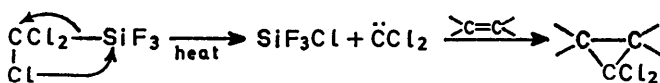


## Cyclopropane Chemistry. Part II.<sup>1</sup> Cyclopropanes as Sources of Difluorocarbene

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The reactions of tetrafluoroethylene, chlorotrifluoroethylene, and 1,1-dichlorodifluoroethylene with dichlorocarbene [generated from trifluoro(trichloromethyl)silane], and of the first two olefins with difluorocarbene (from difluorotrifluoromethylphosphorane), under conditions which give good yields of the corresponding polyhalogenocyclopropanes, are described. 1,1,2,2-Tetrafluorocyclopropane is obtained in only low yield from 1,1-difluoroethylene and difluorotrifluoromethylphosphorane, but is conveniently obtained (98% yield) by reduction of 1,1-dichlorotetrafluorocyclopropane with tributylstannane. Evidence that some of the cyclopropanes undergo a 'chemically activated' decomposition to difluorocarbene and an olefin following their formation is presented, and thermal decomposition of all the cyclopropanes studied leads to difluorocarbene formation at temperatures in the range 150–220°. The difluorocarbene formed in this way undergoes stereospecific addition to hydrocarbon olefins to give high yields of 1,1-difluorocyclopropanes.

ALTHOUGH the addition of carbenes to a wide range of unsaturated compounds, to give cyclopropanes, is now a well established preparative procedure,<sup>2</sup> the number of carbene precursors which have been used successfully with volatile and/or electron-deficient olefins is still severely limited. The addition of dichlorocarbene from the thermal decomposition of trifluoro(trichloromethyl)silane to, *inter alia*, ethylene, tetrachloroethylene, and 1,1-difluoroethylene gives high yields of the corresponding *gem*-dichlorocyclopropanes:<sup>3</sup>



This procedure is also successful with 1,1-dichlorodifluoroethylene, chlorotrifluoroethylene, and tetrafluoro-

ethylene. However, a study of the reaction with the last two olefins reveals complications which have led to an investigation of the thermal decomposition of a number of polyhalogenocyclopropanes.

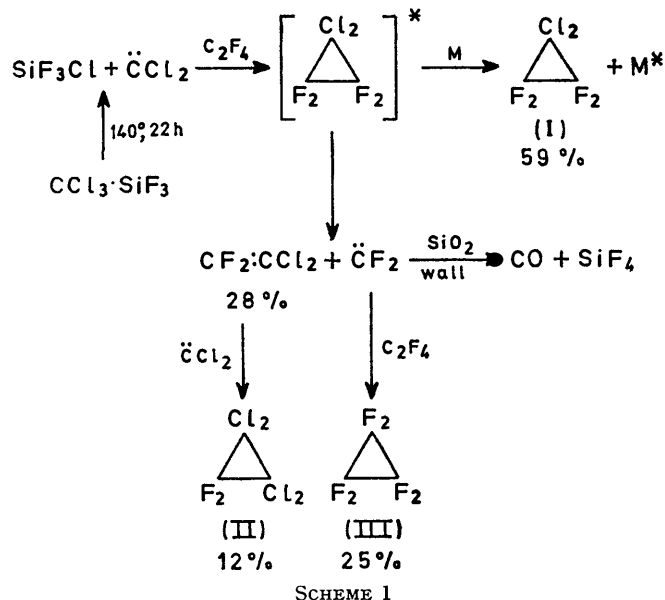
*Reactions of Dichlorocarbene with Polyfluoro-olefins.*—The gas-phase (*ca.* 1 atm) reaction between trifluoro(trichloromethyl)silane and a seven-fold excess of tetrafluoroethylene at 140° yields mainly the expected 1,1-dichlorotetrafluorocyclopropane (I), but appreciable amounts of 1,1,2-tetrachlorodifluorocyclopropane (II), hexafluorocyclopropane (III), and 1,1-dichlorodifluoroethylene, along with traces of polytetrafluoroethylene and carbon monoxide, are also formed. Specimens of all three cyclopropanes have been isolated from the mixture of products and fully characterised by spectroscopic means.

<sup>1</sup> Part I, R. Fields, R. N. Haszeldine, and D. Peter, *J. Chem. Soc.*, 1969, 165.

<sup>2</sup> E. Chinoporos, *Chem. Rev.*, 1963, **63**, 235; W. Kirmse, 'Carbene Chemistry,' Academic Press, London, 2nd edn., 1971; T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes, and Arynes,' Nelson, London, 1969.

<sup>3</sup> W. I. Bevan, J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, 'Organic Reaction Mechanisms,' *Chem. Soc. Special Publ.*, No. 19, p. 174; J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, forthcoming publication; R. N. Haszeldine in 'New Pathways in Inorganic Chemistry,' ed. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 115.

It now seems probable that this reaction follows the path shown in Scheme 1 (yields based on amount of  $\ddot{\text{C}}\text{Cl}_2$  available in the system), the dichlorocyclopropane

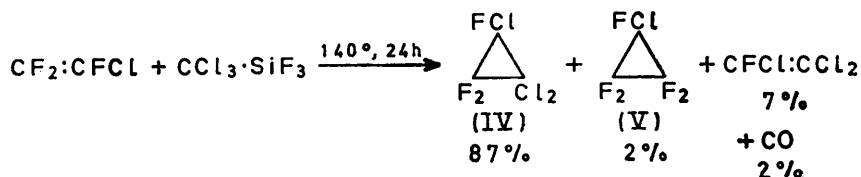


(I) being formed in a 'chemically activated' state, with an excess of vibrational energy sufficient to bring about its decomposition into the dichlorodifluoro-olefin and difluorocarbene unless deactivation by collision occurs quickly. An alternative interpretation, that dichlorotetrafluorocyclopropane undergoes simple thermal decomposition following its formation as a stable entity during the reaction, is not tenable, since longer reaction periods have little effect on the yields of products.

