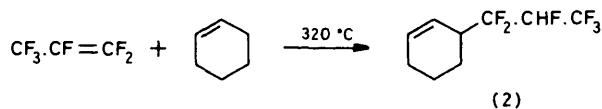
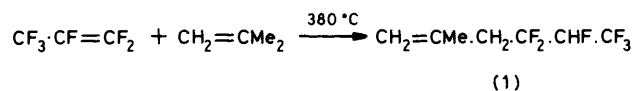


## Fluoro-olefin Chemistry. Part 15.<sup>1</sup> Thermal Reaction of Hexafluoropropene with Hydrocarbon Olefins

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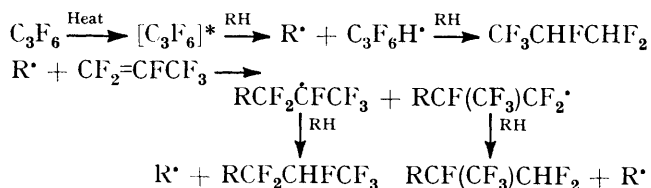
The thermal reaction of hexafluoropropene with hydrocarbon olefins can give three different types of product, 1,1,2-trifluoro-2-trifluoromethylcyclobutanes, hexafluoroalkenes of the type  $R^1R^2C=CR^3\cdot CH_2\cdot CHF\cdot CF_2\cdot CF_3$ , and 1,1,2-trifluoro-2-trifluoromethylcyclopentanes. The cyclobutanes are formed *via* diradical intermediates and the cyclopentanes *via* intermediate allyl-radical attack on the fluoro-olefin, while the hexafluoroalkenes arise *via* either of these radical intermediates or by the 'ene' reaction. With olefins of the type  $CH_2=CHR$  ( $R = Me$  or  $Et$ ), cyclobutanes are formed exclusively, while those such as  $CH_2=CMeR$  ( $R = Et$  or  $Pr^i$ ) give both cyclobutanes and hexafluoroalkenes. However, the olefins  $CH_2=CMe_2$ ,  $CHMe=CMe_2$ , and  $CMe_2=CMe_2$  afford all three types of product, but only with the alkene  $CHMe=CMe_2$  is cyclopentane-formation a major reaction (29% at 270 °C and 35% at 220 °C). Certain of the reactions are complicated by hydrocarbon-olefin isomerisation.

THE thermal cyclodimerisation of tetrafluoroethylene was first reported in 1946<sup>2</sup> and co-dimerisation with many hydrocarbon alkenes was soon investigated.<sup>3</sup> However, it was not until 1966,<sup>4</sup> after confused earlier reports,<sup>5</sup> that the structures of the thermal cyclodimers of hexafluoropropene were established. Since then several cyclodimerisation reactions between hexafluoropropene and hydrocarbon olefins, *e.g.*  $CH_2=CH_2$ ,<sup>6</sup>  $CH_2=CHMe$ ,<sup>7</sup> and  $CH_2=CMe_2$ ,<sup>8</sup> have been investigated; it was observed that the rate of cyclodimer formation was slower than that from tetrafluoroethylene and the same olefins under analogous conditions. With isobutene<sup>8</sup> and cyclohexene,<sup>9</sup> 1 : 1 adducts arising from insertion into allylic C-H bonds, *i.e.* (1) (9%) and (2) (63%), were also observed (Scheme 1).

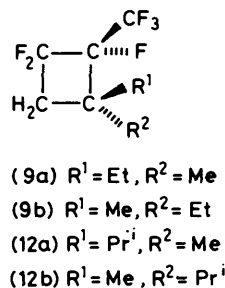
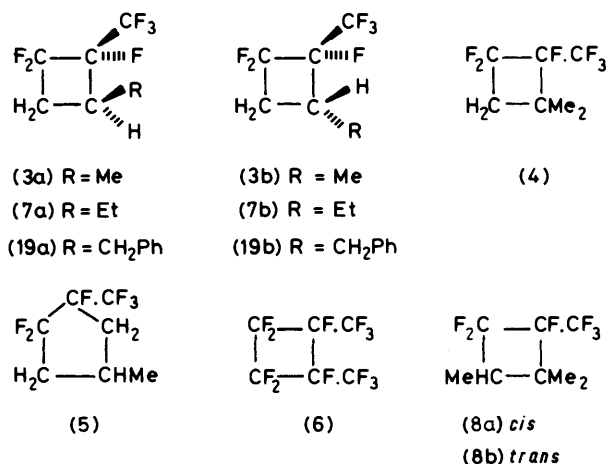


SCHEME 1

Insertion of hexafluoropropene into C-H bonds, *e.g.* in alkanes,<sup>10,11</sup> alkylbenzenes,<sup>12</sup> halogenoalkanes,<sup>9,13</sup> and dialkyl sulphides<sup>14</sup> under comparable conditions, has been observed. A radical chain mechanism initiated by thermally excited hexafluoropropene was proposed, *i.e.*



In the present work, the thermal reactions of hexafluoropropene with the hydrocarbon olefins  $CH_2=CHMe$ ,  $CH_2=CMe_2$ ,  $CH_2=CHEt$ ,  $CH_2=CMeEt$ ,  $Me_2C=CHMe$ ,  $CH_2=CMePr^i$ ,  $Me_2C=CMe_2$ , and  $CH_2=CH\cdot CH_2Ph$  have been



carried out and certain reactions have been investigated under varying conditions. The results obtained are shown in Table 1.

**Mechanisms of Product Formation.**—The major products are of three types, *i.e.* cyclobutanes, hexafluoroalkenes, and cyclopentanes and, in certain cases, a number of the products arose *via* isomerisation of the reactant alkenes. (a) *Cyclobutanes.* It is generally accepted<sup>15</sup> that the formation of cyclobutanes from fluoro-olefins under thermal conditions involves short-lived singlet diradical intermediates in which bond rotation competes with cyclisation. The major, and often exclusive product, is formed *via* the most stable diradical intermediate.

In previously reported thermal cyclisations in which

*cis*- and *trans*-1,2-disubstituted cyclobutanes were formed (e.g. with the alkene  $\text{CF}_2=\text{CFCl}$ )<sup>16</sup> the isomers were obtained in a *ca.* 1:1 ratio. This was explained on the basis of free rotation in the diradical intermediates giving an equal probability for closure to *cis*- or *trans*-structures. In the present work the *cis*- and *trans*-cyclobutanes, formed by reaction between hexafluoropropene and

formed in each case is that in which the  $\text{CF}_3$  group and the 3-substituent (methyl) are *trans*. The importance of 1,3-interactions in cyclobutane formation involving fluoro-olefins has not been reported previously.

