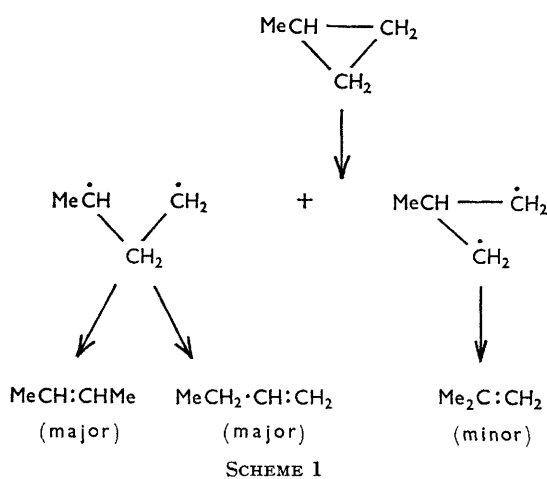


Cyclopropane Chemistry. Part I. Thermal Isomerisation of *gem*-Dichlorocyclopropanes to Olefins¹

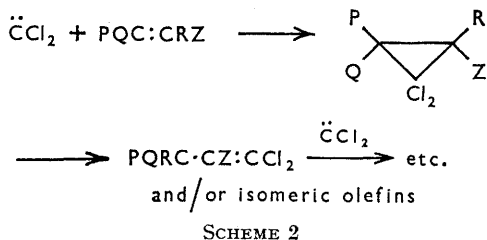
By R. Fields, R. N. Haszeldine,* and D. Peter, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester, 1

A series of 1,1-dichlorocyclopropanes containing various ring substituents has been prepared and the compounds have been pyrolysed in a flow system at 500–670°. This pyrolysis is a useful route to olefins. 1,1-Dichlorocyclopropane gives 2,3-dichloropropene in high yield. Cyclopropanes containing more chlorine substituents also give, in each case, a high yield of a single olefin isomeric with the cyclopropane; for instance 1,1,2-trichlorocyclopropane gives 1,1,3-trichloropropene, the 1,1,2,2-tetrachloro-compound gives 1,1,2,3-tetrachloropropene, and 1,1,2-trichloro-2-chloromethylcyclopropane gives 1,1,3-trichloro-2-chloromethylpropene. Cyclopropanes which contain other substituents give mixtures of isomeric olefins. For instance 1,1-dichloro-2-methylcyclopropane gives 2,3-dichlorobut-1-ene and 1,2-dichlorobut-2-ene. The results are interpreted in terms of a unimolecular concerted chlorine-atom migration and ring-opening mechanism.

PYROLYSIS of alkylcyclopropanes has been studied extensively; in general the reaction is unimolecular, and proceeds mainly *via* the formation of the 'most stabilised diradical,'² followed by migration of hydrogen to either radical site. Formation of the less stable diradical also occurs to a lesser extent, see Scheme 1.³



The ready formation of cyclopropanes containing a *gem*-dichloromethylene group by addition of dichlorocarbene to suitable olefins suggested that the reactions shown in Scheme 2 might represent a useful chain-



lengthening sequence. The pyrolysis of a series of such cyclopropanes has therefore been investigated.

Preparation of 1,1-Dichlorocyclopropanes.—Apart from

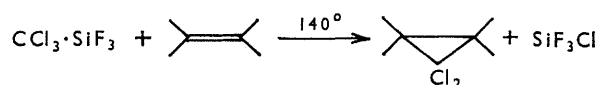
¹ Preliminary communication, R. Fields, R. N. Haszeldine, and D. Peter, *Chem. Comm.*, 1967, 1081.

² R. Breslow in 'Molecular Rearrangements,' Part I, ed. P. DeMayo, Interscience, New York and London, 1963.

³ J. P. Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

⁴ P. G. Stevens, *J. Amer. Chem. Soc.*, 1946, **68**, 620.

1,1-dichlorocyclopropane, which was more conveniently made in quantity by chlorination of cyclopropane,⁴ the cyclopropanes shown in Tables 1 and 2 were prepared in high yield (40–96%) by vapour-phase pyrolysis of trichloromethyltrifluorosilane in an excess of the olefin (Scheme 3).⁵ This procedure is particularly useful



SCHEME 3

for the addition of dichlorocarbene to low-boiling olefins, and to olefins containing electron-withdrawing substituents, for which the basic hydrolysis of chloroform route to dichlorocarbene either fails or, at best, gives only low yields. Apart from the exceptions noted below, the products were shown by their i.r. and n.m.r. spectra to contain no olefinic material.

The addition product from trichloroethylene contained *ca.* 20% of an olefin (by n.m.r.), which was identified by comparison with a sample prepared as shown in Scheme 4⁶ as 1,1,3,3,3-pentachloropropene, evidently formed by



isomerisation of the cyclopropane at 140°. Tobey and West⁷ subsequently reported the isomerisation of pentachlorocyclopropane during distillation above 100°.

The reaction of trichloromethyltrifluorosilane with allene (Scheme 5) gave as the major product (38%) 1,1-dichloro-(2-methylene)cyclopropane, identical with material prepared⁸ by reaction of allene with bromodichloromethyl(phenyl)mercury. The minor product (15%) which we obtained, however, was not the 1,1,4,4-tetrachlorospiropentane observed by Seyferth *et al.*;⁸ its n.m.r. (single unsplit signal) and mass

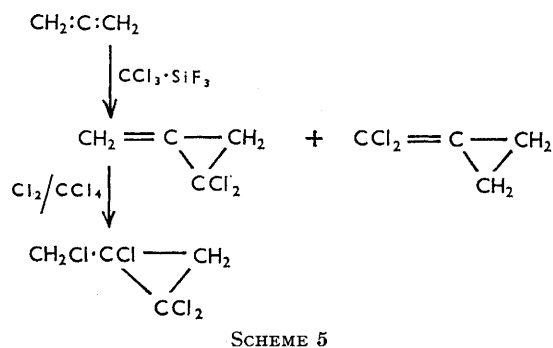
⁵ W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; W. I. Bevan, J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, International Symposium on Reaction Mechanisms, Cork, 1964.

⁶ A. Roedig, F. Bischoff, B. Heinrich, and G. Markl, *Annalen*, 1963, **670**, 8.

⁷ S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, 1966, **88**, 2478.

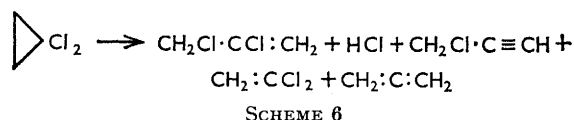
⁸ D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Yick-Pui Mui, H. D. Simmons, A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, 1965, **87**, 4259.

spectra were consistent with its formulation as dichloromethylenecyclopropane, presumably formed by isomerisation of the initial adduct in a manner similar to the known⁹ isomerisation of 1-methyl-2-methylenecyclopropane and of other alkylidenedichlorocyclopropanes since reported.¹⁰ Low temperature chlorination of 1,1-dichloro-(2-methylene)cyclopropane gave 1,1,2-trichloro-2-chloromethylcyclopropane, identical with the compound prepared by reaction of trichloromethyltrifluorosilane with 2,3-dichloropropene.



