# Perfluoroalkyl Derivatives of Nitrogen. Part XXVI.[1] The Preparation and Rearrangement of Polyfluorovinylamines and of Trifluoromethyl Trifluorovinyl Ether[2]

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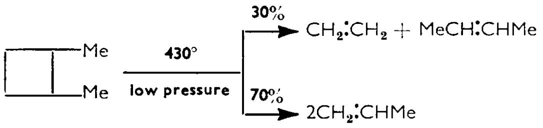
The flow pyrolysis of perfluoro-(1-dimethylamino-2-methoxycyclobutane) at 600°, low pressure (1—2 mm.), and a contact time of *ca.* 1 sec. gives perfluoro-(*NN*-dimethylvinylamine) (76%), perfluoro-2-azapent-2-ene (21%), trifluoromethyl trifluorovinyl ether (22%), and pentafluoropropionyl fluoride (54%). Similar pyrolysis of perfluoro-(1,2-bisdimethylaminocyclobutane) also gives the first two compounds (78 and 17%, respectively). The pyrolysis of bi(perfluoro-2-methoxycyclobutyl) gives more complex products, which include tetrafluoroethylene, perfluorocyclobutene, perfluoro-1,3-butadiene, trifluoromethyl trifluorovinyl ether, and pentafluoropropionyl fluoride. Pyrolysis of perfluoro-(*NN*-dimethylvinylamine) or of trifluoromethyl trifluorovinyl ether gives perfluoro-2-azapent-2-ene (55%) and pentafluoropropionyl fluoride (67%), respectively. The rearrangement of the vinylamine probably occurs by two mechanisms (mainly intramolecular and partly radical), since pyrolysis with a large excess of toluene gives the rearranged azapentene in lower yield (46%) and fluoroform (31%). The vinylamines $(CF_3)_2N{\cdot}CF{:}CF_2$, $(CF_3)_2N{\cdot}CF{:}CHF$, $(CF_3)_2N{\cdot}CH{:}CF_2$, $(CF_3)_2N{\cdot}CBr{:}CF_2$, and $(CF_3)_2N{\cdot}CF{:}CFCl$ are formed in high yield (generally >90%), from the reactions of suitable olefins with *N*-bromobistrifluoromethylamine followed by dehydrohalogenation or dehalogenation reactions. Pyrolysis of the chlorovinylamine $(CF_3)_2N{\cdot}CF{:}CFCl$ gives the rearrangement product $CF_3{\cdot}N{:}CF{\cdot}CFCl{\cdot}CF_3$ (51%) and chlorotrifluoromethane.

Irradiation of perfluoro-(*NN*-dimethylvinylamine) with hydrogen bromide gives the 1 : 1 adduct $(CF_3)_2N{\cdot}CHF{\cdot}CF_2Br$ (99%), which indicates exclusive initial radical addition to the $CF_2$ group of the vinylamine.

*Pyrolysis of Cyclobutanes.*—Both alkyl cyclobutanes and polyfluoro(alkyl cyclobutanes) decompose into olefins when pyrolysed at low pressures (<20 mm.). This cleavage sometimes occurs in both possible ways,[3,4] *e.g.*,



In the present work the three cyclobutane derivatives perfluoro-(1-dimethylamino-2-methoxycyclobutane) (I), perfluoro-(1,2-bisdimethylaminocyclobutane) (II), and

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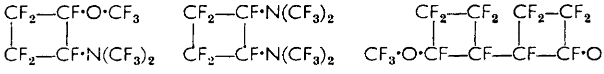
[1] Part XXV, R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.* (*C*), 1967, 1241.

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

[3] H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935.

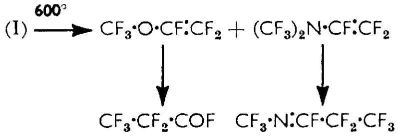
[4] H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 4884.

bi(perfluoro-2-methoxycyclobutyl) (III), prepared by the irradiation of tristrifluoromethylhydroxylamine with



(I) (II) (III)

perfluorocyclobutene,[1] were pyrolysed in platinum; optimum conditions were *ca.* 600° with a contact time of *ca.* 1 sec. at a pressure of 1—2 mm. Under these conditions (I) gave trifluoromethyl trifluorovinyl ether,



$$\text{(I)} \xrightarrow{600^\circ} CF_3{\cdot}O{\cdot}CF{:}CF_2 + (CF_3)_2N{\cdot}CF{:}CF_2;\quad CF_3{\cdot}O{\cdot}CF{:}CF_2 \rightarrow CF_3{\cdot}CF_2{\cdot}COF;\quad (CF_3)_2N{\cdot}CF{:}CF_2 \rightarrow CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3$$

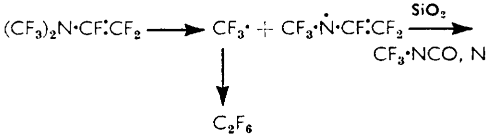
perfluoro-(*NN*-dimethylvinylamine), pentafluoropropionyl fluoride, and perfluoro-2-azapent-2-ene as major products. Trifluoromethyl trifluorovinyl ether was separated from pentafluoropropionyl fluoride by hydrolysis of the latter with aqueous silver carbonate to give silver pentafluoropropionate. The last compound was also obtained by hydrolysis[5] of the $C_4F_9N$ isomer mixture; perfluoro-(*NN*-dimethylvinylamine) was unaffected:

$$CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3 \xrightarrow{H_2O} CF_3{\cdot}CF_2{\cdot}CO_2H + CO_2 + NH_4F + 3HF$$

Although a third $C_4F_9N$ isomer would also have liberated pentafluoropropionic acid on hydrolysis:

$$CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}N{:}CF_2 \xrightarrow{H_2O} CF_3{\cdot}CF_2{\cdot}CO_2H + CO_2 + NH_4F + 3HF,$$

evidence presented later shows that perfluoro-2-azapent-2-ene and perfluoro-(*NN*-dimethylvinylamine) were the only $C_4F_9N$ isomers produced by the pyrolysis. The by-products from the pyrolysis arise by decomposition of the initial products, *e.g.*,



$$(CF_3)_2N{\cdot}CF{:}CF_2 \longrightarrow CF_3{\cdot} + CF_3{\cdot}\dot{N}{\cdot}CF{:}CF_2 \xrightarrow{SiO_2} CF_3{\cdot}NCO,\ N_2,\ COF_2,\ SiF_4;\quad CF_3{\cdot} \rightarrow C_2F_6$$

Products which might have arisen by cleavage of the ring in (I) in the other direction, *e.g.*,

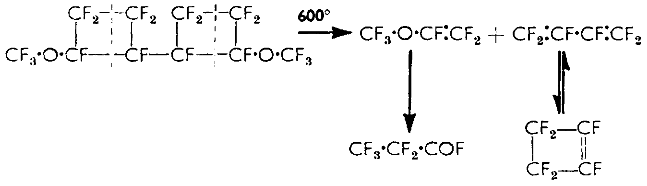
$$\text{(I)} \longrightarrow CF_2{:}CF_2 + CF_3{\cdot}O{\cdot}CF{:}CF{\cdot}N(CF_3)_2$$

were notably absent.

