclopropenium"

Page 69, line 24 - For "cyclosilapropenium", read "silacyclopropenium"

Page 70, line 17 - For "As the experimental evidence indicated", read "As experimental evidence has indicated"

Page 86, line 2 - For "1,1,2-tribromopane", read "1,1,2-tribromopropane"

CONTENTS

FIGURES AND DIAGRAMS

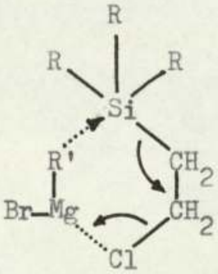
TABLES

I. INTRODUCTION

Although the mechanism of solvolysis of beta-halogenoalkylsilanes has been the subject of many studies over the past twenty years, much of the evidence for the postulated mechanisms is capable of being interpreted in several ways, and some important facets of the work have not been covered. The present investigation has been designed to shed more light on this subject and to arrive at a mechanism which accommodates all the facts.

Interest in the chemistry of beta-halogenoalkylsilanes first arose as a result of their high reactivity in comparison, for example, with other halogenated alkylsilanes. Many investigators have studied the reactions of beta-halogenoalkylsilanes with various reagents, and by way of illustrating the properties of this type of compound some examples will be cited. Initially, the reactions of halogenoalkyltrialkylsilanes were studied by Ushakov and Itenburg[1] who were the first to observe a difference in the reactivity of alpha- and beta-halogenoalkylsilanes. Subsequently, Sommer and Whitmore[2] presented a paper to the American Chemical Society, in which they reported a detailed study of alpha- and beta-chloroalkylsilanes. The subject of this paper was the striking difference in reactivity of a chlorine attached to a carbon atom, alpha to a silicon atom, as compared with that of a chlorine attached to a carbon atom, beta to a silicon atom. As a continuation of this work Sommer and co-workers[3] further investigated the properties of halogenoalkylsilanes, and discovered that the reactivity of chlorine atoms in the alpha and gamma positions differed from those in the beta position. Thus the titration of alpha-chloropropyltrichlorosilane and gamma-chloropropyltrichlorosilane with dilute alkali gave a titre value equivalent to chlorine attached to silicon only, whilst the titration of beta-chloropropyltrichlorosilane gave a value corresponding to chlorine attached to both carbon and silicon.

Sommer also investigated the reactions of beta-chloroethyltrichlorosilane and methyl magnesium bromide,[4] which revealed that the stepwise addition of Grignard reagent proceeded smoothly, to replace three chlorine atoms. However, on addition of a further equivalent, ethylene gas and tetramethylsilane were formed, instead of the expected n-propyltrimethylsilane. Sommer therefore proposed the following cyclic intermediate to account for the evolution of ethylene:



He also suggested that the beta carbon-chlorine bond permitted the formation of a Grignard co-ordination complex, in which the alkyl group R' of the Grignard reagent and the silicon atom are in the 1:6 positions; the silicon atom acting as an electron sink, which attracts the electron pair holding R', with simultaneous electron displacements. Although silicon-carbon cleavage is the major reaction of beta-chloroethylsilanes, not all halogenoalkylsilanes react in this fashion. It has been reported[5] that some beta-bromoalkyl derivatives react partially to give coupling products with highly reactive Grignard reagents. This reaction has been studied extensively, but the significance of the work with respect to the mechanism of silicon-carbon cleavage by Grignard reagents is obscure, because of crude starting materials and incomplete experimental details.

Further studies of beta-eliminations involving silicon by Sommer and co-workers,[6] showed that desilicohalogenation could also be brought about by electrophilic reagents such as aluminium chloride. The reaction was studied in the presence of aluminium chloride and the following mechanism proposed for the elimination:

$$\equiv SiCH_2CH_2Cl + AlCl_3 \xrightarrow{(a)} \equiv SiCH_2CH_2^+ + AlCl_4^-$$

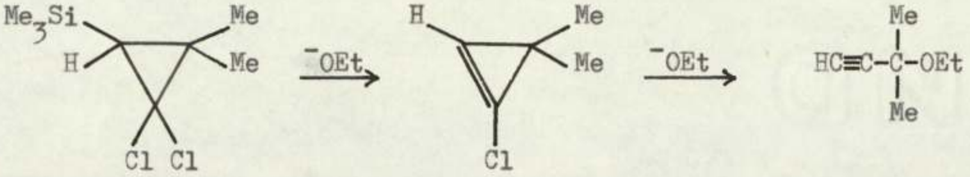
$$\equiv Si-\overset{\curvearrowright}{CH_2}CH_2^+ \xrightarrow{(b)} CH_2{=}CH_2 + \equiv Si^+$$

$$\equiv Si^+ + AlCl_4^- \xrightarrow{(c)} \equiv Si-Cl + AlCl_3$$

Step (a) gives a beta carbonium ion. Step (b) involves electron release from electropositive silicon to electron deficient carbon. Step (c), which may be simultaneous with or subsequent to (b), gives a chlorosilane by combination of chloride ion with "siliconium ion", thus regenerating the catalyst. The ease of thermal elimination of beta-chloroethyltriethylsilane[6] relative to the alpha-chlorinated material was also observed by these investigators, and they suggested that "ionic" bond cleavage was involved in the elimination, although the possibility of free radical cleavage could not be excluded.

Hurd[7] has reported the reaction of beta-chloroethyltrichlorosilane with quinoline, from which he obtained small yields of dehydrochlorinated products, and ascribed their formation to the fact that quinoline is incapable of providing a nucleophile for combination with silicon. However, a better explanation may be provided from a study of the stabilising effect of chlorine attached to silicon: chlorine atoms tend to withdraw electrons from the silicon atom and in so doing, strengthen the silicon-carbon bond of these compounds.

Seyferth and Jula have recently studied the desilicohalogenation of trimethylsilylsubstituted gem-dihalocyclopropanes[8]. They have postulated an initial beta-elimination of trimethylchlorosilane, followed by a further elimination of hydrogen chloride, to account for the acetylenic ether which is formed:

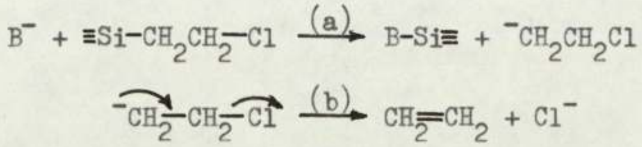


The desilicohalogenation reaction forms part of a general group of elimination reactions, in which an electropositive atom or group and a halide ion are lost from a particular molecule. In this group of reactions one may therefore include the elimination of hydrogen halides, as well as substituted germanium, tin and lead halides. Further examples of this type of reaction, apart from those quoted above may also be found, one of these being Matteson and Liedtke's study of the stereochemistry of deboronobromination of dibutyl erythro-2,3-dibromobutane-2-boronate by treatment with water or base, together with the kinetics of the elimination of ethylene from dibutyl 2-bromoethaneboronate in aqueous ethanol.[9]

The first attempt to formulate a mechanism for the solvolysis of beta-halogenoethyltrialkylsilane was made by Sommer and co-workers:[4]

$$HO^- \dashrightarrow \equiv Si\overset{\curvearrowright}{-}CH_2\overset{\curvearrowright}{-}CH_2-Cl \longrightarrow \equiv SiOH + CH_2{=}CH_2 + Cl^-$$

They suggested that in a silicon compound, the reaction of beta carbon-chlorine bonds with alkali is analogous to the E2 mechanism[10] proposed for beta-eliminations from alkyl halides. The only difference between the two reactions is that the nucleophile attacks tetracovalent silicon, instead of a combined hydrogen atom. Subsequent to a further study, Sommer[6] elaborated on his original proposal and reported the following mechanism:



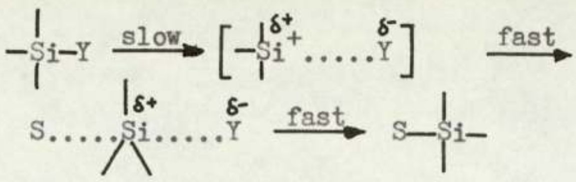
$$B^- + \equiv Si-CH_2CH_2-Cl \xrightarrow{(a)} B-Si\equiv + {}^-CH_2CH_2Cl$$

$$^-CH_2-CH_2-Cl \xrightarrow{(b)} CH_2=CH_2 + Cl^-$$

Step (a) is rate controlling, aided by an increased concentration of nucleophilic anions (B^-). Step (b) is very fast. Thus (a) and (b) were presumed to be effectively simultaneous. Again this mechanism is similar to that established for E2 eliminations of ordinary organic halides.[10]

In 1958, Benkeser and Bennett[11] attempted to establish whether base-catalysed beta-eliminations proceed via a trans-coplanar transition state. A model compound, cis-1-trimethyl-2-bromocyclohexane was synthesised and found to undergo spontaneous decomposition. This was cited as evidence of a four-centre reaction mechanism, which intermediate could be used to explain many of the beta-eliminations.

It was not until 1961 that Sommer and Baughman,[12a] whilst searching to establish the existence of siliconium ions, were led to undertake a quantitative study of the kinetics of beta-eliminations at silicon. Using beta-chloroethyltrimethylsilane as the model compound, they found that the solvolysis in aqueous ethanol at 30°C followed a first order rate law with excellent precision; gave good correlation of variation in rate constant with variation in solvent composition over the range 50-80% aqueous ethanol, by volume, according to the Winstein-Grunwald equation, $\log(k/k_o) = mY$;[13] and yielded a value of m, 1.02, which indicated that the beta-chloroethylsilane and t-butyl chloride are about equally susceptible to the ionizing power of the solvolysis medium. Further conclusions drawn from the data showed that the solvolysis rates are not sensitive to the nucleophilic character of the solvent, but are strongly dependent on its ionizing power. The approximately equal rate constants in corresponding media for the silane and t-butyl chloride, suggested that there is strong participation of electron release from silicon in the rate controlling transition state, without simultaneous nucleophilic attack by solvent at the silicon atom. On these grounds and on the basis of the Hammett rho factor (-2.15), it was stated that the reaction is therefore properly described as proceeding by a limiting siliconium mechanism, as shown below:

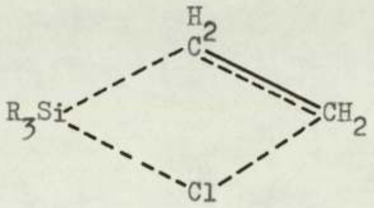


(Y = chloroethyl, S = solvent)

Sommer is essentially proposing an initial, rate-determining cleavage of the silicon-carbon bond with the formation of a carbanion together with a siliconium ion. However, in a footnote,[12b] the alternative suggestion was made of a non-classical siliconium ion intermediate in which the trialkylsilyl ion is π-bonded to the ethylene molecule being formed, which cannot be discarded on the basis of the evidence presented.

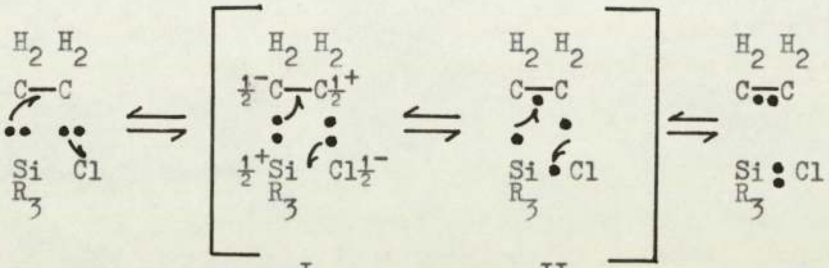
Subsequently Baughman[14] indicated that a cyclic intermediate may account in a more satisfactory fashion for the experimental evidence. He determined values for entropies of activation, which were negative and in the order of 12-14 entropy units, together with the change of electron density on silicon as measured by the Hammett rho factor. This suggested that in the transition state there was considerable positive charge accumulation, relative to the starting state. However, this evidence alone failed to distinguish between the "limiting siliconium ion mechanism" and the "cyclic" mechanism. Baughman also studied the effect on the rate constant caused by changing the halogen from chlorine to bromine. This change resulted in a seventeen-fold increase of the base-catalysed rate, indicating considerable bond stretching in the rate-determining transition state, and also suggesting that the "limiting siliconium ion mechanism" may be at fault. In support of the proposed cyclic intermediate, Kreevoy and Kowitt[15] in 1958, commented on the resemblance between the deoxymercuration of alpha-2-methoxycyclohexylmercuric iodide (in which a cyclic intermediate is proposed) and the elimination of beta-hydroxyethyltrimethylsilane.

Subsequently, Bott et al.[16] reviewed and criticised Sommer and Baughman's results on the basis that the evidence was inconclusive and capable of various interpretations. They suggested instead that the ready unimolecular solvolysis of beta-halogenated trialkylsilanes was related to the ease of thermal decomposition and to the tendency for intramolecular transfer of halogen from carbon to silicon. They postulated that the gas-phase decomposition of beta-chloroalkylsilicon compounds apparently involved a four-centre, unimolecular process,[17] with an intermediate of the type represented below:



They proposed also that the operation of such a process in solution, provided there was charge separation in the transition state, (in order to account for the ionic nature of the reaction) would be consistent with Sommer and Baughman's results.

A more elaborate kinetic study of the gas-phase elimination was made by Davidson et al.[18] Calculation of the A factors for the reaction, together with Raman spectra led them to the conclusion that there is some polar character in the transition state, which they suggest may be described by the semi-ion pair model postulated by Benson and Bose:[19]



I

II

I semi-ion pair

II four-centre system

The above transition states are also indicated as having possible existence in the neutral solvolysis of beta-chloroethyltrialkylsilanes.

The description by Sommer[20] of a reaction mechanism as "... the best hypothesis that can be put forward on the basis of the data available at the time that it is formulated - in short, a reaction mechanism is not necessarily invariant with time ...", is very applicable to the several mechanistic interpretations that have been made concerning the elimination of beta-halogenoalkylsilanes.

It was felt that a study of the stereochemistry of the elimination reaction might provide useful information about the structure of the silicon-containing leaving group; and that further knowledge relating to the transition states may be gained by studying the effect of deuterium substitution on the rate constant. To this end, deuterium was substituted for various hydrogen atoms in the beta-bromoethyltrimethylsilane molecule. In the following dissertation a reaction path with transition states (or intermediates), which appear to account in the most satisfactory fashion for all the experimental evidence accumulated during this and previous investigations, will be proposed.

--o--

II. STEREOCHEMISTRY

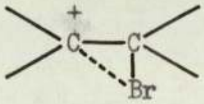
1. Addition of Bromine to 1-propenyltrimethylsilane

It has already been stated in the introduction that useful information concerning the nature of the intermediate in the solvolytic elimination of beta-halogenoalkyltrialkylsilanes, may be gained from a study of the stereochemistry of this reaction. The model compound chosen for this purpose was that obtained by the addition of bromine to 1-propenyltrimethylsilane. It was thought that the addition of bromine to cis-1-propenyltrimethylsilane would yield threo-1,2-dibromopropyltrimethylsilane, whilst the addition of bromine to trans-1-propenyltrimethylsilane would lead to the erythro isomer; hence it was proposed to study the elimination reaction from both threo and erythro isomers. However, as the cis isomer could not be obtained free from the trans, this discussion will be based upon a study of the addition of bromine to the trans isomer only.

In order to be able to study the stereochemistry of elimination, the stereochemistry of the starting material must be known. It has been assumed that the addition of bromine to 1-propenyltrimethylsilane would be stereospecific; the arguments for this assumption are presented below.

The mechanism of the bromination of olefins is generally accepted as proceeding in a trans[21] manner through a bromonium or carbonium ion intermediate. Many investigations have been made on the addition of bromine to unsaturated molecules since Roberts and Kimball[22] first suggested the bromonium ion to account for the stereochemistry of bromine additions to these molecules.

The main feature of this reaction is that the bromine is polarized either before or during its approach to the unsaturated bond. The positive portion of the reagent attacks the π-electrons in the plane perpendicular to that of the olefin. The result of this attack is the formation of a carbonium ion which may be represented by the structure:

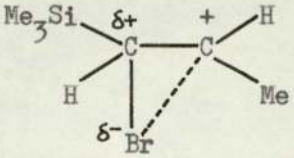


Due to the interaction between the bromine and the positive centre, a measure of configurational stability is ensured, thus restricting the attack of the nucleophilic bromine to the opposite side of the molecule. Attempts[23] have also been made to obtain evidence of a non-stereochemical nature, to substantiate the cyclic intermediate. Determinations of rho value (-2.23) and activation parameters for the reactions studied seem to support the proposition of a cyclic intermediate.

When, however, the olefinic compound contains powerfully electron releasing groups, the stereoselectivity can depend on the solvent.[24] Thus in solvents of high dielectric constant the carbonium ions have sufficiently long life to allow rotation about the carbon-carbon bond, and the product formed is therefore predominately that from the more stable of the two carbonium ions.

Alt and Barton[25] have almost conclusively established the stereochemistry of bromination by the isolation of trans diaxial 1,2-dibromides as major products in the ionic bromination of various cholestenes. Subsequent thermal conversion of the diaxial dibromides to the trans diequatorial dibromides confirmed the original assignment.

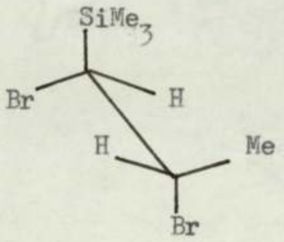
There is every reason to believe that the mode of addition of bromine to 1-propenyltrimethylsilane is normal. The addition consists of a two-stage reaction involving a carbonium, ionic intermediate, which probably resembles the bromonium ion:



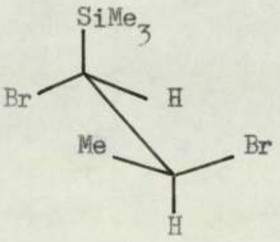
Further attack by the nucleophile leads to the formation of 1,2-dibromopropyltrimethylsilane. Although Benkeser[26] has suggested that the addition of bromine to certain vinylsilanes, that is those containing powerfully electron releasing groups, may not be stereospecifically trans, it was still felt justifiable to discount additions other than trans; the trimethylsilyl group is only weakly electron donating,[27a] as is the methyl group, and also no solvent of high dielectric constant was used.

Some further indication as to the stereochemistry of addition may be gained by considering the nmr coupling constants of the methine protons. Calculations of an approximate nature on the resonance spectra of 2,3-disubstituted n-butanes[28, 29] suggest that rotamer populations may be obtained from a knowledge of the coupling constants of the methine protons.

