Perfluoroalkyl Derivatives of Nitrogen. Part XXV.[1] The Reactions of Tristrifluoromethylhydroxylamine and Mercuric Bistrifluoromethylamide with Unsaturated Systems[2]

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Tristrifluoromethylhydroxylamine reacts with perfluorocyclobutene, on irradiation, to give the 1:1 adduct perfluoro-(1-dimethylamino-2-methoxycyclobutane), and lower yields of other products including perfluoro-(1,2-bisdimethylaminocyclobutane), perfluoro-(2,2′-dimethoxybicyclobutyl), and perfluoro-(2-dimethylamino-2′-methoxybicyclobutyl). Reaction with perfluorobut-2-ene is more complex. Perfluoro-2-azapropene gives low yields of the two isomeric 1:1 adducts perfluoro-(2,3-dimethyl-5-oxa-2,3-diazahexane) and perfluoro-(3,5-dimethyl-2-oxa-3,5-diazahexane).

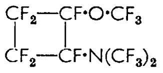
Irradiation of mercuric bistrifluoromethylamide gives perfluorodimethylamine, tetrakistrifluoromethylhydrazine, perfluoro-2-azapropene, and perfluoro-(2,3,5-trimethyl-2,3,5-triazahexane). Photolysis in the presence of perfluorocyclobutene gives perfluoro-(1,2-bisdimethylaminocyclobutane), tetrakistrifluoromethylhydrazine, and smaller amounts of perfluorodimethylamine and perfluoro-2-azapropene.

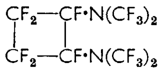
It has previously been shown[3, 4] that tristrifluoromethylhydroxylamine, on photolysis, decomposes by fission of the relatively weak N–O bond.

$$(CF_3)_2N\cdot O\cdot CF_3 \xrightarrow{u.v.} (CF_3)_2N\cdot + CF_3\cdot O\cdot$$

The $(CF_3)_2N\cdot$ radicals formed then either dimerise or react with undissociated hydroxylamine, while the $CF_3\cdot O\cdot$ radicals decompose in the silica reaction tube to give carbon dioxide, carbonyl fluoride, and silicon tetrafluoride. The reactions of the hydroxylamine with perfluorocyclobutene, perfluorobut-2-ene, or perfluoro-2-azapropene are now reported.

Perfluorocyclobutene.—Prolonged photolysis of an equimolar mixture of the hydroxylamine and perfluorocyclobutene under conditions where the olefin is stable (98% recovered) when photolysed alone, gave recovered hydroxylamine (35%), recovered olefin (9%), the 1 : 1 adduct (I) (26%), perfluoro-(2,2′-dimethoxybicyclobutyl) (V) (30%), and a polymeric residue (*ca.* 30% by weight); other products in smaller yields included the diamine (II), the bicyclic compound (VI), carbon dioxide, carbonyl fluoride, and silicon tetrafluoride.


(I)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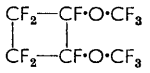
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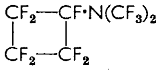
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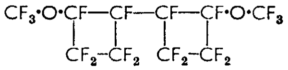
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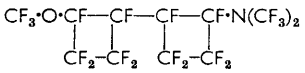
(VI)

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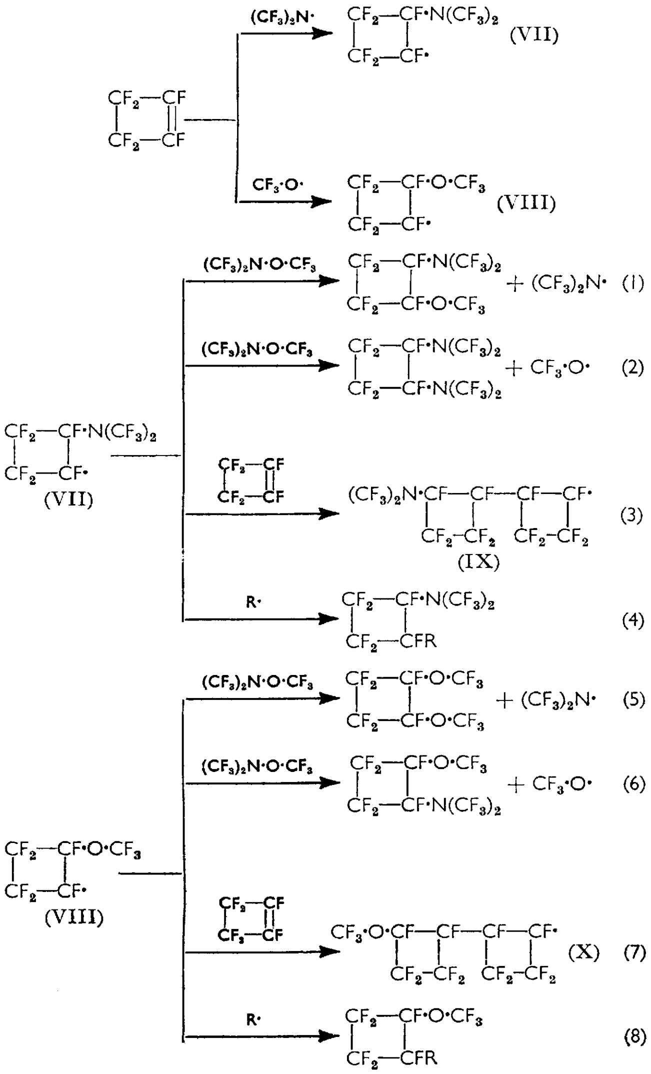
[1] Part XXIV, R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.* (*C*), 1966, 1350.

[2] Presented in part at the Third International Fluorine Symposium, Munich, 1965.

[3] A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1681.

[4] R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.* (*C*), 1966, 1236.



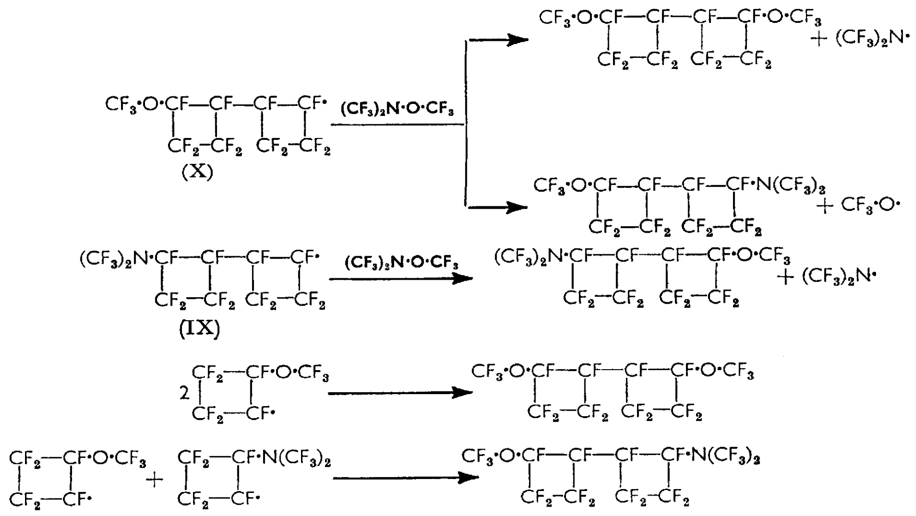
The yield of the higher-boiling polymeric material was much reduced by the use of a 2 : 1 molar ratio of hydroxylamine to butene, and the products were (I) (45%), (II) (16%), (V) (21%), tetrakistrifluoromethylhydrazine (7%), (VI) (*ca.* 5%), various unknown components, and small amounts of breakdown products. The presence of a small amount of (IV) was suggested from mass-spectral evidence.

