THE REACTIONS OF TRIMETHYL TIN HYDRIDE AND TRIMETHYL GERMANIUM HYDRIDE WITH HALOGENOALKANES

David A. Coates

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

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A Thesis Presented

for

The Degree of

Doctor of Philosophy

of

The University of St. Andrews

by

David A. Coates B.Sc.

1972

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Research Training

The candidate entered Kingston-upon-Thames Polytechnical College in October 1966 and graduated with a London University Upper Second Class Honours Degree in Chemistry and Physics in July 1969.

The work described in this thesis was performed in the Chemistry Department, University of St. Andrews, between September 1969 and May 1972 under the supervision of Professor the Lord Tedder.

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The author is also indebted to the members of staff and technical staff for all their help and forbearance.

Finally, the author would like to thank the Scientific Research Council for their financial assistance.

Certificate

I certify that DAVID ASHLEY COATES, B.Sc., has spent eleven terms at research work under my direction and that he has fulfilled the conditions of Ordinance No. 12 and Resolution of the University Court, 1967, No. 1, so that he is qualified to submit the following thesis for the Degree of Doctor of Philosophy.

Professor Lord Tedder

Declaration

I hereby declare that the following Thesis is a record of the results of experiments performed by me, and further that the Thesis is my own composition and has not previously been presented for a higher degree.

To Anne

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ABSTRACT

This thesis deals with the abstraction of halogen atoms by trimethyl tin and trimethyl germanium radicals.

Part I deals with the reactions of trimethyl tin radicals, produced by the photolysis of trimethyl tin hydride, in the presence of halogeno alkanes.

Part II similarly deals with halogen abstraction using trimethyl germanium radicals produced by photolysis of trimethyl germanium hydride. A free radical chain mechanism appears to be operative in which a reaction scheme of the following form has been postulated. Evidence

$$(CH_3)_3M\cdot + RX \xrightarrow{k_2} (CH_3)_3MX + R\cdot$$

$$R\cdot + (CH_3)_3MH \xrightarrow{k_3} (CH_3)_3M\cdot + RH$$

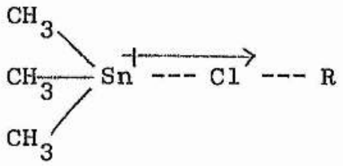
$$(CH_3)_3M\cdot + (CH_3)_3M\cdot \xrightarrow{k_4} (CH_3)_3M\text{-}M(CH_3)_3$$

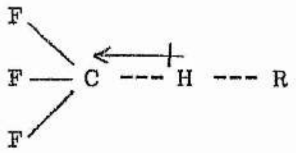
(M = Sn or Ge)

supporting this mechanism includes the dependence of the formation of the alkane on the $\frac{1}{2}$ power of the light intensity, the non-existence of any other termination products and the thermodynamics of the overall initiation and propagation steps.

The observed trends in abstraction rates, Br > Cl > F and for a particular halide tertiary > secondary > primary, are predicted by bond energy data and confirmed experimentally. Breaking of the C-X bond is hence of major importance in determining the relative rates of abstraction.

Polar effects have been discussed in terms of the four factors put forward by Tedder and the properties of these two nucleophilic radicals have been discussed in terms of Coulombic repulsive and attractive forces due to electron displacement in the transition state.





The change in reactivity, following substitution by electron withdrawing groups at the reaction site, provides evidence for the reversal of polar effects in the transition state. Substitution with electron withdrawing groups decreases the activation energy for halogen abstraction by trimethyl tin and trimethyl germanium radicals. However for hydrogen abstraction by chlorine atoms or trifluoromethyl radicals the activation energy is increased.

Introduction

It has been known for some years that the hydrides of tin and germanium will reduce carbon-halogen bonds to carbon-hydrogen bonds in a simple, clean reaction with high yield. Work has been performed in the solution phase and rates of halogen abstraction have been determined. However, prior to the present investigation, no data for gas phase reactions involving trialkyl tin and trialkyl germanium radicals was available.

The purpose of this investigation was to obtain further information about halogen abstraction from alkyl halides and particularly about polar effects in the transition state. It was hoped to see if the firmly established trends in hydrogen abstraction work were similar to those in halogen abstraction, and if not, account for the difference.

In order to account for the observed directive effects in hydrogen abstraction reactions most authors have assumed that the activated complex has considerable polar character with the halogen forming the negative end of the dipole[1,2,3]

$$RH + Cl\cdot \longrightarrow \overset{\delta+}{R} --- H --- \overset{\delta-}{Cl} \longrightarrow R\cdot + HCl$$

However in halogen abstraction by trimethyl tin or trimethyl germanium radicals we would expect the polarisation to be reversed

$$RCl + (CH_3)_3Sn\cdot \longrightarrow R --- \overset{\delta-}{Cl} --- \overset{\delta+}{Sn}(CH_3)_3 \longrightarrow R\cdot + (CH_3)_3SnCl$$

Since the other elements of group IVB are all more electropositive than carbon, $R_3M\cdot$ radicals (where M = Si, Ge, Sn and Pb) should be able to supply electrons, in the transition state of chemical reactions, more easily than the corresponding alkyl radicals. Each reaction should form an interesting contrast with those of electronegative radicals such as hydroxyl or halogen atoms.

Radical transfer reactions of the type:-

$$R_3M\cdot \ + \ X\text{-}Y \longrightarrow R_3M\text{-}X \ + \ Y\cdot$$

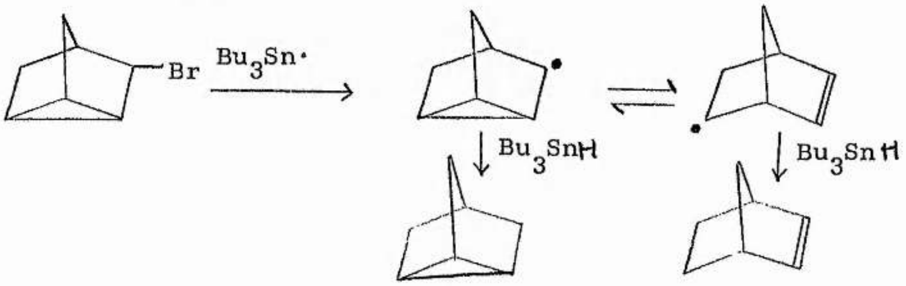
constitute an important class of radical reactions. The rate of such reactions is subject to a variety of factors[4] but one of the most important is the exothermicity or endothermicity of the reaction, which in turn depends on the bond dissociation energies $D(R_3M\text{-}X)$ and $D(X\text{-}Y)$. If the bond formed in the reaction ($R_3M\text{-}X$) is strong, the reaction will tend to be fast, and the reaction will also be facilitated if the bond to be broken (X-Y) is weak. The different pattern of bond dissociation energies for the other group IVB elements tend to form stronger bonds to halogen than to hydrogen whereas the reverse is true for carbon. Tin and germanium free radicals will tend to react by halogen abstraction, rather than by hydrogen abstraction reactions typical of carbon free radicals. This eliminates complicating factors due to hydrogen and halogen abstraction reactions competing for starting material. This point is very important as it makes the kinetics easier to interpret. Germyl radicals are known to abstract hydrogen[5], though this reaction does not proceed particularly readily at low temperatures. However trialkyl tin radicals do not readily abstract hydrogen and organotin hydrides are outstandingly efficient as radical transfer agents, due mainly to the weakness of the tin-hydrogen bond. If chlorine atoms can be abstracted, by trimethyl tin and trimethyl germanium radicals, from some sites that hydrogen atoms have been abstracted from by halogen atoms, direct conformation (or refutation) of the polar concepts should be obtainable.

The earliest work of importance in this field was that of Kuivila and co-workers[6] and others[7] who have shown that in solution the reduction of an alkyl halide, RX, with an organotin hydride, R_3SnH, proceeds by a free radical chain reaction

$$R'X + R_3Sn\cdot \longrightarrow R\cdot + R_3SnX$$

$$R\cdot + R_3SnH \longrightarrow RH + R_3Sn\cdot$$

For tributyltin hydride reductions of alkyl halides, the intermediacy of free alkyl radicals is supported by the fact that optically active $CH_3CHPhCl$ gives racemic α-deuterioethylbenzene with Ph_3SnD[6]. 2-Bromonortricyclene is reduced to a mixture of nortricyclene and norbornene and is inhibited by hydroquinone. Allylic and propargylic halides also give rearranged as well on unrearranged products.



The work by Kaplan[8] supports the high rate of reaction for the hydride abstraction from triorgano tin hydrides

$$Ph_3Sn\cdot + Ph_3C\text{-}CH_2Cl \longrightarrow Ph_3SnCl + Ph_3C\text{-}CH_2\cdot$$

$$Ph_3C\text{-}CH_2\cdot \longrightarrow Ph_2\dot{C}\text{-}CH_2Ph$$

$$Ph_3C\text{-}CH_2\cdot + Ph_3SnH \longrightarrow Ph_3C\text{-}CH_3 + Ph_3Sn\cdot$$

$$Ph_2\dot{C}\text{-}CH_2Ph + Ph_3SnH \longrightarrow Ph_2CH\text{-}CH_2Ph + Ph_3Sn\cdot$$

Kaplan obtained a mixture of 1,1,1-triphenylethane and 1,1,2-triphenylethane containing 30-90% of the 1,1,1-triphenylethane depending on reaction conditions. Since all previous methods of producing 2,2,2-triphenylethane radicals had given exclusively the rearranged product, the hydride abstraction step must be extremely fast.

Kuivila[6] measured the relative reactivities of a number of mono-and poly-substituted alkyl halides with various tin hydrides.

TABLE 1

The Relative rates of reduction of Organic halides by tri-n-butyl tin hydride[(a)]

Alkyl halide	RS
$PhCH_2Cl$	0.05
$cC_6H_{11}Br$	1.46
1-Bromobutane	1.00
t-BuBr	7 ± 1
$1\text{-}IC_7H_{15}$	61.1 ± 5.7
CCl_4	75.1 ± 4.7

(a) At 45°C

The order of reactivity of alkyl halides has been shown to be

$$RF < RCl < RBr < RI$$

and for a particular halogen abstracted tertiary > secondary > primary. Nagai and co-workers[9] found that polyhalogenated compounds are more easily reduced than monohalogenated compounds. Polyhalide reduction has also been studied by others[6,10,11] who found them to be reduced stepwise. This point is of significance later when we present our results for abstraction from polysubstituted groups.

Further work by D.J. Carlsson and K.U. Ingold[12] in solution has shown that the chains are generally terminated by bimolecular radical-radical reactions and in general, with alkyl chlorides the rate controlling step for chain propagation involves chlorine abstraction by the triorgano tin radical, while with bromides and iodides the rate controlling step involves hydrogen abstraction from the hydride by the alkyl radical.

TABLE 2

The relative reactivities of alkyl halides towards the tri-n-butyl tin radical.

Alkyl halide	RS
$cC_6H_{11}F$	< 0.1
1-chloropentane	$1^{(a)}$
$cC_6H_{11}Cl$	1.7
t-BuCl	11
$PhCH_2Cl$	540
$cC_6H_{11}Br$	1.9×10^4
1-bromohexane	1.63×10^4
t-BuBr	7.22×10^4
CH_3I	2.09×10^6

(a) Assumed Standard)

They[13] also found that tri-n-butyl tin hydride was about 10-20 times as good a hydrogen donor to alkyl radicals as was tri-n-butyl germanium hydride. This point will be discussed later.

Work in the gas phase on halogen abstraction is very limited. Polanyi and co-workers[14] investigated the reaction

$RX + Na \longrightarrow R\cdot + NaX$ $\left(X = \text{halogen}\right)$ by the sodium flame technique, while Whittle et al.[15] and Carmichael[16] have investigated the reaction of trifluoromethyl radicals with both aromatic bromo compounds and polyhalogenated methanes. Arrhenius parameters have been measured for all possible reactions involving abstraction of H or Cl.

In solution Szwarc[17] has investigated the abstraction of halogen by methyl radicals.

$$CH_3\cdot + R\text{-}X \longrightarrow CH_3X + R\cdot \qquad X = \text{halogen}$$

The activation energies of these reactions were found to be lowered considerably by the presence of electron withdrawing groups in the parent molecule, and it was emphasised that the repulsion between the approaching methyl radical and the stretched C-X bond was an important factor. Some comment about the work of Szwarc (using methyl radicals) and of Whittle (using trifluoromethyl radicals) is necessary at this point. Both authors draw attention to the fact that methyl radicals and trifluoromethyl radicals preferentially abstract hydrogen atoms in cases where simple bond strength arguments would lead one to expect halogen atom abstraction to be preferred. Szwarc suggests that this relative facility for hydrogen abstraction is due to the presence of Coulombic repulsion between the p-electrons of the attacking radical and the closed shell of the halogen atom. Szwarc also invokes this repulsive concept to explain the fact that even though $D(CF_3-I)$ is slightly greater than $D(CH_3-I)$ abstraction of iodine from trifluoromethyl iodide is about 500 times faster at 338°K than abstraction from methyl iodide. This latter result as Szwarc observes can also be explained in terms of a simple polar argument in which the transition state can be represented thus:-

$$CF_3I + Me\cdot \longrightarrow \overset{\delta-}{CF_3} --- I --- \overset{\delta+}{CH_3} \longrightarrow CF_3\cdot + MeI$$

but he prefers to consider the effect the electronegative trifluoromethyl group will have on the proposed Coulombic repulsion. The same problem also arises with bromotrichloromethane and benzylbromide, where the methyl radical abstracts bromine from the halomethane faster than from the benzylbromide. In the reaction of trimethyl tin radicals with partially halogenated alkanes hydrogen abstraction is thermochemically unfavourable compared with halogen abstraction. Regardless of the interpretations of Szwarc's data we would expect halogen abstraction to predominate.

Pritchard and co-workers[18] have investigated the reaction of methyl radicals with mainly halogenated methanes in the gas phase. They found that the pre-exponential factors are rather higher than for analogous hydrogen abstraction reactions. Their relative rates are below:-

TABLE 3

Relative Rates for the reaction $CH_3^{\cdot} + RX \longrightarrow CH_3X + R\cdot$ at 130°C

Chlorides		Bromides		Iodides	
$CFCl_3$	0.1	CF_3Br	2	C_6H_5I	1.5
$CFCl_2CF_2Cl$	0.1	CF_2Br_2	13	nC_3H_7I	140
C_2Cl_4	0.1	CF_2ClBr	17	$secC_3H_7I$	270
$C_6H_5CCl_3$	0.5	CCl_3Br	1000	CF_3I	2150
C_2Cl_6	0.7	CCl_2Br_2	2300	CH_2I_2	2800
CCl_4	1	CBr_4	4300		
CCl_3COCCl_3	5				
CCl_3CN	7				

Phillip[19] has demonstrated the abstraction of chlorine atoms from gaseous t-butyl hypochlorite by methyl radicals while K.D. King[20] and his co-workers used methyl radicals to abstract chlorine from gaseous ethyl chloride, neopentyl chloride and 1,2-dichloroethane. Cadogan[21] and co-workers have studied the abstraction of halogen from halogenated methanes using both aryl and hexyl radicals. More recently and with the most similar study to the present work, Kerr[22] and co-workers have studied the gas phase abstraction of halogen atoms from alkyl halides with trichlorosilyl radicals. The results they get are shown below.

TABLE 4

Relative rate constants at 275°C based on n-butyl chloride as standard for halogen abstraction by trichlorosilyl radicals.

RX	k[RX]/k[nBuCl]
nBuCl	1.0
secBuCl	2.6
t-BuCl	7.3

These values will be discussed later. It can be seen from this work that little quantitative data is available and no data on highly unusual nucleophilic radicals such as trimethyl tin and trimethyl germanium radicals has appeared in the literature.

PART I

SECTION I

The photochemical reaction of trimethyl tin hydride with mono- and dihalogenated alkanes

SECTION I

Introduction

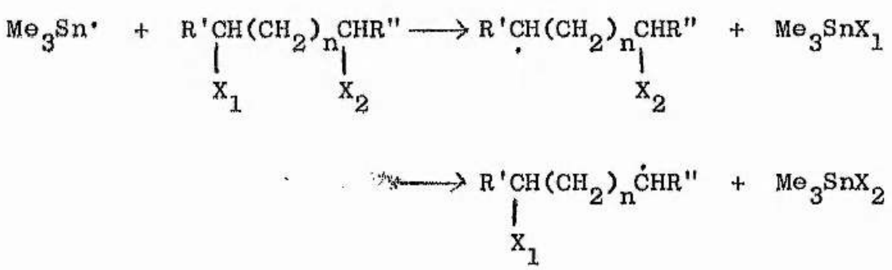
It has been shown[6] that the reaction of triorgano tin hydrides with alkyl halides proceeds via a free radical chain mechanism involving the triorgano tin radical. The radical abstracts a halogen atom to form triorgano tinhalide and an alkyl radical which propagates the chain via abstraction of the hydrogen atom from the radical source, the triorgano tin hydride.

In an attempt to discover quantitative relationships between the relative selectivity values of a series of related free radical abstraction reactions and stabilisation effects of the radicals (i.e. resonance, hyperconjugation and polar effects), a series of experiments using trimethyl tin radicals was studied. Monosubstituted substrates in competition according to the general scheme outlined in I.

$$Me_3Sn\cdot \; + \; RX \longrightarrow R\cdot \; + \; Me_3SnX \quad - \quad I\ (a)$$

$$Me_3Sn\cdot \; + \; R'X \longrightarrow R'\cdot \; + \; Me_3SnX \quad - \quad I\ (b)$$

or a disubstituted substrate



$$Me_3Sn^{\cdot} + R'\underset{X_1}{CH}(CH_2)_n\underset{X_2}{CHR''} \longrightarrow R'\underset{\cdot}{C}H(CH_2)_n\underset{X_2}{CHR''} + Me_3SnX_1$$

$$\longrightarrow R'\underset{X_1}{CH}(CH_2)_n\overset{\cdot}{C}HR'' + Me_3SnX_2$$

were used in which halogen atoms on the same molecule would be in competition.

Studies by Kuivila[6] and co-workers, in solution, have shown that the reduction of an alkyl halide RX with a triorgano tin hydride proceeds by a free radical chain mechanism and the reactivity of alkyl halides towards a given tin hydride increases in the order RF < RCl < RBr < RI. For a particular halogen the reactivities increase in the order primary < secondary < tertiary halide. To verify the chain mechanism and to see if the above relations were the same when performed in the gas phase the forementioned competitive experiments were performed. It was hoped that the results would yield a satisfactory mechanism for the reactions and provide data on the relative rates of halogen abstraction from different sites in substituted alkanes. It was anticipated that the results of this study would provide some insight into the factors influencing the rate of abstraction by this nucleophilic radical.

EXPERIMENTAL

Materials:-

Trimethyl tin hydride was synthesised from trimethyl tin chloride by the method of van der Kerk[23]. Anhydrous stannic chloride (50 g) was added dropwise over a period of 3 hours to a solution of methyl magnesium iodide in di-n-butyl ether (24 g). The stirring was rapid to prevent undue formation of the ether-stannic chloride complex. The reaction mixture was then heated under reflux (85-95°C) for one hour and the crude product distilled from the reaction vessel. A mixture of tetramethyl tin and di-n-butyl ether distilled off at 115°C. This was then fractionated using a simple Vigreaux column and the main fraction of tetramethyl tin distilled over at 76.6-77.2°C (760 mm uncorrected) yield 30g - 87%.

The tetramethyl tin (30 g) dissolved in chloroform (100ml) was heated to boiling point (61°C) and treated with dry hydrogen chloride over a period of 10 hours. The boiling point rose slowly to 105°C. At this point the hydrogen chloride was discontinued and the chloroform removed by fractionation. Fine white needle crystals, with a pungent odour, of trimethyl tin chloride formed on cooling. These were filtered, sucked dry and placed in a vacuum desiccator with paraffin wax at the bottom.
Yield 29.8 g - 93%.

The dry trimethyl tin chloride (70 g) was mixed with dry di-n-butyl ether(100 ml) and added dropwise to a solution of aluminium lithium hydride (8 g) in dry di-n-butyl ether (200 ml). The reaction mixture was heated at 50°C for 1 hour under nitrogen. The volatile trimethyl tin hydride was removed from the reaction mixture by distillation (Widner column, bath at temperature of the boiling point of the ether). Redistillation of the impure hydride afforded 34 g of trimethyl tin hydride of 97% purity. Boiling point 59-60°C of 760 mm . The material was stored under nitrogen at -15°C in the dark to prevent any disproportionation.

The trimethyl tin deutoride was prepared in an analogous manner using aluminium lithium deutoride (supplied by Peninsular Chemicals) in the same quantities as for the trimethyl tin hydride case. The product was purified to >98% by fractionation and stored under nitrogen at -15°C.

<u>Purification of Reactants</u>:- All reactants used were of purity > 98% except for the trimethyl tin hydride which contained <3% of tetramethyl tin as impurity. In view of other work[24] this impurity would have negligible effect on the overall reaction. This was confirmed when a pure sample was prepared. The reaction products as well as k_{1a}/k_{1b} remained the same using both the pure and the impure trimethyl tin hydride. Many of the starting materials listed below had to be prepared and most of the commercial materials had to be purified. This was performed either by using a Pye 105 preparative gas chromatograph if the starting material was small (< 1.0 ml) or by the use of a spinning band column (after Dr. Abby) if the starting sample was larger (> 2.0 ml). Both methods produced materials of 98% minimum purity.

(a) 1-Chloro-4-fluorobutane:- was prepared by the method due to F.W. Hoffman[25]. Purification was by Pye 105 preparative GLC using a 15' glass column packed with 20% dinonylphthalate on 60-100 mesh Embacel.

(b) 1-Bromo-3-chlorobutane:- the commercial material (supplied by Peninsular Chemicals) was found to have approximately 5% impurity. This was removed by preparative GLC using a 7' glass column packed with 20% tritolylphosphate on 60-100 mesh celite.

(c) 1,3-Dichlorobutane:- the commercial material (supplied by Fluka) was fractionated, on the spinning band, under reduced pressure and the middle fraction taken. This was of 99% purity by GLC.

(d) 1,3-Dichloro-3-methylbutane[26] was prepared in 89% yield by the reaction of isoprene and hydrogen chloride under 30 atmospheres. Initial pressure at room temperature. The reaction mixture was purified by GLC using a 7' glass column packed with 20% dinonylphthalate on 60-100 mesh embacel.

(e) 1-Chloro-4-bromobutane[27] was prepared by treating 4-chloro-1-butanol with PBr_3 and then fractionating the resultant products to give a fraction boiling between 175-176°C. This was purified by further fractionation under reduced pressure, to give a product of 98% purity by GLC.

(f) t-Butyl chloride, chlorocyclohexane, 2-chloropentane and 2-chloro-2-methylbutane were commercially available (British Drug Houses) and did not need purifying except for trap to trap distillation.

(g) 1-Chloro-3-methylbutane and 1-chloroheptane were purified by preparative GLC using a 15' glass column packed with 10% silicon oil (Edwards 703 silicone oil) on 60-100 mesh embacel.

(h) The deutrochloroform (supplied by Peninsular Chemicals) was used without further purification.

Apparatus

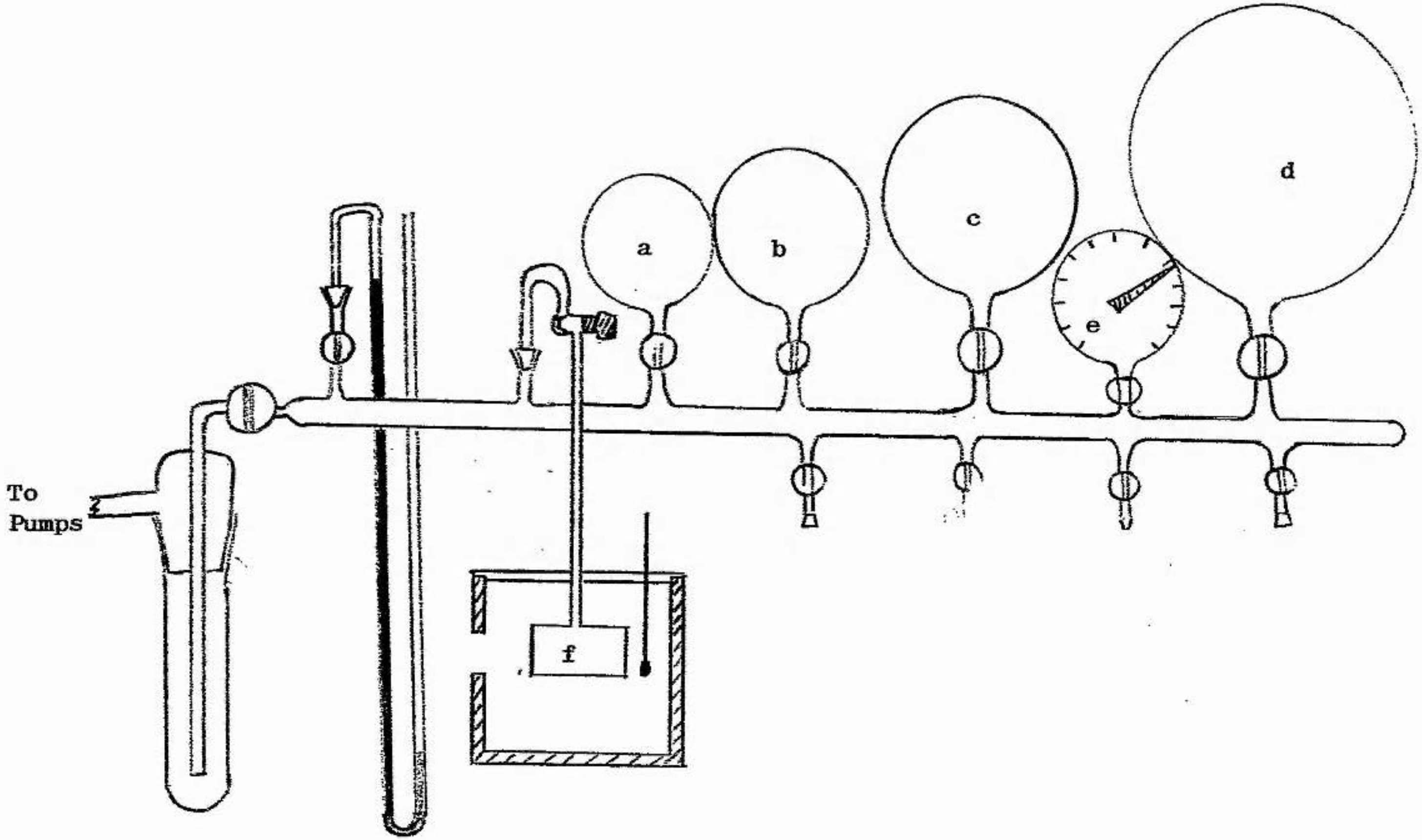
Vacuum Line Assembly

A conventional vacuum line was employed. Fig. 1. The mercury manometer was never used. An Edwards capsular gauge 0-20 torr was used in the measurement of the reactants. The vacuum was maintained by a "Speedivac" silicone oil vapour diffusion pump(model OPW10),using a NGN (model PSRI) single stage rotary pump as a backing pump. The bulbs a, b, c, d were calibrated on the line using methanol. A plot of Pmm/n where n is the number of moles of methanol gave a straight line from which the volumes could be determined to <2%

a = 147.3 ± 0.8 ml
b = 393.7 ± 0.7 ml
c = 1223.9 ± 0.5 ml
d = 5236 ± 1.8 ml

The reaction vessel of quartz was cylindrical with plate quartz windows at each end (volume = 133 ± 1.1 ml). The reactants were initially carefully 'degassed' and then distilled into the reaction vessel using liquid nitrogen as a transfer agent. The reaction vessel was then surrounded by a cylindrical plate heated furnace and adjusted to a chosen reaction temperature by means of a mercury in glass thermometer. When the temperature was constant the reaction vessel was irradiated with light from a Hanovia UVS 220 medium pressure mercury arc placed 13.5 ± 0.2 cm from the reaction vessel. Variable incident light intensity was achieved by placing gauzes of different mesh size between the lamp and the reaction vessel. The gauze transmissions were calibrated on a Unicam SP800 ultraviolet spectrometer at 3650 Å. The mercury arc was allowed a period of 10 minutes to warm up and any final adjustment in temperature of the furnace was made in this time. At the end of

Apparatus Fig. I



the photolysis period the reaction vessel was opened and the contents distilled over, to a small trap, for a period of not less than twenty minutes.

Procedure:-

The reagents were placed on the line ($\sim$0.8 ml) as required in small storage tubes and 'degassed' by allowing the reagent to be alternatively frozen in liquid nitrogen and pumped out and then warmed till liquid again. This process was repeated until no bubbles formed on warming the frozen sample. The 'degassed' reactant was allowed to expand into the main line and one of the evacuated bulbs (b, c or d fig I). When a suitable pressure was registered, on the vacuum gauge, the bulb tap was closed and the reactant in the main line was redistilled back into the small storage tube by cooling in liquid nitrogen. A similar procedure was required for the trimethyl tin hydride. This was always placed in bulb (a) unless concentration effects were being studied. These measured amounts were then distilled from their bulbs into the evacuated quartz reaction vessel by cooling the reaction vessel with liquid nitrogen. After sufficient time for complete distillation (not less than 20 minutes) the reaction vessel was closed and the main line tap opened so the line could be pumped during the photolysis period. The preheated furnace was then raised around the reaction vessel and the mercury arc struck. A ten minute warm-up period was usually needed to stabilise the furnace temperature. When the working temperature was reached the shutter was opened from the illumination aperture in the furnace wall. At the end of the reaction time the reaction mixture was distilled into a small tube attached to the main line. This required about 20-30 minutes. The sample tube was then frozen down and removed from the main line. A sample was then injected into the D6 for analysis. After each run the reaction vessel had to be cleaned out using chromic acid as a thin film formed over the end window. The vessel was pumped for 8 hours before the next run.

Gas Chromatographic Apparatus

Analysis:-

The products were analysed using a Griffin and George D6. This consists basically of an injector, column, amplifier, recorder and a Martin and James density balance. The detector and column were mounted in an oven which could be maintained accurately at temperatures up to 200°C. A 6' x 3/16" stainless steel column packed with support and various liquid phases, to give the most satisfactory separation, was used. A metered flow of oxygen free nitrogen was used as carrier and reference gas. The injector was a fine stainless steel needle of known volume (3.2 μl) attached to a plunger which could be withdrawn into a sheath. The needle was filled by capillary action. The sheath was inserted through rubber seals at the top of the column and the plunger depressed. This placed the known volume at the top of the column which was then carried away by the carrier gas. The detector was a gas density balance which formed part of a Wheatstone bridge resistance network. One leg of the balance was to the effluent from the column and the other to the reference stream of pure carrier gas. While the column effluent contained only pure carrier gas the bridge circuit remained balanced. However, when another gas, a sample constituent, was eluted with the carrier gas the densities of the carrier and reference were changed . The bridge became unbalanced and the small difference was then amplified and fed to a recorder as a potential difference. The recorder, a Honeywell Brown 1 Millivolt potentiometric recorder, then produced a peak on the recording paper.