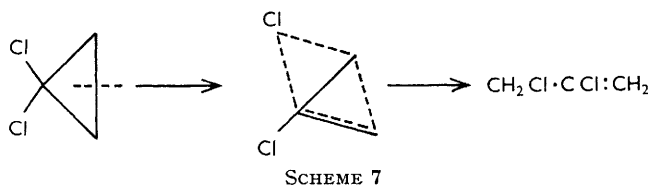
Pyrolysis of 1,1-Dichlorocyclopropane.—Pyrolysis in a flow system gave reasonable conversion (32%) of cyclopropane to olefin at 650–670° with contact times of *ca.* 0.2 sec. At 600° the conversion was only 6%, and at 710° further breakdown and carbonisation occurred.

The only propene formed in these pyrolyses (75% yield based on cyclopropane consumed) was 2,3-dichloropropene, identified unambiguously by microanalysis, by analysis of its n.m.r. spectrum and comparison with that reported previously,¹¹ and by comparison of its properties (*i.e.*, b.p., g.l.c. retention time, *etc.*) with those of known material. Other products, obtained in very low yields, were 3-chloropropyne, allene, and 1,1-dichloroethylene, together with hydrogen chloride (Scheme 6). Another minor product was



tentatively identified (strong C=C=C absorption at 5.1 μ) as chloroallene. These products may arise in part from decomposition of the cyclopropane, but a separate experiment established that 3-chloropropyne, hydrogen chloride, and the presumed chloroallene are also formed from the dichloropropene under the reaction conditions. 2,3-Dichloropropene, although unexpected on the basis of the 'most stable diradical' mechanism, is not a secondary product; it is not formed under the conditions used from either of the products expected to be formed by the most stable diradical mechanism, *i.e.* 1,1- or 3,3-di-

chloropropene. A separate experiment showed the former to be stable; the latter survives similar conditions (*a*) in the chlorination of allyl chloride¹² at 500°, where the other major products are the 1,3-dichloropropenes (not observed at all in the present work), and (*b*) in its formation at 400–600°, under conditions more severe than those used in the present work, from 1,3-dichloropropene.¹³ The isomerisation of 1,1-dichlorocyclopropane therefore does not involve formation of the most stable diradical. In order to account for the observed product, ring-opening opposite the dichloromethylene group must take place, with migration of chlorine (Scheme 7).



The product distribution and conversion were substantially unaltered by the presence (10 moles %) of chlorine, toluene, or oxygen, which implies that a radical chain mechanism is not involved. This is fully substantiated by kinetic studies briefly reported¹⁴ from this department; these are also in accord with a concerted ring-opening and migration of chlorine. Moreover, the activation energy and pre-exponential factor¹⁴ are quite different from those for reactions in which diradical intermediates are involved.

Further evidence against a diradical intermediate is provided by the incomplete pyrolysis of 1,1,2-*cis*,3-tetrachlorocyclopropane. The recovered cyclopropane contained none of the *trans*-isomer.

The observation of a trace of 1,1-dichloroethylene amongst the reaction products suggests extrusion of methylene, but no evidence for this pathway could be found in trapping experiments. Although extrusion of methylene and its re-insertion into a C-Cl bond of 1,1-dichloroethylene could account for the observed product, exclusive insertion into a C-Cl bond would be unexpected. Such a carbene mechanism could not account for the products of the other reactions, and is discarded.

Pyrolysis of Polychlorocyclopropanes.—The results of the pyrolysis of a number of polychlorocyclopropanes, each containing the dichloromethylene group, under conditions similar to those used for 1,1-dichlorocyclopropane, are summarised in Scheme 8.

In each reaction a single olefin was the major product; the minor products arise by loss of hydrogen chloride, either from the cyclopropane, or from the initially produced olefin. The olefins were identified by microanalysis and either unambiguous analysis of their n.m.r. spectra or comparison with samples prepared un-

⁹ E. F. Ullman and W. J. Fanshawe, *J. Amer. Chem. Soc.*, 1961, **83**, 2379.

¹⁰ A. Bezaguet and M. Bertrand, *Compt. rend.*, 1966, **262**, 1697.

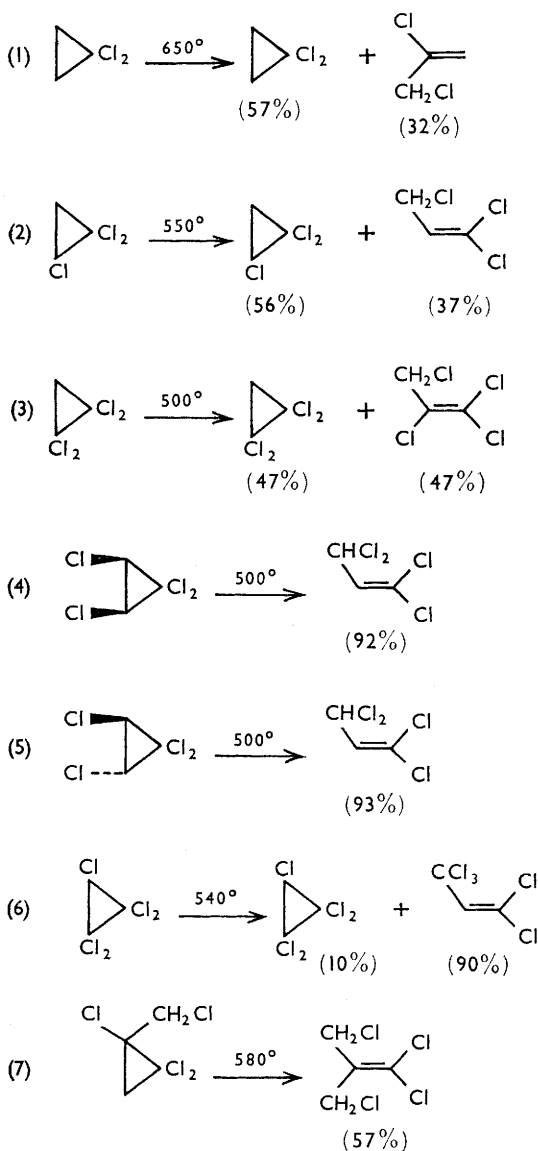
¹¹ Varian Handbook of n.m.r. spectra, vol. I, no. 18.

¹² H. P. A. Groll and G. Hearne, *J. Ind. Eng. Chem.*, 1939, **31**, 1530.

¹³ W. H. Taplin, U.S.P. 2,846,483/1958.