Mechanism of the reaction. Since cyclobutane derivatives were isolated containing two $-O\cdot CF_3$ groups (V) or two $-N(CF_3)_2$ groups (II), it appears that both $(CF_3)_2N\cdot$ and $CF_3\cdot O\cdot$ radicals added initially to the cyclobutene to give the intermediate radicals (VII) and (VIII), respectively, which can then react as in (1)—(4) and (5)—(8), where R· is any radical present in the system, *e.g.*, $(CF_3)_2N\cdot$, $CF_3\cdot O\cdot$, (VII), or (VIII).

The absence of perfluoro-(1,2-dimethoxycyclobutane) (III) in the products is perhaps surprising, and even when a mixture of perfluorodimethyl peroxide and perfluorocyclobutene was photolysed (III) was not formed, the products being (V) (76%), a compound thought to be the tricyclobutyl derivative $CF_3\cdot O\cdot[C_4F_6]_3\cdot O\cdot CF_3$ (6%), and a non-volatile liquid. It was recently reported[5] that the reaction between the peroxide (in large excess) and perfluoropropene gave only telomers, $CF_3\cdot O\cdot[C_3F_6]_n\cdot O\cdot CF_3$, where $n \geqslant 2$, and no 1 : 1 adduct.

This absence of (III) and the presence of the diamine (II) in the reaction products can be explained in several ways: (*a*) that the radical (VIII) is less reactive than radical (VII), is reluctant to participate in the chain-transfer step (5), and hence dimerises to (V), or (*b*) that radical (VIII) abstracts only $(CF_3)_2N$ from the hydroxylamine (6), while radical (VII) can abstract either $CF_3\cdot O\cdot$ (1) or $(CF_3)_2N\cdot$ (2), or (*c*) that the diether (III) is formed but under the reaction conditions decomposes into radical (VIII) and a $CF_3\cdot O\cdot$ radical.

Radical (VIII) probably then reacts either by propagation with the olefin (7), or by radical recombination with another unreactive radical (*e.g.*, dimerisation) (8). The bicyclobutyl ether (V) and the mixed bicyclobutyl derivative (VI) can then arise by the following reactions:



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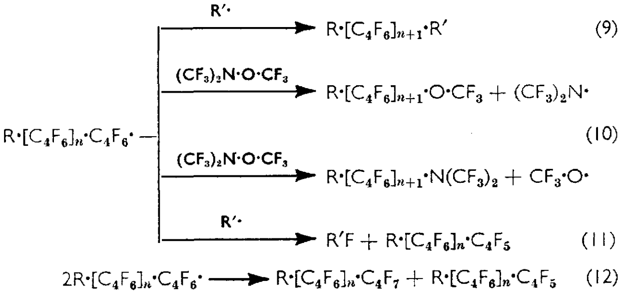
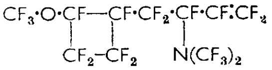
[5] H. L. Roberts, *J. Chem. Soc.*, 1964, 4538.

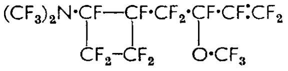
The propagation reactions (3) and (7) lead ultimately to the formation of the higher-boiling polymeric material, and termination of the radical chain will occur either by radical recombination (9), by abstraction (10), by fluorine abstraction (11), or by disproportionation (12). The infrared spectrum of the high-boiling residue contained a strong band at 5·84 μ (>C=C< stretch).



Mass-spectral evidence suggested the presence of compound (IV) in the fraction of b. p. 76—83°. A fraction (b. p. 102—108°) with a boiling point between that of the 1 : 1 adduct (I) and that of the diamine (II) was shown (g.l.c.) to be a mixture of compound (II) and an unknown component, and a comparison of the mass spectrum of the fraction against that of the pure diamine (II), together with the presence of a band at 5·78 μ in the infrared spectrum, suggested the presence of either compound (XI) or compound (XII).

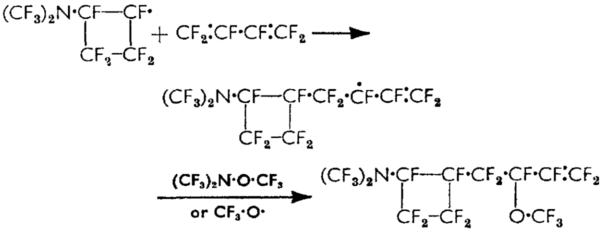


(XI)



(XII)

It is known[6] that under certain conditions perfluorocyclobutene is in equilibrium with perfluorobutadiene, and it is thus possible that compounds (XI) or (XII) are formed by reaction of radicals (VII) or (VIII) with the butadiene followed by abstraction, *e.g.*,

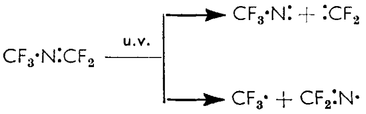


The possibility that the cyclobutane derivatives were 1,3-disubstituted, not 1,2-disubstituted, was rejected because the mass spectra of compounds (I), (II), (V), and (VI) showed ions formed by loss of C_2F_4 from the parent ions.

The mass spectra of compounds (I), (II), (V), and (VI) were in complete agreement with the proposed structures. The b. p. range for compounds (I), (V), and (VI) and g.l.c. and infrared spectroscopic examination of the adducts (I), (V), and (VI) suggested the presence of stereoisomers.

Perfluorobut-2-ene.—Prolonged irradiation of the olefin alone gave polymeric material (90%) and a mixture of the four isomeric butenes (9%). The formation of the butenes $(CF_3)_2C{:}CF_2$ and $CF_3{\cdot}CF_2{\cdot}CF{:}CF_2$ is best explained by rearrangement of the but-2-ene, and presumably they may also take part in polymer formation. Photolysis of a 1 : 1 mixture of the butene and tristrifluoromethylhydroxylamine gave products similar to those obtained on photolysis of the olefin alone, but in addition tetrakistrifluoromethylhydrazine (43%) and at least three additional components (not separable by g.l.c.) were formed.

