Perfluoroalkyl Derivatives of Nitrogen. Part I. Perfluoro-2-methyl-1 : 2-oxazetidine and Perfluoro(alkylenealkylamines).*

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Trifluoronitrosomethane reacts quantitatively with tetrafluoroethylene to give perfluoro-2-methyl-1 : 2-oxazetidine (I) and a polymer of formula $[\cdot N(CF_3)\cdot O\cdot CF_2\cdot CF_2\cdot]_n$ and molecular weight >7000. Pyrolysis of the oxazetidine or of the polymer gives, quantitatively, equimolar amounts of perfluoro(methylenemethylamine), $CF_3\cdot N{:}CF_2$, and carbonyl fluoride. Chemical, physical, and spectroscopic properties are reported for these new compounds. Improved techniques are described for the preparation of trifluoronitrosomethane.

Trifluoronitrosomethane, a deep-blue monomeric gas first prepared by Ruff and Giese (*Ber.*, 1936, **69**, 598, 684) by treatment of a silver cyanide–silver nitrate mixture with fluorine, was subsequently prepared in good yield by the interaction of trifluoroiodomethane and nitric oxide, and its properties were studied.* It is extremely reactive and can readily be converted into trifluoronitromethane, hexafluoroazoxymethane, and an orange dimer which has structure $(CF_3)(CF_3\cdot O)N\cdot NO$ or $(CF_3)_2N\cdot O\cdot NO$. The present communication describes improved techniques for the preparation of trifluoronitrosomethane and similar nitroso-compounds, and its conversion into perfluoro-2-methyl-1 : 2-oxazetidine (I) and perfluoro(methylenemethylamine) (V).

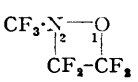
The only disadvantage of the initial preparative method for trifluoronitrosomethane from trifluoroiodomethane and nitric oxide was that sealed tubes or silica reaction flasks were necessary, so that several small-scale experiments were required to obtain substantial quantities of the gas. A simple apparatus has now been developed (see Fig. 1) which

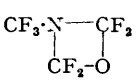
* For earlier work on perfluoroalkyl derivatives of nitrogen see Haszeldine, *Nature*, 1951, **168**, 1028; *J.*, 1953, 2075; Haszeldine and Jander, *J.*, 1953, 4172; 1954, 696, 912, 919; *Naturwiss.*, 1953, **40**, 579.

avoids the use of pressure, is constructed of readily available Pyrex apparatus, yet gives yields as high as those obtained earlier, and in which up to 0·25 mole of trifluoroiodomethane can be used per experiment. These improvements make the pure nitroso-compound readily available.

Trifluoronitrosomethane, as reported earlier, is stable as a gas at room temperature or as a liquid under pressure. Banus (*J.*, 1953, 3755) confirmed the synthesis of the nitroso-compound, but stated that it decomposes spontaneously at room temperature, particularly in the gas phase or when shaken with mercury; this is completely fallacious. The original observations have again been confirmed, and in clean apparatus the nitroso-compound is quite stable to water, to storage, or to shaking with mercury, whereas moist soda-glass surfaces, bases, or light rapidly bring about decomposition. Unless these precautions are taken, therefore, decomposition products soon contaminate the nitroso-compound and cause the difficulties reported by Banus; with these precautions the purification procedure is simple (see p. 1886).

Trifluoronitrosomethane combines slowly and quantitatively with tetrafluoroethylene in the dark at room temperature to give 30—65% of a colourless gas (b. p. −6·8°) and 35—70% of an almost colourless viscous oil. The ratio of gas to oil can be controlled by choice of reaction temperature; higher temperatures favour the former. The gas has molecular formula C_3ONF_7, and is unaffected by water, aqueous alkali or acid, or ultraviolet light. Possible constitutions are (I)—(IV). Heptafluoronitrosopropane (III) can be eliminated since this is known (*J.*, 1953, 2075), and is a deep blue gas showing the very characteristic N:O stretching vibration (6·23 μ) in its infrared spectrum. Compound (II) would be colourless, but its formation would require fission of the C–C bond in tetra-


(I)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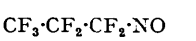
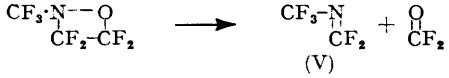

(III)


(IV)

fluoroethylene and of the N–O bond in trifluoronitrosomethane and is thus improbable. Perfluoroamine oxides have not yet been prepared; (IV) would certainly be colourless, however, and, since the compound $(CF_3)_3\overset{+}{P}\overset{-}{O}$ (b. p. 23·5°) boils at only a slightly higher temperature than tristrifluoromethylphosphine (b. p. 17°), it might well be volatile [cf. $(CF_3)_3N$, b. p. −6·5°; Haszeldine, *J.*, 1951, 102]. The P–O stretching vibration in the infrared is at the remarkably low wavelength of 7·53 μ for tristrifluoromethylphosphine oxide (Emeléus, Haszeldine, and Paul, *J.*, 1955, 563), so it might be possible for the nitrogen–oxygen vibration in the compound (IV) to lie below the carbon–fluorine stretching vibrations at 8—9 μ. The infrared spectrum of C_3ONF_7 (C.S. No. 210 *) shows no band in the N:O region, although there is a band at 7·05 μ which might be assigned to the $\overset{+}{N}–\overset{-}{O}$ vibration in (IV) (cf. N:O in CF_3·NO, 6·25 μ). It is unlikely that a three-membered ring of the type in (IV) would be stable, however, or that the co-ordinate $\overset{+}{N}–\overset{-}{O}$ bond could be sufficiently non-polar to account for the low b. p. of −6·8°; perfluoro-amines such as $N(CF_3)_3$ are unable to form amine oxides on account of the markedly decreased availability of the lone pair of electrons on the nitrogen atom. The very weak general absorption of C_3ONF_7 in the ultraviolet, the method used for its synthesis, its physical properties, and its infrared spectrum are all consistent with its alternative formulation as perfluoro-2-methyl-1 : 2-oxazetidine (I). Strong support for this is given by its pyrolysis at 550° at low pressure in absence of air to yield twice the original volume of gas, shown to consist of equimolar amounts of carbonyl fluoride and perfluoro(methylenemethylamine) (V) :


