Trichloromethylsilane Derivatives as Dichloromethylene Transfer Agents; Kinetic Evidence for Free Dichlorocarbene

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The trichloromethylsilane derivatives $CCl_3{\cdot}SiXYZ$ (I; X = Y = Z = Cl; II; X = Y = Cl, Z = OEt; III; X = Cl, Y = Z = OEt; IV; X = Y = Z = OEt; V; X = Y = Cl, Z = Me; VI; X = Y = Cl, Z = CCl_3) give good yields of 1,1-dichloro-2-n-alkylcyclopropane when heated (*ca.* 175—240 °C) with dodec-1-ene and hexadec-1-ene. Insertion of the dichloromethylene group into the tertiary carbon–hydrogen bond of *p*-cymene occurs when (I) or (IV) is heated (*ca.* 175 °C) with *p*-cymene. Kinetic evidence is presented for the intermediacy of free dichlorocarbene in the dichloromethylene transfer reactions of (I) and (IV). The activation energies for the reactions of compounds (I), (IV), and trichloromethyltrifluorosilane with olefins are compared.

TRICHLOROMETHYLTRICHLOROSILANE [1] and trichloromethyltrifluorosilane [2] have been shown to decompose, in the gas phase, at 250 and 140 °C respectively, with the transfer of a dichloromethylene group to olefins.

Trichloromethyltrifluorosilane, owing to its volatility (b.p. 40 °C) and its convenient decomposition temperature, has been found useful in the synthesis of cyclopropanes from volatile olefins.[3] Trichloromethyltrichlorosilane, which is less volatile (b.p. 156 °C) and has a higher decomposition temperature, has not been reported as being used in synthetic organic chemistry. However, there is evidence in the literature that trichloromethyltrichlorosilane decomposes at a lower temperature than originally reported; after heating for 12 h at 160—175 °C under reflux, silicon tetrachloride (90%) and tetrachloroethylene (13%) were obtained.[4] This result suggests that trichloromethyltrichlorosilane might be a good liquid-phase dichloromethylene transfer agent for substrates with suitably high boiling points. It also seemed possible that other trichloromethylsilane derivatives might be useful dichloromethylene transfer agents.

Although the dichloromethylene transfer reactions of trichloromethyltrichlorosilane and trichloromethyltrifluorosilane were originally interpreted as involving dichlorocarbene,[1,2] the evidence so far available does not rule out an alternative bimolecular reaction (later referred to as Mechanism 2) for the dichloromethylene transfer reactions of trichloromethylsilane derivatives.

We now report the preparative utility of several trichloromethylsilane derivatives as dichloromethylene transfer agents, and a kinetic study of the reaction mechanism.

Preparation of Trichloromethylsilane Derivatives.—Trichloromethyltrichlorosilane is conveniently prepared in large quantities by the chlorination of methyltrichlorosilane.[5] Trichloromethyltriethoxysilane is reported to be formed by the reaction of trichloromethyltrichlorosilane with anhydrous ethanol [6] but it was found more convenient to treat trichloromethyltrichlorosilane with ethyl orthoformate, a reagent which has the advantage over ethanol that the conversion $\equiv Si{-}Cl \longrightarrow \equiv Si{-}OEt$ is not accompanied by the formation of siloxanes.[7] Using this reagent we were able,

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[1] W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1966, **80**, 789.

[2] W. I. Bevan, J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, 'Organic Reaction Mechanisms,' *Chem. Soc. Special Publ.*, 1964, No. 19, p. 174.

[3] J. M. Birchall, R. N. Haszeldine, and D. W. Roberts, *Chem. Comm.*, 1967, 287; *J.C.S. Perkin I*, in the press; R. N. Haszeldine, J. M. Birchall, R. A. Burton, S. G. Farrow, R. Fields, G. N. Gilmore, D. W. Roberts, J. G. Speight, and P. Tissington, 4th International Fluorine Symposium, Estes Park, Colorado, July 1967.

[4] G. V. Motsarev and V. R. Rozenberg, *Zhur. priklad. Khim.*, 1964, **37**, 747.

[5] F. Runge and W. Zimmerman, *Chem. Ber.*, 1954, **87**, 282.

[6] G. V. Motsarev, V. R. Rozenberg, and T. Ya. Chashrikova, *Zhur. priklad. Khim.*, 1961, **34**, 430.

[7] L. M. Shorr, *J. Amer. Chem. Soc.*, 1954, **76**, 1390.

by varying the reaction time and the relative proportions of the starting materials, to obtain any of the three possible ethoxylation products in good yield, as shown in Table 1. The compounds $CCl_3{\cdot}Si(OEt)_nCl_{3-n}$ are readily characterised by their mass spectra, which show the ion $[Si(OEt)_nCl_{3-n}]$ as the base peak.

TABLE 1

Reactions of trichloromethyltrichlorosilane with ethyl orthoformate in refluxing benzene

Mole ratio $CCl_3{\cdot}SiCl_3$ to $CH(OEt)_3$	Reaction time/h	Product	Yield/%
1 : 1	6	$CCl_3{\cdot}Si(OEt)Cl_2$	80
1 : 3	2	$CCl_3{\cdot}Si(OEt)_2Cl$	87
1 : 7	24	$CCl_3{\cdot}Si(OEt)_3$	71