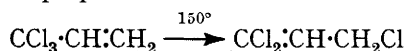
¹⁴ K. A. W. Parry and P. J. Robinson, *Chem. Comm.*, 1967, 1083.

ambiguously. In each case the olefinic product is consistent with ring-opening followed, or accompanied, by migration of chlorine. The ring-opening need not involve the bond opposite to the dichloromethylene group. The products obtained in reactions (2) and



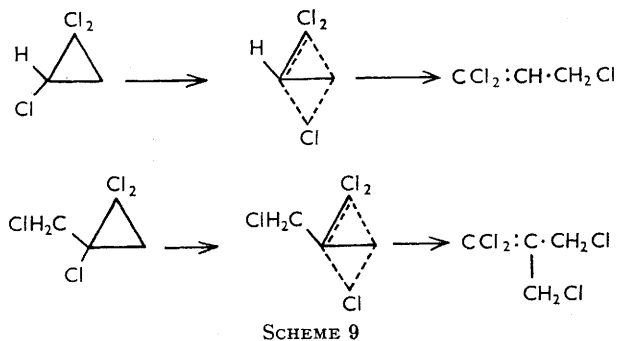
SCHEME 8
Pyrolysis of chlorocyclopropanes

(4)—(7) indicate that where a chloromethylene or 1,2-dichloroethylidene group is also present, the chlorine from that group migrates, with the dichloromethylene group, apparently stabilising the incipient double bond, directing the migration to the other carbon atom (Scheme 9). This is consistent with the known¹⁵ thermal rearrangement of 3,3,3-trichloropropene to the more stable 1,1,3-trichloropropene:



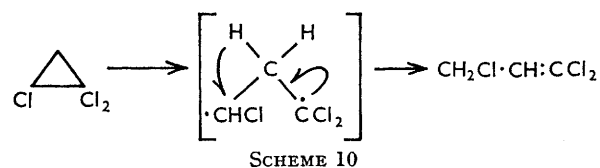
Why migration from the chloromethylene group should

prevail over that from the dichloromethylene group is not clear, but the reaction temperatures for the compounds containing more than two chlorine atoms are

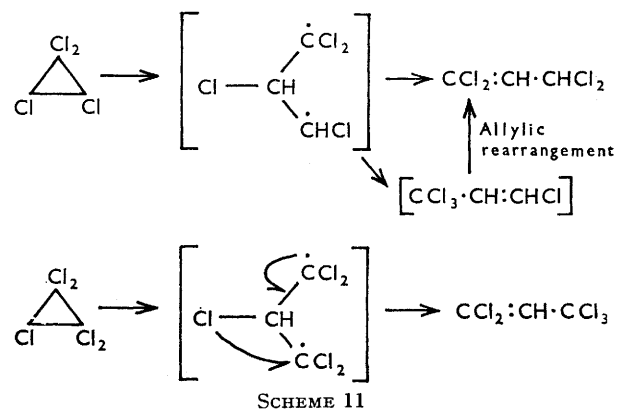


distinctly lower for similar conversions than that required for 1,1-dichlorocyclopropane itself (Scheme 8).

The intervention of diradical intermediates in these reactions cannot be unambiguously ruled out, but would require a number of reaction paths. Only in reaction (2) is the product explicable by the most stable diradical mechanism (Scheme 10). If this mechanism were



modified to permit migration of chlorine rather than hydrogen, the observed products in reactions (4)—(6) are explicable (Scheme 11). The products of reactions

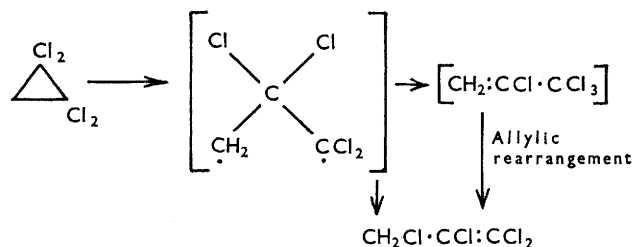


(3) and (7), however, would require exclusive formation of a less stabilised diradical and migration of chlorine, possibly followed by allylic rearrangement (Scheme 12).

Formation of 1,1,3,3-tetrachloropropene [reactions (4) and (5)] *via* the allylic rearrangement of 1,3,3,3-tetrachloropropene under the reaction conditions, however, was excluded by a separate experiment in which the 1,3,3,3-isomer was recovered (>85%). Complete allylic

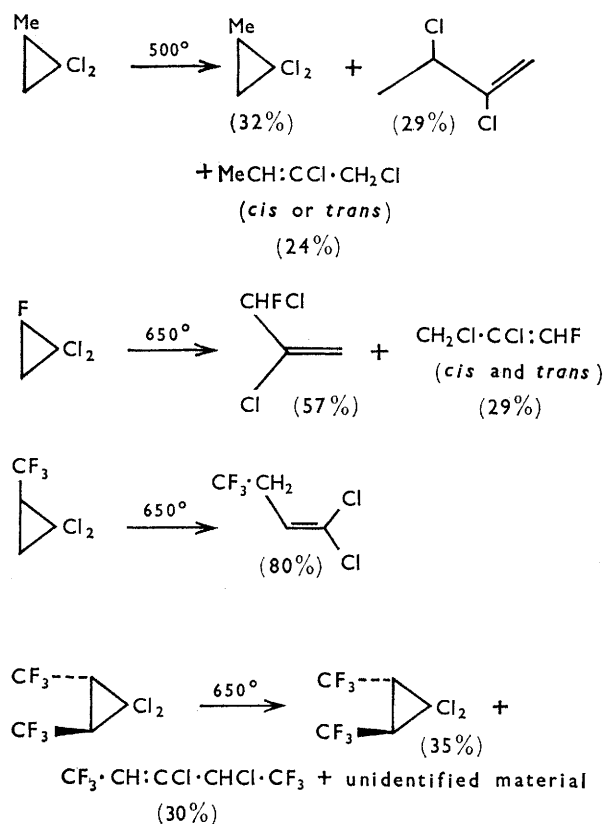
¹⁵ R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3371.

rearrangement in reactions (3) and (7) therefore seems unlikely, and as little as 1% of the 'unrearranged' isomer would certainly have been detected. Kinetic



studies are in progress to clarify the situation, but diradical intermediates seem unlikely to be involved in these reactions.

The pyrolysis of other cyclopropanes containing the dichloromethylene group is sometimes less clear-cut; the results are summarised in Scheme 13. The two olefinic



products from 1,1-dichloro-2-methylcyclopropane can both arise by concerted ring-opening and migration of

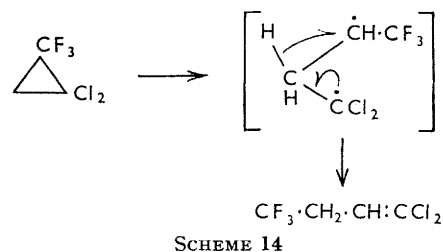
¹⁶ G. W. Hearne and M. L. Adams, U.S.P. 2,391,827/1945 (*Chem. Abs.*, 1946, **40**, 1347).

¹⁷ C. Finger, F. Nerdel, P. Weyerstahl, J. Buddrus, and D. Klamann, G.P. 1,235,293/1967 (*Chem. Abs.*, 1967, **66**, 10,698); P. Weyerstahl, D. Klamann, C. Finger, F. Nerdel, and J. Buddrus, *Chem. Ber.*, 1967, **100**, 1858.