similarly, but the initially formed 1,1,2-trichlorodifluorocyclopropane (IV) is obtained in excellent yield even at a reaction pressure of 1.1 atm (Scheme 2). The chemically activated product decomposes only to a limited extent to give difluorocarbene and (probably) trichlorodifluoroethylene, the former being detected through the formation of carbon monoxide and chloropentafluorocyclopropane (V), its adduct with chlorodifluoroethylene. The spectroscopic properties of the major product (IV) are in good agreement with those reported for specimens obtained by alternative routes.<sup>4</sup>

The reaction of difluorocarbene with glass (even with glass carefully flamed *in vacuo*), to give carbon monoxide and silicon tetrafluoride (and sometimes small amounts of carbon dioxide and carbonyl fluoride<sup>5</sup>), has been observed frequently during this and related work; it tends to occur whenever the carbene is formed in circumstances where its collision with a glass wall is permitted by the relative unreactivity of the olefins or other species present in the gas phase. The formation of carbon monoxide under these circumstances can provide a useful diagnostic test for the presence of difluorocarbene during a reaction, and its detection among the products of the reactions just described is therefore in accord with the suggested mechanism.

The thermal decomposition of trifluoro(trichloromethyl)silane in the presence of an excess of 1,1-dichlorodifluoroethylene at 140° and 7.2 atm gives 1,1,2,2-tetrachlorodifluorocyclopropane (II), identical with the compound formed during the reaction of the silane with tetrafluoroethylene, in 66% yield. Decomposition of the cyclopropane does not apparently occur under these conditions, but small amounts of carbon tetrachloride and tetrachloroethylene are formed, presumably by



Furthermore, pure 1,1-dichlorotetrafluorocyclopropane undergoes less than 20% decomposition during 67 h at 156° (see later). The possibility that the tetrachlorocyclopropane (II) is formed from the dichloro-compound (I) by bimolecular reaction with dichlorocarbene and ejection of difluorocarbene cannot be discarded on the evidence currently available, although Scheme 1 is preferred.

A marked improvement in the yield of dichloro-compound (I) (to 82%) is achieved when the reaction between the silane and an excess of tetrafluoroethylene is carried out at 140° and 10 atm total pressure.

Decomposition of trifluoro(trichloromethyl)silane at 140° in the presence of chlorotrifluoroethylene proceeds

<sup>4</sup> (a) K. L. Williamson and B. A. Braman, *J. Amer. Chem. Soc.*, 1967, **89**, 6183; (b) G. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1970, 178.

side-reactions of the dichlorocarbene permitted by the relatively low reactivity of the dichlorodifluoroethylene.

*Cyclopropanes from Difluorotri(trifluoromethyl)phosphorane.*—Detailed investigation of the mode of cyclopropane decomposition suggested by the foregoing experiments required the preparation of cyclopropanes other than those containing *gem*-dichloromethylene groups. To this end, the use of difluorotri(trifluoromethyl)phosphorane as a precursor of difluorocarbene has been investigated. This compound, prepared from tri(trifluoromethyl)phosphine and sulphur tetrafluoride,<sup>6a</sup> has been shown to decompose during 20 h at 120°, probably in the stepwise manner shown (Scheme 3), the

<sup>5</sup> J. M. Birchall, R. Fields, R. N. Haszeldine, and N. T. Kendall, unpublished observations.

<sup>6</sup> W. Mahler, (a) *Inorg. Chem.*, 1963, **2**, 230; (b) *J. Amer. Chem. Soc.*, 1962, **84**, 4600.

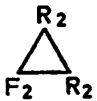

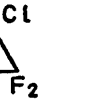



this way is believed to be novel, although the addition of halogenated olefins to hydrocarbon systems under the influence of hydrogen fluoride is well documented.<sup>10</sup>

1,1,2-Tetrafluorocyclopropane may be obtained in almost quantitative yield by the reduction of 1,1-dichlorotetrafluorocyclopropane with tri-*n*-butylstannane, or in 34% yield by reduction of the dichloro-compound

The only mode of decomposition detected for hexafluoro-, chloropentafluoro-, and the dichlorotetrafluorocyclopropane apparently involves the ejection of difluorocarbene, detected mainly as carbon monoxide, carbon dioxide, and silicon tetrafluoride following its reaction with the glass surface. Some dimerisation of the carbene to tetrafluoroethylene can be detected

TABLE I  
Thermal decomposition of the cyclopropanes

Cyclopropane				
Initial amount (mmol)	1.45	2.38	3.74	9.10
Rctn. period (h)	352 <sup>a</sup>	300	453 <sup>b</sup>	185 <sup>c</sup>
Temp. (°C)	160	210	156	200
Pressure (atm.)	0.35	1.1	0.50	1.1
Extent decomp. (%)	21	100	64	100
Yield CR <sub>2</sub> :CR <sub>2</sub> (%) <sup>d</sup>	99	42	77	55
Yield CO (%)	48	61	61	27
Yield CO <sub>2</sub> (%)	52 <sup>e</sup>	Trace	5	Trace
Yield SiF <sub>4</sub> (%)	<i>f</i>	52	60	17
Yield C <sub>2</sub> F <sub>4</sub> (%)		3	6	5
Yield (III) (%)			16	12
Other products		(X) (52%) Un-identified <sup>g</sup> (5%)		CF <sub>2</sub> :CCl <sub>2</sub> (6%) (I) (11%) C <sub>3</sub> Cl <sub>3</sub> F <sub>3</sub> (21%) C <sub>3</sub> Cl <sub>4</sub> F <sub>2</sub> (6%)

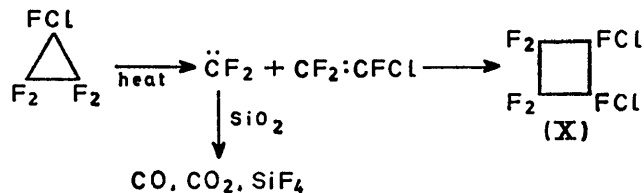
<sup>a</sup> Glass vessel packed with glass wool; remainder in unpacked glass vessels. <sup>b</sup> Little decomp. during 67 h at 156°. <sup>c</sup> Only 4% decomp. during 168 h at 180°. <sup>d</sup> Yields based on cyclopropane decomposed in each case. <sup>e</sup> Produced during subsequent work-up. <sup>f</sup> Detected but not measured. <sup>g</sup> No olefinic i.r. band; *M*, 165.