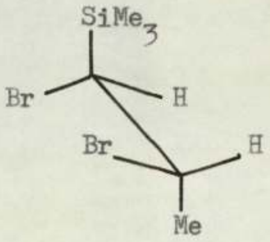
The cis addition of bromine to trans-1-propenyltrimethylsilane would be expected to yield:



I

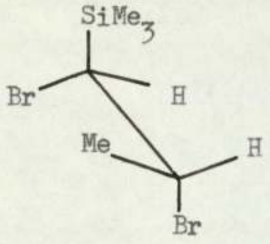


II

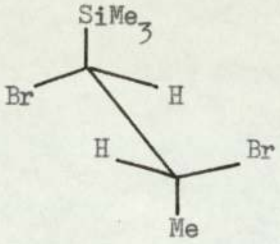


III

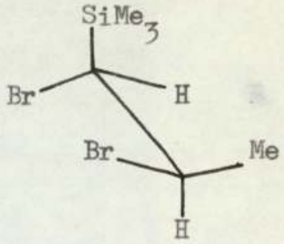
Whilst the trans addition would yield:



IV



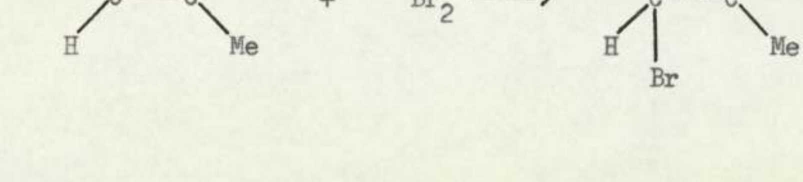
V

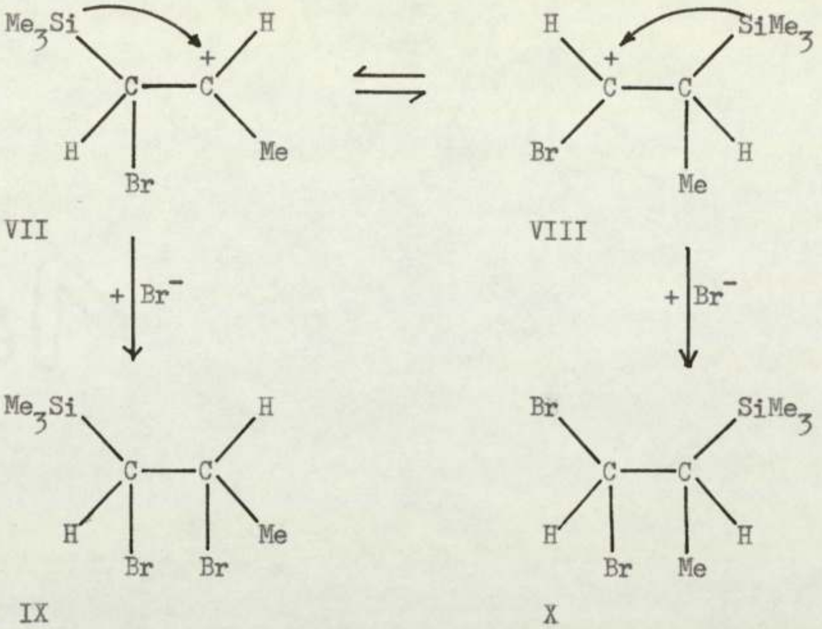


VI

In rotamers I and V, the methine protons are trans and should have a large coupling constant (8-12 cycles per second). In II, III, IV and VI, they are gauche and should have small coupling constants (2-5 cycles per second). It is suggested that with the knowledge of coupling constants, rotamer populations may be estimated. If these are estimated on a qualitative basis it should be possible to determine whether addition has taken place in a cis or trans manner. If it is assumed that the rotamers with the largest groups trans to each other are predominant, then rotamers I and IV should be favoured. Thus a coupling constant of 8-12 cycles per second would indicate that rotamer I predominated and hence the addition was cis, whereas a coupling constant of 2-5 cycles per second would indicate that rotamer IV predominated and that the addition was trans. Therefore, a coupling constant of 4.5 cycles per second obtained for the methine protons, for the addition of bromine to trans-1-propenyltrimethylsilane is consistent with the fact that isomer IV (trans bromine addition) has been synthesised.

It was considered possible that migration of the trimethylsilyl group from the alpha to the beta carbon may affect the stereochemistry of the addition, and therefore the subsequent elimination. Hence the following scheme may represent this migration:





Evidence of a possible migration was sought from the nmr spectrum of the dibrominated material. Although a small absorption at 6.0 p.p.m. (indicative of a $-CHBr_2$ group) was recorded in the spectrum, it was attributed to 1,1,2-tribromopropane (IXa). This material could have been formed from compounds IX or X, by the elimination of bromopropene followed by bromination. If the assumption is made that compounds IX and IXa are present, the absorptions in the nmr spectrum can be rationalized. Whilst this explanation does not necessarily preclude the occurrence of a rearrangement, it does establish the fact that no rearranged product was present during the subsequent solvolysis.

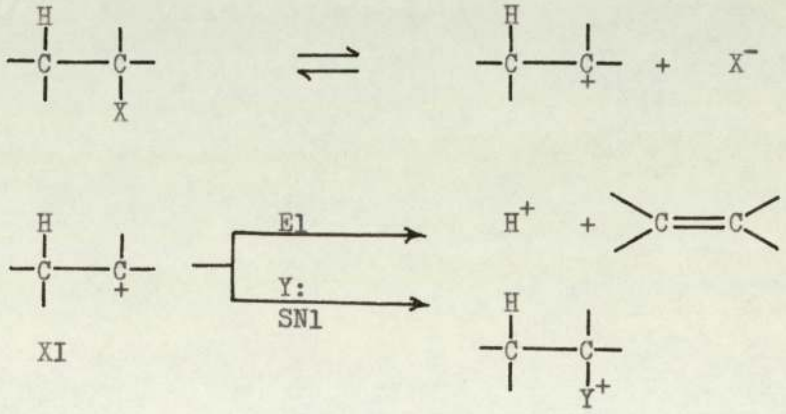
The nmr spectrum of 1,2-dibromoethyltrimethylsilane was also examined. The lack of absorptions in the regions 5.5-6.5 p.p.m. and 1.5-1.2 p.p.m. ($\equiv SiCH_2-$ group), again indicated that no rearranged products were present.

2. Desilicohalogenation of Erythro-1,2-dibromopropyltrimethylsilane

Elimination reactions generally involve the loss of two substituents from a pair of atoms in a chain or ring. The most common eliminations are beta or 1,2-eliminations.[30] These reactions involve two atoms or groups situated on adjacent carbon atoms, which are split off with the formation of a new multiple linkage. Hughes and Ingold[10] first recognised three principal mechanisms for 1,2-eliminations, which are briefly described below.

The E1 mechanism

The initial slow step is the ionization of the substrate, followed by rapid decomposition of the so-formed carbonium ion; added base is not required. The unimolecular mechanism may be represented:

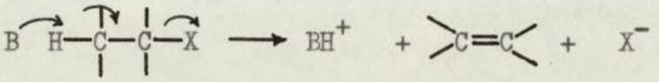


The carbonium ion is partitioned between elimination and substitution, the latter being a result of neutralization by a solvent molecule Y, or any available nucleophile.

The postulation of intermediate XI usually leads to a reaction that is non-stereospecific in nature. Therefore one may expect the products of compounds undergoing E1 eliminations (except in special circumstances, detailed later) to be non-stereospecific.

The E2 mechanism

Ingold[31] noticed that a strong base was almost always required to promote these reactions and put forward a bimolecular mechanism, which is probably the most widespread of all elimination processes, and is formulated:



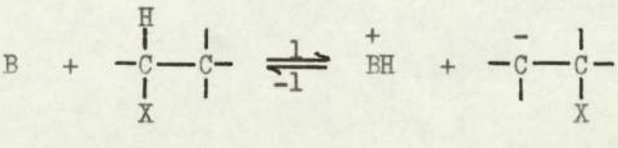
$$\mathrm{B}\quad \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \longrightarrow \mathrm{BH^+} + \mathrm{{>}C{=}C{<}} + \mathrm{X^-}$$

The reagent B is basic and removes a proton from the beta carbon atom of the substrate; the electron attracting group X synchronously splits off. The reaction is second order, first order in each component.

As the postulated mechanism involves a concerted process, one would expect stereospecificity to be a requisite characteristic of this type of elimination.

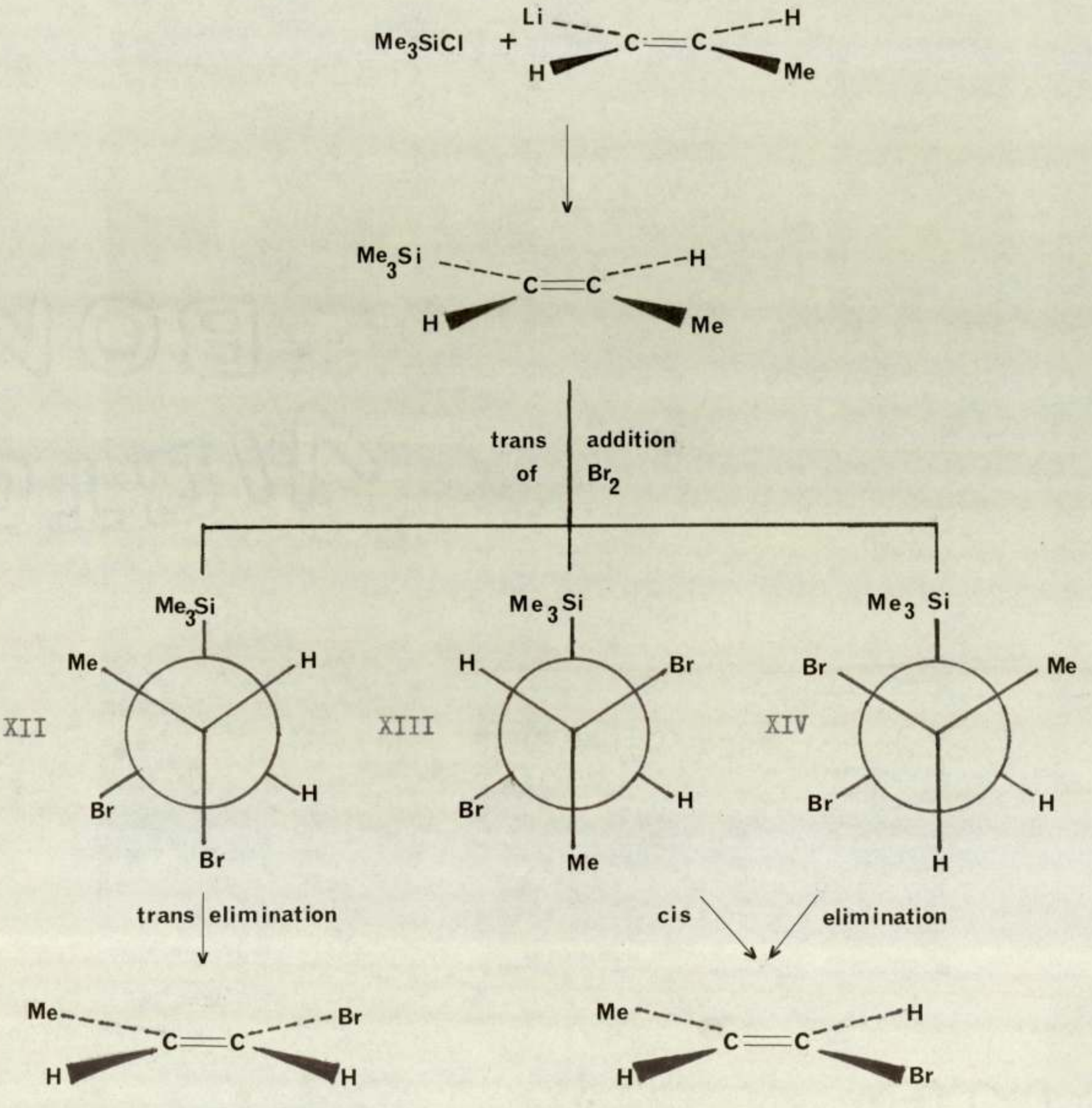
The E1cB mechanism

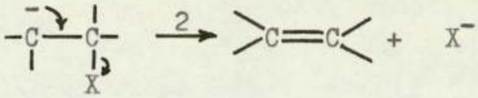
This is another mechanism that is consistent with second order kinetics and involves a two-step process:



$$\mathrm{B} + \mathrm{{-}\overset{H}{\underset{X}{C}}{-}\overset{|}{\underset{|}{C}}{-}} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{\overset{+}{BH}} + \mathrm{{-}\overset{-}{\underset{|}{C}}{-}\overset{|}{\underset{X}{C}}{-}}$$

Flow diagram showing the synthesis of 1-bromopropenes through erythro-1,2-dibromopropyltrimethylsilanes from trimethylchlorosilane and 1-lithiopropene



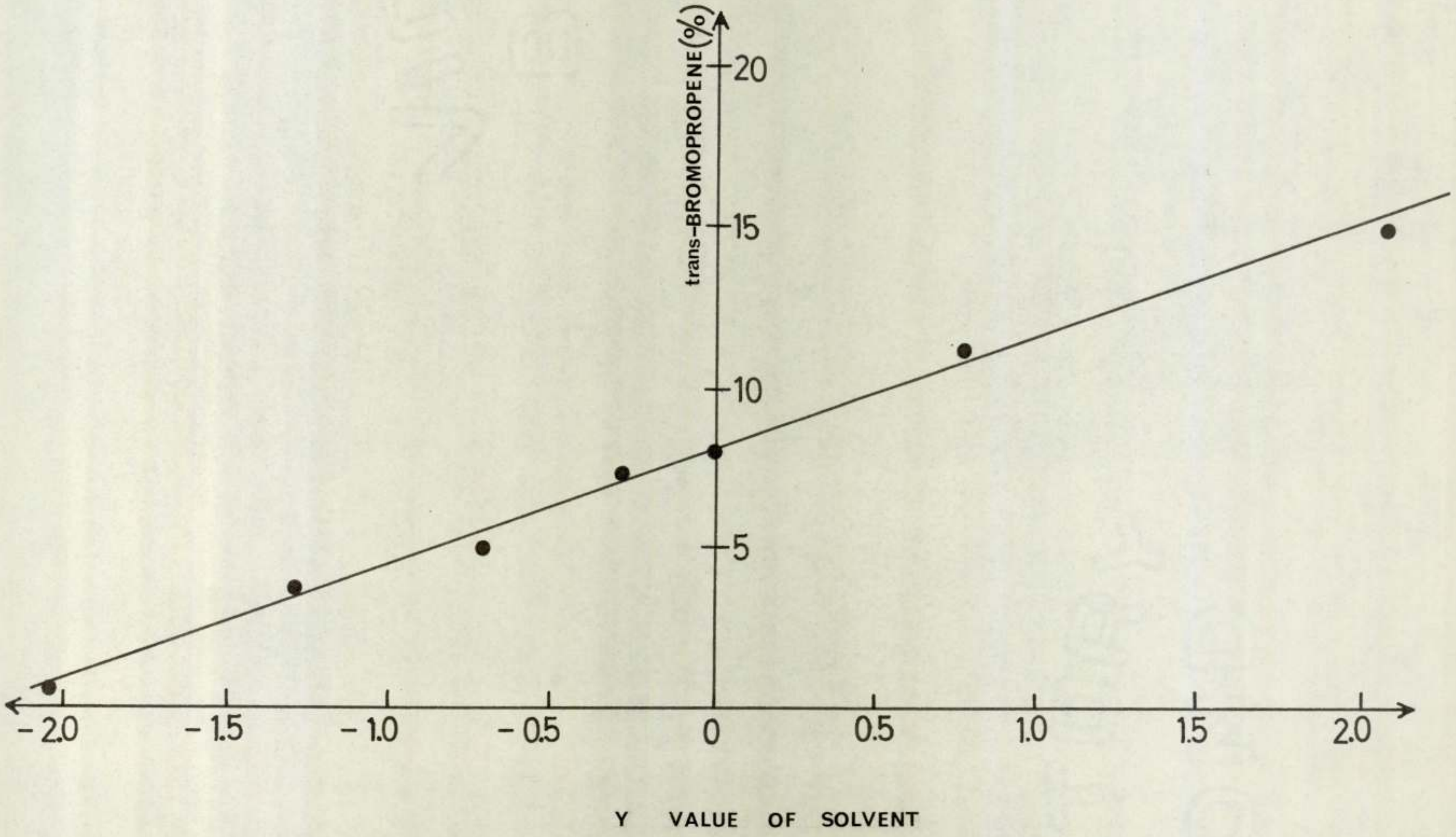


The proton is first abstracted by the base, followed by a unimolecular ejection of X^- from the conjugate base of the substrate. It was originally assumed that step -1 was much faster than step 2 and so the first stage of this process - the formation of the carbanion from the substrate - was in equilibrium. The stereochemistry of the ElcB elimination, proceeding as it does via a free carbanion, may be discussed in similar terms to the El mechanism.

With a knowledge of the possible stereochemical routes of each of these types of mechanism, an attempt has been made to fit the experimental evidence to one of these routes. The desilicohalogenation of XII, XIII or XIV may result in the formation of cis and/or trans-1-bromopropenes. Therefore from a study of the isomer ratios of the products, it is possible to deduce the stereochemical path of elimination. The elimination reaction was studied in various solvents of differing ionic strength, as measured by the Grunwald Winstein Y values.[32] Table I illustrates the results obtained. It is evident that the path leading to cis-1-bromopropene is favoured, that is the elimination has taken place in a predominantly trans fashion. If the percentage of trans-1-bromopropene is plotted against the Y value of the solvent, there is apparently a linear relationship between these two values, the significance of which has not been fully established.

Figure I

Variation of Y value with trans-1-bromopropene (%)



However, the important observation is that the elimination has taken place in a trans fashion, a result which conflicts with the mechanisms proposed by some previous investigators.[11, 12a, 16, 18]

TABLE I

Solvent mixture		Y value	1-Bromopropene product ratio		
			cis	:	trans
Ethanol : Water -	100:0	-2.033	99.7	:	0.3
Ethanol : Water -	95:5	-1.287	97	:	3
Ethanol : Water -	90:10	-0.747	95	:	5
Methanol : Water -	90:10	-0.301	93	:	7
Ethanol : Water -	80:10	0	92	:	8
Formic acid : Acetic acid -	50:50	0.757	88.5	:	11.5
Formic acid : Water -	100:0	2.054	85	:	15

Variation in solvent Y value[32] with 1-bromopropene product ratio

(see also Figure I)

The mechanism proposed by Sommer,[12a] which is analogous to the ElcB mechanism, involves a carbanion intermediate which is unlikely to retain its configuration. On this basis, therefore, a stereospecific elimination would not be expected. Furthermore, as there is no reason to suppose that the trimethylsilyl group would add nucleophilically to the chloroethyl carbanion, the proposal does not meet with the demands of microscopic reversibility.

Other criticisms of this mechanism have been expressed by Bott et al., who regard the evidence as inconclusive for the following reasons:

i) The rate-determining step suggested involves a simple ionization of the Si-CH_2CH_2Cl bond. There is no reason to believe that the chloroethyl carbanion would be particularly stable, and solvolytic cleavages of carbon-silicon bonds involving formation of carbanions which are probably much more stable not only take place much more slowly than the decomposition of the compound beta-chloroethyltrimethylsilane in neutral solution, but are also strongly base-catalysed.

ii) The proposed mechanism implies that the chlorine atom does not participate directly in the rate-determining step, and thus that the rapid rate of solvolysis is only coincidently connected with the well-known ease of decomposition of beta-chloroalkyl silicon compounds under a variety of conditions.[6, 27]

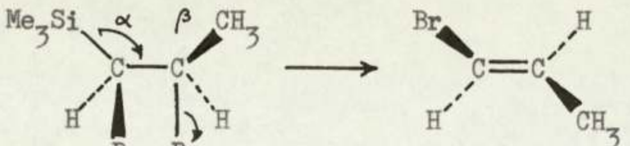
iii) If the proposed mechanism were correct, then beta-chloroethyltrimethylsilane should react in a similar way to 2,2-dimethyl-4-chlorobutane. Although no reports of the solvolysis of the latter could be found, it seems unlikely to undergo the ready fragmentation observed for the silicon compound since, for example, it can be made from a reaction which is, in effect, the reverse of the fragmentation, namely from t-butyl chloride and ethylene in presence of aluminium chloride.[33] (In the presence of aluminium chloride, the compound beta-chloroethyltriethylsilane decomposes rapidly to ethylene and triethylchlorosilane.[27])

The four-centre intermediate may also be excluded as it would require a predominantly cis elimination to account for its stereochemistry. Baughman's thesis, which proposes a cyclic intermediate, is in partial agreement with the stereochemical results.