If the weight (w) of effluent of molecular weight(M) passes through the density balance in the carrier gas of molecular weight (m), then the measured peak area A on the chromatogram is given by

$$w = kA \frac{M}{M-m}$$ where k is a constant of the instrument.

Thus in a chromatogram of a reaction mixture, if the molecular weights of the components and the carrier gas ($N_2 = 28$) are known, the relative concentrations of the products can be readily computed. However in the present work only competitive reactions took place so we have $\frac{w^1}{w_2} = \frac{A^1M^1 \times (M_2-m_2)}{(M^1-m^1)\ A_2M_2}$ and the constant of the instrument need not be known. Attenuation changes increased or decreased the amplification factor of the recorder by a fixed amount allowing both large and small peaks to be measured. Initially integration was by a Honeywell precision integration system but this was quickly changed to a Dupont 310 curve resolver permitting the areas to be measured to 2%.

Identification of reaction products:-

The retention times of the reaction products were compared with those of authentic materials chromatographed under identical conditions. This was performed on at least two separate columns and three columns if the products were very close and hard to identify. As an additional check the authentic materials were added to the reaction products, one at a time. On chromatographing these mixtures, the familiar pattern of products appeared, except that in each case one peak was enlarged. This enlarged peak could then be assigned to the particular material added. In several cases mass spectra of individual products had to be taken to confirm retention time data. This was performed by using the Pye 105 preparative GLC or by means of a Pye 104 GLC coupled to an AEI MS9 mass spectrometer. The glass column used in the 104 was 7' long and packed with 20% dinonylphthalate on 60-80 mesh embacel. This gave excellent separation in all cases making identification of the spectra relatively easy.

Results

Variation of incident light intensity

A series of experiments, at constant temperature, for a fixed reaction time and with a constant concentration of trimethyl tin hydride and 1,3-dichlorobutane were carried out at varying values of the light intensity

Transmission	Temp °C	Time(sec)	%age Conversion $\frac{1\text{-}C_4H_9Cl + 2\text{-}C_4H_9Cl}{CH_2ClCH_2CH(Cl)CH_3} \times 100\%$	No. of Runs
100%	100±2	300	11.11 ± 1.81	4
65%	100±2	300	7.40 ± 1.41	4
61%	100±2	300	8.24 ± 1.43	4
46%	100±2	300	7.17 ± 0.34	4
33%	100±2	300	5.34 ± 0.48	3
25%	100±2	300	5.31 ± 0.32	4

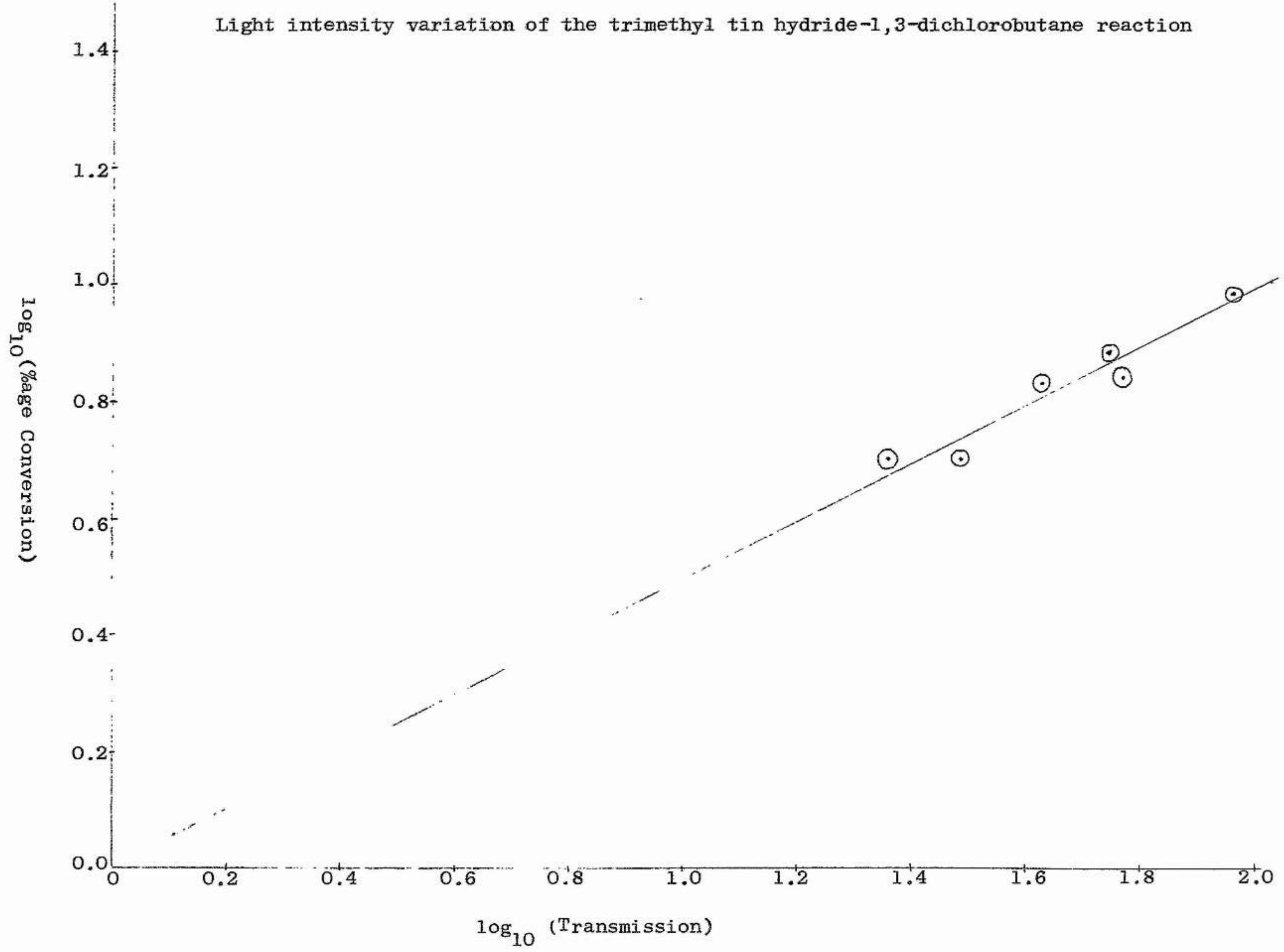
Only 13% conversion (maximum) of the dichloride was carried out so the error in the figure for 1,3-dichlorobutane is very small. The quantity "$\log_{10}\frac{1\text{-}C_4H_9Cl + 2\text{-}C_4H_9Cl}{CH_2ClCH_2CH(Cl)CH_3}$" was plotted against $\log_{10}$ (%age transmission) and gave a straight line. The "least squares" method gave a value of 0.50 ± 0.04 for the slope.

Reaction of Me_3SnH with $CDCl_3$:-

Trimethyl tin hydride (7.76×10^{-4} molar) and deutrochloroform (3.32×10^{-4} molar) were irradiated for 5 minutes at 105 ± 2°C and 145 ± 2°C. The reaction mixtures were analysed for trimethyl tin deutoride using the AEI MS9 GLC coupled mass spectrometer. No trimethyl tin deutoride could be detected.

Reaction of trimethyl tin deutoride with cyclohexane:-

Trimethyl tin deutoride (7.76×10^{-4} molar) and cyclohexane



Light intensity variation of the trimethyl tin hydride-1,3-dichlorobutane reaction

(3.32×10^{-4} molar) were irradiated for 10 minutes at 100 ± 2°C and 130 ± 2°C. The reaction mixtures were then analysed for deutrocyclohexane using the AEI MS9 GLC coupled mass spectrometer. No deutrocyclohexane could be found.

Thermal Reactions:-

Trimethyl tin hydride (7.76×10^{-4} molar), 1,4-dichlorobutane (3.32×10^{-4} molar) and 1-chloro-3-methylbutane (3.32×10^{-4} molar) were heated to 108 ± 2°C and 140 ± 2°C for 20 minutes and then analysed. No detectable products were found and the area ratio of the starting reactants remained constant.

Abstraction from R-Cl

Section AI The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1-chloro-4-fluorobutane (3.32×10^{-4} molar). Photolysed for 15 minutes

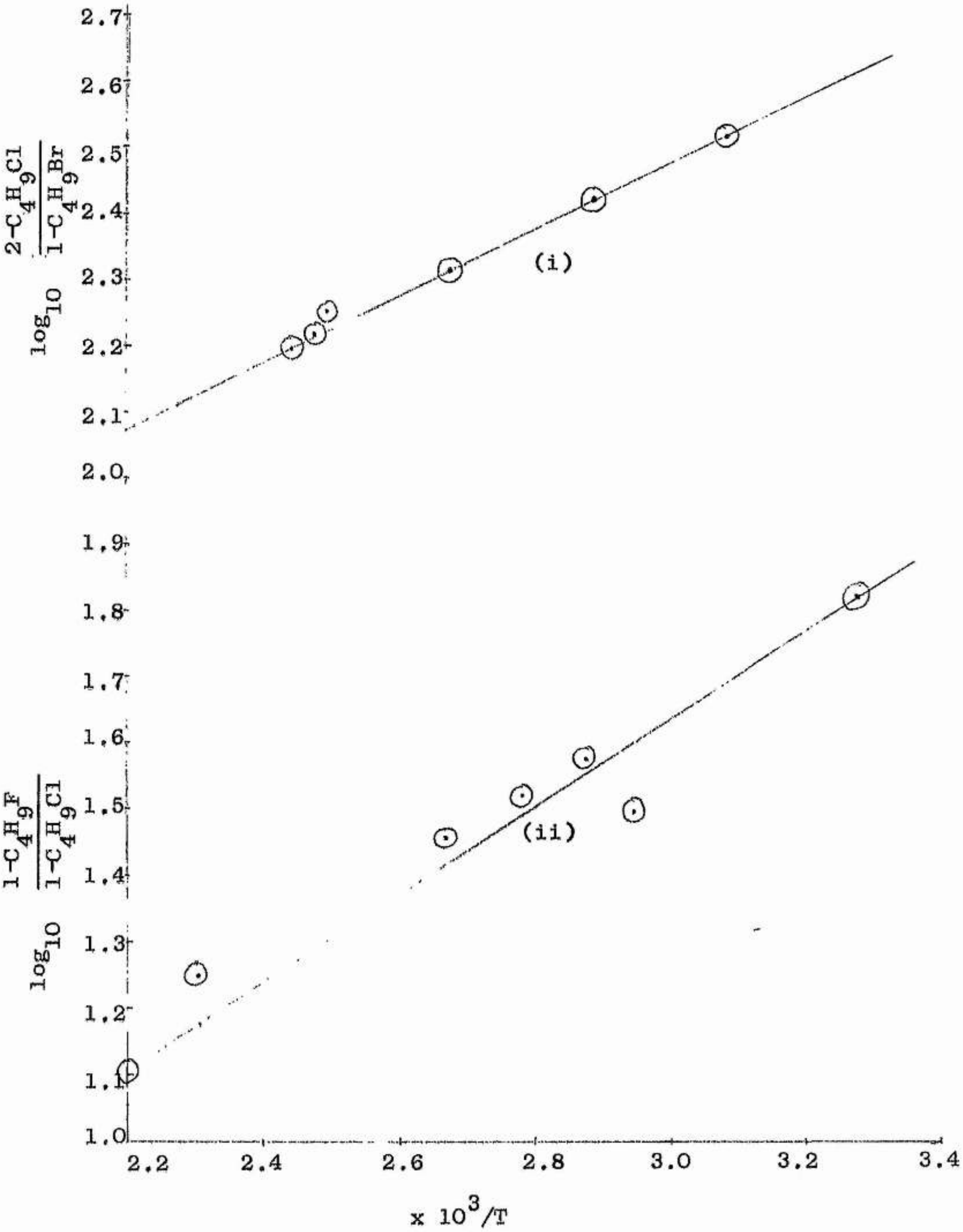
TABLE AI

Run No.	No. of Runs	Temp °C	Product Ratio $[1\text{-}C_4H_9F]/[1\text{-}C_4H_9Cl]$
1	4	184 ± 1	11.41 ± 1.15
2	4	161 ± 1	14.07 ± 0.47
3	4	100 ± 1	23.55 ± 1.58
4	4	83 ± 1	26.14 ± 2.28
5	5	73 ± 1	30.95 ± 2.10
6	4	65 ± 1	25.25 ± 0.53
7	3	30 ± 1	57.06 ± 1.99

A plot of $\log_{10} [nC_4H_9F]/[nC_4H_9Cl]$ vs $10^3/T$ gave a straight line. The "least squares" method gave the gradient $(E_{1^oF} - E_{1^oCl})/2.303R$. $= 0.57 \pm 0.08$ and the intercept $\log_{10}A_{1^oCl} - \log_{10}A_{1^oF} = -0.19 \pm 0.03$.

(i) The reaction of trimethyl tin hydride and 1-bromo-3-chlorobutane

(ii) The reaction of trimethyl tin hydride and 1-chloro-4-fluorobutane



II The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1-bromo-3-chlorobutane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE A II

Run No.	No. of Runs	Temp °C	Product Ratio $[2\text{-}C_4H_9Cl]/[1\text{-}C_4H_9Br]$
1	3	135 ± 1	128.78 ± 2.06
2	3	133 ± 1	135.19 ± 8.93
3	3	126 ± 1	150.42 ± 2.01
4	3	100 ± 1	180.92 ± 9.80
5	3	71 ± 1	227.68 ± 3.48
6	3	50 ± 1	290.36 ± 6.32

A plot of $\log_{10} [2\text{-}C_4H_9Cl]/[n\text{-}C_4H_9Br]$ vs $10^3/T$ gave a straight line. The "least squares" method gave the gradient $(E_{2^oCl}-E_{1^oBr})/2.303R = 0.51 \pm 0.04$ and the intercept $\log_{10}A_{1^oBr}-\log_{10}A_{2^oCl} = 0.87 \pm 0.01$

III The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,3-dichlorobutane (3.32×10^{-4} molar) Photolysed for 10 minutes

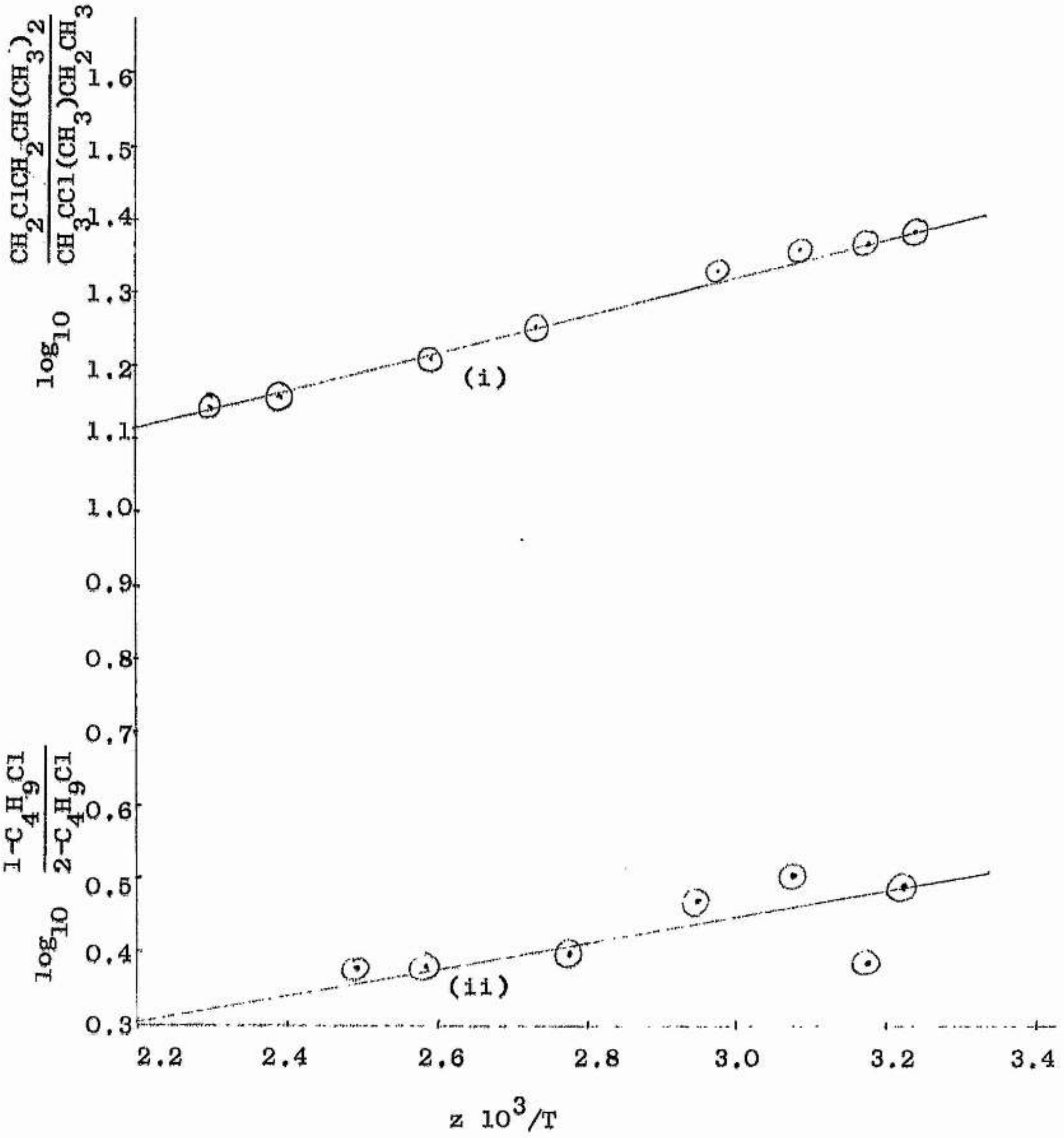
TABLE A III

Run No.	No. of Runs	Temp °C	Product Ratio $[1\text{-}C_4H_9Cl]/[2\text{-}C_4H_9Cl]$
1	5	161 ± 2	1.81 ± 0.05
2	5	128 ± 2	2.50 ± 0.04
3	5	114 ± 2	2.47 ± 0.04
4	5	85 ± 2	2.54 ± 0.14
5	4	65 ± 2	3.07 ± 0.08
6	5	50 ± 2	3.30 ± 0.10
7	4	41 ± 2	2.38 ± 0.14
8	4	36 ± 2	3.12 ± 0.05

A plot of $\log_{10}[n\text{-}C_4H_9Cl]/[2\text{-}C_4H_9Cl]$ vs $10^3/T$ gave a straight line. The "least squares" method gave for the gradient $(E_{1^oCl}-E_{2^oCl})/2.303R = 0.86 \pm 0.35$ and intercept $\log_{10}A_{2^oCl}-\log_{10}A_{1^oCl} = -0.12 \pm 0.02$

(i) The reaction of trimethyl tin hydride with 1,3-dichloro-3-methylbutane

(ii) The reaction of trimethyl tin hydride with 1,3-dichlorobutane



IV The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,3-dichloro-3-methylbutane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE A IV

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_2ClCH_2CH(CH_3)_2]/[CH_3CCl(CH_3)CH_2CH_3]$
1	4	162 ± 2	14.83 ± 0.07
2	5	146 ± 2	15.27 ± 0.37
3	5	111 ± 2	16.72 ± 0.40
4	5	90 ± 2	19.42 ± 0.33
5	5	60 ± 2	22.66 ± 0.40
6	5	49 ± 2	23.68 ± 0.24
7	5	33 ± 2	25.09 ± 0.61

A plot of $\log_{10}$[1-chloro-3-methylbutane]/[2-chloro-2-methylbutane] vs $10^3/T$ gave a straight line. The "least squares" method gave the gradient $[E_{1^oCl} - E_{3^oCl}]/2.303R = 0.25 \pm 0.02$ and intercept $\log_{10}A_{3^oCl} - \log_{10}A_{1^oCl} = 0.58 \pm 0.01$

V The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1-chloro-4-bromobutane (3.32×10^{-4} molar) Photolysed for 60 minutes

TABLE A V

Run No.	No. of Runs	Temp °C	Product Ratio $[1\text{-}C_4H_9Cl]/[1\text{-}C_4H_9Br]$
1	4	161 ± 1	24.55 ± 0.98
2	2	141 ± 1	18.23 ± 1.48
3	3	125 ± 1	19.98 ± 0.91
4	4	118 ± 1	25.85 ± 1.63
5	4	97 ± 1	13.88 ± 0.61
6	4	84 ± 1	14.26 ± 1.88
7	3	70 ± 1	12.71 ± 1.04
8	4	50 ± 1	10.78 ± 0.71

BI The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,4-dichlorobutane (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE B I

Run No.	No. of Runs	Temp °C	Product Ratio $[C_6H_{12}]/[n\text{-}C_4H_9Cl]$
1	5	155 ± 1	2.32 ± 0.07
2	4	139 ± 1	2.05 ± 0.01
3	5	125 ± 1	2.24 ± 0.11
4	5	117 ± 1	1.59 ± 0.04
5	4	85 ± 1	2.43 ± 0.37
6	6	70 ± 1	2.04 ± 0.23
7	3	65 ± 1	1.57 ± 0.01
8	6	40 ± 1	1.98 ± 0.02
9	6	28 ± 1	1.18 ± 0.12

II The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with tertiary butyl chloride (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE B II

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_3CH(CH_3)_2]/[C_6H_{12}]$
1	4	154 ± 1	4.03 ± 0.32
2	4	121 ± 1	4.56 ± 0.01
3	4	105 ± 1	5.52 ± 1.14
4	3	96 ± 1	3.77 ± 0.03
5	4	72 ± 1	2.66 ± 0.08
6	4	58 ± 1	3.18 ± 0.10
7	4	32 ± 1	3.19 ± 0.05

III The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,3-dichloro-3-methylbutane (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE B III

Run No.	No. of Runs	Temp °C	Product Ratio $\frac{[C_6H_{12}]}{[CH_3CCl(CH_3)CH_2CH_3]}$	$\frac{[ClCH_2CH_2CH(CH_3)_2]}{[C_6H_{12}]}$
1	2	145 ± 1	4.28 ± 0.03	4.09 ± 0.22
2	3	113 ± 1	2.52 ± 0.10	5.53 ± 0.24
3	3	89 ± 1	2.47 ± 0.32	5.52 ± 0.64
4	4	73 ± 1	2.41 ± 0.17	11.91 ± 0.92
5	3	68 ± 1	2.24 ± 0.17	8.26 ± 0.46
6	3	35 ± 1	1.98 ± 0.02	13.12 ± 0.01

IV The reaction of trimethyl tin hydride (7.76 x 10^{-4} molar) with 2-chloro-2-methylbutane (3.32 x 10^{-4} molar) and chlorocyclohexane (3.32 x 10^{-4} molar) Photolysed for 10 minutes

TABLE B IV

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_3CH(CH_3)CH_2CH_3]/[C_6H_{12}]$
1	3	147 ± 1	4.24 ± 0.09
2	3	123 ± 1	4.77 ± 0.10
3	3	105 ± 1	3.08 ± 0.08
4	3	92 ± 1	2.63 ± 0.08
5	2	73 ± 1	2.03 ± 0.10
6	3	71 ± 1	2.87 ± 0.15
7	3	62 ± 1	2.12 ± 0.06
8	3	60 ± 1	2.17 ± 0.06
9	5	55 ± 1	1.91 ± 0.04
10	3	45 ± 1	2.49 ± 0.10
11	3	40 ± 1	2.33 ± 0.10
12	3	39 ± 1	2.79 ± 0.16
13	3	32 ± 1	2.45 ± 0.11

C I The reaction of trimethyl tin hydride (7.76 x 10^{-4} molar) with 2-chloropentane (3.32 x 10^{-4} molar) and 1,4-dichlorobutane (3.32 x 10^{-4} molar) Photolysed for 10 minutes

TABLE C I

Run No.	No. of Runs	Temp °C	Product Ratio $[n\text{-}C_4H_9Cl]/[n\text{-}C_5H_{12}]$
1	3	156 ± 1	0.52 ± 0.01
2	3	105 ± 1	0.61 ± 0.01
3	3	90 ± 1	0.67 ± 0.01
4	3	62 ± 1	0.88 ± 0.02
5	3	50 ± 1	1.21 ± 0.01

II The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,4-dichlorobutane(3.32×10^{-4} molar) and 1-chloro-3-methylbutane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE C II

Run No.	No. of Runs	Temp °C	Product Ratio $[n\text{-}C_4H_9Cl]/[C_5H_{12}]$
1	3	160 ± 1	0.54 ± 0.01
2	3	111 ± 1	1.26 ± 0.01
3	3	95 ± 1	1.93 ± 0.03
4	3	56 ± 1	3.10 ± 0.01
5	3	42 ± 1	5.50 ± 0.01

III The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 2-chloropentane (3.32×10^{-4} molar) and 1-chloroheptane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE C III

Run No.	No. of Runs	Temp °C	Product Ratio $[n\text{-}C_5H_{12}]/[n\text{-}C_7H_{10}]$
1	3	165 ± 1	1.71 ± 0.01
2	3	132 ± 1	1.58 ± 0.01
3	3	114 ± 1	1.21 ± 0.01
4	3	78 ± 1	0.72 ± 0.01
5	3	55 ± 1	0.44 ± 0.01
6	3	44 ± 1	0.60 ± 0.03

D I The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with fluorocyclohexane (3.32×10^{-4} molar) and 2,2-dichloropropane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE D I

Run No.	No. of Runs	Temp °C	Product Ratio $[C_6H_{12}]/[CH_3CHClCH_3]$
1	4	150 ± 1	1.20 ± 0.02
2	4	128 ± 1	1.67 ± 0.06
3	5	104 ± 1	1.96 ± 0.02
4	6	70 ± 1	3.74 ± 0.01
5	5	51 ± 1	4.19 ± 0.07
6	5	40 ± 1	4.87 ± 0.01

II The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with chlorocyclohexane (3.32×10^{-4} molar) and 2,2-dichloropropane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE D II

Run No.	No. of Runs	Temp °C	Product Ratio $[C_6H_{12}]/[CH_3CHClCH_3]$
1	5	154 ± 1	1.51 ± 0.01
2	5	129 ± 1	1.93 ± 0.01
3	5	96 ± 1	2.77 ± 0.02
4	5	82 ± 1	3.61 ± 0.01
5	5	68 ± 1	4.70 ± 0.08
6	5	43 ± 1	6.21 ± 0.08

III The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and bromocyclohexane (3.32×10^{-4} molar) Photolysed for 90 seconds

TABLE D III

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_3]/[C_6H_{12}]$
1	4	131 ± 1	0.69 ± 0.01
2	3	123 ± 1	0.80 ± 0.01
3	3	105 ± 1	0.91 ± 0.05
4	3	103 ± 1	0.93 ± 0.01
5	4	74 ± 1	1.01 ± 0.03
6	3	61 ± 1	1.66 ± 0.02
7	2	50 ± 1	1.92 ± 0.01
8	3	50 ± 1	1.98 ± 0.02
9	4	47 ± 1	2.18 ± 0.02

Details of Reactions

In all cases the columns of results under a single compound heading are the peak areas multiplied by the attenuation factor. The ratio of products is the ratio of peak areas corrected for molecular weight and halogen number differences.

Reaction of trimethyl tin hydride with:-

A(I) 1-Chloro-4-fluorobutane:-

Trimethyl tin hydride (7.76×10^{-4} molar) and 1-chloro-4-fluorobutane (3.32×10^{-4} molar) were irradiated for 15 minutes at known temperatures.

Analysis:- Column - 20% Dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 60 ml/min

Recorder chart speed = 24"/h

Temperature = 61 ± 1°C

The products were identified by their retention times in conjunction with a columm of 20% tritolylphosphate on 60-100 mesh embacel.

Run No. 1	Temp = 184 ± 1°C		Run No. 2	Temp = 161 ± 1°C	
nC_4H_9Cl	nC_4H_9F	$\frac{nC_4H_9F}{nC_4H_9Cl}$	nC_4H_9Cl	nC_4H_9F	$\frac{nC_4H_9F}{nC_4H_9Cl}$
67.9x1	31.8x20	12.57	740x1	382x20	13.85
70.0x1	29.9x20	11.46	679x1	368x20	14.55
71.0x1	28.5x20	10.77	724x1	380x20	14.06
70.5x1	28.5x20	10.85	718x1	370x20	13.83

Run No. 3	Temp = 100 ± 1°C		Run No. 4	Temp = 83 ± 1°C	
298x1	244x20	21.98	222x1	224x20	27.08
285x1	263x20	24.77	214x1	203x20	25.46
265x1	239x20	24.21	262x1	233x20	23.87
270x1	234x20	23.26	202x1	212x20	28.17

Run No. 5 Temp = 73 ± 1°C

150.0 x 1	69.0 x 50	30.87
67.0 x 1	33.0 x 50	33.05
69.5 x 1	30.5 x 50	29.45
218.0 x 1	464.0 x 10	28.56
45.0 x 1	55.0 x 20	32.81

Run No. 6 Temp = 65 ± 1°C

51.0 x 1	49.0 x 20	25.79
51.6 x 1	48.0 x 20	24.97
51.7 x 1	48.7 x 20	25.28
51.8 x 1	48.2 x 20	24.97

Run No. 7 Temp = 30 ± 1°C

180 x 1	396 x 20	59.05
190 x 1	396 x 20	55.94
75 x 1	314 x 20	56.19

AII 1-Bromo-3-chlorobutane:-

Trimethyl tin hydride (7.76 x 10^{-4} molar) with 1-bromo-3-chlorobutane (3.32 x 10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 80 ± 1°C

The products were identified by their retention times in conjunction with a column 20% silicon oil on 60-80 mesh celite.

Run No. 1 Temp = 135 ± 1°C

$2\text{-}C_4H_9Cl$	$1\text{-}C_4H_9Br$	$\frac{2\text{-}C_4H_9Cl}{1\text{-}C_4H_9Br}$
88.5 x 10	11.5 x 1	130.05
88.4 x 10	11.6 x 1	128.78
88.4 x 10	11.6 x 1	128.78

Run No. 2 Temp = 133 ± 1°C

$2\text{-}C_4H_9Cl$	$1\text{-}C_4H_9Br$	$\frac{2\text{-}C_4H_9Cl}{1\text{-}C_4H_9Br}$
80.0 x 20	20.0 x 1	135.19
80.0 x 20	20.0 x 1	135.19
81.0 x 20	19.0 x 1	144.09

Run No. 3	Temp 126 ± 1°C		Run No. 4	Temp = 100 ± 1°C	
89.9 x 10	10.1 x 1	150.42	91.0 x 10	8.5 x 1	181.91
89.9 x 10	10.1 x 1	150.42	91.0 x 10	9.0 x 1	170.86
89.8 x 10	10.2 x 1	148.78	91.5 x 10	8.5 x 1	180.92
Run No. 5	Temp = 71 ± 1°C		Run No. 6	Temp = 50 ± 1°C	
93.1 x 10	6.9 x 1	227.68	94.5 x 10	5.5 x 1	290.36
93.1 x 10	6.9 x 1	227.68	94.4 x 10	5.6 x 1	284.87
93.0 x 10	7.0 x 1	224.52	94.5 x 10	5.5 x 1	290.30

AIII 1,3-Dichlorobutane:-

Trimethyl tin hydride (7.76×10^{-4} molar) and 1,3-dichlorobutane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperature.