with lithium aluminium hydride. The value of tri-*n*-butylstannane as a reducing agent for *gem*-dichloro-groups has previously been noted.<sup>11</sup>

*Pyrolysis of the Cyclopropanes Alone.*—The usual mode of thermal decomposition of hydrocarbon and chlorinated hydrocarbon cyclopropanes involves rearrangement to an isomeric alkene,<sup>1</sup> but the results of the reactions of dichlorocarbene with tetrafluoroethylene and chlorotrifluoroethylene suggested that the pyrolysis of polyfluorocyclopropanes could proceed in a totally different way. The observation that octafluorocyclobutane was the main product from the pyrolysis of hexafluorocyclopropane at 450°<sup>12</sup> suggested that difluorocarbene and tetrafluoroethylene had been formed, and this was confirmed by kinetic studies.<sup>13</sup> Carbenoid decomposition has also been observed with arylcyclopropanes<sup>14</sup> and with perfluoroallylcyclopropane.<sup>15</sup>

The results of our experiments, in which the cyclopropanes (I)—(IV) were pyrolysed in sealed glass vessels at pressures in the range 0.35—1.7 atm are shown in Table I. In order that a qualitative idea of the relative ease of decomposition of the cyclopropanes could be obtained, the temperatures employed (156—210°) were about the minimum required to effect a reasonable degree of decomposition in each case.

following pyrolysis of the chloro- and the dichloro-compound, and some hexafluorocyclopropane is also formed from the last compound. The residual olefin is detected in high yield in these three cases, although extensive dimerisation to the cyclobutane (X) occurs with chlorotrifluoroethylene (Scheme 7).



SCHEME 7

Pyrolysis of 1,1-dichlorotetrafluorocyclopropane in a platinum-lined autoclave at 180° (initial pressure 3.8 atm) allows the difluorocarbene formed to survive collision with the wall, and a more complicated mixture of products is formed (Scheme 8). Under these conditions, 90% of the difluorocarbene dimerises to tetrafluoroethylene, most of which (*ca.* 80%) ultimately appears as octafluorocyclobutane (XI), and the co-dimer with dichlorodifluoroethylene, 1,1-dichlorohexafluorocyclobutane (XII) (identified by comparison with a

<sup>10</sup> L. S. German and I. L. Knunyants, *Angew. Chem. Internat. Edn.*, 1969, **8**, 349.

<sup>11</sup> D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, 1963, **28**, 703.

<sup>12</sup> R. D. Chambers, H. Clarke, and C. J. Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 5298.

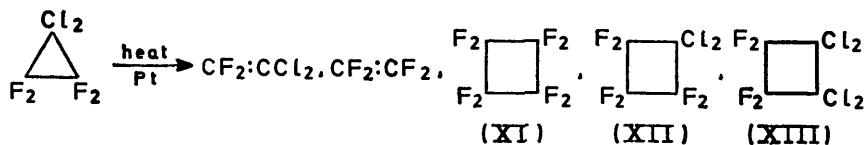
<sup>13</sup> B. Atkinson and D. McKeagan, *Chem. Comm.*, 1966, 189.

<sup>14</sup> D. B. Richardson, L. R. Durrett, J. M. Martin, W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Amer. Chem. Soc.*, 1965, **87**, 2763; P. A. Leermakers and M. E. Ross, *J. Org. Chem.*, 1966, **31**, 301; M. Jones, W. H. Sachs, A. Kulczycki, and F. J. Waller, *J. Amer. Chem. Soc.*, 1966, **88**, 3167.

<sup>15</sup> R. A. Mitsch and E. W. Neuvar, *J. Phys. Chem.*, 1966, **70**, 546.

specimen made separately in *ca.* 50% yield from a mixture of the two olefins at 200° and 50 atm). Self-dimerisation of the dichlorodifluoroethylene to the cyclobutane (XIII) also occurs during this pyrolysis, and unexplained side-reactions give the small amounts of other products shown.

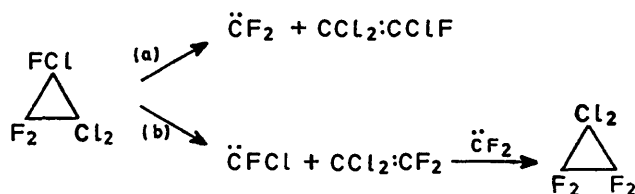
The pyrolysis of 1,1,2-trichlorotrifluorocyclopropane in glass (Table 1) is also more complex than those of the



**CF<sub>2</sub>CCl<sub>2</sub>, CF<sub>3</sub>Cl, unidentified compound (unsaturated)**

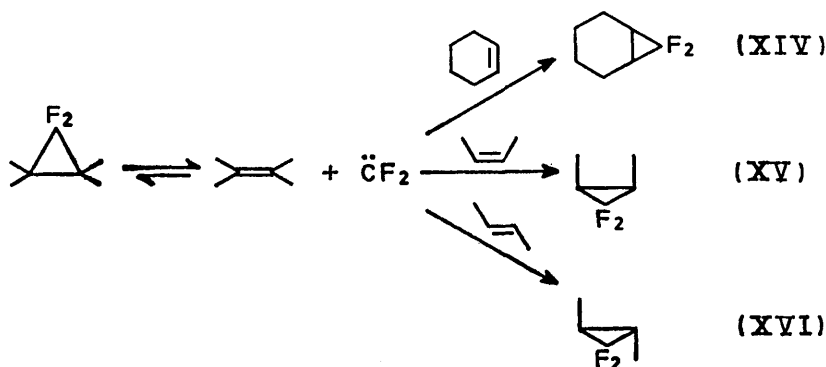
SCHEME 8

first three cyclopropanes under comparable conditions. At least 55% of its decomposition proceeds with the ejection of difluorocarbene and the formation of trichlorofluoroethylene, but the formation of 1,1-dichlorodifluoroethylene and 1,1-dichlorotetrafluorocyclopropane (I) (combined yield 17%) suggests that some breakdown



SCHEME 9

to give chlorofluorocarbene occurs (Scheme 9). Two unidentified compounds, both of whose i.r. spectra



SCHEME 10

indicate the presence of unsaturation, are also formed, and one of these (21% yield) is probably a propene formed by simple rearrangement of the initial cyclopropane. It is tempting to suggest that the other (C<sub>3</sub>Cl<sub>4</sub>F<sub>2</sub>; 6% yield) may be formed as a result of the reaction of the major olefinic product (CCl<sub>2</sub>:CFCl) with chlorofluorocarbene since no other fate for the latter is evident from the results.