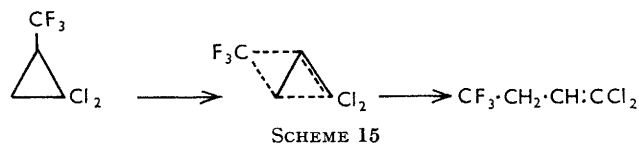
chlorine, but the directing influence of the methyl group is, perhaps expectedly, rather small. 2-Chlorobuta-1,3-diene (13%) was also formed at 500°, either directly or from one or both of the olefins, which are known¹⁶ to lose hydrogen chloride readily. The formation of 2-chlorobuta-1,3-diene by a single-stage reaction involving pyrolysis of propene and chloroform, with¹⁷ or without¹⁸ the presence of ethylene oxide and tetraalkylammonium halide, has been reported.

Pyrolysis of 1,1-dichloro-2-fluorocyclopropane resulted in migration to the fluoromethylene group (57%) and to the methylene group (29%), although, by analogy with the effects of chlorine, the fluorine would have been expected to stabilise the incipient double bond more than hydrogen. The *cis*- and *trans*-isomers of 2,3-dichloro-1-fluoropropene were obtained in approximately equimolar amounts; the possibility of *cis-trans* isomerism under the reaction conditions cannot, however, be ruled out.

The product obtained in high yield from the pyrolysis of 1,1-dichloro-2-trifluoromethylcyclopropane was mainly 1,1-dichloro-4,4,4-trifluorobut-1-ene, together with minor impurities (*ca.* 10% total). This compound cannot be formed by any process involving migration of chlorine. It could be explained by formation of the most stable diradical and migration of hydrogen (Scheme 14) or



by migration of the trifluoromethyl group, acting as a 'pseudohalogen,' with stabilisation of the incipient double bond by the dichloromethylene group (Scheme 15).



It seems unlikely that the stabilisation of the intermediate diradical would be so much preferred in this case alone, even if the increase in stabilisation due to the trifluoromethyl group is allowed for, so that the second route is probably the more likely. Further studies of this reaction are in progress.

This reaction sequence is convenient for the synthesis of certain olefins in two high-yield stages, especially where other routes lead to difficulties. For instance, addition

¹⁸ J. W. Engelsma and R. van Helden, G.P. 1,144,261/1963 (*Chem. Abs.*, 1963, **59**, 6275); J. W. Engelsma, *Rec. Trav. chim.*, 1965, **84**, 187.

of dichlorocarbene to 1,2-dichloroethylene, and pyrolysis of the cyclopropane mixture gives an overall 72% yield of 1,1,3,3-tetrachloropropene (cf. 24% obtained by the reported route¹⁹).

Since our preliminary communication¹ appeared, G. C. Robinson has reported²⁰ a study of the pyrolysis under similar conditions to ours of 1,1-dichlorocyclopropane, 1,1-dichloro-2-methylcyclopropane, and a number of other alkyl-substituted dichlorocyclopropanes. Allowing for the experimental differences, the results for dichlorocyclopropane and the methyl derivative agree well with those reported here and in ref. 1.

Reactions of 1,1-Dichlorocyclopropane with Carbenes.—Methylene generated by photolysis of diazomethane inserted into both C-H and C-Cl bonds of 1,1-dichlorocyclopropane, to give 1,1-dichloro-2-methylcyclopropane and 1-chloro-1-chloromethylcyclopropane in the ratio 1:8. The relative reactivity of C-Cl and C-H bonds in this molecule is thus 16, comparable to that found²¹ for alkyl chlorides. Dichlorocarbene from trichloromethyltrifluorosilane did not attack the dichlorocyclopropane initially produced from reaction with ethylene, even when an excess was introduced and the reaction temperature was raised to 200°. The known products which arise by self-decomposition of trichloromethyltrifluorosilane,⁵ *i.e.* tetrachloroethylene (17%), hexachloroethane (*ca.* 9%), hexachloropropene (*ca.* 45%), hexachlorocyclopropane (*ca.* 3%), and hexachlorobutadiene (*ca.* 4%) were produced.

Spectroscopic Properties.—**Cyclopropanes.** The halogenocyclopropanes usually gave recognisable parent ions in the mass spectrometer. The major peak in all the compounds was formed by loss of chlorine, with the exception of 1,1,2-trichloro-2-(chloromethyl)cyclopropane, from which loss of chloromethyl provided the base peak.

The i.r. spectra of all the cyclopropanes showed the absence of olefinic material. All except pentachlorocyclopropane showed a medium strength band between 9.54 and 9.99 μ , in agreement with the extensive studies reported recently.²² No other common bands could be found. The n.m.r. spectra are summarised in Table 1. Increasing halogen substitution of the cyclopropane ring leads, as expected, to decreasing shielding of the remaining hydrogens.

Olefins. The polychloropropenes and dichlorobutenes examined also showed recognisable parent ions; the base peak was formed by loss of chlorine from the propenes, but of HCl₂ from the butenes; loss of chlorine was also important here. The i.r. spectra are in accord with those of previously reported chloro-olefins.^{10,23} Olefins containing vinylic chlorine show bands at 6.02–6.20 μ . The band is usually strong in those containing terminal dichloromethylene groups. N.m.r.

¹⁹ A. Roedig, R. Manger, and S. Schödel, *Chem. Ber.*, 1960, **93**, 2294; C. Raulet and M. Levas, *Compt. rend.*, 1962, **255**, 1406.

²⁰ G. C. Robinson, *J. Org. Chem.*, 1968, **33**, 607.

²¹ V. Franzen, *Annalen*, 1959, **627**, 22; J. N. Bradley and A. Ledwith, *J. Chem. Soc.*, 1961, 1495.

spectra were sometimes misleading, since the hydrogen of a dichloromethyl group is so deshielded by the chlorine atoms that the resonance signal appears in

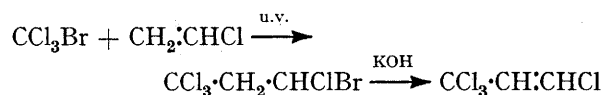
TABLE 1

¹H N.m.r. shifts of 1,1-dichlorocyclopropanes

Substituents at		Chemical shift ^a of ring hydrogens at	
C-2	C-3	C-2	C-3
H ₂	H ₂	1.6	1.6
HCl	H ₂	3.4	1.8
Cl ₂	H ₂		2.2
HCl	HCl ^b	3.51	3.51
HCl	HCl ^c	3.79	3.79
Cl ₂	HCl		3.89
HMe ^d	H ₂	1.0	1.6
HF ^e	H ₂	5.3	2.4
HCF ₃ ^f	H ₂	2.5	2.1
HCF ₃ ^g	HCF ₃ ^g	3.07	3.07
ClCH ₂ Cl ^h	H ₂		4.02
:CH ₂ ⁱ	H ₂		2.14

^a In p.p.m. downfield from tetramethylsilane. ^b *trans*-Isomer. ^c *cis*-Isomer. ^d $\delta(\text{CH}_3)$ 1.3. ^e $\delta(\text{F})$ 127 p.p.m. to high field of external trifluoroacetic acid (TFA). ^f $\delta(\text{CF}_3)$ 14.3 p.p.m. to low field of external TFA. ^g $\delta(\text{CF}_3)$ 13.5 p.p.m. to low field of external TFA. ^h $\delta(\text{CH}_2\text{Cl})$ 2.03. ⁱ $\delta(\text{CH}_2)$ 5.9.

the region usually assigned to vinylic hydrogen. In 1,1,3,3-tetrachloropropene the vinylic and dichloromethyl hydrogens have the same chemical shift. Consequently, suspected reaction products were unambiguously synthesised wherever possible when spectra were not available for comparison. For instance, 1,3,3,3-tetrachloropropene was prepared by the following route:



The possibility that this had undergone allylic rearrangement was excluded by its n.m.r. spectrum.