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 24"/h
Temperature = 61 ± 1°C

The products were identified by their retention times in conjunction with a column 20% silicone oil on 60-80 mesh celite

1-C_4H_9Cl	2-C_4H_9Cl	$\frac{1\text{-}C_4H_9Cl}{2\text{-}C_4H_9Cl}$	1-C_4H_9Cl	2-C_4H_9Cl	$\frac{1\text{-}C_4H_9Cl}{2\text{-}C_4H_9Cl}$
Run No. 1	Temp 161 ± 2°C		Run No. 2	Temp = 128 ± 2°C	
64.5 x 20	35.5 x 20	1.82	71.8 x 10	28.5 x 10	2.55
64.5 x 20	35.5 x 20	1.82	71.4 x 10	28.5 x 10	2.51
64.5 x 20	35.2 x 20	1.83	71.0 x 10	28.8 x 10	2.47
63.5 x 20	36.0 x 20	1.76	71.0 x 10	28.8 x 10	2.47
64.5 x 20	35.2 x 20	1.83	71.7 x 10	28.2 x 10	2.53
Run No. 3	Temp = 114 ± 2°C		Run No. 4	Temp = 85 ± 2°C	
71.0 x 10	29.0 x 10	2.45	72.5 x 10	27.0 x 10	2.69
70.5 x 10	29.1 x 10	2.42	71.0 x 10	29.0 x 10	2.45
71.0 x 10	29.0 x 10	2.45	71.5 x 5	28.5 x 5	2.51
71.5 x 10	28.5 x 10	2.51	71.0 x 10	29.0 x 10	2.45
71.5 x 10	28.5 x 10	2.51	72.5 x 10	27.5 x 10	2.64

Run No. 5 Temp = 65 $\pm 2^{\circ}$C

75.9 x 10	24.1 x 10	3.15
75.0 x 10	25.0 x 10	3.00
75.2 x 10	24.4 x 10	3.08
75.0 x 10	24.5 x 10	3.06

Run No. 6 Temp = 50 $\pm 2^{\circ}$C

77.0 x 10	23.0 x 10	3.35
77.0 x 10	23.0 x 10	3.35
76.2 x 10	23.8 x 10	3.20
76.7 x 10	23.2 x 10	3.31
77.0 x 10	23.0 x 10	3.32

Run No. 7 Temp = 41 $\pm 2^{\circ}$C

69.2 x 10	30.8 x 10	2.25
71.5 x 10	28.3 x 10	2.53
71.2 x 10	28.5 x 10	2.50
69.2 x 10	30.6 x 10	2.26

Run No. 8 Temp = 36 $\pm 2^{\circ}$C

75.8 x 10	24.0 x 10	3.16
75.9 x 10	24.1 x 10	3.15
75.5 x 10	24.5 x 10	3.08
75.6 x 10	24.2 x 10	3.12

AIV 1,3-Dichloro-3-methyl butane:-

Trimethyl tin hydride (7.76×10^{-4} molar) and 1,3-dichloro-3-methylbutane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 24"/h
Temperature = 90 $\pm 1^{\circ}$C

The products were identified by their retention times in conjunction with a column 20% tritolylphosphate on 60-100 mesh embacel.

$ClCH_2CH_2CH(CH_3)_2$	$CH_3C(CH_3)ClCH_2CH_3$	$\frac{ClCH_2CH_2CH(CH_3)_2}{CH_3C(CH_3)ClCH_2CH_3}$
Run No. 1 Temp = 162 $\pm 2^{\circ}$C		
78.7 x 20	21.3 x 5	14.78
78.7 x 20	22.0 x 5	14.31
88.7 x 20	11.4 x 10	15.56
78.7 x 20	21.3 x 5	14.78

$ClCH_2CH_2CH(CH_3)_2$	$CH_3C(CH_3)ClCH_2CH_3$	$\frac{ClCH_2CH_2CH(CH_3)_2}{CH_3C(CH_3)ClCH_2CH_3}$
Run No. 2 Temp = 146 ± 2°C		
61.0 x 50	39.0 x 5	15.64
60.0 x 50	40.0 x 5	15.00
60.2 x 50	39.5 x 5	15.24
60.2 x 50	39.5 x 5	15.24
60.2 x 50	39.5 x 5	15.24
Run No. 3 Temp = 111 ± 2°C		
62.0 x 50	38.0 x 5	16.32
62.4 x 50	37.6 x 5	16.60
62.8 x 50	37.2 x 5	16.88
62.8 x 50	37.2 x 5	16.88
63.0 x 50	37.0 x 5	17.03
Run No. 4 Temp = 90 ± 2°C		
67.0 x 50	33.0 x 5	20.30
65.6 x 50	34.5 x 5	18.99
65.2 x 50	35.6 x 5	18.08
66.5 x 50	34.0 x 5	19.56
66.5 x 50	33.0 x 5	20.15
Run No. 5 Temp = 60 ± 2°C		
69.2 x 50	30.5 x 5	22.69
69.2 x 50	30.2 x 5	22.91
69.0 x 50	31.0 x 5	22.26
69.4 x 50	30.5 x 5	22.75
69.2 x 50	30.5 x 5	22.69
Run No. 6 Temp = 49 ± 2°C		
82.5 x 10	17.5 x 2	23.57
82.4 x 10	17.6 x 2	23.41
83.0 x 10	17.0 x 2	24.41
82.5 x 10	17.6 x 2	23.44
82.5 x 10	17.5 x 2	23.57

Run No. 7 Temp = 33 ± 2°C

71.6 x 50	28.2 x 5	25.39
71.6 x 50	28.2 x 5	25.39
71.2 x 50	28.5 x 5	24.98
71.0 x 50	29.0 x 5	24.48
71.3 x 50	28.3 x 5	25.19

A V 1-Chloro-4-bromobutane:-

Trimethyl tin hydride (7.76 x 10^{-4} molar) and 1-chloro-4-brombutane (3.32 x 10^{-4} molar) were irradiated for 60 minutes at known temperature

Analysis:- Column 20% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 60 ml/min

Recorder chart speed = 24"/h

Temperature = 61 ± 1°C

The products were identifed by their retention times in conjunction with a column 20% silicone oil on 60-80 mesh celite.

1-C_4H_9Cl	1-C_4H_9Br	$\frac{1\text{-}C_4H_9Cl}{1\text{-}C_4H_9Br}$	1-C_4H_9Cl	1-C_4H_9Br	$\frac{1\text{-}C_4H_9Cl}{1\text{-}C_4H_9Br}$
Run No. 1	Temp = 161 ± 1°C		Run No. 2	Temp = 141 ± 1°C	
37.5 x 50	62.0 x 2	25.55	52.1 x 50	47.9 x 5	18.38
36.2 x 50	63.8 x 2	23.97	29.9 x 50	69.9 x 2	18.07
35.2 x 50	64.0 x 2	23.23			
37.8 x 50	62.8 x 2	25.42			
Run No. 3	Temp = 125 ± 1°C		Run No. 4	Temp = 118 ± 1°C	
32.0 x 50	67.5 x 2	20.02	37.0 x 50	62.5 x 2	25.01
32.2 x 20	67.8 x 2	20.06	37.5 x 50	62.5 x 2	25.34
54.0 x 20	46.0 x 2	19.83	38.5 x 50	61.5 x 2	26.44
			38.5 x 50	61.2 x 2	26.57
Run No. 5	Temp = 97 ± 1°C		Run No. 6	Temp = 84 ± 1°C	
26.0 x 50	74.0 x 2	14.84	45.1 x 50	55.0 x 5	13.85
44.5 x 50	55.2 x 5	13.62	48.2 x 50	57.1 x 5	15.93
42.2 x 50	55.6 x 5	12.82	43.9 x 50	56.6 x 5	13.13
44.5 x 50	55.2 x 5	13.62	45.5 x 50	54.5 x 5	14.10

Run No. 7	Temp = 70 ± 1°C		Run No. 8	Temp = 50 ± 1°C	
42.5 x 50	57.2 x 5	12.55	61.8 x 20	37.9 x 5	11.02
44.0 x 50	55.8 x 5	13.32	62.3 x 20	36.9 x 5	11.41
42.0 x 50	58.0 x 5	12.23	60.2 x 20	39.1 x 5	10.40
			60.1 x 20	39.5 x 5	10.28

B I 1-4-Dichlorobutane and chlorocyclohexane:-

Trimethyl tin hydride (7.76 x 10^{-4} molar), 1,4-dichlorobutane (3.32 x 10^{-4} molar) and chlorocyclohexane (3.32 x 10^{-4} molar) were irradiated for 10 minutes at known temperatures

Analysis:- Column 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 24"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a column 20% silicone oil on 60-80 mesh celite.

$1\text{-}C_4H_9Cl$	C_6H_{12}	$\frac{C_6H_{12}}{1\text{-}C_4H_9Cl}$	$1\text{-}C_4H_9Cl$	C_6H_{12}	$\frac{C_6H_{12}}{1\text{-}C_4H_9Cl}$
Run No. 1	Temp = 155 ± 1°C		Run No. 2	Temp = 139 ± 1°C	
50.5 x 5	49.0 x 5	2.23	53.0 x 5	47.0 x 5	2.04
50.0 x 5	50.0 x 5	2.30	53.0 x 5	47.0 x 5	2.04
49.0 x 5	51.0 x 5	2.39	53.0 x 5	47.0 x 5	2.04
49.0 x 5	51.0 x 5	2.37	52.5 x 5	47.0 x 5	2.06
50.0 x 5	50 x 5	2.30			
Run No. 3	Temp = 125 ± 1°C		Run No. 4	Temp = 117 ± 1°C	
72.0 x 2	28.0 x 5	2.24	58.5 x 5	41.5 x 5	1.63
72.0 x 2	28.0 x 5	2.24	59.5 x 5	40.5 x 5	1.57
71.0 x 2	29.0 x 5	2.35	58.5 x 5	41.5 x 5	1.63
72.0 x 2	28.0 x 5	2.24	60.0 x 5	40.0 x 5	1.53
73.0 x 2	27.0 x 5	2.13	59.0 x 5	41.0 x 5	1.60

Run No. 5 Temp = 85 ± 1°C

45.2 x 5	54.8 x 5	2.79
50.0 x 5	50.0 x 5	2.30
49.0 x 5	51.0 x 5	2.39
51.0 x 5	49.0 x 5	2.21

Run No. 6 Temp = 70 ± 1°C

67.0 x 5	33.0 x 10	2.27
70.0 x 5	30.0 x 10	1.97
69.5 x 5	30.5 x 10	2.02
69.5 x 5	30.5 x 10	2.02
70.0 x 5	30.0 x 10	1.97
70.0 x 5	30.0 x 10	1.97

Run No. 7 Temp = 65 ± 1°C

88.0 x 1	12.0 x 5	1.57
88.0 x 1	12.0 x 5	1.57
87.5 x 1	12.0 x 5	1.58

Run No. 8 Temp = 40 ± 1°C

53.5 x 5	46.5 x 5	2.00
54.0 x 5	46.0 x 5	1.96
53.5 x 5	46.5 x 5	2.01
54.0 x 5	46.0 x 5	1.96
53.5 x 5	46.5 x 5	2.00
54.0 x 5	46.0 x 5	1.96

Run No. 9 Temp = 28 ± 1°C

1210 x 5	600 x 5	1.14
357 x 10	199 x 10	1.29
913 x 5	442 x 5	1.11
1216 x 5	580 x 5	1.09
964 x 5	491 x 5	1.17
1493 x 5	845 x 5	1.30

B II t-Butyl chloride and chlorocyclohexane:-

Trimethyl tin hydride (7.76×10^{-4} molar) with t-butyl chloride (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures.

Analysis:- Column 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 24"/h
Temperature = 61 ± 1°C

The products were identifed by their retention times in conjunction with a column 20% tritolylphosphate on 60-80 mesh celite.

C_6H_{12}	C_4H_{10}	$\frac{C_4H_{10}}{C_6H_{12}}$	C_6H_{12}	C_4H_{10}	$\frac{C_4H_{10}}{C_6H_{12}}$
Run No. 1	Temp = 154 ± 1°C		Run No. 2	Temp = 121 ± 1°C	
33.5 x 10	66.5 x 10	3.70	45.1 x 5	55.0 x 10	4.55
30.0 x 10	70.0 x 10	4.35	45.1 x 5	55.0 x 10	4.55
30.0 x 10	70.0 x 10	4.35	45.0 x 5	55.0 x 10	4.56
33.5 x 10	66.5 x 10	3.70	45.0 x 5	55.0 x 10	4.56
Run No. 3	Temp = 105 ± 1°C		Run No. 4	Temp = 96 ± 1°C	
28.8 x 10	71.8 x 10	4.65	49.5 x 5	50.4 x 10	3.79
24.5 x 10	73.5 x 10	5.59	49.7 x 5	50.3 x 10	3.78
24.0 x 10	76.0 x 10	5.90	49.5 x 5	50.1 x 10	3.75
24.0 x 10	76.0 x 10	5.90			
Run No. 5	Temp = 72 ± 1°C		Run No. 6	Temp = 58 ± 1°C	
41.0 x 5	59.0 x 5	2.69	53.2 x 5	46.8 x 10	3.28
42.0 x 5	58.0 x 5	2.58	37.3 x 10	62.7 x 10	3.14
41.0 x 5	59.0 x 5	2.69	37.2 x 10	62.8 x 10	3.15
41.0 x 5	59.0 x 5	2.69	37.3 x 10	62.7 x 10	3.14
Run No. 7	Temp = 32 ±1°C				
36.5 x 10	63.5 x 10	3.25			
37.0 x 10	63.0 x 10	3.18			
37.0 x 10	63.0 x 10	3.18			
37.0 x 10	63.0 x 10	3.18			

B III 1,3-Dichloro-3-methylbutane and chlorocyclohexane:-

Trimethyl tin hydride (7.76 x 10^{-4} molar) with 1,3-dichloro-3-methylbutane (3.32 x 10^{-4} molar) and chlorocyclohexane (3.32 x 10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identifed by their retention times in conjunction with a column 22% tritolylphosphate on 100-140 mesh embacel.

C_6H_{12}	$CH_3CH_2C(CH_3)_2Cl$	$\frac{C_6H_{12}}{CH_3CH_2C(CH_3)_2Cl}$	C_6H_{12}	$(CH_3)_2CHCH_2CH_2Cl$	$\frac{(CH_3)_2CHCH_2CH_2Cl}{C_6H_{12}}$
Run No. 1 Temp = 145 ± 1°C					
75.2x2	24.8 x 2	4.25	31.5x2	68.5 x 5	3.88
75.5x2	24.5 x 2	4.31	14.2x2	85.8 x 2	4.31
Run No. 2 Temp = 113 ± 1°C					
68.3x2	36.2 x 2	2.46	24.8x2	75.2 x 5	5.41
63.8x2	36.2 x 2	2.46	24.8x2	75.2 x 5	5.41
65.2x2	34.8 x 2	2.62	11.0x2	89.0 x 2	5.78
Run No. 3 Temp = 89 ± 1°C					
60.5x2	39.5 x 2	2.14	23.0x2	77.0 x 5	5.98
65.5x2	34.5 x 2	2.66	26.6x2	73.4 x 5	4.93
65.0 x 1	35.0 x 1	2.60	23.8x1	76.2 x 2	5.72
Run No. 4 Temp = 73 ± 1°C					
48.0x2	52.0 x 1	2.58	6.1x2	93.9 x 2	10.99
62.0x1	38.0 x 1	2.29	10.5x1	89.5 x 2	12.17
63.0x1	37.0 x 1	2.38	10.5x1	89.5 x 2	12.17
63.0x1	37.0 x 1	2.38	10.4x1	89.6 x 2	12.30
Run No. 5 Temp = 68 ± 1°C					
62.8x2	37.2 x 2	2.36	17.8x2	82.2 x 5	8.24
59.7x2	40.3 x 2	2.07	18.6x2	81.4 x 5	7.81
62.0x2	38.0 x 2	2.28	17.0x2	83.0 x 5	8.72
Run No. 6 Temp = 35 ± 1°C					
58.8x2	41.2 x 2	2.00	11.8x2	88.2 x 5	13.34
58.4x1	41.6 x 1	1.97	21.4x1	78.6 x 5	13.11
58.4x1	41.6 x 1	1.97	21.4x1	78.6 x 5	13.11

B IV Chlorocyclohexane and 2-chloro-2-methylbutane:-

Trimethyl tin hydride (7.76 x 10^{-4} molar) with chlorocycohexane (3.32 x 10^{-4} molar) and 2-chloro-2-methylbutane (3.32 x 10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 20% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 120 ml/min

Recorder chart speed = 12"/h

Temperature = 61 ± 1°C

The products were identified by their retention times in conjunction with a column 22% tritolylphosphate on 100-140 mesh embacel.

C_6H_{12}	$(CH_3)_2CHCH_2CH_3$	$\frac{(CH_3)_2CHCH_2CH_3}{C_6H_{12}}$	C_6H_{12}	$(CH_3)_2CHCH_2CH_3$	$\frac{(CH_3)_2CHCH_2CH_3}{C_6H_{12}}$
Run No. 1	Temp = 147 ± 1°C		Run No. 2	Temp = 123 ± 1°C	
60.0 x 2	40.0 x 10	4.24	40.0 x 2	60.0 x 5	4.77
60.0 x 2	40.1 x 10	4.25	40.0 x 2	60.0 x 5	4.77
60.0 x 2	40.3 x 10	4.27	41.0 x 2	59.0 x 5	4.57
Run No. 3	Temp = 105 ± 1°C		Run No. 4	Temp = 92 ± 1°C	
80.5 x 1	19.5 x 10	3.08	54.5 x 2	45.1 x 5	2.63
80.4 x 1	19.5 x 10	3.08	54.5 x 2	45.5 x 5	2.63
80.5 x 1	19.6 x 10	3.08	54.3 x 2	45.2 x 5	2.63
Run No. 5	Temp = 73 ± 1°C		Run No. 6	Temp = 71 ± 1°C	
86.1 x 1	13.9 x 10	2.05	52.5 x 2	47.5 x 5	2.88
86.2 x 1	13.8 x 10	2.04	52.5 x 2	47.5 x 5	2.88
			52.6 x 2	47.4 x 5	2.87
Run No. 7	Temp = 62 ± 1°C		Run No. 8	Temp = 60 ± 1°C	
60.0 x 2	40.0 x 5	2.12	74.6 x 1	25.4 x 5	2.16
60.0 x 2	40.0 x 5	2.12	76.3 x 1	25.3 x 5	2.11
60.0 x 2	40.3 x 5	2.14	76.6 x 1	25.3 x 5	2.10
Run No. 9	Temp = 55 ± 1°C		Run No. 10	Temp = 45 ± 1°C	
62.8 x 2	37.2 x 5	1.91	56.1 x 2	43.9 x 5	2.49
62.4 x 2	37.6 x 5	1.92	56.2 x 2	43.8 x 5	2.47
62.8 x 2	37.2 x 5	1.91	56.1 x 2	43.9 x 5	2.49
62.8 x 2	37.2 x 5	1.91			
62.4 x 2	37.6 x 5	1.92			
Run No. 11	Temp = 40 ± 1°C		Run No. 12	Temp = 39 ± 1°C	
73.2 x 1	26.8 x 5	2.33	53.2 x 2	46.8 x 5	2.80
73.2 x 1	26.8 x 5	2.33	53.2 x 2	46.8 x 5	2.80
73.0 x 1	27.0 x 5	2.34	53.2 x 2	46.5 x 5	2.79
Run No. 13	Temp = 32 ± 1°C				
56.5 x 2	43.5 x 5	2.45			
56.0 x 2	43.6 x 5	2.46			
56.5 x 2	43.5 x 5	2.45			

C I 1,4-Dichlorobutane and 2-chlorohexane:-

Trimethyl tin hydride (7.76×10^{-4} molar) and 1,4-dichlorobutane (3.32×10^{-4} molar) and 2-chlorohexane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperature.

Analysis: Column 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a column 20% silicone oil on 60-80 mesh celite.

C_5H_{12}	$n\text{-}C_4H_9Cl$	$\frac{n\text{-}C_4H_9Cl}{C_5H_{12}}$	C_5H_{12}	$n\text{-}C_4H_9Cl$	$\frac{n\text{-}C_4H_9Cl}{C_5H_{12}}$
Run No. 1	Temp = 156 ± 1°C		Run No. 2	Temp = 105 ± 1°C	
39.5 x 2	60.5 x 2	0.52	36 x 2	64 x 2	0.61
39.5 x 2	60.4 x 2	0.52	36 x 2	64 x 2	0.61
39.4 x 2	60.5 x 2	0.52	53 x 1	47 x 2	0.61
Run No. 3	Temp = 90 ± 1°C		Run No. 4	Temp = 62 ± 1°C	
50.5 x 1	49.5 x 2	0.67	43 x 1	57 x 2	0.90
50.0 x 1	50.0 x 2	0.68	44 x 1	56 x 2	0.87
50.5 x 1	49.5 x 2	0.67	44 x 1	56 x 2	0.87
Run No. 5	Temp = 50 ± 1°C				
36.0 x 1	64 x 2	1.21			
36.1 x 1	64.1 x 2	1.21			
36.1 x 1	64.0 x 2	1.21			

C II 1,4-Dichlorobutane and 1-chloro-3-methylbutane:-

Trimethyl tin hydride (7.76×10^{-4} molar), with 1,4-dichlorobutane (3.32×10^{-4} molar) and 1-chloro-3-methylbutane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 20% tritolylphosphate on 60-80 celite column.

C_5H_{12}	n-C_4H_9Cl	$\frac{n\text{-}C_4H_9Cl}{C_5H_{12}}$	C_5H_{12}	n-C_4H_9Cl	$\frac{n\text{-}C_4H_9Cl}{C_5H_{12}}$
Run No. 1	Temp = 160 ± 1°C		Run No. 2	Temp = 111 ± 1°C	
38.3 x 2	61.7 x 2	0.54	35.2 x 1	64.8 x 2	1.26
38.4 x 2	61.6 x 2	0.55	35.1 x 1	64.9 x 2	1.26
38.3 x 2	61.7 x 2	0.54	35.1 x 1	64.9 x 2	1.26
Run No. 3	Temp = 95 ± 1°C		Run No. 4	Temp = 56 ± 1°C	
34.5 x 1	100 x 2	1.98	11.0 x 1	100 x 1	3.10
35.6 x 1	100 x 2	1.92	11.0 x 1	100 x 1	3.10
35.6 x 1	100 x 2	1.92	11.0 x 1	100 x 1	3.10
Run No. 5	Temp = 42 ± 1°C				
11.0 x 1	89.0 x 2	5.52			
11.0 x 1	89.0 x 2	5.52			
11.1 x 1	88.9 x 2	5.46			

C III 2-Chloropentane and 1-chloroheptane:-

Trimethyl tin hydride (7.76×10^{-4} molar) with 2-chloropentane (3.32×10^{-4} molar) and 1-chloroheptane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 24% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 120 ml/min

Recorder chart speed = 12"/h

Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 25% silicone oil column on 60-100 mesh embacel.

n-C_7H_{16}	n-C_5H_{12}	$\frac{n\text{-}C_5H_{12}}{n\text{-}C_7H_{16}}$	n-C_7H_{16}	n-C_5H_{12}	$\frac{n\text{-}C_5H_{12}}{n\text{-}C_7H_{16}}$
Run No. 1	Temp = 165 ± 1°C		Run No. 2	Temp = 132 ± 1°C	
100 x 2	41.9 x 5	1.71	100 x 2	96.0 x 2	1.57
100 x 2	42.0 x 5	1.72	100 x 2	62.8 x 5	1.57
100 x 2	41.8 x 5	1.71	100 x 2	97.0 x 2	1.58
Run No. 3	Temp = 114 ± 1°C		Run No. 4	Temp = 78 ± 1°C	
100 x 1	74.0 x 1	1.21	100 x 1	44.0 x 1	0.72
100 x 1	73.8 x 1	1.21	100 x 1	44.1 x 1	0.72
100 x 1	74.0 x 1	1.21	100 x 1	45.1 x 1	0.72
Run No.5	Temp = 55 ± 1°C		Run No. 6	Temp = 44 ± 1°C	
100 x 1	27.0 x 1	0.44	100 x 1	37.0 x 1	0.61
100 x 2	27.1 x 2	0.44	100 x 1	37.5 x 1	0.61
100 x 2	26.8 x 2	0.44	100 x 1	37.0 x 1	0.61

D I Fluorocyclohexane and 2,2-dichloropropane:-

Trimethyl tin hydride (7.76×10^{-4} molar) with fluorocyclohexane (3.32×10^{-4} molar) and 2,2-dichloropropane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures.

Analysis:- Column 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 36"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a column 20% tritolylphosphate on 60-80 mesh celite.

C_6H_{12}	$CH_3CHClCH_3$	$\frac{C_6H_{12}}{CH_3CHClCH_3}$	C_6H_{12}	$CH_3CHClCH_3$	$\frac{C_6H_{12}}{CH_3CHClCH_3}$
Run No. 1	Temp = 150 ± 1°C		Run No. 2	Temp = 128 ± 1°C	
67.1 x 20	100 x 20	1.21	93.0 x 20	100 x 20	1.68
67.0 x 20	100 x 20	1.20	93.0 x 20	100 x 20	1.68
66.0 x 20	100 x 20	1.19	92.5 x 20	100 x 20	1.67
67.5 x 20	100 x 20	1.22	93.0 x 20	100 x 20	1.68
Run No. 3	Temp = 104 ± 1°C		Run No. 4	Temp = 70 ± 1°C	
100 x 20	91.8 x 20	1.96	100 x 20	48.0 x 20	3.76
100 x 20	90.8 x 20	1.99	100 x 20	48.0 x 20	3.76
100 x 20	91.8 x 20	1.96	100 x 20	48.2 x 20	3.74
100 x 20	91.6 x 20	1.99	100 x 20	48.0 x 20	3.76
100 x 20	91.8 x 20	1.96	100 x 20	48.2 x 20	3.74
			100 x 20	48.0 x 20	3.76
Run No. 5	Temp = 57 ± 1°C		Run No. 6	Temp = 40 ± 1°C	
100 x 20	43.0 x 20	4.19	100 x 20	37.0 x 20	4.87
100 x 20	43.0 x 20	4.19	100 x 20	37.0 x 20	4.87
100 x 20	42.0 x 20	4.29	100 x 20	37.0 x 20	4.87
100 x 20	44.0 x 20	4.10	100 x 20	37.2 x 20	4.85
100 x 20	43.0 x 20	4.19	100 x 20	37.0 x 20	4.87

D II Chlorocyclohexane and 2,2-dichloropropane:-

Trimethyl tin hydride (7.76×10^{-4} molar) with chlorocyclohexane (3.32×10^{-4} molar) and 2,2-dichloropropane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures.

Analysis:- Column 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 36"/h
Temperature = 61 ± 1°C

The products were identified by their retention times in conjunction with a second column of 20% silicone oil on 60-100 mesh embacel.

C_6H_{12}	$CH_3CHClCH_3$	$\frac{C_6H_{12}}{CH_3CHClCH_3}$	C_6H_{12}	$CH_3CHClCH_3$	$\frac{C_6H_{12}}{CH_3CHClCH_3}$
Run No. 1	Temp = 154 ± 1°C		Run No. 2	Temp = 129 ± 1°C	
83.2 x 20	100 x 20	1.50	100 x 20	93.0 x 20	1.94
83.2 x 20	100 x 20	1.50	100 x 20	92.6 x 20	1.95
84.0 x 20	100 x 20	1.51	100 x 20	93.0 x 20	1.94
83.8 x 20	100 x 20	1.51	100 x 20	93.1 x 20	1.94
83.8 x 20	100 x 20	1.51	100 x 20	93.0 x 20	1.94
Run No. 2	Temp = 96 ± 1°C		Run No. 4	Temp = 82 ± 1°C	
100 x 20	64.5 x 20	2.80	100 x 20	50.0 x 20	3.61
100 x 20	65.0 x 20	2.78	100 x 20	49.8 x 20	3.62
100 x 20	65.0 x 20	2.78	100 x 20	49.7 x 20	3.63
100 x 20	65.0 x 20	2.78	100 x 20	50.0 x 20	3.61
100 x 20	64.5 x 20	2.80	100 x 20	50.0 x 20	3.61

D III Carbon tetrachloride and bromocyclohexane:-

Trimethyl tin hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and bromocyclohexane (3.32×10^{-4} molar) were irradiated for 90 seconds at known temperatures.

Analysis:- Column 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a column of 24% silicone oil on 60-80 mesh celite.

