# 458. *Perfluoroalkyl Derivatives of Nitrogen. Part XV.*[1] *The Reaction of Trifluoronitrosomethane with Trifluoroethylene, Vinylidene Fluoride, Vinyl Fluoride, and Ethylene*

By R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis

Trifluoronitrosomethane reacts readily with trifluoroethylene to yield an oxazetidine, which is predominantly (99%) $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CHF{\cdot}C}F_2$, and a tough, rubbery, 1 : 1 copolymer that contains structural units of type $-N(CF_3){\cdot}O{\cdot}CHF{\cdot}CF_2-$ and $-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CHF-$. With vinylidene fluoride, the nitroso-compound yields an oily 1 : 1 (approx.) copolymer considered to be $[-N(CF_3){\cdot}O{\cdot}CH_2{\cdot}CF_2-]_n$, which readily eliminates hydrogen fluoride. Ethylene and vinyl fluoride react only slowly with trifluoronitrosomethane, to give an elastomeric 1 : 1 (approx.) copolymer and an unidentified solid, respectively.

Trifluoronitrosomethane reacts readily at 5—10 atm. pressure with tetrafluoroethylene, chlorotrifluoroethylene, or 1,1-dichlorodifluoroethylene to yield an oxazetidine and a 1 : 1 copolymer;[2] the polymer predominates in reactions carried out at 20°, while the oxazetidine is the major product at 100°. Hexafluoropropene is reluctant to react with trifluoronitrosomethane, but at 100°/30 atm. a mixture of oxazetidine and 1 : 1 copolymer is obtained in which the latter predominates.[2] The structures of the products have been deduced from the identities of the perfluoro(alkylenealkylamines) and carbonyl halides that are produced in essentially quantitative yields by pyrolysis.

| Olefin | Oxazetidine | Copolymer |
|---|---|---|
| $CF_2{:}CF_2$ | $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CF_2{\cdot}C}F_2$ | $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF_2-]_n$ |
| $CF_2{:}CFCl$ | $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CFCl{\cdot}C}F_2$ | $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CFCl-]_n$ predominantly,<br>plus $[-N(CF_3){\cdot}O{\cdot}CFCl{\cdot}CF_2-]_n$ |
| $CF_2{:}CCl_2$ | $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CCl_2{\cdot}C}F_2$ | $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CCl_2-]_n$ predominantly,<br>plus $[-N(CF_3){\cdot}O{\cdot}CCl_2{\cdot}CF_2-]_n$ |
| $CF_2{:}CF{\cdot}CF_3$ | $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CF(CF_3){\cdot}C}F_2$ (90%) | $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF(CF_3)-]_n$ (90%) |
| | $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CF_2{\cdot}C}F{\cdot}CF_3$ (10%) | $[-N(CF_3){\cdot}O{\cdot}CF(CF_3){\cdot}CF_2-]_n$ (10%) |

An interesting feature of the reactions involving unsymmetrical olefins is that the direction of addition of the $N{:}O$ group of trifluoronitrosomethane to a $C{:}C$ bond in oxazetidine formation is opposite to that involved in formation of the predominant copolymer. This can be explained by postulating that copolymerisation occurs by a free-radical mechanism, and that oxazetidine is produced by either a free-radical or molecular process preceded by formation of a 1 : 1 complex of nitroso-compound with olefin.[2]

The reactions between trifluoronitrosomethane and the olefins $CF_2{:}CHF$, $CF_2{:}CH_2$, $CHF{:}CH_2$, and $CH_2{:}CH_2$ have now been studied in order to determine the effect of progressive increase in vinylic hydrogen content.

*Reaction of Trifluoronitrosomethane with Trifluoroethylene.*—Trifluoronitrosomethane reacted with an equimolar amount of trifluoroethylene at 100°/7 atm. to give an oxazetidine and a 1 : 1 copolymer in 90 and 10% yield, respectively; at 20° the respective yields of these two products were 26 and 74%, in keeping with the effect of increase in temperature on product distribution found with other fluoro-olefins.