TABLE 2

Dichloromethylene transfer reactions of trichloromethylsilane derivatives

	Substrate (mole ratio substrate to silane)	T/°C	Reaction time	Product	Yield/%
$CCl_3{\cdot}SiCl_3$	Docec-1-ene (6 : 1)	210	10 min	n-$C_{10}H_{21}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	79 [a]
	p-Cymene (6 : 1)	173	9 h	*p*-$MeC_6H_4{\cdot}CMe_2{\cdot}CCl_2H$	42 [a]
$CCl_3{\cdot}Si(OEt)Cl_2$	Dodec-1-ene (5 : 1)	176·5	7 h	n-$C_{10}H_{21}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	81 [b]
$CCl_3{\cdot}Si(OEt)_2Cl$	Dodec-1-ene (5 : 1)	176·5	75 h	n-$C_{10}H_{21}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	41 [b]
$CCl_3{\cdot}Si(OEt)_3$	Hexadec-1-ene (5 : 1)	238	75 min	n-$C_{14}H_{29}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	73 [c]
	p-Cymene (12 : 1)	176·5	144 h	*p*-$MeC_6H_4{\cdot}CMe_2{\cdot}CCl_2H$	29 [d]
$(CCl_3)_2SiCl_2$	Hexadec-1-ene (12 : 1)	220	1 h	*n*-$C_{14}H_{29}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	70 [e,f]
$CCl_3{\cdot}SiMeCl_2$	Dodec-1-ene (2 : 1)	190—210	6 h	n-$C_{10}H_{21}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	60 [e]

[a] Yield of isolated product. [b] Incomplete reaction. Yield estimated by g.l.c. and based on initial amount of starting material. [c] Yield estimated by g.l.c. [d] 74% Reaction. Yield estimated by g.l.c. and based on amount of starting material consumed. [e] Purity of silanes not known. Yields of isolated products calculated on the assumption that the silanes were pure. [f] Yield calculated on the basis that two dichloromethylene groups are transferred by each molecule of $(CCl_3)_2SiCl_2$.

Trichloromethyltrichlorosilane derivatives were also prepared from dichlorodimethylsilane, chlorination of which can be controlled to give mainly bistrichloromethyldichlorosilane or mainly methyltrichloromethyldichlorosilane.[6]

Dichloromethylene Transfer Reactions of Trichloromethylsilane Derivatives.—The trichloromethylsilane derivatives described above all gave 1,1-dichlorocyclopropanes when heated with olefins, and are thus similar to the phenyl(halogenodichloromethyl)mercury compounds[8] in that both types of compound behave as dichloromethylene transfer agents under neutral conditions.

Phenyl(bromodichloromethyl)mercury gives the dichloromethylene insertion product 1,1-dichloro-2-methyl-2-phenylpropane when heated with cumene[9] and it was therefore of interest to determine whether the trichloromethylsilane derivatives behave similarly. To this end, trichloromethyltrichlorosilane and trichloromethyltriethoxysilane were heated with *p*-cymene.* In both cases, the insertion product 1,1-dichloro-2-methyl-2-(*p*-tolyl)propane was obtained. The alternative insertion product, 1,1-dichloro-2-(*p*-cumyl)ethane was not detected. The isolated yield (42%) of insertion product from trichloromethyltrichlorosilane was strikingly similar to that reported (46%) from cumene and phenyl(bromodichloromethyl)mercury.

Reaction conditions and yields for the dichloromethylene transfer reactions of the trichloromethylsilane derivatives are shown in Table 2.

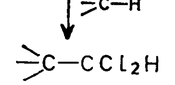
The reactivity of the trichloromethylsilanes depends upon the substituents on silicon. Thus in the series $CCl_3{\cdot}Si(OEt)_nCl_{3-n}$, the reactivity increases with increasing chlorine substitution, as shown by a comparison of first-order rate constants at 176·5 °C (Table 3).

TABLE 3

First-order rate constants for the reactions of trichloromethylsilanes with dodec-1-ene (5 molar excess) at 176·5 °C

Silane	10^6k/s^{-1} with 95% confidence limits
$CCl_3{\cdot}SiCl_3$	118 ± 6
$CCl_3{\cdot}Si(OEt)Cl_2$	72·6 ± 1·6
$CCl_3{\cdot}Si(OEt)_2Cl$	20·2 ± 1·2
$CCl_3{\cdot}Si(OEt)_3$	2·83 ± 0·11

The Mechanism of the Dichloromethylene Transfer Reactions.—The reactions of the trichloromethylsilane derivatives with olefins and with *p*-cymene are readily interpreted either as involving dichlorocarbene (Mech-



MECHANISM 1

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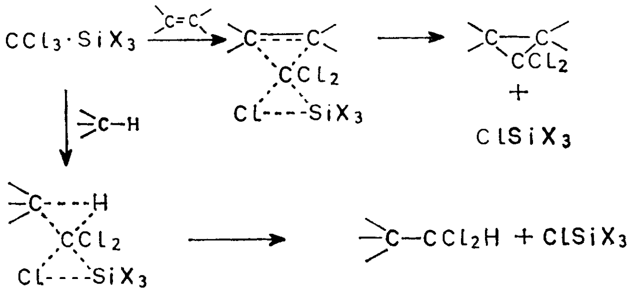
* *p*-Cymene (b. p. 176 °C) was used in preference to cumene (b. p. 156 °C) because its b.p. is closer to the temperature required to give reaction at a reasonable rate.

[8] D. Seyferth, R. J. Minasz, A. J. H. Treiber, J. M. Burlitch, and S. R. Dowd, *J. Amer. Chem. Soc.*, 1965, **87**, 4259.

[9] D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, 1962, **35**, 1989.

anism 1) or in terms of a bimolecular dichloromethylene transfer process (Mechanism 2).



MECHANISM 2

These mechanisms should be distinguishable by kinetic methods. Mechanism 1 may be expressed by reaction (1) where k_1 is the slowest step. Steady-state treatment, assuming no side reactions, gives the expression (2). Kinetics of this form have been observed for

$$\mathrm{CCl_3{\cdot}SiX_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ClSiX_3} + \mathrm{:CCl_2} \xrightarrow[k_2]{\text{Substrate}} \text{Product} \qquad (1)$$

$$\frac{-\mathrm{d}[\mathrm{CCl_3{\cdot}SiX_3}]}{\mathrm{d}t} = \frac{\mathrm{d}[\text{Product}]}{\mathrm{d}t} = \frac{k_1[\mathrm{CCl_3{\cdot}SiX_3}]}{1 + \dfrac{k_{-1}[\mathrm{ClSiX_3}]}{k_2[\text{Substrate}]}} \qquad (2)$$

reactions of phenyl(bromodichloromethyl)mercury with olefins, with the mercurial in excess over olefin.[10] However, if the substrate is in excess over $\mathrm{CCl_3{\cdot}SiX_3}$, and if the volatile $\mathrm{ClSiX_3}$ is distilled out as the reaction proceeds, the rate equation should simplify to the first-order expression (3) * for which the value of the rate

$$-\mathrm{d}[\mathrm{CCl_3{\cdot}SiX_3}]/\mathrm{d}t = k_1[\mathrm{CCl_3{\cdot}SiX_3}] \qquad (3)$$

constant should be independent of the nature and the concentration of the substrate, apart from change of medium effects.