C_6H_{12}	$CHCl_3$	$\frac{CHCl_3}{C_6H_{12}}$	C_6H_{12}	$CHCl_3$	$\frac{CHCl_3}{C_6H_{12}}$
Run No. 1	Temp = 131 ± 1°C		Run No. 2	Temp = 123 ± 1°C	
11.0 x 20	100 x 10	0.70	19.0 x 10	100 x 10	0.81
11.0 x 20	100 x 10	0.70	19.1 x 10	100 x 10	0.80
11.1 x 20	100 x 10	0.69	18.8 x 10	100 x 10	0.81
11.1 x 20	100 x 10	0.69			

Run No. 3 Temp = 105 ± 1°C

16.8 x 10	100 x 10	0.91
16.9 x 10	100 x 10	0.90
16.8 x 10	100 x 10	0.91

Run No. 4 Temp = 103 ± 1°C

16.5 x 10	100 x 10	0.93
16.4 x 10	100 x 10	0.93
16.4 x 10	100 x 10	0.93

Run No. 5 Temp = 74 ± 1°C

15.0 x 10	100 x 10	1.02
15.5 x 10	100 x 10	0.99
15.0 x 10	100 x 10	1.02
15.0 x 10	100 x 10	1.02

Run No. 6 Temp = 61 ± 1°C

9.2 x 10	100 x 10	1.67
9.2 x 10	100 x 10	1.67
9.3 x 10	100 x 10	1.65

Run No. 7 Temp = 50 ± 1°C

8.0 x 10	100 x 10	1.91
8.0 x 10	100 x 10	1.91
7.9 x 10	100 x 10	1.94

Run No. 8 Temp = 50 ± 1°C

3.8 x 20	100 x 10	2.01
3.9 x 20	100 x 10	1.96

Run No. 9 Temp = 47 ± 1°C

14.0 x 5	100 x 10	2.19
14.0 x 5	100 x 10	2.19
14.1 x 5	100 x 10	2.17
13.9 x 5	100 x 10	2.20

PART I

SECTION II

The photochemical reaction of trimethyl tin hydride with substituted 1,1,1-trichloroethane derivatives

Part I

Section II Introduction

It has been shown in section I that the polar effects of substituents have an effect on the relative selectivity. In order to study further the polar effects of various substituents on chlorine abstraction, by trimethyl tin radicals, a series of experiments was designed in which chloroform was used as a reference compound. The reactive hydrogen of chloroform was replaced both by single atoms e.g. chlorine or fluorine, and by substituted alkyl groups e.g. $-CH_2Cl$ or CF_3

Thus it was hoped to study the polar effects following substitution at the reaction centre and also with substituents at a carbon atom one removed from the reaction site. Trimethyl tin hydride was made to react with this series in competition according to the general scheme:-

$$RCCl_3 + Me_3Sn\cdot \longrightarrow R\dot{C}Cl_2 + Me_3SnCl$$

$$R\dot{C}Cl_2 + Me_3SnH \longrightarrow RCHCl_2 + Me_3Sn\cdot$$

In either case the trimethyl tin radical is abstracting a chlorine atom from the $-CCl_3$ functionality. It was thus possible to study the effect of R on the reactivity of the chlorine atoms. It is unfortunate that no comprehensive series of radical abstraction data have appeared in the literature. However a few values for $CHCl_3$, CCl_4 and $CFCl_3$ have been reported. It was hoped that chlorine abstraction, from observable trends using a nucleophilic radical, would give some relative order of magnitude of the polar effects taking part in the transition state.

Experimental

Materials:- Commercial chloroform, carbon tetrachloride, methyl chloroform and pentachloroethane (obtained from BDH) were purified by fractional distillation using the spinning band fractionating column at a reflux ratio of 40:1. This gave a purity > 98% in all cases. Fluorotrichloromethane was kindly given by Imperial Smelters and required no further purification other than trap to trap distillation. 1,1,1-trichlorotrifluoroethane, 1,1,1,3-tetrachloropropane, 1,1,1,2-tetrachloroethane, and 2,2-dichloropropane were obtained from Peninsular Chemicals and all purified by Perkin-Elmer 105 preparative gas chromatogram using a 30' 10% silicon oil on 60-100 mesh embacel column.

Hydrogen pressure	15 lb/sq in
Oxygen pressure	70 lb/sq in
Nitrogen flow rate	120 ml/min
Oven temperature	100-120°C

Purity in excess of 99.5% was obtained.

The trimethyl tin hydride was purified as before.

Procedure:-

The procedure was as before except the polychloro compounds had to be protected from any stray ultra-violet light by wrapping the sample tubes in aluminium foil. They rapidly attacked the vacuum grease used (Apiezon N) and regreasing of the line had to be done after a series was completed. The reaction time had to be limited to a few minutes in several cases as the reaction was very fast and produced a thick film on the end window. Again the reaction vessel had to be washed out with chromic acid after every run.

Identification of Reaction Products:-

Retention times of the reaction products were compared to those of authentic materials chromatographed under identical conditions. However in several cases mass spectra were taken to confirm the products. In the reaction of 1,1,1-trichlorotrifluoroethane with chloroform and trimethyl tin hydride, the peaks were collected using the Perkin-Elmer 105 preparative GLC using a 30' 20% dinonylphthalate glass column on 60-80 mesh celite. The products were then individually identified by mass spectra. This was to discover if any RCF_3 was produced by photolysis of the CCl_3-CF_3 bond. None was found.

Results

Section II Abstraction from R-CCl_3

(i) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichloroethane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE E I

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_3CHCl_2]/[CH_2Cl_2]$
1	6	157 ± 1	1.34 ± 0.09
2	6	132 ± 1	1.45 ± 0.04
3	6	102 ± 1	1.42 ± 0.07
4	6	73 ± 1	1.65 ± 0.08
5	6	67 ± 1	1.59 ± 0.03
6	6	39 ± 1	1.78 ± 0.04
7	6	38 ± 1	1.90 ± 0.11

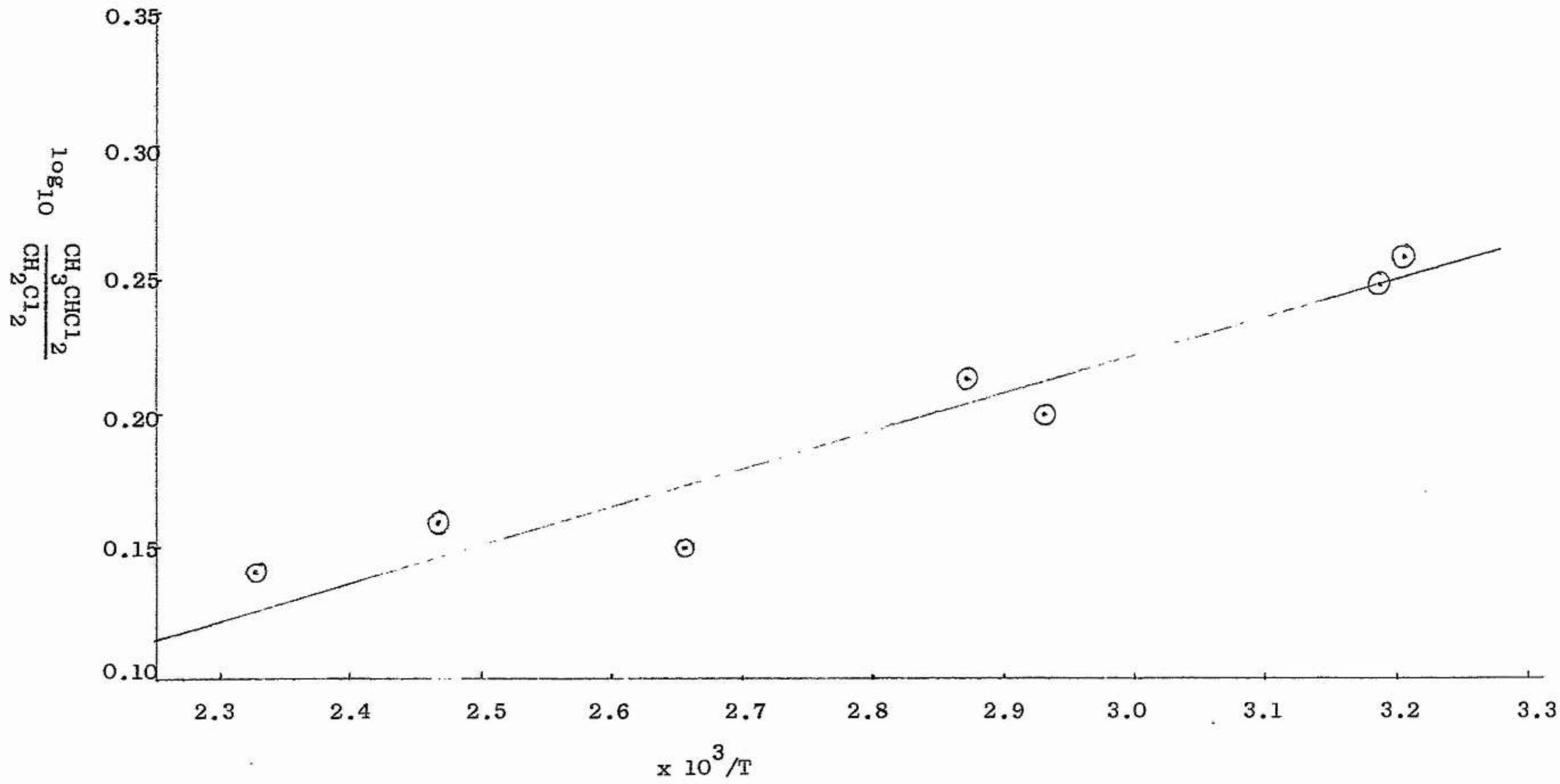
A plot of $\log_{10}[CH_3CHCl_2]/[CH_2Cl_2]$ vs $10^3/T$ gave a line of gradient $(E_{CH_3CHCl_2} - E_{CH_2Cl_2})/2.303R = 0.14 \pm 0.02$ and intercept $\log_{10}A_{CH_3CHCl_2} - \log_{10}A_{CH_2Cl_2} = -0.19 \pm 0.01$ by the "least squares" method.

(ii) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,2-tetrachloroethane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE E II

Run No.	No. of Runs	Temp °C	Product Ratio $\frac{CHCl_2CClH_2}{CH_2Cl_2}$	$\frac{CH_2Cl_2}{CH_3CCl_3}$
1	2	150 ± 1	1.49 ± 0.01	32.39 ± 0.01
2	2	129 ± 1	1.50 ± 0.03	31.36 ± 0.01
3	2	112 ± 1	1.51 ± 0.01	24.96 ± 0.01
4	2	79 ± 1	2.35 ± 0.02	17.83 ± 0.07
5	2	61 ± 1	2.44 ± 0.01	16.62 ± 0.06
6	2	45 ± 1	2.89 ± 0.05	13.68 ± 0.09
7	2	31 ± 1	2.73 ± 0.01	13.19 ± 0.04

The reaction of trimethyl tin hydride, chloroform and 1,1,1-trichloroethane



(iii) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichlorotrifluoroethane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE E III

Run No.	No. of Runs	Temp °C	Product Ratio $[CF_3CHCl_2]/[CH_2Cl_2]$
1	3	155 ± 1	4.90 ± 0.10
2	4	144 ± 1	4.25 ± 0.02
3	4	132 ± 1	3.68 ± 0.03
4	4	105 ± 1	3.78 ± 0.02
5	3	80 ± 1	3.42 ± 0.01
6	3	61 ± 1	3.26 ± 0.02
7	4	50 ± 1	3.25 ± 0.01
8	2	43 ± 1	3.22 ± 0.01

A plot of $\log_{10}[CF_3CHCl_2]/[CH_2Cl_2]$ vs $10^3/T$ gave a line of gradient $(E_{CF_3CHCl_2} - E_{CH_2Cl_2}) = -0.18 \pm 0.05$ and intercept $\log_{10}A_{CF_3CHCl_2} - \log_{10}A_{CH_2Cl_2} = 1.04 \pm 0.02$ by the "least squares" method

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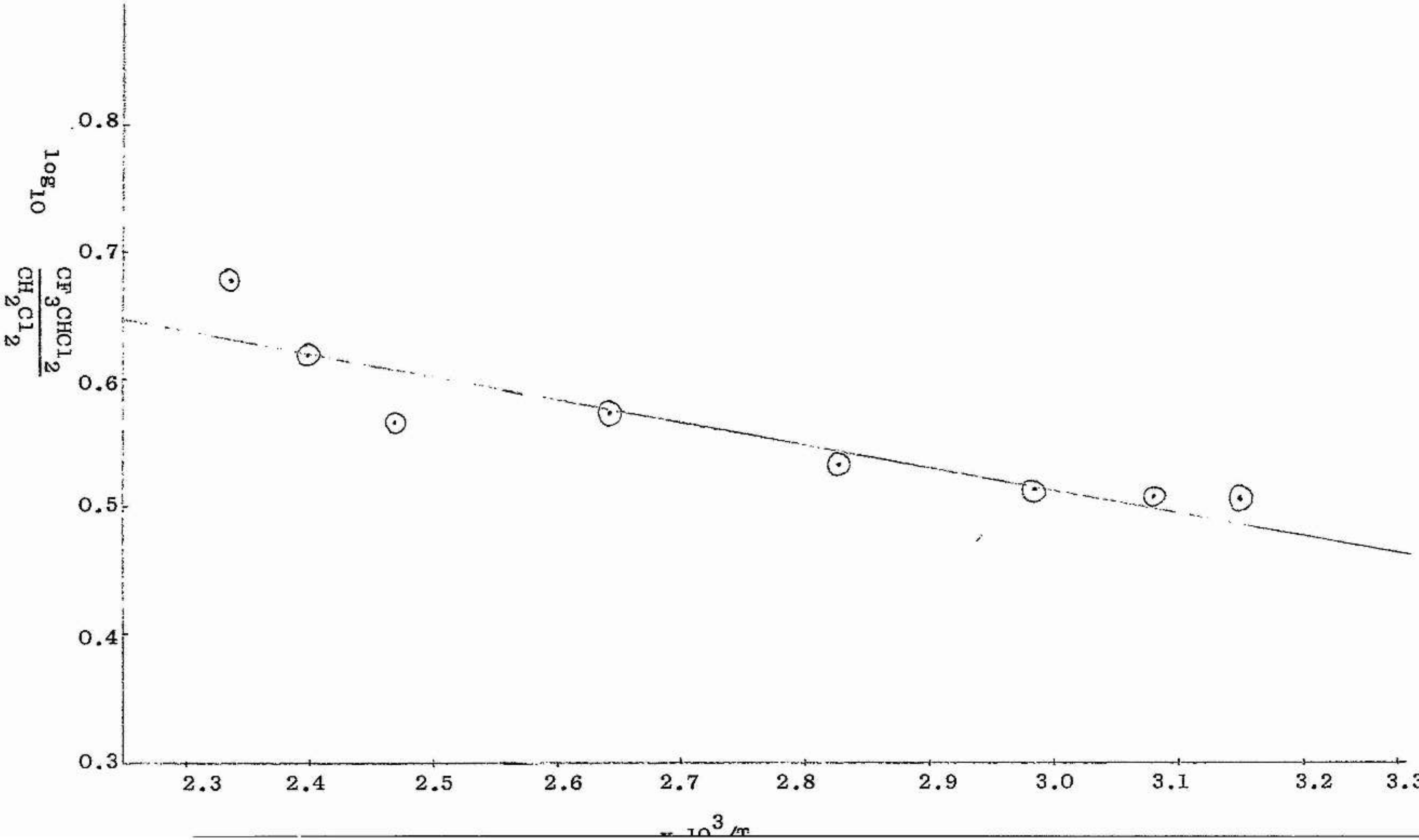
(iv) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,3-tetrachloropropane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE E IV

Run No.	No. of Runs	Temp °C	Product Ratio	
			$\frac{[CH_2Cl_2]}{[CH_3CH_2CCl_3]}$	$\frac{[CH_2ClCH_2CHCl_2]}{[CH_2Cl_2]}$
1	2	156 ± 1	6.37 ± 0.09	1.61 ± 0.01
2	2	128 ± 1	4.47 ± 0.01	3.52 ± 0.01
3	2	105 ± 1	2.58 ± 0.01	4.01 ± 0.01
4	2	94 ± 1	3.73 ± 0.01	3.28 ± 0.01
5	2	92 ± 1	3.56 ± 0.01	4.20 ± 0.02
6	2	72 ± 1	3.54 ± 0.01	4.31 ± 0.02
7	2	67 ± 1	2.47 ± 0.01	4.09 ± 0.09
8	2	64 ± 1	2.95 ± 0.01	3.97 ± 0.01
9	2	61 ± 1	2.59 ± 0.01	5.29 ± 0.01
10	2	50 ± 1	3.14 ± 0.01	4.31 ± 0.02
11	2	43 ± 1	2.66 ± 0.01	4.20 ± 0.02

The reaction of trimethyl tin hydride, chloroform and 1,1,1-trichlorotrifluoroethane



(v) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,1,1-trichloroethane (3.32×10^{-4} molar) and pentachloroethane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE E V

Run No.	No. of Runs	Temp °C	Product Ratio	
			$\frac{[CH_2ClCCl_3]}{[CH_3CCl_2H]}$	$\frac{[CHCl_2CHCl_2]}{[CH_3CCl_2H]}$
1	4	159 ± 1	6.62 ± 0.38	2.48 ± 0.33
2	5	152 ± 1	3.65 ± 0.40	1.53 ± 0.15
3	5	129 ± 1	7.31 ± 0.46	2.85 ± 0.23
4	4	108 ± 1	8.51 ± 1.34	3.13 ± 0.46
5	4	86 ± 1	9.87 ± 0.35	3.85 ± 0.11
6	4	68 ± 1	11.78 ± 0.84	4.86 ± 0.39
7	3	42 ± 1	11.81 ± 0.87	4.62 ± 0.07
8	5	31 ± 1	11.91 ± 0.44	5.06 ± 0.12

(vi) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with 1,1,1-trichloroethane (3.32×10^{-4} molar) and fluorotrichloromethane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE E VI

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_3CHCl_2]/[CHCl_2F]$
1	3	132 ± 2	1.03 ± 0.04
2	4	114 ± 2	0.77 ± 0.08
3	3	93 ± 2	1.06 ± 0.01
4	2	66 ± 2	2.31 ± 0.09
5	4	36 ± 2	1.31 ± 0.13

(vii) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and methylene chloride (3.32×10^{-4} molar) Photolysed for 5 minutes.

TABLE E VII

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_3]/[CH_3Cl]$
1	3	150 ± 2	3.77 ± 0.91
2	3	119 ± 2	2.01 ± 0.16
3	3	82 ± 2	2.01 ± 0.10
4	3	70 ± 2	2.36 ± 0.15

(viii) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE E VIII

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_2Cl_2]/[cC_6H_{12}]$
1	5	163 ± 1	3.12 ± 0.19
2	4	144 ± 1	3.34 ± 0.07
3	5	110 ± 1	4.15 ± 0.21
4	4	79 ± 1	6.52 ± 0.47
5	4	63 ± 1	6.72 ± 0.33
6	4	50 ± 1	10.92 ± 0.55

A plot of $\log_{10}[CH_2Cl_2]/[cC_6H_{12}]$ vs $10^3/T$ gave a line of gradient $E_{CH_2Cl_2} - E_{cC_6H_{12}} = 0.65 \pm 0.08$ and intercept $\log_{10}A_{CH_2Cl_2} - \log_{10}A_{cC_6H_{12}} = -1.03 \pm 0.03$ by the "least squares" method

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(ix) The reaction of trimethyl tin hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 10 minutes

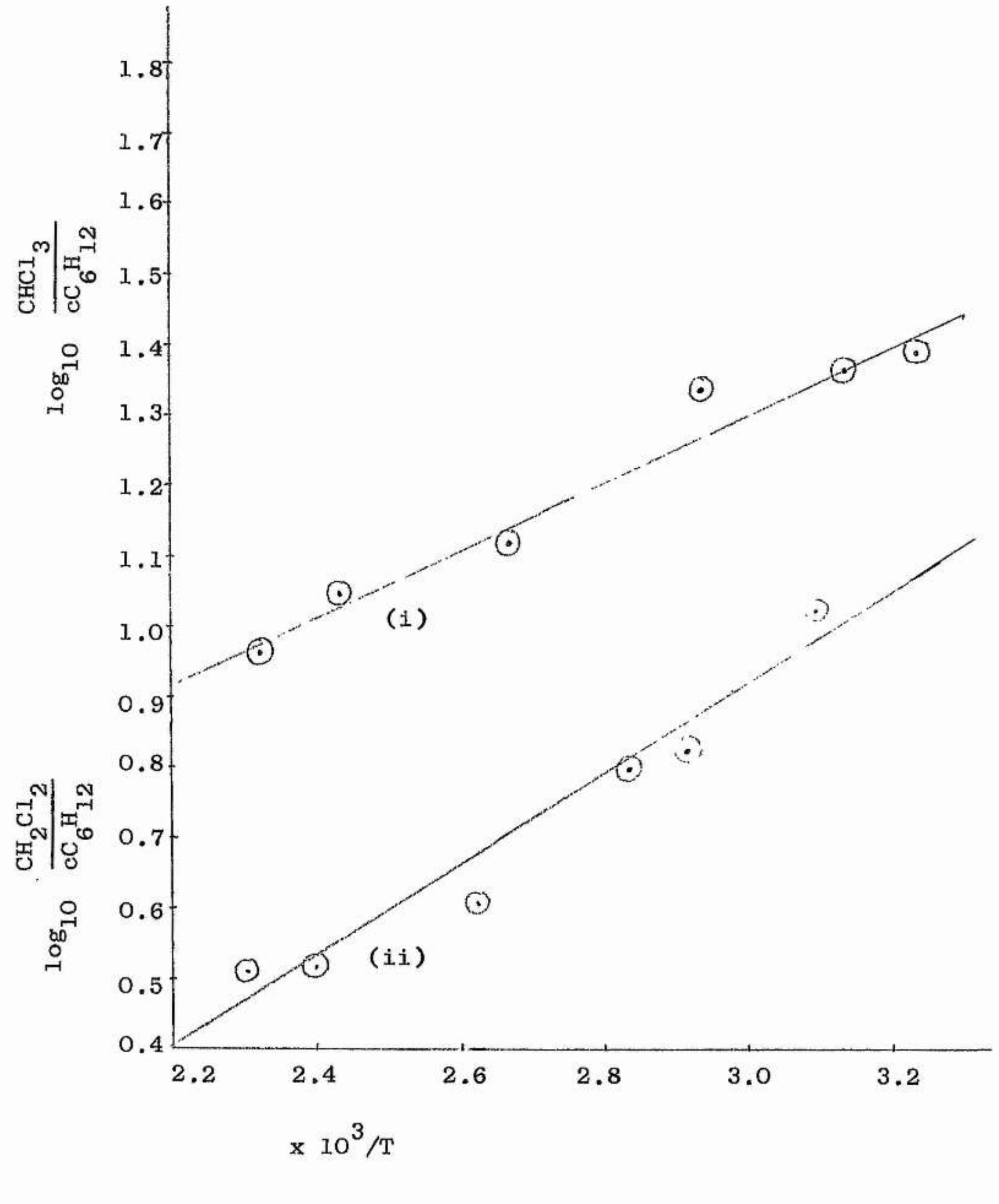
TABLE E IX

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_3]/[cC_6H_{12}]$
1	5	156 ± 1	9.32 ± 0.14
2	6	137 ± 1	11.40 ± 0.61
3	4	100 ± 1	13.46 ± 0.14
4	2	66 ± 1	22.36 ± 0.59
5	4	45 ± 1	24.25 ± 1.30
6	6	35 ± 1	24.88 ± 3.17

A plot of $\log_{10}[CHCl_3]/[cC_6H_{12}]$ vs $10^3/T$ gave a line of gradient $E_{CHCl_3} - E_{cC_6H_{12}} = 0.46 \pm 0.05$ and intercept of $\log_{10}A_{CHCl_3} - \log_{10}A_{cC_6H_{12}} = -0.09 \pm 0.02$ by the "least squares" method.

(i) The reaction of trimethyl tin hydride, carbon tetrachloride and chlorocyclohexane

(ii) The reaction of trimethyl tin hydride, chloroform and chlorocyclohexane



Details of Reactions:

Reaction of trimethyl tin hydride with (i) Chloroform and 1,1,1-trichloroethane.

Trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichloroethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures.

Analysis: Column 6' 20% dinonylphthalate on 60-80 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 24"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a column 6' 24% tritolylphosphate on 60-80 mesh celite.

CH_3CHCl_2	CH_2Cl_2	$\frac{CH_3CHCl_2}{CH_2Cl_2}$	CH_3CHCl_2	CH_2Cl_2	$\frac{CH_3CHCl_2}{CH_2Cl_2}$
Run No. 1	Temp = 157 ± 1°C		Run No. 2	Temp = 132 ± 1°C	
62.5 x 50	37.5 x 50	1.34	65.0 x 10	35.0 x 10	1.50
62.5 x 50	37.5 x 50	1.34	64.0 x 10	36.0 x 10	1.43
62.3 x 50	37.7 x 50	1.33	64.0 x 20	36.0 x 20	1.43
62.4 x 50	37.6 x 50	1.33	64.0 x 20	36.0 x 20	1.43
62.5 x 50	37.5 x 50	1.34	65.0 x 10	35.0 x 10	1.50
62.5 x 50	37.5 x 50	1.34	64 x 10	36 x 10	1.43
Run No. 3	Temp = 102 ± 1°C		Run No. 4	Temp = 73 ± 1°C	
41.0 x 50	49.0 x 20	1.40	67.0 x 50	33.0 x 50	1.63
41.0 x 50	49.0 x 20	1.40	67.0 x 50	33.0 x 50	1.63
41.0 x 50	49.0 x 20	1.40	67.0 x 50	33.0 x 50	1.63
47.0 x 50	53.0 x 10	1.43	67.0 x 50	33.0 x 50	1.63
27.0 x 20	73.0 x 10	1.49	67.5 x 50	32.5 x 50	1.72
41.0 x 50	49.0 x 20	1.40	67.0 x 50	33.0 x 50	1.63

Run No. 5	Temp = 67 ± 1°C		Run No. 6	Temp = 39 ± 1°C	
66.5 x 50	33.5 x 50	1.60	69.0 x 50	31.0 x 50	1.79
66.5 x 50	33.5 x 50	1.60	69.0 x 50	31.0 x 50	1.79
66.5 x 50	33.5 x 50	1.60	69.0 x 50	31.0 x 50	1.79
66.0 x 50	34.0 x 50	1.56	69.0 x 50	31.0 x 50	1.79
66.5 x 50	33.5 x 50	1.60	68.5 x 50	31.5 x 50	1.75
66.5 x 50	33.5 x 50	1.60	69.0 x 50	31.0 x 50	1.79

Run No. 7	Temp = 38 ± 1°C	
70.0 x 50	30.0 x 50	1.88
71.0 x 50	29.0 x 50	1.97
69.0 x 50	31.0 x 50	1.79
70.0 x 50	30.0 x 50	1.89
69.0 x 50	29.0 x 50	1.79
69.0 x 50	29.0 x 50	1.79

(ii) Chloroform and 1,1,1,2-tetrachloroethane

Trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,2-tetrachloroethane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a column 6' 20% silicone oil on 60-100 mesh embacel.

CH_2Cl_2	$CHCl_2CClH_2$	$\frac{CHCl_2CClH_2}{CH_2Cl_2}$	CH_2Cl_2	CH_3CCl_3	$\frac{CH_2Cl_2}{CH_3CCl_3}$
Run No. 1	Temp = 150 ± 1°C				
26.7 x 5	73.3 x 5	1.48	84.0 x 10	16.0 x 1	32.39
26.6 x 5	73.4 x 5	1.49	84.0 x 10	16.0 x 1	32.39
Run No. 2	Temp = 129 ± 1°C				
27.0 x 5	73.5 x 5	1.47	91.5 x 5	9.0 x 1	31.36
26.0 x 5	74.0 x 5	1.54	91.0 x 5	9.0 x 1	31.37

Run No. 3	Temp = 112 ± 1°C				
26.5 x 5	73.5 x 5	1.50	89.0 x 5	11.0 x 1	24.96
26.2 x 5	73.8 x 5	1.52	89.0 x 5	11.0 x 1	24.96
Run No. 4	Temp = 79 ± 1°C				
18.8 x 5	81.2 x 5	2.33	85.2 x 5	14.8 x 1	17.76
18.6 x 5	81.4 x 5	2.36	85.3 x 5	14.7 x 1	17.90
Run No. 5	Temp = 61 ± 1°C				
18.1 x 5	81.9 x 5	2.44	84.4 x 5	15.6 x 1	16.69
18.1 x 5	81.9 x 5	2.44	84.3 x 5	15.7 x 1	16.56
Run No. 6	Temp = 45 ± 1°C				
15.5 x 5	84.5 x 5	2.96	81.5 x 5	18.5 x 1	13.59
16.0 x 5	84.0 x 5	2.84	81.7 x 5	18.3 x 1	13.77
Run No. 7	Temp = 31 ± 1°C				
16.5 x 5	83.5 x 5	2.73	81.0 x 5	19.0 x 1	13.15
16.6 x 5	83.4 x 5	2.71	81.1 x 5	18.9 x 1	13.24

(iii) Chloroform and 1,1,1-trichlorotrifluoroethane

Trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichlorotrifluoroethane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a column 6' 20% silicone oil on 60-80 mesh celite

CF_3CHCl_2	CH_2Cl_2	$\frac{CF_3CHCl_2}{CH_2Cl_2}$	CF_3CHCl_2	CH_2Cl_2	$\frac{CF_3CHCl_2}{CH_2Cl_2}$
Run No. 1	Temp = 155 ± 1°C		Run No. 2	Temp = 144 ± 1°C	
100 x 20	9.5 x 20	4.80	100 x 20	10.8 x 20	4.22
100 x 20	37.5 x 5	5.11	100 x 20	10.8 x 20	4.22
100 x 20	38.0 x 5	4.80	100 x 20	10.7 x 20	4.26
			100 x 20	10.7 x 20	4.26

Run No. 3 Temp = 132 ± 1°C

100 x 20	24.6 x 10	3.71
100 x 20	12.5 x 20	3.65
100 x 20	12.3 x 20	3.71
100 x 20	25.0 x 10	3.65

Run No. 4 Temp = 105 ± 1°C

100 x 20	12.1 x 20	3.77
100 x 20	12.0 x 20	3.80
100 x 20	12.1 x 20	3.77
100 x 20	12.0 x 20	3.80

Run No. 5 Temp = 80 ± 1°C

100 x 20	26.7 x 10	3.42
100 x 20	26.5 x 10	3.44
100 x 20	26.7 x 10	3.42

Run No. 6 Temp = 61 ± 1°C

100 x 20	14.0 x 20	3.26
100 x 20	13.9 x 20	3.28
100 x 20	14.0 x 20	3.26

Run No. 7 Temp = 50 ± 1°C

100 x 20	28.1 x 10	3.25
100 x 20	28.0 x 10	3.26
100 x 20	28.1 x 10	3.25
100 x 20	28.0 x 10	3.26

Run No. 8 Temp = 43 ± 1°C

100 x 20	14.2 x 20	3.21
100 x 20	14.1 x 20	3.23

(iv) Chloroform and 1,1,1,3-tetrachloropropane

Trimethyl tin hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,3-tetrachloropropane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 120 ml/min

Recorder chart speed = 12"/h

Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a column 6' 24% tritolylphosphate on 60-80 mesh celite

CH_2Cl_2	$CCl_3CH_2CH_3$	$\frac{CH_2Cl_2}{CCl_3CH_2CH_3}$	CH_2Cl_2	$CHCl_2CH_2CHCl$	$\frac{CH_2ClCH_2CHCl_2}{CH_2Cl_2}$
Run No. 1	Temp = 156 ± 1°C				
90.0 x 10	100 x 1	6.29	29.6 x 10	100 x 10	1.61
91.0 x 10	100 x 1	6.36	29.4 x 10	100 x 10	1.62
Run No. 2	Temp = 128 ± 1°C				
64.0 x 10	100 x 1	4.47	13.5 x 10	100 x 10	3.53
64.0 x 10	100 x 1	4.47	13.6 x 10	100 x 10	3.50