In all cases the cyclobutanes arose *via* the predicted most stable diradical, and the olefin reactivity order  $\text{CH}_2=\text{CMe}_2 > \text{CHMe}=\text{CMe}_2 > \text{CMe}_2=\text{CMe}_2$  is as expected

TABLE 1  
Reaction of hexafluoropropene with hydrocarbon olefins

Olefin	Ratio $\text{C}_3\text{F}_6$ : hydroalkene	Temp. (°C)	Time (d)	$\text{C}_3\text{F}_6$ recovered (%)	Hydroalkene recovered (%)	Products/% <sup>a</sup>			
						Cyclobutane	Allylic insertion	Cyclopentane	Others
$\text{CH}_2=\text{CHMe}$	1:3	270	3	4	68	(3a) 48 (3b) 48			Eight <sup>c</sup> 2
$\text{CH}_2=\text{CMe}_2$	1:3	270	3	8	48	(4) 78	(1) 12	(5) 4	Four <sup>c</sup> 1 <sup>d</sup>
$\text{CH}_2=\text{CMe}_2$	1:1	270	3	19	19	(4) 81	(1) 10	(5) 2	Four <sup>c</sup> 4
$\text{CH}_2=\text{CMe}_2$	1:1	360	0.5	4	2	(4) 59	(1) 3	(5) 8	(6) 6 Fourteen <sup>c</sup> 6 SiF <sub>4</sub> Five <sup>c</sup> 3
$\text{CH}_2=\text{CMe}_2$	1:1	220	14	78	78	(4) 83	(1) 14		Six <sup>c</sup> 1
$\text{CH}_2=\text{CMe}_2$	1:1	180	28	93	93	(4) 83	(1) 16		Six <sup>c</sup> 1
$\text{CH}_2=\text{CMe}_2$ <sup>b</sup>	1:1	270	3	23	23	(4) 71	(1) 2	(5) 1	Six <sup>c</sup> 4, (6) 3
$\text{CH}_2=\text{CHEt}$	1:3	270	3	5	68	(7a) 42 (7b) 42			Fifteen <sup>c</sup> 11
$\text{CH}_2=\text{CMeEt}$	1:1	270	3	34	34 <sup>e</sup>	(8a) 1 (8b) 3 (9a) 32.5 (9b) 32.5	(10) 9 (11a) 5.5 (11b) 5.5		Five <sup>c</sup> 3
$\text{CH}_2=\text{CMeEt}$	1:1	220	14	78	78 <sup>f</sup>	(9a) 38 (9b) 38	(10) 12 (11a) 5.5 (11b) 5.5		Five <sup>c</sup> 1
$\text{CHMe}=\text{CMe}_2$	1:1	270	3	52	52 <sup>g</sup>	(8a) 6.5 (8b) 19.5 (9a) 6 (9b) 6	(10) 6 (11) 6	29 <sup>h</sup>	Five <sup>c</sup> 3
$\text{CHMe}=\text{CMe}_2$	1:1	220	14	97	97	(8) 50 (9) 6	(10) 9 (11) 9	35 <sup>h</sup>	
$\text{CH}_2=\text{CMePr}^i$	1:1	270	3	46	47 <sup>j</sup>	(1a) 23.5 (12b) 23.5	(13) 9 (14) 9		Five <sup>c</sup> 6 (6) 2
$\text{CMe}_2=\text{CMe}_2$	1:1	270	3	71	72 <sup>k</sup>	(15) 3 (12a) 9 (12b) 9	(13) 2 (14) 6	(16) 2 (17) 2	Seven <sup>c</sup> 9 <sup>l</sup> (6) 2
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Ph}$	1:1	250	3	58	3	(18) 10 <sup>m</sup> (19a) 25 (19b) 25			(6) 2 Five <sup>c</sup> 14 <sup>n</sup>

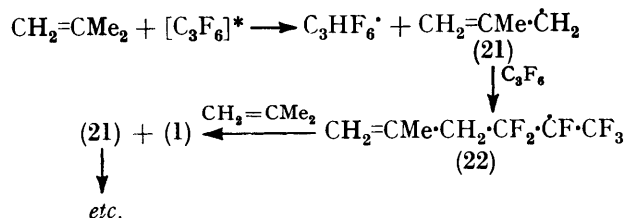
<sup>a</sup> Based on  $\text{C}_3\text{F}_6$  consumed. <sup>b</sup> Autoclave experiment. <sup>c</sup> Number of minor unidentified products (g.l.c.). <sup>d</sup> Isobutene dimers  $\text{CH}_2=\text{CMeCH}_2\cdot\text{CMe}_2$  and  $\text{Me}_2\text{C}=\text{CH}\cdot\text{CMe}_2$  also formed. <sup>e</sup> Consisting of  $\text{CH}_2=\text{CMeEt}$  (2%) and  $\text{Me}_2\text{C}=\text{CHMe}$  (32%). <sup>f</sup> Consisting of  $\text{CH}_2=\text{CMeEt}$  (55%) and  $\text{Me}_2\text{C}=\text{CHMe}$  (23%). <sup>g</sup> Consisting of  $\text{CH}_2=\text{CMeEt}$  (2%) and  $\text{Me}_2\text{C}=\text{CHMe}$  (50%). <sup>h</sup> Mixture of nine isomers. <sup>i</sup> Consisting of  $\text{CH}_2=\text{CMePr}^i$  (7%) and  $\text{Me}_2\text{C}=\text{CMe}_2$  (40%). <sup>j</sup> Consisting of  $\text{CH}_2=\text{CMePr}^i$  (10%) and  $\text{Me}_2\text{C}=\text{CMe}_2$  (62%). <sup>k</sup> Including two unidentified adducts (5 and 2%). <sup>l</sup> Four isomers (75:9:7:9). <sup>m</sup> The compounds PhMe (1%), PhPr<sup>n</sup> (19%), (Z)-PhCH=CHMe (3%), and (E)-PhCH=CHMe (7%) also formed (yields based on hydroalkene consumed).

terminal alkenes (such as  $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{R}$  (R = H, Me, Ph) and  $\text{CH}_2=\text{CMeR}$  (R = Et, Pr<sup>i</sup>), were also obtained in a *ca.* 1:1 ratio despite the increasing bulk of the R group in the two series. Thus, steric factors are apparently unimportant in the formation of these *cis*- and *trans*-1,2-disubstituted cyclobutanes.

With non-terminal olefins, however, there were noticeable deviations from the *ca.* 1:1 ratio, *i.e.* with  $\text{MeCH}=\text{CMe}_2$  the ratio of (8a):(8b) was 1:3, and with  $\text{PhCH}=\text{CHMe}$  (formed by isomerisation of  $\text{PhCH}_2\cdot\text{CH}=\text{CH}_2$ ), four cyclobutanes were obtained (75:9:7:9) and the major adduct was assigned the structure (18a). These results indicate that 1,3-steric interactions in the diradical are important in determining the amounts of individual cyclobutane isomers formed; the major isomer

on the basis of increasing steric hindrance to initial bond formation involving  $\text{CH}_2$ , CHMe, and  $\text{CMe}_2$ , respectively.

