Cyclopropane Chemistry. Part III.[1] Thermal Decomposition of Some Halogenopolyfluorocyclopropanes

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Thermal decomposition of pentafluoro-, perfluoro(methyl)-, 1,1-dichlorotrifluoro(trifluoromethyl)-, bromopentafluoro-, iodopentafluoro-, 1,2-dichlorotetrafluoro-, 1-chloro-1,2,2,3-tetrafluoro-, and 1,1,2-trifluoro-2-trifluoromethyl-cyclopropane, at temperatures in the range 170—250° in glass vessels, is described. The first three compounds decompose exclusively *via* the elimination of difluorocarbene, the last undergoes exclusive rearrangement to an olefin, and the remainder display both types of behaviour. The cyclopropanes were prepared from the appropriate olefins and either difluorotristrifluoromethylphosphorane or trifluoro(trichloromethyl)silane, or by reduction of a dichlorocyclopropane with tributyltin hydride. Application of this last method to 1,2-dichlorotetrafluorocyclopropane gave *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane: the preparation of 3-chloro-1,1,2-trifluoro-2-trifluoromethylcyclopropane from 1,1-dichlorotrifluoro(trifluoromethyl)cyclopropane is also described.

THE earlier papers in this series describe studies of the thermal decomposition of some polychlorocyclopropanes, which undergo rearrangement to isomeric propenes,[2] and of polychloropolyfluorocyclopropanes, which decompose predominantly *via* the expulsion of difluorocarbene.[1] The pyrolysis of a further group of cyclopropanes, each containing at least three fluorine atoms, has now been st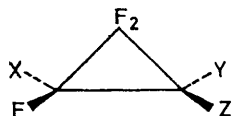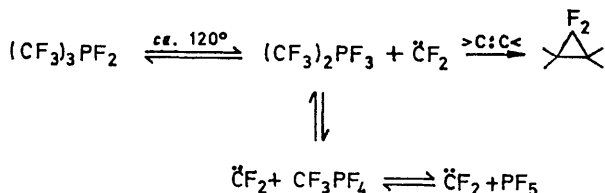udied with the objects of finding common ground between the two types of behaviour and of achieving a better understanding of the factors controlling the nature of the decomposition.

Preparation of the Cyclopropanes.—Pentafluoro- (I) (48%), bromopentafluoro- (II) (61%), iodopentafluoro- (III) (37%), and *cis–trans*-1,2-dichlorotetrafluoro-cyclopropane (IV) (68%), together with perfluoro(methylcyclopropane) (V) (42%), were prepared in the yields

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[1] Part II, J. M. Birchall, R. N. Haszeldine, and D. W. Roberts, *J.C.S. Perkin I*, 1973, 1071.

[2] R. Fields, R. N. Haszeldine, and D. Peter, *J. Chem. Soc. (C)*, 1969, 165.

stated by the reaction of difluorocarbene (from difluoro-tristrifluoromethylphosphorane) with the appropriate olefins.[1,3] The bromo- and iodo-compounds [(II) and (III)] are new, but the cyclopropanes (I), (IV), and (V)

$$(CF_3)_3PF_2 \overset{ca.\ 120°}{\rightleftharpoons} (CF_3)_2PF_3 + \overset{..}{C}F_2 \overset{>C:C<}{\longrightarrow}$$

$$\overset{..}{C}F_2 + CF_3PF_4 \rightleftharpoons \overset{..}{C}F_2 + PF_5$$

(I)   X = Y = F, Z = H
(II) X = Y = F, Z = Br
(III) X = Y = F, Z = I
(IV)a; X = Y = Cl, Z = F
     b; X = Z = Cl, Y = F

(V)   X = Y = F, Z = CF$_3$
(VI)a; X = Cl, Y = H, Z = F
    b; X = Cl, Y = F Z = H
(VII)a; X = Y = H, Z = F
     b; X = Z = H, Y = F

have been prepared previously, both from difluoro-diazirine[4] and from 1,2-epoxyhexafluoropropane.[5,6] The preparation of the dichloro-compounds (IV) from the phosphorane and 1,2-dichlorodifluoroethylene of un-specified stereochemistry has also been reported.[7]

We were unable to effect adequate separation of the cis–trans-1,2-dichlorodifluoroethylene used for our reaction with the phosphorane, but analysis by [19]F n.m.r. spectroscopy showed its composition to be 47% cis, 53% trans. The mixture of cyclopropanes formed is significantly richer in the trans-isomer (35% cis, 65% trans), but no detectable change in the isomeric composition of the large excess of recovered olefin occurs. Although this may indicate a preference for the addition of di-fluorocarbene to trans-1,2-dichlorodifluoroethylene, it seems more likely, in the light of Sargeant's investigation of the addition of difluorocarbene to the chloro-1,2-difluoroethylenes,[5] that the cis–trans-mixture of cyclo-propanes is approaching equilibrium proportions under the conditions employed during the preparation. Preparative separation of the cyclopropane isomers is known to be difficult,[4,5,7] and was not attempted during the work described here.

Reduction of the 1,2-dichlorotetrafluorocyclopropane mixture [(IVa) : (IVb) 35 : 65] with 1 mol. equiv. of tri-n-butyltin hydride[1,8] gives the known[5] 1-chloro-1,2,2,3-tetrafluorocyclopropanes [cis (VIa) : trans (VIb) 23 : 77, separable by g.l.c.] in 85% yield; use of 2 mol. equiv. of the hydride gives the new 1,1,2,3-tetrafluorocyclopropanes [(VIIa and b), again separable by g.l.c.] in 97% yield.

[3] W. Mahler, Inorg. Chem., 1963, 2, 230; J. Amer. Chem. Soc., 1962, 84, 4600.
[4] R. A. Mitsch, J. Heterocyclic Chem., 1964, 1, 271.
[5] P. B. Sargeant, J. Org. Chem., 1970, 35, 678.
[6] P. B. Sargeant and C. G. Krespan, J. Amer. Chem. Soc., 1969, 91, 415.