EXPERIMENTAL

Standard high-vacuum transfer techniques were used whenever possible. N.m.r. spectra were recorded at 35° with a Perkin-Elmer R10 spectrometer, at 60.0 Mc./sec. for ¹H and at 56.46 Mc./sec. for ¹⁹F for neat liquid samples. (d, doublet; t, triplet; q, quartet). δ_{TMS} Values are in p.p.m. to low field of tetramethylsilane; δ_{TFA} values are in p.p.m. to high field of trifluoroacetic acid. Mass spectra were obtained with an A.E.I. model MS2H instrument. Molecular weights were obtained by Regnault's method where practicable. Those obtained from mass spectrometry are indicated thus (MS). In such cases, the molecular weight (found and calculated) is given for the molecule containing entirely the most abundant isotopes.

1,1-Dichlorocyclopropane.—(a) Chlorine and an excess of cyclopropane were irradiated as described previously.⁴ The crude product was washed (aq. NaHCO₃ and water), dried (anhyd. Na₂CO₃) and distilled to give 1,1-dichlorocyclopropane, b.p. 76°/761 mm., n_D^{25} 1.4372 (lit.,⁴ b.p. 75°/760 mm., n_D^{25} 1.4377).

²² H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, 1966, **31**, 295.

²³ (a) C. J. Pennino, *J. Org. Chem.*, 1955, **20**, 530; (b) J. R. Shelton and L.-H. Lee, *J. Org. Chem.*, 1958, **23**, 1876.

(b) Trichloromethyltrifluorosilane (9.1 g., 44.3 mmoles) and ethylene (5.0 g., 177 mmoles) were heated (140°; 24 hr.) in a sealed Pyrex bulb (5 l.). Distillation of the volatile material in the vacuum system gave 1,1-dichlorocyclopropane (3.8 g., 78%) (Found: C, 32.3; H, 3.9; Cl, 64.9%; *M*, 110. Calc. for C₃H₄Cl₂: C, 32.4; H, 3.6; Cl, 64.0%; *M*, 111), identical with that prepared in (a).

Substituted 1,1-Dichlorocyclopropanes.—The following compounds were prepared as in (b) above, by use of the appropriate olefin (6 mol.) and trichloromethyltrifluorosilane (1 mol.): 1,1,2-trichlorocyclopropane (78%) [Found: C, 24.8; H, 2.2; Cl, 72.7%; *M*, 144 (MS). Calc. for C₃H₃Cl₃: C, 24.8; H, 2.1; Cl, 73.2%; *M*, 144], b.p. 123.5°/760 mm., *n*_D²⁵ 1.4780 (lit.,⁴ b.p. 124°/763 mm., *n*_D²⁵ 1.4782); 1,1,2,2-tetrachlorocyclopropane (70%) [Found: C, 20.1; H, 1.2; Cl, 78.8%; *M*, 178 (MS). Calc. for C₃H₂Cl₄: C, 20.0; H, 1.1; Cl, 78.9%; *M*, 178], b.p. 145.5°/758 mm., *n*_D²⁵ 1.4970 (lit.,⁴ b.p. 145.8°/760 mm., *n*_D²⁵ 1.4976); pentachlorocyclopropane (71%) [Found: C, 16.9; H, 0.5; Cl, 82.8%; *M*, 212 (MS). Calc. for C₃HCl₅: C, 16.8; H, 0.5; Cl, 82.6%; *M*, 212], b.p. 53°/7 mm., shown by n.m.r. to contain 1,1,3,3,3-pentachloropropene (ca. 20%); 1,1,2-trichloro-2-(chloromethyl)cyclopropane (71%) [Found: C, 24.7; H, 2.1; Cl, 73.2%; *M*, 192 (MS). C₄H₄Cl₄ requires C, 24.7; H, 2.1; Cl, 73.2%; *M*, 192], b.p. 85°/25 mm.; 1,1-dichloro-2-methylcyclopropane (93%) (Found: C, 38.6; H, 5.0; Cl, 57.0%; *M*, 125. C₄H₆Cl₂ requires C, 38.4; H, 4.8; Cl, 56.8%; *M*, 125), b.p. 100.5°/760 mm.; 1,1-dichloro-2-fluorocyclopropane (96%) [Found: *M*, 130. Calc. for C₃H₃Cl₂F: *M*, 129], identical with an authentic sample;²⁴ 1,1-dichloro-2-trifluoromethylcyclopropane (85%) (Found: C, 26.2; H, 1.7; Cl, 41.4%; *M*, 178. Calc. for C₄H₃Cl₂F₃: C, 26.8; H, 1.7; Cl, 39.6%; *M*, 179), b.p. 102°/760 mm. [g.l.c. and n.m.r. showed no impurity, but the microanalysis suggests the presence of tetrachloroethylene (ca. 4%); and 1,1-dichloro-2-*trans*-3-bistrifluoromethylcyclopropane (40%) (Found: *M*, 254. Calc. for C₅H₂Cl₂F₆: *M*, 247), identical with an authentic sample.²⁵

Reaction of Trichloromethyltrifluorosilane with *cis*-1,2-Dichloroethylene.—(a) *Alone.* Trichloromethyltrifluorosilane (7.9 g., 38.6 mmoles) and *cis*-1,2-dichloroethylene (18.5 g., 191 mmoles), heated (140°; 24 hr.) in a sealed bulb (5 l.), gave a mixture (16.0 g.) of *cis*- and *trans*-1,2-dichloroethylene (ca. 3 : 2 by g.l.c.), 1,1,2-*cis*,3-tetrachlorocyclopropane (1.92 g., 28%) [Found: C, 20.2; H, 1.2; Cl, 78.7%; *M*, 178 (MS). C₃H₂Cl₄ requires C, 20.0; H, 1.1; Cl, 78.9%; *M*, 178], and 1,1,2-*trans*,3-tetrachlorocyclopropane (2.90 g., 42%) [Found: C, 20.0; H, 1.2; Cl, 78.5%; *M*, 178 (MS)], separated by g.l.c. (6 m. silicone oil at 150°). Since *cis*-1,2-dichloroethylene is isomerised²⁶ by chlorine atoms, it seemed likely that the apparent non-stereospecificity of the addition of dichlorocarbene was due to prior isomerisation of the olefin. A control experiment showed that the olefin was not isomerised by the mixed silicon halides formed in the reaction. However, when the olefin (1.00 g., 10.3 mmoles) and bromotrichloromethane (0.20 g., 1.0 mmole) were kept (24 hr.) at 140°, the products were a mixture (1.10 g.) of *cis*- and *trans*-1,2-dichloroethylene (3 : 2 by g.l.c.), contaminated with a little unidentified material, and bromotrichloromethane (0.10 g.). Carbon-silicon bond

in trichloromethyltrifluorosilane takes place⁵ to a small extent under the reaction conditions, and presumably provides sufficient trichloromethyl radicals to promote the isomerisation. Addition of toluene to the reaction mixture reduced the isomerisation and facilitated g.l.c. separation of the major cyclopropane.