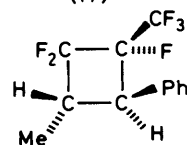
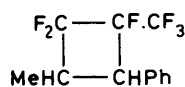
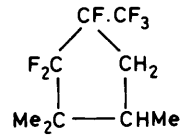
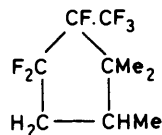
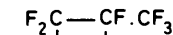
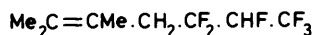
(b) *Hexafluoroalkenes.* In 1966 it was reported<sup>8</sup> that the reaction of hexafluoropropene with isobutene (1:1 molar) at 380 °C (10 h) gave products (4) (28%) and (1) (9%). Details of product characterisation were not given and it was suggested that compound (1) was formed by the 'ene' reaction. Apart from the one-step 'ene' reaction, two other mechanisms need to be considered. These are (i) rearrangement of the diradical precursor (20) to the cyclobutane (4) (a two-step 'ene' reaction) (Scheme 2) and (ii) a chain mechanism initiated by allylic hydrogen abstraction analogous to that proposed previously for insertion of hexafluoropropene into C-H bonds in saturated compounds, *i.e.*



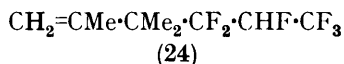
The reaction involving 2-methylbut-1-ene could give compounds (10) and (11) *via* the 'ene' mechanism, and compounds (10), (11), and (23) *via* a radical mechanism,



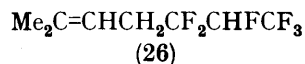
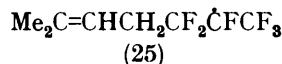
(10) R = Et

(11a) *cis*(13) R = Pr<sup>i</sup>(11b) *trans*

while 2,3-dimethylbut-1-ene could give compounds (13) and (14) *via* the 'ene' mechanism, and compounds (13), (14), and (24) *via* a radical mechanism; compounds (23) and (24) were not detected in the products.



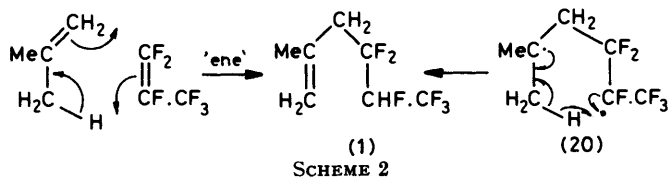
Intermediate radicals such as (22) are considered to be precursors to the cyclopentanes (see later) and, although cyclopentanes derived from radical (25) were observed in the 2-methylbut-2-ene reaction products, the alkene (26) was not detected.



Furthermore, in the isobutene reaction, as the temperature was lowered the yield of alkene (1) increased at the expense of the cyclopentane (5). It is difficult to explain why cyclisation of the radical (22), *via* a five-centre transition state involving attack on the terminal olefinic double-bond, should not be favourable at the lower temperature relative to hydrogen abstraction.

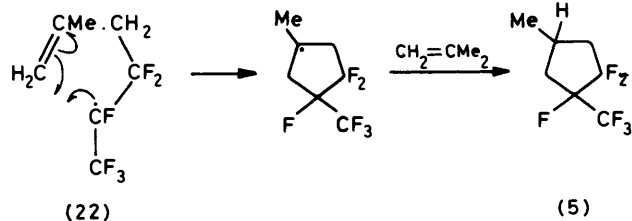
On balance therefore it is more probable that the hexafluoroalkenes are formed *via* the concerted 'ene' or diradical mechanisms.

All of the isolated hexafluoroalkenes were derived from the 2-methylalk-1-enes  $\text{CH}_2=\text{CMeR}$  (R = Me, Et, or Pr<sup>i</sup>)

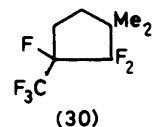
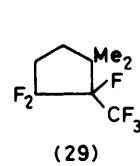
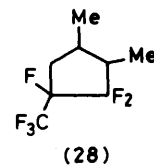
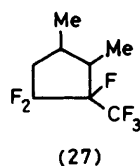


even when internal olefins were the reactants. If the concerted 'ene' mechanism is operative, this observation can be explained on the basis of increased steric hindrance with the non-terminal olefins which renders the 'ene' reaction unfavourable relative to cyclobutane and cyclopentane formation.

(c) *Cyclopentanes*. The original report<sup>8</sup> on the reaction of hexafluoropropene with isobutene did not mention the formation of the cyclopentane (5). In the present work, however, compound (5) was isolated as a mixture of the *cis*- and *trans*-isomers (2% at 270 °C and 8% at 360 °C; 1:1 molar ratio of reactants). It is proposed that the compound arises *via* cyclisation of radical (22) (Scheme 3).



In the other terminal alkene reactions cyclopentanes were not observed, but they were formed in the reactions with non-terminal olefins; in these cyclobutane formation occurred at a slower rate because of steric hindrance. Only with 2-methylbut-2-ene were cyclopentanes obtained in reasonable yields (35% at 270 °C and 29% at 220 °C) at the expense of other 1:1 adducts. Ten cyclopentanes are possible with this alkene, *i.e.* four isomers of structure (27), four isomers of structure (28) (formed *via* the allyl radical  $\dot{\text{C}}\text{H}_2\text{CMe}=\text{CHMe} \longleftrightarrow \text{CH}_2=\text{CMe}\cdot\dot{\text{C}}\text{HMe}$ ), and compounds (29) and (30) (formed *via*



the allyl radical  $\dot{\text{C}}\text{H}_2\cdot\text{CH}=\text{CMe}_2 \leftrightarrow \text{CH}_2=\text{CH}\cdot\dot{\text{C}}\text{Me}_2$ . Nine isomers were detected and they were separated into the following: a mixture of four isomers, a mixture of two isomers, and three individual isomers. Identification of individual isomers was not possible because the n.m.r. spectra were complex, but the isomers were shown to be cyclopentanes by the magnitude of the geminal F-F coupling (*ca.* 250 Hz). Thus allylic hydrogen abstraction occurs from both the CHMe and CMe<sub>2</sub> groups in the alkene. In the reaction involving 2,3-dimethylbut-2-ene, all four isomers of structures (16) and (17) were formed in low yield (2%).

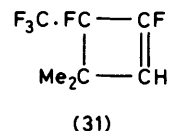
Thus it is probable that three distinct mechanisms can operate for the reactions of hexafluoropropene with hydrocarbon olefins, and the products obtained were dependent on the olefin used. With olefins of the type  $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{R}$  (R = H, Me, or Ph) cyclobutane formation occurred to the exclusion of other 1:1 adducts, while with those such as  $\text{CH}_2=\text{CRMe}$  (R = Me, Et, or Pr<sup>i</sup>) hexafluoroalkene formation became increasingly competitive with cyclobutane formation along the series. For the non-terminal olefins  $\text{Me}_2\text{C}=\text{CHMe}$  and  $\text{Me}_2\text{C}=\text{CMe}_2$ , the formations of cyclobutane and hexafluoroalkene were relatively slow, thus allowing cyclopentane formation *via* allylic hydrogen abstraction to be competitive; this last-named mechanism was also more competitive with isobutene at a higher temperature.