The ^{1}H and [19]F n.m.r. spectra of the trans-isomer (VIIb) are complex, but analysis of the spectra of the cis-isomer (VIIa),[9] and, particularly, the small value of the trans-HF coupling constant across the 2- and 3-positions [0·9 Hz; cf.[5] (VIa), $J_{trans\text{-}HF}$ 1·3; (VIb), $J_{cis\text{-}HF}$ 16·8 Hz], leaves little doubt that the structures have been correctly assigned.

Finally, 1,1-dichlorotrifluoro(trifluoromethyl)cyclo-propane (VIII) was obtained in 88% yield by the reaction of hexafluoropropene with dichlorocarbene from the pyrolysis of trichloromethyltrifluorosilane.[1] Reduction of the dichloro-compound (VIII) with 1 mol. equiv. of the reagent shown yields the 3-chloro-1,1,2-trifluoro-2-tri-fluoromethylcyclopropanes (IX), the two isomers of which were separated by g.l.c. but not on a scale sufficient to clarify their stereochemistry. Complete reduction of the C–Cl systems yields 1,1,2-trifluoro-2-trifluoromethyl-cyclopropane (X).

Pyrolysis of the Cyclopropanes.—The cyclopropanes (VIIa), (VIIb), and (IX) have not been prepared in amounts sufficient for further experiments, but the thermal decompositions of all the other cyclopropanes described here have been studied in glass vessels at temperatures in the region of 170—210° with each cyclo-propane completely in the vapour phase (Table). The precise reaction conditions used for each cyclopropane, determined from a series of preliminary experiments, were usually those which brought about sufficient decomposition for adequate separation and identification
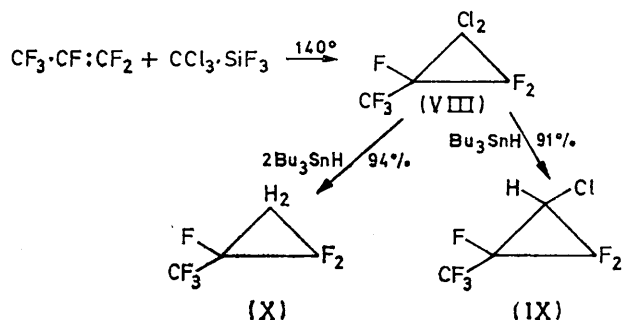
of the products, and no attempt has yet been made to obtain a rigorous order of reactivity.

All the cyclopropanes except the trifluoro(trifluoro-methyl) compound (X) decompose thermally, at least in part, by the carbenoid route (a) to give a halogeno-olefin and difluorocarbene. In each case, the former has been identified as the free olefin and the latter, following its reaction with the wall of the reaction vessel,[1] mainly as carbon monoxide and silicon tetrafluoride; some dimeris-ation to tetrafluoroethylene, which may itself undergo dimerisation and/or carbene addition, also occurs (see Table). No olefins which would be formed by the ejec-

[7] G. Camaggi and F. Gozzo, J. Chem. Soc. (C), 1970, 178.
[8] D. Seyferth, H. Yamagaki, and D. L. Alleston, J. Org. Chem., 1963, 28, 703.
[9] M. G. Barlow, R. Fields, and F. P. Temme, unpublished observations.

tion of carbenes other than difluorocarbene [path (b)] from any of the cyclopropanes described here have been detected. In addition, separate confirmation of the formation of difluorocarbene from pentafluorocyclopropane (I) and from perfluoro(methylcyclopropane) (V) is provided by the stereospecific formation of 1,1-difluoro-cis-2,3-dimethylcyclopropane (80—90% yield) when these cyclopropanes are allowed to decompose in obtained from the two olefins in a separate experiment at 250°.

Concurrent with carbenoid decomposition, all the cyclopropanes except (I), (V), and (VIII) undergo rearrangement to an isomeric propene [path (c)]. The products of this process, shown in the Table, are identified mainly by spectroscopic methods. 3-Bromo- and 3-iodo-pentafluoropropene, arising from cyclopropanes (II)

Pyrolysis of the cyclopropanes

Cyclopropane	Temp. (°C)	Time (h)	Init. press. (atm)	Decomp. (%)	CXF:CYZ (%)	Fate of $\ddot{C}F_2$ (%)	Rearrangement products (%)
(I) [a]	190	240	1·5	88	93	CO (43), C_2F_4 (39), cyclo-C_3F_6, C_4F_8 (6), $[CF_2]_n$	
(II)	170	100	3·0	56	14	CO (63), C_2F_4 (13)	CF_2:CF·CF_2Br (69)[f]
(III)	170	100	0·9	81	8	CO (trace)	CF_2:CF·CF_2I (78)[f]
(IVa and b) [b]	200	197	3·0	100	77	CO (64), C_2F_4, cyclo-C_3F_6, COF_2	cis-CFCl:CF·CF_2Cl (4), trans-CFCl:CF·CF_2Cl (12), CF_3·CF:CCl_2 (6)
(V) [c,d]	200	46	0·5	90	96	CO (76), C_3F_4 (4), cyclo-C_3F_6 (14), cyclo-C_4F_8, $[CF_2]_n$	
(VIa and b) [b,e]	250	167	1·1	100	64 [b]	CO (99), C_2F_4 (trace)	CHF:CF·CF_2Cl (36)
(VIII)	170	100	1·0	31	97	CO, C_2F_4, cyclo-C_3F_6	
(X)	202—240	526	0·7	89			CF_3·CF:CH·CHF_2 (100)

[a] Decomposition also studied in the presence of cis-but-2-ene (see text). [b] For cis : trans ratios see Experimental section. [c] Decomposition also studied in the presence of cis-but-2-ene, trans-but-2-ene, and ethylene. [d] W. Mahler (J. Amer. Chem. Soc., 1968, 90, 523) has also stated that this compound loses difluorocarbene exclusively on pyrolysis, but has provided no evidence for this observation. [e] Reaction vessel packed with glass wool; remainder in empty Pyrex tubes. [f] Unidentified compounds (ca. 17%) also formed. [g] Perfluorohexa-1,5-diene (7%) also formed, presumably by thermal coupling of the major product; traces of unidentified products also present.

the presence of a large excess of cis-but-2-ene [path (d)]; a similar reaction occurs between the perfluoro-compound (V) and trans-but-2-ene, and the yield of carbon monoxide
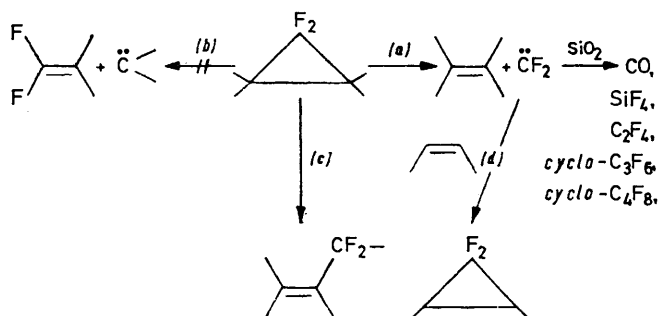

is reduced in these reactions to ca. 10% of the CF_2 produced.