(V)

* Spectra thus designated have been deposited with the Society. Photocopies, price 3*s.* 0*d.* per copy per spectrum, may be obtained on application, quoting the C.S. no., to the General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

Perfluoro(methylenemethylamine) is a colourless gas whose b. p. (−33·7°) is close to that of hexafluoropropene (−29°); as noted earlier for perfluoro-*tert.*-amines, replacement of a >CF– group in a fluorocarbon by a nitrogen atom scarcely affects the b. p. [cf. $(CF_3)_3N$, b. p. −6·5°; *n*-C_4F_{10}, b. p. −0·5°; Haszeldine, *J.*, 1951, 102]. Its infrared spectrum (C.S. No. 211) shows a strong band at 5·53 μ assigned to the N:C stretching vibration (cf. C:C in $CF_3{\cdot}CF{:}CF_2$, 5·56 μ; Haszeldine, *J.*, 1952, 4259). Homologues of perfluoro(methylenemethylamine) have been obtained recently by pyrolysis of perfluoro-*tert.*-amines (Pearlson and Hals, U.S.P. 2,643,267; *Chem. Abs.*, 1954, **48**, 6461).

Ingold and Weaver (*J.*, 1924, **125**, 1456) obtained compounds formulated as "dimethyleneoxamines" (*i.e.*, as oxazetidines) by the reaction between nitrosobenzene and compounds such as 1 : 1-diphenylethylene or diethyl methylenemalonate [*i.e.*, (i) $Ph_2\overset{\frown}{C{\cdot}CH_2{\cdot}O{\cdot}NPh}$ and (ii) $(EtO_2C)_2\overset{\frown}{C{\cdot}CH_2{\cdot}NPh{\cdot}O}$]. Staudinger and Jelagin (*Ber.*, 1911, **44**, 365) prepared related compounds from nitrosobenzene and ketens [*e.g.*, $Ph_2C{:}C{:}O + Ph{\cdot}NO \longrightarrow Ph_2\overset{\frown}{C{\cdot}CO{\cdot}NPh{\cdot}O}$ (iii)]. No yields were given for any of the above compounds, but analytical data were obtained. Proof of structure was given by pyrolysis at 170°: (i) afforded $Ph_2C{:}NPh + CH_2O$; (ii) gave $(EtO_2C)_2C{:}C{:}NPh \longrightarrow (EtO_2C)_2CH{\cdot}CO{\cdot}NHPh$ and (iii) gave $Ph_2CO + Ph{\cdot}NCO$; yields were given only for the last reaction, and were then good. The compound (iii) was cleaved by anhydrous hydrogen chloride to give $Ph_2CCl{\cdot}CO{\cdot}NPh{\cdot}OH$. By contrast, perfluoro-2-methyl-1 : 2-oxazetidine is stable to anhydrous hydrogen chloride and to concentrated aqueous acid.

The lower members of the aliphatic azomethines are believed to be cyclic trimers from molecular-weight and vapour-density determinations (Henry, *Compt. rend.*, 1895, **120**, 839; Thomas, *ibid.*, p. 451); they are hydrolysed to the amine and the aldehyde by dilute acids or aqueous bases, and when treated with ethanolic sodium ethoxide yield both the parent amine and, by reduction, the secondary amine (*e.g.*, $Bu^nN{:}CH_2 \longrightarrow Bu^n{\cdot}NH_2 + Bu^n{\cdot}NHMe$) (Henry, *Bull. Acad. roy. Belg.*, 1895, **29**, 26; Franchimont and Van Epps, *Rec. Trav. chim.*, 1896, **15**, 169).

Perfluoro(methylenemethylamine) is rapidly and quantitatively hydrolysed by water to give carbon dioxide, ammonium fluoride, and hydrogen fluoride:

$$CF_3{\cdot}N{:}CF_2 \xrightarrow{H_2O} CF_3{\cdot}NH_2 + COF_2$$

$$\downarrow -HF \qquad \downarrow H_2O$$

$$CF_2{:}NH \qquad CO_2 + 2HF$$

$$CF_2{:}NH \xrightarrow{H_2O} COF_2 + NH_3 \xrightarrow{H_2O} CO_2 + NH_4F + HF$$

$$CF_2{:}NH \xrightarrow{H_2O} CF_2(OH){\cdot}NH_2 \xrightarrow{-HF} F{\cdot}CO{\cdot}NH_2 \xrightarrow{H_2O} CO_2 + NH_4F$$