Run No. 3 Temp = 105 ± 1°C

36.9 x 10	100 x 1	2.59	11.9 x 10	100 x 10	4.01
36.9 x 10	100 x 1	2.59	11.85 x 10	100 x 10	4.02

Run No. 4 Temp = 94 ± 1°C

53.5 x 10	100 x 1	3.74	14.5 x 10	100 x 10	3.29
53.4 x 10	100 x 1	3.73	14.6 x 10	100 x 10	3.27

Run No. 5 Temp = 92 ± 1°C

51.0 x 10	100 x 1	3.56	11.4 x 10	100 x 10	4.19
51.0 x 10	100 x 1	3.56	11.3 x 10	100 x 10	4.22

Run No. 6 Temp = 72 ± 1°C

50.8 x 10	100 x 1	3.55	11.1 x 10	100 x 10	4.29
50.6 x 10	100 x 1	3.54	11.0 x 10	100 x 10	4.34

Run No. 7 Temp = 67 ± 1°C

35.2 x 10	100 x 1	2.46	11.9 x 10	100 x 10	4.01
			11.9 x 10	100 x 10	4.01

Run No. 8 Temp = 64 ± 1°C

42.2 x 10	100 x 1	2.95	12.0 x 10	100 x 10	3.97
42.1 x 10	100 x 1	2.94	12.0 x 10	100 x 10	3.97

Run No. 9 Temp = 61 ± 1°C

37.0 x 10	100 x 1	2.59	9.0 x 10	100 x 10	5.30
37.0 x 10	100 x 1	2.59	9.0 x 10	100 x 10	5.30

Run No. 10 Temp = 50 ± 1°C

45.0 x 10	100 x 1	3.15	11.0 x 10	100 x 10	4.34
45.0 x 10	100 x 1	3.15	11.0 x 10	100 x 10	4.30

Run No. 11 Temp = 43 ± 1°C

38.0 x 10	100 x 1	2.47	11.3 x 10	100 x 10	4.22
38.0 x 10	100 x 1	2.46	11.4 x 10	100 x 10	4.22

(v) Pentachloroethane and 1,1,1-trichloroethane

Trimethyl tin hydride (7.76×10^{-4} molar) with pentachloroethane (3.32×10^{-4} molar) and 1,1,1-trichloroethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 120 ml/min

Recorder chart speed = 24"/h

Temperature = 90 ± 1°C

The products were identified by their retention times in conjunction with a 10% silicon oil column on 60-100 mesh embacel

Run No. 1 Temp = 159 ± 1°C

CH_2ClCCl_3	CH_3CCl_2H	CH_2ClCCl_3/CH_3CCl_2H
79.0 x 10	21.0 x 5	5.72
90.2 x 10	9.8 x 10	7.00
90.1 x 10	9.9 x 10	6.92
90.0 x 10	10.0 x 10	6.85

CH_2ClCCl_3	$CHCl_2CHCl_2$	$\frac{CH_2ClCCl_3}{CHCl_2CHCl_2}$	$\frac{CHCl_2CHCl_2}{CH_3CCl_2H}$
64.0 x 10	36.0 x 10	2.67	2.15
64.2 x 10	35.8 x 10	2.69	2.60
64.0 x 10	36.0 x 10	2.67	2.60
64.0 x 10	36.0 x 10	2.67	2.57

Run No. 2 Temp = 152 ± 1°C

82.0 x 10	18.0 x 10	3.47
91.0 x 5	9.0 x 10	3.85
91.0 x 5	9.0 x 10	3.85
81.0 x 10	19.0 x 10	3.24
91.0 x 5	9.0 x 10	3.85

43.0 x 10	57.0 x 5	2.26	1.53
61.5 x 5	38.5 x 5	2.40	1.60
62.0 x 5	38.0 x 5	2.45	1.57
44.0 x 10	56.0 x 5	2.36	1.38
62.5 x 10	38.0 x 5	2.45	1.57

Run No. 3 Temp = $129 \pm 1^{\circ}C$

90.0 x 10	10.0 x 10	6.85
90.2 x 10	9.8 x 10	7.00
91.0 x 10	9.0 x 10	7.69
90.8 x 10	9.2 x 10	7.51
90.8 x 10	9.2 x 10	7.51

63.5 x 10	36.5 x 10	2.61	2.62
60.6 x 10	39.4 x 10	2.31	3.03
64.0 x 10	36.0 x 10	2.67	2.88
64.0 x 10	36.0 x 10	2.67	2.82
63.2 x 10	36.7 x 10	2.59	2.90

(vi) 1,1,1-Trichloroethane and fluorotrichloromethane

Trimethyl tin hydride (7.76×10^{-4} molar) with 1,1,1-trichloroethane (3.32×10^{-4} molar) and fluorotrichloromethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 60 ml/min

Recorder chart speed = 24"/h

Temperature = $45 \pm 1^{\circ}C$

The products were identified by their retention times in conjunction with a column 6' 25% silicon oil on 60-80 mesh celite

CH_3CHCl_2	$CHCl_2F$	$\frac{CH_3CHCl_2}{CHCl_2F}$	CH_3CHCl_2	$CHCl_2F$	$\frac{CH_3CHCl_2}{CHCl_2F}$
Run No. 1	Temp = $132 \pm 2^{\circ}C$		Run No. 2	Temp = $114 \pm 2^{\circ}C$	
73.0 x 20	26.2 x 50	1.78	61.0 x 20	39.0 x 50	0.66
48.5 x 50	57.5 x 50	0.99	57.0 x 10	43.0 x 20	0.70
46.2 x 50	53.8 x 50	0.91	63.0 x 20	37.0 x 50	0.72
			76.4 x 10	23.5 x 50	0.69

Run No. 3 Temp = 93 ± 2°C

72.0 x 20	28.0 x 50	1.06
71.0 x 20	28.2 x 50	1.06
71.4 x 20	26.6 x 50	1.06

Run No. 4 Temp = 66 ± 2°C

84.0 x 20	16.0 x 50	2.22
85.0 x 20	15.0 x 50	2.39

Run No. 5 Temp = 36 ± 2°C

52.5 x 20	47.0 x 20	1.78
55.0 x 20	45.0 x 20	1.29
57.0 x 20	43.0 x 20	1.40
56.0 x 20	44.0 x 20	1.34

(vii) Carbon tetrachloride and methylene chloride

Trimethyl tin hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and methylene chloride (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 24"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 25% tritosylphosphate column on 60-80 mesh celite

$CHCl_3$	CH_3Cl	$\frac{CHCl_3}{CH_3Cl}$
Run No. 1	Temp = 150 ± 2°C	
90.2 x 50	9.8 x 10	3.77
90.2 x 50	9.8 x 10	3.77
90.1 x 50	9.8 x 10	3.76
Run No. 3	Temp = 82 ± 2°C	
71.0 x 50	29.0 x 5	2.01
71.1 x 50	28.9 x 5	2.02
71.1 x 50	28.9 x 5	2.02

$CHCl_3$	CH_3Cl	$\frac{CHCl_3}{CH_3Cl}$
Run No.2	Temp = 119 ± 2°C	
71.0 x 50	29.0 x 5	2.01
71.1 x 50	29.0 x 5	2.02
71.0 x 50	29.0 x 5	2.01
Run No. 4	Temp = 70 ± 2°C	
87.8 x 20	12.2 x 5	2.36
87.9 x 20	12.2 x 5	2.37
87.8 x 20	12.2 x 5	2.36

(viii) Chloroform and chlorocyclohexane

Trimethyl tin hydride (7.76×10^{-4} molar) with chloroform(3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 60 ml/min

Recorder chart speed = 12"/h

Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 20% tritosylphosphate on 60-80 mesh celite column

CH_2Cl_2	cC_6H_{12}	$\frac{CH_2Cl_2}{cC_6H_{12}}$	CH_2Cl_2	cC_6H_{12}	$\frac{CH_2Cl_2}{cC_6H_{12}}$
Run No. 1	Temp = 163 ± 1°C		Run No. 2	Temp = 144 ± 1°C	
33.0 x 20	67.0 x 1	3.23	50.5 x 20	49.5 x 2	3.34
33.2 x 20	66.8 x 1	3.26	50.1 x 20	49.9 x 2	3.29
48.0 x 20	52.0 x 2	3.02	50.2 x 20	49.7 x 2	3.31
33.0 x 20	67.0 x 1	3.23	51.0 x 20	49.0 x 2	3.41
33.0 x 20	67.1 x 1	3.23			
Run No. 3	Temp = 110 ± 1°C		Run No. 4	Temp = 79 ± 1°C	
86.2 x 10	13.8 x 5	4.08	66.2 x 10	33.8 x 1	6.42
77.0 x 20	23.0 x 5	4.39	67.8 x 10	32.2 x 1	6.90
75.5 x 20	24.5 x 5	4.04	67.2 x 10	32.8 x 1	6.71
76.0 x 20	24.0 x 5	4.15	48.0 x 20	32.0 x 1	6.06
75.0 x 20	25.0 x 5	3.93			
Run No. 5	Temp = 63 ± 1°C		Run No. 6	Temp = 50 ± 1°C	
50.1 x 20	49.9 x 1	6.58	76.0 x 20	24.0 x 2	10.38
51.8 x 20	48.2 x 1	7.04	77.8 x 20	22.8 x 2	11.18
50.5 x 20	49.5 x 1	6.69	76.0 x 20	24.0 x 2	10.38
50.0 x 20	50.0 x 1	6.55	78.2 x 20	21.8 x 2	11.75

(ix) Carbon tetrachloride and chlorocyclohexane

Trimethyl tin hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures

Analysis:- Column 6' 20% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 26% tritosylphosphate on 60-80 mesh celite column

cC_6H_{12}	$CHCl_3$	$\frac{CHCl_3}{cC_6H_{12}}$	cC_6H_{12}	$CHCl_3$	$\frac{CHCl_3}{cC_6H_{12}}$
Run No. 1	Temp = 156 ± 1°C		Run No. 2	Temp = 137 ± 1°C	
45.0 x 1	54.0 x 50	9.18	57.5 x 1	42.5 x 100	11.32
45.0 x 1	55.0 x 50	9.35	57.0 x 1	43.0 x 100	11.54
45.0 x 1	55.0 x 50	9.35	56.0 x 1	44.0 x 100	12.03
45.0 x 1	55.0 x 50	9.35	57.0 x 1	43.0 x 100	11.54
45.0 x 1	55.0 x 50	9.35	57.0 x 1	44.0 x 100	12.03
			56.0 x 1	44.0 x 100	12.03
Run No. 3	Temp = 100 ± 1°C		Run No. 4	Temp = 66 ± 1°C	
36.5 x 1	63.5 x 50	13.32	25.0 x 1	75.0 x 50	22.95
36.0 x 1	64.0 x 50	13.60	25.0 x 1	74.0 x 50	21.78
36.0 x 1	64.0 x 50	13.60			
36.5 x 1	63.5 x 50	13.32			
Run No. 5	Temp = 45 ± 1°C		Run No. 6	Temp = 35 ± 1°C	
23.0 x 1	77.0 x 50	25.61	23.0 x 1	77.0 x 50	25.61
24.0 x 1	76.0 x 50	24.22	23.0 x 1	77.0 x 50	25.61
24.0 x 1	76.0 x 50	24.22	23.0 x 1	77.0 x 50	25.61
25.0 x 1	75.0 x 50	22.96	23.0 x 1	78.0 x 50	25.88
			26.0 x 1	74.0 x 50	21.71
			23.0 x 1	77.0 x 50	25.61

Part I Discussion

The radical nature of the reaction of organo tin hydrides with alkyl halides has been established by Menapace and Kuivila[6]. Confirmation of a radical chain mechanism is provided by the work of Carlsson and Ingold[12].

In this case, the trimethyl tin hydride requires ultraviolet light of wavelengths below 2600 Å to initiate the process. Moderate temperatures ($\leqslant 160^\circ C$) did not appear to initiate the reaction of trimethyl tin hydride with 1,4-dichlorobutane or 1-chloro-3-methylbutane. This fact indicates that a chain reaction is involved and in view of the short reaction time necessary for 5% conversion, a very long chain is indicated.

The exact nature of the initiation step has yet to be elucidated although it probably involves fission of a carbon-tin bond rather than a hydrogen-tin bond

$$(CH_3)_3SnH \xrightarrow{h\nu} CH_3\cdot + (CH_3)_2\dot{S}nH \qquad (1)$$

$D(Sn\text{-}CH_3)\text{-}D(Sn\text{-}H) \approx 56\text{-}65 = -9$ Kcals mole^{-1}.

In preliminary reactions the photolysis of the alkyl halides alone produced little or no reaction in the time taken for the 5% conversion when trimethyl tin hydride is present. Hence photolysis of the alkyl halide is not the initiating step.

The methyl radical formed in reaction (1) will quickly abstract a hydrogen to form methane. There are three reactions that must now be considered:-

$$(CH_3)_3SnH + CH_3^{\cdot} \longrightarrow (CH_3)_3Sn\cdot + CH_4 \qquad (2\dot{a})$$

$$(CH_3)_2SnH + CH_3^{\cdot} \longrightarrow (CH_3)_2SnHCH_2^{\cdot} + CH_4 \qquad (2\overset{I}{a})$$

$$RCH_2\text{-}X + CH_3^{\cdot} \longrightarrow R\dot{C}HX + CH_4 \qquad (2a^{II})$$

Now D(C-H)-D(Sn-H) $\approx$ 103-65 = + 38 Kcals mole^{-1} and so abstraction of the tin hydrogen (2a) is most probable. Both the dimethyl tin hydride and the trimethyl tin radicals will abstract a halogen from the alkyl halide present in preference to a hydrogen atom D(Sn-Cl)-D(Sn-H)$\approx$+24 Kcals mole^{-1} [28]

$$(CH_3)_2\dot{S}nH + R\text{-}X \longrightarrow (CH_3)_2SnXH + R\cdot \qquad (2a^{III})$$

$$(CH_3)_3Sn\cdot + R\text{-}X \longrightarrow (CH_3)_3SnX + R^{\cdot} \qquad (2)$$

Szwarc and Whittle have shown that hydrogen abstraction has been greatly favoured over halogen abstraction where simple thermochemical studies would predict halogen abstraction to be at least as facile. With trimethyl tin radicals the thermochemistry is so much in favour of halogen abstraction that very little hydrogen abstraction occurs. Deutrochloroform when reacted with trimethyl tin hydride gave $CDCl_2H$, but no trimethyl tin deutroide could be detected by GLC coupled mass spectrographic techniques. Similarly when trimethyl tin deutroide was photolysed in the presence of cyclohexane no deuterium was incorporated in the cyclohexane.

In all the reactions described, one bond is broken and another formed.

$$(CH_3)_3Sn\cdot[(CH_3)_2\dot{S}nH] + RX \longrightarrow (CH_3)_3SnX[(CH_3)_2SnXH] + R\cdot$$

$$\Delta H = D(R\text{-}X)\text{-}D(Sn\text{-}X)$$

The overall enthalpy change accompanying the reaction is thus the difference in bond dissociation energies, and the relative strengths of the bond R-X in the substrate and the bond R_3Sn-X in the triorgano tin hydride determines whether the reaction is endothermic (ΔH positive) or exothermic (ΔH negative). The bond dissociation energies D(R-X)[29,30] are relatively high. In trimethyl tin chloride $D(Me_3Sn-Cl)$[28] $\approx$ 89Kcals mole^{-1} and $D(R_3C-Cl) \leqslant$ 79 Kcals mole^{-1} hence the enthalpy change is always negative for chlorine atom abstraction and so is favoured over hydrogen atom abstraction. The most likely fate of the alkyl radical produced in reaction ($2a^{III}$) and (2) is to propagate the chain by abstraction of hydrogen from trimethyl tin hydride. Thus the same argument applies as was discussed for the fate of the methyl radical produced in the initiation process.

$$R\cdot + (CH_3)_3SnH \longrightarrow RH + (CH_3)_3Sn\cdot \qquad (3)$$

The possible chain termination steps are:-

$$(CH_3)_3Sn\cdot + (CH_3)_3Sn\cdot \longrightarrow (CH_3)_3Sn-Sn(CH_3)_3 \qquad (4)$$

$$(CH_3)_3Sn\cdot + R\cdot \longrightarrow (CH_3)_3SnR \qquad (5)$$

$$R\cdot + R\cdot \longrightarrow R_2 \qquad (6)$$

Hexamethylditin has been detected in all runs though no quantitative analyses were possible due to its very low volatility. Cross termination products (reaction 5) or alkyl radical combination products (reaction 6) have not been found even when the reaction time was considerably increased to give over 40% removal of starting material. Material balance also shows that at least 99.0% of the alkyl halide removed in reaction (2) was converted to the corresponding alkane via reaction (3). Hence all of the available evidence suggests that the recombination of trimethyl tinradicals is the only important chain termination step. It has been shown[24] that although hexamethylditin is thermally stable under our experimental conditions (< 160°C) there is some evidence that very slight decomposition will occur under our photolytic conditions. This photolysis would have the effect of increasing the chain length somewhat by regenerating trimethyl tin radicals

$$(CH_3)_3Sn\text{-}Sn(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3Sn\cdot \tag{7}$$

This reconversion would be so slight in the time taken for reaction that to neglect it would introduce negligible error into our rate equations later on. All the experiments are aimed, however, at finding relative rate data for halogen abstraction at different sites, either in the same molecule or in separate compounds by competitive experimentation. Consequently the regeneration of trimethyl tin radicals in reaction (7) will not effect the relative rate data obtained in the present work.

The complete postulated mechanism under the conditions employed is:-

$$(CH_3)_3SnH + h\nu \xrightarrow{\emptyset Ia} (CH_3)_2\dot{S}nH + CH_3\cdot \tag{1}$$

$$CH_3\cdot + (CH_3)_3SnH \longrightarrow CH_4 + (CH_3)_3Sn\cdot \tag{2a}$$

$$(CH_3)_2\dot{S}nH + RX \longrightarrow (CH_3)_2SnHX + R\cdot \tag{2a^{III}}$$

$$(CH_3)_3Sn\cdot + RX \xrightarrow{k_2} (CH_3)_3SnX + R\cdot \tag{2}$$

$$R\cdot + (CH_3)_3SnH \xrightarrow{k_3} RH + (CH_3)_3S\dot{n} \tag{3}$$

$$(CH_3)_3Sn\cdot + (CH_3)_3Sn\cdot \xrightarrow{k_4} (CH_3)_3Sn\text{-}Sn\ (CH_3)_3 \tag{4}$$

$$(CH_3)_3Sn\text{-}Sn(CH_3)_3 \longrightarrow 2(CH_3)_3Sn\cdot \tag{7}$$

This rather complicated mechanism can be considerably simplified, under the reaction conditions employed, because of the very long chain length of the reaction.

For such systems the main chain carrier is the trimethyl tin radical formed in reaction (2). The dimethyl tin hydride radical produced in the initiation process is unimportant, in these long chains, being simply the initial pathway to the production of trimethyl tin radicals. The reaction scheme can hence be reduced to the following important reactions by considering reactions 2a, $2a^{I}$, $2a^{II}$ and $2a^{III}$ as simply a source of a trimethyl tin radical. The methane and alkyl radicals can be neglected for these very long chains. Hence the reaction scheme for a competitive reaction is:-

$$(CH_3)_3SnH + h\nu \xrightarrow{\emptyset Ia} (CH_3)_3Sn\cdot \qquad (1)$$

$$(CH_3)_3Sn\cdot + RX \xrightarrow{k_2} (CH_3)_3SnX + R\cdot \qquad (2)$$

$$(CH_3)_3Sn\cdot + R_1X \xrightarrow{k_{2_1}} (CH_3)_3SnX + R_1\cdot \qquad (2_1)$$

$$R\cdot + (CH_3)_3SnH \xrightarrow{k_3} (CH_3)_3Sn\cdot + RH \qquad (3)$$

$$R_1\cdot + (CH_3)_3SnH \xrightarrow{k_{3_1}} (CH_3)_3Sn\cdot + R_1H \qquad (3_1)$$

$$2(CH_3)_3Sn\cdot \xrightarrow{k_4} (CH_3)\ Sn\text{-}Sn(CH_3)_3 \qquad (4)$$

where RX and R_1X are two different halogen containing compounds. Application of the steady-state approximations to this simplified mechanism gives the following results:-

$$\frac{d[(CH_3)_3Sn\cdot]}{dt} = 0 = \emptyset I_a - k_2[RX][(CH_3)_3Sn\cdot] + k_3[R\cdot][(CH_3)_3SnH] - 2k_4[(CH_3)_3Sn.]^2 \qquad (a)$$

and

$$\frac{d[R\cdot]}{dt} = 0 = k_2[RX][(CH_3)_3Sn\cdot] - k_3[R\cdot][(CH_3)_3SnH] \qquad (b)$$

Adding (a + b)

$$\emptyset I_a = 2k_4[(CH_3)_3Sn\cdot]^2$$

$$\therefore \quad [(CH_3)_3Sn\cdot] = (\emptyset I_a/2k_4)^{\frac{1}{2}} \qquad (c)$$

Also $\frac{d[RH]}{dt} = k_3[R\cdot][(CH_3)_3SnH]$

and from (b) $[R\cdot] = \dfrac{k_2[RX][(CH_3)_3Sn\cdot]}{k_3[(CH_3)_3SnH]}$

$$\therefore \quad \frac{d[RH]}{dt} = k_2[(CH_3)_3Sn\cdot][RX]$$

$$\therefore \quad \frac{d[RH]}{dt} = k_2[RX](\emptyset I_a/2k_4)^{\frac{1}{2}}$$

For a competitive reaction where RH and R_1H are the two alkanes produced from RX and R_1X alkyl halides respectively, then

$$\frac{d[RH]}{d[R_1H]} = \frac{k_2[RX]}{k_{2_1}[R_1X]} \qquad (A)$$

Now $$\frac{d[(CH_3)_3SnX]}{dt} = \frac{d([RH] + [R_1H])}{dt}$$

$$\therefore \frac{d[(CH_3)_3SnX]}{dt} = k_2[RX][(CH_3)_3Sn\cdot]$$

Multiplying by (c) $$\frac{d[(CH_3)_3SnX]}{dt} = k_2[RX](\varnothing I_a/2k_4)^{\frac{1}{2}}$$

$$\therefore \frac{d[(CH_3)_3SnX]}{dt} = k_2[RX](\varnothing I_a/2k_4)^{\frac{1}{2}} \qquad (B)$$

If the rate of the initiation process (1) is expressed as $\varnothing I_a$, where, $\varnothing$ is the quantum yield of the initiation process and Ia is the light intensity absorbed, then since the extinction coefficient of $(CH_3)_3SnH$ is small, I_a can be equated with

$$I_o\ 2.303\,\varepsilon\, 1\ [(CH_3)_3SnH]$$

where I_o is the incident light intensity and 1 is the length of the reaction cell. In all experiments the overall extent of reaction is small ($\sim$ 5%) and the concentration of starting material remains virtually unchanged. Integration of expressions (A) and (B) yield the final working formula of the equations:-

$$[(CH_3)_3SnX]_f = ([RH]_f + [R_1H]_f) = k_2[RX]\ (\varnothing I_a/2k_4)^{\frac{1}{2}}\ t \qquad (C)$$

and $$\frac{[RH]_f}{[R_1H]_f} = \frac{k_2[RX]}{k_{2_1}[RX_1]} \qquad (D)$$

Under the present experimental conditions $[(CH_3)_3SnX]$ was found to be, within experimental limits, equal to $([RH] + [R_1H])$. The mechanism also predicts that $[RH] + [R_1H]$ is proportional to the ½ power of the light intensity. The results on the light intensity variation with trimethyl tin hydride and 1,3-dichlorobutane confirm this postulation.

Measurement of the final concentrations of the two alkanes formed in competitive reactions RH and R_1H enables the rate constants k_2/k_{2_1} to be determined directly as care was taken to make the concentrations of the two alkyl halides equal. Therefore:-

$$\frac{k_2}{k_{2_1}} = \frac{[RH]_f}{[R_1H]_f}$$

From the results summarised in table 5 the relative rate constants for halogen abstraction from a large variety of alkyl halides can be deduced.

TABLE 5

Abstraction of halogen by trimethyl tin radicals from R-X at 373°K using chlorocyclohexane as a standard, where $[RX]/[cC_6H_{11}Cl] = 1$

R-X	$k_2[RX]/k_{2_1}[cC_6H_{11}Cl]$
$Cl(CH_2)_4$-Cl	0.51 ± 0.03
$Me_2CClCH_2CH_2$-Cl	0.36 ± 0.09
$Me_2CHCH_2CH_2$-Cl	0.34 ± 0.03
$Me(CH_2)_5CH_2$-Cl	0.73 ± 0.09
cC_6H_{11}-Cl	1.00
$CH_3(CH_2)_2CH(Me)$-Cl	0.74 ± 0.09
$Cl(CH_2)_2C(Me)H$-Cl	1.28 ± 0.03
Me_3C-Cl	3.90 ± 0.50
$EtMe_2C$-Cl	3.16 ± 0.21
$Cl(CH_2)_2CMe_2$-Cl	6.30 ± 0.30, 9.30 ± 0.70
$Cl(CH_2)_4$-F	0.02 ± 0.00 (1)

Table 5 (cont)

$Cl(CH_2)_4$-Br	8.37 ± 0.47
$MeCH_2ClCH_2CH_2$-Br	127.10 ± 2.60
cC_6H_{11}-F	0.80 ± 0.02
cC_6H_{11}-Br	16.25 ± 0.92
Me_2CCl-Cl	0.37 ± 0.05

From table 5 it is evident that a trimethyl tin radical will extract a bromine atom from an alkyl bromide very much more readily than it will extract a chlorine atom, which in turn will be extracted much more readily than a fluorine atom from an alkyl fluoride. This, and the fact that ease of abstraction increases from primary through secondary to tertiary carbon-halogen bonds, suggests that the strength of the carbon-halogen bond being broken is a major factor in determination of the activation energy of the reaction.

TABLE 6

	ΔH Kcals $mole^{-1}$
$(CH_3)_3Sn\cdot + RF \longrightarrow (CH_3)_3SnF + R\cdot$	$\approx -10^{(a)}$
$(CH_3)_3Sn\cdot + RCl \longrightarrow (CH_3)_3SnCl + R\cdot$	≈ -9
$(CH_3)_3Sn\cdot + RBr \longrightarrow (CH_3)_3SnBr + R\cdot$	≈ -12

Taking D(R-X) for CH_3-X

(a) estimated value of $\approx$108 K cals $mole^{-1}$ for D(Sn-F) see ref. 43

It can be seen from table 6 that the overall enthalpy changes, for the halogen abstraction process down the series RF to RBr, are virtually unchanged. The decrease in carbon halogen bond energy being largely off set by the increasing strength of the tin halogen bond. Thus the observed trend in abstraction rate Br > Cl > F and tertiary > secondary > primary is indicative that the major factor contributing to the rate of abstraction, is the breaking of the C-X bond and that the change of the $(CH_3)_3Sn$-X bond is of somewhat less importance.

The same trends have been observed for the reaction of sodium[31] atoms with halides, trichlorosilyl[22] radicals with halides and with triorgano tin hydrides in solution[6].

TABLE 7

Relative rate constants at 275°K based on methyl chloride standard for halogen abstraction by trichlorosilyl radicals and sodium atoms

RX	$k[RX]/k[CH_3Cl]$	
	$SiCl_3\cdot$	Na
MeCl	1.0	1
Bu^nCl	4.2	2.9
Bu^sCl	11.2	4.1
Bu^tCl	30.6	6.4
EtBr	117.5	100

TABLE 8

The relative rate constants of alkyl halides towards the tributyl tin radicals[12] at 318°K where $[RX]/[nC_5H_{11}Cl]$ = constant

R-X	$k[RX]/k[nC_5H_{11}Cl]$
$cC_6H_{11}F$	< 0.1
$nC_5H_{11}Cl$	1.0
$cC_6H_{11}Cl$	1.7
Bu^tCl	11
$cC_6H_{11}Br$	1.9×10^{-4}
Bu^tBr	7.2×10^{-4}
$2\text{-}BrC_4H_9$	3.0×10^{-4} (6c)

It is interesting to compare the thermochemistry for chlorine abstraction by trimethyl tin radicals with the thermochemistry of hydrogen abstraction by chlorine atoms

$$RCl + (CH_3)_3Sn\cdot \longrightarrow R\cdot + (CH_3)_3SnCl \qquad \Delta H \approx -9\text{Kcals mole}^{-1}$$ [28]

$$R\cdot + (CH_3)_3SnH \longrightarrow RH + (CH_3)_3Sn\cdot \qquad \Delta H \approx -38\text{Kcals mole}^{-1}$$

So that the overall enthalpy change for chlorine abstraction by trimethyl tin radicals is approximately 47 Kcals exothermic. For hydrogen abstraction by chlorine atoms

$$RH + Cl\cdot \longrightarrow R\cdot + HCl \qquad \Delta H \approx -4\text{Kcals mole}^{-1}$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad \Delta H \approx -23\text{Kcals mole}^{-1}$$

the enthalpy change is approximately 27 Kcals exothermic. It would be expected that chlorine abstraction by trimethyl tin radicals to have approximately the same selectivity as hydrogen abstraction by chlorine atoms. It can be predicted that there would be little difference between the ease of bromine and iodine abstraction since the enthalpy differences, in the reaction with trimethyl tin radicals, are small - of the order of 11 Kcals mole^{-1}. There is little data available for alkyl fluoride bonding or the trimethyl tin fluoride bond, but the great strength of the carbon-fluorine bond ($\approx$ 118 Kcals) suggests that this process is likely to be very slow.

These predictions are based on thermochemical data for the organotin compounds that are far less certain than for alkyl halides or hydrocarbons. Nevertheless the ideas and predictions above do explain the occurrence of very long radical chains and give some idea of the selectivity to be expected. Table 8 shows the selectivity of chlorine radicals for primary, secondary and tertiary hydrogens compared to trimethyl tin radicals for primary, secondary and tertiary chlorines.

TABLE 8

X-	$-CH_2-X$	$>CH-X$	$\rightarrow C-X$
H[a]	1	3.9	5.1
Cl[b]	1	2.5	6.3

a Ref. 32 values at 300°K

b Values at 373°K

The Arrhenius A factor ratios are very close to unity and so the relative selectivity values are a relative measure of the activation energy differences.

The above table shows that the previous predictions are borne out by the experimental results. If the results for the cyclic compounds and for halogens other than chlorine are included, then the general trends appear that are universally accepted.