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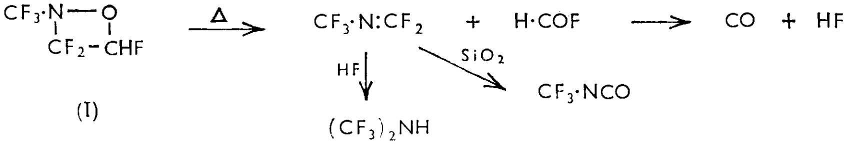
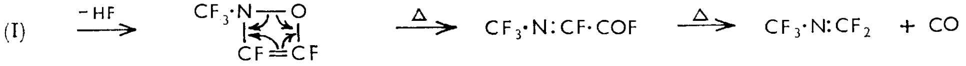
[1] Part XIV, Dinwoodie and Haszeldine, *J.*, 1965, 2266.

[2] Barr, Haszeldine, and Willis, *J.*, 1961, 1351.

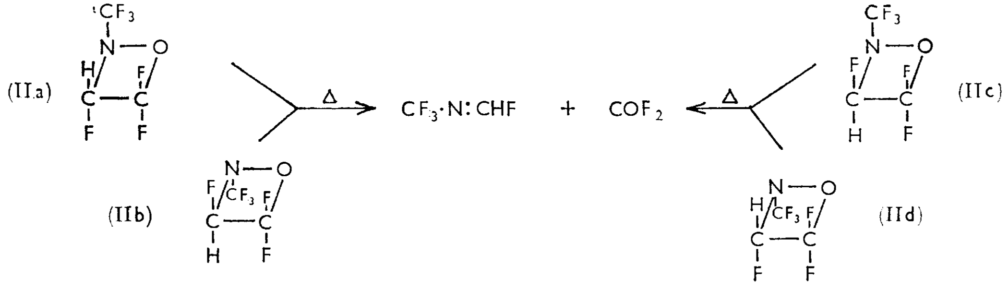
The oxazetidine was separated by gas chromatography into three components that comprised (in order of increasing retention time) 0·5, 99·0, and 0·5%, respectively, of the total material; each component had formula $C_3HF_6NO$ and showed infrared absorption at 7·09, 7·14, and 7·38 μ, respectively, characteristic of polyfluoro-oxazetidines.[2] Pyrolysis at 500°/3 mm. of the major component (b. p. 28·0°) gave carbon monoxide, perfluoro-(methylenemethylamine), bistrifluoromethylamine, and trifluoromethyl isocyanate; carbonyl fluoride was not detected. Structure (I) may thus be assigned:



No evidence was found for thermal dehydrofluorination of (I) before ring fission:



Insufficient of the two minor components of the oxazetidine fraction was available for pyrolysis, but thermal degradation of the original mixture of compounds of formula $C_3HF_6NO$ gave the products obtained from pure (I), together with carbonyl fluoride in 1% molar yield and traces of unknown compounds. The carbonyl fluoride suggests that 1% of the oxazetidine $CF_3\cdot\overline{N\cdot O\cdot CF_2\cdot C}HF$ (II) was present in the mixture as *cis*- and *trans*-isomers, each of which may exist in enantiomorphic forms.



(+)- and (—)-forms of *cis*-isomer

(+)- and (—)-forms of *trans*-isomer

Since n.m.r. studies[3] have revealed that at ambient temperatures rapid Walden inversion occurs at the nitrogen atom of a polyfluoro-oxazetidine, and such inversion would lead to establishment of the equilibria (IIa) $\rightleftharpoons$ (IId) and (IIb) $\rightleftharpoons$ (IIc), the two minor components of the oxazetidine fraction may be mixtures of (IIa) with (IId), and (IIb) with (IIc), respectively. However, isomer (I) for which the same geometrical considerations apply, could not be separated into two components by gas chromatography, although it gave a very broad peak. Clearly, no definite conclusion can be reached regarding the identities of the two minor components: it seems highly unlikely that geometrical forms of isomer (II), can be separated by gas chromatography and not of isomer (I), and, in either case, such separation would mean that optical antipodes had been resolved; the 1% yield of carbonyl fluoride from pyrolysis of the total oxazetidine fraction may be fortuitous. It could be that only one of the minor components is an oxazetidine $CF_3\cdot\overline{N\cdot O\cdot CF_2\cdot C}HF$, and the other a structural isomer [possibly the unknown nitrone $CF_3\cdot\overset{+}{N}(\overset{-}{O})\colon CH\cdot CF_3$] that yields carbonyl

