Free Radical Substitution in Aliphatic Compounds. Part 33.[1] Halogen Atom Abstraction from Alkyl Halides by Trimethylgermanium Radicals in the Gas Phase

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Mixtures of trimethylgermanium hydride and halogenoalkanes have been irradiated by a medium pressure mercury lamp. A rapid reaction has been observed in which a halogen atom on the original halogenoalkane is displaced by a hydrogen atom and trimethylgermanium halide is formed. The reaction is exactly similar to that previously reported for trimethyltin hydride, and is interpreted as a radical chain reaction. The reactivity of different sites in monosubstituted alkanes is in the order tertiary > secondary > primary but trimethylgermanium radicals are *less* selective than trimethyltin radicals. However, in chlorine abstraction from a range of compounds with the general formula $RCCl_3$, trimethylgermanium radicals are considerably *more* selective. These apparently conflicting results are interpreted in terms of polar forces in the transition state.

IN a previous paper[2] we reported the reaction of trimethyltin hydride with halogenoalkanes in the gas phase and the present paper describes a direct continuation of that work in which trimethylgermanium hydride replaced the tin hydride.

EXPERIMENTAL

Trimethylgermanium Hydride.—A solution of trimethylgermanium bromide (Aldrich Chemicals) (20 g) in dibutyl ether (100 cm^3) was added to a suspension of lithium aluminium hydride (3.2 g) in the same solvent (200 cm^3). The combined solution was stirred at 75° and the trimethylgermanium hydride (9.1 g, 75%) distilled over directly (b.p. 26°) and was used without further purification.

Procedure.—The experimental procedure was exactly the same as that described in the earlier work.[2] The main studies involved the photolysis of trimethylgermanium hydride in the presence of two different halogenoalkanes (or with a single polyhalogenoalkane with different halogen sites). The reactions were carried out to $<10\%$ conversion and the products were analysed by g.l.c. using a James and Martin density balance as detector. The products were identified as before.[2]

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 trimethylgermanium hydride and 1,3-dichlorobutane with varying light intensity. Three analytical runs were completed for each light intensity. The quantity $2 + \log_{10}[(1\text{-}C_4H_9Cl + 2\text{-}C_4H_9Cl)/CH_2ClCH_2CHClCH_3]$ was plotted against $\log_{10}$ (percentage transmission) and gave a straight line. The 'least squares' method gave a value of 0.58 ± 0.04 for the slope.

TABLE 1

Transmission (%)	T/°C	t/s	Conversion (%) $\frac{1\text{-}C_4H_9Cl + 2\text{-}C_4H_9Cl}{CH_2ClCH_2CHClCH_3} \times 100$
100	100 ± 2	3 600	3.56 ± 0.01
61	100 ± 2	3 600	1.06 ± 0.03
46	100 ± 2	3 600	0.81 ± 0.08
33	100 ± 2	3 600	0.72 ± 0.05
25	100 ± 2	3 600	0.64 ± 0.01

Effect of Concentration Variation upon the Reaction of Trimethylgermanium Hydride, with 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 $2\text{-}C_6H_{13}Cl : CH_2ClCH_2CH_2CH_2Cl$ constant. The reaction was taken to $<5\%$ conversion.

TABLE 2

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

Investigation of Hydride Transfer.—Trimethylgermanium hydride (7.76×10^{-4} mol) and deuteriochloroform (3.32×10^{-4} mol) were irradiated for 1 h and then the products were analysed by g.l.c.–mass spectrometry. No products of the type Me_3GeD or CD_2Cl_2 could be found.

TABLE 3

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with 1,3-dichlorobutane (3.32×10^{-4} mol). Photolysis for 10 min

No. of runs	T/°C	Product ratio $[1\text{-}C_4H_9Cl]/[2\text{-}C_4H_9Cl]$
3	150 ± 1	0.41 ± 0.01
4	145 ± 1	0.43 ± 0.01
3	135 ± 1	0.37 ± 0.01
3	102 ± 1	0.44 ± 0.01
3	93 ± 1	0.40 ± 0.01
3	72 ± 1	0.35 ± 0.01
5	70 ± 1	0.40 ± 0.01
5	50 ± 1	0.32 ± 0.01
3	44 ± 1	0.33 ± 0.01

TABLE 4

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with carbon tetrachloride (3.32×10^{-4} mol) and chlorocyclohexane (3.32×10^{-4} mol). Photolysis for 30 min

No. of runs	T/°C	Product ratio $[CHCl_3]/[cyclo\text{-}C_6H_{12}]$
3	151 ± 1	18.22 ± 0.22
4	112 ± 1	21.17 ± 0.13
4	66 ± 1	30.67 ± 0.17
3	51 ± 1	96.30 ± 0.42

Thermal Reaction.—Trimethylgermanium hydride (7.76×10^{-4} mol) and 1,3-dichlorobutane (3.32×10^{-4} mol) were heated at 106 ± 2 and 168 ± 2 °C for 60 min and then

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[1] Part 32, D. G. Sanders, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1978, 580.