Perfluoro-2-azapropene.—Free-radical reactions of perfluoro-2-azapropene examined previously include photolysis,[7] and irradiation with halogens[7,8] or trifluoroiodomethane.[7] The products from these reactions may be explained by a dual homolytic breakdown of the azapropene:[7]



Simple 1 : 1 adducts from the addition of free radicals to the double bond of the azapropene were not isolated. In the present work, irradiation (35 days) of a 2 : 1 mixture of the hydroxylamine and the azapropene gave the following products: unchanged $(CF_3)_2N{\cdot}O{\cdot}CF_3$ (32%), $(CF_3)_2N{\cdot}N(CF_3)_2$ (55%), $(CF_3)_3N$ [37% if produced only from $(CF_3)_2N{\cdot}O{\cdot}CF_3$], the isomeric 1 : 1 adducts $(CF_3)_2N{\cdot}CF_2{\cdot}N(CF_3){\cdot}O{\cdot}CF_3$ (XIII) (10%) and $(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}O{\cdot}CF_3$ (XIV) (4%), various unidentified components, and the decomposition products CO_2, SiF_4, CF_4, and C_2F_6.

The adduct (XIII) was not isolated absolutely pure (an extra band was present in the ^{19}F n.m.r. spectrum), but elemental analysis, the molecular weight, and the mass spectrum were in agreement with the structure proposed. A higher-boiling component, separated by g.l.c., showed strong bands at 5·32 μ (–COF group) and 10·12 μ [C–N stretch in $(CF_3)_2N$– group[9,10]]; its molecular weight (*ca.* 400), n.m.r. spectrum, and mass spectrum strongly suggested that it was perfluoro-(2,4,6-trimethyl-1-oxo-2,4,5-triazahexane) (XV).

$(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}N(CF_3){\cdot}COF$ (XV)

The hydrazine and the amine $(CF_3)_3N$ can arise by decomposition of both reactants:

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[6] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 1955, 3880.

[7] R. E. Banks, R. N. Haszeldine, and B. Weller, unpublished results.

[8] D. A. Barr and R. N. Haszeldine, unpublished results.

[9] J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1960, **82**, 396.

[10] R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141.

$$\mathrm{(CF_3)_2N{\cdot}O{\cdot}CF_3 \xrightarrow{u.v.} (CF_3)_2N{\cdot} + CF_3{\cdot}O{\cdot}}$$

$$\mathrm{CF_3{\cdot}N{:}CF_2} \xrightarrow{\text{u.v.}} \begin{cases} \rightarrow \mathrm{CF_3{\cdot}N{:} + {:}CF_2} \\ \rightarrow \mathrm{CF_3{\cdot} + CF_2{:}N{\cdot}} \end{cases}$$

$$\mathrm{CF_3{\cdot}N{:} + CF_3{\cdot} \longrightarrow (CF_3)_2N{\cdot}}$$

$$\mathrm{(CF_3)_2N{\cdot} + CF_3{\cdot} \longrightarrow (CF_3)_3N}$$

$$\mathrm{2\,CF_3{\cdot}N{:} \longrightarrow CF_3{\cdot}N{:}N{\cdot}CF_3 \xrightarrow{2\,CF_3{\cdot}} (CF_3)_2N{\cdot}N(CF_3)_2}$$

$$\mathrm{2\,(CF_3)_2N{\cdot} \longrightarrow (CF_3)_2N{\cdot}N(CF_3)_2}$$

$$\mathrm{(CF_3)_2N{\cdot} + (CF_3)_2N{\cdot}O{\cdot}CF_3 \longrightarrow (CF_3)_2N{\cdot}N(CF_3)_2 + CF_3{\cdot}O{\cdot}}$$

The other products can be explained by the following scheme.

$$\mathrm{CF_3{\cdot}O{\cdot} \xrightarrow{SiO_2} CO_2 + SiF_4}$$

$$\mathrm{2\,CF_3{\cdot} \longrightarrow CF_3{\cdot}CF_3}$$

$$\mathrm{(CF_3)_2N{\cdot}O{\cdot}CF_3 + CF_3{\cdot} \longrightarrow CF_4 + (CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot} \xrightarrow{SiO_2} (CF_3)_2N{\cdot}O{\cdot}COF}$$

$$\mathrm{CF_3{\cdot}N{:}CF_2 + (CF_3)_2N{\cdot}} \longrightarrow \begin{cases} \rightarrow \mathrm{(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}}\ \text{(XVI)} \\ \rightarrow \mathrm{(CF_3)_2N{\cdot}CF_2{\cdot}\dot{N}{\cdot}CF_3}\ \text{(XVII)} \end{cases}$$

$$\mathrm{CF_3{\cdot}N{:}CF_2 + CF_3{\cdot}O{\cdot}} \longrightarrow \begin{cases} \rightarrow \mathrm{CF_3{\cdot}O{\cdot}N(CF_3){\cdot}CF_2{\cdot}}\ \text{(XVIII)} \\ \rightarrow \mathrm{CF_3{\cdot}O{\cdot}CF_2{\cdot}\dot{N}{\cdot}CF_3}\ \text{(XIX)} \end{cases}$$

$$\text{(XVI)—(XIX)} \xrightarrow{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CF_3}} \text{(XIII) and (XIV)}$$

$$\text{(XVI)} + \mathrm{CF_3{\cdot}N{:}CF_2 \longrightarrow (CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}N(CF_3){\cdot}CF_2{\cdot} \xrightarrow{SiO_2}} \text{(XV)}$$

The absence of the compound $\mathrm{(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}N(CF_3)_2}$ (XX), which is a product from the photolysis of mercuric bistrifluoromethylamide alone, suggests that reaction of radicals (XVI) or (XVII) with $\mathrm{(CF_3)_2N{\cdot}}$ radicals does not occur.

Mercuric Bistrifluoromethylamide.—Prolonged irradiation of the mercurial alone gave unchanged material (36%), the hydrazine $\mathrm{(CF_3)_2N{\cdot}N(CF_3)_2}$ (53%), perfluoro-2-azapropene (15%), perfluorodimethylamine (13%), and compound (XX) (15%). These products could have arisen by two distinct primary decompositions of the mercurial, (13) and (14).

$$\mathrm{(CF_3)_2N{\cdot}Hg{\cdot}N(CF_3)_2} \longrightarrow \begin{cases} \rightarrow \mathrm{2\,(CF_3)_2N{\cdot} + Hg} & (13) \\ \rightarrow \mathrm{2\,CF_3{\cdot}N{:}CF_2 + HgF_2} & (14) \end{cases}$$

The mercurial has previously been reported[11] to decompose thermally according to (14). To determine which mechanism was operating under photolytic conditions, the mercurial was irradiated with an excess of isopentane, to give bistrifluoromethylamine (97%) as the only highly-volatile product.[10] This indicated that scheme (13) was operating exclusively, in accord with the reported decompositions of aliphatic hydrocarbon mercurials.[12]

The products $\mathrm{CF_3{\cdot}N{:}CF_2}$ and $\mathrm{(CF_3)_2NF}$ must then be formed by secondary reactions of the $\mathrm{(CF_3)_2N{\cdot}}$ radicals.