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[3] Lee and Orrell, results to be submitted for publication in *Trans. Faraday Soc.*

fluoride on pyrolysis; although both have infrared spectra containing the characteristic polyfluoro-oxazetidine band near 7 μ.

Examination of the original fraction by $^{19}F$ and $^{1}H$ n.m.r. spectroscopy [3] revealed the presence of only isomer (I); at −79° the rate of inversion at the nitrogen was arrested sufficiently to allow resolution of the $^{19}F$ spectrum into components due to the presence of *cis-* and *trans*-forms of the oxazetidine. No spectroscopic distinction exists for enantiomorphs.

Purity of monomers is vital, and the use of reaction temperatures in the range  20° to +20° is desirable, if an elastomeric solid and not an oil or a gel is to be obtained from copolymerisation of trifluoronitrosomethane with tetrafluoroethylene.[2] By contrast, a tough opaque elastomer can be made from trifluoronitrosomethane and trifluoroethylene at 0—20° without difficulty, and even when prepared at 100°, the 1 : 1 copolymer is still an elastomer and not an oil.

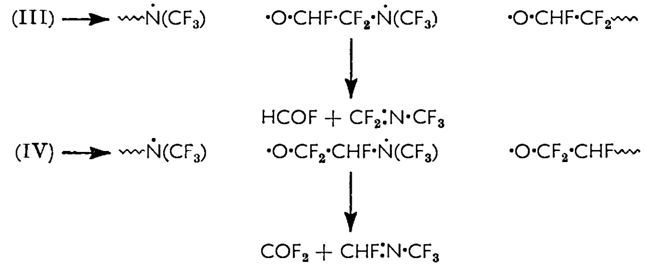
$$-N(CF_3)\cdot O\cdot CHF\cdot CF_2- \quad \text{(III)} \qquad\qquad -N(CF_3)\cdot O\cdot CF_2\cdot CHF- \quad \text{(IV)}$$

If the free-radical mechanism suggested earlier [2] for the copolymerisation of trifluoronitrosomethane with fluoro-olefins is correct, the copolymer of trifluoronitrosomethane with trifluoroethylene should contain both structural units (III) and (IV), with the former predominating, since radical attack on trifluoroethylene occurs preferentially on the CHF group in all the reactions reported,[4-6] except in the reaction with dibromodifluoromethane in the presence of t-butyl perbenzoate [5] (see annexed Scheme).