The pyrolysis of perfluoro-(1,2-bisdimethylaminocyclobutane) (II) under related conditions gave similar products:

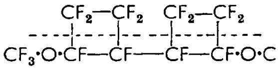
$$\text{(II)} \xrightarrow{600^\circ} (CF_3)_2N{\cdot}CF{:}CF_2 \longrightarrow CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3,$$

but the pyrolysis of the bi-ether (III) was more complex:

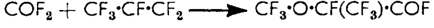


$$\text{(III)} \xrightarrow{600^\circ} CF_3{\cdot}O{\cdot}CF{:}CF_2 + CF_2{:}CF{\cdot}CF{:}CF_2;\quad CF_3{\cdot}O{\cdot}CF{:}CF_2 \rightarrow CF_3{\cdot}CF_2{\cdot}COF$$

It has been established[6] that the equilibrium between perfluoro-1,3-butadiene and perfluorocyclobutene lies well to the cyclobutene side. The presence of small amounts of tetrafluoroethylene amongst the breakdown products from (III), some of which remain unidentified, indicates that cleavage can also occur as follows:



*Trifluoromethyl Trifluorovinyl Ether and Perfluoro-*(NN*-dimethylvinylamine*).—The structure of the ether $CF_3{\cdot}O{\cdot}CF{:}CF_2$ obtained pyrolytically as above follows from physical evidence (n.m.r., i.r., molecular weight, etc.) and from the formation of a dibromide (92%); its b. p. (−26°) is very close to that reported (−22°)[7] for the compound prepared by the passage of perfluoro-(2-methoxypropionyl) fluoride through a bed of dry potassium sulphate pellets at 300°:



$$COF_2 + CF_3{\cdot}\overset{O}{CF{-}CF_2} \longrightarrow CF_3{\cdot}O{\cdot}CF(CF_3){\cdot}COF$$

$$CF_3{\cdot}O{\cdot}CF(CF_3){\cdot}COF \xrightarrow{K_2SO_4} CF_3{\cdot}O{\cdot}CF{:}CF_2 + COF_2$$

Perfluoro-(*NN*-dimethylvinylamine), the first perfluorovinylamine to be reported, is stable and, in contrast to the non-fluorinated vinylamines, does not polymerise spontaneously. Its b. p. (11·1°) is much lower than that of its non-fluorinated analogue $Me_2N{\cdot}CH{:}CH_2$ (b. p. 37—38°),[8] and its structure has been established by physical evidence (n.m.r., i.r., mass spectra, etc.) and by its reaction with bromine or hydrogen bromide. Reaction with bromine gave the dibromide (98%), and photochemical reaction with hydrogen bromide gave only one 1 : 1 adduct (31% conversion), identical with the major product from the reaction of *N*-bromobistrifluoromethylamine with trifluoroethylene.[9]

$$(CF_3)_2NBr + CHF{:}CF_2 \longrightarrow \underset{(78\%)}{(CF_3)_2N{\cdot}CHF{\cdot}CF_2Br} + \underset{(22\%)}{(CF_3)_2N{\cdot}CF_2{\cdot}CHFBr}$$

$$(CF_3)_2N{\cdot}CF{:}CF_2 \xrightarrow{Br{\cdot}} (CF_3)_2N{\cdot}\dot{C}F{\cdot}CF_2Br \xrightarrow{HBr} (CF_3)_2N{\cdot}CHF{\cdot}CF_2Br$$

The 1 : 1 adduct was dehydrobrominated quantitatively to the perfluoro-(*NN*-dimethylvinylamine) by powdered potassium hydroxide at room temperature. An unsuccessful attempt was made to effect ionic addition of hydrogen bromide to perfluoro-(*NN*-dimethylvinylamine).

The attack of a bromine atom on the terminal $CF_2$ group of the vinylamine $(CF_3)_2N{\cdot}CF{:}CF_2$ occurs as expected from a consideration of intermediate radical stability and possible steric effects. The radical reaction of the vinylamine with hydrogen bromide is

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

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

[7] Du Pont de Nemours and Co., B.P. 952,281/1964.

[8] K. H. Meyer and H. Hopff, *Ber.*, 1921, **54***B*, 2274.

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

slower (72% reaction) than that of hexafluoropropene with hydrogen bromide under comparable conditions (96% reaction).

An attempted cyclodimerisation of perfluoro-(*NN*-dimethylvinylamine) at 250° and 60 atmos. to give perfluoro-(1,2-bisdimethylaminocyclobutane) (II) failed; a higher temperature and/or pressure may be required for this.

*Preparation of Other Polyfluorovinylamines*.—The vinylamines $(CF_3)_2N{\cdot}CF{:}CF_2$, $(CF_3)_2N{\cdot}CF{:}CFCl$, $(CF_3)_2N{\cdot}CF{:}CHF$, $(CF_3)_2N{\cdot}CH{:}CF_2$, and $(CF_3)_2N{\cdot}CBr{:}CF_2$ were prepared in excellent yield by utilising the compounds prepared earlier [9] from *N*-bromobistrifluoromethylamine:

$$(CF_3)_2N{\cdot}CHF{\cdot}CF_2Br \xrightarrow[20^\circ]{KOH} (CF_3)_2N{\cdot}CF{:}CF_2 \ (99\%)$$

$$(CF_3)_2N{\cdot}CFCl{\cdot}CFClBr \xrightarrow{Zn-EtOH} (CF_3)_2N{\cdot}CF{:}CFCl \ (87\%)$$

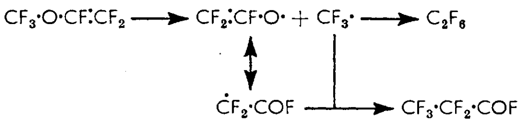
$$(CF_3)_2N{\cdot}CHF{\cdot}CHFBr \xrightarrow[20^\circ]{KOH} (CF_3)_2N{\cdot}CF{:}CHF \ (98\%)$$

$$(CF_3)_2N{\cdot}CH_2{\cdot}CF_2Br \xrightarrow[80^\circ]{KOH} (CF_3)_2N{\cdot}CH{:}CF_2 \ (97\%)$$

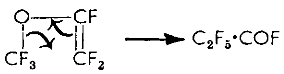
$$(CF_3)_2N{\cdot}CH{:}CF_2 \xrightarrow{Br_2} (CF_3)_2N{\cdot}CHBr{\cdot}CF_2Br \xrightarrow{KOH,\ 20^\circ} (CF_3)_2N{\cdot}CBr{:}CF_2 \ (99\%)$$

The structures of all these vinylamines were in agreement with the physical evidence (n.m.r., i.r., mass spectra, etc.). Dechlorobromination of the compound $(CF_3)_2N{\cdot}CFCl{\cdot}CFClBr$ was accompanied by a small amount of dechlorination to give the olefin $(CF_3)_2N{\cdot}CF{:}CFBr$, identical with that formed by dechlorobromination of the compound [10] $(CF_3)_2N{\cdot}CFBr{\cdot}CFClBr$.

*Pryolytic Rearrangement of Trifluoromethyl Trifluorovinyl Ether*.—The isolation of pentafluoropropionyl fluoride as a pyrolysis product from (I) or (III) suggested that the vinyl ether $CF_3{\cdot}O{\cdot}CF{:}CF_2$ might rearrange thermally. In accord with this, pyrolysis of the ether at 595° (contact time 1·2 sec.) gave pentafluoropropionyl fluoride and the breakdown products $C_2F_6$, $COF_2$, and $SiF_4$. The production of $CF_3$ radicals, implied by the isolation of hexafluoroethane, could arise during free radical rearrangement as follows:



although a 4-centre intramolecular rearrangement could account for the main product without the need for free radical intermediates:



Photolysis of the vinyl ether did not lead to the formation of pentafluoropropionyl fluoride, but gave only carbonyl fluoride and polymer of low molecular weight.