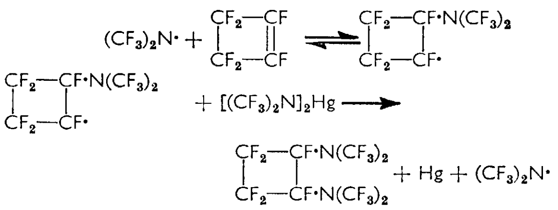
$$\mathrm{2\,(CF_3)_2N{\cdot} \longrightarrow (CF_3)_2NF + CF_3{\cdot}N{:}CF_2}$$

$$\mathrm{2\,(CF_3)_2N{\cdot} + 2Hg \longrightarrow 2\,CF_3{\cdot}N{:}CF_2 + 2HgF\ (or\ HgF_2)}$$

$$\mathrm{(CF_3)_2N{\cdot} \xrightarrow[or\ HgF_2]{HgF} (CF_3)_2NF}$$

The hydrazine $\mathrm{(CF_3)_2N{\cdot}N(CF_3)_2}$ is formed either by dimerisation of $\mathrm{(CF_3)_2N{\cdot}}$ radicals or by reaction of $\mathrm{(CF_3)_2N{\cdot}}$ radicals with undissociated mercurial. The compound $\mathrm{(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}N(CF_3)_2}$ arises from $\mathrm{(CF_3)_2N{\cdot}}$ radical addition to the azapropene to give radicals (XVI) or (XVII) followed by reaction of these with $\mathrm{(CF_3)_2N{\cdot}}$ radicals or with mercuric bistrifluoromethylamide.

Photolysis of a 2 : 1 molar mixture of the mercurial and perfluorocyclobutene (31 days) gave unchanged mercurial (56%) and unchanged butene (75%). The products were $\mathrm{(CF_3)_2N{\cdot}N(CF_3)_2}$ (47%), $\mathrm{CF_3{\cdot}N{:}CF_2}$ (13%), $\mathrm{(CF_3)_2NF}$ (6%), and the adduct (II) (25%). The low yield of the last compound indicates either that reaction of the $\mathrm{(CF_3)_2N{\cdot}}$ radicals with the butene is slow and the secondary reactions leading to the other products have time to occur, or that the initial addition is reversible, or that the abstraction reaction (15) is not favoured.



(15)

An attempt to prepare the unknown primary alcohol $\mathrm{CF_3OH}$ by the reaction of $\mathrm{CF_3{\cdot}O{\cdot}}$ radicals, produced by photolysis of perfluorodimethyl peroxide, with isopentane was unsuccessful.

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Irradiation reactions were normally carried out in silica tubes (380 ml. capacity), at a distance of 6 in. from an Hanovia S.500 ultraviolet lamp, with the liquid phase shielded. The products were partially separated by distillation *in vacuo*, and the resultant fractions analysed by infrared spectroscopy and gas–liquid chromatography (g.l.c.). Pure components were normally separated by repeated distillation *in vacuo*, or by fractional distillation, or by preparative-scale g.l.c., and were examined by infrared spectroscopy (Perkin-Elmer 21 instrument), ^{19}F n.m.r. spectroscopy (A.E.I. R.S.2 instrument operating at 56·46 Mc./sec.), and mass spectrometry

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[11] J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

[12] E. W. R. Steacie, " Atomic and Free Radical Reactions," 2nd edn., Reinhold, New York, 1954, pp. 386—394.

(A.E.I. MS. 2H instrument). Perkin-Elmer 154B or 451 instruments were used for g.l.c., with nitrogen as the carrier gas, and were calibrated with known mixtures of pure compounds. Analytical columns (2 m., 4 mm. i.d.) or preparative-scale columns (4 m., 4 mm. i.d.), packed with various organic compounds (30%) on Celite at various temperatures, were used.

Tristrifluoromethylhydroxylamine.—The hydroxylamine was prepared in 85% yield by the irradiation of a mixture of trifluoroiodomethane and trifluoronitrosomethane in a 2 : 1 molar ratio.[4]

Photolysis of Tristrifluoromethylhydroxylamine with Perfluorocyclobutene.—(a) 1 : 1 *Molar ratio.* The hydroxylamine (22·2 g., 0·098 mole) and the olefin (18·7 g., 0·116 mole), sealed in four silica tubes and irradiated for 30 days, gave (i) a mixture (0·114 g., 2·0 mmoles; *M*, 71) of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride, (ii) unchanged hydroxylamine (7·80 g., 32·9 mmoles, 35%), (iii) unchanged perfluorocyclobutene (1·6 0g., 9·9 mmoles, 9%), and (iv) a higher-boiling liquid fraction (31·3 g.), which was distilled through a Podbielniak Heli-pak column (30 cm., 8 mm. i.d.), to give the results shown in Table 1.

TABLE 1

Distillation of products from the reaction of

$(CF_3)_2N\cdot O\cdot CF_3$ with $\overline{CF_2\cdot CF{:}CF\cdot CF_2}$

Fraction (b. p.)	Amount collected (g.) (mmoles)	Mol. wt.	G.l.c. analysis	
			Column temp.	Components
76—83°	0·85 (2·3)	370	50°	A (15%), B (65%), (I) (20%)
83—90	6·67 (16·7)	397	50 100	(I) (100%) (I) (100%)—2 isomers
102—108	2·08 (4·5)	475	100	C (40%), (II) (60%)
119—129·5	4·77 (9·7)	492	100	(V) (80%), D (10%), (VI) isomer " a " (10%)
129·5—145·5	0·84 (Intermediate fraction)		—	—
145·5—153·5	3·50 (6·0)	570	100	(VI) isomer " a " (50%), isomer " b " (50%)
Residue	10·40	—	—	

Percentages given for mixtures are ±5%, since complete resolution of the fractions by g.l.c. (2 and 4 m. silicone columns) was not achieved. Components A, B, C, and D were not identified.

The brown liquid residue remaining after distillation contained strong bands in its infrared spectrum at 5·84 μ (olefinic double bond stretch) and 10·12 μ [C–N stretch in a $(CF_3)_2N-$ group].

Compound (I) was identified as *perfluoro-*(1-*dimethylamino-*2-*methoxycyclobutane*) (6·86 g., 17·2 mmoles, 26%) (Found: C, 21·3; N, 3·7%; *M*, 397. $C_7F_{15}NO$ requires C, 21·1; N, 3·5%; *M*, 399); compounds (II) and (V) were later identified as perfluoro-(1,2-bisdimethylaminocyclobutane) (1·26 g., 2·7 mmoles, 8%) and perfluoro-(2,2′-dimethoxybicyclobutyl) (3·83 g., 7·8 mmoles, 24%), respectively, and compound (VI) was identified as *perfluoro-*2-*dimethylamino-*2′-*methoxybicyclobutyl*) (4·04 g., 7·0 mmoles, 11%) (Found: C, 23·6; N, 2·9%; *M*, 560. $C_{11}F_{21}NO$ requires C, 23·5; N, 2·5%; *M*, 561).

(b) 2 : 1 *Molar ratio.* The hydroxylamine (285·4 g., 1·09 moles) and perfluorocyclobutene (94·1 g., 0·58 mole), sealed in ten silica tubes and irradiated for 30 days, gave (i) a mixture (1·70 g., 23·1 mmoles; *M*, 74) of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride contaminated with a small amount of hexafluoroethane, (ii) unchanged hydroxylamine (183·5 g., 0·775 mole, 71%), (iii) unchanged olefin (30·4 g., 0·188 mole, 32%), and (iv) higher-boiling material (134·8 g.). The results of the distillation of the high-boiling fraction are shown in Table 2.