If the stereochemistry alone were taken as evidence of a particular mechanism, the E2 type elimination may be suggested as a possible explanation of the stereospecificity. This synchronous mechanism requires a stereospecific trans (or more recently, cis[34]) elimination. However, the evidence from the kinetic results cannot be reconciled with an E2 mechanism.

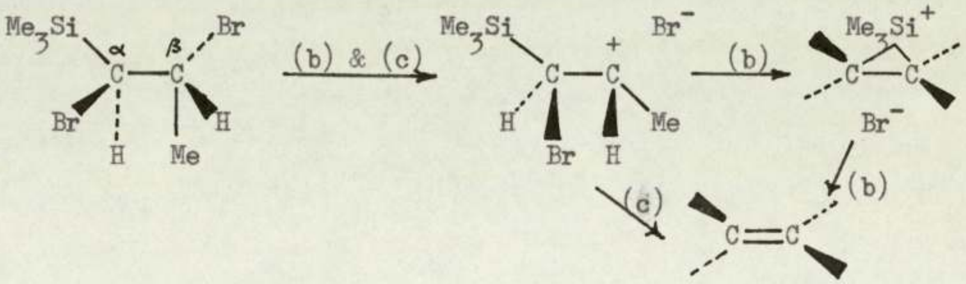
Cram has postulated four mechanisms,[35] which are essentially similar, in order to explain trans-stereospecificity in E1 reactions. The Cram treatment has been applied to the molecule in question and the mechanisms are delineated below:

Mechanism (a)



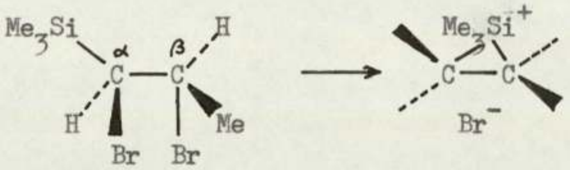
Mechanism (a) involves a bimolecular one-stage process, in which a solvent molecule removes the trimethylsilyl group from the alpha carbon at the same time that an anion leaves from the beta carbon. In this mechanism trimethylbromosilane could be lost from the molecule, only from that conformation about the carbon-carbon bond that places trimethylsilyl and bromine groups trans to one another. This is caused by the necessity for the pair of electrons initially in the carbon-silicon bond to displace Br^- from the rear, as in a Walden inversion type displacement reaction. The difference between the mechanism proposed, and the conventional E2 mechanism, is that the latter reaction is provoked by the attack of strong base on the carbon-silicon bond, the transition state being stabilized by the formation of two new covalent bonds. In the former mechanism the breaking of the carbon-bromine bond to form a stable anion initiates the reaction.

Mechanisms (b) and (c)



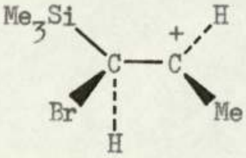
Mechanism (c) is consistent with the stereospecificity only if several assumptions are made. The ion pair involved as an intermediate in the mechanism would have to be capable of holding configuration at the beta carbon, and the electron pair initially in the carbon-silicon bond, would have to become attached to the beta carbon only when trimethylsilyl and bromine groups were trans to one another.

Mechanism (d)



In Mechanism (d), the reason for the trans course lies in the necessity for the trimethylsilyl group to become bonded at the rear of the beta carbon, the latter becoming inverted as Br$^-$ is displaced. The trimethylsilyl bridge would be capable of participating in the displacement of bromine from the beta carbon, and is responsible for the stereospecific mechanism.

If Table I is examined, the dependence of the product ratio on ionic strength becomes apparent. Taking formic acid, for example, as a solvolysis medium, some contributions from ions of a classical type are necessary in order to account for the non-stereospecific products obtained. Thus contributions from ionic intermediates (or transition states) of the following type must be invoked:



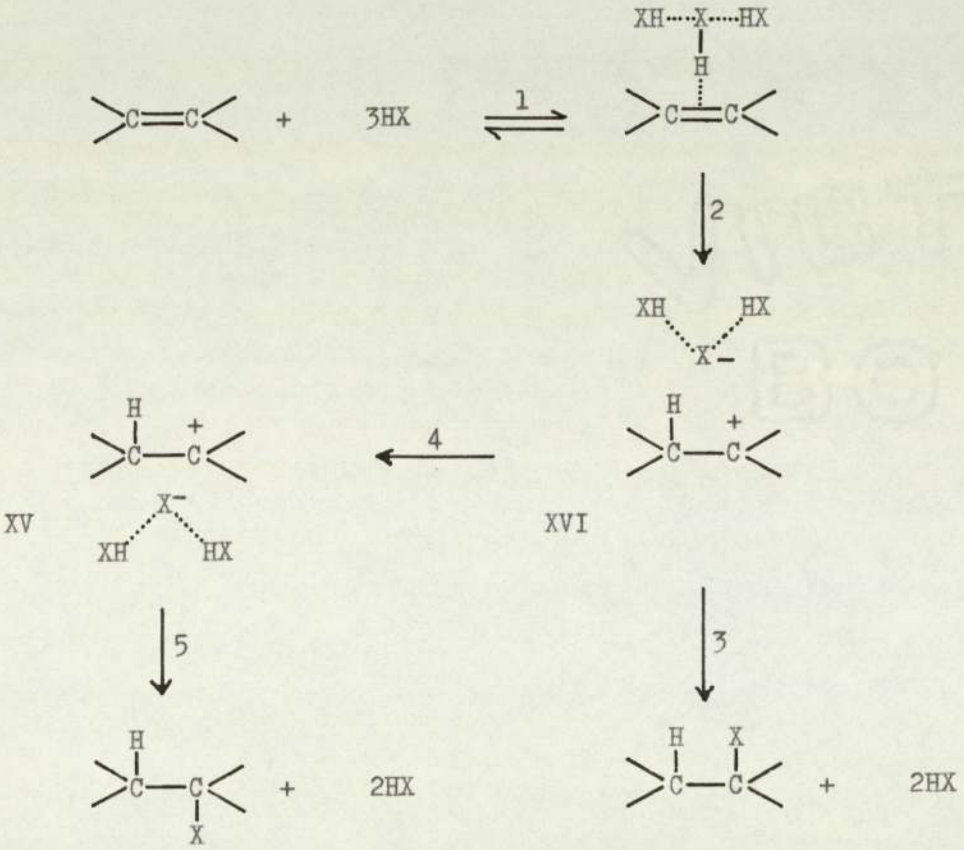
This free carbonium ion is postulated[36] to be electrostatically solvated by the surrounding solvent shell. Collapse of this solvent shell will lead to non-stereospecific products. The more ionizing the solvent and the more stable the carbonium ion, the longer will be the lifetime of the intermediate. Thus the reaction becomes less stereospecific. Mechanism (b) seems to account most satisfactorily for the observed facts. The stereochemical study thus implies the following as possible explanation for the mechanism. An initial rate-determining breakage of the carbon-bromine bond which may be assisted by the trimethylsilyl group, followed by the formation of a non-classical intermediate (or transition state) together with some contributions from a classical structure. The collapse of these intermediates (or transition states) then gives rise to the olefin.

Further evidence in support of an intermediate (or transition state) in which the trimethylsilyl group interacts with the developing positive charge, is found in the tendency for the trimethylsilyl group to migrate. This evidence is fully discussed in Chapter IV.

3. Addition of Deuterium bromide to Trans-1-propenyltrimethylsilane and the Desilicohalogenation of the Resulting Material

At the outset of this study it was hoped to be able to prepare a molecule of known stereochemistry, by the addition of deuterium bromide to trans-1-propenyltrimethylsilane. As the investigation progressed it became apparent that deuterium bromide did not add to propenyltrialkylsilanes stereospecifically. Nevertheless, an attempt was made to elucidate the stereochemistry of this addition. The procedure adopted by Dewar and Fahey[37] was followed, the results of which are presented below. Although the stereochemical course of addition of halogen acids to unsaturated systems[38] has been studied in detail, it was initially assumed that trans addition predominated,[39] but evidence has recently been accumulating which suggests that the ionic addition halogen acids may proceed in a cis fashion.[37, 40]

The scheme proposed by Dewar and Fahey, and criticised by de la Mare,[38] accommodates all the evidence in terms of a reaction mechanism involving a classical carbonium ion, formed in the rate-determining step as an ion pair with the halide ion.

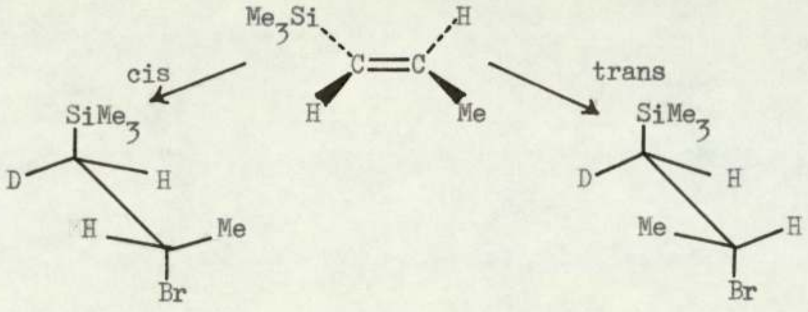


Three molecules of hydrogen halide associate with the olefin to form a loose complex in a reversible step 1. Step 2 is rate-determining and leads to an ion pair XVI; collapse of XVI leads exclusively to cis adduct. Alternatively, XVI can rearrange to the isomeric ion pair XV; collapse of XV leads to trans adduct. In order to explain cis addition products, the postulation that step 3 proceeds at a faster rate than step 4 has to be made.

The direction of the ionic addition of hydrogen halides to vinyl substituted silanes has been studied,[27, 41] and an explanation for the reverse Markovnikov addition to certain silanes has been given. It is suggested that the inductive effect of the trialkylsilyl group is overcome by a tautomeric effect, and that several canonical forms make contributions to the structure, one of which is presented below:

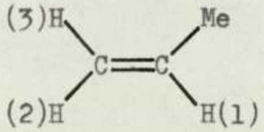
$$R_3\overset{-}{Si}{=}CH{-}\overset{+}{CH_2}$$

Thus the addition of deuterium bromide to trans-1-propenyltrimethylsilane may yield two products, depending on whether the addition is cis or trans:



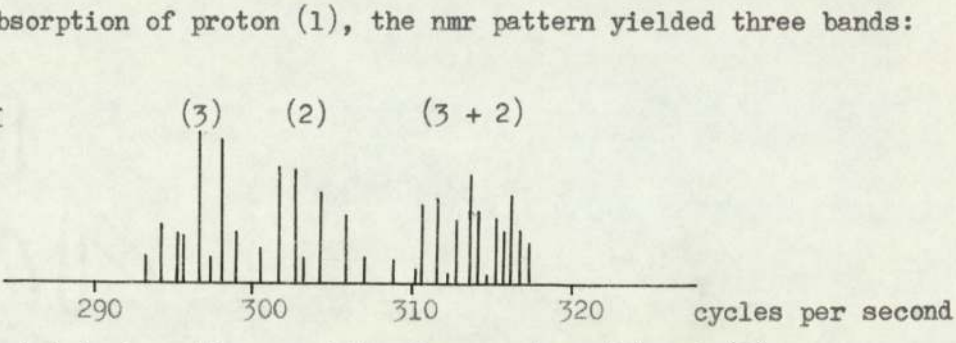
The addition products were treated with absolute ethanol and under these conditions it was assumed (from the evidence presented in the previous section) that stereospecific trans-desilicohalogenation would take place. The cis addition to trans-1-propenyltrimethylsilane followed by elimination gives trans-1-deutero-1-propene; whilst the trans addition followed by elimination yields cis-1-deutero-1-propene.

The ratio of cis to trans-deuteropropene was obtained from a study of the nmr spectrum (contamination by undeuterated propene was not greater than 3%). The nmr spectrum of propene has been analysed.[42]



The absorptions in the vinylic region consist of: sixteen lines arising from proton (1) which occur at lowest field; then a closely-spaced group of lines at slightly higher field, which constitutes one member of a doublet and arises from proton (3); the next complex arises similarly from proton (2); the band at highest field in the vinylic region includes members of the doublets from protons (2) and (3). Thus, neglecting the absorption of proton (1), the nmr pattern yielded three bands:

Figure II



Calculated absorptions arising from protons (2) and (3)

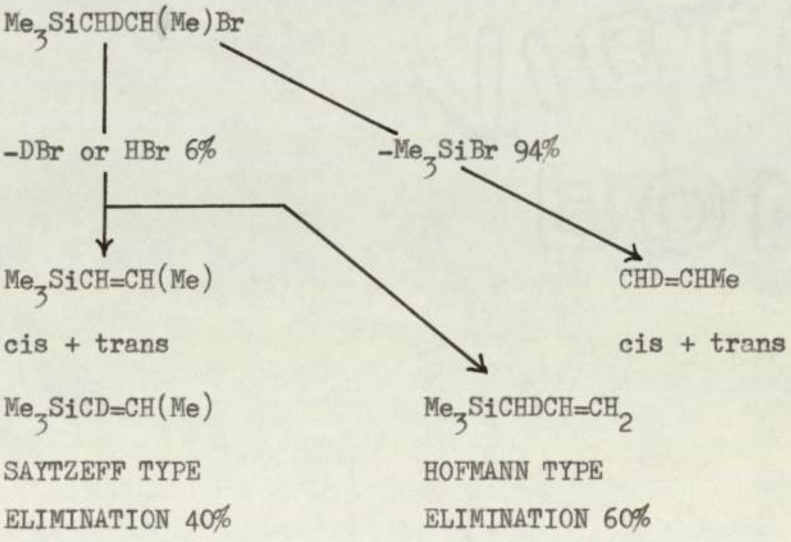
This is represented in Figure II as three lines (3), (2) and (3 + 2), due to the absorptions of the protons with the same designations. By using a simplified formula,[43] involving chemical shifts and coupling constants, it is possible to calculate the contributions of each of these protons, from the intensity of the bands in this region. Thus total "quantity" of proton (3) is the intensity of band (3) plus a portion of band (3 + 2), whose ratio is 65.86:32.24. Similarly for proton (2), where the ratio of band (2) to the portion of band (3 + 2) is 62.47:42.43. The observed intensity of the three bands was in the ratio 3.29 (3): 1.19 (2):2.37 (3 + 2). From the calculated ratio, 1.61 parts of band (3 + 2) can be attributed to proton (3), and 0.81 parts attributed to proton (2). This results in a theoretical total of 2.42; the observed result was 2.37, which is within experimental error.

The ratio, therefore, of proton (3) to proton (2), which is the ratio of trans to cis deuterated isomers, is calculated to be approximately 70:30. This result suggests that the addition of hydrogen halides to vinyl silanes, although in no sense stereospecific, favours a cis addition path, and is consistent with the interpretation rendered by Dewar and Fahey for similar systems.

4. Dehydrohalogenation of Beta-halogenoethyltrialkylsilanes

An attempt was made to eliminate hydrogen halides from beta-halogenoethyltrialkylsilanes. By this means it was hoped to be able to gain further information concerning the stereochemistry of hydrogen halide addition to vinyl silanes. A similar procedure to that described in the previous section was employed in aiming to confirm this result.

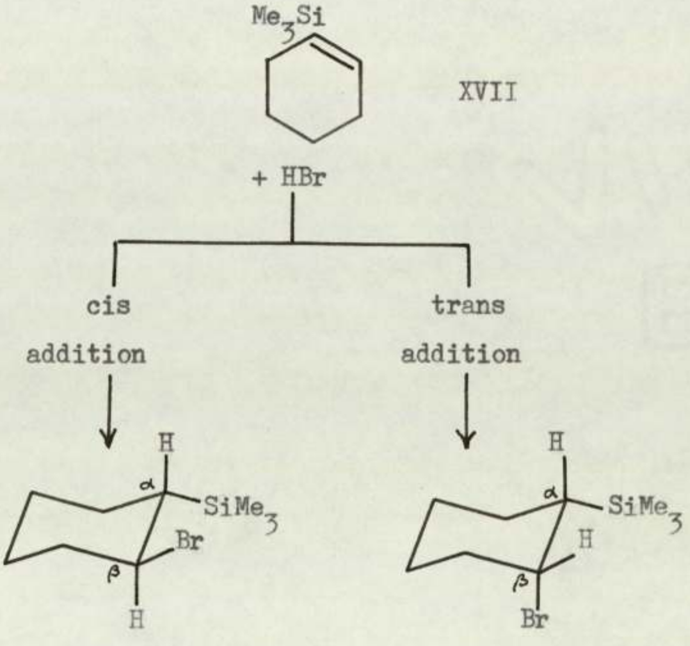
Unlike the beta-halogenoethyltrichlorosilanes,[6, 7, 44] beta-halogenoethyltrialkylsilanes have a low thermal stability and it was this fact that led to the abandonment of this particular facet of the work. However, some time was spent examining the products of the elimination reaction with quinoline. Deuterium bromide was added to trans-1-propenyltrimethylsilane and the product subjected to an elimination process with dry quinoline. The following flow diagram provides the information that was obtained:



The major portion of the reaction is presumably due to the thermal elimination process (reaction carried out at 90-110°C). Due to the fact that reaction in the desired direction was limited, only small yields of the required products were obtained. It was therefore decided that any conclusions based on these minor reaction products would be meaningless.

5. Addition of Hydrogen Bromide to 1-trimethylsilylcyclohex-1-ene (XVII)

Initial attempts to clarify the stereochemistry of addition were made using the cyclic molecule - (XVII). By observing the nmr spectrum of the product obtained by the addition of hydrogen bromide, it was hoped that the stereochemistry of the molecule could be elucidated:



XVII

XVIII

XIX

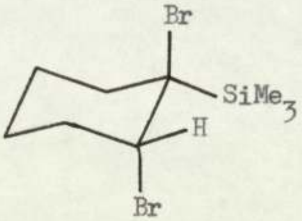
1-trimethyl-2-bromocyclohexane was therefore prepared by the addition of hydrogen bromide to XVII. Thus cis addition produces isomer XVIII; whilst trans addition produces isomer XIX. The nmr absorption of the proton situated on the beta carbon atom is at sufficiently low field to enable its coupling constants to be determined. The coupling of this proton with the proton on the alpha carbon would provide information leading to the stereochemistry of addition. The protons in compound XVIII, being trans, should have relatively large coupling constants; whereas the protons in compound XIX, having a cis configuration, should have relatively small coupling constants. However, the results obtained from the nmr spectrum were inconclusive. It was postulated that the spontaneous decomposition of the hydrobrominated material could be responsible for the complex nature of this spectrum. The spontaneous decomposition of this compound has already been observed by Bennett,[11] who suggested that it may be due to the intervention of a four-centre intermediate.