[2] D. A. Coates and J. M. Tedder, *J.C.S. Perkin II*, 1973, 1570.

analysed for products. No detectable products were obtained and the ratio of reactants before and after heating remained constant.

TABLE 5

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with 1,3-dichloro-3-methylbutane (3.32×10^{-4} mol) and chlorocyclohexane (3.32×10^{-4} mol). Photolysis for 30 min

No. of runs	T/°C	Product ratios $[CH_2ClCH_2CH(CH_3)_2]$/$[cyclo\text{-}C_6H_{12}]$	$[CH_3CCl(CH_3)CH_2CH_3]$/$[cyclo\text{-}C_6H_{12}]$
3	140 ± 2	14.16 ± 1.01	2.81 ± 0.05
3	101 ± 2	17.25 ± 0.16	3.53 ± 0.20
3	86 ± 2	16.87 ± 0.03	3.88 ± 0.06
3	52 ± 2	29.01 ± 0.04	8.17 ± 0.06

TABLE 6

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with 1,4-dichlorobutane (3.32×10^{-4} mol) and 2-chlorohexane (3.32×10^{-4} mol). Photolysis for 20 min

No of runs	T/°C	Product ratio $[n\text{-}C_6H_{14}]/[1\text{-}C_4H_9Cl]$
3	150 ± 2	1.54 ± 0.01
3	130 ± 2	1.29 ± 0.01
3	110 ± 2	1.22 ± 0.01
3	106 ± 2	1.24 ± 0.06
3	80 ± 2	1.10 ± 0.02
3	76 ± 2	1.14 ± 0.01
3	67 ± 2	1.21 ± 0.01
3	60 ± 2	1.26 ± 0.01
3	50 ± 2	1.55 ± 0.03
3	49 ± 2	1.62 ± 0.01

TABLE 7

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with 1,4-dichlorobutane (3.32×10^{-4} mol) and chlorocyclohexane (3.32×10^{-4} mol). Photolysis for 30 min

No. of runs	T/°C	Product ratio $[1\text{-}C_4H_9Cl]/[cyclo\text{-}C_6H_{12}]$
3	150 ± 2	1.25 ± 0.03
3	131 ± 2	1.24 ± 0.04
3	118 ± 2	1.55 ± 0.04
3	92 ± 2	2.17 ± 0.03
3	82 ± 2	1.97 ± 0.02
3	72 ± 2	1.50 ± 0.01

TABLE 8

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with chloroform (3.32×10^{-4} mol) and 1,1,1-trichloroethane (3.32×10^{-4} mol). Photolysis for 30 min

No. of runs	T/°C	Product ratio $[CH_3CHCl_2]/[CH_2Cl_2]$
4	180 ± 3	3.19 ± 0.01
4	126 ± 2	2.89 ± 0.02
3	100 ± 1	3.59 ± 0.05
5	80 ± 1	3.03 ± 0.02
4	48 ± 1	2.54 ± 0.01

TABLE 9

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with chloroform (3.32×10^{-4} mol) and 1,1,1,2-tetrachloroethane (3.31×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratio $[CH_2ClCHCl_2]/[CH_2Cl_2]$
4	168 ± 2	5.13 ± 0.01
4	118 ± 2	9.28 ± 0.01
4	98 ± 1	11.46 ± 0.01
4	68 ± 1	12.97 ± 0.01

TABLE 10

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with chloroform (3.32×10^{-4} mol) and 1,1,1-trichlorotrifluoroethane (3.32×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratio $[CF_3CHCl_2]/[CH_2Cl_2]$
4	163 ± 1	14.72 ± 0.01
4	145 ± 1	19.69 ± 0.10
4	130 ± 1	21.89 ± 0.01
3	110 ± 1	30.43 ± 0.20
4	85 ± 1	38.99 ± 0.11

A plot of $\log_{10}[CF_3CHCl_2]/[CH_2Cl_2]$ *versus* $10^3/T$ gave a line of gradient $E_{CF_3CHCl_2} - E_{CH_2Cl_2} = 3.83 \pm 0.4$ and intercept $\log_{10}A_{CF_3CHCl_2} - \log_{10}A_{CH_2Cl_2} = -0.73 \pm 0.04$.