Attempts to prepare the still-unknown trifluoromethylamine, $CF_3{\cdot}NH_2$, by the reaction of perfluoro(methylenemethylamine) with a deficit of water ($CF_3{\cdot}N{:}CF_2 + H_2O \longrightarrow CF_3{\cdot}NH_2 + COF_2$) were unsuccessful. Unchanged perfluoro(methylenemethylamine) and breakdown compounds [silicon tetrafluoride (from reaction of hydrogen fluoride with the reaction vessel) and carbonyl fluoride] were the main products, and infrared spectroscopic examination failed to detect more than traces of gaseous compounds containing N–H bonds. Small amounts of a volatile compound showing absorption in the infrared at 4·4 μ (not carbon dioxide) were always formed under these conditions. Final identification must be deferred, since attempts to isolate the compound failed, but it seems possible that it is cyanogen fluoride produced by the reaction $CF_3{\cdot}NH_2 \longrightarrow FCN + 2HF$, and that the C:N absorption is appearing at 4·4 μ. Trifluoromethyl *iso*cyanate, produced by the reaction

$$CF_3{\cdot}NH_2 + COF_2 \xrightarrow{-HF} CF_3{\cdot}NH{\cdot}COF \xrightarrow{-HF} CF_3{\cdot}NCO$$

is also possible, since the N:C:O vibration would be expected to appear near 4·4 μ. The same unknown product is produced when perfluoro(methylenemethylamine) is heated in

silica, and the formation of cyanogen fluoride or of trifluoromethyl *iso*cyanate (*e.g.*, $CF_3{\cdot}N{:}CF_2 \xrightarrow{SiO_2} CF_3{\cdot}N{:}C{:}O$) concurrently with silicon tetrafluoride can be visualised.

Anhydrous methanol reacts rapidly with perfluoro(methylenemethylamine) to yield dimethyl ether, dimethyl carbonate, and ammonium fluoride, but not carbon dioxide. Methanolysis probably occurs as follows :

$$CF_3{\cdot}N{:}CF_2 + 2CH_3{\cdot}OH \longrightarrow CF_3{\cdot}NH_2 + COF_2 + (CH_3)_2O$$
$$COF_2 + 2CH_3{\cdot}OH \longrightarrow (CH_3{\cdot}O)_2CO + 2HF$$
$$2CH_3{\cdot}OH \xrightarrow{HF} (CH_3)_2O + H_2O$$
$$CF_3{\cdot}NH_2 \xrightarrow{-HF} CF_2{:}NH$$
$$CF_2{:}NH + 2CH_3{\cdot}OH \longrightarrow NH_3 + COF_2 + (CH_3)_2O$$

although an alternative mechanism, involving nucleophilic attack on the C:N (cf. the ease of nucleophilic attack on fluoro-olefins such as C_2F_4, C_3F_6), can be visualised :

$$CF_3{\cdot}N{:}CF_2 \xrightarrow{MeOH} CF_3{\cdot}NH{\cdot}CF_2{\cdot}OMe \xrightarrow{-HF} CF_2{:}N{\cdot}CF_2{\cdot}OMe \xrightarrow{MeOH} MeO{\cdot}CF_2{\cdot}NH{\cdot}CF_2{\cdot}OMe$$
$$MeO{\cdot}CF_2{\cdot}NH{\cdot}CF_2{\cdot}OMe \xrightarrow[\text{repeated}]{-HF;\ MeOH} (MeO)_3C{\cdot}NH{\cdot}C(OMe)_3 \longrightarrow C(OMe)_4 + NH_3$$
$$C(OMe)_4 \xrightarrow{HF} (CH_3O)_2CO + (CH_3)_2O$$

The colourless viscous oil formed by the reaction of trifluoronitrosomethane with tetrafluoroethylene is insoluble in the common organic solvents. Its infrared spectrum (C.S. No. 212) fails to show the presence of groups such as N:O, NO_2, $N{:}\overset{+}{N}(\overset{-}{O})$, ONO, or ONO_2, and N=O, N=N, C=N, and C=C double bonds are absent. The ultraviolet spectrum fails to show specific absorption, again indicating the absence of N:O or NO_2 groups (see *J.*, 1953, 2525; 1954, 691, 912, 919 for infrared and ultraviolet spectra of compounds containing nitrogen and oxygen). The oil has empirical formula C_3ONF_7, *i.e.*, the same as perfluoro-2-methyl-1 : 2-oxazetidine, and this eliminates the possibility that it is a tetrafluoroethylene polymer $(\cdot CF_2{\cdot}CF_2\cdot)_n$, with end groups derived from trifluoronitrosomethane. Two alternatives seemed possible : that the oil was similar to perfluoro-2-methyl-1 : 2-oxazetidine but contained a larger ring system ; or that it was an amine oxide. Both of these possibilities were favoured by the analytical data which indicated a 1 : 1 ratio of $CF_3{\cdot}NO : C_2F_4$. The formation of cyclic compounds was possible in the method used, *e.g.*,

$$2CF_3{\cdot}NO + 2C_2F_4 \longrightarrow CF_3{\cdot}N\begin{<}\begin{matrix}O{\cdot}CF_2{\cdot}CF_2\\ CF_2{\cdot}CF_2{\cdot}O\end{matrix}\end{>}N{\cdot}CF_3$$