TABLE 9

Relative selectivities for halogen abstraction by trimethyl tin radicals at 373°K using chlorocyclohexane as a standard base

X-	$-CH_2-X$	$>CH-X$	$\rightarrow C-X$	X
F	0.016	-	-	0.8
Cl	0.36	0.9	2.3	1.0
Br	126	-	-	16.25

In order to account for the observed directive effects in hydrogen abstraction reactions,most authors have assumed that the activated complex has considerable polar character with the halogen forming the negative end of the dipole e.g hydrogen abstraction by chlorine atoms and $CF_3\cdot$ radicals

$$RH + Cl \longrightarrow \overset{\delta+ \quad \longmapsto \quad \delta-}{R --- H --- Cl} \longrightarrow R\cdot + HCl$$

$$RH + CR_3^{\bullet} \longrightarrow \overset{\delta+ \quad \longmapsto \quad \delta-}{R --- H --- CF_3} \longrightarrow R\cdot + CF_3H$$

In halogen abstraction by trimethyl tin radicals it would be expected that the polarisation be reversed

$$RCl + (CH_3)_3Sn\cdot \rightarrow \overset{\delta-\ \longleftarrow\!\!\!\!-\!\!\!+\ \delta+}{R\ \text{---}\ Cl\ \text{---}\ Sn(CH_3)_3} \longrightarrow R\cdot + (CH_3)_3SnCl$$

Hence, if chlorine can be abstracted by trimethyl tin radicals from the same site as hydrogen has been abstracted by halogens, then substituents which decrease the reactivity of the site towards hydrogen abstraction by chlorine will increase the ease of abstraction of halogen by trimethyl tin radicals from the same site. From table 10, the results relating to compounds of the type $RCCl_3$ can be examined.

TABLE 10

Abstraction from $RCCl_3$ at 373°K on a chloroform standard for abstraction of chlorine by trimethyl tin radicals

R =	$RS^{RCCl_3}_{CHCl_3}$	$D(RCCl_2-Cl)$
$-H$	1.0	77.5^a
$-CH_3$	1.5 ± 0.1	-
$-CH_2CH_2Cl$	3.3 ± 0.6	$(70.2)^b$
$-CH_2Cl$	2.0 ± 0.1	$(70.2)^b$
$-CHCl_2$	4.65 ± 0.3	$(70.2)^b$
$-Cl$	2.78 ± 0.1	70.5^a
$-F$	~1.5	-
$-CF_3$	3.7 ± 0.2	-

(a) Ref. 29
(b) Ref. 30 Bond dissociation Energy D, in Kcals mole^{-1}

It can be seen from the above that the relative selectivity varies very little in going from chloroform to 1,1,1-trichlorotrifluoroethane. However bond dissociation energy arguments would predict abstraction from CCl_3CF_3 to be more difficult than from chloroform, since $D(CF_3CCl_2-Cl) > D(CHCl_2-Cl)$, whereas it is easier by a factor of 3.7.

This would indicate that in the transition state, polar forces are present that are capable of reversing the results expected on a purely thermochemical argument. The quantitative importance of polar effects can be seen for the abstraction of hydrogen by $CH_3\cdot$, Cl and $CF_3\cdot$ radicals. The results in table 11 are of interest for comparison purposes with the present data and are worthy of some discussion.

TABLE 11

The influence of halogen substituents on hydrogen abstraction reactions

	E	D(→C-H)		E	D(→C-H)
$Cl\cdot + CH_4$	3.85^{36}	104^{33}	$CH_3\cdot + CH_4$	14.3^{37}	104^{33}
$+ CH_3Cl$	3.30	100.9^{34}	$+ CH_3F$	11.4^{38}	100 ± 2^{38}
$+ CH_2Cl_2$	3.00	99.0^{34}	$+ CH_2F_2$	10.2^{38}	101 ± 2^{35}
$+ CHCl_3$	3.35	99.5^{34}	$+ CHF_3$	11.4^{39}	106 ± 1^{33}

	E^{40}	D(→C-H)
$CF_3\cdot + CH_4$	11.2	104^{33}
$+ CH_3F$	11.2	100 ± 2^{35}
$+ CH_2F_2$	11.2	101 ± 2^{35}
$+ CHF_3$	-	106 ± 1^{33}

D(R-H) is in Kcals $mole^{-1}$

It might be expected that the activation energies for abstraction of hydrogen from a particular halomethane would be related to the bond strength of the formed methane. Thus as $D(CH_3-H) \sim 104$ Kcals $mole^{-1}$ and $D(CF_3-H) \sim 106$ Kcals $mole^{-1}$, the activation energies for hydrogen abstraction should be in the order $CH_3\cdot > CF_3\cdot$. Consideration of table 11 shows that, although the activation energy for hydrogen abstraction from methane by methyl radicals is some 3Kcals $mole^{-1}$ higher than for trifluoromethyl radicals, the activation energies for hydrogen abstraction from fluoromethanes can be actually lower for methyl radicals than for trifluoromethyl radicals. There is apparently no decrease in the activation energy for trifluoromethyl radicals going down the series[40,41] $CH_4 \longrightarrow CH_2F_2$ in comparison with the data for methyl radicals in this series.

It has been suggested that in the particular series where the $\geq$C-H bond strength is decreasing, the repulsion between the electrophilic $CF_3\cdot$ radical and the fluoromethane counteracts the effect of decreasing bond strength. In the case of the essentially non-polar methyl radical it is the bond strength that is the controlling factor. Similar arguments can be applied to the results for hydrogen abstraction from substituted methanes by chlorine atoms also shown in table 11; where the decrease in $\geq$C-H bond strength with increasing chlorination of the methane is partly offset by polar effects and the drop in activation energy from methane to methylene chloride is lower than expected and indeed there is a rise in activation energy for the chlorination of chloroform. In this case there will be no repulsion between the attacking, non-polar, chlorine atom and the substrate, but the HCl molecule formed is highly polar and consequently there is a marked

$$\overset{\longleftarrow\!\!\!\!+}{\mathrm{Cl}\ ---\ \mathrm{H}}\ ---\ \mathrm{C}\leqslant$$

change in electron density at the reaction site and substitution of chlorine atoms at the reaction site lowers the reactivity of the molecule due to these polar effects.

The factors influencing hydrogen abstraction reactions have been discussed by Tedder[4] and can be adapted to halogen abstraction reactions.

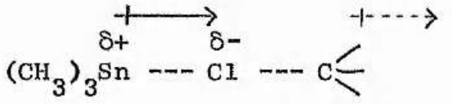
(1) The strength of the bond Me_3Sn-X which is formed

(2) The strength of the bond R-X being broken

(3) The repulsion between the new radical R' and the new molecule Me_3SnX

(4) The repulsion between the incoming radical $Me_3Sn\cdot$ and the molecule RX

In chlorine abstraction the strength of the bond being formed is the same in each case, though in any case the fact that Br > Cl > F and tertiary > secondary > primary suggests that the strength of the bond broken has a larger effect than the strength of the bond formed. Point two has already been discussed and would give, for example, chlorine abstraction from chloroform to be easier than abstraction from carbon tetrachloride purely on the strength of the R-Cl bond broken. The repulsion between the new molecule $(CH_3)_3Sn-Cl$ and the new radical $R\cdot$ (factor 3) is likely to be important in the present reactions. The trimethyl tin chloride will be highly polar and polar substituents in the methane will exert a considerable effect.



$$(CH_3)_3\overset{\delta+}{Sn} \text{ --- } \overset{\delta-}{Cl} \text{ --- } C<$$

An electron attracting substituent on the methyl carbon atom would be expected to lower the activation energy for chlorine abstraction by increasing the attractive forces between the new molecule $(CH_3)_3Sn-Cl$ and the new radical $R\cdot$ in the transition state.

The fourth factor considers the Coulombic forces between the attacking trimethyl tin radical and the initial molecule. This factor can only be important if the trimethyl tin radical has polar properties. Certainly it is reasonable to suppose that for a highly polar radical such as the trifluoromethyl radical this effect may be important and indeed it has been indicated[42] that even a methyl radical is slightly nucleophilic.

An interesting point is the abstraction of hydrogen by methyl radicals from the fluoromethane series. The abstraction from CF_3H has an activation energy of about 3 Kcals $mole^{-1}$ less than that of the corresponding abstraction of hydrogen from methane, despite the fact that $D(CF_3-H) > D(CH_3-H)$ by some 2 Kcals. In this case factor four may be important i.e. reduced repulsion between $CH_3\cdot$ and CF_3H lowers the activation energy for attack on CF_3H compared to CH_4 owing to reduced electron density on the hydrogen of CF_3H. It can be argued that the trimethyl tin radical will have slight nucleophilic properties due to the electron donating effect of three methyl radicals, and thus only electron with-drawing substituents at the reaction site in the initial molecule will tend to increase the rate of chlorine abstraction. This effect is expected to be relatively minor compared with factor 3 discussed above.

The carbon-chlorine bond dissociation energy decreases passing down table 12 as more chlorine substituents are introduced into the substituted methane.

TABLE 12

Relative selectivites of chlorine abstraction by trimethyl tin radicals at 373^oK using chlorocyclohexane as standard, where $[RCl]/[cC_6H_{11}Cl] = 1$

$$R\text{-}Cl + Me_3Sn\cdot \longrightarrow R\cdot + Me_3SnCl$$

R=	$k[RCl]/k[cC_6H_{11}Cl]$	D(C-Cl)
Me_3C-	3.9	80
Me_2Cl-	0.37	-
$MeCl_2$-	7.69	70.2
CCl_3-	14.29	70.5

Consequently the decrease in the strength of the bond being broken will reduce the activation energy for chlorine abstraction in agreement with the experimental observations. For these reactions it is difficult to assess the influence of the polar factors quantitatively since increasing chlorination of the reaction site will also affect the strength of the bond broken due to the factors discussed previously. Finally any influence on the activation energy of abstraction from factor four, the attractive forces between $Me_3Sn\cdot$ and RCl, will also lower the activation energy down the series but the effect is expected to be minor.

The environment at the reaction centre is being radically altered in the previous discussion, but in table 13, the substituents are changed at the C_2 carbon atom, reducing the change to the environment at the centre.

TABLE 13

Relative selectivities of chlorine abstraction by trimethyl tin radicals at 373°K using chlorocyclohexane as standard where $[RCCl_3]/[cC_6H_{11}Cl] = 1$

$$RCCl_2{-}Cl \;+\; Me_3Sn. \longrightarrow RCCl_2\cdot \;+\; Me_3SnCl$$

R=	$k[RCCl_3]/k[cC_6H_{11}Cl]$
-Me	1.5 ± 0.1
$-CH_2Cl$	2.0 ± 0.1
$-CHCl_2$	4.65 ± 0.3
$-CF_3$	3.7 ± 0.2

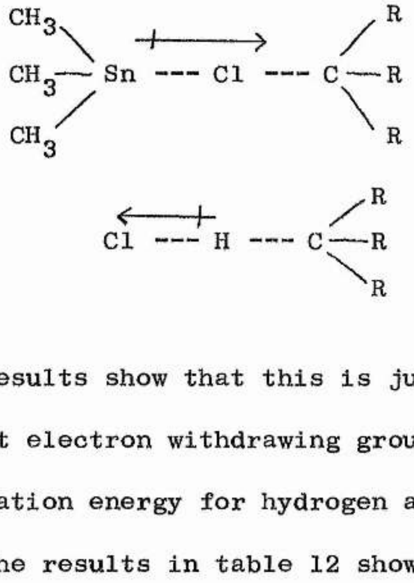
The bond dissociation energies for the first three compounds are given as being the same[28] and the 1,1,1-trifluorotrichloroethane would probably be slightly greater than these, due to the electron attracting effect of the highly electronegative CF_3- grouping.

In this series factor 2, relating to the strength of the alkyl chloride bond broken, is virtually constant and the change in selectivities can almost entirely be related to the polar factors 3 and to a lesser extent 4.

It is immediately obvious that the increase in reactivity passing down the series, CH_3CCl_3, CH_2ClCCl_3 and $CHCl_2CCl_3$ can be attributed to

Coulombic effects due to electrostatic displacements in the transition state. Again it is to be expected increased chlorination at C_2 of the substrate will lower the activation energy down the series (factor 3). A similar though less important lowering of the activation energy will result from the increased attraction between $(CH_3)_3Sn\cdot$ and the initial molecule (factor 4). Similar arguments can be applied for the reactivity of 1,1,1-trifluorotrichloroethane, but the polar effects may now be partly offset by a slight increase in the C-Cl bond energy.

Comparing the results for halogen abstraction by trimethyl tin radicals with those discussed by Tarr[44] et al, it is seen that the polar effects are exactly reversed,



and the results show that this is just what is observed. Table 11 shows that electron withdrawing groups at the reaction site raises the activation energy for hydrogen abstraction by chlorine atoms, whereas the results in table 12 show the opposite effect for chlorine abstraction by $(CH_3)_3Sn^{\cdot}$ where a lowering of the activation energy results with increasing chlorination at the reaction site.

PART II

SECTION I

The photochemical reactions of trimethyl germanium hydride with mono-and di-halogenated alkanes

Part II Introduction

Section I

In Part I it has been shown that the nucleophilic radical trimethyl tin follows the general trends of radical abstraction reactions in that the ease of halogen abstraction follows the order F < Cl < Br and for a particular halogen primary < secondary < tertiary. It has also been shown that a halogen abstraction is greatly assisted by polar effects when a nucleophilic radical is used due to the pre- and post-transitional repulsive forces.

In this section of the work it is hoped to show that the polar effects of the trimethyl tin radical abstractions are further exemplified by trimethyl germanium radicals. Germanium is more electronegative than tin so the polar effects will be slightly reduced, with respect to trimethyl tin, in the transition state. However the difference[29] in the bond energy of a germanium-hydrogen and a germanium-chlorine is very small leading to a greater selectivity, and therefore it would be expected that the contributions from the polar effects would be readily apparent.

Halogen abstraction by triorganogermanium hydrides has been performed in solution by Carlsson and Ingold[13] and by Massol[45]. Gar et al[46] have used trihalogermanes to abstract iodine from alkyl iodides but this was a minor reaction in his work. Carlsson and Ingold give $D(nBu_3Ge-Cl)-D(nBu_3Ge-H) \approx 17$ Kcals mole^{-1} so the difference for the trimethyl germanium compounds will be smaller as suggested by Jackson[28]. Dessy and co-workers[5] have found that triphenyl germyl radicals will abstract hydrogen from organic solvents though these reactions do not proceed particularly readily. They suggest that in some reactions the rate determining step could change from halogen abstraction to hydrogen abstraction. This point will be discussed later. The mechanism postulated is similar to that of trimethyl tin hydride and it is hoped that the following work will add to the understanding of the polar effects involved in nucleophilic radical abstractions and confirm the general trends observed in the case of trimethyl tin hydride.

Experimental

Materials

Trimethyl germanium hydride was synthesised from trimethyl germanium bromide in a similar manner to the trimethyl tin hydride. The trimethyl germanium bromide was purchased from Aldrich Chemicals and required no further purification.

Anhydrous di-n-butyl ether (100 ml) and trimethyl germanium bromide (20 g) were added dropwise to aluminium lithium hydride (3.2 g) in anhydrous di-n-butyl ether (200 ml). The mixture was heated and rapidly stirred at 75°C. The trimethyl germanium hydride distilled over at 26.3°C (760 mm uncorrected) and required no further purification yield 9.1 g (75%). The material was "degassed" and stored under nitrogen, to prevent oxidation and formation of trimethyl germanium hydroxide, at -15°C.

All the alkyl halides had been purified previously for reaction with the trimethyl tin hydride and only required "degassing" and a short trap to trap fractionation.

Procedure

The procedure was as for trimethyl tin hydride. The trimethyl germanium hydride was degassed and stored on the line in a sample tube fitted with its own tap. Again the reaction vessel had to be washed out after every reaction. A thin, initially transparent, film built up on the quartz vessel end window making the results irreproducible if, when repeated, several runs separated them.

Chromatography and identification of products

The Griffin and George D6 was used as for the trimethyl tin hydride. A new column of 24% dinonylphthalate on 60-100 mesh embacel had to be made up as the previous column had deteriorated and blocked due to its constant use.

The products were again identified by their retention times compared with authentic samples using the above 24% dinonylphthalate column and a second 6' column.

Initially mass spectra were taken to identify the trimethyl germanium halide and trimethyl germanium hydride peaks.

Results

Variation of incident light intensity

A series of experiments, performed at constant temperature for a fixed reaction time, were carried out with a constant concentration of trimethyl germanium hydride and 1,3-dichlorobutane with varying light intensity.

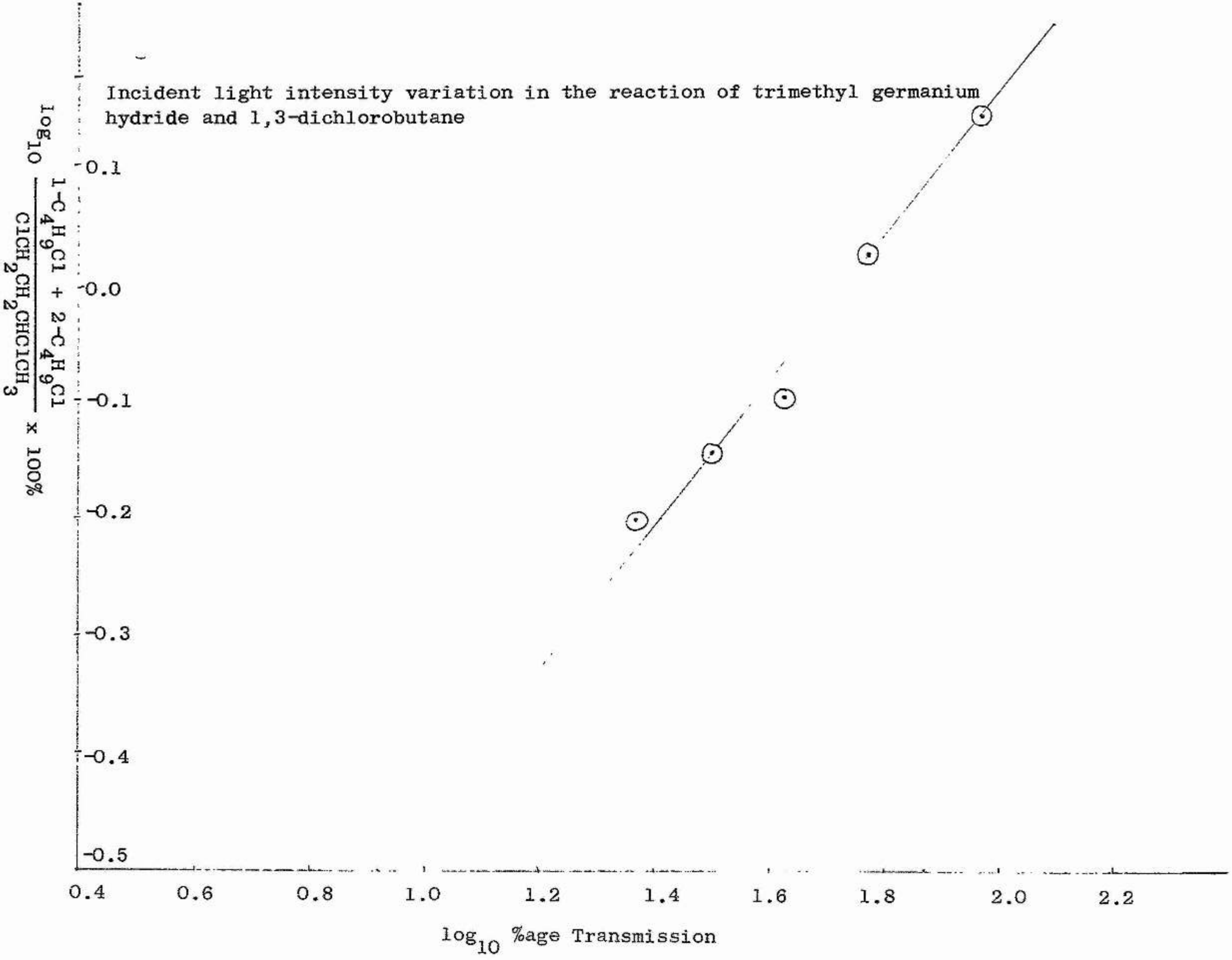
TABLE F I

Transmission	Temp °C	Time (sec)	%age Conversion $\frac{1\text{-}C_4H_9Cl + 2\text{-}C_4H_9Cl}{CH_2ClCH_2CHClCH_3} \times 100\%$	No. of Runs
100%	100 ± 2	3600	3.56 ± 0.01	3
61%	100 ± 2	3600	1.06 ± 0.03	3
46%	100 ± 2	3600	0.81 ± 0.08	3
33%	100 ± 2	3600	0.72 ± 0.05	3
25%	100 ± 2	3600	0.64 ± 0.01	3

Less than 4% conversion of the dichloride was carried out so the error due to error in the denominator is very small. The quantity $\log_{10} \frac{1\text{-}C_4H_9Cl + 2\text{-}C_4H_9Cl}{CH_2ClCH_2CHClCH_3} \times 100\%$ was plotted against $\log_{10}$ (%age transmission) and it gave a straight line. The "least squares" method gave a value of 0.58 ± 0.04 for the slope.

Effect of concentration variation upon the reaction of trimethyl germanium hydride, 2-chlorohexane and 1,4-dichlorobutane

A series of experiments, performed at a constant temperature of 100 ± 2°C, were performed varying the concentration of Me_3GeH and keeping the ratio $2\text{-}C_6H_{13}Cl:CH_2ClCH_2CH_2CH_2Cl$ a constant.



Incident light intensity variation in the reaction of trimethyl germanium hydride and 1,3-dichlorobutane

TABLE F II

Run No.	No. of Runs	$\frac{[n\text{-}C_6H_{14}]}{[1\text{-}C_4H_9Cl]}$	$\frac{[Me_3GeH]}{[2\text{-}C_6H_{13}Cl]}$
1	2	1.05 ± 0.04	0.50
2	2	1.28 ± 0.01	1.84
3	2	1.32 ± 0.01	2.50
4	2	1.71 ± 0.01	4.74
5	2	1.66 ± 0.01	7.50
6	2	1.37 ± 0.01	9.78

The reaction was taken to < 5% conversion.

Investigation of hydride tranfer

Trimethyl tin hydride (7.76×10^{-4} molar) and deutrochloroform (3.32×10^{-4} molar) were irradiated for 1 hour and then the products analysed by GLC coupled mass spectrometer.

No products of the type Me_3SnD or CD_2Cl_2 could be found.

Thermal Reaction

Trimethyl germanium hydride (7.76×10^{-4} molar) and 1,3-dichlorobutane (3.32×10^{-4} molar) were heated at 106 ± 2°C and 168 ± 2°C for 60 minutes and then analysed for products. No detectable products were obtained and the ratio of reactants before and after heating remained constant.

Section I

Abstraction from R-Cl

Reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with 1,3-dichlorobutane (3.32×10^{-4} molar) Photolysed for 10 minutes

TABLE G I

Run No.	No. of Runs	Temp °C	Product Ratio $[1\text{-}C_4H_9Cl]/[2\text{-}C_4H_9Cl]$
1	3	150 ± 1	0.41 ± 0.01
2	4	145 ± 1	0.43 ± 0.01
3	3	135 ± 1	0.37 ± 0.01
4	3	102 ± 1	0.44 ± 0.01
5	3	93 ± 1	0.40 ± 0.01
6	3	72 ± 1	0.35 ± 0.01
7	5	70 ± 1	0.40 ± 0.01
8	5	50 ± 1	0.32 ± 0.01
9	3	44 ± 1	0.33 ± 0.01

Reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Phtolysed for 30 minutes

TABLE G II

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_3]/[cC_6H_{12}]$
1	3	151 ± 1	18.22 ± 0.22
2	3	131 ± 1	32.08 ± 0.10
3	2	123 ± 1	23.80 ± 0.22
4	4	112 ± 1	21.17 ± 0.13
5	3	102 ± 1	18.83 ± 0.06
6	4	95 ± 1	17.66 ± 0.21
7	4	66 ± 1	30.67 ± 0.17
8	3	51 ± 1	96.30 ± 0.42

Reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with 1,3-dichloro-3-methylbutane (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 30 minutes

TABLE G III

Run No.	No. of Runs	Temp ^{o}C	Product Ratio $\frac{[CH_2ClCH_2CH(CH_3)_2]}{[CH_3CCl(CH_3)CH_2CH_3]}$	$\frac{[CH_3CCl(CH_3)CH_2CH_3]}{[cC_6H_{12}]}$	$\frac{[CH_2ClCH_2CH(CH_3)_2]}{[cC_6H_{12}]}$
1	6	140 ± 2	5.33 ± 0.21	2.81 ± 0.05	14.16 ± 1.01
2	6	101 ± 2	3.86 ± 0.02	3.53 ± 0.20	17.25 ± 0.16
3	6	86 ± 2	4.15 ± 0.01	3.88 ± 0.06	16.87 ± 0.03
4	6	52 ± 2	3.17 ± 0.01	8.17 ± 0.06	29.01 ± 0.04

Reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with 1,4-dichlorobutane (3.32×10^{-4} molar) and 2-chlorohexane (3.32×10^{-4} molar) Photolysed for 20 minutes

TABLE G IV

Run No.	No. of Runs	Temp ^{o}C	Product Ratio $[n\text{-}C_6H_{14}]/[1\text{-}C_4H_9Cl]$
1	3	150 ± 2	1.54 ± 0.01
2	3	130 ± 2	1.29 ± 0.01
3	3	110 ± 2	1.22 ± 0.01
4	3	106 ± 2	1.24 ± 0.06
5	3	80 ± 2	1.10 ± 0.02
6	3	76 ± 2	1.14 ± 0.01
7	3	67 ± 2	1.21 ± 0.01
8	3	60 ± 2	1.26 ± 0.01
9	3	50 ± 2	1.55 ± 0.03
10	3	49 ± 2	1.62 ± 0.01

Reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with 1,4-dichlorobutane (3.32×10^{-4} molar) and chlorocyclohexane (3.32×10^{-4} molar) Photolysed for 30 minutes

TABLE G V

Run No.	No. of Runs	Temp °C	Product Ratio $[1\text{-}C_4H_9Cl]/[cC_6H_{12}]$
1	3	150 ± 2	1.25 ± 0.03
2	3	131 ± 2	1.24 ± 0.04
3	3	118 ± 2	1.55 ± 0.04
4	3	92 ± 2	2.17 ± 0.03
5	3	82 ± 2	1.97 ± 0.02
6	3	72 ± 2	1.50 ± 0.01

Details of Results

Reaction of trimethyl germanium hydride with (i) 1,3-Dichlorobutane:-

Trimethyl germanium hydride (7.76 x 10^{-4} molar) and 1,3-dichlorobutane (3.32×10^{-4} molar) were irradiated for 10 minutes at known temperatures.

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1^{o}C

The products were determined by their retention times in conjunction with a 6' column of 20% tritolylphosphate on 60-80 mesh celite.

A GLC coupled mass spectrograph was taken initially to determine the position of the trimethyl germanium compounds.