TABLE 11

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with chloroform (3.32×10^{-4} mol) and 1,1,1,3-tetrachloropropane (3.32×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratios $[CHCl_2CH_2CH_2Cl]$/$[CH_2Cl_2]$	$[CH_3CH_2CCl_3]$/$[CH_2Cl_2]$
3	193 ± 2	6.08 ± 0.01	0.66 ± 0.01
3	159 ± 2	10.12 ± 0.01	1.36 ± 0.01
3	125 ± 2	14.66 ± 0.01	4.04 ± 0.01
4	110 ± 2	22.89 ± 0.01	8.02 ± 0.01
3	95 ± 2	37.22 ± 0.03	46.27 ± 0.01

A plot of $\log_{10}[CHCl_2CH_2CH_2Cl]/[CH_2Cl_2]$ *versus* $10^3/T$ gave a line of gradient $E_{CHCl_2CH_2CH_2Cl} - E_{CH_2Cl_2} = 6.01 \pm 0.50$ and intercept $\log_{10}A_{CHCl_2CH_2CH_2Cl} - \log_{10}A_{CH_2Cl_2} = -2.08 \pm 0.06$.

TABLE 12

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with pentachloroethane (3.32×10^{-4} mol) and 1,1,1-trichloroethane (3.32×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratio $[CHCl_2CHCl_2]/[CH_3CHCl_2]$
3	154 ± 2	253.0 ± 4.9
3	144 ± 2	222.0 ± 4.7
3	137 ± 2	198.0 ± 3.3
3	128 ± 3	126.0 ± 3.1

TABLE 13

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with 1,1,1-trichloroethane (3.32×10^{-4} mol) and fluorotrichloromethane (3.32×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratio $[CHCl_2F]/[CH_3CHCl_2]$
4	181 ± 1	1.63 ± 0.01
4	154 ± 1	1.88 ± 0.01
4	133 ± 1	2.11 ± 0.01
4	99 ± 1	2.35 ± 0.01

TABLE 14

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with carbon tetrachloride (3.32×10^{-4} mol) and 1,1,1-trichlorotrifluoroethane (3.32×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratio $[CHCl_3]/[CF_3CHCl_2]$
3	180 ± 2	1.42 ± 0.02
3	153 ± 2	1.67 ± 0.01
3	122 ± 2	2.05 ± 0.01
3	110 ± 1	1.80 ± 0.02
3	102 ± 1	1.45 ± 0.02

TABLE 15

Reaction of trimethylgermanium hydride (7.76×10^{-4} mol) with chloroform (3.32×10^{-4} mol) and 2,2-dichloropropane (3.32×10^{-4} mol). Photolysis for 5 min

No. of runs	T/°C	Product ratio $[CH_2Cl_2]/[CH_3CHClCH_3]$
3	201 ± 2	7.79 ± 0.01
3	148 ± 1	4.75 ± 0.02
3	129 ± 1	4.19 ± 0.02
3	124 ± 1	3.95 ± 0.01
3	115 ± 1	3.36 ± 0.02
3	102 ± 1	2.70 ± 0.02

DISCUSSION

As in the previous study with trimethyltin hydride the exact initiation process remains uncertain, the most probable being either photolysis of the trimethylgermanium hydride [reaction (1)] or photolysis of the alkyl halide [reaction (2)]. In either case the radicals pro-

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

$$RCl \xrightarrow[?]{h\nu} R\cdot + Cl\cdot \qquad (2)$$

duced will abstract hydrogen from the trimethylgermanium hydride [reaction (3)]. The trimethylgermanium radical then abstracts a halogen atom from the halogenoalkane, so that a chain reaction is set up. The

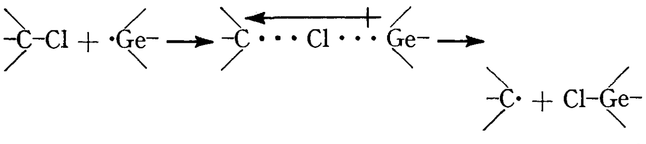
$$(CH_3)_3GeH + R\cdot\ [\text{or } CH_3\cdot] \longrightarrow (CH_3)_3Ge\cdot + RH\ [\text{or } CH_4] \qquad (3)$$

$$(CH_3)_3Ge\cdot + RCl \longrightarrow (CH_3)_3GeCl + R\cdot \qquad (4)$$

$$R\cdot + (CH_3)_3GeH \longrightarrow RH + (CH_3)_3Ge\cdot \qquad (5)$$

termination process is uncertain but the half-power light dependence of the reaction and the isolation of hexamethyldigermanium suggests that combination of two trimethylgermanium radicals is an important process. Considerable effort was devoted to a search for cross combination products [$(CH_3)_3GeR$] without success.