The lower reactivity of ethylene towards difluorocarbene is reflected by an experiment in which perfluoro-(methylcyclopropane) was heated at 180—190° in the presence of an excess of this olefin; only 4% of the carbene was trapped as 1,1-difluorocyclopropane, the remainder yielding the usual products of decomposition and dimerisation. A small proportion (5%) of the hexafluoropropene formed during this experiment undergoes co-dimerisation with the ethylene to form 1,1,2-trifluoro-2-trifluoromethylcyclobutane (XI), the identity of which was confirmed by spectroscopic analysis of a specimen

and (III), respectively, are well established compounds, and the spectroscopic properties (particularly the [19]F n.m.r. spectra) of 1,1-dichlorotetrafluoropropene and of the two previously unreported 1,3-dichlorotetrafluoropropenes, the products from the rearrangement of cis-trans-1,2-dichlorotetrafluorocyclopropane (IVa and b), are in excellent agreement with the proposed structures.

However, although the base peak in the mass spectrum of the propenes formed during the isomerisation of cis-trans-1-chloro-1,2,2,3-tetrafluorocyclopropane (VIa and b) corresponds to $[M - H]^+$, suggesting the presence of an allylic hydrogen atom and hence the structure of cis-trans-1-chloro-1,2,3,3-tetrafluoropropene, the rather weak [19]F n.m.r. spectrum obtained indicates the presence of chlorodifluoromethyl rather than difluoromethyl groups (no gem-HF coupling in the allylic fluorine bands). The

(XI)
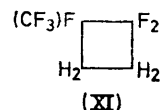
structure of cis-trans-3-chloro-1,2,3,3-tetrafluoropropene is therefore preferred for the product of this isomerisation, and the coupling constants observed for the more intense ^{19}F absorption indicate that the trans-isomer predominates. The position of the C:C stretching band (5·78 μm) in the i.r. spectrum of the mixture is consistent with this interpretation, but does not rule out the alternative

1-chloro-compound (cf. $CF_3 \cdot CF \colon CHF$,[10] 5·74 μm; $CF_3 \cdot CF \colon CFCl$,[11] 5·82 μm).

The product from the isomerisation of 1,1,2-trifluoro-2-trifluoromethylcyclopropane (X) shows a C:C stretching band at 5·80 μm (cf. $CF_3 \cdot CF \colon CH \cdot CF_3$:[12] cis 5·81, trans 5·74 μm). The base peak in the mass spectrum corresponds to loss of hydrogen from the parent, and strong peaks of equal intensity appear at m/e 69 ($\overset{+}{C}F_3$) and 51 ($\overset{+}{C}HF_2$). The weak [19]F n.m.r. spectrum confirms the presence of a CF_3 group (band at +5·6 p.p.m. from external trifluoroacetic acid). Two formulations, $CF_3 \cdot CF \colon CH \cdot CHF_2$ and $CHF_2 \cdot CF \colon CH \cdot CF_3$, are consistent with these results and the former is strongly preferred since its formation requires the migration only of hydrogen during the rearrangement; the much less probable migration of both hydrogen and trifluoromethyl is required for formation of the latter.

Discussion.—The observation that the ejection of only difluorocarbene occurs during carbenoid decomposition of all the cyclopropanes described here is consistent with the known stability of this entity in the gas phase [1] and in solution,[13] and requires little further comment. However, in view of the observation that the thermal decomposition of 1,1,2-trichlorotrifluorocyclopropane at 200° leads to the formation of some 1,1-dichlorodifluoroethylene, implying that chlorofluorocarbene is ejected to a limited extent (17%),[1] it is a little surprising that no comparable products are observed during the decomposition of 1,2-dichlorotetrafluorocyclopropane (IVa and b).

Although none of the rearrangement products observed here provides a completely unambiguous indication of the nature of the migration which has occurred [e.g. the olefin $CHF \colon CF \cdot CF_2Cl$ could in principle be formed from the parent cyclopropane (VI) by the migration either of fluorine from or of chlorine to the CF_2 group], the results are completely consistent with the concerted mechanism suggested earlier.[1,2] One of the main factors affecting

(XII)
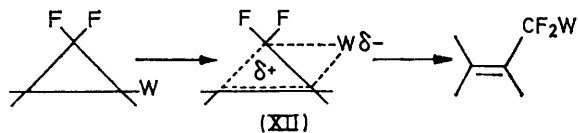
the formation of the transition state (XII) would be expected to be the strength of the bond to the migrating group (W), and consequently it is likely that the migration of bromine is involved during the rearrangement of (II), of iodine during the rearrangement of (III), mainly of chlorine in (IV), of chlorine in (VI), and of hydrogen in (X). In each case the migration would be towards the CF_2 group, the most electron-deficient centre in each molecule, perhaps implying the charge separation indicated in the transition state. The migration of

fluorine as well as chlorine must be involved in the formation of the minor product (XIII) during the re-

$CF_3 \cdot CF \colon CCl_2$

(XIII)
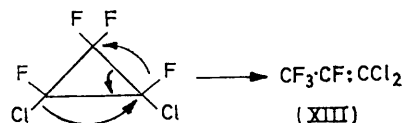
arrangement of dichlorotetrafluorocyclopropane (VI), and the reason for this unexpected behaviour is at present unclear.