$1\text{-}C_4H_9Cl$	$2\text{-}C_4H_9Cl$	$\frac{1\text{-}C_4H_9Cl}{2\text{-}C_4H_9Cl}$	$1\text{-}C_4H_9Cl$	$2\text{-}C_4H_9Cl$	$\frac{1\text{-}C_4H_9Cl}{2\text{-}C_4H_9Cl}$
Run No. 1	Temp = 155 ± 1^{o}C		Run No. 2	Temp = 145 ± 1^{o}C	
100 x 2	38.2 x 2	2.62	100 x 1	37.0 x 1	2.70
100 x 1	38.1 x 1	2.63	100 x 1	37.1 x 1	2.71
100 x 2	38.1 x 2	2.63	100 x 1	37.1 x 1	2.71
			100 x 1	37.0 x 1	2.70
Run No. 3	Temp = 135 ± 1^{o}C		Run No. 4	Temp = 102 ± 1^{o}C	
100 x 1	42.0 x 1	2.38	100 x 1	36.5 x 1	2.74
100 x 1	42.0 x 1	2.38	100 x 1	36.4 x 1	2.75
100 x 1	42.1 x 1	2.38	100 x 1	36.5 x 1	2.74
Run No. 5	Temp = 93 ± 1^{o}C		Run No. 6	Temp = 72 ± 1^{o}C	
100 x 1	39.6 x 1	2.53	18.0 x 1	8.0 x 1	2.25
100 x 1	39.6 x 1	2.53	18.2 x 1	8.1 x 1	2.25
100 x 1	39.5 x 1	2.53	18.0 x 1	8.0 x 1	2.25
Run No. 7	Temp = 70 ± 1^{o}C		Run No. 8	Temp = 50 ± 1^{o}C	
100 x 1	39.5 x 1	2.53	34.0 x 1	16.0 x 1	2.13
100 x 1	39.5 x 1	2.53	34.0 x 1	16.1 x 1	2.13
100 x 1	39.6 x 1	2.52	34.0 x 1	16.2 x 1	2.10

Run No. 9 Temp = 44 ± 1°C

15.0 x 1	7.0 x 1	2.14
15.1 x 1	7.0 x 1	2.16
15.0 x 1	7.0 x 1	2.14

(ii) Carbon tetrachloride and chlorocyclohexane:- Trimethyl germanium hydride (7.76 x 10^{-4} molar) with carbon tetrachloride (3.32 x 10^{-4} molar) and chlorocyclohexane (3.32 x 10^{-4} molar) were irradiated for 30 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 120 ml/min

Recorder chart speed = 12"/h

Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a 20% silicon oil column on 60-100 mesh embacel

cC_6H_{12}	$CHCl_3$	$\frac{CHCl_3}{cC_6H_{12}}$	cC_6H_{12}	$CHCl_3$	$\frac{CHCl_3}{cC_6H_{12}}$
Run No. 1	Temp = 151 ± 1°C		Run No. 2	Temp = 131 ± 1°C	
8.3 x 1	100 x 10	18.43	4.6 x 1	95.4 x 10	31.73
8.5 x 1	100 x 10	18.00	4.5 x 1	95.5 x 10	32.44
8.4 x 1	100 x 10	18.21	4.6 x 1	95.4 x 10	31.73
Run No. 3	Temp = 123 ± 1°C		Run No.4	Temp = 112 ± 1°C	
6.0 x 1	94.0 x 10	23.97	7.0 x 1	93.0 x 10	20.33
6.1 x 1	94.2 x 10	23.63	3.2 x 1	96.8 x 5	23.14
			3.2 x 1	96.8 x 5	23.14
			7.1 x 1	93.0 x 10	20.04
Run No. 5	Temp = 102 ± 1°C		Run No. 6	Temp = 95 ± 1°C	
7.5 x 1	92.5 x 10	18.87	4.1 x 1	95.8 x 5	17.88
14.0 x 1	86.0 x 20	18.81	4.2 x 1	95.8 x 5	17.45
3.9 x 1	96.1 x 5	18.83	4.2 x 1	95.8 x 5	17.45
			4.1 x 1	95.8 x 5	17.88

Run No. 7 Temp = 66 ± 1°C

2.5 x 1	97.5 x 5	29.84
2.4 x 1	97.5 x 5	31.07
2.5 x 1	97.5 x 5	29.84
2.4 x 1	97.6 x 5	31.11

Run No. 8 Temp = 51 ± 1°C

1.6 x 1	98.4 x 10	94.09
1.5 x 1	98.5 x 10	100.47
7.5 x 1	92.5 x 5	94.35

(iii) Chlorocyclohexane and 1,3-dichloro-3-methylbutane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with chlorocyclohexane (3.32×10^{-4} molar) and 1,3-dichloro-3-methylbutane (3.32×10^{-4} molar) were irradiated for 30 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/10 sec
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 20% tritolylphosphate column on 60-80 mesh celite

cC_6H_{12}	$CH_3CCl(CH_3)CH_2CH_3$	$\frac{CH_3CCl(CH_3)CH_2CH_3}{cC_6H_{12}}$
Run No. 1	Temp = 140 ± 2°C	
20.2 x 1	79.8 x 1	2.82
20.0 x 1	80.0 x 1	2.86
20.5 x 1	79.5 x 1	2.77
20.2 x 1	79.8 x 1	2.82
20.0 x 1	80.0 x 1	2.86
20.5 x 1	79.5 x 1	2.77

cC_6H_{12}	$CH_2ClCH_2CH(CH_3)_2$	$\frac{CH_2ClCH_2CH(CH_3)_2}{cC_6H_{12}}$
20.5 x 1	79.5 x 5	13.84
32.0 x 1	68.0 x 10	15.17
20.2 x 1	79.8 x 5	14.10
20.5 x 1	79.5 x 5	13.84
20.2 x 1	79.8 x 5	14.10
32.0 x 1	68.0 x 10	15.17

Run No. 2 Temp = 101 ± 2°C

16.0 x 1	83.5 x 1	3.73
16.0 x 1	84.0 x 1	3.75
17.0 x 1	83.0 x 1	3.49
17.0 x 1	83.0 x 1	3.49
17.0 x 1	83.1 x 1	3.49
16.0 x 1	84.0 x 1	3.75

29.5 x 1	70.5 x 10	17.06
17.1 x 1	83.1 x 5	17.35
17.0 x 1	83.0 x 5	17.43
29.5 x 1	70.5 x 10	17.06
29.6 x 1	70.7 x 10	17.06
17.1 x 1	83.1 x 5	17.35

Run No. 3 Temp = 86 ± 2°C

15.5 x 1	84.5 x 1	3.89
15.6 x 1	84.5 x 1	3.87
15.4 x 1	84.6 x 1	3.92
15.4 x 1	84.6 x 1	3.92
15.6 x 1	84.5 x 1	3.87
15.5 x 1	84.5 x 1	3.89

7.8 x 1	92.2 x 2	16.88
7.8 x 1	92.4 x 2	16.92
7.8 x 1	92.2 x 2	16.88
7.8 x 1	92.2 x 2	16.88
7.8 x 1	92.4 x 2	16.92
7.8 x 1	92.4 x 2	16.92

Run No. 4 Temp = 52 ± 2°C

8.0 x 1	92.0 x 1	8.21
8.1 x 1	92.0 x 1	8.11
14.8 x 1	85.2 x 2	8.22
8.1 x 1	92.0 x 1	8.11
8.0 x 1	92.0 x 1	8.21
14.8 x 1	85.2 x 2	8.22

2.4 x 1	97.6 x 1	29.04
2.4 x 1	97.6 x 1	29.04
4.7 x 1	95.3 x 2	28.92
4.7 x 1	95.3 x 2	29.04
2.4 x 1	97.6 x 1	29.04
2.4 x 1	97.6 x 1	29.04

(iv) 1,4-Dichlorobutane and 2-chlorohexane:-

Trimethyl germanium hydride (7.76 x 10^{-4} molar) with 1,4-dichlorobutane (3.32 x 10^{-4} molar) and 2-chlorohexane (3.32 x 10^{-4} molar) were irradiated for 20 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 20% silicon oil column on 60-100 mesh embacel

$1\text{-}C_4H_9Cl$	$n\text{-}C_6H_{14}$	$\frac{n\text{-}C_6H_{14}}{1\text{-}C_4H_9Cl}$	$1\text{-}C_4H_9Cl$	$n\text{-}C_6H_{14}$	$\frac{n\text{-}C_6H_{14}}{1\text{-}C_4H_9Cl}$
Run No. 1	Temp = 150 ± 2°C		Run No. 2	Temp = 130 ± 2°C	
100 x 2	70.0 x 2	1.54	100 x 1	58.5 x 1	1.29
100 x 2	70.0 x 2	1.54	100 x 1	58.9 x 1	1.30
100 x 2	70.1 x 2	1.55	100 x 1	58.5 x 1	1.29

Run No. 3	Temp = 110 ± 2°C		Run No.4	Temp = 106 ± 2°C	
100 x 1	56.0 x 1	1.24	100 x 1	58.5 x 1	1.29
100 x 1	55.0 x 1	1.24	100 x 1	58.3 x 1	1.19
100 x 1	56.0 x 1	1.21	100 x 1	29.2 x 2	1.29

Run No. 5	Temp = 80 ± 2°C		Run No. 6	Temp = 75 ± 2°C	
100 x 1	49.0 x 1	1.08	100 x 1	52.0 x 1	1.15
100 x 1	50.0 x 1	1.10	100 x 1	52.2 x 1	1.15
100 x 1	50.0 x 1	1.10	100 x 1	52.0 x 1	1.15

Run No. 7	Temp = 67 ± 2°C		Run No. 8	Temp = 60 ± 2°C	
18.2 x 1	10.0 x 1	1.21	63.5 x 1	36.5 x 1	1.27
18.5 x 1	10.2 x 1	1.22	63.8 x 1	36.2 x 1	1.25
18.2 x 1	10.0 x 1	1.21	63.5 x 1	36.5 x 1	1.27

Run No. 9	Temp = 50 ± 2°C		Run No. 10	Temp = 49 ± 2°C	
11.9 x 1	8.4 x 1	1.56	10.0 x 1	7.4 x 1	1.63
11.8 x 1	8.4 x 1	1.57	9.9 x 1	7.3 x 1	1.62
11.9 x 1	8.3 x 1	1.54	10.0 x 1	7.4 x 1	1.63

(v) Chlorocyclohexane and 1,4-dichlorobutane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with chlorocyclohexane (3.32×10^{-4} molar) and 1,4-dichlorobutane (3.32×10^{-4} molar) were irradiated for 30 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel

Nitrogen flow rate = 120 ml/min

Recorder chart speed = 12"/h

Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6'25% tritolylphosphate column on 60-100 mesh embacel

$1-C_4H_9Cl$	cC_6H_{12}	$\frac{1-C_4H_9Cl}{cC_6H_{12}}$	$1-C_4H_9Cl$	cC_6H_{12}	$\frac{1-C_4H_9Cl}{cC_6H_{12}}$
Run No. 1	Temp = 150 ± 2°C		Run No. 2	Temp = 131 ± 2°C	
100 x 1	34.8 x 1	1.25	100 x 1	35.1 x 1	1.24
100 x 1	34.9 x 1	1.24	100 x 1	34.9 x 1	1.23
100 x 1	34.7 x 1	1.26	100 x 1	35.9 x 1	1.25

Run No. 3 Temp = 118 ± 2°C

100 x 1	28.0 x 1	1.55
100 x 1	28.0 x 1	1.55
100 x 1	28.1 x 1	1.55

Run No. 4 Temp = 92 ± 2°C

100 x 1	29.0 x 1	1.50
100 x 1	29.1 x 1	1.49
100 x 1	28.9 x 1	1.51

Run No. 5 Temp = 82 ± 2°C

100 x 1	22.0 x 1	1.97
100 x 1	22.0 x 1	1.97
100 x 1	22.0 x 1	1.97

Run No. 6 Temp = 72 ± 2°C

100 x 1	20.0 x 1	2.17
100 x 1	19.8 x 1	2.21
100 x 1	20.2 x 1	2.13

PART II

SECTION II

The photochemical reaction of trimethyl germanium hydride with 1,1,1-trichloroethane derivatives

Part II

Section II

Introduction

In the preceding section the general trends established with trimethyl tin radicals have been followed although the relative magnitude of the selectivity values are not as large as anticipated. In the next piece of work the same series of compounds as used in Part I Section II was used to identify the relative magnitudes of the polar substituents R in the $RCCl_3$ series. It was hoped to show that trimethyl germanium radicals would follow the same trends as trimethyl tin radicals but to be more selective.

The identification of products and experimental procedures were the same as for the previous section.

Results

Abstraction from R-CCl_3

The reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichloroethane (3.32×10^{-4} molar) Photolysed for 30 minutes

TABLE H I

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_3CHCl_2]/[CHCl_3]$
1	4	180 ± 3	3.19 ± 0.01
2	4	126 ± 2	2.89 ± 0.02
3	3	100 ± 1	3.59 ± 0.05
4	5	80 ± 1	3.03 ± 0.02
5	4	48 ± 1	2.54 ± 0.01

The reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,2-tetrachloroethane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE H II

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_2ClCHCl_2]/[CH_2Cl_2]$
1	4	168 ± 2	5.13 ± 0.01
2	4	118 ± 2	9.28 ± 0.01
3	4	98 ± 1	11.46 ± 0.01
4	4	68 ± 1	12.97 ± 0.01

The reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichlorotrifluorobutane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE H III

Run No.	No. of Runs	Temp °C	Product Ratio $[CF_3CHCl_2]/[CH_2Cl_2]$
1	4	163 ± 1	14.72 ± 0.01
2	4	145 ± 1	19.69 ± 0.10
3	4	130 ± 1	21.89 ± 0.01
4	3	110 ± 1	30.43 ± 0.20
5	4	85 ± 1	38.99 ± 0.11

A plot of $\log_{10}[CF_3CHCl_2]/[CH_2Cl_2]$ vs $10^3/T$ gave a line of gradient $E_{CF_3CHCl_2} - E_{CH_2Cl_2} = 0.84 \pm 0.11$ and intercept $\log_{10}A_{CF_3CHCl_2} - \log_{10}A_{CH_2Cl_2} = -0.73 \pm 0.04$ by the "least squares" method.

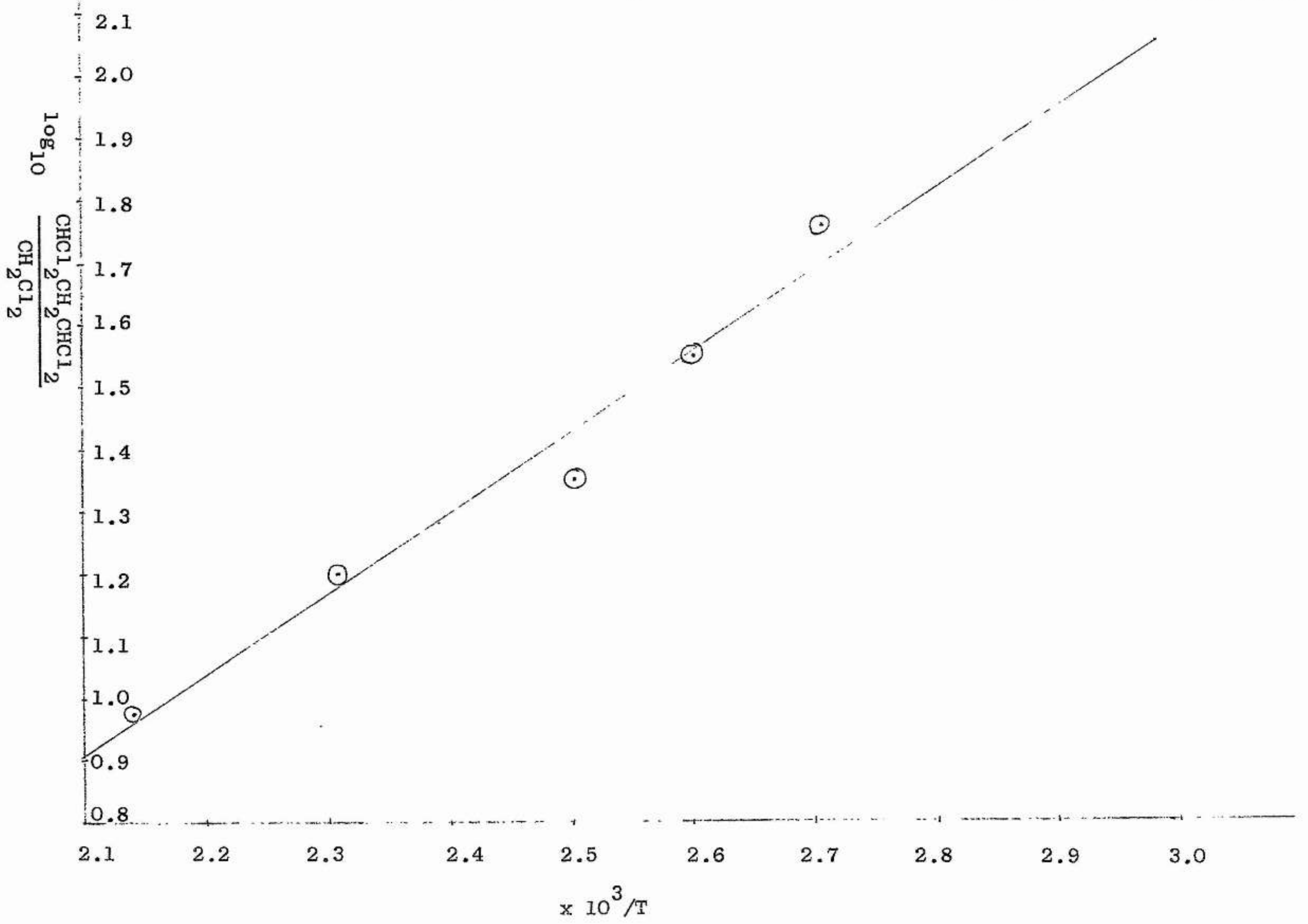
The reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,3-tetrachloropropane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE H IV

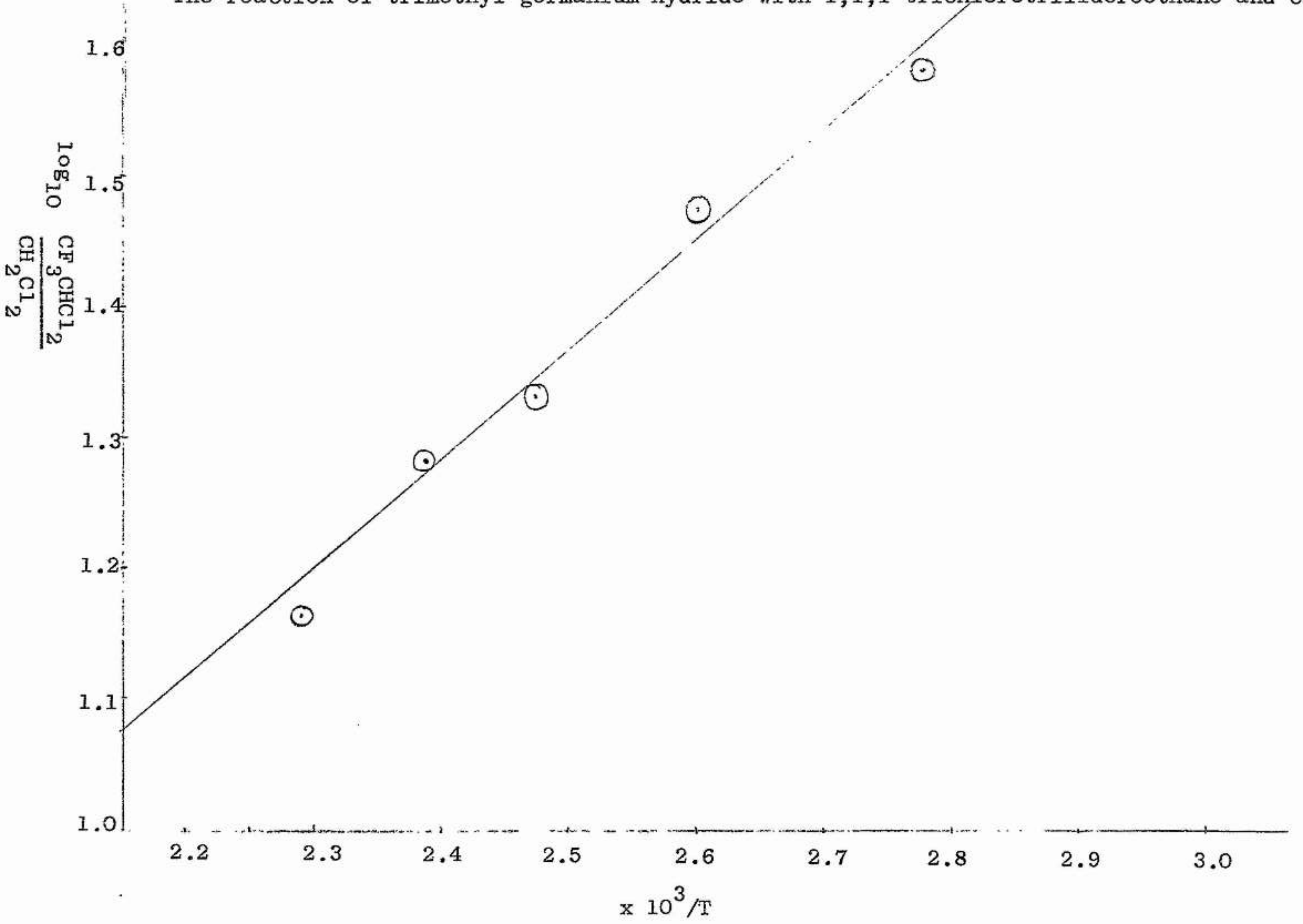
Run No.	No. of Runs	Temp °C	Product Ratio $\frac{[CHCl_2CH_2CH_2Cl]}{[CH_2Cl_2]}$	$\frac{[CH_3CH_2CCl_3]}{[CH_2Cl_2]}$
1	3	193 ± 2	6.08 ± 0.01	0.66 ± 0.01
2	3	159 ± 2	10.12 ± 0.01	1.36 ± 0.01
3	3	125 ± 2	14.66 ± 0.01	4.04 ± 0.01
4	4	110 ± 2	22.89 ± 0.01	8.02 ± 0.01
5	3	95 ± 2	37.22 ± 0.03	46.27 ± 0.01

A plot of $\log_{10}[CHCl_2CH_2CH_2Cl]/[CH_2Cl_2]$ vs $10^3/T$ gave a line of gradient $E_{CHCl_2CH_2CH_2Cl} - E_{CH_2Cl_2} = 1.32 \pm 0.16$ and intercept $\log_{10}A_{CHCl_2CH_2CH_2Cl} - \log_{10}A_{CH_2Cl_2} = -2.08 \pm 0.06$ by the "least squares" method.

The reaction of trimethyl germanium hydride with chloroform and 1,1,1,3-tetrachloropropane



The reaction of trimethyl germanium hydride with 1,1,1-trichlorotrifluoroethane and chloroform



The reaction of trimethyl germanium hydride (7.76 x 10^{-4} molar) with pentachloroethane (3.32 x 10^{-4} molar) and 1,1,1-trichloroethane (3.32 x 10^{-4} molar) Photolysed for 5 minutes

TABLE H V

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_2CHCl_2]/[CH_3CHCl_2]$
1	3	154 ± 2	253.0 ± 4.9
2	3	144 ± 2	222.0 ± 4.7
3	3	137 ± 2	198.0 ± 3.3
4	3	128 ± 2	126.0 ± 3.1

The reaction of trimethyl germanium hydride (7.76 x 10^{-4} molar) with 1,1,1-trichloroethane (3.32 x 10^{-4} molar) and fluorotrichloromethane (3.32 x 10^{-4} molar) Photolysed for 5 minutes

TABLE H VI

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_2F]/[CH_3CHCl_2]$
1	4	181 ± 1	1.63 ± 0.01
2	4	154 ± 1	1.88 ± 0.01
3	4	133 ± 1	2.11 ± 0.01
4	4	99 ± 1	2.35 ± 0.01

The reaction of trimethyl germanium hydride (7.76 x 10^{-4} molar) with carbon tetrachloride (3.32 x 10^{-4} molar) and 1,1,1-trichlorotrifluoroethane (3.32 x 10^{-4} molar) Photolysed for 5 minutes

TABLE H VII

Run No.	No. of Runs	Temp °C	Product Ratio $[CHCl_3]/[CF_3CHCl_2]$
1	3	180 ± 2	1.42 ± 0.02
2	3	153 ± 2	1.67 ± 0.01
3	3	122 ± 2	2.05 ± 0.01
4	3	110 ± 1	1.80 ± 0.02
5	3	102 ± 1	1.45 ± 0.02

The reaction of trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 2,2-dichloropropane (3.32×10^{-4} molar) Photolysed for 5 minutes

TABLE H VIII

Run No.	No. of Runs	Temp °C	Product Ratio $[CH_2Cl_2]/[CH_3CHClCH_3]$
1	3	201 ± 2	7.79 ± 0.01
2	3	148 ± 1	4.75 ± 0.02
3	3	129 ± 1	4.19 ± 0.02
4	3	124 ± 1	3.95 ± 0.01
5	3	115 ± 1	3.36 ± 0.02
6	3	102 ± 1	2.70 ± 0.02

Details of Reactions

The reaction of trimethyl germanium hydride with (i) Chloroform and 1,1,1-trichloroethane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichloroethane (3.32×10^{-4} molar) were irradiated for 30 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a 20% tritolylphosphate column on 60-80 mesh celite

$CHCl_2CH_3$	CH_2Cl_2	$\frac{CH_3CHCl_2}{CH_2Cl_2}$
Run No. 1	Temp = 180 ± 3°C	
80.0 x 1	20.0 x 1	3.21
80.0 x 2	20.2 x 2	3.18
80.0 x 1	20.2 x 1	3.18
80.0 x 2	20.2 x 2	3.18
Run No. 3	Temp = 100 ± 1°C	
81.8 x 2	18.0 x 2	3.65
82.0 x 1	18.6 x 1	3.54
81.8 x 1	18.0 x 1	3.65
Run No. 5	Temp = 48 ± 1°C	
76.0 x 1	24.0 x 1	2.54
76.0 x 2	24.0 x 2	2.54
76.0 x 1	24.0 x 1	2.54
76.1 x 2	24.1 x 2	2.53

$CHCl_2CH_3$	CH_2Cl_2	$\frac{CH_3CHCl_2}{CH_2Cl_2}$
Run No. 2	Temp = 126 ± 2°C	
59.2 x 5	40.8 x 2	2.91
59.0 x 5	41.0 x 2	2.89
59.0 x 5	41.0 x 2	2.89
59.1 x 5	41.0 x 2	2.89
Run No. 4	Temp = 80 ± 1°C	
79.0 x 2	21.0 x 2	3.02
79.0 x 2	21.0 x 2	3.02
79.2 x 2	20.8 x 2	3.06
79.2 x 1	20.8 x 1	3.06
79.0 x 2	21.0 x 2	3.02

(ii) Chloroform and 1,1,1,2-tetrachloroethane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,2-tetrachloroethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 25% silicon oil column on 60-100 mesh celite

CH_2Cl_2	$CH_2ClCHCl_2$	$\frac{CH_2ClCHCl_2}{CH_2Cl_2}$	CH_2Cl_2	$CH_2ClCHCl_2$	$\frac{CH_2ClCHCl_2}{CH_2Cl_2}$
Run No. 1	Temp = 168 ± 2°C		Run No. 2	Temp = 118 ± 2°C	
34.5 x 1	65.5 x 5	5.13	5.5 x 1	94.5 x 1	9.28
34.5 x 1	65.5 x 5	5.13	5.5 x 1	94.5 x 1	9.28
34.6 x 1	65.4 x 5	5.12	5.4 x 1	94.5 x 1	9.28
34.4 x 1	65.6 x 5	5.14	5.5 x 1	94.5 x 1	9.28
Run No. 3	Temp = 98 ± 1°C		Run No. 4	Temp = 68 ± 1°C	
4.5 x 1	95.5 x 1	11.46	4.0 x 1	96.0 x 1	12.96
4.5 x 1	95.5 x 1	11.46	4.0 x 1	96.1 x 1	12.98
4.6 x 1	95.4 x 1	11.45	4.0 x 1	96.0 x 1	12.96
4.4 x 1	95.6 x 1	11.47	4.0 x 1	96.1 x 1	12.98

(iii) Chloroform and 1,1,1-trichlorotrifluoroethane:-

Trimethyl germanium hydride 7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1-trichlorotrifluoroethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis: Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 25% tritolylphosphate column on 60-80 mesh celite

CF_3CHCl_2	CH_2Cl_2	$\frac{CF_3CHCl_2}{CH_2Cl_2}$	CF_3CHCl_2	CH_2Cl_2	$\frac{CF_3CHCl_2}{CH_2Cl_2}$
Run No. 1	Temp = 163 ± 1°C		Run No. 2	Temp = 145 ± 1°C	
86.5 x 10	13.5 x 2	14.72	89.5 x 10	10.5 x 2	19.59
86.5 x 10	13.5 x 2	14.72	89.6 x 10	10.4 x 2	19.80
86.4 x 10	13.6 x 2	14.70	89.6 x 5	10.4 x 1	19.80
86.6 x 10	13.4 x 2	14.74	89.5 x 5	10.5 x 1	19.59
Run No. 3	Temp = 130 ± 1°C		Run No. 4	Temp = 110 ± 1°C	
90.5 x 10	9.5 x 2	21.89	93.0 x 10	7.0 x 2	30.53
90.5 x 10	9.5 x 2	21.89	87.0 x 10	13.0 x 1	30.76
90.5 x 10	9.5 x 2	21.89	93.0 x 10	7.0 x 2	30.53
90.6 x 10	9.6 x 2	21.90			
Run No. 5	Temp = 85 ± 1°C				
89.5 x 10	10.6 x 1	38.81			
89.5 x 10	10.5 x 1	39.18			
89.4 x 10	10.6 x 1	38.78			
89.6 x 10	10.4 x 1	39.84			

(iv) Chloroform and 1,1,1,3-tetrachloropropane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 1,1,1,3-tetrachloropropane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 102 ± 2°C

The products were identified by their retention times in conjunction with a 20% tritolylphosphate column on 60-80 mesh celite

$CHCl_2CH_2CH_2Cl$	CH_2Cl_2	$\frac{CHCl_2CH_2CH_2Cl}{CH_2Cl_2}$	$CCl_3CH_2CH_3$	CH_2Cl_2	$\frac{CCl_3CH_2CH_3}{CH_2Cl_2}$
Run No. 1	Temp = 193 ± 2°C				
83.6 x 5	16.4 x 2	6.08	48.2 x 1	51.8 x 2	0.67
83.7 x 5	16.4 x 2	6.08	48.0 x 1	52.0 x 2	0.66
83.6 x 5	16.4 x 2	6.08	48.0 x 1	52.0 x 2	0.66

Run No. 2 Temp = 159 ± 2°C

95.5 x 2	4.5 x 2	10.12	65.5 x 1	34.5 x 2	1.36
95.5 x 2	4.5 x 2	10.12	65.5 x 1	34.5 x 2	1.36
95.5 x 2	4.5 x 2	10.12	65.4 x 1	34.4 x 2	1.36

Run No. 3 Temp = 125 ± 2°C

98.4 x 1	1.6 x 2	14.66	85.0 x 1	15.0 x 2	4.05
98.4 x 1	1.6 x 2	14.66	84.9 x 1	15.1 x 2	4.02
98.3 x 1	1.5 x 2	14.66	85.0 x 1	15.0 x 2	4.05

Run No. 4 Temp = 110 ± 2°C

96.0 x 2	4.0 x 1	22.89	84.9 x 1	15.1 x 1	8.05
96.0 x 2	4.0 x 1	22.89	84.8 x 1	15.2 x 1	7.98
96.0 x 2	4.0 x 1	22.89	84.9 x 1	15.1 x 1	8.05
96.1 x 2	3.9 x 1	22.87	84.8 x 1	15.2 x 1	7.98

Run No. 5 Temp = 95 ± 2°C

97.5 x 2	2.5 x 1	37.20	97.0 x 1	3.0 x 1	46.27
97.5 x 2	2.5 x 1	37.20	97.1 x 1	3.1 x 1	46.27
97.6 x 2	2.5 x 1	37.24	97.0 x 1	3.0 x 1	46.27

(v) Pentachloroethane and 1,1,1-trichloroethane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with pentachloroethane (3.32×10^{-4} molar) and 1,1,1-trichloroethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 120 ml/min
Recorder chart speed = 12"/h
Temperature = 102 ± 2°C

The products were identified by their retention times in conjunction with a 6' 20% silicon oil column in 60-80 mesh celite. In this reaction the peaks could not be measured together. A third peak had to be used (x) and the CH_3CHCl_2 and $CHCl_2CHCl_2$ peaks measured relative to this. Then by dividing out (x) was eliminated and the desired ratio obtained.

CH_3CHCl_2	x	$\frac{x}{CH_3CHCl_2}$	$CHCl_2CHCl_2$	x	$\frac{CHCl_2CHCl_2}{x}$	$\frac{CHCl_2CHCl_2}{CH_3CHCl_2}$
Run No. 1 Temp = 154 $\pm$ 2°C						
5.0 x 1	95.0 x 1	19.0	84.0 x 5	16.0 x 1	26.3	253
5.0 x 1	94.0 x 1	18.9	84.0 x 5	16.0 x 1	26.3	250
5.0 x 1	96.0 x 1	19.1	84.0 x 5	16.0 x 1	26.3	256
Run No. 2 Temp = 144 $\pm$ 2°C						
51.5 x 1	48.5 x 10	9.41	97.9 x 10	2.1 x 10	46.6	222
51.5 x 1	48.5 x 10	9.41	97.9 x 10	2.1 x 10	46.6	222
51.4 x 1	48.4 x 10	9.40	97.8 x 10	2.2 x 10	46.4	219
Run No. 3 Temp = 137 $\pm$ 2°C						
19.5 x 1	80.5 x 5	20.6	94.9 x 10	5.1 x 1	19.0	198
19.5 x 1	80.6 x 5	20.8	94.8 x 10	5.2 x 1	18.8	196
19.4 x 1	80.5 x 5	20.6	94.9 x 10	5.1 x 1	19.0	198
Run No. 4 Temp = 128 $\pm$ 2°C						
11.4 x 1	88.6 x 1	7.7	86.5 x 5	13.5 x 1	31.8	126
11.4 x 1	88.6 x 1	7.7	86.5 x 5	13.5 x 1	31.8	126
11.4 x 1	88.6 x 1	7.7	86.5 x 5	13.5 x 1	31.8	126

(vi) 1,1,1-Trichloroethane and fluorotrichloromethane:-

Trimethyl germanium hydride (7.76 x 10^{-4} molar) with 1,1,1-trichloroethane (3.32 x 10^{-4} molar) and fluorotrichloroethane (3.32 x 10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh celite
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a 6' 20% silicon oil column on 60-80 mesh celite and a 6' 24% tritolylphosphate column on 40-60 mesh celite.