$$CF_2{:}CHF \xrightarrow{\text{HBr, u.v.}} CHF_2\cdot CHFBr\ (58\%) + CF_2Br\cdot CH_2F\ (42\%)$$
$$CF_2{:}CHF \xrightarrow{CF_3I,\ \text{u.v.}} CF_3\cdot CHF\cdot CF_2I\ (80\%) + CF_3\cdot CF_2\cdot CHFI\ (20\%)$$
$$CF_2{:}CHF \xrightarrow{CFCl_2I,\ Bz_2O_2} CFCl_2\cdot CHF\cdot CF_2I\ * + CFCl_2\cdot CF_2\cdot CHFI$$
$$CF_2{:}CHF \xrightarrow{CF_2Br_2,\ Bz_2O_2,\ 100^\circ} CF_2Br\cdot CHF\cdot CF_2Br\ (70\%) + CF_2Br\cdot CF_2\cdot CHFBr\ (30\%)$$
$$CF_2{:}CHF \xrightarrow{CF_2Br_2,\ PhCO_3Bu^t,\ 120^\circ} CF_2Br\cdot CHF\cdot CF_2Br\ (50\%) + CF_2Br\cdot CF_2\cdot CHFBr\ (50\%)$$
$$CF_2{:}CHF \xrightarrow{CH_3\cdot SH,\ \text{X-ray}} CH_3\cdot S\cdot CHF\cdot CHF_2\ (75\%) + CH_3\cdot S\cdot CF_2\cdot CH_2F\ (25\%)$$
$$CF_2{:}CHF \xrightarrow{CF_3\cdot SH,\ \text{u.v.}} CF_3\cdot S\cdot CHF\cdot CHF_2\ (98\%) + CH_3\cdot S\cdot CF_2\cdot CH_2F\ (2\%)$$
$$CF_2{:}CHF \xrightarrow{SiHCl_3,\ \text{u.v.}} Cl_3Si\cdot CHF\cdot CHF_2\ (99\%) + Cl_3Si\cdot CF_2\cdot CH_2F\ (1\%)$$
$$CF_2{:}CHF \xrightarrow{SF_5Cl,\ Bz_2O_2} SF_5\cdot CHF\cdot CF_2Cl\ (100\%)$$

* Said [6] to be the predominant product but no supporting figures given.

If pyrolytic breakdown of the copolymer occurred by N–O fission followed by elimination of an acyl or carbonyl fluoride from the polyhalogenoalkoxy-radical thus produced, the ratio of perfluoro(methylenemethylamine) to carbonyl fluoride formed should equal the ratio of (III) to (IV):



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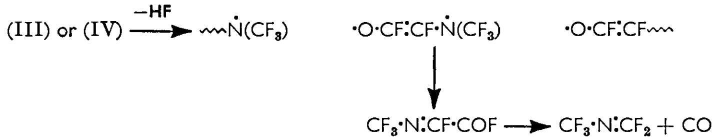
[4] Haszeldine and Steele, *J.*, 1957, 2800; Harris and Stacey, *J. Amer. Chem. Soc.*, 1961, **83**, 841; Haszeldine and Young, *J.*, 1960, 4503; Case, Ray, and Roberts, *ibid.*, 1961, 2070.

[5] Coseia, *J. Org. Chem.*, 1961, **26**, 2995.

[6] Fried and Miller, *J. Amer. Chem. Soc.*, 1959, **81**, 2078.

Pyrolysis of the copolymer gave the compounds CO (by decomposition of formyl fluoride), $COF_2$, $CF_3\cdot N:CF_2$, $(CF_3)_2NH$ (by reaction of HF with $CF_3\cdot N:CF_2$), possibly $CF_3\cdot N:CHF$ and, by reaction of the last compound with hydrogen fluoride, $(CF_3)(CHF_2)NH$. Although consistent with the presence of units both of (III) and (IV), it was not possible to obtain an accurate quantitative analysis for the content of these in the copolymer, since carbonisation occurred during pyrolysis and the pyrolysate soon reacted further with the glass of the traps to liberate carbon monoxide and carbonyl fluoride. The ratio $[CF_3\cdot N:CF_2 + (CF_3)_2NH]:COF_2$ in pyrolysate that was immediately analysed was 1·2 : 1, implying the same value for the ratio of (III) : (IV), but this figure could be much in error, particularly since elimination of hydrogen fluoride from $-CHF\cdot CF_2-$ units in the polymer before N–O fission would give $CF_3\cdot N:CF_2$ from both (III) and (IV):