(b) *In the presence of toluene.* Trichloromethyltrifluorosilane (2.3 g., 11.1 mmoles), *cis*-1,2-dichloroethylene (6.5 g., 66.4 mmoles), and toluene (1.0 g., 11.1 mmoles), heated (140°, 24 hr.) in a bulb (2 l.), gave 1,1,2-*cis*,3-tetrachlorocyclopropane (1.42 g., 71%), and 1,1,2-*trans*,3-tetrachlorocyclopropane (0.13 g., 6%), identified by g.l.c., recovered toluene, and *cis*-1,2-dichloroethylene containing a trace of the *trans*-isomer.

Reaction of Trichloromethyltrifluorosilane with *trans*-1,2-Dichloroethylene.—(a) *Alone.* Reaction with the *trans*-olefin similarly gave a mixture of *cis*- and *trans*-1,2-dichloroethylene, and a mixture (78%) of *cis*- and *trans*-1,1,2,3-tetrachlorocyclopropanes (4 : 5 by g.l.c.).

(b) *In the presence of toluene.* Reaction as in (b) above gave 1,1,2-*trans*,3-tetrachlorocyclopropane (1.37 g., 69%) and the *cis*-isomer (0.07 g., 3%), together with *trans*-1,2-dichloroethylene (86%) containing the *cis*-olefin (ca. 5%), and recovered toluene.

1,1,2-Trichloro-2-(chloromethyl)cyclopropane.—Trichloromethyltrifluorosilane (5.5 g., 26.9 mmoles) and allene (6.5 g., 161 mmoles) were heated (140°; 24 hr.) in a sealed bulb (5 l.). Distillation in the vacuum system, followed by g.l.c. separation (2 m. DNP at 90°) of the fraction which condensed at -78°, gave 1,1-dichloro-2-methylenecyclopropane (1.25 g., 38%) [Found: *M*, 122 (MS). Calc. for C₄H₄Cl₂: *M*, 122], identified by its i.r. spectrum (C=CH₂ at 5.55, 5.75, and 11.0 μ, cf. 5.6—5.8 and 11 μ for methylenecyclopropane²⁷ and 5.51, 5.66, and 11.05 μ for 1-methylenecyclopropane²⁸) and by analysis of its n.m.r. spectrum. The spectra are in agreement with those reported⁸ for the product of the reaction of allene with bromodichloromethyl(phenyl)mercury, but under high resolution the 'three triplets' reported⁸ at δ_{TMS} 6.03, 5.62, and 2.1 are resolved into a triplet (3.0 c./sec.) of doublets (ca. 0.8 c./sec.) (1H), a triplet (2.6 c./sec.) of doublets (ca. 0.8 c./sec.) (1H), and a doublet (3.0 c./sec.) of doublets (2.6 c./sec.) (2H) in which the two centre bands are barely resolved, for the ring hydrogens; this confirms the structure.

The minor product from the g.l.c. separation (0.50 g., 15%) [Found: *M*, 122 (MS)] showed a singlet in the n.m.r. (δ_{TMS} 1.53 p.p.m.).

1,1-Dichloro-2-methylenecyclopropane (0.30 g., 2.5 mmoles) and carbon tetrachloride (5 ml.) were condensed at -196° into an ampoule containing chlorine (2.5 mmoles), and the mixture was warmed slowly to room temperature. Removal of the solvent left 1,1,2-trichloro-2-(chloromethyl)cyclopropane (0.21 g., 43%), identical with that prepared from trichloromethyltrifluorosilane and 2,3-dichloropropene.

Pyrolysis of 1,1-Dichlorocyclopropane.—1,1-Dichlorocyclopropane (5.00 g., 45.0 mmoles) was pyrolysed in an unpacked silica tube (i.d. 0.8 cm., heated length 44 cm.) at ca. 2 mm. and 650°. The products were separated by distillation into (i) a mixture (0.25 g., 6.7 mmoles) of hydrogen chloride (95%) and allene (5%); (ii) a mixture (0.14 g.)

²⁴ J. M. Birchall, G. S. Farrow, and R. N. Haszeldine, unpublished results.

²⁵ J. M. Birchall, R. N. Haszeldine, and P. Tissington, unpublished results.

²⁶ C. Steel, *J. Phys. Chem.*, 1960, **64**, 1588.

²⁷ J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 1953, **75**, 3344.

²⁸ J. H. Atherton and R. Fields, *J. Chem. Soc. (C)*, 1968, 1507.

shown by comparison of its i.r. spectrum and g.l.c. retention times with those of authentic compounds to contain 3-chloropropyne, 1,1-dichloroethylene, and possibly chloroallene; (iii) unchanged 1,1-dichlorocyclopropane (2.87 g., 57%); and (iv), separated from (iii) by preparative g.l.c., 2,3-dichloropropene (1.61 g., 32%) [Found: C, 32.2; H, 3.7; Cl, 63.9%; M , 110. Calc. for $C_3H_4Cl_2$: C, 32.4; H, 3.6; Cl, 64.0%; M , 111], identical with an authentic sample.

Pyrolysis of 2,3-Dichloropropene.—2,3-Dichloropropene (2.39 g., 21.7 mmoles) was similarly pyrolysed at 630°, to give hydrogen chloride (0.08 g., 2.2 mmoles), 2,3-dichloropropene (2.22 g., 93%), 3-chloropropyne (0.02 g., 1%), and the component tentatively identified above as chloroallene (0.04 g., 2%).

Pyrolysis of Cyclopropanes.—The substituted cyclopropanes were pyrolysed as described above.

(a) 1,1,2-Trichlorocyclopropane (2.24 g., 15.4 mmoles) at 650° gave hydrogen chloride (0.12 g.), 1,1,3-trichloropropene^{15,23b} (1.87 g., 83%) (Found: C, 25.0; H, 2.3; Cl, 73.0%; M , 145. Calc. for $C_3H_3Cl_3$: C, 24.8; H, 2.1; Cl, 73.2%; M , 145), unidentified material (0.12 g.), and a little carbon. The n.m.r. spectrum of 1,1,2-trichloropropene showed a triplet (J 8.0 c./sec.), δ_{TMS} 6.1 (=CH) and a doublet (J 8.0 c./sec.), δ_{TMS} 4.1 (CH_2Cl gem to vinylic hydrogen), confirming the structure.