As with the series of polyfluorocyclopropanes studied earlier,[1] it is difficult at this stage to provide a simple explanation of the variations in stability and in the ratio of carbenoid decomposition to rearrangement. Some observations [e.g. the high proportion of rearrangement in the reactions of the bromo- and iodo-compounds, (II) and (III)] are easy to interpret, but others [e.g. the apparently greater effect of the presence of hydrogen than of chlorine in favouring rearrangement over carbenoid fission [cf. (VIII) and (X), see Table] are more obscure. The possibility that the rearrangement products are formed in part via carbenoid fission followed by carbene attack at the vinylic position cannot be excluded yet. We anticipate that some of these points will be clarified by the more rigorous kinetic study which is in progress.

EXPERIMENTAL

Air was rigorously excluded from all reactions carried out in sealed vessels. Spectroscopic and chromatographic techniques have been described previously.[1] I.r. spectra were recorded for compounds in the vapour state and n.m.r. spectra for neat liquids; recorded ^{19}F chemical shifts are positive to high field of external trifluoroacetic acid and ^{1}H values to high field of external benzene, with coupling constants quoted as moduli. Molecular weights were determined by Regnault's method.

Cyclopropanes from the Phosphorane.—(a) *Bromopentafluorocyclopropane* (II). Bromotrifluoroethylene (10·63 g, 66·0 mmol) and difluorotristrifluoromethylphosphorane (36·98 g, 134·0 mmol) [3] were kept at 110—120° for 53 h in a 200 ml stainless steel rocking autoclave. Volatile products were fractionated *in vacuo* to give decomposition products of the phosphorane (23·3 g), bromotrifluoroethylene (3·95 g, 37% recovery), a mixture of unidentified components (0·26 g), and a fraction (6·66 g) which was treated with aqueous 2M-sodium hydroxide to hydrolyse the phosphorus derivatives it contained. The recovered product (6·52 g) was treated with an excess of bromine (the excess being removed by the addition of mercury) to remove bromotrifluoroethylene, then redistilled to give pure *bromopentafluorocyclopropane* (6·44 g, 61% based on $CF_2 \colon CFBr$ consumed) (Found: C, 17·1%; M, 210. C_3BrF_5 requires C, 17·1%; M, 211), b.p. 20·5°, $\lambda_{max.}$ 6·65, 7·50, 7·86, 8·16, 9·53, 12·20, and 15·40 μm, m/e 162, 160 (C_3BrF_3), 131 ($C_3F_5 + CBrF_2$), 112 ($C_3F_4 + CBrF$), 110 (CBrF), 93

[10] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1953, 1592.
[11] J. H. Fried and W. T. Miller, *J. Amer. Chem. Soc.*, 1959, **81**, 2080.

[12] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, unpublished observations; T. J. Maynard, *J. Org. Chem.*, 1963, **28**, 112.
[13] J. Hine and S. J. Ehrenson, *J. Amer. Chem. Soc.*, 1958, **80**, 824.

(C_3F_5 + CBr), 81 (C_2F_3 + Br), 69 (CF_3), and 31 (CF); the [19]F n.m.r. spectrum has been reported previously.[14]

(b) *Iodopentafluorocyclopropane* (III). Iodotrifluoroethylene (3·70 g, 17·8 mmol) and the phosphorane (1·63 g, 5·9 mmol) were kept in a sealed 1 l Pyrex flask at 125° for 20 h. Fractionation *in vacuo* then gave iodotrifluoroethylene (2·27 g, 61% recovery) and a fraction purified by g.l.c. (4 m column of Silicone MS550; 33°) to give *iodopentafluorocyclopropane* (1·70 g, 37% based on phosphorane) (Found: C, 14·0%; *M*, 256. C_3F_5I requires C, 14·0%; *M*, 258), b.p. 48·5°, $\lambda_{max.}$ 6·69, 7·58, 7·88, 8·20, 9·90, 12·20, 12·25, and 15·75 μm, *m/e* 208 (C_2F_3I), 158 (CFI), 131 (C_3F_5), 127 (I), 112 (C_3F_4), 93 (C_3F_3), 81 (C_2F_3), 69 (CF_3), and 31 (CF); the [19]F n.m.r. spectrum has been reported previously.[14]

(c) *1,2-Dichlorotetrafluorocyclopropane* (IV). The phosphorane (3·545 g, 12·8 mmol) and *cis–trans*-1,2-dichlorodifluoroethylene (19·57 g, 147 mmol; *cis* : *trans* 47 : 53 by n.m.r.), kept at 105—115° for 100 h in the 200 ml autoclave, similarly gave *cis–trans*-1,2-dichlorotetrafluorocyclopropane (4·80 g, 68%) (Found: C, 19·6%; *M*, 183. Calc. for $C_3Cl_2F_4$: C, 19·7%; *M*, 183), b.p. 41° (lit.,[7] 40—41·5°). The n.m.r. spectrum of the product was in agreement with reported data[5,15] and indicated a *cis* : *trans* ratio of 35 : 65. The *cis* : *trans* ratio of the recovered olefin (15·3 g, 79%) was virtually unchanged.

(d) *Pentafluorocyclopropane* (I) *and perfluoro(methylcyclopropane)* (V). These were prepared and purified by the method described in (a). The spectra of both pentafluorocyclopropane (48% yield) (Found: C, 27·6; H, 0·9%. Calc. for C_3HF_5: C, 27·3; H, 0·7%) and perfluoro(methylcyclopropane) (42% yield) (Found: C, 24·2%; *M*, 199. Calc. for C_4F_8: C, 24·0%; *M*, 200), b.p. −9°, were in full agreement with reported data.[4,5] Final traces of hexafluorocyclopropane were removed from the pentafluorocompound by g.l.c. (4 m column of Kel-F oil; 21°).

1,1-Dichlorotrifluoro(trifluoromethyl)cyclopropane (VIII).— Hexafluoropropene (4·60 g, 30·6 mmol) and trifluoro(trichloromethyl)silane (1·79 g, 8·84 mmol) were kept in a sealed 1 l Pyrex flask at 155° for 18 h. Repeated fractionation *in vacuo* gave pure (g.l.c.) *1,1-dichlorotrifluoro(trifluoromethyl)cyclopropane* (1·80 g, 88%) (Found: C, 20·3%; *M*, 231. $C_4Cl_2F_6$ requires C, 20·6%; *M*, 233), b.p. 48°, $\lambda_{max.}$ 6·90, 7·48, 7·81, 8·16, 8·33, 9·43, 9·66, 9·71, 10·58, 12·22, 12·66, 12·99, 13·55, and 15·04 μm, n.m.r. $ABMX_3$ system with δ_{AB} 65·0, δ_M 119·4, and δ_X −8·4 p.p.m.; its mass spectrum shows a weak parent ion at *m/e* 236, 234, and 232.