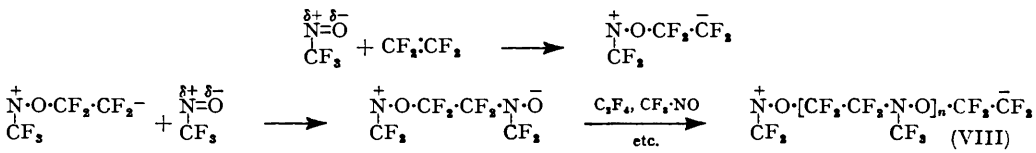
but this possibility is rejected, since compounds with 8-, 12-, or 16-membered rings would be appreciably volatile (cf. $C_{16}F_{34}$, b. p. 234°), whereas the oil has low volatility (decomposes *in vacuo* about 400° without distillation). A cyclic compound containing more than 20 atoms in the ring would therefore have to be postulated, and it would have to be formed without the concurrent formation of cyclic compounds containing smaller rings, since products intermediate in volatility between perfluoro-2-methyl-1 : 2-oxazetidine and the oil were not present ; this is unlikely. The second possibility was more probable, and was examined in detail. An amine oxide such as (VI) would explain the 1 : 1 ratio of $CF_3{\cdot}NO$ to C_2F_4 and the high b. p. could be attributed to the polar nature of the $\overset{+}{N}{-}\overset{-}{O}$ bonds ; this polarity would also make the nitrogen–oxygen infrared vibration tend towards that for

(VI) $\overset{-}{O}\!\!\begin{<}\begin{matrix}\overset{+}{N}(CF_3)\\ \overset{+}{N}(CF_3)\end{matrix}\end{>}\!\!\begin{matrix}CF_2{\cdot}CF_2\\ CF_2{\cdot}CF_2\end{matrix}\!\!\begin{>}\overset{-}{O}$ $\qquad$ $CF_3{\cdot}N\begin{<}\begin{matrix}CF_2{\cdot}CF_2\\ CF_2{\cdot}CF_2\end{matrix}\end{>}N{\cdot}CF_3$ (VII)

a nitrogen–oxygen single bond and towards that for hydrocarbon amine oxides (8—10·8 μ) so that it would appear in the same region as the carbon–fluorine vibrations, and

make assignment difficult. Attempts were made to reduce the oil to the perfluoro-amine (VII), since it can be predicted with certainty that this amine would be a liquid with about the same volatility as perfluorodimethyl*cyclo*hexane (b. p. 101°) and could be synthesised by fluorination of the corresponding unsubstituted compound. Zinc-dust distillation, sodium amalgam and methanol, zinc and hydrochloric acid, lithium aluminium hydride in ethyl ether, and distillation with sulphur were tried without success. The insolubility of the oil in common solvents rendered use of lithium aluminium hydride difficult. Perfluoromethyl*cyclo*hexane readily dissolves the oil, but even the use of mixtures of this with ethyl ether as solvents for lithium aluminium hydride and the oil failed to cause change in the latter.

A third possibility for the constitution of the oil was therefore considered, namely, that it was a polymer of type (VIII), formed by copolymerisation of tetrafluoroethylene and trifluoronitrosomethane by an ionic mechanism favoured by low temperatures :

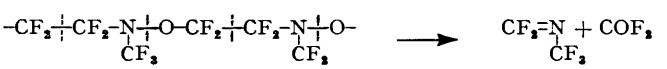


The formation of perfluoro-2-methyl-1 : 2-oxazetidine (I) from the intermediate $CF_3\cdot\overset{+}{N}\cdot O\cdot CF_2\cdot\overset{-}{C}F_2$ is also readily visualised. The facility of nucleophilic attack on tetrafluoroethylene and other polyfluoro-olefins is well established, and the above mechanism, and the fact that formation of the oil occurs preferentially at low temperatures when the reactants are in the liquid phase, are in accord with this. A polymer such as (VIII) thus contains alternate trifluoronitrosomethane and tetrafluoroethylene units, so that the analytical data agree with the empirical formula C_3ONF_7. Chain termination in the polymer might involve disproportionation reactions such as

Infrared spectroscopic examination shows that if the $\cdot CF{:}CF_2$ end group is present at all the molecular weight of the polymer must be high, since only slight absorption can be seen near the C:C stretching vibration region (5·6 μ). A high molecular weight would clearly allow end groups other than those postulated above to be present without marked effect on the analysis of the polymer.

Distinction between (VI) and (VIII) was made on the basis of molecular-weight determination in perfluoromethyl*cyclo*hexane, for which the ebullioscopic constant was determined as 13·0. The mean molecular weight was at least 7000 and possibly much higher [cf. (VI), $M = 398$], and the oil is thus clearly the polymer (VIII).

The polymer is unaffected by hot concentrated sulphuric acid or hot concentrated aqueous potassium hydroxide, but when heated *in vacuo* at 400° in absence of air it yields equimolar amounts of perfluoro(methylenemethylamine) and carbonyl fluoride quantitatively :



This reaction strongly supports the formulation of the polymer as above, and is analogous to the pyrolysis of perfluoro-2-methyl-1 : 2-oxazetidine. The formation of carbonyl fluoride by fission of a carbon–carbon bond in a system such as $CF_3\cdot CF_2\cdot CF_2\cdot O\cdot$ has been postulated recently to explain the rapid degradation of a fluorocarbon chain by photochemical oxidation (Francis and Haszeldine, *J.*, 1955, in the press). Degradation of a fluorocarbon chain containing oxygen by this reaction of carbonyl fluoride elimination will probably prove to be of general application.