For Mechanism 2, reactions should be of the first order in $\mathrm{CCl_3{\cdot}SiX_3}$ and of the first order in substrate, *i.e.*, of the second order overall. Although the use of excess of substrate would lead to pseudo-first-order kinetics, the value of the observed rate constant should depend on the nature and the concentration of the substrate.

Kinetics.—Kinetic runs were carried out over a range of temperatures for reactions of trichloromethyltrichlorosilane and trichloromethyltriethoxysilane with excess of olefin, and also for reactions of these silanes with *p*-cymene at reflux temperature. The reactions with olefin were followed by the appearance of the 1,1-dichlorocyclopropane (CP). In a run with trichloromethyltrichlorosilane and olefin at 190 °C, which was followed to completion, a quantitative yield was observed, so the inital quantity of trichloromethylsilane (Sil) derivative was taken as the $[\mathrm{CP}]_\infty$ value for all runs. The reactions with *p*-cymene were followed by the appearance of the insertion product (IP) and also, in the case of trichloromethyltriethoxysilane, by the disappearance of starting material. Plots of log $([\mathrm{Sil}]_0 - [\mathrm{CP}]_t)$, $\log([\mathrm{IP}]_\infty - [\mathrm{IP}]_t)$†, and log $[\mathrm{Sil}]_t$† against time were substantially linear. The observed rate constants are shown in Tables 4 and 5.

TABLE 4

Rate constants for reactions of $\mathrm{CCl_3{\cdot}SiCl_3}$

Run	T/°C ±0·5 °C	Substrate (mole ratio substrate to $\mathrm{CCl_3{\cdot}SiCl_3}$)	$10^6 k_{\mathrm{obs}}$ [a]/$\mathrm{s^{-1}}$ with 95% confidence limits	Extent of reaction followed/%
1	190	Dodec-1-ene (5 : 1)	499 ± 58	100
2	176·5	Dodec-1-ene (5 : 1)	118 ± 8	86
3	176·5	Dodec-1-ene (2·36 : 1) [b]	131 ± 17	57
4	155·8	Dodec-1-ene (5 : 1)	14·8 ± 1·3	26
5	145·5	Dodec-1-ene (5 : 1)	5·60 ± 0·64	15
6	140	Dodec-1-ene (5 : 1)	2·61 ± 0·33	15
7	171 (±1·0)	*p*-Cymene (12 : 1)	75·2 ± 7·2	100
7′	171	Dodec-1-ene [c]	74·1	

[a] From plots of log $([\mathrm{Sil}]_0 - [\mathrm{CP}]_t)$ against t (runs 1—6) or log $([\mathrm{IP}]_\infty - [\mathrm{IP}]_t)$ against t (run 7), where [Sil] = number of mmoles of trichloromethylsilane derivative, [CP] = number of mmoles of cyclopropane derivative, and [IP] = number of mmoles of insertion product $p\text{-}\mathrm{Me{\cdot}C_6H_4{\cdot}CMe_2{\cdot}CCl_2H}$. [b] n-Hexadecane was added to adjust the initial concentration of $\mathrm{CCl_3{\cdot}SiCl_3}$ to the same value as in the other runs with dodec-1-ene. [c] Rate constant calculated from an Arrhenius plot for runs 1—6.

TABLE 5

Rate constants for reactions of $\mathrm{CCl_3{\cdot}Si(OEt)_3}$

Run	T/°C ±0·5 °C	Substrate [mole ratio substrate to $\mathrm{CCl_3{\cdot}Si(OEt)_3}$]	$10^6 k_{\mathrm{obs}}/\mathrm{s^{-1}}$ with 95% confidence limits	Extent of reaction followed/ %
8	222	Hexadec-1-ene [5 : 1]	134 ± 8	45
9	209	Hexadec-1-ene [5 : 1]	45·0 ± 3·4	63
10	209	Dodec-1-ene [5 : 1]	45·4 ± 3·0	50
11	190	Dodec-1-ene [5 : 1]	9·19 ± 0·30	18
12	176·5	Dodec-1-ene [5 : 1]	2·83 ± 0·11	22
13	176·5	*p*-Cymene [12 : 1]	2·47 ± 0·26 [a] 2·43 ± 0·31 [b]	73 *ca.* 75

[a] From plot of log $[\mathrm{Sil}]_t$ against t. [b] From plot of log $([\mathrm{IP}]_\infty - [\mathrm{IP}]_t)$ against t.

The results show that the rate constant is unaffected by a change in initial substrate concentration (Runs 2 and 3 for $\mathrm{CCl_3{\cdot}SiCl_3}$) or by a change in the nature of the substrate [Runs 7 and 7′ for $\mathrm{CCl_3{\cdot}SiCl_3}$, Runs 12 and 13 for $\mathrm{CCl_3{\cdot}Si(OEt)_3}$], as would be predicted for the carbene mechanism (Mechanism 1). Mechanism 2 is untenable unless it is assumed that: (i) the similarity of the observed rate constants in Runs 2 and 3 is the result of mutually compensating change of medium and change of initial concentration effects, and (ii) the relative reactivity of dodec-1-ene and *p*-cymene towards both trichloromethylsilane derivatives is *ca.* 0·8 : 1.

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* In this expression, the formulae in square brackets represent quantities of material, not concentrations. This distinction, which is not experimentally significant, arises because, as a result of removing $\mathrm{ClSiX_3}$, the kinetic system is non-closed.