Abstraction of chlorine atoms by trimethylgermanium radicals from alkyl chlorides is likely to be a thermoneutral or slightly exothermic processes. The second chain propagating step (hydrogen abstraction from trimethylgermanium hydride) is very exothermic and the experimental observation is that the chains are very long. Finally germanium is almost as electropositive (relative to carbon) as tin, so that if there is a polar effect, we would expect it to be apparent with trimethylgermanium as it was with trimethyltin radicals.



Trimethylgermanium hydride has been photolysed with 1,3-dichlorobutane and with mixtures of (a) 1,3-dichloro-3-methylbutane and chlorocyclohexane, (b) 1,4-dichlorobutane and 2-chlorohexane, and (c) 1,4-dichlorobutane and chlorocyclohexane. The results are summarised in Table 16. As in the previous experiments with trimethyltin radicals there is considerable scatter in the results (see Experimental section).

TABLE 16

Relative selectivities of $(CH_3)_3Ge\cdot$ and $(CH_3)_3Sn\cdot$ radicals in the gas phase at 100°

$$(CH_3)_3M\cdot + RCl \longrightarrow (CH_3)_3MCl + R\cdot$$

Primary, secondary, or tertiary position	$(CH_3)_3Ge\cdot$	$(CH_3)_3Sn\cdot$
RCH_2Cl	1	1
R_2CHCl	2.5	3.6
R_3CCl	4.0	8.8
cyclo-$C_6H_{11}Cl$	0.3	2.8

Quite contrary to our expectation trimethylgermanium radicals proved *less* selective than trimethyltin, and initially we were at a loss to explain these results. In the previous paper [2] we commented that the observed ease of chlorine abstraction by tin radicals (tertiary > secondary > primary) showed that this well established sequence for hydrogen abstraction must principally be due to changes in the strength of the bond being broken and not to a polar effect as had earlier been suggested by Ash and Brown [3] on the basis of chlorination studies. If polarity was important then selectivity of chlorine atom abstraction by trimethyltin radicals would occur in the reverse order. The present results show that although bond strength is the governing factor the polar effect invoked by Ash and Brown for hydrogen abstraction does affect chlorine abstraction by trimethylgermanium radicals. In other words chlorine abstraction by trimethylgermanium radicals is more affected by polar forces than the similar reaction involving trimethyltin radicals. Examination of the variation of product ratios in this paper with those reported previously for trimethyltin radicals [2] shows a considerably larger temperature coefficient for trimethylgermanium radicals. In other words the difference in activation energies for attack at different sites is greater for trimethylgermanium radicals.

There remains a further puzzling feature of Table 16 and that is the reactivity of the chlorine atom in chlorocyclohexane. It appears that the pre-exponential term for hydrogen abstraction from cyclohexane (by $Br\cdot$,[4] $CF_3\cdot$,[5] and $CH_3\cdot$ [5]) is appreciably greater than that for the secondary positions in n-butane and the activation energy is also greater. The high pre-exponential term is probably associated with the change from a rigid cyclohexane ring to a comparatively ' floppy ' cyclohexyl radical; no similar change occurs with the other rings (however see ref. 6). Chlorine abstraction by the bulky trimethyltin radicals appears to be substantially influenced by the pre-exponential term, while chlorine abstraction by trimethylgermanium radicals is, as we

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[3] A. B. Ash and H. C. Brown, *Records Chem. Progr.*, 1948, **9**, 81.

[4] K. C. Ferguson and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2618.

[5] S. H. Jones and E. Whittle, *Internat. J. Chem. Kinetics*, 1970, **2**, 479.

[6] D. A. Whytock, J. D. Clarke, and P. Gray, *J.C.S. Faraday I*, 1974, **411**.

have seen, more affected by changes in activation energy. The combined result is that chlorine abstraction from chlorocyclohexane by trimethyltin radicals is almost as fast as from the secondary position in 1,3-dichloro*butane*, while the chlorine abstraction by trimethylgermanium radicals occurs much faster from the secondary position in 1,3-dichlorobutane than from chlorocyclohexane.