Reaction of trifluoronitrosomethane with tetrafluoroethylene followed by pyrolysis

of both the products thus gives perfluoro(methylenemethylamine) quantitatively and extension of the reaction to longer-chain perfluoronitrosoalkanes provides the simplest general route to the compounds $CF_3{\cdot}[CF_2]_n{\cdot}N{:}CF_2$. The reactions of the perfluoro(alkylene-alkylamines), *e.g.*, their reaction with hydrogen fluoride to give bis(perfluoroalkyl)amines such as $(CF_3)_2NH$, will be described in subsequent papers.

Experimental

Preparation and Purification of Trifluoronitrosomethane.—The apparatus is shown in Fig. 1. Into a 20-l. Pyrex flask is fitted, *via* a B24 joint, a clear silica tube *A* sealed at the lower end. A 12″ Hanovia cold mercury lamp (200 v, 15 w), type SNC, which generates mainly 2537 Å radiation, fits loosely inside *A*, whose length is such that the lower end clears by 2—3″ a pool of mercury (400 ml.) inside the flask. The apparatus is evacuated and trifluoroiodomethane (41 g., 0·210 mole) is condensed into the small attached receiver *B*, then, with tap *C* closed, is allowed to expand into the flask. Tap *D* is closed and nitric oxide (12·7 g., 0·422 mole) is condensed into *B* and then allowed to expand into the flask *via D*, which is then closed; the small amount of nitric oxide remaining in *B* is neglected. The flask is mounted on a mechanical shaker which is agitated at such a rate (75 strokes/min.) that the mercury pool swirls up the sides of the flask as shown in Fig. 1, and can thus react readily with any dinitrogen tetroxide

Fig. 1.
Preparation of trifluoronitrosomethane.

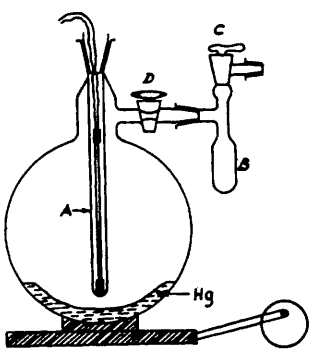
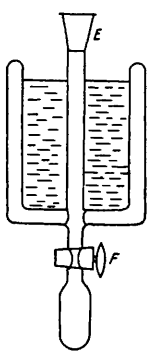


Fig. 2.
Purification of trifluoronitrosomethane.



produced. Irradiation of the gas mixture soon produces a blue colour, which reaches maximum intensity after 20—25 hr.; the surface of the mercury becomes covered with oxide film.

Oxygen is then let into the flask *via C* and *D* until the pressure is atmospheric, and the flask is set aside for 1 hr. to complete the oxidation of unchanged nitric oxide. The gases are slowly (2 hr.) pumped out through three traps cooled by liquid oxygen to separate condensable products from the excess of oxygen, etc., and are then fractionated twice *in vacuo* to remove unchanged trifluoroiodomethane. The trifluoronitrosomethane is freed from carbon dioxide by bubbling it twice through two wash-bottles containing 30% aqueous sodium hydroxide (*ca.* 20 min. per pass). Further fractionation *in vacuo* readily gives a product (Found : *M*, 99. Calc. for $CONF_3$: *M*, 99) contaminated by only traces of trifluoroiodomethane.

Further purification is effected when necessary by use of the apparatus (Fig. 2) constructed from two thick-walled beakers. With the B10 joint *E* attached to a vacuum system, liquid nitrogen is poured into the Dewar vessel to the height indicated and the receiver below tap *F* is cooled in liquid nitrogen. When trifluoronitrosomethane is passed slowly into the evacuated apparatus through *E*, it condenses on the walls and runs down through *F* into the cooled receiver, whereas impurities such as trifluoroiodomethane remain as solid in the centre tube. When drainage of the nitroso-compound has ceased (30 min.), tap *F* is closed, the liquid nitrogen is removed from the Dewar vessel, and the solid impurities, together with some occluded trifluoronitrosomethane, are pumped away through *E* as the temperature rises. The pure trifluoronitrosomethane is then transferred *via F* into the vacuum system and its purity is checked by its infrared spectrum. The ultraviolet spectrum of trifluoronitrosomethane shows only weak absorption in the region 250—300 mμ where trifluoroiodomethane absorbs heavily

(*J.*, 1953, 1764), and contamination with the latter is thus readily detected. The band at 266 mμ in the spectrum of the nitroso-compound reported earlier (*J.*, 1954, 912) is caused partly by trifluoroiodomethane.

In a typical experiment the yield of trifluoronitrosomethane is 85% (7·6 g.) based on the trifluoroiodomethane used (45%).