TABLE 2

Distillation of products from the reaction of

$(CF_3)_2N\cdot O\cdot CF_3$ with $\overline{CF_2\cdot CF{:}CF\cdot CF_2}$

Fraction (b. p.)	Amount collected (g.) (mmoles)	Mol. wt.	G.l.c. analysis
31—40°	3·25 (10·7)	299	97% $(CF_3)_2N\cdot N(CF_3)_2$
40—80	9·61 (—)	—	6 Components
80—83	1·39 (4·1)	—	A (20%), B (30%), (I) (50%)
83—90	52·9 (133)	398	(I) (100%)
90—101	2·01 (4·6)	441	(I) (50%), C (20%), (II) (15%)
101—113·2	7·63 (15·9)	480	(I) (15%), C (45%), (II) (40%)
113·2—116·5	7·10 (15·2)	466	(II) (100%)
116·5—122·5	8·00 (6·2)	482	(II) (40%), (V) (60%)
122·5—129	14·76 (29·9)	492	(V) (100%)
129—154	9·15 (—)	—	(V) (5%), (VI) (95%)
Residue	19·0		

The identified products were thus tetrakistrifluoromethylhydrazine (3·16 g., 10·4 mmoles, 7%), (I) (56·0 g., 140·4 mmoles, 45%), (II) (11·5 g., 24·7 mmoles, 16%), (V) (16·6 g., 33·6 mmoles, 21%), and (VI) (*ca.* 8·6 g., 15·3 mmoles, 5%).

Photolysis of Perfluorobut-2-ene.—The olefin (10·83 g., 54·1 mmoles), irradiated for 30 days, gave (i) a mixture (0·95 g., 4·6 mmoles, 9%) (Found: *M*, 209. Calc. for C_4F_8: *M*, 200) of perfluorobut-2-ene, perfluorobut-1-ene, and perfluoroisobutene contaminated with a small amount of an unknown component, (ii) a higher-boiling mixture (7·2 g., 17·7 mmoles) shown by g.l.c. (4 m. Kel-F oil at 100°) to contain twelve components, which did not analyse correctly for $(C_4F_8)_n$ and contained strong bands in its infrared spectrum at 5·72 and 5·78 μ (olefinic double bond stretch), and (iii) a non-volatile residue (2·60 g.) which contained a strong band at 5·82 μ in its infrared spectrum. Analysis of the butene fraction by g.l.c. (8 m. Kel-F grease at room temperature) showed perfluorobut-1-ene and *cis*- and *trans*-perfluorobut-2-ene (0·41 g., 2·1 mmoles, 4%), and perfluoroisobutene (0·46 g., 2·3 mmoles, 4%) to be present.

Photolysis of Tristrifluoromethylhydroxylamine with Perfluorobut-2-ene.—The hydroxylamine (6·45 g., 27·2 mmoles) and the olefin (5·45 g., 27·2 mmoles), irradiated for 30 days, gave (i) a mixture (0·83 g., 10·5 mmoles; *M*, 79) of carbonyl fluoride, silicon tetrafluoride, tetrafluoromethane, and hexafluoroethane, (ii) unchanged hydroxylamine (1·41 g., 5·9 moles, 22%), (iii) tetrakistrifluoromethylhydrazine (1·41 g., 4·65 mmoles, 43%) (Found: *M*, 302. Calc. for $C_4F_{12}N_2$: *M*, 304) identified by a comparison of its infrared spectrum with that of a known pure sample, (iv) a mixture of the isomeric perfluorobutenes (0·87 g., 4·4 mmoles, 16%), (v) a fraction of lower volatility (7·42 g.) shown by g.l.c. (4 m. Kel-F oil at 100°) to contain thirteen components, three of which were not formed by irradiation of the butene alone, and (vi) a non-volatile residue (0·3 g.).

Perfluoro-2-azapropene.—The azapropene was prepared in 69% overall yield by the reaction of tetrafluoroethylene with trifluoronitrosomethane in an autoclave at 70°, to give perfluoro-(2-methyl-1,2-oxazetidine) which was then pyrolysed by passage through a platinum tube (1—2 mm./550°).[13]

Photolysis of Tristrifluoromethylhydroxylamine with Perfluoro-2-azapropene.—The hydroxylamine (7·40 g., 31·2 mmoles) and the azapropene (2·08 g., 15·6 mmoles), irradiated for 35 days, gave (i) a volatile mixture (0·98 g., 11·4 mmoles; *M*, 86) of tetrafluoromethane, hexafluoroethane, carbon dioxide, silicon tetrafluoride, and an unknown component E containing a strong band in the infrared spectrum at 5·25 μ, (ii) unchanged hydroxylamine (2·37 g., 10·0 mmoles, 32%), (iii) tetrakistrifluoromethylhydrazine (1·76 g., 5·8 mmoles, 55%) (Found: *M*, 304. Calc. for $C_4F_{12}N_2$: *M*, 304), identified by a comparison of its g.l.c. retention time and infrared spectrum with those of a known pure sample, (iv) *perfluoro-*(3,5-*dimethyl-*2-*oxa-*3,5-*diazahexane*) (XIII) (0·80 g., 2·15 mmoles, 10%) (Found: C, 16·3; N, 7·6%; *M*, 367. $C_5F_{14}N_2O$ requires C, 16·2; N, 7·6%; *M*, 370), (v) *perfluoro-*(2,3-*dimethyl-*5-*oxa-*2,3-*diazahexane*) (XIV) (0·28 g., 0·75 mmole, 4%) (Found: C, 16·2; N, 7·8%; *M*, 372. $C_5F_{14}N_2O$ requires C, 16·2; N, 7·6%; *M*, 370), (vi) tristrifluoromethylamine (1·75 g., 7·9 mmoles, 22%) (Found: C, 16·2; N, 6·4%; *M*, 221. Calc. for C_3F_9N: C, 16·3; N, 6·4%; *M*, 221) identified by comparison of its infrared spectrum with that of a known pure sample, (vii) perfluoro-(3-methyl-1-oxo-2-oxa-3-azabutane), $(CF_3)_2N\cdot O\cdot COF$ (0·08 g., 0·35 mmole, 2%), identified by a comparison of its g.l.c. retention time and infrared spectrum with those of a pure sample,[4] and (viii) a component tentatively identified as perfluoro-(2,4,6-trimethyl-1-oxo-2,4,5-triazahexane) (XV) (0·07 g., 0·17 mmole, 1%) (Found: *M*, *ca*. 400. Calc. for $C_6F_{15}N_3O$: *M*, 415). Seven further components were shown to be present by g.l.c. (3·25 m. Fluorolube at 0° and 20°); of these three were present in low yield and were not isolated. The other four components were separated as two mixtures: (i) containing components E (80%) and F (20%) (Found: *M*, 141); the infrared spectrum showed bands at 5·26s (assigned to the C=O stretch in a –COF group), 7·35s, 7·56s, 7·82sh,s, 8·00vs, 8·55vs, 9·75s, 10·05m, 10·28s, 10·35sh,s, 13·96m, 14·30s, 14·45s, and 14·53sh,m μ, and (ii) containing components G (33%) and H (67%) (Found: *M*, 271); the infrared spectrum showed bands at 5·33s (–COF group), 5·45s, 7·25m, 7·36s, 7·70vs, 7·98vs, 8·55s, 8·70sh,s, 8·85s, 9·45m, 10·10s [assigned to the C–N stretch in a $(CF_3)_2N-$ group], 10·45s, 10·60sh,s, 10·95s, 11·37s, 13·50s, 14·50s, and 14·82sh,s μ.