Reduction of the Dichlorocyclopropanes.—(a) *1,2-Dichlorotetrafluorocyclopropane* (IV) *with* 1 *mol. equiv. of tributyltin hydride.* Tri-n-butyltin hydride (2·56 g, 8·8 mmol)[16] and *cis–trans*-1,2-dichlorotetrafluorocyclopropane (1·611 g, 8·8 mmol), in a sealed 50 ml Pyrex tube at 55°, were irradiated with light from a 200 W tungsten-filament lamp for 46 h. The volatile products (1·273 g) gave three peaks (5 : 35 : 1) on g.l.c. (4 m column of Kel-F oil; 20°), and isolation of the largest yielded *cis–trans*-1-chloro-1,2,2,3-tetrafluorocyclopropane (VI) (1·110 g, 85%), identified by spectroscopy. Separation of the geometrical isomers was achieved with difficulty by g.l.c. (8 m column of 2,4-dimethyltetrahydrothiophen dioxide; 23°), and the *cis* : *trans* ratio was shown to be 23 : 77; isolation of the isomers gave *cis*-1-chloro-1,2,2,3-tetrafluorocyclopropane (VIa) (Found: C, 24·4; H, 1·1%; *M*, 148. Calc. for C_3HClF_4: C, 24·2; H, 0·7%;

[14] M. G. Barlow, R. Fields, and F. P. Temme, *Chem. Comm.*, 1968, 1671.

M, 149) and *trans*-1-chloro-1,2,2,3-tetrafluorocyclopropane (VIb) (Found: C, 24·6; H, 0·9%; *M*, 147), b.p. 24·5°, with n.m.r. and mass spectra in agreement with published data.[5]

(b) *Dichlorotetrafluorocyclopropane* (IV) *with an excess of tributyltin hydride.* The hydride (4·01 g, 13·8 mmol) and *cis–trans*-1,2-dichlorotetrafluorocyclopropane (1·11 g, 6·1 mmol) were allowed to react under the conditions used for the previous experiment. Involatile tin compounds were removed by fractionation *in vacuo*, and the product isomers (combined yield 0·673 g, 97%) were separated by g.l.c. (4 m column of Kel-F oil; 22°), to give *cis*-1,1,2,3-tetrafluorocyclopropane (Found: C, 31·8; H, 1·5%; *M*, 114. $C_3H_2F_4$ requires: C, 31·6; H, 1·7%; *M*, 114), b.p. 34°, and *trans*-1,1,2,3-tetrafluorocyclopropane (Found: C, 31·3; H, 1·9%; *M*, 113), b.p. 6°; the *trans*-isomer had the shorter retention time. The *cis*-compound shows $\lambda_{max.}$ 6·62, 6·67, 7·57, 8·13, 8·16, 8·19, 8·40, 8·47, 8·50, 9·90, 10·36, 11·69, 13·79, 13·88, 15·33, and 15·38 μm, n.m.r. $ABPP'XX'$ system with δ_{AB} (mean) 67·15, δ_{AB} (internal) 21·8, δ_P 170·0 p.p.m., and δ_X 1·81 p.p.m. (J_{AB} 205·8, J_{AP} 4·8, J_{BP} 3·1, J_{AX} 11·2, J_{BX} 1·2, $J_{PP'}$ 18·6, $J_{XX'}$ 6·4, J_{PX} 57·8, and $J_{PX'}$ = 0·9 Hz).[9] The *trans*-compound shows $\lambda_{max.}$ 6·56, 6·60, 7·50, 7·52, 7·87, 7·94, 8·47, 8·55, 9·66, 9·71, 9·80, 9·90, 9·99, 10·38, 10·47, 10·53, 13·33, and 14·49 μm, n.m.r. complex $AA'PP'XX'$ system with ^{19}F bands (AA' and PP') at +72·0 and +154·8 p.p.m. and a ^{1}H band (XX') at +1·58 p.p.m.[9] The mass spectra of the two isomers are very similar; both show *m/e* 113 (C_3HF_4), 95 ($C_3H_2F_3$), 82 (C_2HF_3), 75 (C_3HF_2), 69 (CF_3), 64 ($C_2H_2F_2$), 63 (C_2HF), 51 (CHF_2), 50 (CF_2), 45 (C_2H_2F), 44 (C_2HF), 33 (CH_2F), 32 (CHF), and 31 (CF).

(c) *1,1-Dichlorotrifluoro(trifluoromethyl)cyclopropane* (VIII) *with* 1 *mol. equiv. of tributyltin hydride.* The cyclopropane (3·91 g, 16·8 mmol) and the hydride (4·88 g, 16·8 mmol), in a 300 ml Pyrex tube, were irradiated as in (a) for 120 h. The total volatile products were shown by i.r. and g.l.c. (8 m column of 2,4-dimethyltetrahydrothiophen dioxide; 22°) to consist of unchanged starting material (0·47 g, 9%) and a reduced product (3·06 g, 91%), two isomers (48 : 52%) of which were isolated by g.l.c. and characterised as 3-*chloro*-1,1,2-*trifluoro*-2-*trifluoromethylcyclopropane* (IX), isomer (i) (Found: C, 24·3; H, 0·5%; *M*, 198. C_4HClF_6 requires C, 24·2; H, 0·5%; *M*, 199), b.p. 41°, and isomer (ii) (Found: C, 24·6; H, 0·5%; *M*, 197), b.p. 44°, by i.r. spectroscopy on the separated isomers and n.m.r. and mass spectrometry on the mixed isomers. Isomer (i) shows $\lambda_{max.}$ 6·80, 7·35, 7·72, 7·94, 8·07, 8·30, 9·17, 9·71, 12·12, 12·99, and 15·62 μm, and isomer (ii) shows $\lambda_{max.}$ 6·83, 7·23, 7·72, 7·94, 8·17, 8·33, 9·30, 11·72, 12·20, 12·99, and 14·18 μm. The [19]F n.m.r. spectrum of the mixture consisted of two overlapping $ABMX_3$ systems, with centres of absorption at δ_{AB} (mean) 66·6, δ_{AB} (internal) 9·9 (δ_{AB} 182·5 Hz), δ_M 140·5, and δ_X −5·2 p.p.m. in the ratio 2 : 1 : 3; the ^{1}H spectrum showed δ_H 2·73 p.p.m.