An Alternative to Mercury in the Preparation of Trifluoronitrosomethane.—Dinitrogen tetroxide reacts rapidly with trifluoronitrosomethane on irradiation (though only slowly in absence of light), and must thus be removed during the reaction of trifluoroiodomethane with nitric oxide. Mercury was used in the original synthesis (*J.*, 1953, 2075) and is still the best for this purpose, but acidified potassium iodide can be used instead, although it gives somewhat lower yields of trifluoronitrosomethane. The 20-l. reaction flask is charged with potassium iodide (200 g.), water (1 l.), and concentrated hydrochloric acid (200 ml.), then freed from air by pumping; trifluoroiodomethane (42·9 g., 0·219 mole) and nitric oxide (13·2 g., 0·438 mole) are then introduced and the flask is irradiated (63 hr.) without shaking. With this technique it was found best to use only the lower 2″ of the ultraviolet light, so that any dinitrogen tetroxide formed was near the surface of the liquid and reacted instantly with it. Fractionation gave unchanged trifluoroiodomethane (24·5 g., 0·125 mole, 57%), carbon dioxide (1·93 g., 0·044 mole), and trifluoronitrosomethane (4·36 g., 0·044 mole, 47%) as volatile products, identified by means of their molecular weights and infrared spectra.

Trifluoronitrosomethane reacts slowly with acidified potassium iodide solution: a sample of the gas (0·0214 g.) in contact with 0·5 ml. of acidified iodide solution (2 g. KI, 2 ml. conc. HCl, 10 ml. H_2O) in a sealed 5-ml. tube in the dark was completely decomposed only after 18 hr., and yielded carbon dioxide (0·17 mmole, 80%) as volatile product. The reaction was accelerated when gas and liquid were intimately mixed by vigorous shaking.

Stability of Trifluoronitrosomethane.—(*a*) Trifluoronitrosomethane stored as vapour in a clean bulb in the dark for 5 weeks failed to show change in properties, molecular weight (98·6. Calc. for $CONF_3$: *M*, 99), or infrared or ultraviolet spectrum. A specimen kept as liquid for several years had undergone <1% decomposition.

(*b*) Trifluoronitrosomethane (0·022 g., 0·223 mmole) and mercury (1 g.), shaken (4 days) in a sealed 5-ml. Pyrex tube covered with tinfoil to exclude light, showed no change in properties (CF_3·NO recovered: 0·022 g. Found: *M*, 98·6). Banus (*loc. cit.*), who reported that the nitroso-compound is completely decomposed in 20 hr. under these conditions, has considerably exaggerated the difficulties of working with perfluoroalkyl nitroso-compounds.

(*c*) The nitroso-compound (0·0215 g., 0·217 mmole) and water (0·5 ml.) were unchanged when shaken (2 days) in a sealed Pyrex tube in absence of light (CF_3·NO recovered: 0·0212 g.).

Trifluoronitrosomethane is completely stable in a vacuum system and can be stored as gas or as liquid with negligible decomposition for many months. Light, alkali, etc., bring about decomposition.

Reaction of Trifluoronitrosomethane with Tetrafluoroethylene.—In a typical low-temperature reaction, trifluoronitrosomethane (1·48 g., 0·015 mole) and tetrafluoroethylene (1·50 g., 0·015 mole) in an evacuated 85-ml. sealed silica tube were kept at −45° (1 hr.), then allowed to warm to room temperature during 24 hr., and finally kept at 20° for 5 days (probably excessive). Fractionation of the volatile products *in vacuo* gave unchanged reactants (8%) and *perfluoro-2-methyl-1 : 2-oxazetidine* (0·85 g., 28%), b. p. (isoteniscope) −6·8° (Found: C, 18·1; N, 7·2%; *M*, 199. C_3ONF_7 requires C, 18·1; N, 7·0%; *M*, 199). The reaction vessel contained an involatile colourless viscous oil (*ca.* 1·8 g., 64%) (see below) on the walls and at the bottom of the tube; the oil sometimes had a gel-like appearance.

In an experiment at room temperature, trifluoronitrosomethane (1·19 g., 0·012 mole) and tetrafluoroethylene (0·60 g., 0·006 mole) kept in a sealed 85-ml. silica tube (14 hr.) gave unchanged tetrafluoroethylene (0·23 g., 37%), unchanged trifluoronitrosomethane (0·82 g., 69%), perfluoro-2-methyl-1 : 2-oxazetidine (0·45 g., 62%), and the oil (0·29 g., 38%). Reaction at a higher temperature thus favours production of the oxazetidine. Other experiments have given similar results.

Properties of Perfluoro-2-methyl-1 : 2-oxazetidine.—This compound is a colourless gas showing only general absorption in the ultra-violet (ε at λ 260, 250, 240, 230, and 220 mμ = 2, 5, 11·5, 24, and 51).

(a) *Stability to aqueous reagents.* Perfluoro-2-methyl-1 : 2-oxazetidine (0·078 g.) and water (0·5 ml.), heated in a sealed 5-ml. Pyrex tube at 155° (14 hr.), gave only unchanged starting material (0·076 g., 97%). When the oxazetidine (0·098 g.) and 10% aqueous sodium hydroxide (1 ml.) were heated in a sealed 5-ml. tube at 110° (14 hr.), 96% (0·094 g.) was recovered

unchanged. Almost quantitative (97%) recovery of the oxazetidine was obtained when it (0·048 g.) and concentrated hydrochloric acid (0·5 ml.) were shaken at room temperature (10 days).

(b) *Irradiation.* Pure perfluoro-2-methyl-1 : 2-oxazetidine showed no signs of decomposition after exposure to ultraviolet radiation (mainly 2537 Å) for 3 days.