Photolysis of Perfluorodimethyl Peroxide with Perfluorocyclobutene.—The peroxide (2·24 g., 13·3 mmoles) and the olefin (2·15 g., 13·3 mmoles), irradiated for 7 days, gave (i) a mixture (1·45 g., 16·4 mmoles; *M*, 88) of carbon dioxide and silicon tetrafluoride, (ii) unchanged peroxide (0·26 g., 1·5 mmoles, 11%) (Found: *M*, 171. Calc. for $C_2F_6O_2$: *M*, 170), (iii) an unidentified three-component mixture (0·28 g., 0·8 mmole; *M*, 356) with bands in the infrared spectrum at 5·30w, 5·40w, 7·29s, 7·82vs, 8·05vs, 8·24s, 8·33sh,s, 8·68vs, 9·55m, 10·20s, 10·50m, 10·65m, 11·10m, 11·40s, 11·62s, 11·82m, 12·45s, 12·72m, 13·45s, and 14·90m μ, (iv) *perfluoro-*(2,2′-*dimethoxybicyclobutyl*) (V) (2·49 g., 5·0 mmoles; 76%) (Found: C, 24·4%; *M*, 487. $C_{10}F_{18}O_2$ requires C, 24·3%; *M*, 494), (iv) a higher-boiling component thought to be the tricyclobutyl derivative $CF_3\cdot O\cdot[C_4F_6]_3\cdot O\cdot CF_3$ (0·17 g., 6%) with bands in the infrared spectrum at 7·26s, 7·40m, 7·85vs, 8·00vs, 8·20vs, 8·35s, 8·67vs, 9·45m, 9·56m, 10·10m, 10·48m, 11·35m, 11·80m, 12·50s, 12·75m, 13·20w, 13·45m, 13·90m, and 14·86w μ, and (v) an unidentified non-volatile liquid (0·25 g.).

Photolysis of Perfluorodimethyl Peroxide with Isopentane.—The peroxide (1·01 g., 6·0 mmoles) and isopentane (0·81 g., 11·3 mmoles), irradiated for 5 days, gave (i) a mixture (1·05 g., 16·3 mmoles; *M*, 65) of carbon dioxide and silicon tetrafluoride, (ii) unchanged isopentane (0·79 g., 10·6 mmoles, 94%) (Found: *M*, 75. Calc. for C_5H_{12}: *M*, 72) contaminated with unknown material having infrared absorption bands at 7·85s, 8·18m, 8·73s, 9·22w, and 12·10w μ, and (iii) a fraction (0·13 g., 1·3 mmoles; *M*, 102) containing isopentane and unknown material with infrared absorption bands at 7·35w, 7·90s, 8·20s, 8·75s, 9·22w, 11·60w, 12·10w, and 14·00w μ. This latter fraction decomposed at room temperature *in vacuo* in glass to form silicon tetrafluoride.

Preparation of Mercuric Bistrifluoromethylamide.—The mercurial was prepared in 81% yield by the reaction of mercuric fluoride with perfluoro-2-azapropene at 105° for 38 hr.[11]

Photolysis of Mercuric Bistrifluoromethylamide.—The mercurial (7·2 g., 14·3 mmoles), sealed in a 250-ml. silica tube and irradiated at a distance of 4 in. from the lamp (30 days), gave (i) unchanged mercurial (2·62 g., 5·2 mmoles, 36%), (ii) a volatile fraction (0·93 g., 5·6 mmoles; *M*, 166) consisting of perfluoro-2-azapropene, perfluorodimethylamine, and smaller amounts of bistrifluoromethylamine, trifluoromethyl isocyanate, and tetrakistrifluoromethylhydrazine, (iii) tetrakistrifluoromethylhydrazine (1·28 g., 4·3 mmoles, 48%) (Found: *M*, 300. Calc. for $C_4F_{12}N_2$: *M*, 304), (iv) *perfluoro-*(2,3,5-*trimethyl-*2,3,5-*triazahexane*) (XX) (0·39 g., 0·9 mmole, 15%) (Found: C, 16·3; N, 9·8%; *M*, 440. $C_6F_{17}N_3$ requires C, 16·5; N, 9·6%; *M*, 437), and (v) a residue containing mercury, mercurous and mercuric ions, and fluoride ion.

The volatile fraction (ii), shaken in a sealed tube with 20% aqueous sodium hydroxide (10 ml.) for 4 hr., gave perfluorodimethylamine (0·40 g., 2·4 mmoles, 13%) and a further quantity of tetrakistrifluoromethylhydrazine (0·16 g., 0·5 mmole, 5%).

Photolysis of Mercuric Bistrifluoromethylamide with Perfluorocyclobutene.—The mercurial (10·39 g., 20·4 mmoles) and the olefin (1·80 g., 11·2 mmoles), sealed in a 300-ml. silica tube and irradiated at a distance of 4 in. from the lamp (30 days), gave (i) a mixture (2·59 g., 13·5 mmoles; *M*, 193) of perfluorocyclobutene, perfluoro-2-azapropene, and tetrakistrifluoromethylhydrazine, contaminated with small amounts of perfluorodimethylamine and trifluoromethyl isocyanate, (ii) a mixture of perfluorocyclobutene (0·27 g., 1·6 mmoles, 15%) and tetrakistrifluoromethylhydrazine (0·20 g., 0·7 mmole, 8%), (iii) *perfluoro-*(1,2-*bisdimethylaminocyclobutane*) (II) (1·04 g., 2·2 mmoles, 25%) (Found: C, 20·4; N, 6·2%; *M*, 462. $C_8F_{18}N_2$ requires C, 20·6; N, 6·0%; *M*, 466), and (iv) unchanged mercurial (5·77 g., 11·5 mmoles, 56%).

Fraction (i), sealed with water (10 ml.) in a Pyrex tube and shaken at room temperature for 4 hr., gave a mixture (2·31 g., 11·2 mmoles; *M*, 208) of perfluorodimethylamine, tetrakistrifluoromethylhydrazine, and perfluorocyclobutene. Further reaction of this mixture with 20% aqueous sodium hydroxide (10 ml.) at room temperature for 20 days gave

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[13] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881; 1956, 3416.