*Reaction of Trifluoronitrosomethane with Vinylidene Fluoride.*—In complete contrast to tetrafluoroethylene and trifluoroethylene, vinylidene fluoride failed to react with trifluoronitrosomethane at 20—100°/10 atm., and even at 150°/46 atm. a tan-coloured, oily 1 : 1 copolymer was obtained in only 18% yield. Distillation of this product was accompanied by decomposition to yield a colourless mobile liquid and a solid brown residue, both of which showed infrared absorption at 5·98 $\mu$ characteristic of compounds containing a $\cdot CH:CF\cdot$ group, and had analyses consistent with the elimination of 25% of the hydrogen of the original 1 : 1 copolymer as hydrogen fluoride. In view of this it was not expected that pyrolysis of the polymer would yield precise information regarding structure. This proved to be the case: pyrolysis afforded carbon and a complex mixture containing the products HCN, CO, $COF_2$, $C_2F_6$, $CF_3\cdot N:CF_2$, $(CF_3)_2NH$, $CF_3\cdot NCO$, $SiF_4$, and at least six unknown compounds. The predicted structure of the polymer is $[-N(CF_3)\cdot O\cdot CH_2\cdot CF_2-]_n$, since radical attack on vinylidene fluoride occurs exclusively on the $CH_2$ group,[7] and the products found are consistent with this structure.

The reaction between trifluoronitrosomethane and vinylidene fluoride at 150° failed to yield an oxazetidine, and only the compounds $CF_3\cdot CH_3$ (from reaction of HF with $CH_2:CF_2$), $CF_3\cdot NO_2$, and $CF_3\cdot\overset{+}{N}(\bar{O}):N\cdot CF_3$ (from disproportionation of $CF_3\cdot NO$ in the presence of carbon),[8] $(CF_3)_2NH$ (from reaction of HF with $CF_3\cdot N:CF_2$),[9] and $CF_3\cdot N:N\cdot CF_3$ (from the pyrolytic decomposition of $CF_3\cdot NO$ [10]) were present.

In an attempt to minimise the decomposition of trifluoronitrosomethane and to increase the yield of the copolymer, the reaction between the nitroso-compound and vinylidene fluoride was repeated at 100°/46 atm. over a period of 17 weeks (the reaction at 150° took 5 weeks). A 62% yield of a tan-coloured oil was obtained which was analytically and spectroscopically identical with the olefinic oil obtained by distillation of the 1 : 1 copolymer obtained at 150°. A possible structure for this product is $[-N(CF_3)\cdot O\cdot CH_2\cdot CF_2\cdot N(CF_3)\cdot O\cdot CH:CF-]_n$, although it is not implied that loss of hydrogen fluoride has occurred regularly from alternate repeating units. Slow elimination of hydrogen fluoride from the 1 : 1 copolymer probably occurs during the long reaction period. The yield of 1,1,1-trifluoroethane also obtained accounted almost entirely for the amount of free hydrogen fluoride expected, and the other products arose from self-decomposition of trifluoronitrosomethane. No oxazetidine was found among the products.

*Reaction of Trifluoronitrosomethane with Vinyl Fluoride.*—An equimolar mixture of

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[7] Haszeldine and Steele, *J.*, 1954, 923.

[8] Haszeldine and Jander, *J.*, 1954, 919.

[9] Barr and Haszeldine, *J.*, 1955, 2532; Young, Tsoukalas, and Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

[10] Banks, Barlow, Haszeldine, McCreath, and Sutcliffe, unpublished results.

trifluoronitrosomethane and vinyl fluoride was recovered unchanged after being kept in the dark at 20°/10 atm. for almost 2 years; an attempt to force a reaction at 20° and high pressure gave a brown viscous liquid, which evolved acid fumes and solidified to a black solid on contact with glass. In a reaction at 100° and low pressure, the reactants were converted during 6 months into a brown involatile solid (46%), which did not correspond to a 1 : 1 copolymer on analysis, and a mixture of nitrogen and the compounds $CF_3{\cdot}NO_2$, $CF_3{\cdot}N{:}N{\cdot}CF_3$, $CF_3{\cdot}\overset{+}{N}(\overset{-}{O}){:}N{\cdot}CF_3$, $SiF_4$, and $CO_2$. Pyrolysis of the solid yielded a mixture of the compounds HCN, CO, $CO_2$, $CF_3{\cdot}NCO$, $(CF_3)_2NH$, and $SiF_4$ (from the glass traps), leaving a residue of carbon, and no deductions can be made concerning structure.