In order that this type of decomposition may be possible, the silicon, alpha carbon, beta carbon and bromine atoms must become coplanar. This coplanarity will only be achieved with some difficulty. However the coplanar arrangement of these atoms is less probable for compound XVIII than it is for compound XIX. This can be explained by the fact that in compound XIX the bonds bearing the bromine and silicon atoms are cis (ea); the movement of these two bonds from a dihedral angle of 60° to a dihedral angle of 0° leads to a flattening of the chair, against a relatively soft potential energy barrier. But in compound XVIII the bonds in question are trans (ee); the movement of these bonds from a dihedral angle of 60° to 0° would require an increased puckering of the chair, against a relatively steep potential energy barrier.[45] In this connection it is of interest to note that Reppe and coworkers[46] in their synthesis of bicyclo(4.2.0.)octane, starting from cyclooctatetraene, were able to prepare only the cis isomer. The stable nature of this bicyclic structure was also noted. Thus, if it is postulated that the decomposition proceeds through a four-centre intermediate, compound XIX must be assumed to have been formed predominantly, hence implying a trans addition of hydrogen bromide.

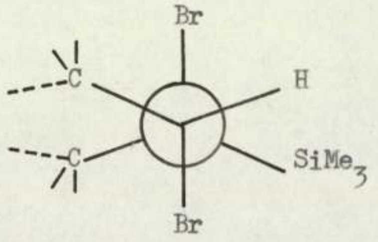
It would seem that a more likely explanation of the spontaneous decomposition lies in the fact that the initial addition has taken place in a predominantly cis manner, and the subsequent elimination process is trans. The cis addition is consistent with the evidence presented by Dewar and Fahey and also with that put forward in Section 3 of this chapter, whilst the trans elimination is coincident with the observation made in Section 2.

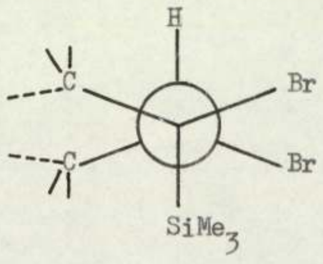
6. Addition of Bromine to 1-trimethylsilylcyclohex-1-ene (XVII)

In attempting to gain still further stereochemical evidence for trans-desilicohalogenation from beta-halogenoalkyltrialkylsilanes, bromine was added to compound XVII, and on the basis of the arguments stated in Section 1 of this chapter, addition was assumed to be trans, thus yielding compound XX:



XX





This leads to a cis arrangement of bromine and trimethylsilyl groups. Compound XX was not observed to decompose over a period of some days, and in this case decomposition was not expected. The trimethylsilyl and bromine substituents are locked in the molecule in such a way that a trans arrangement of these groups is impossible. Therefore decomposition does not occur as readily as in the previous case (see Section 5). This result again indicates that the trimethylsilyl group and the halogen atom will eliminate only when they are in the trans configuration.

--o--

III. REARRANGEMENT

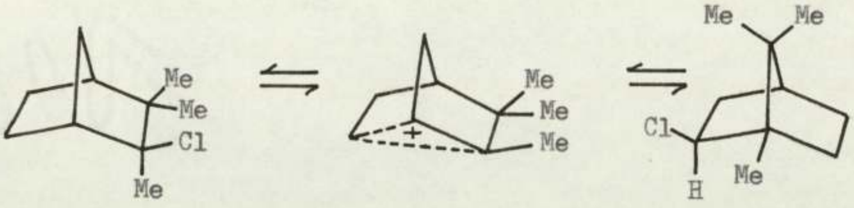
1. Introduction

Many criteria have been cited as indicative of the intervention of a non-classical carbonium ion in solvolytic reactions,[47] one of these being that skeletal rearrangements occur during the reaction. By analogy with the non-classical carbonium ion system, if the silacyclopropenium mechanism is correct, it seems possible that rearrangement might either accompany the elimination reaction or occur under milder conditions.

This elimination process occurs so readily in beta-halogenoalkyltrialkylsilanes that it would be difficult to establish that rearrangement does occur in this system. However, it has been possible to establish that rearrangement takes place in some reactions of the related beta-hydroxyalkyltrialkylsilanes.

2. Rearrangements involving carbon

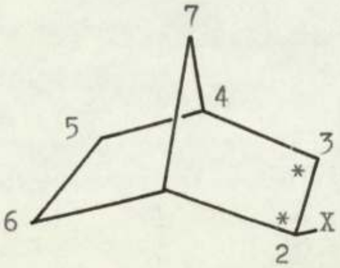
In a paper published in 1939, Nevell, de Salas and Wilson[48] advanced the hypothesis that a mesomeric, bridged ion (XXI) is involved in the rearrangement of camphene hydrochloride to isobornyl chloride, which is the classic example of the Wagner-Meerwein rearrangement. According to following sequence, camphene hydrochloride is converted to a non-classical carbonium ion without the intervention of a classical carbonium ion:



XXI

The concept of a non-classical ion was also taken up by Winstein and Trifan[49] to explain the reason why exo-norbornyl p-bromobenzenesulphonate undergoes acetolysis 350 times faster than its endo isomer, and yields as the product of substitution almost exclusively exo-norbornyl acetate.

The structural rearrangement required by the intervention of the bridged ion was subjected to experimental scrutiny by Roberts, Lee and Saunders.[50] Exo-2-norbornyl brosylate, labelled with ^{14}C at the 2- and 3- positions (see molecule XXII), was subjected to acetolysis and the product, exo-2-norbornyl acetate, was systematically degraded:



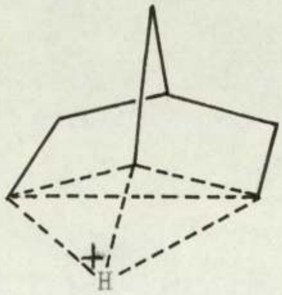
XXII

TABLE II

Calculated for Bridged Ion	^{14}C Activity (%) at			
	C(2) + C(3)	C(1) + C(4)	C(7)	C(5) + C(6)
Bridged ion	50	25	25	0
6←2 hydride shift	50	0	0	50
3←2 hydride shift	100	0	0	0
Nortricyclonium ion (XXIII)	33	17	17	33
55% (bridged ion) 45% (XXIII)	42.5	21.25	21.25	15
Found	40	23	22	15

Calculated and observed ^{14}C activity (%) for the acetolysis of labelled exo-2-norbornyl brosylate

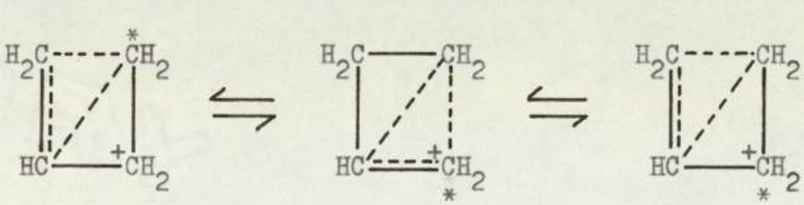
If the racemization of optically active brosylate results, either from intervention of the bridged ion, or from rapid equilibration of a classical 2-norbornyl cation with its enantiomer by means of a Wagner-Meerwein migration of C(6) from C(1) to C(2), 25% of the total initial ^{14}C should be found at each of the 1-, 2-, 3-, and 7- positions, in the acetate produced. The experimental result is presented in Table II. This result clearly establishes that the complex racemization attending solvolysis of the exo-brosylate, cannot result primarily from a 6↔2 hydride shift or from a 3→2 hydride shift. However, the presence of ^{14}C at the 5- and 6- positions establishes that 6↔2 hydride migrations do occur to a significant extent during this reaction. To account for the observed ^{14}C distribution, Roberts suggested the intervention of an even more highly symmetrical ion than the bridged ion - the nortricyclonium ion (XXIII):



XXIII

Another class of compounds in whose solvolysis the intervention of non-classical ions has been postulated are derivatives of cyclopropylmethyl alcohol. The evidence for this is that the solvolyses of these compounds frequently yield rearranged products as for example, cyclobutyl and 3-butenyl derivatives. Thus the acetolysis of cyclopropylmethyl chloride yields cyclopropylmethyl and cyclobutyl acetates in the ratio 2.6:1; a small amount of 3-butenyl acetate and a 1.7:1 mixture of cyclobutyl and 3-butenyl chlorides.[51]

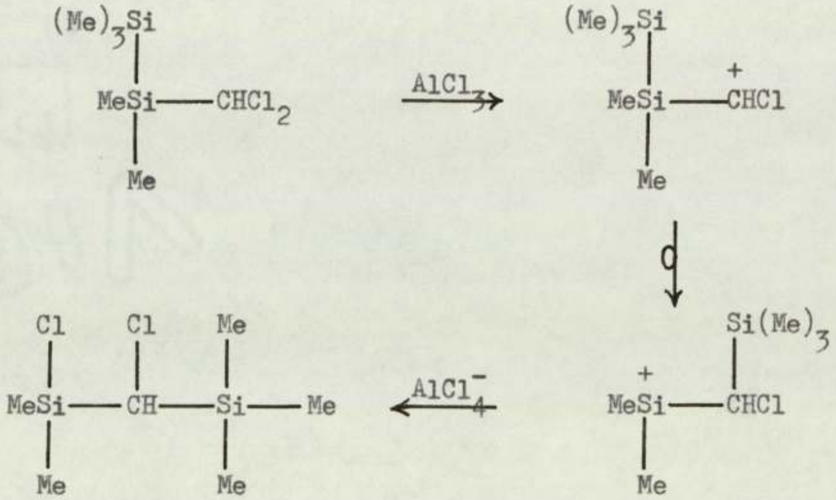
An experiment with specifically deuterated cyclopropylmethyl chloride indicated considerable rearrangement in the cyclopropylmethyl chloride isolated from the partly solvolysed reaction mixture.[52] The solvolysis of this chloride also proceeds at enhanced rates (one of the criteria[47] used for postulating non-classical ions). These results suggest that the ionization of cyclopropylmethyl, cyclobutyl and 3-butenyl compounds yields the same ion, or readily interconvertible ions which may either react with solvent or reform chloride or toluene p-sulphonates, by ion pair return. Roberts and coworkers have favoured the intervention of an equilibrating set of cyclobutonium ions:



These were preferred to the single tricyclobutonium ion, because in certain non-solvolytic reactions there was incomplete equilibration of methylene groups.

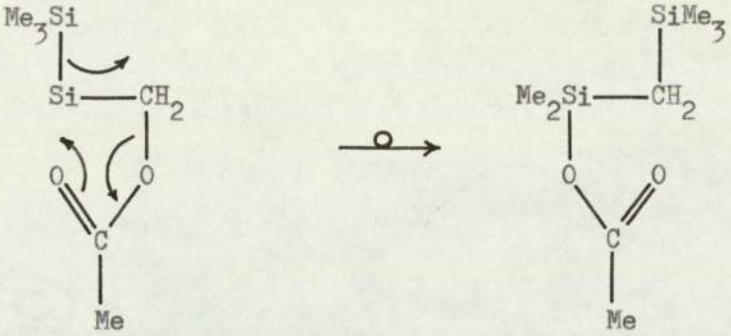
3. Rearrangements involving silicon

Rearrangements are not without precedent in the silicon field. Rearrangements involving migration of alkyl,[53, 54, 55, 56,] aryl[16] and trialkylsilyl groups[57, 58, 59] from silicon to carbon have been noted. Kumada and Ishikawa[58] observed that the migration of a trimethylsilyl group from silicon to carbon, took place in the presence of aluminium chloride at 70-80°C:



A similar migration of the trimethylsilyl group from carbon to oxygen, with a variety of catalysts, has also been reported.[59]

A further example of intramolecular rearrangement has been shown to occur by Kumada et al. They postulate a cyclic transition state as the intermediary for the 1,2-migration of the trimethylsilyl group from silicon to carbon:[60]



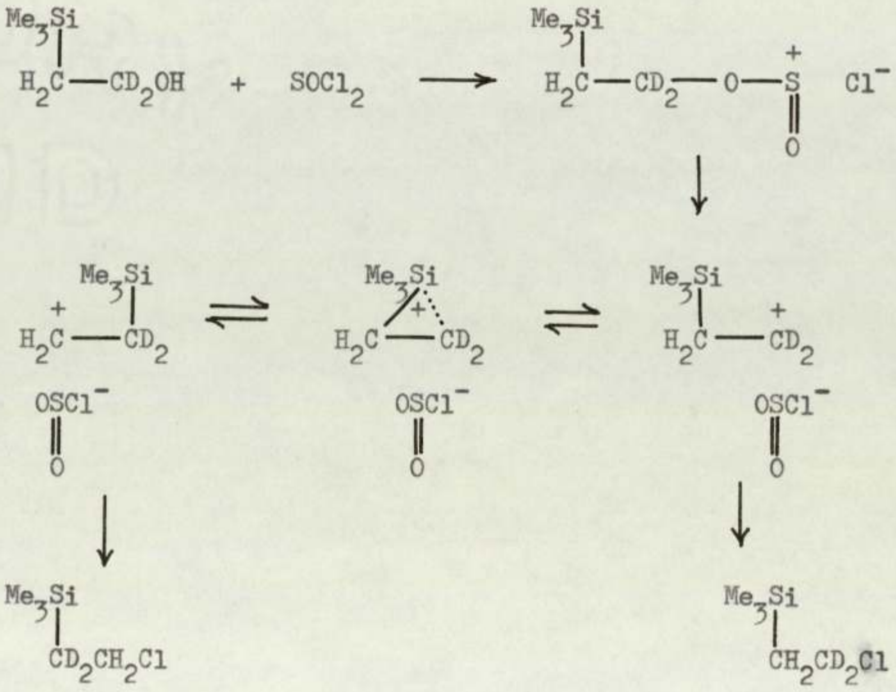
The migration of the trimethylsilyl group of beta-hydroxyethyltrimethylsilane was noted in the reaction of this compound with phosphorus tribromide. A similar migration was also observed when thionyl chloride was used. The fact that rearrangement was occurring in these reactions was established from the nmr spectra of the resulting materials; beta-dideutero-beta-hydroxyethyltrimethylsilane was synthesised and analysed by nmr. The spectrum obtained showed the expected pattern of absorptions, consisting of a singlet at 3.9 p.p.m. of intensity one (due to the proton of the hydroxyl group); a singlet at 0.9 p.p.m. of intensity two (due to the protons of the methylene group attached alpha to the silicon atom); and finally a singlet of intensity nine due to the trimethylsilyl group. However, on reaction of this alcohol with phosphorus tribromide, instead of the expected singlet absorption at approximately 1.3 p.p.m. and the trimethylsilyl group absorption, a third singlet at 3.6 p.p.m. of similar intensity to the absorption at 1.3 p.p.m. was observed. The ratio of the intensities of these two singlets with respect to the trimethylsilyl group was 2:9.

It was also noted that these two peaks were slightly broader than usual and on further examination it was found that each singlet consisted of a series of lines, with a coupling of 1.4 cycles/second between them. The magnitude of the ratio of the coupling constants of the protonated to the deuterated materials, suggested that the value of 1.4 cycles/second may be considered to be a result of protium-deuterium coupling. The relative intensity of each of these singlets also made it possible to calculate the percentage of each isomer formed. This result showed that the quantity of alpa-deuterated compound produced (45%) was slightly less than the quantity of beta-deuterated compound (55%).

In this connection it is of interest to note the work of Roberts and Mazur,[51] who suggest that the prediction of the product obtained from a given carbonium ion reaction, depends on the knowledge of several factors, one of the more important ones being that of the relative carbonium ion stabilities. In the present study it is probable that the carbonium ions $Me_3SiCH_2CD_2^+$ and $Me_3SiCD_2CH_2^+$ are formed. In this case one could predict that the positive charge on the beta-deuterated carbonium ion would be stabilized by the deuterium atoms through inductive and hyperconjugative effects (see Chapter IV), to the extent of approximately 10-12% over the non-deuterated molecule.

Roberts and Mazur[51] make a further observation on the reactions of alcohols with thionyl chloride. They state that these reactions generally proceed without rearrangement, but in some cases for example 2-methyl-2-phenyl-1-butanol, rearrangements do occur. These workers found that cyclobutanol and cyclopropylcarbinol reacted with thionyl chloride to give mixtures of chlorides, and that similar mixtures were obtained from each alcohol. They also state that their results indicated that the reaction proceeds irreversibly (or with rearrangement), and that similar considerations apply to the reactions with phosphorus tribromide.

A reaction scheme is suggested to account for the migration observed in the case being studied:



A similar scheme may be drawn for the reaction with phosphorus tribromide, in which the ratio of alpha to beta-deuterated compounds is identical with that of the reaction with thionyl chloride. In order to account for the rearranged products observed from the nmr spectrum, it may be supposed that a cyclic intermediate (or transition state) must be postulated.

A related rearrangement occurs on reacting nucleophilic reagents with acetoxymethyldisilanes,[61] which does not occur with the methoxy compounds:

$$\mathrm{MeCO_2^-} + \mathrm{(Me)_5Si_2CH_2Cl} \xrightarrow{\mathrm{MeCO_2H}}$$

$$\mathrm{(Me)_5Si_2CH_2O_2CMe} \xrightarrow{\circ} \mathrm{(MeCO_2)(Me)_2SiCH_2Si(Me)_3}$$

It would appear that these rearrangements are promoted by the interaction of silicon with the developing positive charge on the beta-carbon atom. Evidence that this is the case may be deduced from the fact that the methoxymethyldisilanes do not rearrange. The halogens and acetoxy groups are good leaving groups and bond breaking would probably progress considerably in the transition state, with stabilization due to interaction with the silicon atom gaining importance. The methoxy group is a poor leaving group, and it is probable that bond stretching would not occur sufficiently to allow interaction with the silicon atom to become important; thus no rearrangement occurs.

The occurrence of these rearrangement reactions provides evidence that silicon interacts with the developing positive charge on the beta-carbon atom, and thus further substantiates the proposal that solvolysis of beta-halogenoalkyltrialkylsilanes proceeds via a cyclopropenium intermediate (or transition state).

--o--

IV. SECONDARY ISOTOPE EFFECTS

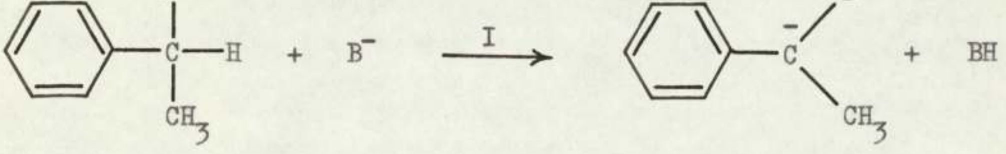
Definition

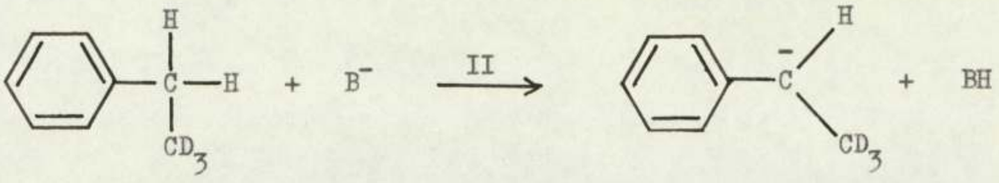
The deuterium secondary isotope effect may be defined as the perturbation on a property or process, caused by the substitution of hydrogen by deuterium, on atoms in the molecule other than those linked by the bond to the nucleide in question.