*Pyrolysis of the Cyclopropanes in the Presence of Olefins.*—The results obtained by pyrolysis of all the

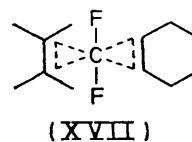
<sup>18</sup> Compare P. B. Sargeant, *J. Org. Chem.*, 1970, **35**, 678.

cyclopropanes described here in the presence of a large excess of cyclohexene or of *cis*- or *trans*-butene (Table 2) also provide strong evidence that difluorocarbene is formed in each case. The addition of reactive hydrocarbon olefins apparently accelerates the decomposition of the cyclopropanes, at the same time preventing the formation of significant amounts of carbon monoxide and silicon tetrafluoride; this may be

attributed to rapid removal of the difluorocarbene, which prevents reversal of the initial fission of the polyhalogenocyclopropane (Scheme 10). The alternative explanation, that a bimolecular reaction through a transition state such as (XVII) results in transfer of the carbene without its formation as a free entity,<sup>16</sup> is reasonable but less probable, since the kinetics of the thermal decomposition of hexafluorocyclopropane have been shown to be first-order in the early stages of the decomposition.<sup>13</sup>

In most of the experiments summarised in Table 2, very high yields of the expected difluorocarbene adduct [(XIV), (XV), or (XVI)] were obtained, and correspondingly large amounts of the residual olefin from the cyclopropane decomposition were also detected. The additions to the butenes were completely stereospecific except for the reaction of 1,1,2,2-tetrachlorodifluoro-

cyclopropane with *cis*-but-2-ene, which gave the *cis*-2,3-dimethylcyclopropane (XV) contaminated with 2%



(XVII)

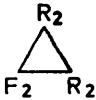
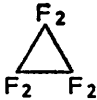

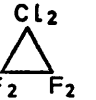
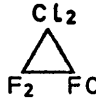
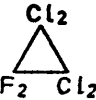
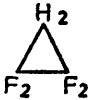
of the *trans*-isomer (XVI). However, this last case involved the most drastic conditions used for either but-2-ene, and a separate experiment showed that

1,1-difluoro-*cis*-2,3-dimethylcyclopropane itself undergoes 7% isomerisation to the *trans*-isomer and 3% decomposition to an unidentified compound during 450 h at 200° in glass. It seems safe to conclude, therefore, that decomposition of the polyhalogenocyclopropanes under these conditions leads to difluorocarbene in the familiar singlet state.

The decomposition of 1,1,2-trichlorotrifluorocyclo-

clear that the tendency for a polyhalogenocyclopropane to rearrange rather than to expel a carbene fragment is favoured by the presence of chlorine, whereas the more strongly bonded fluorine has the opposite effect. No rearrangement of the hydrogen-containing cyclopropane (VI) is observed during its decomposition at 220° in the presence of cyclohexene, 1,1-difluoroethylene and 7,7-difluoronorcarane being formed in high yields.

TABLE 2  
Reactions of the cyclopropanes with olefins

Cyclopropane	F <sub>2</sub>		FCl		Cl <sub>2</sub>		Cl <sub>2</sub>		Cl <sub>2</sub>		H <sub>2</sub>	
												
Initial amount (mmol)	2.73	6.87	6.87	6.43	5.88	6.88	9.29	5.91	6.57			
Rctn. period (h)	471	255	255	246	257	253	145	206	260			
Temp. (°C)	160	170	170	170	170	170	200	200	220			
Press. (atm)	1.5	10	10	10 <sup>a</sup>	1.5	10	1.6	1.1	0.9			
Olefin (mmol)	cyclo- C <sub>6</sub> H <sub>10</sub> (42.8)	<i>cis</i> - C <sub>4</sub> H <sub>6</sub> (68.2)	<i>cis</i> - C <sub>4</sub> H <sub>6</sub> (68.3)	<i>trans</i> - C <sub>4</sub> H <sub>6</sub> (68.2)	cyclo- C <sub>6</sub> H <sub>10</sub> (42.3)	<i>cis</i> - C <sub>4</sub> H <sub>6</sub> (68.1)	cyclo- C <sub>6</sub> H <sub>10</sub> (87.8)	<i>cis</i> - C <sub>4</sub> H <sub>6</sub> (61.7)	cyclo- C <sub>6</sub> H <sub>10</sub> (44.5)			
Extent decomp. (%)	52	92	82	90	97	100	100	97	66			
Yield $\dot{C}F_2$ adduct (%) <sup>b</sup>	92 <sup>c</sup>	42 <sup>d</sup>	84	71 <sup>d</sup>	100	98	67	87 <sup>e</sup>	93			
Yield CR <sub>2</sub> :CR <sub>2</sub> (%)	70	19	97	95	99	100	92	88	100			
CO (%)	5		Trace		Trace							
SiF <sub>4</sub> (%)	<i>f</i>	Trace	6	6	Trace	Trace	Trace					
Other products		(XI) 4% unident. products (ca. 21%)		Unident. products		C <sub>2</sub> F <sub>4</sub> (trace) (III) (trace)	Trace C <sub>2</sub> F <sub>4</sub> (trace) CF <sub>2</sub> :CCl <sub>2</sub> (trace) PhCl (14%) <sup>h</sup>	C <sub>2</sub> F <sub>4</sub> (trace)	C <sub>2</sub> F <sub>4</sub> (trace) C <sub>3</sub> Cl <sub>4</sub> F <sub>3</sub> <sup>g</sup> (12%)			

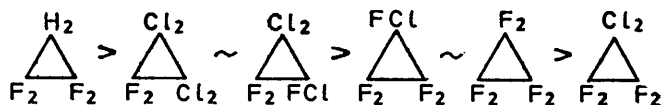
<sup>a</sup> An experiment at 1 atm with a six-molar excess of *trans*-butene gave CF<sub>2</sub>:CFCl (96%), CO (29%), and the  $\dot{C}F_2$  adduct (43%).