† In the reactions with *p*-cymene, the yields of insertion product did not approach 100%. The nature of the side reactions is not known; only traces of volatile by-products were detected, the major by-product being a tar containing carbon, hydrogen, and chlorine. It is not therefore necessarily legitimate to plot log $([\mathrm{IP}]_\infty - [\mathrm{IP}]_t)$ and log $[\mathrm{Sil}]_t$ against time. However, the results of run 13 (Table 5) in which plots of log $([\mathrm{IP}]_\infty - [\mathrm{IP}]_t)$ and log $[\mathrm{Sil}]_t$ against time gave essentially the same result, show that for the $\mathrm{CCl_3{\cdot}SiX_3}$–*p*-cymene system this treatment is justified.

[10] D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1967, **89**, 4953.

The second assumption was checked by competition experiments in which trichloromethyltrichlorosilane and trichloromethyltriethoxysilane were separately heated with a mixture of dodec-1-ene and *p*-cymene, in the molar proportions $CCl_3{\cdot}SiX_3$ to 1-dodecene to *p*-cymene of 1 : 1·35 : 5·57. The relative reactivities of dodec-1-ene (D) and *p*-cymene (Cy) towards the silanes were calculated from the yields of 1,1-dichloro-2-n-decylcyclopropane (CP) and insertion product (IP) by use of expression (4).

$$\frac{k_D}{k_{Cy}} = \frac{\log\{[D]_0/([D]_0 - [CP])\}}{\log\{[Cy]_0/([Cy]_0 - [IP])\}} \qquad (4)$$

The relative reactivity of dodec-1-ene to *p*-cymene was found to be 13·0 ± 0·6 for trichloromethyltrichlorosilane and 13·4 ± 0·6 for trichloromethyltriethoxysilane. These values are sufficiently different from 0·8 to make Mechanism 2 untenable. Further, the fact that the values are, within the limits of experimental error, identical, suggests that the same reactive species is produced from either of the trichloromethylsilane derivatives, which means that there is no significant interaction between dichlorocarbene and silicon halide SiX_3Cl in the transition state leading to product.

The evidence thus indicates a carbene mechanism in the reactions of trichloromethyltrichlorosilane and trichloromethyltriethoxysilane as dichloromethylene transfer agents. This is consistent with the observation made by Skell and Cholod[11] to the effect that there remains no substantive evidence for an intermediate other than free dichlorocarbene in dichlorocyclopropanation of olefins, regardless of source.

Activation Parameters.—Arrhenius plots for the reactions of trichloromethyltrichlorosilane and trichloromethyltriethoxysilane with olefins gave good straight lines, from which the activation energy and the entropy of activation were calculated. These values are shown in Table 7. First-order rate constants were also obtained for the reaction of trichloromethyltrifluorosilane with oct-1-ene, mainly in the vapour phase. These rate constants are shown in Table 6.

TABLE 6

Rate constants for reactions of $CCl_3{\cdot}SiF_3$ with oct-1-ene (mole ratio C_8H_{16} to $CCl_3{\cdot}SiF_3$ = 5 : 1)

Run	T/°C ± 1 °C	$10^5k_{obs}/s^{-1}$ with 95% confidence limits
14	130	38·3 ± 3·0
15	127	24·7 ± 2·4
16	122·5	20·2 ± 3·4
17	114	6·62 ± 0·91
18	105·5	3·63 ± 0·30
19	98	2·37 ± 0·23

The activation parameters from an Arrhenius plot for trichloromethyltrifluorosilane are also shown in Table 7. The Arrhenius line for this silane was not as good as for the chloro- and ethoxy-analogues; this may be a result of the narrower temperature range and the larger temperature error.

There appears to be a correlation between the electronegativities of the group attached to silicon and the activation energies. Thus the silanes bearing chlorine and oxygen, which have similar electronegativities, have similar activation energies, whilst the silane bearing the more electronegative fluorine has a lower activation energy. It would thus seem that in the transition state the silicon bears some negative charge, which would imply that silicon–chlorine bond formation is more advanced than silicon–carbon bond cleavage.

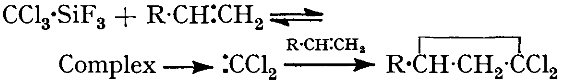
TABLE 7

Activation parameters for formation of dichlorocarbene from silanes $CCl_3{\cdot}SiX_3$ [a]

Silane	E_a/kcal mol^{-1} with 95% confidence level	$\Delta S^{\ddagger}_{450\,K}$/cal mol^{-1} K^{-1}	Temp. range used/°C	No. of points
$CCl_3{\cdot}SiCl_3$	39·1 ± 1·9	8·1 ± 4·4	140—190	6
$CCl_3{\cdot}Si(OEt)_3$	37·2 ± 1·2	−3·7 ± 2·7	176—222	5
$CCl_3{\cdot}SiF_3$	26·3 ± 5·6	−11·9 ± 14·6	98—130	6
ΔH_{calc} for $CCl_3{\cdot}SiX_3 \longrightarrow {:}CCl_2 + SiX_3Cl$	45 ± 14 [b]			

[a] It is presumed, by analogy with $CCl_3{\cdot}SiCl_3$ and $CCl_3{\cdot}Si(OEt)_3$, that $CCl_3{\cdot}SiF_3$ behaves as a dichlorocarbene precursor. The results of competition experiments[3] with $CCl_3{\cdot}SiF_3$ support, but do not prove, this assumption. [b] Calculated from the published data: ΔH_fCCl_2 = 56·5 ± 5,[c] ΔH_fCCl_3 = 18·5,[d] ΔH_fCl = 29,[d] E_{Si-O} = 69 ± 9,[e] E_{Si-Cl} = 91 kcal mol^{-1}.[e] [c] J. S. Shapiro and F. P. Lossing, *J. Phys. Chem.*, 1968, **72**, 1552. [d] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968. [e] T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, London, 1958.