*Reaction of Trifluoronitrosomethane with Ethylene.*—Trifluoronitrosomethane was found to react very slowly with ethylene at temperatures in the range 20—100° at low pressure (<10 atm.), but in one experiment a mixture of the reactants at *ca.* 0° and 40 atm. exploded violently, causing severe damage to an autoclave. In a low-pressure reaction at 20°, 80% of the reactants were recovered after 22 months, and a 75% net yield of a transparent elastomeric gum was obtained which analytical evidence suggested was the 1 : 1 copolymer $[\text{-}N(CF_3){\cdot}O{\cdot}CH_2{\cdot}CH_2\text{-}]_n$. A similar reaction at 100° yielded, during 6 months, decomposition products of trifluoronitrosomethane and a 57% yield (based on 41% of reactants converted) of a brown solid of unknown structure, which was shown by analysis to contain $CF_3{\cdot}NO$ and $C_2H_4$ residues combined in the approximate ratio of 2 : 1.

*General Comments.*—The formation of an oxazetidine and a 1 : 1 copolymer from trifluoronitrosomethane occurs most readily with the olefins $CF_2{:}CF_2$, $CF_2{:}CHF$, $CF_2{:}CFCl$, and $CF_2{:}CCl_2$, and less readily with perfluoro-olefins containing more than two carbon atoms, or with ethylenes containing two or more vinylic hydrogens. Chlorotrifluoroethylene and trifluoroethylene yield elastomers more readily than the perfluoro-olefins $C_2F_4$ and $C_3F_6$ and although presence of hydrogen introduces thermal instability, the polymer becomes much more readily soluble in common organic solvents and hence more convenient for technological study.

## EXPERIMENTAL

Trifluoroethylene, vinylidene fluoride, vinyl fluoride, and ethylene were commercial samples treated by standard procedures to yield material of spectroscopic and chromatographic purity.

Low-pressure reactions (<10 atm.) were carried out in sealed, evacuated, Dreadnought tubes; high-pressure reactions (>10 atm.) were carried out in stainless steel autoclaves fitted with bursting discs and pressure gauges.

Volatile reaction products were distilled *in vacuo* or at atmospheric pressure, and analysed by infrared spectroscopy and by gas–liquid chromatography (8 m. long × 5 mm. i.d. Pyrex column in the form of a folded W packed with a 30% w/w mixture of Kel-F No. 1 oil and 80—100 mesh Celite, and operated at room temperature with a nitrogen flow-rate of 26 ml./min.).

*Reaction of Trifluoronitrosomethane with Trifluoroethylene.*—The nitroso-compound (4·11 g., 41·5 mmole) and trifluoroethylene (3·40 g., 41·5 mmole), sealed in a 300-ml. Dreadnought tube and heated at 100° for 65 hr., gave (i) unchanged reactants (4%), (ii) a 99 : 1 mixture of 3,3,4-*trifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine* and 3,4,4-*trifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine* (6·55 g., 36·2 mmole; 90% based on $CF_3{\cdot}NO$ converted) (Found: C, 19·8; H, 0·5; N, 7·5%; *M*, 182. $C_3HF_6NO$ requires C, 19·9; H, 0·6; N, 7·7%; *M*, 181), and (iii) a sticky elastomeric colourless *copolymer* $[\text{-}N(CF_3){\cdot}O{\cdot}C_2HF_3\text{-}]_n$ (0·7 g.; 10% based on $CF_3{\cdot}NO$ consumed) (Found: C, 19·9; H, 0·5; N, 7·8%. $C_3HF_6NO$ requires C, 19·9; H, 0·6; N, 7·7%).

A similar reaction mixture kept at 20° for 16 days yielded only 5% of the oxazetidine mixture and mainly a tough, white, elastomeric 1 : 1 copolymer (74% based on $CF_3{\cdot}NO$ converted) of trifluoronitrosomethane with trifluoroethylene (Found: C, 20·0; H, 0·5; N, 7·8%. Calc. for $C_3HF_6NO$: C, 19·9; H, 0·6; N, 7·7%).