<sup>b</sup> Yields based on cyclopropane decomposed in each case. <sup>c</sup> J. M. Birchall, G. W. Cross, and R. N. Haszeldine, *Proc. Chem. Soc.*, 1960, 81. <sup>d</sup> N.m.r. spectra in reasonable agreement with R. A. Mitsch, *J. Amer. Chem. Soc.*, 1965, **87**, 758; i.r. and mass spectra in good agreement with structures; analytically pure samples had b.p. (isoteniscope) *cis* 51.5° at 760 mmHg, *trans* 46° at 760 mmHg. <sup>e</sup> Contained some *trans*-isomer (see text). <sup>f</sup> Detected but not measured. <sup>g</sup> Identified as CCl<sub>2</sub>:CCl:CClF<sub>2</sub> by i.r. (O. Paleta, A. Posta, and Z. Novotna, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2970), n.m.r., and mass spectroscopy. <sup>h</sup> Yield based on 1C<sub>3</sub>F<sub>3</sub>Cl<sub>3</sub> → 1C<sub>6</sub>H<sub>5</sub>Cl.

propane in the presence of cyclohexene poses further, at present unresolved, problems in relation to this particular cyclopropane. The main mode of reaction is again ejection of difluorocarbene (difluoronorcarane is formed in 67% yield), and apart from the formation of a trace of 1,1-dichlorodifluoroethylene, no clear evidence for the alternative reaction path [(b), Scheme 9] is obtained (*i.e.* 7-chloro-7-fluoronorcarane was not detected). The formation of the polyhalogenopropenes isolated from the earlier decomposition of 1,1,2-trichlorotrifluorocyclopropane alone is apparently suppressed in the presence of cyclohexene, and the detection of an appreciable amount of chlorobenzene as a product of the latter reaction is unexpected. It seems likely that the chlorobenzene arises from a free-radical reaction involving chlorine atoms, but only a speculative mechanism could be proposed at present.

The decomposition of 1,1,2,2-tetrachlorodifluorocyclopropane, which has not been studied in the absence of added olefins, gives a 12% yield of 1,1,2,3-tetrachlorodifluoropropene (CCl<sub>2</sub>:CCl:CClF<sub>2</sub>) together with the high yield of 1,1-difluoro-2,3-dimethylcyclopropane produced in the reaction with *cis*-butene (Table 2). It seems

*Discussion.*—As a result of the experiments shown in Tables 1 and 2, the cyclopropanes studied may be placed in approximate order of decreasing stability as follows:

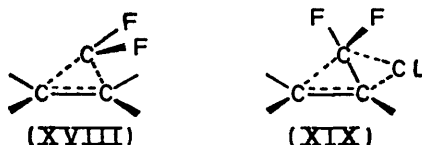


With the one possible exception already discussed, carbenoid decomposition yields only difluorocarbene in each case, a fact which may be attributed to the mesomeric effect of the fluorine atoms and its stabilising influence on the empty orbital of the carbene.<sup>17</sup> The differences in stability between the cyclopropanes studied are not large, and one important influence on their relative stabilities must be the statistical possibility of difluorocarbene expulsion; on this basis alone, hexafluorocyclopropane would decompose three times as fast as tetrachlorodifluorocyclopropane under the same conditions. However, it also seems clear that the introduction of a *gem*-dichloro-group tends to accelerate

<sup>17</sup> J. Hine and S. J. Ehrenson, *J. Amer. Chem. Soc.*, 1958, **80**, 824.

carbenoid decomposition, whereas the presence of hydrogen in a cyclopropane molecule has the opposite effect. Whether these influences are steric or electronic in origin is yet to be elucidated.

The principle of microscopic reversibility demands that the expulsion of a carbene from a cyclopropane follows a path identical with that of cyclopropane formation from the carbene and olefin. The addition reactions of methylene<sup>18</sup> and of dihalogenocarbenes<sup>19</sup> to olefins have been the subject of extensive discussion, and the 'concerted' character of the addition is widely recognised. However, completely synchronous formation or fission of two carbon-carbon bonds in a cyclopropane ring is forbidden,<sup>18</sup> and an unsymmetrical transition state of the type shown (XVIII) is envisaged at present.



The transition state for the competing rearrangement to a propene [e.g. (XIX)] need differ comparatively little from that for carbene expulsion, and a more detailed discussion of the factors controlling the two processes will be included in a subsequent paper.

#### EXPERIMENTAL

Air was rigorously excluded from all reactions carried out in sealed vessels. I.r. spectra (vapour) were measured with a Perkin-Elmer 21 instrument, n.m.r. spectra with a Perkin-Elmer R10 instrument, and mass spectra with an A.E.I. MS/2H instrument. N.m.r. coupling constants are quoted as moduli and <sup>19</sup>F chemical shifts as positive to high field of the reference. G.l.c. analysis was carried out with a Perkin-Elmer No. 116 (thermistor detector) or Griffin and George D6 (gas-density balance) instrument; columns (ca. 4 mm int. diam.) were packed with 30% w/w of the stationary phase on Celite, and the carrier gas was nitrogen. Molecular weights were measured by Regnault's method.