The reactant olefin isomerisations observed were probably acid-catalysed, involving the walls of the Pyrex (fluorosilicate) reaction ampoules.

Attempted dehydrofluorination of the cyclobutane (4)

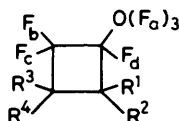
with an excess of powdered potassium hydroxide at 200 °C (72 h) gave unchanged starting material (66% recovered) and 2,3-difluoro-4,4-dimethyl-3-trifluoromethylcyclobutene (31) in very low yield (<1%).

*Structural Assignments.*—These were made mainly on the basis of <sup>19</sup>F n.m.r. and mass spectral evidence, although g.l.c. retention times (in general cyclopentanes > hexafluoroalkenes > cyclobutanes) and the absence or presence of vinylic protons (as shown by <sup>1</sup>H n.m.r. and i.r. spectra) were also helpful.



*Cyclobutanes.*—(a) <sup>19</sup>F N.m.r. spectra. The major features observed in the spectra are shown in Table 2. All the spectra, except for those of compounds (18b—d) [obtained for a mixture containing (18a) as the major component] and (12b), showed a geminal F-F coupling in the range 209—220 Hz as expected for cyclobutanes (reported range 195—240 Hz). The *cis*- and *trans*-assignments for compounds derived from terminal olefins, which contain an alkyl group on the carbon (C-2) adjacent to the CF·CF<sub>3</sub> group, were made on the basis that (i) a CF<sub>3</sub> group *cis* to the hydrogen on C-2 absorbs at higher field than a CF<sub>3</sub> group *cis* to alkyl, and (ii) the fluoromethine fluorine atom (F<sub>a</sub>; see Table 2) *cis* to hydrogen on C-2 absorbs at lower field than if it is *cis* to alkyl [*cf.* compounds (29) and (4)]. The compounds

TABLE 2

<sup>19</sup>F n.m.r. data for cyclobutanes

Compound	Compound				Chemical shifts (p.p.m.) <sup>a</sup>				J(Hz) <sup>b</sup> b-c
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	F <sub>a</sub>	F <sub>b</sub>	F <sub>c</sub>	F <sub>d</sub>	
(29)	H	H	H	H	+3.6	+24.2	+37.6	+99.2	214
(3b)	H	Me	H	H	+3.2	+28.7	+31.8	+119.7	218
(3a)	Me	H	H	H	-1.7	+25.0	+42.4	+98.0	219
(4)	Me	Me	H	H	-2.8	+25.0	+34.2	+109.2	219
(7b)	H	Et	H	H	+3.2	+29.3	+32.2	+121.2	220
(7a)	Et	H	H	H	-2.4	+24.8	+42.1	+97.2	216
(9b)	Me	Et	H	H	-3.6	+25.9	+31.5	+108.9	220
(9a)	Et	Me	H	H	-3.0	+23.6	+32.7	+104.4	220
(8b)	Me	Me	H	Me	-2.6	+23.9	+50.1	+108.0	220
(8a)	Me	Me	Me	H	-3.8	+26.9	+49.2	+109.2	209
(12b)	Me	Pr <sup>i</sup>	H	H	-4.4	+29.1	+29.1	+110.6	
(12a)	Pr <sup>i</sup>	Me	H	H	-3.9	+21.4	+33.1	+102.3	216
(15)	Me	Me	Me	Me	-4.0	+40.7	+43.3	+106.4	216
(19b)	H	Bz	H	H	+1.9	+27.6	+29.9	+115.0	214
(19a)	Bz	H	H	H	-2.7	+23.7	+39.9	+93.6	212
(18a)	Ph	H	H	Me	-3.3	+25.2	+54.4	+91.1	210
(18b)	Ph	H	Me	H	-0.5				
(18c)	H	Ph	Me	H	+2.1 or +1.0				
(18d)	H	Ph	H	Me	+1.0 or +2.1				

<sup>a</sup> Shifts to low field of reference (CF<sub>3</sub>-CO<sub>2</sub>H) are negative. <sup>b</sup> The coupling constants *J*<sub>ab</sub>, *J*<sub>ad</sub>, and *J*<sub>cd</sub> were *ca.* 8, *ca.* 8, and *ca.* 16 Hz, respectively.

which contain two alkyl groups on C-2 were designated *cis* and *trans* by the relative dispositions of the  $\text{CF}_3$  and bulkier alkyl group, and were differentiated by (i) the fact that the  $\text{CF}_3$  group *cis* to the smaller alkyl group absorbs at lower field than the  $\text{CF}_3$  group *cis* to the bulkier alkyl group, and (ii) atom  $\text{F}_a$  *cis* to the smaller alkyl group absorbs at lower field than when it is *cis* to the bulkier alkyl group. With the cyclobutanes (8a and b) and (18a), the disposition of the methyl group on C-3 was assigned by its effect on the chemical shifts of the fluorines  $\text{F}_b$  and  $\text{F}_c$  [a *cis*-methyl group causes a high-field shift relative to a *cis*-hydrogen atom, *cf.* compounds (29) and (4)].

(b) *Mass spectra.* All the spectra showed a parent-ion peak and the most typical mass spectral breakdown observed involved cross-ring cleavage, as indicated, with major cleavage occurring by either path A or B depending on the particular cyclobutane: *e.g.* compound (3b), *m/e* 64 (72%,  $\text{CF}_2\text{CH}_2^+$ ) and 128 (70%,  $\text{CF}_3\text{CFCHMe}^+$ ) *via* path A, and *m/e* 42 (87%  $\text{CH}_2\text{CHMe}^+$ ) *via* path B; compound (4), *m/e* 64 (16%) and 142 (78%,  $\text{CF}_3\text{CFCMe}_2^+$ ) *via* path A, and *m/e* 56 (98%,  $\text{CH}_2\text{CMe}_2^+$ ) *via* path B.

*Hexafluoroalkenes.*—(a) *N.m.r. spectra.* All of the six compounds prepared contained the  $\text{CH}_2\text{CF}_2\text{CHFCF}_3$  grouping, and the relevant chemical shifts and coupling constants observed in the spectra are as follows:  $\text{C}(\text{H}_a)_2$ :  $\text{CF}_a\text{CF}_b\text{CH}_b\text{F}_c$ :  $\text{C}(\text{F}_d)_3$ ;  $\tau$  7.60  $\pm$  0.1 ( $\text{H}_a$ ), 5.68  $\pm$  0.6 ( $\text{H}_b$ ), *ca.* +30 ( $\text{F}_a\text{F}_b$ ), +133  $\pm$  1 ( $\text{F}_c$ ), and  $-2.4 \pm 0.3$  ( $\text{F}_d$ ) p.p.m.;  $J_{AB}$  264  $\pm$  4 Hz,  $J_{bc}$  43–44 Hz. These chemical shifts and coupling constants are in the expected ranges as the  $\text{CH}_2$  group is also allylic. Vinylic protons and allylic methyl groups also absorbed in the expected regions,  $\tau$  5.15  $\pm$  0.35 and  $\tau$  8.65  $\pm$  0.05, respectively.