It is interesting that whereas the energies of activation for trichloromethyltrichlorosilane and trichloromethyltriethoxysilane are close to the calculated heat of reaction, as expected, in the case of trichloromethyltrifluorosilane the error limits barely overlap. This could be the result of inadequate data for the strength of the carbon–silicon bond in these systems, or it could indicate a different mechanism such as (5) for the reaction of



$$CCl_3{\cdot}SiF_3 + R{\cdot}CH{:}CH_2 \rightleftharpoons$$
$$\text{Complex} \longrightarrow {:}CCl_2 \xrightarrow{R\cdot CH:CH_2} R{\cdot}CH{\cdot}CH_2{\cdot}CCl_2 \qquad (5)$$

trichloromethyltrifluorosilane with oct-1-ene. A mixture of oct-1-ene and trichloromethyltrifluorosilane rapidly becomes brown at room temperature; this may be indicative of complex formation.

Our present data do not enable us to distinguish between the simple decomposition mechanism and mechanisms such as the above for trichloromethyltrifluorosilane, and further work in this area would be desirable.

EXPERIMENTAL

I.r. spectra were measured with a Perkin-Elmer spectrophotometer model 457, n.m.r. spectra with a Perkin-Elmer R14 instrument operating at 100 MHz, and mass spectra with an A.E.I. MS 902 spectrometer. Spectral data for new compounds and compounds whose spectra have not been described previously are shown in Table 8.

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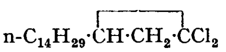
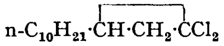
[11] P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, 1969, **91**, 6035.

TABLE 8

Spectral data

Compound	I.r. spectrum/cm^{-1}	Main features of mass spectrum
$CCl_3{\cdot}Si(OEt)_3$	2980m, 2940w, 2900w, 2870sh, 1390w, 1170sh, 1105s, 1090sh, 975m, 790m, 728m, 6702, 485m,	245 (2Cl) R.I. 0·7 235 (3Cl) R.I. 5 190 (3Cl) R.I. 7 183 (1Cl) R.I. 8 173 (2Cl) R.I. 4 163 R.I. 100 119 R.I. 76 103 R.I. 68 79 R.I. 52
$CCl_3{\cdot}Si(OEt)_2Cl$	2967m, 2890w 1473w, 1433w, 138w 1361sh, 1284w, 1163s 1104vs, 1087sh, 977w 960w, 896w, 785w, 729s Not recorded below 670 cm^{-1}	234 (3Cl) R.I. 1·9 225 (4Cl) R.I. 4 181 (3Cl) R.I. 13·5 153 (1Cl) R.I. 100 97 (1Cl) R.I. 73
$CCl_3{\cdot}Si(OEt)Cl_2$	2980m, 2940w, 2910w, 2890w, 2890w, 1980w, 1445w 1395w, 1168m, 1110s 975w, 898m, 744s, 610s, 530s	231 (5Cl) R.I. 11 225 (4Cl) R.I. 6 215 (5Cl) R.I. 25 181 (4Cl) R.I. 21 143 (2Cl) R.I. 100 115 (2Cl) R.I. 75 82 (2Cl) R.I. 68
 $n\text{-}C_{14}H_{29}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	3080w, 3010w, 2960sh 2930s, 2870s, 1470s 1380m, 1228m, 1120s, 1040s, 1010sh, 810sh 750s, 740sh, 720sh, 460w	306 (2Cl) R.I. 0·9 (parent) 270 (1Cl) R.I. 2·5 235 R.I. 2·3 57 R.I. 100
 $n\text{-}C_{10}H_{21}{\cdot}CH{\cdot}CH_2{\cdot}CCl_2$	The i.r. spectrum was indistinguishable from that listed immediately above	250 (2Cl) R.I. 2·0 (parent) 214 (1Cl) R.I. 2·0 179 R.I. 3·7 116 (1Cl) R.I. 2·1 102 (1Cl) R.I. 2·6 56 R.I. 100
$p\text{-}MeC_6H_4{\cdot}CMe_2{\cdot}CCl_2H$	3100w, 3060w, 3015w, 2980m 2920w, 2880w, 1610vw 1515m, 1470w, 1390m, 1370m 1210w, 1095w, 1022w, 860m 820s, 767s, 730m, 560m	216 (2Cl) R.I. 6 (parent) 133 R.I. 100 105 R.I. 22 Metastable peak at 82·0 (133 $\longrightarrow$ 105)

Gas chromatographic analysis was carried out on a Pye 104 model 24 dual-column gas chromatograph, fitted with flame ionisation detectors. The 5 ft colums were packed with 5% 20M Carbowax or 3% UCC-W-928 Silicone Gum Rubber on Chromosorb W 80/100 A.W. D.C.M.S. treated packing. Peak areas were measured by a Digital Equipment Corporation GLC-8 computer which was directly connected to the gas chromatograph.

Materials.—Oct-1-ene, dodec-1-ene, hexadec-1-ene, n-dodecane, n-hexadecane, and n-eicosane (B.D.H.) and methyltrichlorosilane and dichlorodimethylsilane (Hopkin and Williams) were used as supplied. *p*-Cymene (Koch-Light) and ethyl orthoformate (B.D.H.) were distilled before use. Trichloromethyltrichlorosilane was prepared from methyltrichlorosilane and chlorine by the published method.[5] It was freshly sublimed *in vacuo* before use in kinetic runs. Trichloromethyltrifluorosilane was prepared from trichloromethyltrichlorosilane and antimony trifluoride by the published method.[12]

Preparation of the Trichloromethylethoxychlorosilanes, $CCl_3{\cdot}Si(OEt)_nCl_{3-n}$.—The reactions were carried out in a flask fitted with a dropping funnel and a reflux condenser leading to a cold trap (−78 °C) protected from the atmosphere by an air-lock. For each experiment the apparatus was flushed with nitrogen and a slow stream of nitrogen was maintained throughout. The solvent, benzene, was dried over sodium.