(b) 1,1,2,2-Tetrachlorocyclopropane (1.58 g., 8.8 mmoles) at 550° gave hydrogen chloride (0.072 g.), unchanged 1,1,2,2-tetrachlorocyclopropane (0.55 g., 35%), 1,1,2,3-tetrachloropropene¹⁵ (0.78 g., 50%) [Found: C, 20.3; H, 1.3; Cl, 78.7%; M , 178 (MS). Calc. for $C_3H_2Cl_4$: C, 20.0; H, 1.1; Cl, 78.9%; M , 178], δ_{TMS} 4.74 (single unsplit band), and unidentified material (0.075 g.).

(c) 1,1,2-*cis*,3-Tetrachlorocyclopropane (0.87 g., 4.8 mmoles) at 500° gave hydrogen chloride (0.003 g.) and 1,1,3,3-tetrachloropropene (0.80 g., 92%) [Found: C, 20.1; H, 1.3; Cl, 78.8%; M , 178 (MS). Calc. for $C_3H_2Cl_4$: C, 20.0; H, 1.1; Cl, 78.9%; M , 178], b.p. 51°/19 mm. (lit.,¹⁹ 50–50.5°/18.5 mm.) δ_{TMS} 6.37 (single unsplit band), identical with a sample prepared by an established¹⁹ route. The 3,3-dichloroacraldehyde used in this synthesis showed doublets of equal intensity at δ_{TMS} 6.61 (J 6.0 c./sec., =CH) and 9.95 (J 6.0 c./sec., CHO).

At 410°, with the same contact time, the tetrachlorocyclopropane (0.187 g., 1.04 mmole) gave hydrogen chloride (trace), 1,1,3,3-tetrachloropropene (0.037 g., 20%), and recovered 1,1,2-*cis*,3-tetrachlorocyclopropane (0.148 g., 80%) containing none of the *trans*-isomer.

(d) 1,1,2-*trans*,3-Tetrachlorocyclopropane (0.60 g., 3.3 mmoles) at 500° gave hydrogen chloride (0.002 g.) and 1,1,3,3-tetrachloropropene (0.56 g., 93%).

(e) Pentachlorocyclopropane (1.19 g., 5.6 mmoles), containing 1,1,3,3,3-pentachloropropene (20%), at 540° gave hydrogen chloride (0.004 g.), pentachlorocyclopropane (0.11 g., 9%), and 1,1,3,3,3-pentachloropropene (1.01 g., 85%) [Found: C, 16.7; H, 0.5; Cl, 82.9%; M , 212 (MS). Calc. for C_3HCl_5 : C, 16.8; H, 0.5; Cl, 82.6%; M , 212], b.p. 62°/12 mm. (lit.,⁶ 60–61°/11 mm.), δ_{TMS} 6.88(s), identical with that prepared by an established route.⁶

(f) 1,1,2-Trichloro-2-(chloromethyl)cyclopropane (2.59 g., 13.3 mmoles) at 580° gave hydrogen chloride (0.15 g.), 1,1,3-trichloro-2-(chloromethyl)propene (1.48 g., 57%), identical with that described below, and a mixture (0.56 g.)

¹⁹ M. G. Barlow, unpublished results.

[Found: M , 156 (MS). Calc. for $C_4H_3Cl_3$: M , 156] tentatively identified by its n.m.r. spectrum [singlets at δ_{TMS} 7.16, ($CH_2=C$) and 6.04 ($CH=C$)] as 1,1,3-trichlorobuta-1,3-diene (30%) and 1,2,3-trichlorobuta-1,3-diene (47%) [δ_{TMS} 5.76 and 5.60 (AB pattern, J_{AB} ca. 2 c./sec., $CH_2=C$) and 6.40 (s, $CHCl:C$)], together with unidentified material. Isomers with hydrogen atoms *cis* or *trans* to one another were precluded by the absence of any couplings >3 c./sec.

(g) 1,1-Dichloro-2-methylcyclopropane (1.19 g., 9.5 mmoles) at 500° gave hydrogen chloride (0.06 g.), 2-chlorobuta-1,3-diene (0.11 g., 13%), a mixture separated by g.l.c. (2 m. DNP at 80°) to give (i) 2,3-dichlorobut-1-ene (0.34 g., 29%) [Found: M , 124 (MS). Calc. for $C_4H_6Cl_2$: M , 124], δ_{TMS} 2.15 (d, J 6.8 c./sec., $CH_3\cdot CH$), 5.12 (qd, J , 6.8 and ca. 0.6 c./sec., $CH\cdot CH_3$), and 5.83 and 6.07 (AB pattern, J_{AB} 1.8 c./sec., with further doublet splitting, J ca. 0.6 c./sec. in the high-field bands, $:CH_2$); (ii) 1,2-dichlorobut-2-ene (0.28 g., 24%) [Found: M , 124 (MS)], δ_{TMS} 2.23 (dt, J 6.7 and ca. 1 c./sec., $CH_3\cdot CH$), 6.43 (qt, J 6.7 and ca. 1 c./sec., $CH_3\cdot CH$), and 4.58 (2H, quintet, J ca. 1 c./sec., CH_2Cl); and (iii) unchanged starting material (0.38 g., 32%).

(h) 1,1-Dichloro-2-fluorocyclopropane (0.63 g., 4.9 mmoles) at 650° gave hydrogen chloride (0.03 g.) and a mixture (0.55 g., 87%) (Found: M , 128. Calc. for $C_3H_3Cl_2F$: M , 129) unresolved by g.l.c., but shown by analysis of the n.m.r. spectra²⁹ to be a mixture of 2,3-dichloro-3-fluoropropene (57%), and equimolar amounts of *cis*- and *trans*-2,3-dichloro-1-fluoropropene (29%). The spectral data are shown in Table 2.

TABLE 2

N.m.r. parameters of the product from 1,1-dichloro-2-fluorocyclopropane

Chemical shift ^a	Splittings (c./sec.)	Assignment
¹ H		
5.95	2.4 (AB), 2.0 (d)	} $H_2C=C^b$
6.20	2.4 (AB), 0.9 (d), 0.9 (d)	
6.90	49 (d), 0.9 (d)	$-CHFCl^b$
7.18	79.5 (d), 0.5 (t)	$HFC=C^c$
4.56	4.0 (d), 1.0 (t)	CH_2Cl^c
7.46	76.8 (d), 0.5 (t)	$HFC=C^d$
4.70	3.6 (d), 0.5 (t)	CH_2Cl^d
¹⁹ F		
+54	49 (d), 2 (d), 0.9 (d)	$CHFCl^b$
+45.3	79.5 (d), 3.6 (t)	$HFC=C^c$
+45	76.8 (d), 4.0 (t)	$HFC=C^d$

^a For ¹H, δ_{TMS} ; for ¹⁹F, δ_{TFA} . ^b In $H_2C:CCI-CHClF$. ^c In *cis*- or *trans*- $CHF:CCI-CH_2Cl$. ^d In *trans*- or *cis*- $CHF:CCI-CH_2Cl$.