Table 17 shows the relative rates of chlorine abstraction from the trichloromethyl group for a range of compounds of the type $RCCl_3$, by both trimethylgermanium and trimethyltin radicals (the values are calculated from the Arrhenius equation where possible, otherwise they represent average values). We see at once that in abstracting chlorine atoms from this series of compounds trimethylgermanium radicals are very much more selective and the expected polar effect is very manifest. The increase in reactivity in going from chloroform to carbon tetrachloride can be accounted for on both a polar and [depending on $D(Me_3Ge{-}Cl)$] a bond strength argument, but the high rate of attack on trichlorofluoromethane relative to chloroform can only be accounted for on polar grounds. If we compare hydrogen abstraction by bromine atoms from analogous sites at 100° we obtain the pattern (in Table 18). The contrast in the relative reactivity of $CFCl_2H$ and $CFCl_3$ to bromine atoms and trimethylgermanium radicals respectively is very striking.

TABLE 17

Relative rates of chlorine atom abstraction from substituted chloroforms [$R{-}CCl_3$] by trimethylgermanium and trimethyltin radicals at 100°

$R{-}CCl_3$	$(CH_3)_3Ge\cdot$	$(CH_3)_3Sn\cdot$[2]
$H{-}CCl_3$	1	1
$F{-}CCl_3$	9.1	1.5
$Cl{-}CCl_3$	41.6	2.8
$CH_3{-}CCl_3$	3.6	1.5
$ClCH_2{-}CCl_3$	10.0	2.0
$Cl_2CH{-}CCl_3$	26.9	4.7
$CF_3{-}CCl_3$	33.1	3.7
$ClCH_2CH_2{-}CCl_3$	26.9	3.3

TABLE 18

Relative rates of hydrogen abstraction by bromine atoms [7] and chlorine atoms by trimethylgermanium radicals from similar sites at 100°

	$X{-}CCl_2{-}H + Br\cdot$	$X{-}CCl_2{-}Cl + Me_3Ge\cdot$
X = H	1	1
X = Cl	2.4	41.6
X = F	0.04	9.1

The importance of the ' reverse ' polar effect can also be seen in the results with 1,1,1-trichloroethane and 1,1,1-trichlorotrifluoroethane. Chlorine abstraction by trimethylgermanium radicals from trichlorotrifluoroethane is 30 times faster than abstraction from trichloroethane. In comparison chlorine abstraction by trifluoromethyl radicals is three times slower from trichlorotrifluoroethane than from trichloroethane.[8]

In the previous studies with trimethyltin radicals evidence for a ' reverse ' polar effect was good but the trimethyltin radicals were very unselective. The present results with trimethylgermanium radicals show much greater evidence for the ' reverse ' polar effect and, although the scatter in the results make calculation of Arrhenius parameters have little meaning, the temperature coefficients are greater than with the analogous trimethyltin experiments, showing that the effect is manifest in the activation energy.

Unfortunately there is very little agreement in the literature about the metal–halogen bond dissociation energies of the trimethyltin and trimethylgermanium halides. In a review article Jackson constructed a table of bond strengths which could be used to rationalise the results in the present paper.[9] However more recent work throws doubt on some of these figures, especially Jackson's values for $D[(CH_3)_3Ge{-}Cl]$ and $D[(CH_3)_3Sn{-}Cl]$.[10] Until accurate values of these two particular bond dissociation energies are available it is impossible to rationalise the present results completely. The principle experimental observations are that abstraction of halogen atoms from alkyl halides by both trimethyltin and trimethylgermanium radicals shows good evidence of the ' reverse polar effect ' predicted by current qualitative theories of radical transfer reactions [11] The experimental results also show that trimethylgermanium radicals are affected by polarity much more strongly than trimethyltin radicals. This second observation must wait on better data for both bond strengths and relative electronegativity before it can be completely understood.

[7/1611 *Received*, 9*th September*, 1977]

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[7] D. E. Copp and J. M. Tedder, *Internat. J. Chem. Kinetics*, 1972, **4**, 69.

[8] L. M. Quick and E. Whittle, *J.C.S. Faraday I*, 1972, 878.

[9] R. A. Jackson, *Adv. Free Radical Chem.*, 1969, **3**, 231.

[10] J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. S. Poland, *J.C.S. Dalton*, 1972, 1943.

[11] J. M. Tedder, *Quart. Rev.*, 1960, **14**, 336.