Trichloromethylethoxydichlorosilane, $CCl_3{\cdot}Si(OEt)Cl_2$.—Ethyl orthoformate (11·6 g, 0·078 mol) was added during 10 min to a solution of trichloromethyltrichlorosilane (20 g, 0·078 mol) in benzene (50 ml). The mixture was heated under reflux for 6 h, then benzene was distilled off at atmospheric pressure. The residue was distilled at reduced pressure to give a fraction (19·5 g), b.p. 68—70 °C at 10 mmHg, from which was isolated by redistillation through a lagged Vigreux column (5 cm) *trichloromethylethoxydichlorosilane* (16·3 g, 80%), b.p. 69 °C at 10 mmHg, n_D^{20} 1·4643 (Found: C, 12·9; H, 1·9; Cl, 68·6. $C_3H_5Cl_5OSi$ requires C, 13·7; H, 1·9; Cl, 68·5%).

Trichloromethylethoxychlorosilane, $CCl_3{\cdot}Si(OEt)_2Cl$.—Ethyl orthoformate (27·6 g, 0·189 mol) in benzene (50 ml) was added to a solution of trichloromethyltrichlorosilane (15·8 g, 0·0625 mol) in benzene (50 ml). The mixture was heated under reflux for 2 h, then benzene was distilled off at atmospheric pressure. Low-pressure distillation of the residue gave *trichloromethyldiethoxychlorosilane* (12·1 g, 71%), b.p. 60 °C at 2 mmHg, n_D^{20} 1·4472 (Found: C, 22·7; H, 3·8; Cl, 53·3. $C_5H_{10}Cl_4O_2Si$ requires C, 22·0; H, 3·7; Cl, 52·0%). A lower-boiling fraction (6·1 g), b.p. 50—60 °C at 2 mmHg, was shown by i.r. and n.m.r.

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[12] R. Müller, S. Reichel, and C. Dathe, *Chem. Ber.*, 1964, **97**, 1673.

to contain trichloromethyldiethoxychlorosilane (2·7 g, 16% yield) and ethyl orthoformate (3·4 g).

Trichloromethyltriethoxysilane.—Ethyl orthoformate (238 g, 1·6 mol) was added during 30 min to trichloromethyltrichlorosilane (60·0 g, 0·237 mol) in benzene (100 ml). The mixture was heated under reflux and the progress of the reaction was followed by weighing the product in the cold trap from time to time. After 24 h the volatile products collected amounted to 49·5 g (theoretical yield of ethyl chloride: 46 g) and the reaction was terminated. The mixture was distilled to give trichloromethyltriethoxysilane (47·0 g, 71%), b.p. 94 °C at 9·5 mmHg, n_D^{20} 1·4350 (lit.,[6] b.p. 99·5—101 °C at 10 mmHg, n_D^{20} 1·4360) (Found: C, 30·0; H, 5·4; Cl, 37·3; Si, 10·2. Calc. for $C_7H_{15}Cl_3O_3Si$: C, 29·9; H, 5·35; Cl, 37·9; Si, 10·0%).

Chlorination of Dichlorodimethylsilane.[6]—The apparatus consisted of a Pyrex test tube (3·5 × 35 cm) with a B34 neck fitted with a gas inlet reaching to 5 cm from the bottom and a cold-finger condenser (−78 °C) leading *via* a buffer trap and gas bubbler (containing paraffin oil) to an inverted funnel dipping into sodium hydroxide solution. The reaction tube was irradiated with a 125 W Hanovia medium-pressure mercury lamp and heated by means of a Baird and Tatlock 275 W i.r. heater. A thermometer was placed inside the reaction tube.

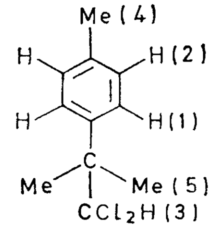
$(CCl_3)_2SiCl_2$. The reaction tube was loaded with dichlorodimethylsilane (199·8 g, 1·54 mol) and carbon tetrachloride (35 ml) and a rapid stream of chlorine was passed through the mixture, with irradiation and heating. After 50 h at 40—60 °C, the reaction was terminated. Volatile material was removed under vacuum. Trap-to-trap distillation (60—100 °C at 0·05—3 mmHg) of the residue gave a semi-solid product (185 g, 36%) which was presumed to be mainly bistrichloromethyldichlorosilane.

$CCl_3{\cdot}SiMeCl_2$. The reaction tube was loaded with dichlorodimethylsilane (193·0 g, 1·49 mol) and carbon tetrachloride (20 ml). The sodium hydroxide solution contained 372·4 g (9·31 mol) sodium hydroxide. A rapid stream of chlorine was passed through the mixture, with irradiation and heating. After 14 h at 57—60 °C, titration of the sodium hydroxide solution with N-hydrochloric acid showed that 4·91 mol hydrogen chloride had been produced (assuming that no chlorine had passed through the cold-finger condenser) and the reaction was terminated. Volatile material was removed under vacuum and the residue was sublimed *in vacuo* to give a white solid (288 g, 83%) whose spectral properties (n.m.r. and m.s.) were consistent with methyltrichloromethyldichlorosilane as the major constituent, although the low m.p. (79—83 °C; lit.,[6] 100 °C) was indicative of impurities.

Preparative Reactions with Trichloromethylsilane Derivatives.—In these experiments a trichloromethylsilane derivative and a substrate were heated together in a flask fitted with a nitrogen inlet, a thermometer (immersed in the mixture), and a Vigreux column (40 × 2·5 cm) surmounted by a cold trap (−78 °C) protected from the atmosphere by an air-lock containing liquid paraffin. The apparatus was flushed with nitrogen and a slow stream of nitrogen was maintained throughout the reaction.

Trichloromethyltrichlorosilane with Dodec-1-*ene*.—Trichloromethyltrichlorosilane (25·0 g, 0·097 mol) and dodec-1-ene (100 g, 5·95 mol) were heated together. After 10 min at 210 °C, evolution of volatile material {shown by molecular-weight determination to be silicon tetrachloride (13·5 g, 81% yield). [Found: *M* (Regnault), 173. Calc. for $SiCl_4$: *M*, 170]} ceased. The mixture was distilled twice, to give 1,1-*dichloro*-2-*n*-*decylcyclopropane* (20·5 g, 79%), b.p. 83 °C at 0·3 mmHg, n_D^{23} 1·4596 (Found: C, 62·9; H, 9·7; Cl, 28·6. $C_{13}H_{24}Cl_2$ requires C, 62·2; H, 9·6; Cl, 28·2%) and dodec-1-ene (76 g, 88% of theoretical recovery).