(d) *1,1-Dichlorotrifluoro(trifluoromethyl)cyclopropane* (VIII) *with an excess of tributyltin hydride.* The cyclopropane (1·51 g, 6·49 mmol) and the hydride (7·50 g, 25·8 mmol) were irradiated as in (a) in a 300 ml Pyrex tube for 336 h. The volatile product was washed with aqueous 2M-sodium hydroxide, dried by redistillation, and shown by g.l.c. (4 m column of 2,4-dimethyltetrahydrothiophen dioxide; 20°) to be one component, identified as 1,1,2-trifluoro-2-trifluoromethylcyclopropane (X) (Found: C, 29·8; H, 1·7%; *M*,

[15] L. Cavalli, *Org. Magnetic Resonance*, 1970, **2**, 233.

[16] G. J. M. Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, 1957, **7**, 366.

164. Calc. for $C_4H_2F_6$: C, 29·3; H, 1·2%; M, 164), b.p. 21·5°, by spectroscopy. The i.r. spectrum shows $\lambda_{max.}$ 6·74, 7·22, 7·35, 7·81, 8·32, 8·85, 9·11, 9·66, 11·35, 12·17, 12·99, 13·07, 14·88, and 15·67 μm. The complicated n.m.r. spectra are consistent with the assigned structure; the ^{19}F spectrum is an $ABMX_3$ system with δ_{AB} (mean) 66·8, δ_M 137·4, and δ_X −1·9 p.p.m., J_{AB} 184·0 Hz, and the ^1H spectrum shows δ_H 4·7 p.p.m.; no geminal HF coupling is present. The mass spectrum shows a weak parent ion at m/e 164 and intense peaks at m/e 113 (C_3HF_4), 100 (C_2F_4), 95 ($C_3H_2F_3$), 75 (C_3HF_2), 69 (CF_3), 64 (C_2H_2F), 56 (C_3HF), 55 (C_3F), 51 (CHF_2), 50 (CF_2), 45 (C_2H_2F), 43 (C_2F), 41, 39, and 31 (CF). The preparation of this cyclopropane from hexafluoropropene and diazomethane has been claimed by Misani, Speers, and Lyon,[17] who report b.p. −15·8° but provide no spectroscopic evidence in support of the suggested structure.
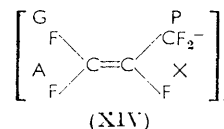
Pyrolysis of the Cyclopropanes.—(a) *Pentafluorocyclopropane* (I). (i) *Alone*. A preliminary experiment showed that only 8% decomposition of the cyclopropane occurred during 100 h at 170°. The cyclopropane (2·046 g, 15·5 mmol), kept in a 300 ml Pyrex tube at 190° for 240 h (initial pressure *ca.* 1·5 atm), gave (i) carbon monoxide (0·164 g, 5·86 mmol, 43% of $\ddot{C}F_2$) (Found: M, 28), (ii) *via* g.l.c. (10 m column of Kel-F oil; 20°), tetrafluoroethylene (0·265 g, 2·65 mmol, 39% of $\ddot{C}F_2$) and trifluoroethylene (1·041 g, 12·7 mmol, 93% of converted cyclopropane), (iii) *via* g.l.c. (8 m column of Silicone MS550; 19°), a mixture of pentafluorocyclopropane (0·249 g, 1·89 mmol, 12% recovery), hexafluorocyclopropane, and octafluorocyclobutane (combined amount *ca.* 0·075 g, accounting for 6% of $\ddot{C}F_2$ produced), and two unidentified components.

(ii) *With* cis-*but-2-ene*. Pentafluorocyclopropane (0·660 g, 5·00 mmol) and *cis*-butene (1·680 g, 30·0 mmol), kept in a sealed 1 l Pyrex flask at 220° for 48 h, gave, by fractionation *in vacuo*, (i) carbon monoxide (0·40 mmol, 8% of $\ddot{C}F_2$), (ii) a mixture (0·407 g) of trifluoroethylene (0·354 g, 4·32 mmol, 95% based on pentafluorocyclopropane consumed), tetrafluoroethylene, hexafluorocyclopropane, silicon tetrafluoride, and a trace of fluoroform, (iii) a mixture of *cis*-butene (1·389 g, 83% recovery) and pentafluorocyclopropane (0·059 g, 9% recovery), and (iv) a fraction (0·471 g) which contained *cis*-butene (removed by treatment with bromine) and 1,1-difluoro-*cis*-2,3-dimethylcyclopropane (0·445 g, 4·20 mmol, 84%) (Found: M, 104. Calc. for $C_5H_8F_2$: M, 106), identified by comparison of its i.r. spectrum with that of a sample prepared earlier.[1] G.l.c. (4 m Kel-F oil; 21° and 4 m Silicone MS550; 21°) did not reveal any of the corresponding *trans*-cyclopropane.

(b) *Bromopentafluorocyclopropane* (II). The cyclopropane (0·441 g, 2·09 mmol), kept in a sealed 25 ml Pyrex tube at 170° for 100 h (initial pressure *ca.* 3·0 atm), gave carbon monoxide (0·10 mmol, 63% of $\ddot{C}F_2$), tetrafluoroethylene (*ca.* 0·01 mmol, 13% of $\ddot{C}F_2$), silicon tetrafluoride, and *via* g.l.c. (4 m column of 2,4-dimethyltetrahydrothiophen dioxide; 38°), bromopentafluorocyclopropane (0·194 g, 0·92 mmol, 44% recovery), bromotrifluoroethylene (0·026 g, 0·16 mmol, 14% of converted cyclopropane), 3-bromopentafluoropropene (0·170 g, 0·81 mmol, 69% of converted cyclopropane), and four unidentified components (0·032 g). The

n.m.r. spectrum of a pure sample of the 3-bromopropene, separated by g.l.c., was in full accord with previously reported data.[18]