(b) *Mass spectra.* Relatively strong parent-ion peaks were present in all the spectra, and major breakdown was observed involving cleavage of the  $\text{RCH}_2\text{-CF}_2$  bond to give the  $\text{RCH}_2^+$  ion as the base peak.

(c) *I.r. spectra.* All the alkenes, except compound (14), showed an absorption between 6.00 and 6.20  $\mu\text{m}$  ( $\text{C}=\text{C}$  stretch) in their i.r. spectra.

*Cyclopentanes.*—These compounds showed the absence of a CHF group and the presence of a tertiary fluorine (85–117 p.p.m.) in their  $^{19}\text{F}$  n.m.r. spectra; the cyclopentane ring was confirmed by the magnitude of the geminal F–F coupling (246–254 Hz). The  $^1\text{H}$  n.m.r. spectra showed only the presence of methine, methylene, and methyl hydrogens (no absorptions at lower field than  $\tau$  7.7). However, the spectra were complex and, in a number of cases, mixtures of isomers were present, so it was not possible to assign definite structures except in the case of the isobutene adducts (5); for these the low-field fluoromethine absorption (92.8 p.p.m.) was assigned to the *cis*-isomer (F and H *cis*) and the high-field absorption (104.5 p.p.m.) was assigned to the *trans*-isomer (F and H *trans*).

The mass spectra were of little help in structural assignment although parent ions were always present. The isobutene adduct showed a base peak in its spectrum at *m/e* 91 [ $(M - \text{C}_2\text{F}_4\text{Me})^+$ , *i.e.*  $\text{C}_4\text{H}_5\text{F}_2^+$ ], while the

spectra of all the 2-methylbut-2-ene adducts and the mixture of 2,3-dimethylbut-2-ene adducts showed a base peak due to the ion  $(M - \text{C}_3\text{HF}_6)^+$  at *m/e* 69 ( $\text{C}_5\text{H}_9^+$ ) and 83 ( $\text{C}_6\text{H}_{11}^+$ ), respectively.

## EXPERIMENTAL

Reactants and products were manipulated in a vacuum system, where possible, to avoid contamination with air or moisture. Tube and autoclave reactions were carried out *in vacuo* in Pyrex tubes (*ca.* 300  $\text{cm}^3$ ) and Hastelloy autoclaves (*ca.* 500  $\text{cm}^3$ ), respectively. Products were partially separated by fractional condensation *in vacuo* and individual components were separated from the fractions obtained by preparative scale g.l.c. [Perkin-Elmer F 21 instrument; columns of trixylyl phosphate (TXP), Apiezon L grease (APL), polyethyleneglycol adipate (PEGA), or Silicone SE 30 oil (15–25% on Celite)]. They were examined by i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R 10 spectrometer operating at 60.0 MHz for  $^1\text{H}$  and 56.46 MHz for  $^{19}\text{F}$ , or a Varian HA-100 spectrometer operating at 100.0 MHz for  $^1\text{H}$  and 94.1 MHz for  $^{19}\text{F}$ , with external tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS 902 spectrometer). The mass spectra of individual components of mixtures were obtained by coupled g.l.c.–mass spectrometry. B.p.s were determined by Siwoloboff's method.

*Thermal Reactions of Hexafluoropropene with Hydrocarbon Alkenes.*—(a) *With propene.* A mixture of hexafluoropropene (2.25 g, 15.0 mmol) and propene (1.89 g, 45.0 mmol) was sealed *in vacuo* in a Pyrex ampoule and heated at 270  $^\circ\text{C}$  (3d) to give (i) a mixture (1.37 g, 31.2 mmol; *M*, 44) of unchanged hexafluoropropene (0.09 g, 0.6 mmol, 4% recovered) and unchanged propene (1.28 g, 30.6 mmol, 68% recovered); (ii) a mixture (2.71 g) of two major components (1:1 ratio) and eight minor components (*ca.* 2% of the fraction), which, on separation by g.l.c. (7-m SE 30 at 30  $^\circ\text{C}$ ), afforded *trans*-1,1,2-trifluoro-3-methyl-2-trifluoromethylcyclobutane (3b) (1.33 g, 6.9 mmol, 48%) (Found: C, 37.5; H, 3.1; F, 58.9%; *M*<sup>+</sup>, 192.  $\text{C}_6\text{H}_5\text{F}_6$  requires C, 37.5; H, 3.2; F, 59.3%; *M*, 192), b.p. 85  $^\circ\text{C}$ , and *cis*-1,1,2-trifluoro-3-methyl-2-trifluoromethylcyclobutane (3a) (1.33 g, 6.9 mmol, 48%) (Found: C, 37.6; H, 3.3; F, 59.1%; *M*<sup>+</sup> 192), b.p. 91  $^\circ\text{C}$ ; and (iii) a small amount of charred material which remained in the tube and was not examined further.

(b) *With isobutene.* A mixture of hexafluoropropene (2.25 g, 15.0 mmol) and isobutene (2.52 g, 45.0 mmol) was sealed *in vacuo* in a Pyrex ampoule and heated at 270  $^\circ\text{C}$  (3d) to give (i) a mixture (1.39 g, 22.9 mmol; *M*, 61) of unchanged hexafluoropropene (0.18 g, 1.2 mmol, 8% recovered) and unchanged isobutene (1.21 g, 21.7 mmol, 48% recovered); (ii) a liquid mixture (3.19 g), shown by g.l.c. (2-m SE 30 at 45  $^\circ\text{C}$ ) to contain four major components (80:3:11:6) and four minor components (*ca.* 1% of fraction); and (iii) a small amount of charred material which remained in the tube and was not examined further. The four major components of the liquid mixture were separated by g.l.c. (7-m SE 30 at 65  $^\circ\text{C}$ ), but the first component was shown to be a mixture of two further components (87:13) and was re-separated (7-m TXP at 85  $^\circ\text{C}$ ) to give 1,1,2-trifluoro-3,3-dimethyl-2-trifluoromethylcyclobutane (4) (2.21 g, 10.7 mmol, 78%) (Found: C, 40.9; H, 4.1; F, 55.1%; *M*<sup>+</sup>, 206. Calc. for  $\text{C}_7\text{H}_8\text{F}_6$ : C, 40.8; H, 3.9; F,