Trichloromethyltrichlorosilane with p-*Cymene*.—Trichloromethyltrichlorosilane (26·5 g, 0·104 mol) and *p*-cymene (85·6 g, 0·638 mol) were mixed and heated under reflux for 9 h. Excess of *p*-cymene (73·3 g) was removed by evaporation at reduced pressure, and the residual material was fractionated with a packed column (10 × 2·5 cm) to give the insertion product 1,1-*dichloro*-2-*methyl*-2-(p-*tolyl*)*propane* (9·45 g, 42%), b.p. 76 °C at 0·03 mmHg, n_D^{20} 1·5320 (Found: C, 60·8; H, 6·6; Cl, 32·4. $C_{11}H_{14}Cl_2$ requires C, 60·8; H, 6·5; Cl, 32·7%). The n.m.r. spectrum (CCl_4) of the insertion product (I) showed five absorptions of relative intensities 2 : 2 : 1 : 3 : 6 at δ 7·15 (1-H), 7·02 (2-H), 5·74 (s, 3-H), 2·27 (s, 4-H), and 1·49 (s, 5-H). The absorptions at 7·15 and 7·02 formed an AA′BB′ system with $J_{1,2}$ 9 Hz.



(I)

Impure Bistrichloromethyldichlorosilane with Hexadec-1-*ene*.—Material presumed to be mainly bistrichloromethyldichlorosilane (13·1 g, *ca*. 0·039 mol) was heated with hexadec-1-ene (102·2 g, 0·455 mol) at 220 °C for 1 h. Distillation of the reaction mixture gave 1,1-*dichloro*-2-*n*-*tetradecylcyclopropane* (16·8 g, 70%), b.p. 122 °C at 0·5 mmHg, n_D^{20} 1·4842 (Found: C, 66·0; H, 10·0. $C_{17}H_{32}Cl_2$ requires C, 66·4; H, 10·4%).

Impure Methyltrichloromethyldichlorosilane with Dodec-1-*ene*.—Impure methyltrichloromethyldichlorosilane (53·8 g, 0·231 mol) and dodec-1-ene (76·8 g, 0·457 mol) were heated together at 190—210 °C for 6 h. Distillation of the reaction mixture gave 1,1-dichloro-2-n-decylcyclopropane (35·1 g, 60%).

Kinetics.—*Method*. The method was essentially the same for all kinetic runs, except those involving trichloromethyltrifluorosilane. The apparatus consisted of a flask fitted with a stirrer, a thermometer (arranged so as to dip into the reaction mixture), a gas inlet, and a condenser (for runs involving trichloromethyltrichlorosilane, *i.e.*, Runs 1—7, an air condenser was used) protected from the atmosphere by an air-lock. Nitrogen (dried over conc. H_2SO_4) was passed through the apparatus throughout each run. The requisite amounts of olefin (or *p*-cymene), silane, and an internal standard for g.l.c. analysis (see below) were weighed out and mixed. The mixture was then added rapidly to the preheated reaction flask, which was maintained at the required temperature by a stirred oil-bath heated by a 1 kW immersion heater controlled by a contact thermometer and Sunvic relay. The maximum temperature fluctuation observed during any run was 0·5 °C.

Analysis.—Samples (*ca*. 0·5 ml) were removed at appropriate intervals from the stirred reaction mixture and analysed by g.l.c. The amount of product that had been produced at the time the sample was taken was calculated from the relative peak areas corresponding to the product and to the internal standard, using previously determined response factors. In run 13 [$CCl_3{\cdot}Si(OEt)_3$] an analogous method was used to calculate the amount of starting material remaining.

Run 7 ($CCl_3{\cdot}SiCl_3$ with *p*-cymene) was carried out without an internal standard. Instead weighed samples (*ca.* 0·1 g) were removed, mixed with measured amounts of a g.l.c. standard (n-hexadecane), and examined by g.l.c. From the relative peak areas it was possible to calculate the number (n) of mmoles of product per gram of reaction mixture. The total number (m) of mmoles in the solution was then calculated from the expression: $m = nw_0/(1 + 17n/y)$ where w_0 is the initial total weight of the reaction mixture and y is the percentage yield of insertion product observed after completion of the reaction. This expression takes into account the loss in weight due to the removal of silicon tetrachloride as the reaction proceeds.

TABLE 9

Run 13; Reaction of trichloromethyltriethoxysilane with *p*-cymene

Time/h	$10^3[IP]_t$/mol	$10^3[Sil]$/mol	$\frac{10^2[IP]_t}{[Sil]_0 - [Sil]_t}$	$[IP]_\infty - [IP]_t$	$\log([IP]_\infty - [IP]_t)$	$\log[Sil]_t$
0	0·0	28·8		8·41	0·9248	1·4594
1	0·08			8·33	0·9206	
7	0·61	26·3	24·4	7·80	0·8921	1·4200
23·5	1·67	21·8	23·9	6·74	0·8287	1·3385
53·5	2·85	20·2	33·2	5·56	0·7451	1·3054
76	4·07	15·3	30·2	4·34	0·6375	1·1847
76	4·22	13·8	28·2	4·19	0·6222	1·1399
96	5·06	12·5	31·1	3·35	0·5250	1·0969
104	5·60	11·1	31·8	2·81	0·4487	1·0453
104	5·30			3·11	0·4928	
120	5·93	10·0	31·5	2·48	0·3945	1·0000
144	6·12	7·7	29·0	2·29	0·3598	0·8854
176	6·23			2·18	0·3385	
			Mean 29·2			

Hence $[IP]_\infty = [Sil]_0 \times 29{\cdot}2 \times 10^{-2} = 8{\cdot}41$.