1. Introduction

It was initially assumed that significant isotopic differences in equilibrium or rate constants, were to be expected in reactions in which a bond to an isotopic atom was either broken or formed. It was subsequently found[62] that deuteration beta to the leaving group could affect the rate of reaction. Such isotope effects on rate and equilibrium constants were termed secondary.

A further subdivision of these secondary isotope effects has also been defined.[63] The following example illustrates this division:





Reaction I exemplifies a secondary isotope effect of the first kind, whereas reaction II is of the second kind, the criterion being whether or not bonds to isotopic atoms have undergone spatial reorientation.

Certain physical properties have long been recognised as being closely related to chemical reactivity. Properties such as dipole moment, molecular refraction, optical activity, nmr and nuclear quadrupole coupling constant, serve as probes into the electronic environment of the nucleus. From a study of the effect that deuterium substitution has on these properties, one may conclude that deuterium bonded to carbon is effectively more electropositive but less polarizable than protium.

The principal factor responsible seems to be the anharmonicity of the vibrations involving motion of the hydrogen atoms, which leads to different average bond lengths and angles in deuterated and protonated molecules. Also there is a contribution from the greater mean square amplitude of the protium motions, (since the motions of the protonated molecules lie above the deuterated molecules, in the potential energy well). Although these effects are vibrational in origin and can be dealt with in vibrational terms to a limited extent, they can be regarded as genuine substituent effects for all practical purposes. Thus the effect of CD_3 relative to CH_3 on a given property is qualitatively of the same nature as that of ethyl or tert-butyl, and may be discussed in similar terms.

2. Theoretical Considerations

A starting point in the study of the effect of isotopic substitution on reaction rates must be furnished by a theoretical model of chemical reactions. A theory is required which makes use of a detailed description of the roles of the individual atoms, and the forces exerted by the electron cloud. The absolute reaction rate theory presented by Glasstone, Laidler and Eyring[64] has proved very useful for this case.

The transition state theory assumes that there is a single potential energy surface, along which the reaction takes place. For the usual reaction there will be a barrier between the part of co-ordinate space corresponding to reactants, and the part of space corresponding to products. The reaction will then take place over the path corresponding to the lowest barrier. The transition state is located at the top of the barrier along the decomposition path, and in general will be stable along all degrees of freedom except along the path of decomposition. Thus the transition state theory leads to the following expression for the rate equation constant:

$$\text{Rate} = \frac{kT}{h} \text{x} K' \qquad \ldots\ldots 1.$$

where k is the Boltzmann constant, T is the absolute temperature, h is

Planck's constant, x is the transmission coefficient, and K' is the equilibrium constant between the activated state molecules and the reactants.

By using statistical mechanics, K' may be expressed in terms of partition functions of the activated complex and reactants:

$$K' = \frac{Q^*}{Q_A Q_B} \qquad \text{..... 2.}$$

Thus one is effectively dealing with an equilibrium reaction, an example of which may be expressed as follows:

$$\begin{aligned} AH + R &\overset{K'_H}{\rightleftharpoons} BH + S \\ AD + R &\overset{K'_D}{\rightleftharpoons} BD + S \end{aligned} \qquad \text{..... 3.}$$

The ratio of the equilibrium constants representing the isotope effects is:

$$\frac{K'_H}{K'_D} = K'_{Ex} \qquad \text{..... 4.}$$

where K'_{Ex} is the equilibrium constant of the isotopic exchange reaction:

$$AH + BD \rightleftharpoons AD + BH \qquad \text{..... 5.}$$

The evaluation of such an equilibrium constant has been discussed[65] and may be expressed in terms of the respective partition functions:

$$K'_{Ex} = \frac{Q_{AD}Q_{BH}}{Q_{AH}Q_{BD}} \qquad \text{..... 6.}$$

Assuming the Born-Oppenheimer approximation, which regards electronic and nuclear partition functions as separable, the ratios in equation 6 reduce to the ratios of the corresponding partition functions for nuclear motion. Further assumptions imply that the vibration-rotation interaction is neglible; the rotations are classical and the vibrations harmonic.

If the structure of each molecular species is known, the moments of inertia can be calculated and corrections applied for the rotation partition function not having reached its classical value. Also an approximate correction for neglect of anharmonicity can be made. Subsequently, the isotope effect can be calculated.

a). <u>Bigeleisen-Mayer Formulation</u>

The necessity for a knowledge of the moments of inertia can be avoided by using the Teller-Redlich rule, which allows isotope effects to be expressed as a function of vibrational frequencies only. This treatment by Bigeleisen and Mayer[66] permits the ratio of the equilibrium constants to be expressed:

$$\frac{K'_H}{K'_D} = \frac{\prod_i \frac{u_i(D)}{u_i(H)} \frac{1 - \exp\left[-u_i(H)\right]}{1 - \exp\left[-u_i(D)\right]} \exp\left[\frac{1}{2}\left(u_i(H) - u_i(D)\right)\right]}{\prod_j \frac{u_j(D)}{u_j(H)} \frac{1 - \exp\left[-u_j(H)\right]}{1 - \exp\left[-u_j(D)\right]} \exp\left[\frac{1}{2}\left(u_j(H) - u_j(D)\right)\right]} \quad \ldots\ldots 7.$$

where $u_i = hcw_i/kT$ and the product in the numerator is over all of the i normal modes of AH and AD, and in the denominator over the j normal modes of BH and BD.

If u_i and $u_j \gg 1$, that is the frequencies are high, equation 7 reduces to:

$$\frac{K'_H}{K'_D} \cong \frac{\prod_i \exp\left[\frac{1}{2}\left(u_i(H) - u_i(D)\right)\right]}{\prod_j \exp\left[\frac{1}{2}\left(u_j(H) - u_j(D)\right)\right]} \quad \ldots\ldots 8.$$

$$\ln(K'_H/K'_D) \cong \sum_i \tfrac{1}{2}\left[u_i(H) - u_i(D)\right] - \sum_j \tfrac{1}{2}\left[u_j(H) - u_j(D)\right] \ldots\ldots 9.$$

$$\ln(K'_H/K'_D) \cong \frac{hc}{2kT}\left[\sum_i \left(w_i(H) - w_i(D)\right) - \sum_j \left(w_j(H) - w_j(D)\right)\right] \quad \ldots\ldots 10.$$

This equation refers to the case where both reactants and both products are at their lowest vibrational levels, and equates the isotope effect on the standard free energy change for the reaction with changes in total zero point energy. This may be illustrated by Figure III:

Potential energy diagram showing zero-point energy levels of isotopic reactants and products

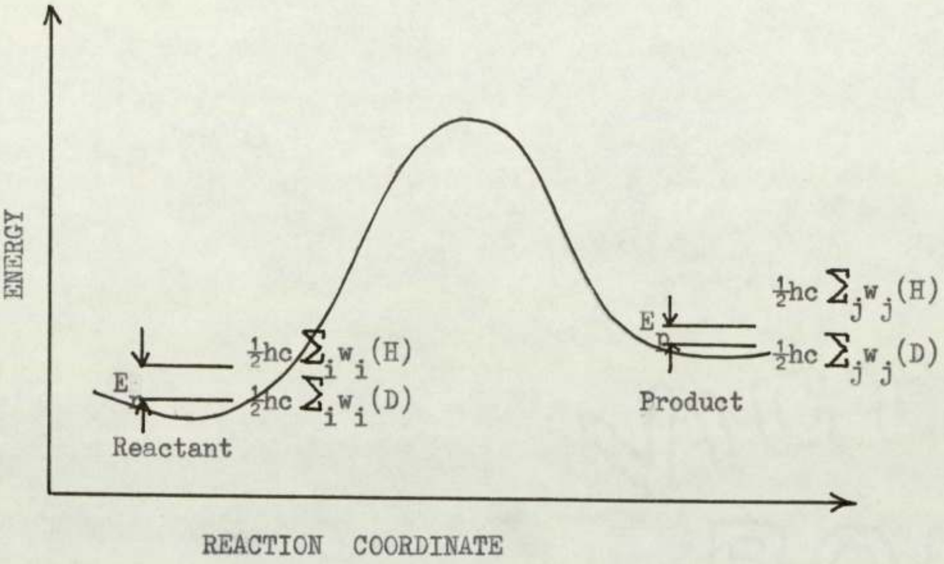


Figure III

where, if $\Delta E_r > \Delta E_p$ then an isotope effect in the direction $K'_H > K'_D$ is observed.

b). Streitwieser's Approximation

The previous treatment, however, necessitates a knowledge of the vibrational analyses of the protonated as well as the deuterated molecules. Usually the information concerning deuterated molecules is not available. The Streitwieser approximation,[67] therefore, makes use of a technique whereby it is possible to estimate the frequencies of the deuterated molecules, from a knowledge of the frequencies of the protonated ones.

Streitwieser's assumptions are as follows:

1. Deuterium substitution will change significantly only those frequencies primarily associated with the motion of the isotopically substituted hydrogen atoms, therefore the factors in equation 7 involving the vibrational modes can be neglected.
2. Carbon-hydrogen and carbon-deuterium stretching and bending modes are of sufficiently high frequency, that only zero-point energy differences need be considered.
3. C - H to C - D frequencies are in the ratio of approximately 1:1.35.

With these approximations equation 7 becomes:

$$\ln(K'_H/K'_D) = \frac{0.187}{T}\sum_i\Big[w_i(AH) - w_i(BH)\Big] \qquad \text{.... 11.}$$

The summation is carried out only over the C - H stretching and bending modes of the protonated molecules, and the condition for an isotope effect in the direction $K'_H > K'_D$ is that the zero-point energy associated with these modes be higher in the reactant than in the product.

c). Kinetics

Having established an equation for the equilibrium case, one can now revert to the absolute reaction rate theory and, using a similar procedure, the Bigeleisen equation may be derived for the kinetic case:

$$\frac{k_H}{k_D} = \frac{\dfrac{v^*_H}{v^*_D} \displaystyle\prod_{i=1}^{3N^*-7} \frac{u^*_i(H)}{u^*_i(D)} \frac{\left[1 - \exp\left(-u^*_i(D)\right)\right]}{\left[1 - \exp\left(-u^*_i(H)\right)\right]} \frac{\exp\left(-\frac{1}{2}u^*_i(H)\right)}{\exp\left(-\frac{1}{2}u^*_i(D)\right)}}{\displaystyle\prod_{j=1}^{3N-6} \frac{u_j(H)}{u_j(D)} \frac{\left[1 - \exp\left(-u_j(D)\right)\right]}{\left[1 - \exp\left(-u_j(H)\right)\right]} \frac{\exp\left(-\frac{1}{2}u_j(H)\right)}{\exp\left(-\frac{1}{2}u_j(D)\right)}} \quad .... 12.$$

* values refer to the properties concerned with the activated complex. The only difference from equation 7 is that the product in the numerator is over $3N^* - 7$ real frequencies of the transition state. The effect of motion along the reaction co-ordinate appears in the temperature independent factor v^*_H/v^*_D which is the ratio of the imaginary frequencies of motion over the barrier.

If all the frequencies are high relative to kT/h then:

$$\ln(k_H/k_D) = \tfrac{1}{2}\ln(m^*_D/m^*_H)$$

$$- \frac{hc}{2kT} \sum_i \left[w^*_i(H) - w^*_i(D)\right] - \sum_j \left[w_j(H) - w_j(D)\right] \quad .... 13.$$

The temperature independent factor has been expressed in terms of the masses along the reaction co-ordinate.

Streitwieser's approximation, now including the assumption that the ratio of the mass terms can be set equal to unity, leads to:

$$\ln(k_H/k_D) = \frac{0.187}{T} \sum_i \left[w_i(H) - w^*_i(H)\right] \quad .... 14.$$

Thus for $k_H > k_D$ it is necessary that the sum of the frequencies in the transition state is lower than that in the reactant. In the derivation of the equations, tunneling through the potential energy barrier as well as the effect due to the transmission coefficient were neglected.

3. Qualitative Aspects

The introduction of deuterium into an organic molecule has qualitatively much the same effect as that of other substituents. Consequently, secondary isotope effects are currently discussed in terms of the effect on the induction, hyperconjugation and steric interactions of a molecule into which deuterium has been substituted. No satisfactory quantitative treatment for any of these effects is yet available. Qualitative predictions make it possible to account for an observed result, but usually make confident prognoses impossible. Nevertheless, wide use has been made of secondary isotope effects in exploring reaction mechanisms. Some examples of these qualitative interpretations will be discussed in order to demonstrate their utility in mechanistic elucidations.

Theories on secondary isotope effects are involved, and in part contradictory.[63, 68, 69] Fundamentally two views may be traced:

1. Halevi's view[63] - that the secondary isotope effects may be treated as substituent effects, for example, a carbon-deuterium bond would be more strongly electron donating than a carbon-hydrogen bond; also a CD_3 group would exhibit weaker hyperconjugation than

a CH_3 group.[70]

2. The proposal by Bartell[71] in which he suggests that the secondary isotope effect can be based entirely on non-bonded interactions. He explains that the effect can be accounted for in terms of the smaller bulk of deuterium; that is the smaller amplitude of vibration of the deuterated molecules.

We have preferred to interpret our results in the terms of the proposals made by Halevi and Streitwieser et al.,[67] as these are currently more widely accepted. Some examples of the interpretation in terms of the classical effects (already mentioned at the beginning of Section 3), will be shown.

a). Inductive Effect

According to Halevi, the secondary isotope effect can be attributed largely to an inductive effect. This inductive effect is caused as a result of the anharmonicity of the Morse function. Because of this anharmonicity, the electrons in the carbon-deuterium bond are more localized on the carbon atom than those in the carbon-hydrogen bond. The accumulation of negative charge at this carbon atom is reflected in other bonds in the molecule.

i). Acid-Base Equilibria

The characteristic inductive effect which is altered by the substitution of deuterium for hydrogen, results in a decrease in the acidity of acids and an increase in their basicity. This is ascribed to the more effective electron release from the shorter carbon-deuterium bond.[72, 73] The result can be generalized for all carboxylic acids which have been studied; Halevi and Streitwieser both agreeing over the interpretation of the results, the following characteristics being present (see Table III):

A. The effect is attenuated by the interposition of a saturated carbon atom.

B. The isotope effects are of an expected magnitude, having regard to the dipole moment of the carbon-deuterium bond.

C. Deuteration in the alpha position in the benzylic group has a comparable effect in both acids and bases.

TABLE III

Acid	K_H/K_D	$\Delta\Delta F^o/n$[(a)]
CD_3COOH	1.06	12
CH_3CD_2COOH	1.08	23
$C_6H_5CD_2COOH$(b)	1.12	33
CD_3CH_2COOH	1.01	4
$(CD_3)_3CCOOH$	1.04	3

Base	K_H/K_D	$\Delta\Delta F^o/n$
$C_6H_5CD_2NH_2$ (b)	1.13	38
$(NO_2)_2C_6H_3NHCD_3$ (c)	1.14	26
$(NO_2)_3C_6H_2NHCD_3$ (c)	1.11	22

Secondary isotope effects on the strength of acids and bases in water at 25°C

(a) Corrected for incomplete deuteration and expressed per deuterium atom: $\Delta\Delta F^o/n = (RT/n)\ln(K_H/K_D)$, where n is the number of equivalent deuterium atoms.

(b) At 27°C.

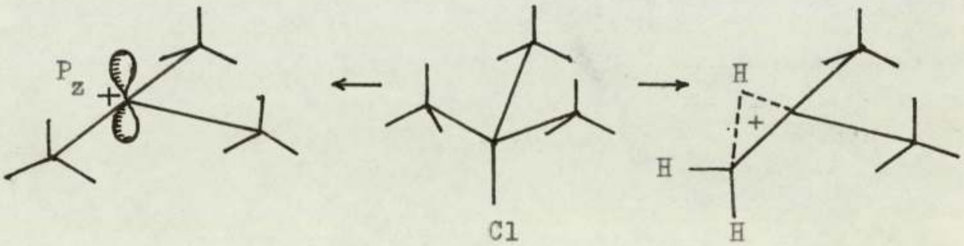
(c) At 33°C and in aqueous H_2SO_4.

ii). Rate Constants

The inductive effect has also been suggested as an explanation for the influence that deuterium substitution (in the ring and side chain) has on the rate of solvolysis of various benzhydryl chlorides.[74] Halevi and coworkers[75] have gained further insight into the mechanism of N-nitration of trinitro-N-methyl-aniline, by using the inductive effect in their postulation.

b). Hyperconjugation

Although this effect has been the subject of much controversy over the past few years[76] it has nevertheless been proposed as one of the explanations of a secondary isotope effect. Hydrogen attached to a carbon atom beta to a carbonium ion is therefore capable of stabilising the latter by hyperconjugation to a greater extent than deuterium could in the same position. This induces a retarding effect on the rate of reaction (normal effect) as the carbonium ion is formed in the slow step, and a speeding up (inverse effect) of reaction rate as the ion disappears. However, the decrease in stability of the carbonium ion could equally well be explained, in a qualitative manner, by a steric effect. In order to study this problem further, tert-butyl chloride is taken as an example together with the ion derived from it, and represented by XXIV and XXV below:



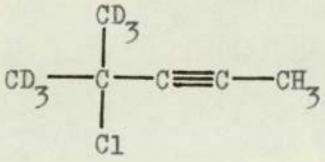
XXIV XXV

Two arguments can be presented for the stabilizing effect of the beta hydrogen atoms.

A. By the overlap of the vacant p_z orbital of the alpha carbon with the beta carbon-hydrogen bonds represented by XXIV. If these hydrogen atoms are replaced by deuterium atoms, the carbon-deuterium length, being shorter, will be less capable of overlap, thereby decreasing the hyperconjugative stabilization.

B. By the formation of a bridged structure XXV. In this instance also the substitution of hydrogen by deuterium will reduce the stabilization. The lengthening of the carbon-hydrogen bond which is required for the formation of the bridge, results in a partial loss of the zero-point energy, which is greater for the carbon-deuterium bond than for the carbon-hydrogen bond.

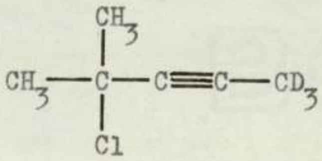
In XXIV the isotope effect would be cumulative; thus as CH_3 is replaced by CD_3 one would expect the ratios of k_H/k_D to increase in a geometric progression. However, it is difficult to distinguish this type of effect from a steric effect. In order to differentiate between the two effects, Shiner and Kritz[70] have made a study of the following two compounds:



$$CD_3-\underset{\displaystyle Cl}{\overset{\displaystyle CD_3}{C}}-C\equiv C-CH_3$$

$k_H/k_D = 1.65$

XXVI



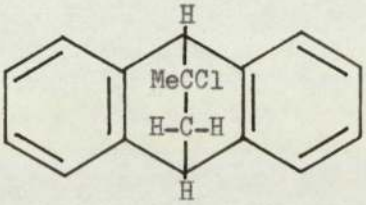
$$CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{C}}-C\equiv C-CD_3$$

$k_H/k_D = 1.092$

XXVII

According to these authors, the isotope effect observed in XXVII cannot be attributed in any extent to an inductive effect, as it is solvent independent; neither can it be steric in nature by virtue of the distance of the group from the reaction centre. Thus this observation seems to confirm the original conclusion that beta-deuterium isotope effects are caused by an electronic interaction with the reaction centre.