55.3%; *M*, 206), b.p. 102 °C (lit.,<sup>8</sup> 99 °C), and 4,4,5,6,6,6-hexafluoro-2-methylhex-1-ene (1) (0.33 g, 1.6 mmol, 12%) (Found: C, 41.0; H, 4.0; F, 55.7%; *M*<sup>+</sup>, 206), b.p. 98 °C (lit.,<sup>8</sup> 95 °C). The remaining components were found to be 1,1,2-trifluoro-4-methyl-2-trifluoromethylcyclopentane (5) (0.10 g, 0.5 mmol, 4%) (Found: C, 41.0; H, 4.0; F, 54.8%; *M*<sup>+</sup>, 206) as a mixture of the *cis*- and *trans*-isomers in the ratio 1 : 1, b.p. 121 °C; 2,4,4-trimethylpent-1-ene (0.35 g, 3.1 mmol, 27% based on isobutene) identified by a comparison of its i.r., n.m.r., and mass spectra with those of an authentic sample; and a mixture (0.18 g, 1.6 mmol, 14% based on isobutene) of 2,4,4-trimethylpent-2-ene and two other, unidentified octenes (ratio 64 : 27 : 9) with the major olefin identified by a comparison of its i.r., n.m.r., and mass spectra with those of an authentic sample.

Further experiments using a 1 : 1 molar ratio of reactants (30.0 mmol of each) at (i) 270 °C (3 d), (ii) 360 °C (12 h), (iii) 220 °C (14 d), and (iv) 180 °C (28 d) in Pyrex tubes, and an autoclave experiment (1 : 1 ratio of reactants, 0.30 mol of each) at 270 °C (3 d) were also carried out; the results are given in Table 1.

(c) *With but-1-ene*. A mixture of hexafluoropropene (2.25 g, 15.0 mmol) and but-1-ene (2.25 g, 45.0 mmol) was sealed *in vacuo* in a Pyrex ampoule and heated at 270 °C (3d) to give (i) a mixture (1.83 g, 31.4 mmol; *M*, 59) of unchanged hexafluoropropene (0.12 g, 0.8 mmol, 5% recovered) and unchanged but-1-ene (1.71 g, 30.6 mmol, 68% recovered); (ii) a liquid fraction (2.76 g), which was shown by g.l.c. (3-m TXP at 65 °C) to contain two major components (1 : 1) and fifteen minor components (11% of fraction) with different retention times to those of the major components; and (iii) a small amount of charred residue which remained in the tube and was not examined further. The two major components of the liquid fraction were separated by g.l.c. (7-m TXP at 85 °C) and identified as *trans*-3-ethyl-1,1,2-trifluoro-2-trifluoromethylcyclobutane (7b) (1.24 g, 6.0 mmol, 42%) (Found: C, 41.2; H, 4.1; F, 54.8%; *M*<sup>+</sup>, 206. C<sub>7</sub>H<sub>8</sub>F<sub>8</sub> requires C, 40.8; H, 3.9; F, 55.3%; *M*, 206), b.p. 104 °C, and *cis*-3-ethyl-1,1,2-trifluoro-2-trifluoromethylcyclobutane (7a) (1.21 g, 6.0 mmol, 42%) (Found: C, 41.0; H, 4.1; F, 54.9%; *M*<sup>+</sup>, 206), b.p. 108 °C.

(d) *With 2-methylbut-1-ene*. A mixture of hexafluoropropene (4.50 g, 30.0 mmol) and 2-methylbut-1-ene (2.10 g, 30.0 mmol) was sealed *in vacuo* in a Pyrex ampoule and heated at 270 °C (3 d) to give (i) unchanged hexafluoropropene (1.53 g, 10.2 mmol, 34% recovered); (ii) a mixture (0.71 g, 10.2 mmol; *M*, 70) of unchanged 2-methylbut-1-ene (0.04 g, 0.6 mmol, 2% recovered) and 2-methylbut-2-ene (0.67 g, 9.6 mmol, 32% on initial alkene), as shown by their g.l.c. (2-m SE 30 at 25 °C) retention times and i.r. and mass spectral data; (iii) a higher-boiling liquid fraction (3.94 g) which was shown by g.l.c. (2-m PEGA at 60 °C) to contain four major components (5 : 73 : 10 : 12) and five minor components (*ca.* 3% of fraction); and (iv) a small amount of charred material (0.4 g) which remained in the tube and was not examined further. The major components of the liquid fraction were separated by g.l.c. (6-m PEGA at 90 °C) and identified as: a mixture of *cis*- and *trans*-1,1,2-trifluoro-3,3,4-trimethyl-2-trifluoromethylcyclobutane (8) (0.17 g, 0.8 mmol, 4%) (Found: C, 43.8; H, 4.8; F, 51.7%; *M*<sup>+</sup>, 220. C<sub>8</sub>H<sub>10</sub>F<sub>8</sub> requires C, 43.6; H, 4.6; F, 51.8%; *M*, 220), b.p. 120 °C, present in the ratio 1 : 3 (<sup>19</sup>F n.m.r. spectroscopy); a mixture of *cis*- and *trans*-3-ethyl-1,1,2-trifluoro-3-methyl-2-trifluoromethylcyclobutane (9) (2.83 g, 12.9 mmol, 65%) (Found: C, 43.8; H, 4.6; F, 51.7%; *M*<sup>+</sup>,

220), b.p. 124 °C, present in the ratio 1 : 1 (<sup>1</sup>H and <sup>19</sup>F n.m.r. spectroscopy); 2-ethyl-4,4,5,6,6,6-hexafluorohex-1-ene (10) (0.37 g, 1.7 mmol, 9%) (Found: C, 43.4; H, 4.6; F, 51.6%; *M*<sup>+</sup>, 220), b.p. 119 °C; λ<sub>max</sub> 6.05 μm (C=C str.); and a mixture of *cis*- and *trans*-5,5,6,7,7,7-hexafluoro-3-methylhept-2-ene (11) (0.47 g, 2.1 mmol, 11%) (Found: C, 43.6; H, 4.6; F, 51.5%; *M*<sup>+</sup>, 220), b.p. 123 °C; λ<sub>max</sub> 6.16 μm and 6.25 μm (C=C stretch), present in the ratio 1 : 1 (<sup>1</sup>H and <sup>19</sup>F n.m.r. spectroscopy).

A second reaction using the same quantities of reactants and carried out at 220 °C (14 d) gave the results shown in Table 1.