(c) *Reaction with hydrogen chloride.* The oxazetidine (0·050 g.) and anhydrous hydrogen chloride (0·018 g.) underwent no reaction at 100° (24 hr.) in a 5-ml. sealed tube.

Perfluoro(methylenemethylamine).—(a) *Preparation from perfluoro-2-methyl-1 : 2-oxazetidine.* The oxazetidine (0·320 g., 1·65 mmoles) was passed at 5 mm. pressure in absence of air through a silica tube (15 mm. internal diam.) heated at 550° over a length of 30 cm., and the reaction products were condensed in a trap cooled by liquid oxygen. Fractionation *in vacuo* gave carbonyl fluoride (0·108 g., 1·63 mmoles) (Found : *M*, 66. Calc. for COF_2 : *M*, 66) and *perfluoro(methylenemethylamine)* (0·217 g., 1·63 mmoles), b. p. (isoteniscope) −33·7° (Found : C, 18·3; N, 10·4%; *M*, 133. C_2NF_5 requires C, 18·1; N, 10·5%; *M*, 133). The carbonyl fluoride was identified by means of its infrared spectrum. Perfluoro(methylenemethylamine) shows only very weak general absorption in the ultraviolet. The oxazetidine has been pyrolysed to perfluoro(methylenemethylamine) on a larger scale in essentially quantitative yield.

(b) *Hydrolysis.* Perfluoro(methylenemethylamine) (0·102 g., 0·77 mmole) and water (0·5 ml., 0·03 mole) were sealed in a 10-ml. Pyrex tube in absence of air and kept at 20° (12 hr.). Fractionation of the volatile products *in vacuo* gave only carbon dioxide (0·067 g., 1·52 mmoles) (Found : *M*, 44. Calc. for CO_2 : *M*, 44). The aqueous solution gave a positive test for fluoride and ammonium ions.

In a second experiment perfluoro(methylenemethylamine) (0·067 g., 0·50 mmole) in a sealed 5-ml. ampoule was inserted in a 3-l. flask which was then evacuated. Water vapour (0·037 g., 2·0 mmoles) was then introduced into the flask; in this volume all the water is in the vapour phase. The tip of the perfluoro(methylenemethylamine) tube was next broken to allow the fluorine compound and the water vapour to mix rapidly. After 24 hr. at 20° the volatile contents of the flask were fractionated *in vacuo* to give unchanged perfluoro(methylenemethylamine) (0·043 g., 0·32 mmole, 64%) identified by its molecular weight and infrared spectrum, silicon tetrafluoride, a small amount of carbon dioxide, and an unknown compound. The N–H band near 3 μ could not be detected in any fraction from the distillation.

The unknown material obtained in the above and several other hydrolysis reactions is volatile (b. p. $< -25°$) and is characterised by infrared absorption at 4·33, 4·38 (doublet), 6·83, and 8·61, 8·65 μ (doublet). The first doublet is readily distinguished from the band of carbon dioxide which appears in this region (4·30 μ), and appears in material which is free from carbon dioxide. The unknown is also produced during the reaction of perfluoro(methylenemethylamine) with silica at 210° (75 hr.), but on the present scale cannot be separated from the silicon tetrafluoride which accompanies it. It is decomposed by aqueous bases.

In a further experiment perfluoro(methylenemethylamine) (0·0350 g.) and 5% aqueous sodium hydroxide (2 ml.), kept at 20° (2 hr.) in a sealed tube, gave fluoride (Found : 70·9, 70·9. Calc. for C_2NF_5 : F, 71·2%), determined as fluorosilicate by thorium nitrate titration. Determination of the fluoride produced by aqueous hydrolysis of perfluoro(methylenemethylamine) gave low results (*e.g.*, Found : F, 67%), since hydrogen fluoride was lost from the aqueous solution during manipulation.

(c) *Reaction with methanol.* Perfluoro(methylenemethylamine) (0·497 g., 3·74 mmoles) and anhydrous methanol (0·960 g., 30 mmoles), sealed in a Pyrex tube *in vacuo*, then warmed to room temperature, reacted exothermally (5 min.). After 40 hr., the volatile products were transferred to a vacuum system and fractionated to give unchanged methanol, dimethyl ether (0·185 g., 4 mmoles; some ether was lost by the method of separation used), and dimethyl carbonate (0·570 g., 6·35 mmoles). The methyl ether, dimethyl carbonate (80% of theory for complete alcoholysis), and ammonium fluorosilicate produced during the reaction were identified by means of their infrared spectra.

Investigation of the Polymer produced from Trifluoronitrosomethane and Tetrafluoroethylene.—The oil referred to above was analysed [Found : C, 18·2; N, 6·9. $(C_3ONF_7)_n$ requires C, 18·1; N, 7·0%]; its ultraviolet spectrum, recorded for a thin film on silica plates, shows only weak general absorption. The oil is substantially insoluble in ether, carbon tetrachloride, chloroform, acetone, benzene, ethanol, light petroleum, trifluoroacetic acid, methyl heptafluorobutyrate, and benzotrifluoride, but readily soluble in perfluoromethyl*cyclo*hexane.

(a) *Behaviour with acid or alkali.* A specimen of the polymer heated with concentrated sulphuric acid failed to undergo reaction. No change could be detected when a sample was heated under reflux with 50% aqueous potassium hydroxide.