*Pyrolytic Rearrangement of Polyfluorovinylamines*.—The rearrangement of perfluoro-(*NN*-dimethylvinylamine) at 600°:

$$(CF_3)_2N{\cdot}CF{:}CF_2 \longrightarrow CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3$$

was slower (contact time *ca.* 7 sec.) than that of the ether; perfluoro-2-azapent-2-ene (55%) was the major product. The structure of the last compound, $CF_3{\cdot}N{:}CF{\cdot}C_2F_5$, follows from its hydrolysis to pentafluoropropionic acid, the similarity of its b. p. (11·9°) to that (13·2°) reported [11] for perfluoro-2-azapent-2-ene prepared by fluorination of trispentafluoroethyl-*s*-triazine, and its n.m.r. spectrum, which is almost identical with that of the compound prepared from the *s*-triazine and consistent with the proposed structure as distinct from its isomer, perfluoro-2-azapent-1-ene $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}N{:}CF_2$. The last compound, which would also have given pentafluoropropionic acid on hydrolysis, is a product (b. p. 25·6°) [5] from the pyrolysis of perfluoro-(2-n-propyl-1,2-oxazetidine), and has a much higher b. p. than its isomer. Perfluoro-2-azapent-1-ene has also been reported [12] as the major product (b. p. 12·5°) from the pyrolysis of the amine $(C_3F_7)_3N$, but this product was probably perfluoro-2-azapent-2-ene, since pyrolysis of the homologue $(C_4F_9)_3N$ originally reported [12] to yield the compound $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}N{:}CF_2$ is now known [13] to give the isomer $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}N{\cdot}CF_3$.

Distinction between isomers which contain $N{:}CF_2$ or $N{:}CF{\cdot}CF_3$ groups can now be made on the basis of i.r. and b. p. data (Table 1).

TABLE 1

I.r. and b. p. data

| | N=C stretch ($\mu$) | B. p. | Difference |
|---|---|---|---|
| $CF_3{\cdot}N{:}CF_2$ [a] | 5·53 | −33·7° | 27·7 |
| $CF_3{\cdot}CF_2{\cdot}N{:}CF_2$ [b] | 5·52 | −6 | 31·6 |
| $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}N{:}CF_2$ [a] | 5·51 | 25·6 | |
| $CF_3{\cdot}N{:}CF{\cdot}CF_3$ | 5·60 | −15 | 26·9 |
| $CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3$ | 5·65 | 13·2,[c] 12·5,[d] 11·9 | 27·1 |
| $CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_2{\cdot}CF_3$ | 5·64 | 39 | |

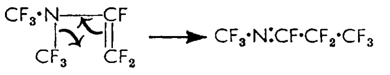
[a] Ref. 5. [b] D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1961, 1351. [c] Ref. 11. [d] Ref. 12.

The rearrangement of the perfluoro-(*NN*-dimethylvinylamine) to perfluoro-2-azapent-2-ene could occur by a radical process (A) or by an intramolecular process (B):

$$\text{(A)}\ (CF_3)_2N{\cdot}CF{:}CF_2 \longrightarrow CF_3{\cdot}\dot{N}{\cdot}CF{:}CF_2 + CF_3{\cdot}$$

$$CF_3{\cdot}\dot{N}{\cdot}CF{:}CF_2 \longleftrightarrow CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot} \xrightarrow{CF_3\cdot} CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3$$

(B)



Pyrolysis of perfluoro-(*NN*-dimethylvinylamine) in the presence of a large excess of toluene (610°, contact time 0·66 sec.) gave unchanged vinylamine (60%

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[10] M. G. Barlow and A. E. Tipping, unpublished results.

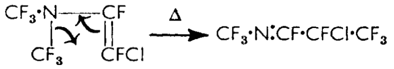
[11] J. B. Hynes, B. C. Bishop, P. Bandyopadhyay, and L. A. Bigelow, *J. Amer. Chem. Soc.*, 1963, **85**, 83.

[12] W. H. Pearlson and L. J. Hals, U.S.P. 2,643,267/1953.

[13] R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

recovery), perfluoro-2-azapent-2-ene (46% yield), fluoroform (31%), 1,1-difluoroethylene (38%), and the breakdown products $COF_2$, $CF_3\cdot NCO$, and $SiF_4$. Hexafluoroethane was formed (*ca.* 50%) when the vinylamine was pyrolysed alone. Its absence when the pyrolysis was carried out in presence of toluene suggests that the trifluoromethyl radicals reacted with the toluene; however, the yield of perfluoro-2-azapent-2-ene (46%) was only slightly lower than that (55%) obtained by pyrolysis in absence of toluene, which implies that the rearrangement occurs mainly by an intramolecular process, and perhaps to a minor extent by a free-radical process. The yield of fluoroform was greater than that calculated for the loss of only one $CF_3$ group from the vinylamine lost by decomposition as distinct from rearrangement; presumably the radical $CF_3\cdot\dot{N}\cdot CF{:}CF_2$ breaks down to generate another $CF_3$ radical. 1,1-Difluoroethylene accounted for *ca.* 70% of the $CF_2{:}C$ present in the vinylamine which decomposed but did not rearrange; the mechanism for its formation is at present obscure.

The pyrolysis of 2-chloro-1,2-difluorovinylbistrifluoromethylamine under conditions similar to those used for the pyrolysis of perfluoro-(*NN*-dimethylvinylamine) gave unchanged material (15% recovery), 4-chloro-octafluoro-2-azapent-2-ene (51%), and a low-boiling fraction containing chlorotrifluoromethane, hexafluoroethane, silicon tetrafluoride, carbonyl fluoride, and unknown material with i.r. bands at 5·65 (C=C or C=N stretch) and 5·80 (C=C stretch) μ:



with a minor contribution from the radical process:

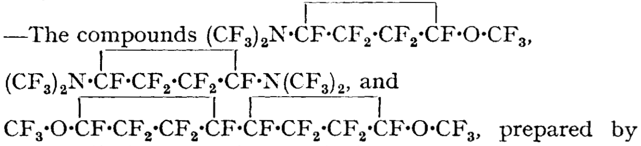
$$(CF_3)_2N\cdot CF{:}CFCl \xrightarrow{\Delta} CF_3\cdot\dot{N}\cdot CF{:}CFCl + CF_3\cdot$$

$$CF_3\cdot\dot{N}\cdot CF{:}CFCl \longleftrightarrow CF_3\cdot N{:}CF\cdot\dot{C}FCl \xrightarrow{CF_3\cdot} CF_3\cdot N{:}CF\cdot CFCl\cdot CF_3$$

Photolysis of perfluoro-(*NN*-dimethylvinylamine) did not cause its rearrangement. Instead it gave (80%) a 9 : 1 mixture of two dimers which contained bands in the infrared at 5·63 (C=C or C=N) and 5·78 (C=C) μ; possible structures include
$(CF_3)_2N\cdot CF{:}CF\cdot CF_2\cdot CF_2\cdot N(CF_3)_2$,
$(CF_3)_2N\cdot CF{:}CF\cdot CF(CF_3)\cdot N(CF_3)_2$, and
$(CF_3)_2N\cdot CF_2\cdot CF_2\cdot C({:}CF_2)\cdot N(CF_3)_2$.