(e) *With 2-methylbut-2-ene*. A mixture of hexafluoropropene (4.50 g, 30.0 mmol) and 2-methylbut-2-ene (2.10 g, 30.0 mmol) was sealed *in vacuo* in a Pyrex tube and heated at 270 °C (3 d) to give (i) unchanged hexafluoropropene (2.34 g, 15.6 mmol, 52% recovered); (ii) a mixture (1.09 g, 15.6 mmol; *M*, 70) of unchanged 2-methylbut-2-ene (1.05 g, 15.0 mmol, 50% recovered) and 2-methylbut-1-ene (0.04 g, 0.6 mmol, 2% on initial alkene), as shown by g.l.c. (2-m SE 30 at 25 °C); (iii) a higher-boiling liquid fraction (2.42 g) which was shown by g.l.c. (3-m TXP at 80 °C) to contain nine major components (36 : 19 : 6 : 6 : 18 : 4 : 4 : 4 : 3) and five minor components (*ca.* 3% of the fraction); and (iv) a charred residue (0.7 g) which remained in the reaction tube and was not examined further. The major components of this liquid fraction were separated by g.l.c. (7-m TXP at 110 °C) to give (a) a mixture of the *cis*- and *trans*-cyclobutanes (8) (0.84 g, 3.8 mmol, 26%) in the ratio 1 : 3 (<sup>19</sup>F n.m.r.), (b) a mixture of three components as shown by g.l.c. (2-m PEGA at 65 °C) in the ratio 64 : 10 : 26, which was re-separated by g.l.c. (6-m PEGA at 80 °C) into its components; these were identified as a mixture of the *cis*- and *trans*-cyclobutanes (9) (0.38 g, 1.7 mmol, 12%) in the ratio 1 : 1 (<sup>19</sup>F n.m.r.), a mixture of hexafluoro-octenes (0.06 g, 0.3 mmol, 2%), and a mixture of hexafluoro-octenes (0.13 g, 0.6 mmol, 4%) (Found: C, 43.8; H, 4.6; F, 52.2%; *M*<sup>+</sup>, 220. Calc. for C<sub>8</sub>H<sub>10</sub>F<sub>8</sub>: C, 43.6; H, 4.6; F, 51.8%; *M*, 220), (c) a mixture of four unidentified trifluorodimethyltrifluoromethylcyclopentanes (A—D) (0.56 g, 2.5 mmol, 17%) (Found: C, 43.6; H, 4.7; F, 52.2%; *M*<sup>+</sup>, 220), b.p. 134 °C, present in the ratio 30 : 9 : 4 : 7 (<sup>19</sup>F n.m.r.), (d) an unidentified trifluorodimethyltrifluoromethylcyclopentane (E) (0.09 g, 0.4 mmol, 3%) (Found: C, 43.3; H, 4.6; F, 51.3%; *M*<sup>+</sup>, 220), b.p. 136 °C, (e) a mixture of two unidentified trifluorodimethyltrifluoromethylcyclopentanes (F and G) (0.10 g, 0.4 mmol, 3%) (Found: C, 43.9; H, 4.7; F, 51.5%; *M*<sup>+</sup>, 220), b.p. 138 °C, in the ratio 31 : 19 (<sup>19</sup>F n.m.r.), (f) an unidentified trifluorodimethyltrifluoromethylcyclopentane (H) (0.10 g, 0.4 mmol, 3%) (Found: C, 43.8; H, 4.6; F, 51.8%; *M*<sup>+</sup>, 220), b.p. 140 °C, and (g) an unidentified trifluorodimethyltrifluoromethylcyclopentane (I) (0.08 g, 0.4 mmol, 3%) (Found: C, 43.7; H, 4.7; F, 51.3%; *M*<sup>+</sup>, 220), b.p. 142 °C.

A second reaction (1 : 1 molar ratio) carried out at 220 °C (14 d) gave the results shown in Table 1.

(f) *With 2,3-Dimethylbut-1-ene*. A mixture of hexafluoropropene (4.50 g, 30.0 mmol) and 2,3-dimethylbut-1-ene (2.52 g, 30.0 mmol) was sealed *in vacuo* in a Pyrex ampoule and heated at 270 °C (3 d) to give (i) unchanged hexafluoropropene (2.07 g, 13.8 mmol, 46% recovered), (ii) a mixture of *cis*- and *trans*-1,2-bis(trifluoromethyl)hexafluorocyclobutane (6) (0.09 g, 0.3 mmol, 2%), (iii) a mixture (1.18 g, 14.1 mmol; *M*, 84) of unchanged 2,3-dimethylbut-1-ene (0.18 g, 2.1 mmol, 7% recovered) and 2,3-dimethylbut-2-ene (1.00 g,

12.0 mmol, 40% based on initial alkene) as shown by their g.l.c. (3-m TXP at 60 °C) retention times and i.r. spectra, (iv) a higher-boiling liquid fraction (2.62 g) which was shown by g.l.c. (3-m TXP at 90 °C) to contain three major components (14 : 73 : 13) and five minor components (*ca.* 6% of fraction), and (v) a charred residue (*ca.* 1.0 g) which was not examined further. The three major components of the liquid fraction were separated by g.l.c. (7-m TXP at 125 °C) and were identified as 4,4,5,6,6,6-hexafluoro-2-isopropylhex-1-ene (13) (0.35 g, 1.5 mmol, 9%) (Found: C, 46.1; H, 5.1; F, 48.7%;  $M^+$ , 234.  $C_9H_{12}F_6$  requires C, 46.2; H, 5.2; F, 48.7%;  $M$ , 234), b.p. 135 °C;  $\lambda_{\max}$  6.06  $\mu\text{m}$  (C=C stretch) a mixture of *cis*- and *trans*-1,1,2-trifluoro-3-isopropyl-3-methyl-2-trifluoromethylcyclobutane (12) (1.78 g, 7.6 mmol, 47%) (Found: C, 46.2; H, 5.2; F, 48.5%;  $M^+$ , 234), b.p. 144 °C, present in the ratio 1 : 1 ( $^{19}\text{F}$  n.m.r.) and 5,5,6,7,7,7-hexafluoro-2,3-dimethylhept-2-ene (14) (0.32 g, 1.4 mmol, 9%) (Found: C, 46.2; H, 4.9; F, 48.5%;  $M^+$ , 234), b.p. 143 °C.