TABLE 3

Vapour pressure data

Compound	Range measured	*A*	*B*	L_v	*T*	B. p.
$(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}O{\cdot}CF_3$	29—58°	8·255	−1811	8390	24·9	63·8°
$(CF_3)_2N{\cdot}CF_2{\cdot}N(CF_3){\cdot}O{\cdot}CF_3$	9—50	8·233	−1759	8150	24·8	55·4
$(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}N(CF_3)_2$	52—80	8·253	−1920	8790	24·6	84·0
$(CF_3)_2N{\cdot}N(CF_3){\cdot}CF_2{\cdot}N(CF_3){\cdot}COF$ *	23—62	8·289	−1828	8510	25·2	64·9

* Structure not proven.

TABLE 4

Main mass-spectral bands; the intensities in the data shown are all relative to CF_3^+ intensity 100

Compound	Ions		
	Mass	Intensity	Assignment
(I)	399	Trace	Parent+ $(C_7F_{15}NO^+)$
	299	1·5	$C_5F_{11}NO^+$
	292	2·5	$C_6F_{10}NO^+$
	233	1·3	$C_4F_9N^+$
	202	0·7	$C_3F_8N^+$
	176	3·4	$C_4F_6N^+$
	166	0·7	$C_3F_6O^+$
	100	2·7	$C_2F_4^+$
Fraction, b. p. 102—108° *	480	Trace	$C_9F_{18}NO^+$
	461	Trace	$C_9F_{17}NO^+$
	454	Trace	$C_{10}F_{16}NO^+$
	442	Trace	$C_9F_{16}NO^+$
	430	Trace	$C_8F_{16}NO^+$
	414	Trace	$C_8F_{16}N^+$
	394	0·2	$C_8F_{14}O_2^+$
	380	0·2	$C_7F_{14}NO^+$
	349	1·5	$C_6F_{13}NO^+$
	328	2·3	$C_7F_{12}O^+$
	293	3·5	$C_7F_{11}^+$
	262	1·1	$C_6F_{10}^+$
	261	0·3	$C_5F_9NO^+$
	259	0·2	$C_6F_9O^+$
	255	0·2	$C_7F_9^+$
	243	1·7	$C_6F_9^+$
	228	1·4	$C_5F_8O^+$
	193	2·1	$C_5F_7^+$
	And all the bands of (II)		
(XIII)	370	Trace	Parent+ $(C_5F_{14}N_2O^+)$
	304	0·2	$C_4F_{12}N_2^+$
	285	5·5	$C_4F_{11}N_2^+$
	263	2·8	$C_4F_9N_2O^+$
	202	8·1	$C_3F_8N^+$
(XIV)	301	2·8	$C_4F_{11}N_2O^+$
	235	0·7	$C_3F_9N_2^+$
	135	17·8	$C_2F_5O^+$

Compound	Ions		
	Mass	Intensity	Assignment
(II)	466	0·2	Parent+ $(C_8F_{18}N_2^+)$
	447	0·3	$C_8F_{17}N_2^+$
	366	Trace	$C_6F_{14}N_2^+$
	359	1·6	$C_7F_{13}N_2^+$
	314	4·5	$C_6F_{12}N^+$
	226	7·7	$C_5F_8N^+$
	202	9·0	$C_3F_8N^+$
	100	1·7	$C_2F_4^+$
VI)	561	Trace	$C_{11}F_{21}NO^+$
	542	0·4	$C_{11}F_{20}NO^+$
	461	0·3	$C_9F_{17}NO^+$
	454	0·4	$C_{10}F_{16}NO^+$
	293	0·8	$C_7F_{11}^+$
	226	0·7	$C_5F_8N^+$
	214	0·6	$C_4F_8N^+$
	202	5·8	$C_3F_8N^+$
	162	1·1	$C_4F_6^+$
	135	1·3	$C_2F_5O^+$
	114	10·5	$C_2F_4N^+$
	100	4·9	$C_2F_4^+$
(V)	394	5·7	$C_8F_{14}O_2^+$
	328	0·3	$C_7F_{12}O^+$
	305	2·8	$C_8F_{11}^+$
	294	2·1	$C_6F_{10}O_2^+$
	228	7·7	$C_5F_8O^+$
	166	1·4	$C_3F_6O^+$
	162	1·2	$C_4F_6^+$
	100	5·6	$C_2F_4^+$
(XV)	368	0·5	$C_5F_{14}N_3^+$
	299	0·7	$C_4F_{11}N_3^+$
	266	0·2	$C_4F_{10}N_2^+$
	235	3·6	$C_3F_9N_2^+$
	216	1·6	$C_3F_8N_2^+$
	128	1·6	$C_2F_4N_2^+$
	114	2·3	$C_2F_4N^+$

* Fraction from $(CF_3)_2N{\cdot}O{\cdot}CF_3/\overline{CF_2{\cdot}CF{:}CF{\cdot}CF_2}$ experiment.

TABLE 5

^{19}F N.m.r. spectra; assignments and chemical shifts

Compound				Band 1			Band 2		
1	2	3	4	P.p.m.	Type	Intensity	P.p.m.	Type	Intensity
$(CF_3)_2N$—	$N(CF_3)$—	CF_2—	$O{\cdot}CF_3$	−18·0	Broad	6	−10·8	Broad	3
$(CF_3)_2$—	$N(CF_3)$—	CF_2—	$N(CF_3)_2$	−18·1 or −16·8	Broad	6	−16·5	Complex	3
* $(CF_3)_2N$—	CF_2—	$N(CF_3)$—	$O{\cdot}CF_3$	−21·8	Triplet	6	−15·3	Complex	2
† $(CF_3)_2N$—	$N(CF_3)$—	CF_2—	$N(CF_3){\cdot}COF$	−16·7	Broad quartet	6	−16·6 or 19·2	Complex	3

Compound				Band 3			Band 4		
1	2	3	4	P.p.m.	Type	Intensity	P.p.m.	Type	Intensity
$(CF_3)_2N$—	$N(CF_3)$—	CF_2—	$O{\cdot}CF_3$	−4·8	Complex	2	−19·3	Triplet	3
$(CF_3)_2N$—	$N(CF_3)$—	CF_2—	$N(CF_3)_2$	−12·3	Complex	2	−16·8 or −18·1	Complex	6
* $(CF_3)_2N$—	CF_2—	$N(CF_3)$—	$O{\cdot}CF_3$	−16·4	Complex	*ca.* 2·5	−15·8	Sextet	3
† $(CF_3)_2N$—	$N(CF_3)$—	CF_2—	$N(CF_3){\cdot}COF$	−12·3	Broad septet	*ca.* 2	−19·2 or −16·6	Complex	3

* An extra weak band observed at −18·9 (triplet) p.p.m. is considered to be due to impurity. † The band due to the COF fluorine atom, expected at *ca.* −80 p.p.m. [cf. $(CF_3)_2N{\cdot}COF$ −79·5 p.p.m.],[14] was not observed; but this group was shown to be present by the infrared spectrum of the compound; weak impurity bands were also present at −8·8, −11·6, and −15·6 p.p.m.

perfluorodimethylamine (0·16 g., 1·0 mmoles, 6%) and tetrakistrifluoromethylhydrazine (1·07 g., 3·5 mmoles, 39%). Thus, fraction (i) originally contained perfluorocyclobutene (1·35 g., 8·3 mmoles, 75%) and perfluoro-2-azapropene (0·31 g., 2·3 mmoles, 13%).