## EXPERIMENTAL

All materials were manipulated in a conventional high-vacuum apparatus. Reaction components were separated by fractional condensation *in vacuo* or by gas–liquid chromatography (g.l.c.), and were identified by molecular weight determination (Regnault's method), infrared spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), n.m.r. spectroscopy (A.E.I. RS2 spectrometer), mass spectrometry (A.E.I. MS/2H instrument), and g.l.c. (Perkin-Elmer Fraktometer models 154B or 451). The g.l.c. column [2 m. × 4 mm. (i.d.)] was packed with Fluorolube (30%) on Celite and operated at 0° or at room temperature.



*Synthesis of the Vinylamines from Cyclobutane Derivatives.*—The compounds $(CF_3)_2N\cdot\overline{CF\cdot CF_2\cdot CF_2\cdot CF}\cdot O\cdot CF_3$, $(CF_3)_2N\cdot\overline{CF\cdot CF_2\cdot CF_2\cdot CF}\cdot N(CF_3)_2$, and $CF_3\cdot O\cdot\overline{CF\cdot CF_2\cdot CF_2\cdot CF}\cdot\overline{CF\cdot CF_2\cdot CF_2\cdot CF}\cdot O\cdot CF_3$, prepared by the irradiation of a mixture of tristrifluoromethylhydroxylamine and perfluorocyclobutene,[1] were passed at low pressure (1—2 mm.) through a platinum tube (41 cm. heated length, 1 cm. i.d.). Small amounts of nitrogen and/or oxygen were formed during the pyrolyses.

(a) *Pyrolysis of perfluoro-*(1-*dimethylamino-*2-*methoxycyclobutane*). The cyclobutane (8·56 g., 21·4 mmoles), pyrolysed at 590° (6·8 hr.; contact time *ca.* 1 sec.) gave (i) unchanged cyclobutane (5·12 g., 13·1 mmoles, 61%), (ii) a mixture (0·27 g., 3·0 mmoles; *M*, 126) shown by its infrared spectrum to be mainly hexafluoroethane contaminated with carbonyl fluoride, silicon tetrafluoride, and trifluoromethylisocyanate, (iii) a mixture of pentafluoropropionyl fluoride and trifluoromethyl trifluorovinyl ether (1·04 g., 6·3 mmoles, 76%) (Found: C, 21·5%; *M*, 167. Calc. for $C_3F_6O$: C, 21·7%; *M*, 166), in the ratio 63 : 37, and (iv) a mixture of perfluoro-2-azapent-2-ene and perfluoro-(*NN*-dimethylvinylamine) (1·89 g., 8·1 mmoles, 97%) (Found: C, 20·8; N, 5·9%; *M*, 232. Calc. for $C_4F_9N$: C, 20·6; N, 6·0%; *M*, 233).

The mixture of acyl fluoride and vinyl ether (1·04 g.), shaken with water (4 ml.) in a sealed tube at room temperature for 4 hr., gave, as the only volatile product, trifluoromethyl trifluorovinyl ether (0·31 g., 1·9 mmoles, 22%) (Found: C, 21·9%; *M*, 166. Calc. for $C_3F_6O$: C, 21·7%; *M*, 166). The aqueous solution remaining in the tube was treated with a slight excess of freshly prepared silver carbonate, the excess was filtered off, and the solution was extracted with ether. Removal of the ether by pumping *in vacuo* for 48 hr. gave silver pentafluoropropionate (1·04 g., 3·8 mmoles, 46%) (Found: C, 13·6; Ag, 39·6. Calc. for $C_3AgF_5O_2$: C, 13·3; Ag, 39·8%).

The mixture of perfluoro-2-azapent-2-ene and perfluoro-(*NN*-dimethylvinylamine) (1·89 g.), hydrolysed with water (8 ml.) in a sealed tube for 8 hr., gave *perfluoro-*(NN-*dimethylvinylamine*) (1·46 g., 6·3 mmoles, 76%) (Found: C, 20·6; N, 6·0%; *M*, 233. $C_4F_9N$ requires C, 20·8; N, 6·0%; *M*, 233). Treatment of the aqueous solution with silver carbonate gave silver pentafluoropropionate (0·43 g., 1·6 mmoles, 19%) (Found: C, 13·6; Ag, 39·5%).

TABLE 2

Pyrolysis of perfluoro-(1-dimethylamino-2-methoxycyclobutane)

| Contact time (sec.) | Temp. | Recovered unchanged (%) | Products (%) | | | |
|---|---|---|---|---|---|---|
| | | | A | B | C | D |
| 0·99 | 500° | 99 | | | | |
| 0·80 | 545 | 90 | 42 | 47 | 88 | 6 |
| 1·00 | 595 | 59 | 22 | 54 | 76 | 21 |
| 0·85 | 595 | 62 | 24 | 44 | 80 | 14 |
| 1·07 | 700 | 11 | 8 | 58 | 39 | 30 |

A, $CF_3\cdot O\cdot CF{:}CF_2$; B, $C_2F_5\cdot COF$; C, $(CF_3)_2N\cdot CF{:}CF_2$; D, $CF_3\cdot N{:}CF\cdot CF_2\cdot CF_3$. The decomposition products $C_2F_6$, $CF_3\cdot NCO$, $SiF_4$, and $COF_2$ were also formed.

Table 2 shows the products obtained under various conditions.

(b) *Pyrolysis of perfluoro-*(1,2-*bisdimethylaminocyclobutane*). This compound (2·63 g., 5·6 mmoles), pyrolysed through the platinum tube at 600° (100 min.; contact time 0·93 sec.), gave (i) unchanged material (1·53 g., 3·3 mmoles, 58%), (ii) a mixture (0·67 g., 0·70 mmole; *M*, 96) of hexafluoroethane, silicon tetrafluoride, trifluoromethylisocyanate, and carbonyl fluoride, (iii) perfluoro-2-azapent-2-ene (0·18 g., 0·78 mmole, 17%), and (iv) perfluoro-(*NN*-dimethylvinylamine) (0·86 g., 3·6 mmoles, 78%).

(c) *Pyrolysis of bi*(*perfluoro-2-methoxycyclobutyl*). The compound (1·45 g., 3·0 mmoles), passed through the platinum tube at 600° (80 min.; contact time 1·4 sec.), gave (i) unchanged biether (0·30 g., 0·59 mmole, 21% recovery), (ii) a low-boiling mixture (0·26 g., 2·1 mmoles; *M*, 119) of hexafluoroethane, tetrafluoroethylene, silicon tetrafluoride, carbonyl fluoride, and unknown material with i.r. bands at 5·60w, 7·18m, 8·80m, 9·80m, and 10·0m μ, and (iii) three complex higher-boiling fractions (I—III).

Fraction (ii) treated *in vacuo* with 5% aqueous potassium hydroxide (5 ml.) for 30 min. gave a mixture (0·21 g., 1·6 mmoles; *M*, 133) of hexafluoroethane, tetrafluoroethylene, and the same unknown components as in (ii).

Fraction I (0·53 g., 3·2 mmoles; *M*, 167), which condensed *in vacuo* at −130°, was shown by i.r. spectroscopy to be a mixture of trifluoromethyl trifluorovinyl ether, pentafluoropropionyl fluoride, perfluorocyclobutene, and perfluoro-1,3-butadiene. Hydrolysis [as fraction (ii)] removed the acyl fluoride and left the other three components (0·24 g., 1·4 mmoles; *M*, 166), identified by i.r. spectroscopy since g.l.c. showed only one peak.