(i) 1,1-Dichloro-2-trifluoromethylcyclopropane (1.28 g., 7.15 mmoles) at 650° gave hydrogen chloride (0.04 g.) and a mixture (1.1 g., 86%) (Found: M , 177. Calc. for $C_4H_3Cl_2F_3$: M , 179) identified by i.r. ($C=C$ at 6.11s μ) and n.m.r. [δ_{TMS} 6.27 (t, J 7.2 c./sec., $:CH$) and 3.35 (qd, J 10.5 and 7.2 c./sec., CH_2), δ_{TFA} -11.6 (t, J 10.5 c./sec., CF_3)] as mainly 1,1-dichloro-4,4-trifluorobut-1-ene, with minor impurities.

(j) 1,1-Dichloro-2-*trans*,3-bis(trifluoromethyl)cyclopropane (1.01 g., 4.1 mmoles) at 650° gave hydrogen chloride (0.03 g.) and a mixture (0.93 g.) unresolved by g.l.c., but shown by n.m.r. to contain the cyclopropane (ca. 35%), 1,1,1,5,5,5-hexafluoro-3,4-dichloropent-2-ene (ca. 30%), (doublets, J 6 and 7 c./sec. at δ_{TFA} -5.0 and -16.2, together

with quartets, J 6 and 7 c./sec. at δ_{TMS} 6.65 and 6.97, and unidentified material.

Static Pyrolysis of 1,1,2,2-Tetrachlorocyclopropane.—1,1,2,2-Tetrachlorocyclopropane (0.50 g., 2.8 mmoles) was heated (210°; 72 hr.) in a sealed tube (50 ml.). The volatile products were hydrogen chloride (0.15 mmole), the cyclopropane (0.31 g., 61%), and 1,1,2,3-tetrachloropropene (0.14 g., 28%). At 250° (200 hr.) extensive carbonisation took place.

Preparation of 1,3,3,3-Tetrachloropropene.—U.v. irradiation (16 hr.; silica vessel) of a mixture of bromotrichloromethane (40.0 g., 202 mmoles) and vinyl chloride (3.1 g., 50 mmoles) gave 3-bromo-1,1,1,3-tetrachloropropene (7.6 g., 58%), b.p. 126°/83 mm., and unchanged starting materials. The n.m.r. spectrum consisted of a doublet (δ_{TMS} 4.65) and a triplet (δ_{TMS} 6.83, J 5.5 c./sec.). Cold (0°) ethanolic potassium hydroxide (1.2 g. in 60 ml.) was added (1 hr.) to 3-bromo-1,1,1,3-tetrachloropropene (5.0 g., 19.2 mmoles) vigorously stirred at 0°. After a further 1 hr., water (50 ml.) was added, and the organic layer was separated, dried (CaCl_2), and distilled to give 1,3,3,3-tetrachloropropene (2.7 g., 79%) [Found: C, 20.9; H, 1.4; Cl, 77.7%; M , 178 (MS). Calc. for $\text{C}_3\text{H}_2\text{Cl}_4$: C, 20.0; H, 1.1; Cl, 78.9%; M , 178], b.p. 92°/122 mm., which analysis suggested might contain some impurity, although it was apparently pure by g.l.c. and by n.m.r. which showed an AB pattern (J_{AB} 13.0 c./sec.) with centre at δ_{TMS} 7.29, confirming the structure $-\text{CH}:\text{CH}-$.

1,1,3-Trichloro-2-chloromethylpropene.—Chloroform (11.0 g., 92 mmoles) and dry light petroleum (b.p. 60–80°; 30 ml.) were added slowly under nitrogen to a stirred suspension (0°) of triphenylphosphine (24.0 g., 92 mmoles) and potassium *t*-butoxide (10.4 g., 92 mmoles) in dry light petroleum. After a further 1 hr., a suspension of $\alpha\alpha'$ -dichloroacetone (6.4 g., 50 mmoles) in light petroleum (50 ml.) was added in portions, and the temperature of the mixture was allowed to rise to 20°. Filtration and distillation of the filtrate gave 1,1,3-trichloro-2-(chloromethyl)propene (1.9 g., 20%) [Found: C, 25.3; H, 2.1; Cl, 72.9%;

M , 192 (MS). $\text{C}_4\text{H}_4\text{Cl}_4$ requires C, 24.7; H, 2.1; Cl, 73.2%; M , 192], b.p. 40°/1 mm. The n.m.r. spectrum contained only a single unsplit band at δ_{TMS} 4.44.

Reaction of Diazomethane with 1,1-Dichlorocyclopropane.—Gaseous diazomethane, generated from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in anisole, was dissolved at –20 to –30° in 1,1-dichlorocyclopropane (22 g.), and photolysed (500 w Hanovia lamp; Pyrex vessels) at 0–10°. Diazomethane (112 mmoles), estimated by reaction of an aliquot portion with benzoic acid, was used. Preparative g.l.c. (Autoprep; 6 m. silicone oil at 125°) gave 1,1-dichloro-2-methylcyclopropane (0.15 g., 1.2%), identical with that described above, and 1-chloro-1-(chloromethyl)cyclopropane (1.26 g., 9%) [Found: C, 38.7; H, 4.9; Cl, 57.0%; M , 124 (MS). $\text{C}_4\text{H}_6\text{Cl}_2$ requires C, 38.4; H, 4.8; Cl, 56.8%; M , 124], b.p. 127°/760 mm., δ_{TMS} 3.81 (s, CH_2Cl) and 1.20 (A_2B_2 pattern, ring hydrogens). An attempt to prepare this compound by reaction of 2,3-dichloropropene with methylene iodide and zinc-copper couple gave instead a low yield (11%) of a compound tentatively identified by mass spectrum [Found: M , 216 (MS). Calc. for $\text{C}_4\text{H}_6\text{ClI}$: M , 216, base peak at 89, $\text{C}_4\text{H}_6\text{Cl}$], n.m.r. [δ_{TMS} 2.85 (t, J 6 c./sec., CH_2), 3.30 (t, J 6 c./sec., CH_2Hal), and 5.28 (s, $\text{CH}_2=$)], and i.r. [λ_{max} 6.1 (C=C) and 5.8 and 11.3 ($=\text{CH}_2$) μ] as 2-chloro-4-iodobut-1-ene, b.p. 50°/20 mm.

Reaction of 1,1-Dichlorocyclopropane with Trichloromethyltrifluorosilane.—The silane (3.4 g., 16.7 mmoles) and 1,1-dichlorocyclopropane (11.0 g., 99.3 mmoles) were heated *in vacuo* in a Pyrex bulb (3 l.) at 200° for 24 hr. to give tetrachloroethylene (0.23 g., 17%), hexachloroethane (0.2 g., 9%), hexachlorocyclopropane (*ca.* 0.04 g., 3%), hexachloropropene (0.6 g., 45%), hexachlorobutadiene (*ca.* 0.05 g., 4%), and unchanged 1,1-dichlorocyclopropane (11.0 g., 100%).

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