(b) *Attempted reduction.* The following methods of reduction were tried: (i) The oil (0·20 g.), intimately mixed with zinc powder then treated with concentrated hydrochloric acid, showed no change even on heating. (ii) The oil (0·20 g.) failed to react with 80% formic acid (2 ml.) in a sealed tube at 110° (24 hr.). (iii) A paste of sodium amalgam and the oil was treated with "AnalaR" methanol under reflux, and, in a separate experiment, with water under reflux. The oil remained unchanged, and products containing fluorine [*e.g.*, (VII), predicted b. p. *ca.* 100°] were not detected. (iv) Zinc-dust distillation of the oil caused only a sudden vigorous decomposition at high temperatures to breakdown products such as carbon dioxide. (v) Lithium aluminium hydride (0·2 g.) in diethyl ether (15 ml.) was without effect on the oil (0·300 g.) during 12 hr. at reflux temperature. The experiment was repeated with perfluoromethyl*cyclo*hexane–ethyl ether as solvent. To the oil (0·80 g.) in perfluoromethyl*cyclo*hexane (15 ml., pretreated with lithium aluminium hydride in ether) was quickly added 0·5M-lithium aluminium hydride in ethyl ether (60 ml.), and the mixture stirred (3 hr.). Hydrolysis, distillation, etc., gave only recovered solvent with no indication of products such as (VII); the oil was recovered unchanged. (vi) An intimate mixture of the oil (0·100 g.) and sulphur (*ca.* 5 g.) was heated at 200° (30 min.) without change. When it was heated with a free flame decomposition occurred, and examination of the volatile products collected in a cooled trap showed them to be carbonyl fluoride and perfluoro(methylenemethylamine) produced by pyrolysis of the oil. No indication of reduction products was obtained.

(c) *Pyrolysis.* In a typical experiment, the polymer (1·56 g.) was placed in a silica tube (25 mm. internal diam.), closed at one end, and with the other end connected, through a trap cooled by liquid oxygen, to an oil-pump. The closed end of the tube was slowly inserted in a horizontal tube furnace (400°) so that the polymer was pyrolysed during a total period of 1 hr. Pyrolysis occurred without charring and without formation of non-condensable gas. The pyrolysate consisted of unchanged polymer (0·15 g.) and volatile products, distillation of which gave carbonyl fluoride (0·472 g., 7·17 mmoles) (Found: *M*, 66. Calc. for COF_2: *M*, 66) and perfluoro(methylenemethylamine) (0·930 g., 7·01 mmoles, 99%) (Found: *M*, 133. Calc. for C_2NF_5: *M*, 133). The products were identified spectroscopically.

(d) *Molecular weight.* An ebullioscopic method with a Cottrell-type apparatus was used with a glycol–water-cooled condenser at −5°. Perfluoromethyl*cyclo*hexane (b. p. 75·8°, d_D^{25} 1·79) was a suitable solvent, and its ebullioscopic constant was determined by use of perfluorohexadecane (Found: C, 23·1; H, 0. Calc. for $C_{16}F_{34}$: C, 23·1; H, 0%) and of perfluoro-1 : 2-di*cyclo*hexylethane (Found: C, 25·2; H, 0. Calc. for $C_{14}F_{26}$: C, 25·3; H, 0%). Spectroscopically pure perfluorohexadecane (1·325 g.), dissolved in perfluoromethyl*cyclo*hexane (50·0 ml.), caused an elevation in b. p. of 0·23°, whence $K = 13·1$. A second determination gave 12·9. Perfluoro-1 : 2-di*cyclo*hexylethane (0·1263 g.), dissolved in perfluoromethyl*cyclo*hexane (5·0 ml.), caused an elevation in b. p. of 0·27°, whence $K = 12·8$; a second determination using 0·1323 g. of the solid gave an elevation of 0·29°, whence $K = 13·1$.

The polymer from trifluoronitrosomethane and tetrafluoroethylene (0·580 g.), dissolved in 50·0 ml. of perfluoromethyl*cyclo*hexane, caused no detectable change in the b. p. of the pure solvent. A b. p. elevation of 0·01° would have been detected, and would correspond to a molecular weight of 7000. The molecular weight of the polymer is thus >7000. A duplicate experiment gave the same result.

For comparison, a short-chain polymer of chlorotrifluoroethylene was used. This had CF_3 or CF_2Cl end-groups, and analysis (Found: C, 19·8, 19·8; H, 0%) indicates $CF_2Cl{\cdot}[CF_2{\cdot}CFCl]_5{\cdot}CF_2{\cdot}CF_2Cl$ (Calc.: C, 19·5%; *M*, 800) or $CF_3{\cdot}[CF_2{\cdot}CFCl]_5{\cdot}CF_2{\cdot}CF_2Cl$ (Calc.: C, 19·9%; *M*, 784). A b. p. elevation of 0·39° was observed when this polymer (2·055 g.) was dissolved in perfluoromethyl*cyclo*hexane (50·0 ml.), whence $M = 765$, in reasonable agreement with the molecular weight of *ca.* 790 deduced from b. p. and analysis. The ebullioscopic method using a fluorocarbon solvent is thus easily sufficiently sensitive to distinguish between compounds (VI) (*M*, 398) and (VIII), and the oil obtained from the reaction of trifluoronitrosomethane and tetrafluoroethylene must thus be a polymer (VIII).

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