(c) *Iodopentafluorocyclopropane* (III). The cyclopropane (0·713 g, 2·76 mmol) was kept in a sealed 45 ml Pyrex tube at 170° for 100 h (initial pressure *ca.* 2·2 atm) and yielded a trace of carbon monoxide. The condensable volatile products were shown by i.r. spectroscopy and g.l.c. (8 m column of Kel-F oil; 43°) to contain iodopentafluorocyclopropane (0·129 g, 0·50 mmol, 18% recovery), iodotrifluoroethylene (0·042 g, 0·02 mmol, 8% of converted cyclopropane), 3-iodopentafluoropropene (0·464 g, 1·80 mmol, 78%), perfluorohexa-1,5-diene (0·021 g, 0·008 mmol, 7%), and traces of three unidentified compounds; small amounts of iodine were also formed. The n.m.r. spectrum of a pure (g.l.c.) sample of the 3-iodopropene was in accord with published data;[18] the n.m.r. spectrum of the hexadiene was identical with that of a specimen obtained by a coupling reaction of 3-iodopropene[19] and showed δ_A 11·0, δ_G 28·5, δ_P 42·4, and δ_X 113·2 p.p.m. (J_{AG} 53, J_{AP} 5·5, J_{AX} 40, J_{GP} 31, and J_{GX} 120 Hz) [*cf.* (XIV)].

(XIV)

(d) cis–trans-1,2-*Dichlorotetrafluorocyclopropane* (IV). A preliminary experiment showed that only 15% decomposition of this mixture of isomers occurred during 100 h at 170°. 1,2-Dichlorotetrafluorocyclopropane (0·968 g, 5·30 mmol; cis : trans 35 : 65), kept in a sealed 50 ml Pyrex tube at 200° for 197 h (initial pressure *ca.* 3·2 atm), yielded carbon monoxide (0·074 g, 2·64 mmol, 64% of $\ddot{C}F_2$) and, *via* g.l.c. (4 m column of Kel-F oil; 22° and 8 m column of Silicone MS550; 22°), i.r., mass spectrometry, and n.m.r., silicon tetrafluoride, tetrafluoroethylene, hexafluorocyclopropane, a trace of carbonyl fluoride (combined weight 0·206 g), cis–trans-1,2-dichlorodifluoroethylene (0·545 g, 4·10 mmol, 77% yield), 1,1-dichlorotetrafluoropropene (0·060 g, 0·33 mmol, 6% yield) (*see later*), *cis*-1,3-dichlorotetrafluoropropene (0·038 g, 0·21 mmol, 4%), and *trans*-1,3-dichlorotetrafluoropropene (0·115 g, 0·63 mmol, 12%). Chlorotrifluoroethylene was not detected. The ^{19}F n.m.r. spectrum of the *cis*-dichloropropene showed δ_1 16·0 (dt $J_{1,2}$ 19, $J_{1,3}$ 7 Hz), δ_2 67·0 (dt, $J_{2,1}$ 19, $J_{2,3}$ 15 Hz), and δ_3 −23·0 p.p.m. (dd, $J_{3,2}$ 15, $J_{3,1}$ 7 Hz) and the *trans*-dichloropropene showed δ_1 30·6, (dt, $J_{1,2}$ 133, $J_{1,3}$ 31 Hz), δ_2 80·0 (dt, $J_{2,1}$ 133, $J_{2,3}$ 16·5 Hz), and δ_3 −21·8 p.p.m. (dd, $J_{3,2}$ 16·5, $J_{3,1}$ 31 Hz).

(e) *Perfluoro(methylcyclopropane)* (V). (i) *Alone*. A preliminary experiment showed that 40% decomposition of this compound occurred during 100 h at 170°. The cyclopropane (1·076 g, 5·38 mmol), kept in a 300 ml tube at 200° for 46 h (initial pressure *ca.* 0·5 atm), gave carbon monoxide (0·105 g, 3·75 mmol, 76% of $\ddot{C}F_2$), unchanged cyclopropane (0·108 g, 0·54 mmol, 10%), hexafluoropropene (0·698 g, 4·65 mmol, 96% of converted cyclopropane), hexafluorocyclopropane (0·031 g, 0·21 mmol, 14% of $\ddot{C}F_2$), tetrafluoroethylene (0·010 g, 0·10 mmol, 4% of $\ddot{C}F_2$), and octafluorocyclobutane (trace).

[17] F. Misani, L. Speers, and A. M. Lyon, *J. Amer. Chem. Soc.*, 1956, **78**, 2801.
[18] K. C. Ramey and W. S. Brey, *J. Chem. Phys.*, 1964, **40**, 2349.

[19] A. H. Fainberg and W. T. Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 4170; I. H. Bruce, R. N. Haszeldine, and A. E. Tipping, unpublished observations.

(ii) *With but-2-ene.* Perfluoro(methylcyclopropane) (0·435 g, 2·17 mmol) and *cis*-butene (0·729 g, 13·0 mmol), kept in a 150 ml tube at 220° for 48 h, gave carbon monoxide (0·20 mmol, 10% of $\ddot{C}F_2$), unchanged cyclopropane (0·017 g, 0·11 mmol, 4% recovery), *cis*-butene (0·605 g), hexafluoropropene (0·296 g, 1·97 mmol, 94%), 1,1-difluoro-*cis*-2,3-dimethylcyclopropane (0·193 g, 1·82 mmol, 88%) (Found: *M*, 105. Calc. for $C_5H_8F_2$: *M*, 106), and traces of tetrafluoroethylene, carbonyl fluoride, and silicon tetrafluoride. A similar experiment, in which perfluoro(methylcyclopropane) (0·178 g, 0·89 mmol) and *trans*-butene (0·168 g, 3·00 mmol) were heated at 200° for 16 h gave pure 1,1-difluoro-*trans*-2,3-dimethylcyclopropane (0·065 g, 69%), identified by i.r. and n.m.r. spectroscopy.[1]

(iii) *With ethylene.* The cyclopropane (0·804 g, 4·02 mmol) and ethylene (1·014 g, 36·2 mmol) were kept in a 300 ml tube at 180° for 16 h and then at 190° for 28 h. Carbon monoxide (0·9 mmol, 21% of $\ddot{C}F_2$) was formed, together with ethylene (0·996 g), hexafluoropropene (0·570 g, 3·80 mmol, 95%), hexafluorocyclopropane (0·078 g, 0·52 mmol, 39% of $\ddot{C}F_2$), octafluorocyclobutane (0·045 g, 0·23 mmol, 23% of $\ddot{C}F_2$), 1,1-difluorocyclopropane (0·012 g, 0·15 mmol, 4% of $\ddot{C}F_2$),[17,20] traces of tetrafluoroethylene and silicon tetrafluoride, and a fraction shown by comparison with a fully characterised specimen (*see later*) to be 1,1,2-trifluoro-2-trifluoromethylcyclobutane.