(g) *With 2,3-dimethylbut-2-ene.* A mixture of hexafluoropropene (4.50 g, 30.0 mmol) and 2,3-dimethylbut-2-ene (2.52 g, 30.0 mmol) was sealed *in vacuo* in a Pyrex ampoule and heated at 270 °C (3 d) to give (i) unchanged hexafluoropropene (3.20 g, 21.3 mmol, 71% recovered), (ii) compound (6) (0.09 g, 0.3 mmol, 2%), (iii) a mixture (1.81 g, 1.6 mmol;  $M$ , 84) of unchanged 2,3-dimethylbut-2-ene (1.56 g, 18.6 mmol, 62% recovered) and 2,3-dimethylbut-1-ene (0.25 g, 3.0 mmol, 10% based on initial alkene), as shown by g.l.c. (3-m TXP at 60 °C) and i.r. spectroscopy, (iv) a higher-boiling liquid fraction (0.72 g) which was shown by g.l.c. (3-m TXP at 90 °C) to contain seven major components (J—P) (8 : 6 : 12 : 50 : 5 : 15 : 4) and five minor components (*ca.* 2% of the fraction), and (v) a charred residue (1.2 g) which was not examined further. The seven major components of the liquid fraction were separated by g.l.c. (7-m TXP at 130 °C) into four fractions; a mixture (0.18 g, 0.8 mmol, 10%) of components (J—L), 1,1,2-trifluoro-3,3,4,4-tetramethyl-2-trifluoromethylcyclobutane (15) (0.06 g, 0.2 mmol, 3%), the alkene (13) (0.04 g, 0.2 mmol, 2%) and an unidentified adduct (0.08 g, 0.4 mmol, 5%); a mixture of components (M and N), *cis*- and *trans*-cyclobutanes (12) (0.35 g, 1.5 mmol, 18%) in the ratio 1 : 1 ( $^{19}\text{F}$  n.m.r.), and an unidentified adduct (0.04 g, 0.2 mmol, 2%); component (O), the alkene (14) (0.11 g, 0.5 mmol, 6%); and component (P), a mixture (0.03 g, 0.1 mmol, 2%) (Found: C, 46.5; H, 5.3; F, 48.4%;  $M^+$ , 234. Calc. for  $C_9H_{12}F_6$ : C, 46.2; H, 5.2; F, 48.7%;  $M$ , 234), b.p. 155 °C, of *cis*- and *trans*-1,1,2-trifluoro-3,3,4-trimethyl-2-trifluoromethylcyclopentane (16) and *cis*- and *trans*-1,2,2-trifluoro-3,3,4-trimethyl-1-trifluoromethylcyclopentane (17) in the ratio 31 : 31 : 22 : 16 ( $^{19}\text{F}$  n.m.r.).

(h) *With 3-phenylpropene.* A mixture of hexafluoropropene (4.50 g, 30.0 mmol) and 3-phenylpropene (3.54 g, 30.0 mmol) was sealed under reduced pressure in a Pyrex ampoule and heated at 250 °C (3 d) to give (i) unchanged hexafluoropropene (2.61 g, 17.4 mmol, 58% recovered), (ii) cyclobutane (6) (0.09 g, 0.3 mmol, 2%), (iii) a high-boiling liquid (3.74 g), and (iv) a charred residue (1.5 g) which was not examined further. The high-boiling liquid was fractionated on a spinning band column (2 m) into two fractions a mixture (1.06 g), b.p. <180 °C, and a mixture (2.68 g), b.p. >180 °C. The lower-boiling fraction was shown by g.l.c. (2-m PEGA at 140 °C) to contain four components identified, by their g.l.c. retention times and g.l.c.-mass spectrometry, as toluene (0.04 g, 0.4 mmol, 1% on alkene),

*n*-propylbenzene (0.69 g, 5.7 mmol, 19%), unchanged 3-phenylpropene (0.24 g, 2.0 mmol, 7% recovered), and (*Z*)-1-phenylpropene (0.09 g, 0.8 mmol, 3%). The higher-boiling fraction was shown by g.l.c. (2-m PEGA at 140 °C) to contain three major components (26 : 37 : 37) and five minor components (*ca.* 14% of fraction). The three major components were separated by g.l.c. (6-m PEGA at 140 °C) to give (a) a mixture (0.60 g) of two components in the ratio 60 : 40 ( $^1\text{H}$  n.m.r.) which was re-separated (6-m PEGA at 120 °C) to afford (*E*)-1-phenylpropene (0.25 g, 2.1 mmol, 7% based on reactant alkene), and 1,1,2-trifluoro-4-methyl-3-phenyl-2-trifluoromethylcyclobutane (18) (0.35 g, 1.3 mmol, 10%) (Found: C, 54.1; H, 4.0; F, 41.9%;  $M^+$ , 268.  $C_{12}H_{10}F_6$  requires C, 53.7; H, 3.8; F, 42.5%;  $M$ , 268), b.p. 198 °C, present as a mixture of four isomers in the ratio 75 : 9 : 7 : 9 ( $^{19}\text{F}$  n.m.r.); (b) *trans*-3-benzyl-1,1,2-trifluoro-2-trifluoromethylcyclobutane (19b) (0.85 g, 3.2 mmol, 25%) (Found: C, 54.1; H, 3.7; F, 42.2%;  $M^+$ , 268), b.p. 210 °C; and (c) *cis*-3-benzyl-1,1,2-trifluoro-2-trifluoromethylcyclobutane (19a) (0.85 g, 3.2 mmol, 25%) (Found: C, 53.9; H, 4.0; F, 42.8%;  $M^+$ , 268), b.p. 215 °C.

*Thermolysis of Reactant Hydrocarbon Alkenes.*—All reactions were carried out on a 15.0-mmol scale in Pyrex ampoules (*ca.* 100  $\text{cm}^3$ ) at 270 °C (3 d) unless stated otherwise.

(a) *With isobutene.* The products were the unchanged alkene (90%) and a mixture of octene isomers (10%).

(b) *With but-1-ene.* The olefin was recovered quantitatively.

(c) *With 2-methylbut-1-ene.* The products were the unchanged alkene (16%) and 2-methylbut-2-ene (84%); at 220 °C (14 d) the same olefins (68 : 32) were obtained.

(d) *With 2-methylbut-2-ene.* This gave the unchanged alkene (94%) and 2-methylbut-1-ene (6%); at 220 °C (14 d) the alkene ratio was 98 : 2.

(e) *With 2,3-dimethylbut-1-ene.* The products were the unchanged alkene (64%) and 2,3-dimethylbut-2-ene (36%) at 250 °C (3 d).

(f) *With 2,3-dimethylbut-2-ene.* The products were the unchanged alkene (82%) and 2,3-dimethylbut-1-ene (18%).

(g) *With 3-phenylpropene.* This gave benzene (trace), toluene (18%), ethylbenzene (3%), a methylethylbenzene (trace), *n*-propylbenzene (45%), unchanged alkene (3% recovered), an unidentified compound of formula  $C_{12}H_{14}$  (trace), (*Z*)-1-phenylpropene (2%), (*E*)-1-phenylpropene (5%), and a charred residue (27% by weight).

*Attempted Dehydrofluorination of the Cyclobutane (4).*—A mixture of the cyclobutane (1.28 g, 6.2 mmol) and powdered potassium hydroxide (1.85 g, 33.0 mmol) was sealed in a Pyrex ampoule (*ca.* 100  $\text{cm}^3$ ) *in vacuo* and heated at 200 °C (3 d) to give a mixture (0.87 g) which was shown by g.l.c. (3-m TXP at 65 °C) to contain one major and four minor components (*ca.* 2% of fraction). The major component and one of the minor components were identified as unchanged cyclobutane (4) (0.85 g, 4.6 mmol, 66% recovered) and 2,3-difluoro-4,4-dimethyl-3-trifluoromethylcyclobutane (31) (<1%) (Found:  $M^+$ , 186. Calc. for  $C_7H_7F_5$ :  $M$ , 186), respectively, by g.l.c.-mass spectrometry.

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