Fraction II (0·17 g., 0·80 mmole; *M*, 207), which condensed *in vacuo* at −95°, was a mixture of perfluorocyclobutene, perfluoro-1,3-butadiene, and unknown material [bands at 2·68w, 5·32s, (COF), 8·12s, 8·87s, 9·55m, 10·36ssh, 11·56w, 11·92w, 13·30s, and 14·50s μ]. Hydrolysis as before gave a mixture (0·10 g., 0·51 mmole; *M*, 197) of perfluorocyclobutene, perfluoro-1,3-butadiene, and unknown material (bands at 8·12s, 11·56w, and 11·92w μ).

Fraction III (0·21 g., 0·62 mmole; *M*, 340) condensed *in vacuo* at −78°, and was a mixture of unchanged biether and unknown material [bands at 5·32m (COF), 5·42m, 5·63m and 5·76m (C=C), 9·15w, 9·58s, 11·56s, 11·92m, 12·10wsh, 13·45w, and 14·30w μ].

*Synthesis of the Vinylamines from* 1 : 1-*Adducts from* N-*Bromobistrifluoromethylamine and Fluoro-olefins*.—The adducts were prepared from the olefins $CHF{:}CF_2$, $CFCl{:}CFCl$, $CH_2{:}CF_2$, and $CHF{:}CHF$.[9]

(a) *Perfluoro-*(NN-*dimethylvinylamine*). The mixture (2·29 g., 7·3 mmoles) of the adducts $(CF_3)_2N{\cdot}CHF{\cdot}CF_2Br$ (80%) and $(CF_3)_2N{\cdot}CF_2{\cdot}CHFBr$ (20%) was treated *in vacuo* with powdered potassium hydroxide (10 g., 0·18 mole) at room temperature for 3 hr. to give unchanged *NN*-bistrifluoromethyl-2-bromo-1,1,2-trifluoroethylamine (0·46 g., 1·5 mmoles; 100% recovery) and perfluoro-(*NN*-dimethylvinylamine) (1·34 g., 5·8 mmoles, 99%) (Found: *M*, 233. Calc. for $C_4F_9N$: *M*, 233).

(b) 2-*Chloro*-1,2-*difluorovinylbistrifluoromethylamine*. 2-Bromo-1,2-dichloro-1,2-difluoroethylbistrifluoromethylamine (5·01 g., 13·7 mmoles) in ethyl alcohol (30 ml.), added slowly (2 hr.) to a well stirred slurry of previously activated zinc dust (30 g.) in ethyl alcohol (150 ml.) under reflux, gave 2-*chloro*-1,2-*difluorovinylbistrifluoromethylamine* (2·87 g., 11·5 mmoles, 87%) (Found: C, 19·4; N, 5·4%; *M*, 249. $C_4ClF_8N$ requires C, 19·2; N, 5·6%; *M*, 250) and a small higher-boiling fraction (*ca.* 2%), identified as 2-bromo-1,2-difluorovinylbistrifluoromethylamine (Found: *M*, 290. Calc. for $C_4BrF_8N$: *M*, 294) by comparison of its infrared and mass spectra with those of an authentic sample.[10]

(c) 2,2-*Difluorovinylbistrifluoromethylamine*. 2-Bromo-2,2-difluoroethylbistrifluoromethylamine (7·45 g., 25·6 mmoles), heated under reflux (2 hr.) over powdered potassium hydroxide (20 g., 0·36 mole) at *ca.* 80° and 650 mm., gave 2,2-*difluorovinylbistrifluoromethylamine* (4·49 g., 20·9 mmoles, 97%) (Found: C, 22·4; H, 0·7; N, 6·2%; *M*, 215. $C_4HF_8N$ requires C, 22·3; H, 0·5; N, 6·5%; *M*, 215) and unchanged starting material (0·95 g., 3·2 mmoles, 14%).

Reaction with powdered potassium hydroxide at room temperature (24 hr.) and with triethylamine at 50° (2 hr.) gave unchanged adduct (99 and 91%, respectively). Reaction with an excess of powdered potassium hydroxide in a sealed tube at 80° (12 hr.) gave only involatile products; the solid remaining in the tube gave positive tests for bromide, fluoride, carbonate, and cyanate ions.

(d) 1,2-*Difluorovinylbistrifluoromethylamine*. 2-Bromo-1,2-difluoroethylbistrifluoromethylamine (2·56 g., 8·6 mmoles) kept *in vacuo* with powdered potassium hydroxide (10 g., 0·18 mole) at room temperature for 6 hr. gave 1,2-*difluorovinylbistrifluoromethylamine* (1·70 g., 7·9 mmoles, 98%) (Found: C, 22·5; H, 0·4; N, 6·4%; *M*, 215. $C_4HF_8N$ requires C, 22·3; H, 0·5; N, 6·7%; *M*, 215) and unchanged starting material (0·15 g., 0·5 mmole, 6%).

(e) 1-*Bromo*-2,2-*difluorovinylbistrifluoromethylamine*. 2,2-Difluorovinylbistrifluoromethylamine (2·12 g., 9·8 mmoles) was shaken with bromine (3·20 g., 20·0 mmoles) in a sealed 200 ml. ‘ Pyrex ’ ampoule in light for 1 hr. The excess of bromine was destroyed by shaking with mercury (5 ml.). The product was 1,2-dibromo-2,2-difluoroethylbistrifluoromethylamine (3·62 g., 9·6 mmoles, 98%) (Found: *M*, 374. Calc. for $C_4HBr_2F_8N$: *M*, 375). The dibromide (2·59 g., 6·9 mmoles), treated *in vacuo* with powdered potassium hydroxide (10 g., 0·18 mole) at room temperature for 30 min., gave 1-*bromo*-2,2-*difluorovinylbistrifluoromethylamine* (1·62 g., 5·8 mmoles, 99%) (Found: C, 16·5; N, 4·5%; *M*, 298. $C_4BrF_8N$ requires C, 16·3; N, 4·8%; *M*, 296), and unchanged dibromide (0·39 g., 1·1 mmoles, 15%).

*Reactions of Perfluoro*-(N,N-*dimethylvinylamine*).—(a) *With bromine*. The vinylamine (0·30 g., 1·3 mmoles) and bromine (0·60 g., 3·8 mmoles) were shaken together in a sealed tube *in vacuo* at room temperature for 3 hr. and the excess of bromine was destroyed with mercury (2 ml.). The product was 1,2-*dibromotrifluoroethylbistrifluoromethylamine* (0·49 g., 1·25 mmoles, 98%) (Found: C, 12·4; H, 3·6%; *M*, 392. $C_4Br_2F_9N$ requires C, 12·2; N, 3·6%; *M*, 393).

(b) *Free-radical reaction with hydrogen bromide*. The vinylamine (0·61 g., 2·6 mmoles) and hydrogen bromide (0·22 g., 2·7 mmoles), sealed in a 150 ml. ‘ Pyrex ’ ampoule, and irradiated with a Hanovia S 500 ultraviolet lamp at a distance of 6 in. for 14 days gave 2-bromo-1,2,2-trifluoroethylbistrifluoromethylamine (0·26 g., 0·84 mmole, 99%) (Found: *M*, 313. Calc. for $C_4HBrF_9N$: *M*, 314), identical with the major product from the reaction of *N*-bromobistrifluoromethylamine with trifluoroethylene, hydrogen bromide (0·15 g., 1·9 mmoles, 69%), and unchanged vinylamine (0·42 g., 1·85 mmoles, 68%).