**Reaction of Tetrafluoroethylene with Dichlorocarbene.**—(a) *At ca. 1 atm.* (i) Tetrafluoroethylene (14.03 g, 140.3 mmol) and trifluoro(trichloromethyl)silane (4.28 g, 20.2 mmol),<sup>3,20</sup> heated at 140° for 24 h in a sealed 5 l Pyrex flask (initial calc. pressure 1.1 atm), gave, by fractionation *in vacuo*, (i) a mixture (14.4 g; *M*, 103) of tetrafluoroethylene and chlorofluorosilanes, (ii) a mixture (9.90 g; *M*, 152), shown by g.l.c. (4 m Kel-F oil; 21°) and i.r. spectroscopy to contain hexafluorocyclopropane (0.76 g, 25% yield), 1,1-dichlorodifluoroethylene (0.06 g), and 1,1-dichlorotetrafluorocyclopropane (0.07 g), (iii) a mixture (2.80 g; *M*, 167) of 1,1-dichlorodifluoroethylene (0.69 g, total yield 28%) and 1,1-dichlorotetrafluorocyclopropane (2.11 g, total yield 59%), and (iv) 1,1,2,2-tetrachlorodifluorocyclopropane (0.28 g, 13%), identified by i.r. spectroscopy. Irradiation of fraction (iii) for 60 h in the presence of bromine (3.0 g) followed by fractionation *in vacuo* yielded pure 1,1-dichlorotetrafluorocyclopropane (Found: C, 19.3;

Cl, 38.3%; *M*, 183. Calc. for C<sub>3</sub>Cl<sub>2</sub>F<sub>4</sub>: C, 19.7; Cl, 38.7%; *M*, 183), b.p. (isoteniscope) 40° at 760 mmHg, *L*<sub>v</sub> 7150 cal mol<sup>-1</sup>, λ<sub>max</sub> 6.70, 7.88, 8.33, 8.36, 10.45, 12.24, 12.31, 12.36, 12.62, and 12.99 μm (lit.,<sup>21</sup> 6.68 μm).

(ii) A similar experiment, in which tetrafluoroethylene (11.93 g, 119.3 mmol) and trifluoro(trichloromethyl)silane (4.98 g, 24.5 mmol) were heated at 140° for 88 h in a 5 l flask (initial pressure 1.0 atm) gave carbon monoxide (0.014 g, 2%), hexafluorocyclopropane (1.01 g, 28%), 1,1-dichlorodifluoroethylene (1.09 g, 33%), 1,1-dichlorotetrafluorocyclopropane (2.42 g, 56%), and 1,1,2,2-tetrachlorodifluorocyclopropane (0.29 g, 11%).

(b) *At ca. 10 atm.* Tetrafluoroethylene (14.87 g, 148.7 mmol) and the silane (6.40 g, 31.5 mmol) were divided equally, sealed in two 300 ml heavy-wall Pyrex tubes, and heated at 140° for 24 h (initial pressure 10.0 atm). Treatment of the combined products as before gave 1,1-dichlorotetrafluorocyclopropane (4.70 g, 82%) and 1,1,2,2-tetrachlorodifluorocyclopropane (0.06 g, 2%); hexafluorocyclopropane and 1,1-dichlorodifluoroethylene were detected but not estimated.

**Reaction of Chlorotrifluoroethylene with Dichlorocarbene.**—Chlorotrifluoroethylene (15.10 g, 129.6 mmol) and trifluoro(trichloromethyl)silane (3.86 g, 18.9 mmol), kept at 140° for 24 h in a 5 l flask (initial pressure 1.1 atm), gave, by fractionation *in vacuo*, carbon monoxide (0.02 g, 3%), (i) a mixture (1.01 g; *M*, 111) of chlorotrifluoroethylene and chlorofluorosilanes, (ii) a mixture (14.10 g) of chlorotrifluoroethylene, chlorofluorosilanes, 1,1,2-trichlorotrifluorocyclopropane (0.15 g after redistillation), and chloropentafluorocyclopropane (total yield 0.06 g, 2%, after treatment with an excess of bromine water then 40% aqueous sodium hydroxide, identified by i.r.), (iii) a mixture of 1,1,2-trichlorotrifluorocyclopropane (0.60 g), an unidentified compound (0.08 g), and a product which decolourised bromine water and was presumed to be trichlorofluoroethylene (0.20 g, 7%), and (iv) 1,1,2-trichlorotrifluorocyclopropane (2.44 g; total yield 3.19 g, 85%) (Found: C, 17.9; Cl, 54.3%; *M*, 200. Calc. for C<sub>3</sub>Cl<sub>3</sub>F<sub>3</sub>: C, 18.0; Cl, 53.5%; *M*, 199.5), b.p. (isoteniscope) 76° at 760 mmHg, *L*<sub>v</sub> 7132 cal mol<sup>-1</sup>. The i.r. and n.m.r. spectra of the last compound were in good agreement with those reported for a sample (b.p. 56–62°) obtained in 8.5% yield from chlorotrifluoroethylene and sodium trichloroacetate.<sup>4a</sup> The trichlorotrifluorocyclopropane has also been obtained (in 25% yield) by reaction of 1,1,2-trichlorofluoroethylene with difluorotri(trifluoromethyl)phosphorane.<sup>4b</sup>

**Tetrachlorodifluorocyclopropane.**—1,1-Dichlorodifluoroethylene (8.09 g, 60.8 mmol) and trifluoro(trichloromethyl)silane (1.95 g, 9.6 mmol), kept at 140° for 24 h in a sealed 330 ml tube (initial pressure 7.2 atm), gave 1,1-dichlorodifluoroethylene (7.23 g, 89% recovery), a mixture (0.21 g) of 1,1-dichlorodifluoroethylene, carbon tetrachloride, tetrachloroethylene, and 1,1,2,2-tetrachlorodifluorocyclopropane, and pure 1,1,2,2-tetrachlorodifluorocyclopropane (1.36 g, 66%) (Found: C, 17.0; Cl, 66.6%; *M*, 215. Calc. for C<sub>3</sub>Cl<sub>4</sub>F<sub>2</sub>: C, 17.0; Cl, 66.1%; *M*, 216), b.p. 119° at 763 mmHg (lit.,<sup>22</sup> 121° at 740 mmHg), i.r. spectrum as reported.<sup>22</sup>

**Hexafluorocyclopropane.**—(i) Tetrafluoroethylene (10.5 g, 105 mmol) and difluorotri(trifluoromethyl)phosphorane

<sup>20</sup> R. Mueller, S. Reichel, and C. Dathe, *Chem. Ber.*, 1964, **97**, 1673.