(f) *cis–trans*-1-*chloro*-1,2,2,3-*tetrafluorocyclopropane* (VI). Only 7% decomposition of this material occurred during a preliminary experiment at 170° for 100 h. 1-Chloro-1,2,2,3-tetrafluorocyclopropane (0·048 g, 0·32 mmol; *cis* : *trans* 23 : 77) was kept in a sealed 25 ml Pyrex tube, packed with glass wool, at 250° for 167 h (initial pressure *ca.* 1·1 atm). Fractionation gave carbon monoxide (0·19 mmol, 100% of $\ddot{C}F_2$), a mixture (0·10 mmol) of silicon tetrafluoride with a trace of tetrafluoroethylene, a fraction (0·035 g) shown by i.r. spectroscopy and g.l.c. (4 m column of 2,4-dimethyl-tetrahydrothiophen dioxide; 35°) to contain chloro-1,2-difluoroethylene (0·019 g, 0·19 mmol, 60%; *cis* : *trans* 52 : 48), and probably (see above) *cis*- and *trans*-3-chloro-1,2,3,3-tetrafluoropropene (0·015 g, 0·10 mmol, 31%). The mass spectrum of the propenes showed intense peaks at *m/e* 150 (C_3HClF_4), 149 (C_3ClF_4), 148 (C_3HClF_4), 147 (C_3ClF_4), 131 (C_3HClF_3), 129 (C_3HClF_3), 118 (C_2ClF_3), 116 (C_2ClF_3), 113, 101, 100, 98, 97, 93, 91, 69, 55, 51, 50, 49, 47, 44, 43, 37, 35, and 31.

[20] J. M. Birchall, R. Fields, R. N. Haszeldine, and D. G. Summers, unpublished observations.

(g) 1,1-*Dichlorotrifluoro*(*trifluoromethyl*)*cyclopropane* (VIII). The cyclopropane (0·960 g, 4·13 mmol) was kept in a 150 ml tube at 170° for 100 h; analysis of the products by fractionation *in vacuo*, g.l.c., and i.r. spectroscopy then showed them to consist only of unchanged cyclopropane (0·661 g, 2·84 mmol, 69%), 1,1-dichlorotetrafluoropropene (0·229 g, 1·25 mmol, 97% of converted cyclopropane), carbon monoxide, silicon tetrafluoride, tetrafluoroethylene, and hexafluorocyclopropane. A pure specimen of the propene (Found: C, 19·6%; *M*, 184. Calc. for $C_3Cl_2F_4$: C, 19·7%; *M*, 183) was isolated by g.l.c., and its n.m.r. spectrum showed δ_2 41·1 and δ_3 −10·6 p.p.m., with $J_{2,3}$ 8·5 Hz; its i.r. (C:C str. 6·02 μm) and mass spectra were also in accord with the assigned structure. The propene was first prepared by Henne, Whaley, and Stevenson,[21] but its spectra have not been published; however, the n.m.r. spectra of *cis*- and *trans*-1,2-dichlorotetrafluoropropene exclude these isomers.[22]

(h) 1,1,2-*Trifluoro*-2-*trifluoromethylcyclopropane* (X). A preliminary experiment showed that no detectable decomposition of this compound occurred during 100 h at 170°. The cyclopropane (0·045 g, 0·28 mmol) was kept in a 25 ml tube at 202° for 118 h, at 230° for 168 h, and at 240° for 240 h (initial pressure *ca.* 0·7 atm). No carbon monoxide was detected, and separation of the products by g.l.c. (4 m column of Kel-F oil; 19°) yielded unchanged cyclopropane (0·005 g, 0·03 mmol, 11%) and a product believed to be (see above) *cis–trans*-1,1,1,2,4,4-hexafluorobut-2-ene (0·041 g, 0·025 mmol, 100% of converted cyclopropane).

1,1,2-*Trifluoro*-2-*trifluoromethylcyclobutane* (XI).—Hexafluoropropene (4·410 g, 29·4 mmol) and ethylene (0·818 g, 29·2 mmol) were kept in a 300 ml rocking autoclave at 250° for 18 h. Fractionation *in vacuo* gave a mixture of hexafluoropropene (3·390 g, 22·6 mmol, 77% recovery) and ethylene (0·627 g, 22·4 mmol, 77%), and a fraction purified by g.l.c. (4 m column of Silicone MS550; 55°) to give 1,1,2-*trifluoro*-2-*trifluoromethylcyclobutane* (1·120 g, 6·29 mmol, 93% based on olefins converted) (Found: C, 33·7; H, 2·3%; *M*, 178. $C_5H_4F_6$ requires C, 33·7; H, 2·3%; *M*, 178), b.p. 67·5°, $\lambda_{max.}$ 6·85, 6·96, 7·35, 7·60, 7·80, 8·00, 8·20, 8·35, 8·90, 9·60, 10·35, 13·37, and 15·45 μm, [19]F n.m.r. ABMX$_3$ system with δ_{AB} (mean) 31·4, δ_M 96·6, and δ_X 3·8 p.p.m. (J_{AB} 222 Hz), *m/e* 95 ($C_3H_2F_3$), 69 (CF_3), 64 ($C_2H_2F_2$), 45 (C_2H_2F), 31 (CF), and 28 (C_2H_4).

[21] A. L. Henne, A. W. Whaley, and J. K. Stevenson, *J. Amer, Chem. Soc.*, 1941, **63**, 3478.
[22] C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, 1961, **34**, 2122.