Irradiation in a 100 ml. silica tube under similar conditions for 6 days gave the 1 : 1 adduct (72% conversion, 99% yield), and a comparison experiment run under the same conditions with a mixture of hydrogen bromide and perfluoropropene gave 1-bromo-1,1,2,3,3,3-hexafluoropropane (96% conversion, 96% yield) shown by its i.r. spectrum to be contaminated with a small amount of 1,2-dibromohexafluoropropane.

(c) *Attempted ionic reaction with hydrogen bromide.* A mixture of the vinylamine (0·71 g., 3·1 mmoles) and hydrogen bromide (0·25 g., 3·1 mmoles), sealed in a 150 ml. 'Pyrex' tube and kept in the dark at room temperature for 14 days gave only unchanged reactants which were resealed with aluminium bromide (0·10 g., 0·40 mmole) and kept in the dark at room temperature for 14 days; again no reaction occurred.

(d) *Photolysis.* The vinylamine (0·61 g., 2·6 mmoles), sealed in a 35 ml. silica tube, and irradiated with a Hanovia S 500 ultraviolet lamp at a distance of 6 in. for 14 days gave unchanged vinylamine (0·25 g., 1·1 mmoles, 41%), a higher-boiling dimer fraction (0·28 g., 0·60 mmole, 80%) (Found: C, 20·8; N, 6·1%; *M*, 470. Calc. for $C_8F_{18}N_2$: C, 20·6; N, 6·0%; *M*, 466) shown by g.l.c. to consist of two components in the ratio 9 : 1, and a non-volatile residue (0·07 g.).

The dimer fraction showed strong i.r. bands at 5·63, 5·78, 7·45, 7·82, 8·05, 8·18, 8·55, 10·08 (C–N), 13·0, and 13·75 $(CF_3)$ μ.

(e) *Pyrolysis.* The vinylamine (0·55 g., 2·4 mmoles), pyrolysed at 1—2 mm. through the platinum tube (40 min.; contact time 1·1 sec.) at 595° gave a mixture of hexafluoroethane, silicon tetrafluoride, trifluoromethylisocyanate, and carbonyl fluoride, and a higher-boiling fraction (0·51 g., 2·2 mmoles, 92%). This higher-boiling fraction was repassed five times through the platinum tube (total time 4 hr., contact time *ca.* 7 sec.), with the low-boiling decomposition products separated after each pass to give (i) a mixture (0·10 g., 1·0 mmoles; *M*, 100) of hexafluoroethane, silicon tetrafluoride, trifluoromethylisocyanate, and carbonyl fluoride, and (ii) a higher-boiling fraction (0·35 g., 1·5 mmoles, 63%) (Found: *M*, 232. Calc. for $C_4F_9N$: *M*, 233) shown by i.r. spectroscopy to contain unchanged starting material and another component.

The higher-boiling fraction was sealed in a 50 ml. 'Pyrex' tube with bromine (0·30 g., 1·9 mmoles) and shaken at room temperature for 60 hr., and the excess of bromine was destroyed with mercury (2 ml.). The products were 1,2-dibromotrifluoroethylbistrifluoromethylamine (0·14 g., 0·40 mmole, 16%) and perfluoro-2-azapent-2-ene (0·27 g., 1·1 mmoles, 46% conversion, 55% yield) (Found: C, 20·7; N, 5·9%; *M*, 232. Calc. for $C_4F_9N$: C, 20·6; N, 6·0%; *M*, 233).

(f) *Pyrolysis with toluene.* The vinylamine (0·77 g., 3·3 mmoles) and toluene (3·0 g., 33·0 mmoles) passed through the platinum tube at 610° (100 min.; contact time 0·66 sec.) gave (i) a small amount of non-condensable material (4 ml.), (ii) a low-boiling fraction (0·11 g., 1·5 mmoles; *M*, 72), (iii) an intermediate boiling fraction (0·61 g., 2·6 mmoles, 80%; *M*, 233) containing unchanged vinylamine (0·46 g., 2·0 mmoles, 60% recovery) and perfluoro-2-azapent-2-ene (0·15 g., 0·60 mmoles, 18% conversion, 46% yield), and (iv) a high-boiling fraction (3·0 g., 32·9 mmoles; *M*, 94), containing unchanged toluene, bibenzyl, and unknown material with bands in the i.r. at 7·25w, 7·42w, 7·80w, 7·99m, 8·24m, 8·70m, 10·10w, and 10·80w μ, which decomposed slowly and liberated silicon tetrafluoride from glass.

The low-boiling fraction, shown by i.r. spectroscopy to be a mixture of fluoroform, silicon tetrafluoride, trifluoromethylisocyanate, 1,1-difluoroethylene, and carbonyl fluoride, was treated with 5% aqueous sodium hydroxide (5 ml.) at room temperature for 30 min. to give a mixture (0·09 g., 1·3 mmoles; *M*, 67) of fluoroform, 1,1-difluoroethylene, and unknown material with weak i.r. bands at 4·0, 4·4, 5·4, and 8·1 μ. This hydrolysed fraction, sealed with bromine (0·24 g., 1·5 mmoles) for 2 hr., gave fluoroform (0·06 g., 0·80 mmole, 31%) (Found: *M*, 70. Calc. for $CHF_3$: *M*, 70) identified by its i.r. spectrum and shown to contain the impurity bands at 4·0, 4·4, 5·4, and 8·1 μ, and 1,2-dibromo-1,1-difluoroethane (0·11 g., 0·50 mmole) (Found: *M*, 226. Calc. for $C_2H_2Br_2F_2$: *M*, 224), identified by a comparison of its i.r. spectrum with that of a pure sample.

(g) *Attempted cyclodimerisation.* The vinylamine (3·85 g., 16·5 mmoles) was unchanged when heated at 250° for 48 hr. in a 12 ml. autoclave (max. pressure possible 60 atmos.).

*Reactions of Trifluoromethyl Trifluorovinyl Ether.*—(a) *With bromine.* The vinyl ether (0·11 g., 0·66 mmole) and bromine (0·40 g., 2·50 mmoles), shaken in a 100 ml. 'Pyrex' tube at room temperature for 2 hr., gave *1,2-dibromotrifluoroethyl trifluoromethyl ether* (0·20 g., 0·61 mmole, 92%) (Found: C, 10·9%; *M*, 327. $C_3Br_2F_6O$ requires C, 11·0%; *M*, 326).

(b) *Photolysis.* The vinyl ether (0·24 g., 1·45 mmoles), irradiated in a 35 ml. silica tube (Hanovia S 500 lamp at 6 in.) for 15 days gave (i) a mixture (0·01 g., 0·10 mmole) of carbonyl fluoride and silicon tetrafluoride, (ii) a mixture (0·06 g., 0·30 mmole; *M*, 187) of unchanged vinyl ether and unknown material, (iii) a higher-boiling fraction (0·13 g., 0·34 mmole) (Found: C, 19·3%; *M*, 378), and (iv) a non-volatile residue (0·04 g.).

(c) *Pyrolysis.* The vinyl ether (0·26 g., 1·5 mmoles), passed through the platinum tube at 595° (35 min.; contact time 1·2 sec.), gave (i) a non-condensable fraction (*ca.* 2 ml. gas), (ii) a volatile mixture (0·07 g., 0·53 mmole; *M*, 127) of carbonyl fluoride, silicon tetrafluoride, and hexafluoroethane, and (iii) a mixture of unchanged vinyl ether (0·05 g., 0·30 mmole, 20% recovery) and pentafluoropropionyl fluoride (0·13 g., 0·80 mmole, 67%).