Shiner[77] has effectively demonstrated the relationship between beta isotope effects and hyperconjugation, using the solvolysis of a bicyclic chloride (XXVIII) as a model reaction:



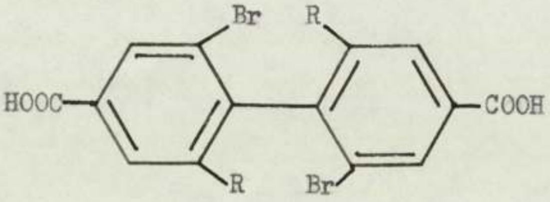
XXVIII

His results show that the occurrence of the beta isotope effect depends not only on the position, but also on the orientation of the isotopic bond. He suggests that hyperconjugative intramolecular transmission of electronic charge is an essential factor, causing beta-deuterium substituted compounds to give a slower reaction rate in S_N1 solvolyses, than their protium analogues. Therefore, whether XXIV or XXV is the correct representation for hyperconjugation, it is evident that a necessary condition for stabilization of the carbonium ion is that the hydrogen on the beta-carbon atom is in a position parallel to the vacant p orbital. The replacement of this hydrogen causes a greater isotope effect than the replacement of any other, and furthermore if the interaction between the beta-hydrogen and p_z orbital is prohibited, then only a small effect is likely.

c). Steric Effect

The replacement of hydrogen by deuterium in a molecule modifies the geometry of the molecule, this being described as the steric effect. The causes of the effect stem from the fact that a carbon-deuterium bond is shorter than a carbon-hydrogen bond, and also that the CD_3 group is sterically smaller than the CH_3 group. As a consequence, modifications in physical properties and reaction rate are observed.

Melander and Carter[78] have studied the racemization of certain biphenyls:



R = H and D respectively. The geometry of the transition state of this reaction had already been evaluated, and is believed to be planar. The bromine and hydrogen atoms are within van der Waals' radius of each other. This geometry corresponds to a calculated energy of activation of approximately 18 kilocalories/mole,[79] where the experimental value is 18.5 kilocalories/mole.[80]

It was found that the deuterated molecule racemized faster than the protonated equivalent - $k_D/k_H = 1.19$. In this reaction it is postulated that the entire potential energy barrier is due to the hydrogen-bromine non-bonded interactions. An alternative explanation that the increased rate of racemization is a result of inductive effects is ruled out, as the isotope effect is independent of the properties of the solvent. A difference in inductive effect, that is essentially a difference in the ability of protium or deuterium to support a movement of charge, might be expected to be influenced by solvent properties.

Brown et al.[69] suggest that the successful correlation of so many secondary isotope effects in terms of the relative steric requirements of hydrogen and deuterium, is ample evidence that the data should be re-evaluated in these terms. It is recognised by these workers, however, that the suggestion of the dominant factor in the secondary isotope effect being steric in origin, can only be considered as speculative.

4. Interpretation of Isotope Effects in Beta-halogenoalkyltrialkylsilanes

Although the stereochemical investigation had provided some indication of the mechanistic pathway for the reaction, more evidence to support this proposed mechanism was still required. It was hoped that by studying the effect of deuterium substitution on the rate of solvolysis of beta-halogenoalkyltrialkylsilanes, more detailed information concerning the nature of the intermediate (or transition state) would be gained. With this aim the following deuterated silanes were synthesised:

$$(CH_3)_3SiCH_2CD_2Br$$

TABLE IV

Compound	Solvent	10^2k	Av. 10^2k	k_H/k_D	$\Delta\Delta F^*/n$
$(CH_3)_3SiCH_2CH_2Br$	80% aq. ethanol	4.48 4.49 4.59 4.59 4.44	4.52	-	-
$(CH_3)_3SiCHDCH_2Br$	80% aq. ethanol	4.42 4.39 4.44 4.44 4.47 4.38	4.42	1.02	12
$(CH_3)(CD_3)_2SiCH_2CH_2Br$	80% aq. ethanol	4.66 4.62 4.62 4.63	4.63	0.98	-3
$(CH_3)_3SiCH_2CD_2Br$	80% aq. ethanol	3.96 4.03 4.14 3.94	4.02	1.12	61
$(CH_3CH_2)_2CH_3SiCH_2CH_2Br$	80% aq. ethanol	3.37 3.30	3.34	-	-
$(CH_3CD_2)_2CH_3SiCH_2CH_2Br$	80% aq. ethanol	3.39	3.39	0.985	-3
$(CH_3)_3SiCH_2CH_2OH$	8.5 M H_2SO_4 in 50% aq. methanol	14.14 14.19	14.17	-	-
$(CH_3)_3SiCH_2CD_2OH$	8.5 M H_2SO_4 in 50% aq. methanol	10.91 11.39	11.15	1.27	71

Secondary isotope effects on beta-substitutedethyltrialkylsilanes at 25.22°C

The values of the first order rate constants (minutes^{-1}) were calculated using a method of least squares program, on an Elliot 803 Computer.

$\Delta\Delta F^*/n$ has been corrected for incomplete deuteration and expressed per deuterium atom. k_H/k_D values are accurate to plus or minus 2%.

$(CH_3)_3SiCHDCH_2Br$

$(CD_3)_2CH_3SiCH_2CH_2Br$

Initially other materials were also prepared, which are listed in Table IV. The neutral solvolysis rates of each compound in 80% ethanol, were determined and compared with the solvolysis rate (in the same medium) of the undeuterated silane. The results of this study are summarized in Table IV.

In the following section, the term alpha-deuterium effect, refers to the effect of a deuterium atom linked to the carbon atom beta to the silicon; whilst beta-deuterium effect refers to the effect of a deuterium atom attached to the carbon atom in the alpha position.

The ratio $k_H:k_D$ has been calculated for each compound, and the significance of the secondary isotope effects (or lack of them) will be discussed in the light of interpretations made by previous investigators, who have worked with similar systems.

Lewis and Boozer[62] were the first to present experimental evidence for a secondary isotope effect. They studied the rate of decomposition of 2-pentylchlorosulphite and recorded a decrease in rate when beta-hydrogen atoms were replaced by deuterium. Many examples of secondary isotope effects on solvolysis rates have accumulated since this work, and most of them are similar in magnitude: about 10-30% rate retardation per deuterium atom. Data from a large number of papers dealing with these effects in S_N1 solvolytic reactions (in which the rate-determining step is the formation of a carbonium ion), are summarized in Table V. This type of effect has been exploited considerably since it was exposed by Streitwieser and coworkers.[67] The explanation for the relative consistency of the isotope effect of 10-12% per deuterium atom[81-84] (a requirement being that the reaction be genuinely S_N1), substituted on an alpha-carbon atom, will be discussed below.

TABLE V[63]

Compound	Solvent	T °C	$\Delta\Delta F^*/n$
Benzyl-1d-tosylate[(a)]	CH_3COOH	50	73 ± 22
Benzyl-1,1d_2-tosylate	CH_3COOH	50	71 ± 8
Isopropyl-1d-brosylate[(b)]	CH_3COOH	70	77 ± 6
2,2-Dipheylethyl-1,1d_2-tosylate	CH_3COOH	75	66 ± 8
2(p-Methoxyphenyl)ethyl-1,1d_2-tosylate	CH_3COOH	75	57 ± 2
2,2-Diphenylethyl-1,1d_2-tosylate	HCOOH	75	66 ± 5
2(p-Methoxyphenyl)ethyl-1,1d_2-tosylate	HCOOH	50	58 ± 10
2 Phenylethyl-1,1d_2-tosylate	HCOOH	75	59 ± 6
Methyl tolyl carbinyl 1-d-chloride	80% aq $(CH_3)_2CO$	38	63 ± 9
1-Methylheptyl-1d-brosylate	CH_3OH	70	63

Solvolytic α-Effects at an Aliphatic Carbon Atom in Non-aqueous Media

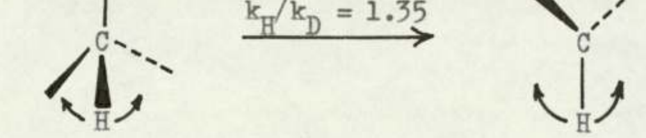
(a) Tosylate = p-toluenesulphonate

(b) Brosylate = p-bromobenzenesulphonate

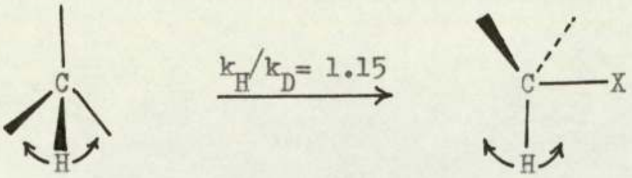
If the secondary isotope effect is considered in terms of the Streitwieser hypothesis, that is by considering zero-point energy differences between the protonated and deuterated molecules in the ground state, the constancy of the effect[85] becomes less surprising. It is known for instance, that complex molecules differing in several respects, exhibit similar vibrational frequencies which are characteristic of certain functional groups. The carbon-hydrogen group frequencies, for example, are sensitive to the degree of hybridization at that carbon, but relatively insensitive to the substituents at that carbon atom. Because of these similarities, systems which undergo reaction where a bond is broken in a unimolecular rate-controlling process, generally should exhibit an alpha-deuterium isotope effect in the range 1.10-1.12.

According to Streitwieser,[67] the most important factor involved in the alpha-deuterium effect is ascribed to the isotopic inhibition of the out-of-plane bending vibration of the cation, which is weaker than the corresponding vibration in the ground state. Streitwieser suggests that the isotope effect which should be experienced in proceeding from a tetrahedrally hybridized atom to a trigonally hybridized atom, should be of the order of 1.35. This may be illustrated as follows:

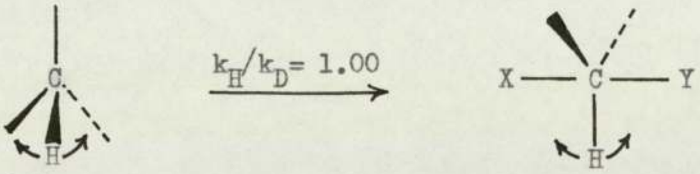
A.



B.



C.



In A. the maximum effect may be expected, whereas in C. the transition state would contain both entering and leaving groups and the wagging motion would be impeded. Streitwieser further suggests that it would not be surprising to find that this motion was approximately the same as the tetrahedral carbon-hydrogen bending. B. is postulated as being equivalent to a transition state that is independent of solvent participation, but the leaving group X is still associated with the carbonium ion and its presence probably impedes the carbon-hydrogen wagging motion. Streitwieser also comments that should these implications be substantiated by further work, the alpha-deuterium effect may provide a new tool for determining the structural degree of solvent or neighbouring group assistance at the transition state of solvolytic displacement reactions.

a). Alpha-deuterium Effect

The effect observed in the case of the solvolysis of 1-dideutero-1-bromoethyltrimethylsilane is consistent with a transition state similar to that of type B. This result leads to a postulation for the structure of the transition state and a possible mechanistic route. Thus, an explanation of the observed isotope effect is that the rate-determining step in the reaction, involves the separation of the halogen from the alpha-carbon atom. Simultaneously the hybridization of this carbon atom changes from tetrahedral to trigonal so that a p orbital becomes available. Interaction between this orbital and the alpha-carbon-silicon bond is now possible. In order that new bonds can form as old ones are broken, the silicon, the two carbon atoms and the bromine atoms must be coplanar.[15] It is further suggested that if the silicon atom is trans to the bromine atom, the transitions can take place without any great increase in the repulsions between non-bonded atoms.

The solvolysis of 1-dideutero-1-hydroxyethyltrimethylsilane in acid media was also studied, and a rate retardation similar to that in the previous case was observed. On this basis the rate-determining step was postulated as including a similar transition state to the halogenated molecule. In this instance, however, a rapid pre-rate-determining equilibrium step, involving the protonated species, is suggested:

$$H^+ + Me_3SiCH_2CH_2OH \xrightleftharpoons{\text{fast}} Me_3SiCH_2CH_2OH_2^+$$

The protonated hydroxy group will finally separate from the carbon atom to which it is bound, thereby liberating a molecule of water. Bonds will then rearrange in a similar fashion to that proposed in the case of the halogenated silane.

The evidence obtained from the observed effect suggests therefore, that the rate-determining step involves the rupture of the carbon-bromine bond.

b). Beta-deuterium Effect

Although Brown prefers to interpret beta-deuterium effects in terms of a steric effect, much evidence[86, 87] has accumulated supporting the hyperconjugative interpretation, which is now widely favoured. Karabatsos[87] et al. come to the conclusion that in ordinary systems with hyperconjugation possible, probably only 2-5% of the observed effect can be attributed to non-bonded interactions. In this instance an interpretation on the basis of hyperconjugation has been invoked and certain conclusions have been drawn. The rate of solvolysis of 2-deutero-1-bromoethyltrimethylsilane was examined, as it seemed a suitable compound in which to test Sommer's hypothesis that a rate-determining step involved the cleavage of the carbon-silicon bond. If the alpha-carbon-hydrogen bonds were becoming more planar due to the partial detachment of the trimethylsilyl group, an effect of the first kind in the direction $k_H/k_D > 1$, may be expected. The lack of an effect indicates that the transition state does not require much spatial rearrangement of the alpha-hydrogens; faced with the normal alpha effect it must be concluded that bond rupture has progressed reasonably far, but that the trimethylsilyl group has not become substantially less firmly bonded to the alpha-carbon, or attached to the beta-carbon. This would imply that the reaction is a simple carbonium ion-forming solvolysis. However, from this the normal beta effect $k_H/k_D \simeq 1.15$ per deuterium atom, might still be expected. In order to account for the lack of effect it must be assumed that the alpha-hydrogens are constrained to remain below the nodal plane of the $2p_z$ alpha-carbon orbital.

Thus the overlap with the asymmetric combination of the carbon-hydrogen bond orbitals is prevented; overlap with the less important symmetric carbon-hydrogen bond orbital combination is still possible, and should produce a retardation of approximately 4% per deuterium atom, according to previous investigators. However, even this small effect is absent in the systems which are believed to involve neighbouring group participation. In the present investigation an effect of approximately 2% per deuterium atom was observed.

Assuming participation from the trimethysilyl group predominates, the alpha-carbon-hydrogen bonds will be almost orthoganol to the developing p orbital on the beta-carbon atom in the transition state, and as a consequence hyperconjugation will be prevented, which is reflected by the lack of an isotope effect. This lack of isotope effect, coupled with the normal effect observed in the previous case (4. a).), tends to reinforce the mechanism implied in the stereochemical study, in which a non-classical cyclosilapropenium intermediate (or transition state) was suggested as the predominating ion.

c). Delta-deuterium Effect

The study of the effect of deuteration of the methyl group attached to silicon, was undertaken because hyperconjugation has been proposed to explain the dipole moment and bond shortening of the carbon-silicon bond length.[88] Had the rate-determining step involved a rupture of the carbon-silicon bond, then hyperconjugation might have been expected to contribute to an isotope effect. According to Streitwieser, two factors affect hyperconjugation:

i). The extent of the delocalized carbon-hydrogen bond orbital overlap with the electron deficient p orbital (developing on the carbonium ion).

ii). The degree of electron deficiency on the neighbouring carbon atom. The greater the overlap and the greater the electron deficiency, the greater the extent of hyperconjugation.

As the experimental evidence indicated a large positive charge accumulation on the silicon atom, this would be a suitable reaction in which to observe a beta-deuterium effect. However, in view of the fact that a negligible isotope effect was noted in Section 4. b)., the lack of a normal effect in this case is hardly surprising. On the other hand, Jewett and Dunlap[86] have studied the solvolysis of $(CD_3)_3CCH_2C(CH_3)Cl$ in 80% ethanol and have found a small inverse isotope effect. They suggest that in this instance hyperconjugation is prevented and therefore the effect is steric in nature, being due to the steric assistance to ionization. By analogy with the preceding observation, it is considered possible that the small inverse effect recorded in the case under consideration, may also be attributed to some steric assistance to the ionization.

--o--

V. CONCLUSION

Previous investigators have shown that the solvolytic elimination of beta-halogenoalkyltrialkylsilane in aqueous ethanol has the following characteristics:

1. First order kinetics are followed precisely.
2. The rate of elimination is susceptible to the ionizing power of the medium.
3. The rate of elimination is insensitive to the nucleophilic character of the medium.
4. The Hammett rho factor = -2.15.
5. Entropies of activation are negative and in the order of 12-14 entropy units.
6. Approximately equal rates in corresponding media for the silane and tert-butyl chloride.
7. The rate of solvolysis varies with the halogen substituted on the beta-alkyl group ($k_{Br} = 17k_{Cl}$, in the base-catalysed reaction).

This study has been principally concerned with the investigation of the solvolysis of beta-bromoethyltrimethylsilane. The work has yielded further information concerning the mechanism of the reaction, from three differing aspects:

1. Stereochemistry

   The stereochemical study indicated that the elimination reaction was stereospecific, with predominant trans elimination of trimethylbromosilane.

2. Rearrangement

   The migration of the trimethylsilyl group observed in the reaction of a related molecule, provided some evidence that this group could interact with the developing positive charge on the beta-carbon atom, during the reaction.

3. Isotope Effects

   The magnitude of the effects experienced from the substitution of deuterium in the three positions in the molecule, suggested that carbon-bromine bond cleavage (with the possibility of assistance from the trimethylsilyl group), has occurred in the rate-determining step.

Thus the conclusion drawn from the total available evidence indicates that in the rate-determining step, the carbon-halogen bond is ruptured, which may be assisted by the trimethylsilyl group interacting with the developing positive charge on the beta-carbon atom, to form a non-classical intermediate (or transition state).

--o--

VI. EXPERIMENTAL

The boiling points quoted in the following text are uncorrected. Physical constants are mainly taken from "Organosilicon Compounds", volume 2, part I, by Bazant et al.[89] The interpretations of nmr spectra were based on the texts of Jackman,[90] and Emsley, Feeney and Sutcliffe,[91] and infra-red assignments on Bellamy.[92] Any other sources used in either of the above are referred to in the section concerned.

Nmr Spectra

The proton resonance spectra were obtained using a Perkin Elmer R10 Spectrometer, operating at 60 Mc/sec. and 35°C. Tetramethylsilane was used as an internal reference.

Infra-red Spectra

The spectra were determined using a Perkin Elmer Infracord - 237.

Vapour-phase Chromatography

Gas chromatographic analyses and separations were carried out using the following apparatus:

i). Analytical

5' x $\frac{1}{8}$" o.d. stainless steel 4 mm bore, packed with:

a). Saturated silver nitrate in purified ethylene glycol[93] (17 ml) on Chromosorb P (39 g).

b). 40% $\beta\beta'$oxydipropionitrile on Chromosorb P.[94]

A Pye series 104 chromatograph was used, operating at 35°C with a katharometer sensing device, current 195-200 mA and a flow rate of 60 ml/min, helium carrier gas.

ii). Preparative

20' x $\frac{3}{8}$" o.d. aluminium column with packings as in a). and b). above. An Aerograph Autoprep model A-70 was used, operating at 35°C with helium as the carrier gas (50 p.s.i.), at a flow rate of 120 ml/min.

Mass Spectra

The mass spectral data were obtained using the AEI MS9 double focussing, high resolution mass spectrometer.