CH_3CHCl_2	$CHCl_2F$	$\frac{CHCl_2F}{CH_3CHCl_2}$	CH_3CHCl_2	$CHCl_2F$	$\frac{CHCl_2F}{CH_3CHCl_2}$
Run No. 1	Temp = 181 ± 1°C		Run No. 2	Temp = 154 ± 1°C	
85.5 x 2	14.5 x 20	1.63	83.7 x 2	16.3 x 20	1.87
85.5 x 2	14.5 x 20	1.63	83.6 x 2	16.4 x 20	1.88
85.5 x 2	14.5 x 20	1.63	83.6 x 2	16.4 x 20	1.88
85.5 x 2	14.5 x 20	1.63	83.7 x 2	16.3 x 20	1.87
Run No. 3	Temp = 133 ± 1°C		Run No.4	Temp = 99 ± 1°C	
82.0 x 2	18.0 x 20	2.11	80.3 x 2	19.7 x 20	2.35
82.0 x 2	18.0 x 20	2.11	80.3 x 2	19.7 x 20	2.35
82.0 x 2	18.0 x 20	2.11	80.4 x 2	19.6 x 20	2.34
82.0 x 2	18.0 x 20	2.11	80.4 x 2	19.6 x 20	2.34

(vii) Carbon tetrachloride and 1,1,1-trichlorotrifluoroethane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with carbon tetrachloride (3.32×10^{-4} molar) and 1,1,1-trichlorotrifluoroethane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 12"/h
Temperature = 45 ± 1°C

The products were identified by their retention times in conjunction with a 6' 20% silicon oil column on 60-80 mesh celite.

$CHCl_3$	$CHCl_2CF_3$	$\frac{CHCl_3}{CHCl_2CF_3}$	$CHCl_3$	$CHCl_2CF_3$	$\frac{CHCl_3}{CHCl_2CF_3}$
Run No. 1	Temp = 180 ± 2°C		Run No. 2	Temp = 153 ± 2°C	
73.5 x 10	26.5 x 20	1.42	76.5 x 10	23.5 x 20	1.67
73.4 x 10	26.6 x 20	1.41	76.6 x 10	23.4 x 20	1.68
73.5 x 10	26.5 x 20	1.42	76.5 x 10	23.5 x 20	1.67
Run No. 3	Temp = 122 ± 2°C		Run No. 4	Temp = 110 ± 1°C	
80.0 x 10	20.0 x 20	2.05	77.8 x 10	22.2 x 20	1.80
80.0 x 10	20.0 x 20	2.05	77.9 x 10	22.1 x 20	1.80
80.0 x 10	20.0 x 20	2.05	77.8 x 10	22.2 x 20	1.80

Run No. 5	Temp = 102 ± 1°C	
73.7 x 10	26.3 x 20	1.44
59.0 x 20	41.0 x 20	1.47
73.7 x 10	26.3 x 20	1.44

(viii) Chloroform and 2,2-dichloropropane:-

Trimethyl germanium hydride (7.76×10^{-4} molar) with chloroform (3.32×10^{-4} molar) and 2,2-dichloropropane (3.32×10^{-4} molar) were irradiated for 5 minutes at known temperatures

Analysis:- Column 6' 24% dinonylphthalate on 60-100 mesh embacel
Nitrogen flow rate = 60 ml/min
Recorder chart speed = 12"/h
Temperature = 34 ± 1°C

The products were identified by their retention times in conjunction with a 6' 25% tritolylphosphate column on 60-80 mesh celite

CH_2Cl_2	$CH_3CHClCH_3$	$\frac{CH_2Cl_2}{CH_3CHClCH_3}$	CH_2Cl_2	$CH_3CHClCH_3$	$\frac{CH_2Cl_2}{CH_3CHClCH_3}$
Run No. 1	Temp = 201 ± 2°C		Run No.2	Temp = 148 ± 1°C	
72.5 x 5	27.5 x 1	7.79	89.0 x 1	11.0 x 1	4.78
72.5 x 5	27.5 x 1	7.79	88.9 x 1	11.1 x 1	4.73
72.5 x 5	27.5 x 1	7.79	88.9 x 1	11.1 x 1	4.73
Run No. 3	Temp = 129 ± 1°C		Run No. 4	Temp = 124 ± 1°C	
87.6 x 1	12.4 x 1	4.17	87.0 x 1	13.0 x 1	3.95
87.7 x 1	12.3 x 1	4.21	87.0 x 1	13.0 x 1	3.95
87.6 x 1	12.4 x 1	4.17	87.0 x 1	13.0 x 1	3.95
Run No. 5	Temp = 115 ± 1°C		Run No. 6	Temp = 102 ± 1°C	
85.0 x 1	15.0 x 1	3.34	90.2 x 1	9.8 x 2	2.72
85.1 x 1	14.9 x 1	3.37	90.1 x 1	9.9 x 2	2.68
85.0 x 1	15.0 x 1	3.34	90.2 x 1	9.8 x 2	2.72

Part II Discussion

The photolytic reaction between trimethyl germanium hydride and alkyl chlorides is experimentally very similar to that of the corresponding trimethyl tin hydride reaction; however, there appears to be a marked reduction in chain length. It is convenient to discuss the mechanism in a similar manner to that outlined previously for the reactions of the tin analogue and compare the thermodynamic properties of both systems.

It seems reasonable that the initiation process can be well represented by the following scheme:-

$$(CH_3)_3GeH \xrightarrow{h\nu} (CH_3)_2\dot{G}eH + CH_3\cdot \qquad (1)$$

$$CH_3\cdot + (CH_3)_3GeH \longrightarrow CH_4 + (CH_3)_3Ge\cdot \qquad (2a)$$

The photolytic rupture of the Ge-CH_3 bond is far more likely, on thermochemical considerations, than the Ge-H bond:-

$$D[(CH_3)_2HGe\text{-}CH_3] = 58^{(a)}$$
$$D[(CH_3)_3Ge\text{-}H] = 81^{(a)}$$

(a) See Ref 28

Experimentally it was found light of shorter wavelengths than 2600 Å were required to initiate the reaction. Trimethyl germanium hydride with 1,3-dichlorobutane gave no detectable products when heated for one hour at 106 ± 2°C and 168 ± 2°C and hence under the present experimental conditions the reactants are thermally stable.

The trimethyl germanium radical produced in the initiation process can either abstract chlorine or hydrogen from the alkyl halide:-

$$RCH_2Cl + (CH_3)_3Ge\cdot \longrightarrow (CH_3)_3GeCl + RCH_2\cdot \qquad (2)$$

$$\Delta H \approx 0 \text{ Kcals}^{(a)}$$

$$RCH_2Cl + (CH_3)_3Ge\cdot \longrightarrow (CH_3)_3GeH + RCHCl\cdot \qquad (2a^{II})$$

$$\Delta H \approx +9 \text{ Kcals}^{(a)}$$

(a) See ref 28 and footnote

and the fate of the alkyl radical produced in (2) and $(2a^{II})$ will be expected to follow the reactions (3) and (3^1)

$$RCH_2\cdot + (CH_3)_3GeH \longrightarrow RCH_3 + (CH_3)_3Ge\cdot \qquad (3)$$

$$\Delta H \approx -9 \text{ Kcals}^{(a)}$$

$$RCHCl\cdot + (CH_3)_3GeH \longrightarrow RCH_2Cl + (CH_3)_3Ge\cdot \qquad (3^1)$$

$$\Delta H \approx 0 \text{ Kcals}^{(a)}$$

(a) Ref. 28

Thermodynamically it would be expected that reactions (2) and (3) will constitute the chain reaction of trimethyl germanium radicals with alkyl chlorides. Experimental evidence for this comes from the reactions of $(CH_3)_3GeH$ with $CDCl_3$ where no evidence for $(CH_3)_3GeD$ was detected and, hence reaction $(2a^{II})$ is unimportant compared to reaction (2). It should be noted, however, that since the net result of reactions $(2a^{II})$ and (3^1) is to leave the system unchanged the only effect of this chain would be to reduce the chain length of the propagation reactions (2) and (3). In the present experiments, in which only the relative

---

Footnote (a):- Taking $D(RCH_2\text{-}Cl)$ = 81 Kcals as for $D(C_2H_5\text{-}Cl)$ which has a higher bond energy than any of the alkyl chlorides studied in these experiments.

Taking $D(RCHCl\text{-}H)$ = 90 Kcals as for $D(CCl_3\text{-}H)$, which has the lowest C-H bond energy of the molecules studied.

rates of chlorine abstraction from two different sites, either in the same or different molecules, was determined, reaction ($2a^{II}$) and (3^1) would be kinetically unimportant.

It is interesting at this point in the discussion to compare the thermodynamic properties of the propagation steps (2) and (3) for the reactions of $(CH_3)_3Ge\cdot$ and $(CH_3)_3Sn\cdot$ radicals. The differences will be influenced by the increase in the Ge-H bond strength over the corresponding value for Sn-H ($\sim$16 Kcals higher) and the decrease in bond strength of some 8 Kcals for Ge-Cl compared with that for Sn-Cl. The abstraction of Cl by $(CH_3)_3Sn\cdot$ radicals, is approximately 8 Kcals exothermic compared with the thermoneutrality of the corresponding reaction of $(CH_3)_3Ge\cdot$ radicals. It might be expected, therefore, that chlorine abstraction by $(CH_3)_3Ge\cdot$ radicals will have a higher activation energy than that for abstraction by $(CH_3)_3Sn\cdot$ radicals and consequently a greater selectivity.

Reaction (3) for both systems is exothermic, $\sim$ 25 Kcals for hydrogen abstraction from $(CH_3)_3SnH$ by alkyl radicals compared to $\sim$ 9 Kcals for the analogous reaction in the germanium system. Whereas for the tin system it appears that reaction (3) was sufficiently exothermic to remove all the alkyl radicals formed in reaction (2), there must now be a real question as to whether the same arguments can be used for the germanium case. If reaction (3) is slow it might be expected that alkyl radicals will be important in the termination steps of the chains. Ingold et al[13] have previously found evidence for the participation of alkyl radicals in the termination steps in the solution phase.

Possible chain termination steps are:-

$$(CH_3)_3Ge\cdot + (CH_3)_3Ge\cdot \longrightarrow (CH_3)_3Ge\text{-}Ge(CH_3)_3 \qquad (4)$$

$$(CH_3)_3Ge\cdot + RCH_2\cdot \longrightarrow (CH_3)_3Ge\text{-}CH_2R \qquad (5)$$

$$RCH_2\cdot + RCH_2\cdot \longrightarrow RCH_2CH_2R \qquad (6)$$

Evidence for the formation of hexamethyl digermanium comes from the presence of the Ge-Ge absorption frequency at 228-234 cm^{-1} when the reaction vessel was scanned at the end of a number of runs. Unfortunately $(CH_3)_3Ge-Ge(CH_3)_3$ was nearly as involatile as hexamethyl ditin and could not be analysed for quantitatively by gas chromatography. After a long photolysis period, for mass spectrographic purposes, some hexamethyl digermanium was distilled out of the reaction vessel and identified by its retention time compared with an authentic sample.

A careful attempt was made to detect the cross-termination products of reaction (5) and the dialkyl compounds from reaction (6) using long reaction times and high intensity photolysis. The method of mass spectra coupled GLC gave no evidence to support the formation of these products. Agreement with this finding comes from the material balance of $(CH_3)_3GeCl$ with RCH_3 in the experiments, suggesting that practically every $RCH_2\cdot$ radical formed in reaction (2) utlimately forms the corresponding alkane by abstraction of hydrogen from $(CH_3)_3GeH$ in reaction (3).

It can, therefore, be concluded that the combination of two $(CH_3)_3Ge\cdot$ radicals is the main chain terminating step and reaction (3) is sufficiently fast to exclude alkyl radicals from participating in the chain termination process.

The complete mechanism is then identical to that for the tin analogue:-

$$(CH_3)_3GeH \xrightarrow{h\nu \quad \emptyset I_a} (CH_3)_3Ge. \qquad (1)$$

$$(CH_3)_3Ge\cdot \xrightarrow{k_2} (CH_3)_3GeCl + R\cdot \qquad (2)$$

$$R\cdot + (CH_3)_3GeH \xrightarrow{k_3} RH + (CH_3)_3Ge\cdot \qquad (3)$$

$$2(CH_3)_3Ge\cdot \xrightarrow{k_4} (CH_3)_3Ge-Ge(CH_3)_3 \qquad (4)$$

and relationships (E) and (F) can be deduced by similar arguments used for the formulation of equations (B), (C), and (D) in the trimethyl tin radical reaction scheme.

$$[(CH_3)_3GeCl]_f = [RH]_f + [RH]_f = k_2[RX](\phi I_a/2k_4)_t^{\frac{1}{2}} \qquad (E)$$

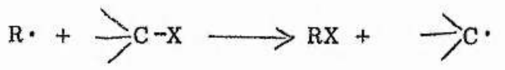
$$\frac{[RH]_f}{[R_1H]_f} = \frac{k_2}{k_1}\frac{[RX]}{[RX_1]} \qquad (F)$$

The results in table F I show the rate of alkane, $[RH]_f$, formed is dependent to the half power on the light intensity in agreement with equation (E).

As previously mentioned the equality $[(CH_3)_3GeCl]_f = [R^1H]_f + [RH]_f$ of equation (E) has also been verified. Equation (F) predicts no change in selectivity if the ratio $[R^1Cl]_i/[RCl]_i$ is constant and therefore the selectivity should be independent of the ratio $[R^1Cl]_i + [RCl]_i/[(CH_3)_3GeH]$. This was found to be true within the limits of experimental error (See Table F II). The relative selectivities for primary, secondary and tertiary chlorine abstraction by trimethyl germanium radicals have been estimated using the chlorine abstraction data for 1,3-dichlorobutane (primary and secondary) and 1,3-dichloro-3-methylbutane (primary and tertiary).

TABLE 14

Relative selectivities of chlorine abstraction by trimethyl germanium radicals and trimethyl tin radicals at 373°K. The relative selectivities for hydrogen abstraction by chlorine atoms are also given together with the enthalpy changes for the reaction



$$R\cdot + \rangle C{-}X \longrightarrow RX + \rangle C\cdot$$

X	R =	$-CH_2-X$	ΔH	>CH-X	ΔH	C-X	ΔH
Cl	$(CH_3)_3Ge$	1	0	2.5	- 2	3.9	- 4
Cl	$(CH_3)_3Sn$	1	- 8	2.5	-10	6.3	-12
H(a)	Cl·	1	-21	3.9	-22	5.1	-24

(a) See Refs. 32, 48 values at 300°K ΔH in K cals $mole^{-1}$

The ratio of the A factors are approximately unity and hence the differences are due to differences in activation energies.

The selectivities for chlorine abstraction by trimethyl germanium radicals are somewhat lower than were anticipated from bond energy data by comparison with the values for chlorine and hydrogen abstraction by trimethyl tin radicals and chlorine atoms respectively. However, the selectivities do provide evidence for the importance of the strength of the carbon-chlorine bond broken in chlorine abstraction by trimethyl germanium radicals.

Further consideration of the data for chlorine abstraction from primary, secondary and tertiary sites show some interesting and unexpected results, specifically the selectivities expected on bond energy data are in fact reversed.

Consider the results for the competitive abstraction of chlorine from chlorocyclohexane and 1,3-dichloro-3-methylbutane by means of the trimethyl germanium radical. The product ratio:

2-chloro-2-methylbutane/cyclohexane = 3.53 ± 0.20

(abstraction of a 1° chlorine relative to a 2° cyclic chlorine),

and 1-chloro-3-methylbutane/cyclohexane = 17.3 ± 0.20

(abstraction of a 3° chlorine relative to a 2° cyclic chlorine),

yield a value of 4.7 for the relative selectivity of a tertiary chlorine compared to the primary site. This is in reasonable agreement with the value of 3.9 derived directly from 1,3-dichloro-3-methylbutane.

However, these results also indicate that a primary chlorine is about 3.5 times more reactive than the secondary chlorine of chlorocyclohexane, whereas the data from 1,3-dichlorobutane suggests a secondary chlorine is some 2.5 times more reactive than the primary. This abnormality is also evidence in the competitive chlorine abstraction from 1,4-dichlorobutane with chlorocyclohexane in which a value of 2.0 was found for primary relative to secondary abstraction. The above results can be rationalised in one of two ways: either chlorine abstraction from chlorocyclohexane is unusually slow or enhanced abstraction from the 1,3- and 1,4-dichlorobutanes occurs. It is difficult to see why chlorine abstraction from chlorocyclohexane should be unusual. The rates of chlorine abstraction from the primary site in 1,4-dichlorobutane and the secondary position in the straight chain molecule, 2-chlorohexane, are nearly equal and this suggests that perhaps the abnormality is associated with the dihalogenoalkane. Thus it seems as though attention must be focussed on the high reactivity of the disubstituted butanes, specifically the activating influence of a chlorine substituent at either the 3 or 4 position to the reaction site. The results shown in table 15 below provide some insight into the problem and further comment is given in the discussion pertaining to the results in the table.

TABLE 15

Rates of chlorine abstraction by trimethyl germanium radicals at 373°K relative to chlorine abstraction from chloroform. Data for trimethyl tin radicals is also presented for comparison purposes.

R=	$(CH_3)_3Ge\cdot$ $RS^{RCCl_3}_{CHCl_3}$	$(CH_3)_3Sn\cdot$ $RS^{RCCl_3}_{CHCl_3}$	$D(RCCl_2-Cl)$ Kcals mole^{-1}
$-H$	1.00	1.00	77.5[34]
$-CH_3$	3.65	1.50	-
$-Cl$	47.70	2.75	70.5[34]
$-CH_2Cl$	10.00	2.00	70.2[30]
$-CHCl_2$	52.00	4.65	70.2[30]
$-CH_2CH_2Cl$	26.90	3.30	70.2[30]
$-F$	9.05	1.50	72.0 ± 2[49]
$-CF_3$	33.10	3.70	-

The ratio of A factors is approximately unity and hence differences in reactivity are due to differences in activation energy.

The most noticeable feature of the results in table 15 is the large increase in the rate of chlorine abstraction by trimethyl germanium radicals in the substituted chloroform derivatives, not only with respect to chloroform itself but also in the magnitude of these increases in reactivity compared to the corresponding reactions with trimethyl tin radicals. The results for chlorine abstraction by trimethyl tin radicals were rationalised in terms of two major components, the strength of the C-Cl bond broken and polar effects in the transition state. It is convenient to discuss the present results within this simple framework. It can be seen that a reduction in the Ge-Cl bond strength leads to an increase in reactivity, though since for each case the electron withdrawing substituents will also increase the reactivity, it is impossible to correlate the increase with bond energy quantitatively. Basically all the derivatives of chloroform studied have approximately the same C-Cl bond dissociation energy which is some 7 Kcals mole^{-1} weaker than in the parent chloroform molecule. If the enthalpy changes in the rate determining step for these abstractions is considered, then it can be seen why substituents which weaken the

$$(CH_3)_3Ge\cdot + CHCl_3 \longrightarrow (CH_3)_3GeCl + \cdot CHCl_2 \qquad \Delta H = -3.5 \text{ Kcals mole}^{-1}$$

$$(CH_3)_3Sn\cdot + CHCl_3 \longrightarrow (CH_3)_3SnCl + \cdot CHCl_2 \qquad \Delta H = -11.5 \text{ Kcals mole}^{-1}$$

C-Cl bond should have such a pronounced effect on the reactivity of trimethyl germanium radicals compared with the much smaller increase in abstraction rate for the tin analogue. Since the abstraction step is only just exothermic for trimethyl germanium radicals, a decrease of 7 Kcals in the C-Cl bond of the substrate represents a substantial increase in the exothermicity of the reaction, whereas for trimethyl tin radicals the reaction is already appreciably exothermic. Thus for example the difference of ~ 50 in the reactivity of CCl_4 over $CHCl_3$ is probably due to the weakening of the C-Cl bond. A similar, though much less pronounced, increase is observed for trimethyl germanium radicals.

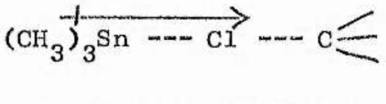
Of more interest in the present work is the series R = $-Cl$, $-CH_2Cl$, $-CHCl_2$ and $-CH_2CH_2Cl$ where the C-Cl bond energy is approximately constant and polar effects are the most likely cause of reactivity changes. These trends in the polar effects are exemplified further by relating the rates of chlorine abstraction for this series relative to the rate of abstraction from CCl_4.

TABLE 16

Rates of chlorine abstraction by $(CH_3)_3Ge\cdot$ and $(CH_3)_3Sn\cdot$ radicals from $R-CCl_3$ at 373°K relative to chlorine abstraction from carbon tetrachloride.

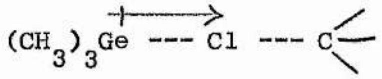
R=	$(CH_3)_3Ge\cdot$ $RS^{RCCl_3}_{CCl_4}$	$(CH_3)_3Sn\cdot$ $RS^{RCCl_3}_{CCl_4}$
$-Cl$	1.00	1.00
$-CH_2Cl$	0.20	0.71
$-CHCl_2$	10.90	1.67
$-CH_2CH_2Cl$	0.56	1.18

The Coulombic forces due to electronic displacements acting in the transition state for the abstraction of chlorine by $(CH_3)_3Sn\cdot$ radicals were discussed in terms ofthe model



$$\overset{\longmapsto}{(CH_3)_3Sn --- Cl} --- C\lessgtr$$

where electron withdrawing substituents at the reaction site increased the attractive forces between the new molecule $(CH_3)_3SnCl$ and the new radical $\cdot\mathrm{C}\leqq$; thus reducing the activation energy. A similar model for the present case can also be invoked, and close similarities in the effect of substituents on the substrate



$$(\mathrm{CH_3})_3\overset{+\!\!\longrightarrow}{\mathrm{Ge\ ---\ Cl}}\ ---\ \mathrm{C}\leqq$$

are to be expected.

Table 17 showsthat germanium is slightly more electronegative than tin and also has a smaller covalent radius and hence is less polarizable.

TABLE 17

Element	Covalent Radius	Electronegativity	
		Allred-Rochand(a)	Pauling(b)
C	0.77	2.50	2.55
Si	1.18	1.74	1.90
Ge	1.22	2.02	2.01
Sn	1.40	1.72	1.96
Pb	1.75	1.55	2.33

(a) Ref. 50

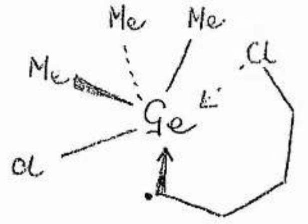
(b) Ref. 51

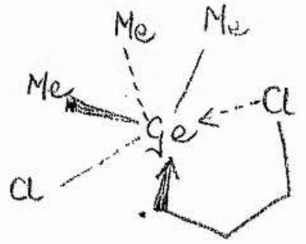
At first sight, therefore, it would be expected that changes in reactivity due to polar effects in the transition state would be slightly smaller in the transition state containing the less polarizable germanium-chlorine bond than for the corresponding transition state involving tin. In absolute terms it would be expected that the polar effects for chlorine abstraction by trimethyl tin radicals are greater than those for abstraction by trimethyl germanium radicals. Such small differences are probably well within the present experimental errors and are not obvious from the data in table 17. The most important features of the results in table 17 are that the trends for $(CH_3)_3Ge\cdot$ and $(CH_3)_3Sn\cdot$ radicals are exactly analogous. Removal of the chlorine substituent one carbon from the reaction site (CCl_4 compared with CH_2ClCCl_3) results in a drop in reactivity, as expected. The high reactivity of $CH_2Cl_2CCl_3$ with $(CH_3)_3Ge\cdot$radicals compared with that with CCl_4 is difficult to explain at present, although a similar, smaller, effect is observed for $(CH_3)_3Sn'$ radicals.

The effect on reactivity of a chlorine atom in the three position is most surprising. The rate of abstraction by $(CH_3)_3Ge\cdot$ and $(CH_3)_3Sn\cdot$ radicals of chlorine from $CH_2ClCH_2CCl_3$ is virtually the same as when the chlorine substituent is actually at the reaction site (i.e. for CCl_4). Normally it is expected that Coulombic effects are rapidly reduced as the substituent is removed from the reaction site and are negligible beyond the two position. This is just what was observed previously when the selectivities of primary, secondary and tertiary chlorine abstractions were discussed. In this case the results were rationalised in terms of the enhanced reactivity of 1,3- and 1,4-disubstituted butanes.

In the data for abstraction by $(CH_3)_3Sn\cdot$ radical and halogen atom, the relative selectivities are for abstraction from monosubstituted compounds in which polar effects would be relatively unimportant, and bond energies very important. However in the case of $(CH_3)_3Ge\cdot$ radicals there is a contribution to the activation energy from polar effects since disubstituted alkanes were used. Hence selectivities will be correspondingly reduced since the bond energy is only part of the overall energy change. The results for $CH_2ClCH_2CCl_3$ confirm this finding and it must be concluded that substituents at the 3 and 4 positions have observable effects on the rate of abstractions. It is difficult to rationalize these results in terms of normal short-range Coulombic effects and it is felt that for these molecules some other factors are operative.

A possible explanation of this anomaly is that a loose ring type of intermediate is formed in which the germanium and tin atoms partially accept electrons from the closed shells of the chlorine atoms and hence produce additional stability to the new radical formed.





The transfer of a halogen would then be of a lower energy process than the thermochemical data would suggest. The new radical formed would have the odd electron delocalised around the ring giving it greater stability over a non ring system. The 1,4-dichlorobutane could form a loose six membered ring system and the 1,3-substituted butanes form a five membered system.

It has been shown by many authors[52] that both germanium and tin will form pentacoordinate and hexacoordinate complexes fairly readily. Thus abstraction from the 1 position of the dichlorinated alkanes produces a species that is capable of being stabilised by using the vacant orbitals of the tin and germanium atom to form a five or six membered ring system. This would make the abstraction from a primary position of a dihalogenated alkane relatively easier than from a primary monohalogenated alkane or a cyclic secondary compound that is unable to form a ring system of this type. It would however make no difference to the rate of abstraction of primary to tertiary in 1,3-dichloro-3-methylbutane or primary to secondary in 1,3-dichlorobutane as they are both in the same environment and subject to the same delocalising factors.

The postulations put forward do not adequately deal with the few anomalous results that occur, but until further work can be carried out on these systems and more data accumulated, no other ideas seem to fit the experimental data as well. Kaplan[53] has shown that with di-iodoalkanes there is the possibility of ring formation by abstraction of the halogens. It may be that formation of a loose ring complex is the first stage to ring closure. However, no cyclic compounds were identified in the reaction systems in which dichloroalkanes were used.

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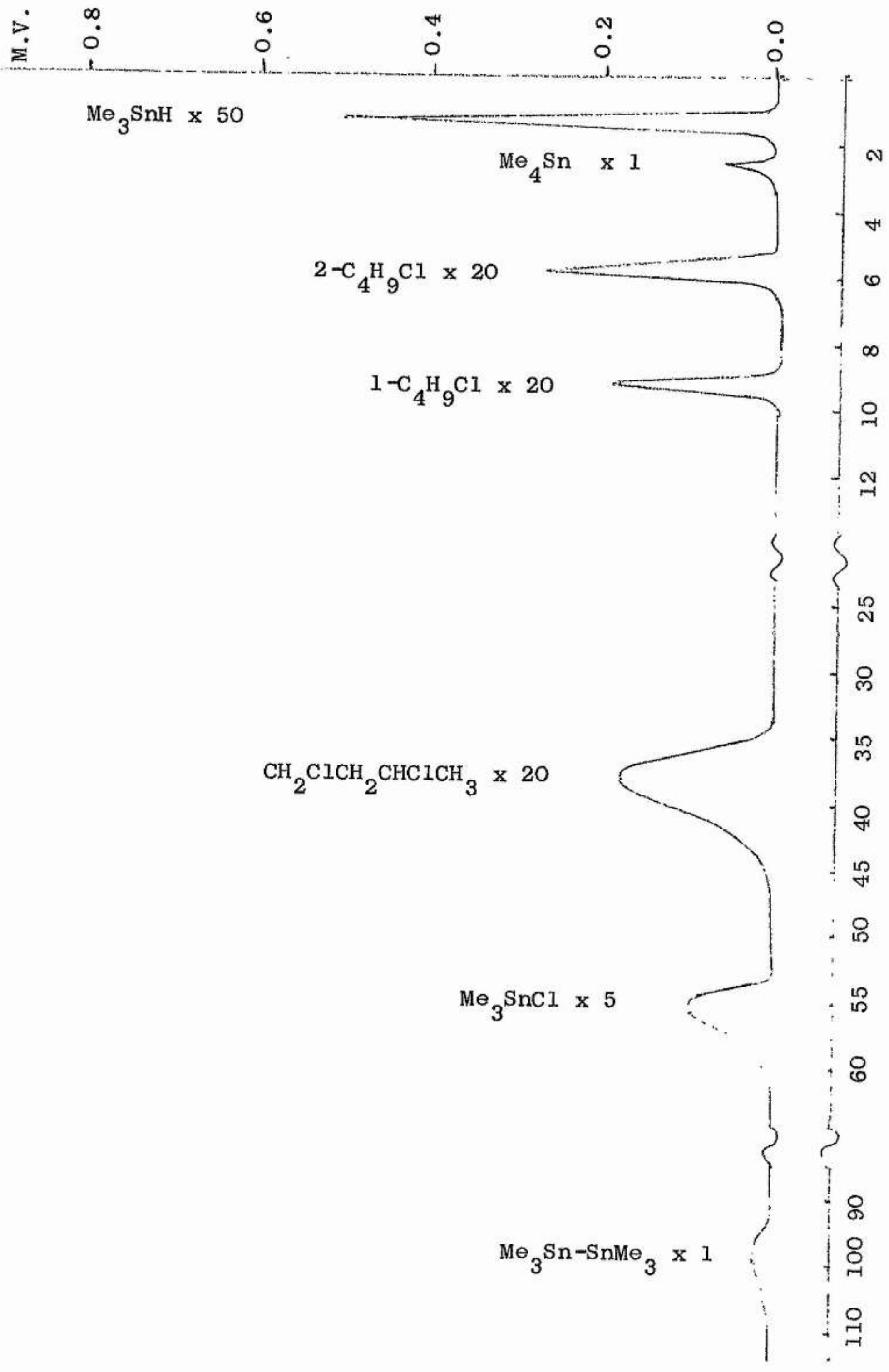

(a) $Me_3SnH + CH_2ClCH_2CHClCH_3$

(b) $Me_3GeH + CH_2ClCH_2CHClCH_3$