*Pyrolysis of 2-Chlorodifluorovinylbistrifluoromethylamine.*—This vinylamine (1·20 g., 4·8 mmoles), passed through the platinum tube at 600° (4 hr.), gave (i) a low-boiling mixture (0·32 g., 3·1 mmoles; *M*, 104) of carbonyl fluoride, silicon tetrafluoride, hexafluoroethane, and unknown material with weak i.r. bands at 5·65 and 5·80 μ, and (ii) a higher-boiling fraction (0·84 g., 3·4 mmoles; *M*, 247) containing unchanged vinylamine and unknown material.

Treatment of (i) with 10% aqueous potassium hydroxide (5 ml.) *in vacuo* at room temperature for 30 min. gave a mixture (0·20 g., 1·7 mmoles; *M*, 117) of hexafluoroethane and chlorotrifluoromethane contaminated with the same unknown material. Fraction (ii) and bromine (1·50 g., 9·4 mmoles) irradiated in a 100 ml. silica tube for 24 hr. gave (i) *4-chloro-octafluoro-2-azapent-2-ene* (0·53 g., 2·1 mmoles, 47%) (Found: C, 19·2; N, 5·8%; *M*, 249. $C_4ClF_8N$ requires C, 19·2; N, 5·6%; *M*, 250), (ii) 1,2-dibromo-2-chlorodifluoroethylbistrifluoromethylamine (0·15 g., 0·36 mmole, 8%) identical with the product obtained from the reaction of bromine with the chlorovinylamine,[14] and (iii) a mixture (0·19 g., 0·70 mmole) of two unknown components.

*Vapour Pressure Equations.*—The constants *A* and *B*

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[14] R. N. Haszeldine and A. E. Tipping, unpublished results.

TABLE 3

Vapour pressure data

| | Range measured | *A* | *B* | $L_v$ | *T* | B. p. |
|---|---|---|---|---|---|---|
| $(CF_3)_2N{\cdot}CF{:}CF_2$ | −16 to 7° | 7·936 | −1437 | 6580 | 23·1 | 11·1° |
| $(CF_3)_2N{\cdot}CH{:}CF_2$ | 1·5—18 | 7·817 | −1447 | 6620 | 22·6 | 20·0 |
| $(CF_3)_2N{\cdot}CBr{:}CF_2$ | 20—47 | 7·935 | −1637 | 7490 | 23·1 | 50·7 |
| $(CF_3)_2N{\cdot}CF{:}CHF$ | 3—23 | 7·922 | −1503 | 6880 | 23·1 | 24·9 |
| $(CF_3)_2N{\cdot}CF{:}CFCl$ | 0—39 | 7·724 | −1522 | 6970 | 22·2 | 41·2 |
| $(CF_3)_2N{\cdot}CFBr{\cdot}CF_2Br$ | 53—93 | 7·624 | −1790 | 8290 | 22·0 | 104·1 |
| $CF_3{\cdot}N{:}CF{\cdot}CF_2{\cdot}CF_3$ * | −28 to 7 | 7·763 | −1392 | 6450 | 22·6 | 11·9 |
| $CF_3{\cdot}O{\cdot}CF{:}CF_2$ † | −65 to −32 | 7·711 | −1194 | 5470 | 22·7 | −26·1 |
| $CF_3{\cdot}O{\cdot}CFBr{\cdot}CF_2Br$ | 26—62 | 8·184 | −1806 | 8360 | 24·6 | 67·4 |

* Lit.,[11] b. p. 13·2°; *T*, 22·7. † Lit.,[7] b. p. −22°.

TABLE 4

Main mass spectral bands

| | Mass | Ion | *I* |
|---|---|---|---|
| $(CF_3)_2N{\cdot}CF{:}CF_2$ | 233 | Parent$^+$ | 8·1 |
| | 145 | $C_3F_5N^+$ | 10·4 |
| | 126 | $C_3F_4N^+$ | 9·4 |
| | 114 | $C_2F_4N^+$ | 5·2 |
| $(CF_3)_2N{\cdot}CH{:}CF_2$ | 215 | Parent$^+$ | 16·7 |
| | 146 | $C_3HF_5N^+$ | 6·7 |
| | 96 | $C_2HF_3N^+$ | 10·2 |
| $(CF_3)_2N{\cdot}CF{:}CHF$ | 215 | Parent$^+$ | 8·0 |
| | 127 | $C_3HF_4N^+$ | 13·4 |
| | 114 | $C_2F_4N^+$ | 4·4 |
| | 77 | $C_2HF_2N^+$ | 4·7 |
| | 63 | $C_2HF_2^+$ | 2·4 |
| $CF_3{\cdot}N{:}CF{\cdot}C_2F_5$ | 233 | Parent$^+$ | 0·2 |
| | 214 | $C_4F_8N^+$ | 10·2 |
| | 164 | $C_3F_6N^+$ | 9·1 |
| | 119 | $C_2F_5^+$ | 1·5 |
| | 114 | $C_2F_4N^+$ | 41·8 |
| $(CF_3)_2N{\cdot}CFBr{\cdot}CF_2Br$ | 312<br>314 | $C_4BrF_9N^+$ | 5·3 |
| | 239<br>241<br>243 | $C_2Br_2F_3^+$ | 5·8 |
| | 233 | $C_4F_9N^+$ | 2·5 |
| | 129<br>131 | $CBrF_2^+$ | 4·3 |
| | 114 | $C_2F_4N^+$ | 10·3 |
| $CF_3{\cdot}O{\cdot}CFBr{\cdot}CF_2Br$ | 245<br>247 | $C_3BrF_6O^+$ | 7·2 |
| | 239<br>241<br>243 | $C_2BrF_3^+$ | 4·5 |
| | 195<br>197 | $C_2BrF_4O^+$ | 1·3 |
| $(CF_3)_2N{\cdot}CF{:}CFBr$ | 293<br>295 | Parent$^+$ | 7·9 |
| | 224<br>226 | $C_3BrF_5N^+$ | 2·1 |
| | 114 | $C_2F_4N^+$ | 43·7 |
| $(CF_3)_2N{\cdot}CF{:}CFCl$ | 249 | Parent$^+$ | 11·2 |
| | 161 | $C_3ClF_4N^+$ | 19·1 |
| | 114 | $C_2F_4N^+$ | 3·1 |
| | 66 | $CClF^+$ | 1·6 |
| $(CF_3)_2N{\cdot}CBr{:}CF_2$ | 293<br>295 | Parent$^+$ | 10·2 |
| | 224<br>226 | $C_3BrF_5N^+$ | 7·7 |
| | 174<br>176 | $C_2BrF_3N^+$ | 1·4 |
| $CF_3{\cdot}N{:}CF{\cdot}CFCl{\cdot}CF_3$ | 249 | Parent$^+$ | 0·9 |
| | 230 | $C_4ClF_7N^+$ | 4·1 |
| | 180 | $C_3ClF_5N^+$ | 3·5 |
| | 135 | $C_2ClF_4N^+$ | 1·8 |
| | 114 | $C_2F_4N^+$ | 49·6 |
| $(CF_3)_2N{\cdot}CHBr{\cdot}CF_2Br$ | 294<br>296 | $C_4HBrF_8N^+$ | 36·7 |
| | 244<br>246 | $C_3HBrF_6N^+$ | 1·6 |
| | 221<br>223<br>225 | $C_2HBr_2F_2^+$ | 14·7 |
| | 142<br>144 | $C_2HBrF_2$ | 5·3 |
| | 129<br>131 | $CBrF_2^+$ | 3·4 |
| | 127 | $C_3HF_4N^+$ | 13·4 |
| | 96 | $C_2HF_3N^+$ | 12·4 |

Both the bromovinylamines also showed a peak due to the ion $CF_2Br^+$ and the chlorovinylamine showed a peak due to the ion $CF_2Cl^+$, probably arising by rearrangements, like the ion $C_2HBrF_3^+$ found in the spectrum of the compound $(CF_3)_2N{\cdot}CHBr{\cdot}CF_2Br$.