The silanes were for the most part purchased from Messrs. Hopkin and Williams. The rest were kindly donated by:

ICI Nobel Division
Midland Silicones Ltd.
Dow Corning Corporation, Michigan

1. Vinyltrimethylsilane (XXIX)

A method similar to that used by Nagel and Post[95] was employed. Methyl magnesium iodide in sodium dried di-n-butyl ether (2.4 g Mg, 6.3 ml MeI) (0.006M solution) was contained in a 250 ml, 3-necked flask equipped with stirrer, reflux condenser (with $CaCl_2$ guard tube) and addition funnel. Methylvinyldichlorosilane (6.5 ml, 0.05 mole) was added over a period of 0.5 hours. After the addition, the reaction mixture was refluxed for 2 hours. Compound XXIX was then fractionated (using a 12" glass helix packed column) directly from the reaction vessel. Refractionation yielded the pure product (5 ml, 70% yield) b.p. 56°C (Lit.[95] 54.4°C/745.4 mm); nmr,[96] neat liquid, at 5.63-6.11 p.p.m. a multiplet of intensity one (vinylic protons), at 0.06 p.p.m. a singlet of intensity three (trimethylsilyl protons); infra-red, neat liquid,[97] maxima (cm^{-1}) at 3030m, 1600w (stretching), 950m (out of plane deformation) - vinylic, 1250s (symmetric deformation), 850m (stretching) - silicon methyl, 1412s (bending) - carbon hydrogen; mass spectrum, neat liquid, peaks at 100 and 85 a.m.u. due to $(Me_3SiCH{=}CH_2)^+$ and $(Me_2SiCH{=}CH_2)^+$ respectively, both exhibiting a typical silicon cracking pattern.

2. <u>2-Bromoethyltrimethylsilane</u>

The halogenosilane was prepared following the method used by Sommer et al.[41] Hydrogen bromide, generated by the action of water on phosphorus tribromide, was passed through acetone dry-ice traps, in order to freeze out water vapour. The gas was then bubbled through ice-cooled, dry XXIX (10 g, 0.1 mole) containing benzoyl peroxide (0.10 g), until the infra-red absorption bands due to unsaturation disappeared. Fractionation using a 4" column (packed with glass helices) yielded 14 g (77% yield) of 2-bromoethyltrimethylsilane, b.p. 65°C/42 mm, (Lit.[89] 64-65°C/39 mm); nmr, neat liquid, a triplet of intensity two centred at 3.5 p.p.m. (protons on beta-carbon atom), at 1.3 p.p.m. a triplet of intensity two (protons on alpha-carbon), at 0 p.p.m. a singlet of intensity nine (trimethylsilyl protons); infra-red, neat liquid, maxima (cm^{-1}) at 1250s (symmetric deformation), 850s (stretching) - silicon methyl, 1415w (bending) - carbon hydrogen. An accurate determination of the amount of halide present was made by titrating with standard base. The material was previously dissolved in neutralised acetone and titrated to a phenolphthalein end point; (Found: Br, 43.5. Calc. for $C_5H_{13}BrSi$: Br, 44.1%).

3. 1-Deutero-2-bromoethyltrimethylsilane

A procedure similar to that adopted for producing the undeuterated[41] material (see previous section) was employed. Deuterium bromide,[37] prepared by the addition of deuterium oxide (99.7%) to phosphorus tribromide, was bubbled through XXIX. The resulting material, after fractionation (b.p. 65°C/40 mm), was subjected to nmr analysis. Contamination of the deuterated silane, by the protonated material did not exceed 3% ± 1.5%.

Nmr, neat liquid, centred at 3.5 p.p.m. a doublet of intensity two (protons on beta-carbon), centred at 1.3 p.p.m. a triplet of intensity 1.03 (protons on alpha-carbon), at 0 p.p.m. a singlet of intensity nine (trimethylsilyl protons); infra-red, neat liquid, maxima (cm^{-1}) at 1253s (symmetric deformation), 845s (stretching) - silicon methyl, 1410w (bending) - carbon hydrogen; (Found: Br, 43.5. Calc. for $C_5H_{12}BrDSi$: Br, 43.9%).

4. 2-Hydroxyethyltrimethylsilane[98]

Chloromethylmethyldichlorosilane was methylated using methyl magnesium bromide, in the normal way.[53] The Grignard reagent of chloromethyltrimethylsilane was prepared in the manner suggested in the literature;[99] it was however, initiated using 1,2-dibromoethane in lieu of ethyl bromide. By adding this Grignard reagent to ethyl chloroformate, ethyltrimethylsilyl acetate[100] was synthesised.

Ether (20 ml) (freshly distilled from lithium aluminium hydride) and lithium aluminium hydride (1.0 g) were charged to a 50 ml, 3-necked flask equipped with addition funnel, reflux condenser (with drying tube) and magnetic stirrer. Ethyltrimethylsilyl acetate (4.0 g) in ether (10 ml) was added to the contents of the flask, over 0.5 hours, and allowed to react for a further 0.75 hours. The reaction mixture was then hydrolysed by carefully adding distilled water, and the organic layer separated. The aqueous layer was extracted with several 5 ml portions of ether. The organic extracts were than combined and dried over magnesium sulphate for 12 hours. Fractionation afforded 2-hydroxyethyltrimethylsilane (2.0 g, 0.017 mole) b.p. 66°C/24 mm (Lit.[101] 95°C/100 mm); nmr, neat liquid, at 4.9 p.p.m. a singlet of intensity one (hydroxyl proton), at 2.9 p.p.m. a triplet of intensity two (protons on beta-carbon), at 0.9 p.p.m. a triplet of intensity two (protons on alpha-carbon), at 0 p.p.m. a singlet of intensity nine (trimethylsilyl protons); infrared, neat liquid, maxima (cm^{-1}) at 3330s broad (stretching) - hydroxyl group, 1248s (symmetric deformation), 835s, 860s (stretching) - silicon methyl, 1415w (bending) - carbon hydrogen; (Found: C_2H_4, 23.3. Calc. for $C_5H_{14}OSi$: C_2H_4, 23.7%).

5. 2-Dideutero-2-hydroxyethyltrimethylsilane

The same procedure as that adopted in the previous section was followed, with the exception that ethyltrimethylsilyl acetate was reduced with lithium aluminium deuteride (obtained from CIBA laboratories; isotopic purity greater than 99% per molecule), in place of the hydride. Nmr spectral analysis of the pure deuterated hydroxysilane (b.p. 85°C/63 mm) revealed that contamination by the protonated silane did not exceed one percent. Nmr, neat liquid, at 3.6 p.p.m. variable, a singlet of intensity one (hydroxyl proton), at 0.9 p.p.m. a singlet of intensity two (protons on alpha-carbon), at 0 p.p.m. a singlet of intensity nine (trimethylsilyl protons); infra-red, neat liquid, maxima (cm^{-1}) at 3330s broad (stretching) - hydroxyl group, 2200w, 2100w (stretching) - carbon deuterium, 1250s (symmetric deformation), 850s (stretching) - silicon methyl; (Found: $C_2H_2D_2$, 25.0. Calc. for $C_5H_{12}D_2OSi$: $C_2H_2D_2$, 25.4%).

6. Bromination of 2-dideutero-2-hydroxyethyltrimethylsilane

Phosphorus tribromide (3.0 g) was charged to a 2-necked, 50 ml flask equipped with a magnetic stirrer, condenser (with guard tube) and an addition funnel. The flask and contents were cooled to below 0°C in an ice-salt bath, and 2-dideutero-2-hydroxyethyltrimethylsilane was added dropwise with stirring. Two fractionations with a 4" column yielded 2-dideutero-2-bromoethyltrimethylsilane (2.0 g, 70%) b.p. 68°C/42 mm; nmr, neat liquid, at 3.6 p.p.m. a singlet of intensity 0.905 (protons on beta-carbon), at 1.3 p.p.m. a singlet of intensity 1.095 (protons on alpha-carbon), at 0 p.p.m. a singlet of intensity nine (trimethylsilyl protons);

(Found: Br, 43.1. Calc. for $C_5H_{11}D_2BrSi$: Br, 43.6%).

7. 2-Bromoethyl-bis-(trideuteromethyl)methylsilane

Using the method described by Cotton et al.[102] trideuteromethyl iodide was prepared. Following the procedure described in Section 1. (page 75), the Grignard reagent of the deuterated iodide was added to methylvinyldichlorosilane; bis-(trideuteromethyl)methylvinylsilane (b.p. 56°C) was then fractionated, yield 5ml, 70%; nmr, neat liquid, at 5.6-6.1 p.p.m. a multiplet of intensity three (vinylic protons), at 0 p.p.m. a singlet of intensity 4.75 (bis-(trideuteromethyl)methylsilyl protons); mass spectrum, neat liquid, peaks between 100-106 a.m.u., corresponding to material containing 0-6 deuterium atoms per molecule substituted on the deuterated silyl group. Both mass and nmr spectral data indicated that the bis-(trideuteromethyl)methylsilyl group contained 71% deuterium.

Dry hydrogen bromide bubbled through this vinylsilane (following the procedure described in Section 2. (page 76)) yielded 2-bromoethyl-bis-(trideuteromethyl)methylsilane, b.p. 66°C/42 mm; nmr, neat liquid, centred at 3.5 p.p.m. a triplet of intensity two (protons on beta-carbon), centred at 1.3 p.p.m. a triplet of intensity two (protons on alpha-carbon), at 0 p.p.m. a singlet of intensity 4.75 (bis-(trideuteromethyl)methylsilyl protons); infra-red, neat liquid, maxima (cm^{-1}) at 2210w (stretching) - carbon deuterium, 1260s (symmetric deformation), 840s, 800s, (stretching) - silicon methyl, 1415w (bending) - carbon hydrogen; (Found: Br, 42.5. Calc. for $C_5H_{7.75}D_{4.25}BrSi$: Br, 42.8%).

8. 2-Bromoethyl-bis-(1-dideuteroethyl)methylsilane

The described procedure for the preparation[103] and saponification of monomethylethyl malonate was followed, and the acid[104] synthesised. Several exchanges[105] of this acid with deuterium oxide, followed by reaction with silver nitrate, led to the formation of deuterated silver propionate.[106] Brominative degradation of the silver salt yielded 1-dideutero-1-bromoethane.[106]

Methylvinyldichlorosilane (12.5 ml, 0.096 mole) was added to the Grignard reagent prepared from 1-dideutero-1-bromoethane (4.8 g, 0.2 mole, magnesium; 15.2 ml, 0.2 mole, deuterated bromoethane; 120 ml, dry tetrahydrofuran) over 0.5 hours and then refluxed for 2 hours. The solution was then cooled and carefully added to iced water containing 10% hydrochloric acid, from which the organic layer separated and the aqueous layer twice extracted with ether. The combined organic extracts were washed twice with dilute sodium bicarbonate solution, followed by a washing with water, and finally dried over sodium sulphate. Fractionation yielded bis-(1-dideuteroethyl)methylvinylsilane, b.p. 117°-118°C[107] (7.2 g, 58% yield). This silane was shown by its nmr spectrum to contain not less than 3.9 deuterium atoms per molecule.

Dry hydrogen bromide gas bubbled through the vinylsilane, as previously described, yielded 2-bromoethyl-bis-(1-dideuteroethyl)methylsilane, b.p. 80°-82°C/10 mm; nmr, neat liquid, centred at 3.6 p.p.m. a triplet of intensity two (protons on beta-carbon), centred at 1.4 p.p.m. a triplet of intensity two (protons on alpha-carbon), at 0.6-1.2 p.p.m. a multiplet of intensity 6.1 (protons on deuterated ethyl group), at 0.1 p.p.m. a singlet of intensity three (methylsilyl protons); infra-red, neat liquid, maxima (cm^{-1}) 2100w, 2160w, 2200w (stretching) - carbon deuterium, 1255s (symmetric deformation), 825s (stretching) - silicon methyl, 1410m (bending) - carbon hydrogen; (Found: Br, 37.0. Calc. for $C_7H_{13}D_4BrSi$: Br, 37.4%).

9. <u>2-Bromoethyl(diethyl)methylsilane</u>

Ethylmagnesium bromide was prepared in the normal way using bromoethane and magnesium turnings. The method then followed the preparation of the deuterated material as shown in the previous section. The resulting 2-bromoethyl(diethyl)methylsilane was fractionated, b.p. 79°C/10 mm (7.5 g, 60% yield). The nmr shifts of the protons of this material were similar to those reported in the previous section. The only difference in the spectrum is the intensity of the protons of the ethyl group (in this case, ten). The infra-red spectrum was also similar except for the carbon deuterium stretching vibrations, which were absent. (Found: Br, 37.7. Calc. for $C_7H_{17}BrSi$: Br, 38.2%).

10. <u>Trans-1-chloropropene</u>

The method described by Allinger and Hermann[108] was followed. A seven foot column, packed with Dixon gauzes, fitted with a take-off head, was used for the final fractionation (a reflux ratio of 30:1 was employed). The purity of the isomer isolated from this fractionation was checked by infra-red and v.p.c. (using the oxydipropionitrile column, described on page 75).

11. Trans-1-propenyltrimethylsilane

The synthetic route followed was similar to that employed by Seyferth and Vaughan.[109] Lithium wire (11.0 g, 1.6 mole, 1.1% sodium content) was contained in a one litre, 3-necked flask, equipped with addition funnel, reflux condenser and stirrer, (the usual precautions were taken to exclude moisture from the reaction vessel), together with sufficient dry ether to just cover the wire. Trans-1-chloropropene (2 g) was used to initiate the reaction, which was then maintained at gentle reflux by adding a mixture consisting of trans-1-chloropene (37 g, 0.48 mole) and dry ether (140 ml). On the completion of the addition, the contents of the flask were stirred for a further 0.5 hours, before trimethylchlorosilane (50 g, 0.46 mole) was added, at a rate aimed at maintaining a gentle reflux. Additional refluxing for 1.5 hours completed the reaction. The reaction mixture was then filtered to remove the remaining lithium metal, plus salts, and the filtrate carefully added to water (300 ml). The aqueous layer was extracted twice with ether and the combined ether extracts washed with water, and dried over magnesium sulphate for 12 hours. The ether was distilled from the material, which was then fractionated (using a 12" column, packed with glass helices). The fraction, which boiled at 85°-89°C, proved to be pure trans-1-propenyltrimethylsilane (35 g, 65% yield); nmr, neat liquid, at 5.6-6.6 p.p.m. a multiplet of intensity two (vinylic protons), at 1.9 p.p.m. a doublet of intensity three (methyl protons), at 0.2 p.p.m. a singlet of intensity nine (trimethylsilyl protons);[110] infra-red,[110] neat liquid, maxima (cm^{-1}) 1625s (stretching), 897s (out of plane deformation) - trans vinylic, 1252s (symmetric deformation), 840-865s (stretching) - silicon methyl, 1445w (bending) - carbon hydrogen; v.p.c., silver nitrate/ethylene glycol column (see i). a)., page 75) indicated that contamination of this isomer by the cis isomer was less than 0.5%.

12. Addition of deuterium bromide to trans-1-propenyltrimethylsilane

Deuterium bromide[37] was bubbled through trans-1-propenyltrimethylsilane at -40°C, until the infra-red absorption bands due to unsaturation disappeared. Traces of trimethylbromosilane, formed during the reaction, were removed by evacuating the flask at room temperature. The nmr spectrum of the remaining material was consistent with the predicted spectrum of the deuterobrominated compound. Contamination with non-deuterated material did not exceed 3% ± 1%; a negligible quantity of trimethylbromosilane was also detected.

13. Elimination reaction of 1-deutero-2-bromopropyltrimethylsilane with quinoline[111]

Quinoline (17 ml), dried over potassium hydroxide pellets, was charged to a 50 ml, 3-necked flask fitted with reflux condenser, addition funnel and thermometer. The quinoline was heated to 95°C and the 1-deutero-2-bromopropyltrimethylsilane (8 ml) added dropwise. During the addition, the temperature in the reaction vessel rose to 100°-120°C. The reaction was allowed to continue for an additional 0.25 hours at 95°C, before being cooled to room temperature. Excess water was added slowly and the silicon-containing compounds separated, forming an upper layer, which was removed and dried over magnesium sulphate. Attempts were made to separate the various organosilicon compounds by v.p.c., but as the desired products - cis and/or trans-1-propenyltrimethylsilane, had only been formed in less than 6% yield (see Chapter II, Section 4), this project was abandoned.

14. Attempted isomerization of propenylsilanes in quinoline

As it had been proposed to study the ratio of the products of reaction in the previous experiment, it was necessary to know if any isomerization of propenylsilanes occurred in the presence of quinoline.

Trans-1-propenyltrimethylsilane was heated with excess quinoline for several hours. A similar procedure was adopted using a mixture of cis and trans-propenylsilanes. Analysis by v.p.c. of the resulting products from both reactions, showed that no isomerization had taken place under the conditions of the elimination reaction.

15. Erythro-1,2-dibromopropyltrimethylsilane[112]

Bromine (8 g, 0.05 mole), redistilled from phosphorus pentoxide, was added carefully to trans-1-propenyltrimethylsilane (5.5 g, 0.048 mole), contained in a 3-necked, 50 ml flask, fitted with stirrer, reflux condenser and addition funnel. The flask was maintained at -20°C throughout the reaction. Traces of excess bromine were finally removed under vacuum, at room temperature. Nmr, neat liquid, at 5.5-5.0 p.p.m. a multiplet of intensity one (protons on beta-carbon), at 3.8 p.p.m. a doublet of intensity one (protons on alpha-carbon), at 1.75 p.p.m. a doublet of intensity three (methyl protons), at 0.2 p.p.m. a singlet of intensity nine (trimethylsilyl protons). Absorptions due to a negligible quantity of 1,1,2-tribromopane were also recorded.

16. 1,2-dibromoethyltrimethylsilane

The method of preparation of 1,2-dibromoethyltrimethylsilane was identical with that employed in the previous section. Nmr, neat liquid, at 3.1-4.1 p.p.m. a multiplet of intensity one (protons on alpha and beta-carbons), at 0.2 p.p.m. a singlet of intensity three (trimethylsilyl protons).

17. Identification of products of solvolysis of 1,2-dibromopropyltrimethylsilane

98% aqueous ethanol was used in the desilicohalogenation of the silane. The resulting material was subjected to v.p.c. (see i). b)., page 75). Two peaks with low retention times were identified as hexamethyldisiloxane and ethoxytrimethylsilane. A third peak which was later collected using the Autoprep A700, was analysed by nmr and v.p.c. Both techniques showed, by comparison with authentic samples of cis and trans-bromopropenes, that the collected peak was cis-bromopropene. Quantitative measurements of the reaction products (using v.p.c.), indicated that bromopropene was formed in approximately 80% yield.

18. Attempted isomerization of bromopropenes in the solvents listed in Table I

Cis-1-bromopropene and trans-1-bromopropene were allowed to stand in the solvents listed in Table I (page 21). After 24 hours at room temperature, the solutions were examined by v.p.c. using the oxydipropionitrile column (see Section i). b)., page 75). No detectable isomerization had occurred.

19. Cis-1-bromopropene

This compound was prepared by the method described by Braude and Coles,[113] with some minor modifications, listed as follows:

i). The dibromobutyric acid, prepared according to the instructions, was allowed to stand for only one hour after the completion of the bromine addition.

ii). The steam distillation stage was omitted and the cis-1-bromopropene distilled and collected in three traps, cooled to -80°C. The material was finally dried over calcium chloride for 12 hours. Fractionation yielded cis-1-bromopropene, the purity of which was checked by infrared and v.p.c.

20. Cis-1-propenyltrimethylsilane

Several attempts to prepare the pure cis isomer, by modification of the method employed in the preparation of the trans isomer, failed. The purest material isolated contained 20% trans-1-propenyltrimethylsilane.