<sup>21</sup> R. A. Mitsch, *J. Heterocyclic Chem.*, 1964, **1**, 271.

<sup>22</sup> S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, 1966, **88**, 2481.

<sup>18</sup> R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475.

<sup>19</sup> See, for example, P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, 1956, **78**, 5430; P. S. Skell and M. S. Cholod, *ibid.*, 1969, **91**, 7131; R. A. Mitsch and A. S. Rodgers, *Internat. J. Chem. Kinetics*, 1969, **1**, 439.

(1.50 g, 5.45 mmol),<sup>6a</sup> kept at 120° for 65 h in a 200 ml stainless-steel rocking autoclave (initial pressure 17.8 atm), gave hexafluorocyclopropane (1.87 g, 86% after washing with aqueous 40% sodium hydroxide) (Found: *M*, 150. Calc. for C<sub>3</sub>F<sub>6</sub>: *M*, 150), identified by i.r. spectroscopy.<sup>23</sup>

(ii) An experiment in which tetrafluoroethylene (6.65 g, 66.5 mmol) and the phosphorane (1.05 g, 3.81 mmol) were kept in a 2350 ml Pyrex flask at 100° for 156 h gave carbon monoxide (0.06 g, 20%) and hexafluorocyclopropane (0.34 g, 22%) (*M*, 152).

*Chloropentafluorocyclopropane*.—Chlorotrifluoroethylene (10.10 g, 86.9 mmol) and difluorotriethylphosphorane (2.35 g, 8.5 mmol), kept at 110° for 143 h in the 200 ml rocking autoclave (initial pressure 15.0 atm), gave, after removal of phosphorus compounds by treatment with aqueous 2*M*-sodium hydroxide, chlorotrifluoroethylene (4.97 g, 49% recovery), chloropentafluorocyclopropane (3.83 g, 91%) (Found: C, 21.6%; *M*, 166.5. Calc. for C<sub>3</sub>ClF<sub>5</sub>: C, 21.6%; *M*, 166.5), b.p. (isoteniscope) 3° at 760 mmHg, *L*<sub>v</sub> 6316 cal mol<sup>-1</sup>, i.r. and n.m.r. data as reported,<sup>21</sup> and 1,2-dichlorohexafluorocyclobutane (0.25 g, 2%).

*Tetrafluorocyclopropane*.—(a) *From the phosphorane*. (i) 1,1-Difluoroethylene (33.0 g, 516 mmol) and difluorotriethylphosphorane (2.81 g, 10.2 mmol), kept at 120° for 44 h in a 1 l stainless-steel rocking autoclave (initial pressure 17.0 atm), gave, after treatment with aqueous 2*M*-sodium hydroxide where necessary, 1,1-difluoroethylene (30.4 g, 92% recovery), hexafluorocyclopropane (0.39 g, 31%), tetrafluorocyclopropane (0.49 g, 13%), and 1,1,1,3,3-pentafluorobutane (1.66 g, 7%) (Found: *M*, 148. Calc. for C<sub>4</sub>H<sub>5</sub>F<sub>5</sub>: *M*, 148), b.p. (isoteniscope) 41° at 760 mmHg (lit.,<sup>24</sup> b.p. 40.14°), *L*<sub>v</sub> 7247 cal mol<sup>-1</sup>. Redistillation gave a pure sample of 1,1,2,2-tetrafluorocyclopropane (Found: C, 31.6; H, 1.8%; *M*, 115. Calc. for C<sub>3</sub>H<sub>2</sub>F<sub>4</sub>: C, 31.8; H, 2.0%; *M*, 114), b.p. (isoteniscope) -6° (lit.,<sup>8</sup> -6°), *L*<sub>v</sub> 5630 cal mol<sup>-1</sup>, i.r. as reported.<sup>8</sup> The pentafluorobutane was identified mainly by its n.m.r. spectra: <sup>19</sup>F (external reference CF<sub>3</sub>CO<sub>2</sub>H) δ<sub>1</sub> -14.7 (tt, *J*<sub>FF</sub> 9.5, *J*<sub>F,2-H</sub> 10 Hz) and δ<sub>3</sub> 9.7 p.p.m. (qtq, *J*<sub>F,4-H</sub> 19, *J*<sub>F,2-H</sub> 14, *J*<sub>FF</sub> 9.5 Hz); <sup>1</sup>H τ<sub>2</sub> 7.30 (tq, *J*<sub>H,3-F</sub> 14, *J*<sub>H,1-F</sub> 10 Hz) and τ<sub>4</sub> 8.30 (t, *J*<sub>H,3-F</sub> 19 Hz), with integrated intensities in agreement with the proposed structure. The mass spectrum showed strong peaks at *m/e* 64 (C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>), 65 (C<sub>2</sub>H<sub>3</sub>F<sub>2</sub>), 69 (CF<sub>3</sub>), and 133 (C<sub>3</sub>H<sub>2</sub>F<sub>3</sub>); i.r. λ<sub>max</sub> 7.20, 7.78, 8.05, 8.20, and 8.98 μm.

(ii) Reaction of 1,1-difluoroethylene (6.05 g, 94.6 mmol) with the phosphorane (1.12 g, 4.1 mmol) at 95–100° for 141 h in a sealed 2350 ml Pyrex flask (initial pressure 1.3 atm) gave carbon monoxide (>45%), tetrafluoroethylene (trace), hexafluorocyclopropane (0.22 g, 34%), and 1,1,2,2-tetrafluorocyclopropane (0.09 g, 6%).

(b) *From 1,1-dichlorotetrafluorocyclopropane*. (i) The dichlorotetrafluorocyclopropane (3.18 g, 17.4 mmol) and tri-*n*-butylstannane<sup>25</sup> (11.20 g, 38.5 mmol), in a 20 ml silica tube, irradiated with u.v. light (500 W Hanovia lamp) for 17 h, gave 1,1,2,2-tetrafluorocyclopropane (1.95 g, 98%).