TABLE 5

$^{19}$F N.m.r. spectra

| 1 | 2 | 3 | Band 1 |  |  | Band 2 |  |  | Band 3 |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | P.p.m. | Type | Intensity | P.p.m. | Type | Intensity | P.p.m. | Type | Intensity |
| $(CF_3)_2N$— | —CF= | =$CF_2$ | −17·5 | s, br | 6 | 35·5 | dd | 1 | 69·3<br>22·2 | dd<br>t | 1<br>1 |
| $(CF_3)_2N$— | —CF= | =CFCl *cis* | −19·2 | dd | 6 | 32·5 | dsep | 1 | 19·0 | dsep | 1 |
|  |  | *trans* | −19·2 | t | 6 | 32·6 | dsep | 1 | 47·2 | dsep | 1 |
| $(CF_3)_2N$— | —CF= | =CHF *cis* | −19·5 | dd | 6 | 32·8 | c | 1 | 70·6 | ddsep | 1 |
|  |  | *trans* | −20·0 | t | 6 | 58·0 | c | 1 | 86·6 | ddsep | 1 |
| $(CF_3)_2N$— | —CH= | =$CF_2$ | −16·1 | s, br | 6 |  |  |  | 14·5<br>5·0 | cd<br>ddsep | 1<br>1 |
| $(CF_3)_2N$— | —CBr= | =$CF_2$ | −18·8 | dd | 6 |  |  |  | 1·3<br>3·2 | dsep<br>dsep | 1<br>1 |
| $(CF_3)_2N$— | —CFBr— | —$CF_2Br$ | −25·4 | c | 6 | 23·2 | c | 1 | −21·8 | c | 1 |
| $CF_3{\cdot}O$— | —CF= | =$CF_2$ | −13·8 | t | 3 | 62·8 | ddq | 1 | 41·4<br>48·4 | ddq<br>ddq | 1<br>1 |
| $CF_3{\cdot}O$— | —CFBr— | —$CF_2Br$ | −22·7 | d | 3 | −6·5 | q | 1 | −15·1 | d | 2 |

s = Singlet, br = broad, d = doublet, t = triplet, q = quartet, sep = septet, c = complex, dd = doublet of doublets, ddq = doublet of doublets of quartets, etc.

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

*Mass Spectral Data.*—The intensities in the data shown in Table 4 are relative to $CF_3^+$, intensity 100.

*Nuclear Magnetic Resonance Spectra.*—The data shown in Tables 5 and 6 were recorded using trifluoroacetic acid and tetramethylsilane as $^{19}$F and $^{1}$H references, respectively.

TABLE 6

$^{1}$H N.m.r. spectra

|  | Multiplicity | $\tau$ |
|---|---|---|
| $(CF_3)_2N{\cdot}CH{:}CF_2$ | dsex * | 4·84 |
| *cis*-$(CF_3)_2N{\cdot}CF{:}CHF$ | dd | 3·42 |
| *trans*-$(CF_3)_2N{\cdot}CF{:}CHF$ | dd | 2·94 |

dsex = Doublet of sextets, dd = doublet of doublets.

* Observation of a doublet of sextets is presumably due to weakness of the outer bands in the expected doublet of octets.

The $^{19}$F chemical shifts established for various groups are as follows:

| Group | Chemical shift (p.p.m.) | Reference |
|---|---|---|
| $(CF_3)_2N{\cdot}C$ | *ca.* −20 | 15, 16 |
|  | −19·5 to −26·1 | 9 |
|  | −17 to −22 | 1 |
| $CF_2{:}C$ | 1—20 and 12—32 | 17 |
|  | *ca.* 30 and *ca.* 50 | 18 |
| $CFCl{:}C$ | *ca.* 70 | 18 |
| $CHF{:}C$ | *ca.* 110 | 18 |
|  | 30—40 | 19 |
| $CF_2Br{\cdot}C$ | −11·4 to −21·9 | 9 |
|  | −13 to −22 | 20 |
|  | −23·4 | 19 |
| $C{\cdot}CFBr{\cdot}N$ | −15·9 | 9 |
| $CF_3{\cdot}O{\cdot}C$ | *ca.* −20 | 1 |

The spectra of the two azapentenes prepared in the present work are compared with the reported [11] spectrum of perfluoro-2-azapent-2-ene, and with that of perfluoro-2-azahex-2-ene [13] (Table 7; abbreviations as in footnote to Table 5 and quin = quintet).

*Infrared Spectra.*—The spectra of all the vinylamines showed strong bands between 7 and 8·5 μ (C–F stretch), between 5·5 and 5·85 μ (C=C stretch), between 10·0 and 10·2 μ (C–N stretch) and between 13·6 and 13·8 μ ($CF_3$ deformation); certain of these are shown in Table 8.

TABLE 7

|  | $CF_3$— | —$CF_2$— | —CF=N— | —$CF_3$ |
|---|---|---|---|---|
| Found | 7·7 dt | 44·7 d | −50·1 s | −18·3 d |
| Reported | 7·3 | 44·6 | −51·2 | −18·3 |
|  | $CF_3$— | —$(CF_2)_2$— | —CF=N— | —$CF_3$ |
|  | 5·2 td | 42·5 quin<br>50·8 d | −52·9 s | −18·3 d |
|  | $CF_3$— | —CFCl— | —CF=N— | —$CF_3$ |
|  | 4·1 t | 55 br | −52 s | −19 d |

TABLE 8

Infrared spectra of vinylamines (μ)

|  | C=C stretch | C–N stretch | $CF_3$ deformation |
|---|---|---|---|
| $(CF_3)_2N{\cdot}CF{:}CF_2$ | 5·52 | 10·09 | 13·73 |
| $(CF_3)_2N{\cdot}CF{:}CFCl$ | 5·78, 5·83 | 10·11 | 13·70 |
| $(CF_3)_2N{\cdot}CH{:}CF_2$ | 5·68 | 10·16 | 13·64 |
| $(CF_3)_2N{\cdot}CF{:}CHF$ | 5·72 | 10·07 | 13·67 |
| $(CF_3)_2N{\cdot}CBr{:}CF_2$ | 5·73 | 10·02 | 13·79 |
| $(CF_3)_2N{\cdot}CF{:}CFBr$ | 5·65 | 10·05 | 13·58 |

The vinyl ether $CF_3{\cdot}O{\cdot}CF{:}CF_2$ gave strong bands at 5·57 (C=C) and 13·70 ($CF_3$) μ. Both of the azapentenes prepared gave strong bands in the C=N stretching region; 5·65 μ for $CF_3{\cdot}N{:}CF{\cdot}C_2F_5$ (lit.,[11] 5·60 μ) and 5·64 μ for $CF_3{\cdot}N{:}CF{\cdot}CFCl{\cdot}CF_3$.

The authors thank Dr. J. Lee and Dr. D. J. Mowthorpe for the n.m.r. data, Dr. R. D. Sedgwick and Mr. E. Henderson for the mass spectra data, and the D.S.I.R. for a Research Studentship (to A. E. T.).

[7/579 *Received, May* 10*th*, 1967]

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