Vapour Pressure Equations.—The constants A and B for the vapour pressure equation $\log_{10}p$(mm.) $= A + B/T$, the b. p., latent heat of vaporisation L_v (cal. mole^{-1}), and Trouton's constant T (cal. mole^{-1} deg.$^{-1}$) for the new compounds prepared are shown in Table 3.

Mass Spectral Data.—Table 4 records the main mass spectral bands of the compounds prepared. The mass spectrum of the compound suspected to be $(CF_3)_2N\cdot N(CF_3)\cdot CF_2\cdot N(CF_3)\cdot COF$ contains a peak at mass 368 attributed to loss of COF from the parent, and the peaks at lower mass are consistent with the proposed structure.

The mass spectra of the fractions obtained from the $(CF_3)_2N\cdot O\cdot CF_3/CF_2\cdot CF{:}CF\cdot CF_2$ reaction gave helpful information. (*a*) Fraction b. p. 76—83° contained a peak at mass 314 due to the ion $C_6F_{12}N^+$, as might be expected by loss of F from the compound $(CF_3)_2N\cdot CF\cdot CF_2\cdot CF_2\cdot CF_2$. (*b*) Fraction b. p. 102—108° contained all the bands due to the diamine (II), but many additional peaks were present. Those in the lower region of the spectrum are assigned to fluorocarbon ions up to C_7 and are interpreted as being due to a compound containing two butene residues. The strong peak at mass 349 due to $C_6F_{13}NO^+$ (isotopic ratios measured) shows that the N and the O are separated by six or less carbon atoms and, if the assignment of the peak at mass 261 to $C_5F_9NO^+$ is correct, by five or less carbon atoms. Since the infrared spectrum showed the presence of an olefin double bond (band at 5·78 μ) in the fraction, it is suggested that either the compound

$$(CF_3)_2N\cdot CF\cdot CF_2\cdot CF_2\cdot CF\cdot CF_2\cdot CF(O\cdot CF_3)\cdot CF{:}CF_2 \qquad \text{(XII)}$$

or the compound

$$CF_3\cdot O\cdot CF\cdot CF_2\cdot CF_2\cdot CF\cdot CF_2\cdot CF[N(CF_3)_2]\cdot CF{:}CF_2 \qquad \text{(XI)}$$

is present in this fraction. The peak at mass 461 then arises by loss of C_2F_4 from the parent; a similar breakdown to that obtained with the other cyclobutane derivatives. All the other peaks except that at mass 394 can be explained by the presence of either of the above compounds; the peak at mass 394 due to the ion $C_8F_{14}O_2^+$ suggests that in addition a compound containing two $-O\cdot CF_3$ groups is present.

Nuclear Magnetic Resonance Spectra.—The data in Table 5 were recorded with trifluoroacetic acid as the external reference.

The cyclobutane derivatives $(CF_3)_2N\cdot C_4F_6\cdot O\cdot CF_3$ (I), $CF_3\cdot O\cdot C_4F_6\cdot C_4F_6\cdot O\cdot CF_3$ (V), and $(CF_3)_2N\cdot C_4F_6\cdot N(CF_3)_2$ (II) each showed a low-intensity region (ring fluorines) and a high-intensity region [$(CF_3)_2N-$ and $CF_3\cdot O-$ fluorines] at 50—65 p.p.m. and *ca.* −21 p.p.m. (I), at 50—63 p.p.m. and *ca.* −20 p.p.m. (V), and at 50—65 p.p.m. and *ca.* −22 p.p.m. (II), respectively. The ring fluorines in the cyclobutane $CBrF\cdot CF_2\cdot CF_2\cdot CBrF$ absorb at *ca.* 43 p.p.m. and in the acyl fluoride $CF_2\cdot CF_2\cdot CF_2\cdot CF\cdot COF$ at 52—55 p.p.m.[14]

Infrared Spectra.—Table 6 records the spectra of some of the compounds.

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[14] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1962, **84**, 4275.

TABLE 6

Infrared spectra

(I) *	(I) †	(II)	(V) ‡	(VI)	(XX)	(XIV)	(XIII)	(XV)	Assignment
								5·32s	−COF
							7·05m		
7·35s	7·35s		7·26m	7·26m	7·26s	7·28s	7·35s	7·35s	
7·40sh,s	7·40s	7·42vs	7·40m	7·45s	7·43s	7·43s			
	7·55s	7·52s					7·52vs	7·52s	
					7·59vs	7·63vs	7·68vs	7·64s	
7·81s	7·81s	7·80s	7·83vs	7·80s	7·78vs			7·80s	
						7·90s	7·90s		
8·00s	8·00s	8·02sh,s	7·99vs	8·05s	8·00s	8·02vs	8·05s	8·05s	C–F stretch
8·15s	8·15s	8·15s	8·21vs	8·18s					
			8·33s			8·28s	8·28s		
8·55s	8·55s				8·49s	8·49s	8·49s	8·43s	
	8·68s		8·67s	8·70m		8·65s	8·60s		
8·90m	8·85s	9·04m			8·94m	8·82s	8·90s	8·85s	
9·38m		9·19m	9·55m						
9·71s	9·71s		9·90m						
10·08s	10·08s	10·07s		10·08s	10·22s	10·08s	10·09s	10·12s	C–N stretch [3, 4, 9, 10]
	10·43m								
10·60m				10·65m	10·70s	10·72s	10·78s	10·86s	
	10·91w				10·97s				
11·14m	11·12s	11·06m							
11·26m		11·50m		11·23m	11·38s	11·34m	11·24s		
				11·54m		11·49s	11·46s		
11·87s	11·78s					11·60m	11·72s	11·88s	$\begin{smallmatrix}C\\C\end{smallmatrix}\!>\!N$ bending [3, 4, 9, 10]
	11·97s	11·92m		12·08w					
		12·15m		12·50m		12·26m	12·10s		
13·15s	13·12s					13·02m	13·05s	13·10m	
		13·26s		13·20m			13·22s		
13·72m	13·60m	13·70s	13·43m	13·68m	13·65s	13·50s	13·60s	13·50s	CF_3 deformation [3, 4]
14·10m	14·10m			13·90m	13·90s	14·00s	13·84s	13·88s	
14·85m	14·95m		14·90w			14·80s	14·56s	14·65m	

* B. p. 83—86°. † B. p. 88—90°. ‡ This compound also contained absorption bands at 10·10m, 10·48m, 11·33m, 12·50s, and 12·72m μ.

The presence of the *cis*- and *trans*-isomers of compound (I) was inferred from the variation in intensity of bands common to the 83—86° and 88—90° fractions, and the absence and presence of certain bands in these fractions; both fractions analysed correctly for (I).

It is interesting that only the compounds which contained an $-O{\cdot}CF_3$ group showed a strong absorption band at 8·60—8·66 μ, and also that only the symmetrical compounds (V) and (II) contained one band in the CF_3 deformation region while the others showed two.

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