(ii) Reaction of 1,1-dichlorotetrafluorocyclopropane (0.61 g) with lithium aluminium hydride (0.50 g) in di-*n*-butyl ether (20 ml), at 20° for 15 h and then at 30° for 2 h, also gave 1,1,2,2-tetrafluorocyclopropane (0.14 g, 34%), but a compound believed to be chloro-1,1,2,2-tetrafluorocyclopropane was also formed.

<sup>23</sup> J. Heicklen, F. Wachi, and V. Knight, *J. Phys. Chem.*, 1965, **69**, 693.

<sup>24</sup> A. L. Henne and J. B. Hinkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 1194.

*Reaction of Difluoroethylene with Boron Trifluoride*.—1,1-Difluoroethylene (4.88 g, 76.3 mmol) and boron trifluoride (0.89 g, 13.1 mmol), heated at 120° for 70 h in a 200 ml stainless-steel rocking autoclave, gave a fraction (4.60 g), which was washed with aqueous 40% sodium hydroxide and then shown by i.r. spectroscopy and mol. wt. measurement to consist of 1,1-difluoroethylene (2.17 g, 45% recovery) and 1,1,1-trifluoroethane (0.81 g, 46% based on olefin transformed and on the hypothetical assumption that 2CF<sub>2</sub>:CH<sub>2</sub> → CF<sub>3</sub>·CH<sub>3</sub>). A less volatile fraction was passed over phosphorus pentoxide (to remove water formed by the attack of HF on the glass apparatus) and identified by i.r. spectroscopy as 1,1,1,3,3-pentafluorobutane (0.52 g, 25% based on 3CF<sub>2</sub>:CH<sub>2</sub> → C<sub>4</sub>H<sub>5</sub>F<sub>5</sub>) (Found: *M*, 149. Calc. for C<sub>4</sub>H<sub>5</sub>F<sub>5</sub>: *M*, 148).

*Pyrolysis of the Cyclopropanes in Glass*.—The products from the experiments shown in Tables 1 and 2 were separated by fractional condensation *in vacuo* and identified by i.r., n.m.r., and/or mass spectroscopy. Fractions were washed with water (to remove silicon tetrafluoride) or treated with bromine and refractionated (to remove olefins) when this was necessary to facilitate analysis. Quantitative analyses of complex fractions were achieved by g.l.c., which was also used to isolate pure components where necessary for identification.

*Pyrolysis of 1,1-Dichlorotetrafluorocyclopropane in Platinum*.—The cyclopropane (0.616 g, 3.37 mmol), heated at 180–200° for 300 h in a 33 ml platinum-lined autoclave, gave tetrafluoroethylene (0.013 g, 8%), dichlorodifluoromethane and chlorotrifluoromethane (0.016 g, combined yield 12%), and material which was separated by g.l.c. (2 m dinonyl phthalate; 23°) into the two chlorofluoromethanes (0.013 g, 10%), octafluorocyclobutane (0.07 g, 41%), 1,1-dichlorodifluoroethylene (0.13 g, 29%), 1,1-dichlorohexafluorocyclobutane (0.16 g, 20% based on CF<sub>2</sub>:CCl<sub>2</sub>, 41% based on CF<sub>2</sub>), 1,1,2,2-tetrachlorotetrafluorocyclobutane (0.107 g, 21%),<sup>26</sup> and (probably) a dichlorotetrafluoropropene (*ca.* 0.04 g, 7%).

*1,1-Dichlorohexafluorocyclobutane*.—Tetrafluoroethylene (10.39 g, 104 mmol) and 1,1-dichlorodifluoroethylene (14.87 g, 112 mmol), heated at 200° for 20 h in a 200 ml stainless steel rocking autoclave, gave tetrafluoroethylene (4.25 g, 41% recovery), a mixture of 1,1-dichloroethylene (5.68 g, 38% recovery) and octafluorocyclobutane (3.26 g), 1,1-dichlorohexafluorocyclobutane (7.38 g, 52% based on C<sub>2</sub>F<sub>4</sub> consumed, 47% based on C<sub>2</sub>Cl<sub>2</sub>F<sub>2</sub> consumed) containing a trace of 1,1-dichlorodifluoroethylene, and 1,1,2,2-tetrachlorotetrafluorocyclobutane (0.92 g, 3%), m.p. *ca.* 70° (lit.,<sup>26</sup> 84°), identified by i.r. spectroscopy. Treatment of the dichlorohexafluorocyclobutane fraction with bromine and refractionation gave pure 1,1-dichlorohexafluorocyclobutane (Found: C, 20.5; Cl, 30.8%; *M*, 233. C<sub>4</sub>Cl<sub>2</sub>F<sub>6</sub> requires C, 20.3; Cl, 30.3%; *M*, 233), b.p. (isoteniscope) 59°, *L*<sub>v</sub> 7171 cal mol<sup>-1</sup>; λ<sub>max</sub> 7.13, 7.64, 7.75, 8.11, 8.14, 8.36, 8.89, 10.16, 10.92, and 11.83 μm; <sup>19</sup>F n.m.r. spectrum (neat; external CF<sub>3</sub>·CO<sub>2</sub>H) δ<sub>2,4</sub> 44 and δ<sub>3</sub> 51 p.p.m., *m/e* 31 (CF), 69 (CF<sub>3</sub>), 93 (C<sub>3</sub>F<sub>3</sub>), 100 (C<sub>2</sub>F<sub>4</sub>), 132, 134, and 136 (C<sub>2</sub>Cl<sub>2</sub>F<sub>2</sub>), 147 and 149 (C<sub>3</sub>ClF<sub>4</sub>), and 163 and 165 (C<sub>3</sub>Cl<sub>2</sub>F<sub>3</sub>).

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<sup>25</sup> G. J. M. Kerk, J. G. Noltes, and J. G. A. Luitjen, *J. Appl. Chem.*, 1957, **7**, 366.

<sup>26</sup> A. L. Henne and R. P. Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279.