Treatment of Data.—In runs 1—6 and 8—12, log ($[Sil]_0 - [P]_t$) was plotted against time t {$[Sil]_0$ = number of mmoles $CCl_3{\cdot}SiCl_3$ or $CCl_3{\cdot}Si(OEt)_3$ initially, $[P]_t$ = number of mmoles of product at time t}. In run 13, log $[Sil]_t$ was plotted against t. In run 13, $[P]_t$ was also measured. Since the reaction was too slow for $[P]_\infty$ to be measured directly, $[P]_\infty$ was calculated from the average value of $[P]_t \times [Sil]_0/([Sil]_0 - [Sil]_t)$ at all points where both $[P]_t$ and $[Sil]_t$ were measured. It was then possible to plot log ($[P]_{\infty,\mathrm{calc}} - [P]_t$) against t for run 13. In run 7, $[P]_\infty$ was measured directly. Regression analysis for the plots gave 95% confidence limits. As an example of the method, readings for run 13 are shown in Table 9.

$CCl_3{\cdot}SiF_3$ *Kinetics.*—As trichloromethyltrifluorosilane is a volatile liquid (b.p. 40 °C), highly sensitive to atmospheric moisture, it was not possible to carry out kinetic runs in the manner described above for the other silanes. The method used was as follows. A storage ampoule (47 ml) fitted with a Rotaflo polytetrafluoroethylene tap and a B10 cone was loaded with oct-1-ene (19·5 g, 0·174 mol) and an internal standard (n-dodecane, 0·81 g).

The ampoule was then attached to a high-vacuum line and degassed. Trichloromethyltrifluorosilane (6·0 g, 0·0295 mol) was then condensed into the ampoule from the vacuum line. The ampoule was next connected by a tube with B10 joints (socket at the top end, cone at the bottom) to a reaction tube (46 ml) fitted with a B10 socket. The connecting tube was fitted with a Rotaflo polytetrafluoroethylene tap near the bottom and a side arm leading *via* a Rotaflo polytetrafluoroethylene tap to the vacuum line. The connecting tube and reaction tube were evacuated, isolated from the vacuum line, and the bottom tap was closed. The tap on the storage ampoule was then opened to allow a portion of the mixture (*ca.* 0·5 ml) to flow into the connecting tube, then closed again. This portion of mixture was then run into the reaction tube, which was next cooled to −196 °C and sealed, then replaced by another tube. In this manner 57 tubes were loaded with approximately equal amounts of the mixture.

Batches of 8 (run 15), 9 (run 17), or 10 (runs 14, 16, 18, and 19) reaction tubes, were placed in an oil-bath with provision for gentle mechanical agitation. The oil-bath was heated by a 1 kW immersion heater controlled by a contact thermometer and Sunvic relay, and the oil was stirred. The maximum temperature fluctuation observed during any run was 1 °C. Tubes were removed at regular intervals (ranging from 5 min at 130 °C to 15 min at 98 °C). Timing was started 1 min after placing the batch of tubes in the bath. In run 14 (130 °C) one tube was left in the heated oil-bath for 23 h (*ca.* 46 half-lives) to give the infinity reading which was used for all the runs. Immediately on removal from the oil-bath, tubes were cooled (water) and opened. The contents were removed from the tubes and examined by g.l.c. (Carbowax, 50 °C). The areas (A) of the peaks due to the internal standard (IS) and to 1,1-dichloro-2-n-hexylcyclopropane (CP) were measured. Values of expression (6) were plotted against time. Regression analysis gave 93% confidence limits.

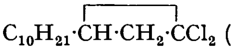
$$\log\left[\left(\frac{A_{\mathrm{CP}}}{A_{\mathrm{IS}}}\right)_\infty - \left(\frac{A_{\mathrm{CP}}}{A_{\mathrm{IS}}}\right)_t\right] \qquad (6)$$

Competition Experiments.—$CCl_3{\cdot}SiCl_3$. A mixture of trichloromethyltrichlorosilane (3·80 g, 0·0150 mol), dodec-1-ene (3·40 g, 0·0202 mol), *p*-cymene (11·10 g, 0·0830 mol), and internal standard (n-hexadecane, 0·95 g) was heated under reflux (184 °C) under nitrogen for 7·5 h. Comparison of g.l.c. (Carbowax, 80—200 °C at 6 °C/min) peak areas gave the yields shown in expressions (7) and (8).

$C_{10}H_{21}{\cdot}\overline{CH{\cdot}CH_2{\cdot}CCl_2}$ (2·03 ± 0·04) g, (8·13 ± 0·16) × 10^{-3} mol, (54 ± 1)% yield (7)

p-$MeC_6H_4{\cdot}CMe_2{\cdot}CCl_2H$ (0·67 ± 0·01) g, (3·12 ± 0·06) × 10^{-3} mol, 21% yield (8)

$CCl_3\cdot Si(OEt)_3$. A mixture of trichloromethyltriethoxysilane (4·21 g, 0·0150 mol), dodec-1-ene (3·40 g, 20·2 mol), *p*-cymene (11·20 g, 0·0835 mol), and internal standard (n-hexadecane, 0·95 g) was heated under reflux (184 °C) under nitrogen for 72 h. Comparison of g.l.c. (Carbowax, 80—200° at 6 °C/min) peak areas gave the yields shown in expressions (9) and (10).



$C_{10}H_{21}\cdot CH\cdot CH_2\cdot CCl_2$ (1·51 ± 0·03) g, (6·03 ± 0·12) × 10^{-3} mol, (40 ± 1)% yield * (9)

p-$MeC_6H_4\cdot CMe_2\cdot CCl_2H$ (4·9 ± 0·01) g, (2·26 ± 0·04) × 10^{-3} mol, 15% yield * (10)

We thank Dr. D. Bethell (Liverpool University) and Drs. K. Jones and P. W. Vipond (Unilever Research Port Sunlight Laboratory) for discussions.

[2/1575 *Received, 4th July,* 1972]

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* Based on initial starting material, although the reaction had not gone to completion.