21. 1-Trimethylsilylcyclohex-1-ene[114]

Trimethylchlorosilane (50 ml, 0.4 mole) was slowly added to cyclo-1-enyl lithium[115] (53.0 g, 0.46 mole chlorocyclohex-1-ene, 6.9 g, 1.0 mole lithium metal in ether), taking the usual precautions to exclude moisture, at a rate aimed at maintaining a gentle reflux. Subsequent to the addition, the material was refluxed for one hour. The contents of the flask were then filtered, and the filtrate added to 200 ml, 10% ammonia solution. The organic layer was separated and dried over calcium chloride for 12 hours. Fractionation yielded 1-trimethylsilylcyclohex-1-ene, b.p. 172°C (Lit.[114] 171°C/752 mm)(38 g, 61% yield); nmr, neat liquid, centred at 6.2 p.p.m. a multiplet of intensity one (vinylic proton), two broad bands in the region 1.6-2.4 p.p.m. of intensity eight (methylene protons), at 0.3 p.p.m. a singlet of intensity nine (trimethylsilyl protons); infra-red, neat liquid, maxima (cm^{-1}) 1622m (stretching), 945m (out of plane deformation) - vinylic, 1255s (symmetric deformation), 840s, 860s, (stretching) - silicon methyl, 1440m, 1450m (bending) - carbon hydrogen.

22. Addition of hydrogen bromide to 1-trimethylsilylcyclohex-1-ene (XVII)

Following a similar procedure to that described on page 76, dry hydrogen bromide was bubbled through an ice-cold solution containing compound XVII and benzoyl peroxide. Attempts made by nmr to study the stereochemistry of the 1-trimethylsilyl-2-bromocyclohexane formed by this reaction, were unsuccessful, (see page 32).

23. Addition of bromine to 1-trimethylsilylcyclohex-1-ene

Bromine was added to XVII under similar conditions to those described in Section 15 (page 85). No change was observed in the nmr spectrum after several days, when a second spectrum of the dibrominated material was obtained.

24. Desilicohalogenation of erythro-1,2-dibromopropyltrimethylsilane

Trimethylbromosilane was obtained by reacting erythro-1,2-dibromopropyltrimethylsilane with the solvents listed in Table I (page 21). The desilicohalogenation was carried out at room temperature, by adding the erythro diastereoisomer to the solvent in a ratio of 1:10 v/v respectively. The elimination of trimethylbromosilane gave a mixture of cis and trans-1-bromopropenes. These were separated by preparative v.p.c. (column packing as described in ii). b). - page 75), and their configuration determined by nmr, by considering the proton coupling constants. The proportions in which the cis and trans isomers were formed initially, were determined using analytical v.p.c. (column packing as described in i). b). - page 75).

25. Threo-1,2-dibromopropyltrimethylsilane

The addition of bromine to the material prepared in Section 20 (page 87), followed a similar procedure to that described in Section 15 (page 85), and produced threo and erythro-1,2-dibromopropyltrimethylsilanes.

26. Desilicohalogenation of threo-1,2-dibromopropyltrimethylsilane

Although the pure threo diastereoisomer was not isolated, the elimination of trimethylbromosilane from the contaminated threo isomer served as a useful check on the proposed stereochemical route for the elimination reaction. Desilicohalogenation of the impure threo isomer, using the solvents listed in Table VI, yielded results which were consistent with those in Table I (page 21).

TABLE VI

Threo to erythro isomer ratio	Solvent mixture (ethanol : water)	1-Bromopropene product ratio cis : trans
80:20	100:0	79 : 21
80:20	95:5	78.5 : 21.5
80:20	80:20	75 : 25
28:72	100:0	70 : 30
28:72	80:20	68 : 32

Effect of varying erythro:threo isomer ratio and solvent composition on 1-bromopropene product ratio

27. Desilicohalogenation of 1-deutero-2-bromopropyltrimethylsilane

The elimination of trimethylbromosilane from 1-deutero-2-bromopropyltrimethylsilane in 98% aqueous ethanol, resulted in the formation of 1-deuteropropene. The method of the collection and analysis of this deuteropropene has been described by Bothner-By and Naar-Colin.[42]

28. Reaction of thionyl chloride with 2-dideutero-2-hydroxyethyltrimethylsilane

Excess thionyl chloride was added carefully to cooled 2-dideutero-2-hydroxyethyltrimethylsilane, in an nmr tube. The nmr spectrum of the resulting material indicated that it contained 55.0% 2-dideutero-2-

chloroethyltrimethylsilane together with 45.0% 1-dideutero-2-chloroethyltrimethylsilane, (cf. Section 6, page 79).

Kinetic Measurements

The value of the first order rate constants for the various materials synthesised, were determined by following the rate of ethylene evolution, which was observed on a relatively simple apparatus. This consisted of a thermostated reaction vessel, in which a liquid could be agitated, connected to a manometer. The reaction vessel was attached to a shaker, and connected to a fixed burette via a flexible coupling. To avoid errors due to ambient temperature changes, the burette was also thermostated. The volume of the burette was kept small in relation to the gas space in the reaction vessel.

The silane was weighed into a small glass-stoppered container, which was then introduced into the reaction vessel containing the previously equilibrated solvent. The reaction vessel was reconnected to the manometer, and the agitation of the vessel was sufficient to cause the release of the stopper from the container and allow the reaction to proceed. Timing began as soon as the two liquids came into contact. The final reading was taken when the reaction had been in progress for at least ten half-lives. However, in order to eliminate errors due to final reading, the Guggenheim plot was employed.[116] This method obviates the need for an accurate infinity value.

The variation in temperature was not greater than ±0.02°C over each run, and not greater than ±0.05°C over the entire series.

In order to check that the observed rate values were not functions of impurities, the materials were prepared in duplicate and separate kinetic runs performed on each one. In the case of the "mother" compound, that is, 2-bromoethyltrimethylsilane, three preparations were made:

i). From hydrogen bromide (commercially produced) bubbled through the vinylsilane.

ii). From hydrogen bromide (produced in the laboratory by the action of water on phosphorus tribromide) bubbled through the vinylsilane.

iii). From the addition of phosphorus tribromide to 2-hydroxyethyltrimethylsilane.

Kinetic measurements were performed on solutions containing the silane in 80% aqueous ethanol, at $25.22^\circ C \pm 0.05^\circ C$. Kinetic measurements on the hydroxyethylsilanes were observed using 8.5 M sulphuric acid in 50% aqueous methanol as solvent, at the same temperature.

The volume of ethylene evolved during the kinetic runs was recorded, and was 85-90% of the theoretical volume for each of the silanes.

--o--

BIBLIOGRAPHY

1. S. N. Ushakov and A. M. Itenburg, J. Gen. Chem. (U.S.S.R.), 7, 2495, (1937); Chem. Abs., 32, 2083, (1938).
2. L. H. Sommer and F. C. Whitmore, J. Amer. Chem. Soc., 68, 485, (1946).
3. L. H. Sommer, E. Dorfman, G. M. Goldberg and F. C. Whitmore, J. Amer. Chem. Soc., 68, 488, (1946).
4. L. H. Sommer, G. M. Goldberg, E. Dorfman and F. C. Whitmore, J. Amer. Chem. Soc., 68, 1083, (1946).
5. A. D. Petrov and V. F. Mironov, Izvest. Akad. Nauk S.S.S.R., (1952), 635; Chem. Abs., 47, 10471, (1953); 48, 4462, 5078, (1954).
6. L. H. Sommer, D. L. Bailey and F. C. Whitmore, J. Amer. Chem. Soc., 70, 2869, (1948).
7. D. T. Hurd, J. Amer. Chem. Soc., 67, 1813, (1945).
8. D. Seyferth and T. F. Jula, J. Organometal. Chem., 14, 109, (1968).
9. D. S. Matteson and J. D. Liedtke, J. Amer. Chem. Soc., 87, 1526, (1965).
10. E. D. Hughes and C. K. Ingold, Trans. Faraday Soc., 37, 657, (1941).

11. E. W. Bennett, Diss. Abs., 19, 3121, (1959).

12. (a) L. H. Sommer and G. A. Baughman, J. Amer. Chem. Soc., 83, 3346, (1961).

(b) See (a), Ref. 7.

13. E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 70, 846, (1948).

14. G. A. Baughman, Diss. Abs., 22, 2187, (1961).

15. M. M. Kreevoy and F. R. Kowitt, J. Amer. Chem. Soc., 82, 739, (1960).

16. R. W. Bott, C. Eaborn and B. M. Rushton, J. Organometal. Chem., 3, 455, (1965).

17. C. Eaborn, I. M. T. Davidson and M. Lilly, J. Chem. Soc., (1964), 264.

18. I. M. T. Davidson, M. R. Jones and C. Pett, J. Chem. Soc. (B), (1967), 937.

19. S. W. Benson and A. N. Bose, J. Chem. Phys., 39, 3463, (1963).

20. L. H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, 1965.

21. P. F. Franklin, J. Chem. Soc., (1912), 654.

22. I. Roberts and G. E. Kimball, J. Amer. Chem. Soc., 59, 947, (1937).

23. K. Yates and W. V. Wright, Tetrahedron Letters, (1965), 1927.

24. R. E. Buckles, J. M. Badar and R. J. Thurmaier, J. Org. Chem.,

27, 4523, (1962).

25. G. H. Alt and D. H. R. Barton, J. Chem. Soc., (1954), 4284.

26. R. A. Benkeser, Private Communication.

27. C. Eaborn, "Organosilicon Compounds", Butterworths Scientific Publications, 1960. (a) page 98.

28. A. A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc., **84**, 743, (1962).

29. F. A. L. Anet, J. Amer. Chem. Soc., **84**, 747, (1962).

30. D. V. Banthorpe, "Elimination Reactions", Elsevier, 1963.

31. W. Hanhart and C. K. Ingold, J. Chem. Soc., (1927), 997.

32. A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc., **78**, 2770, (1956).

33. L. Schmerling, J. Amer. Chem. Soc., **67**, 1152, (1945).

34. C. H. de Puy, G. F. Morris, J. S. Smith and R. J. Smat, J. Amer. Chem. Soc., **87**, 2421, (1965).

35. D. J. Cram, J. Amer. Chem. Soc., **74**, 2137, (1952).

36. L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, J. Chem. Soc., (1940), 979.

37. M. J. S. Dewar and R. C. Fahey, J. Amer. Chem. Soc., **85**, 2245, 2248, 3645, (1963).

38. P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, 1966.

39. M. S. Newman, "Steric Effects in Organic Chemistry", John Wiley

and Sons Inc., New York, N. Y., 1956, page 242.

40. H. Kwart and K. L. Nyce, J. Amer. Chem. Soc., 86, 2601, (1964).

41. L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, J. Amer. Chem. Soc., 76, 1613, (1954).

42. A. A. Bothner-By and C Naar-Colin, J. Amer. Chem. Soc., 83, 231, (1961).

43. J. Homer, Private Communication.

44. C. L. Agre and W. Hilling, J. Amer. Chem. Soc., 74, 3895, (1952).

45. E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, "Conformational Analysis", Interscience Publishers, New York, London, Sydney, 1965, page 228.

46. W. Reppe, O. Schlichting, K. Klage and T. Toepel, Annalen, 560, 1, (1948).

47. G. D. Sargent, Quart. Rev., 20, 301, (1966).

48. T. P. Nevell, E. de Salas, and C. L. Wilson, J. Chem. Soc., (1939), 1188.

49. S. Winstein and D. Trifan, J. Amer. Chem. Soc., 71, 2953, (1949); 74, 1147, 1154, (1952).

50. J. D. Roberts, C. C. Lee and W. H. Saunders, J. Amer. Chem. Soc., 76, 4501, (1954).

51. J. D. Roberts and R. H. Mazur, J. Amer. Chem. Soc., 73, 2509, (1951).

52. M. C. Caserio, W. H. Graham and J. D. Roberts, Tetrahedron, 11, 171, (1960).

53. F. C. Whitmore, L. H. Sommer and J. R. Gould, J. Amer. Chem. Soc., 69, 1976, (1947).

54. L. H. Sommer, D. L. Bailey, J. R. Gould and F. C. Whitmore, J. Amer. Chem. Soc., 76, 801, (1954).

55. L. H. Sommer and F. J. Evans, J. Amer. Chem. Soc., 76, 1186, (1954).

56. M. Kumada, M. Ishikawa, S. Maeda and K. Ikura, J. Organometal. Chem., 2, 146, (1964).

57. M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, J. Org. Chem., 23, 292, (1958).

58. M. Kumada, and M. Ishikawa, J. Organometal. Chem., 1, 411, (1964).

59. I. F. Lutsenko, Yu. I. Baukov, O. V. Dudukina and E. N. Kramarova, J. Organometal. Chem., 11, 35, (1968).

60. M. Kumada, M. Ishikawa and K. Tamao, J. Organometal. Chem., 5, 226, (1966).

61. M. Kumada and K. Tamao, "Advances in Organometallic Chemistry", 6, 19, (1968).

62. E. S. Lewis and C. E. Boozer, J. Amer. Chem. Soc., 74, 6306, (1952).

63. E. A. Halevi, Secondary Isotope Effects in S. G. Cohen, A. Streitwieser Jr. and R. W. Taft, Ed., "Progress in Physical

Organic Chemistry", Vol. 1, Interscience Publishers, New York, 1963.

64. S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", M^{c}Graw-Hill Book Company Inc., New York and London, 1941.

65. H. C. Urey, J. Chem. Soc., (1947), 562.

66. J. Bigeleisen and M. G. Mayer, J. Chem. Phys., **15**, 261, (1947).

67. A. Streitwieser Jr., R. H. Jagow, F. C. Fahey and S. Suzuki, J. Amer. Chem. Soc., **80**, 2326, (1958).

68. H. C. Brown and G. J. M^{c}Donald, J. Amer. Chem. Soc., **88**, 2514, (1966).

69. H. C. Brown, M. E. Azzaro, J. G. Koelling and G. J. M^{c}Donald, J. Amer. Chem. Soc., **88**, 2520, (1966).

70. V. J. Shiner and G. S. Kritz, J. Amer. Chem. Soc., **86**, 2643, (1964).

71. L. S. Bartell, J. Amer. Chem. Soc., **83**, 3567, (1961).

72. E. A. Halevi, M. Nussim and A. Ron, J. Chem. Soc., (1963), 866.

73. A. Streitwieser Jr., and H. S. Klein, J. Amer. Chem. Soc., **85**, 2759, (1963).

74. A. Streitwieser Jr., and H. S. Klein, J. Amer. Chem. Soc., **86**, 5170, (1964).

75. E. A. Halevi, A. Ron and S. Speiser, J. Chem. Soc., (1965), 2560.

76. "Conference on Hyperconjugation", University of Indiana,

Tetrahedron, 5, 105-274, (1959).

77. V. J. Shiner Jr., J. Amer. Chem. Soc., 82, 2655, (1960).

78. L. E. Melander and R. E. Carter, Acta Chem. Scand., 18, 1138, (1964).

79. F. J. Westheimer, J. Chem. Phys., 15, 252, (1947).

80. M. M. Harris and R. E. Mitchell, J. Chem. Soc., (1960), 1905.

81. W. H. Saunders Jr., S. Asperger and D. H. Edison, J. Amer. Chem. Soc., 80, 2421, (1958).

82. R. R. Johnson and E. S. Lewis, Proc. Chem. Soc., (1958), 52.

83. K. Mislow, S. Borcic and V. Prelog, Helv. Chim. Acta, 40, 2477, (1957).

84. S. Borcic, M. Nikoletic and D. E. Sunko, J. Amer. Chem. Soc., 84, 1615, (1962).

85. S. Seltzer, J. Amer. Chem. Soc., 83, 2625, (1961).

86. J. G. Jewett and R. P. Dunlap, J. Amer. Chem. Soc., 90, 809, (1968).

87. G. J. Karabatsos, G. C. Sonnichsen, C. G. Papaioannou, S. E. Scheppele and R. L. Shone, J. Amer. Chem. Soc., 89, 463, (1967).

88. L. E. Sutton, Tetrahedron, 5, 118, (1959).

89. V. Bazant, V. Chvalovsky and J. Rathousky, "Organosilicon Compounds", Publishing House of the Czechoslovak Academy of Sciences, Prague 1965.

90. L. M. Jackman, "Application of Nuclear Magnetic Resonance in Organic Chemistry", Pergamon, 1962.

91. J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vols. 1 and 2, Pergamon, 1966.

92. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen, 1958.

93. M. E. Bednas and D. S. Russell, Canad. J. Chem., **36**, 1272, (1958).

94. H. S. Knight, Analyt. Chem., **30**, 9, (1958).

95. R. Nagel and H. W. Post, J. Org. Chem., **17**, 1379, (1952).

96. R. T. Hobgood, J. H. Goldstein and G. S. Reddy, J. Chem. Phys., **35**, 2038,(1961).

97. M. Kanazashi, Bull. Chem. Soc. Japan, **26**, 2245, (1963).

98. I. F. Lutsenko, Yu. I. Baukov, G. S. Burlachenko and B. N. Khasapov, J. Organometal. Chem., **5**, 20, (1966).

99. F. C. Whitmore and L. H. Sommer, J. Amer. Chem. Soc., **68**, 481, (1946).

100. J. R. Gould, L. H. Sommer and F. C. Whitmore, J. Amer. Chem. Soc., **70**, 2874, (1948).

101. J. L. Speier, J. A. Webster and G. H. Barnes, J. Amer. Chem. Soc., **79**, 974, (1957).

102. F. A. Cotton, J. H. Fassnacht, W. D. Horrocks and N. A. Nelson,

J. Chem. Soc., (1959), 4138.

103. N. Weiner, "Organic Syntheses", John Wiley and Sons Inc., New York, Collective Vol. 2, page 279.

104. "The Dictionary of Organic Compounds", Eyre and Spottiswoode, Publishers Ltd., E. and F. N. Spon Ltd., (1965).

105. A. Murray and D. L. Williams, "Organic Syntheses with Isotopes", Part II, Interscience Publishers, (1958), page 1265.

106. B. Nolin, Canad. J. Chem., 31, 1257, (1953).

107. B. M. Mikhailov and A. N. Blokhina, J. Gen. Chem. U.S.S.R., 30, 3583, (1960).

108. N. L. Allinger and R. B. Hermann, J. Org. Chem., 26, 1040, (1961).

109. D. Seyferth and L. G. Vaughan, J. Amer. Chem. Soc., 86, 883, (1964).

110. D. Seyferth and L. G. Vaughan, J. Organometal. Chem., 1, 138, (1963-64).

111. V. F. Mironov and A. Petrov, Doklady Akad. Nauk S.S.S.R., 80, 761, (1951).

112. B. N. Dolgov, G. V. Golodnikov and I. B. Genser, Zhur. obshchei Khim., 30, 2988, (1960); Chem. Abs., 55, 19765, (1961).

113. E. A. Braude and R. A. Coles, J. Chem. Soc., (1951), 2085.

114. A. Petrov, V. F. Mironov and V. G. Glukhovtsev, J. Gen. Chem. U.S.S.R., 27, 1609, (1957).

115. E. A. Braude and R. A. Coles, *J. Chem. Soc.*, (1950), 2014.

116. E. A. Guggenheim, *Phil. Mag.*, **2**, 538, (1926).

-----o-----