*Pyrolysis of the* 99 : 1 *Mixture of the Oxazetidines* $CF_3\overline{N{\cdot}O{\cdot}CHF{\cdot}CF_2}$ *and* $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CF_2{\cdot}CHF}$.—The oxazetidine mixture (1·16 g., 6·41 mmole) was passed at 3 mm. pressure (contact time 1 min.) through a platinum tube (100 cm. long × 1 cm. i.d.) heated electrically to 430° over 55 cm. of its length. Air was vigorously excluded. Carbon monoxide (1·74 mmole., 0·049 g.) was collected in a charcoal-filled trap at −196°, while the other products, carbonyl fluoride (0·09 mmole., 1%), perfluoro(methylenemethylamine) (0·72 g., 5·41 mmole), bistrifluoromethylamine (0·14 g., 0·92 mmole) and unidentified material were collected in a glass trap cooled to −196°.

*Separation of the* 99 : 1 *Mixture of* $CF_3\cdot N\cdot O\cdot CHF\cdot CF_2$ *and* $CF_3\cdot N\cdot O\cdot CF_2\cdot CHF$.—The oxazetidine mixture was separated by large-scale gas–liquid chromatography (8 m. × 1 cm. i.d. column packed with 30% w/w of Kel-F No. 1 oil on Celite) into three components with chromatogram peak area ratios, in order of retention time, 0·5 : 99 : 0·5; since the compounds were isomers it was assumed that the response of the thermistor detector was the same for each of them.

| Compound | % of total | Analysis (%) [a] C | H | N | $M$ [a] | $\log_{10} p$ (mm.) [b] | B. p. calc. | Trouton const. | Ring vibrn. |
|---|---|---|---|---|---|---|---|---|---|
| $CF_3\cdot N\cdot O\cdot CF_2\cdot CHF$ ... | 0·5 | 20·1 | 0·5 | 7·5 | 178 | $6{\cdot}56 - \frac{1060}{T}$ | 15·1° | 16·8 | 7·09 |
| $CF_3\cdot N\cdot O\cdot CHF\cdot CF_2$ ... | 99 | 20·1 | 0·6 | 7·7 | 181 | $7{\cdot}81 - \frac{1483}{T}$ | 28·0 | 22·5 | 7·14 |
| $CF_3\cdot N\cdot O\cdot CF_2\cdot CHF$ ... | 0·5 | 20·1 | 0·7 | * | 181 | * | * | * | 7·38 |

[a] Calc. for $C_3HF_6NO$: C, 19·9; H, 0·6; N, 7·7%; $M$, 181. [b] Isoteniscope.

* Insufficient material available.

*Pyrolysis of* 3,3,4-*Trifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine*.—Pyrolysis of the oxazetidine (0·25 g., 1·38 mmole) at 500°/3 mm. (contact time 1 min.) in the platinum tube described above gave carbon monoxide (0·035 g., 1·25 mmole; 14%), perfluoro(methylenemethylamine) (0·04 g., 0·30 mmole), bistrifluoromethylamine (0·15 g., 0·98 mmole), trifluoromethyl isocyanate (0·02 g., 0·18 mmole), and silicon tetrafluoride. No carbonyl fluoride was detected.

*Pyrolysis of the* 1 : 1 *Copolymer of Trifluoronitrosomethane with Trifluoroethylene*.—Weighed samples of the copolymer contained in a platinum boat were placed near the closed end of a 100 cm. × 1 cm. i.d. platinum tube; the other end of the tube was connected *via* three traps cooled to −196°, the last one of which was filled with activated charcoal, to a vacuum system. The platinum tube was fitted with two electric furnaces; the first, 10 cm. long, was placed so that the platinum boat was at its centre; the second, 60 cm. long, was placed immediately adjacent to the first.

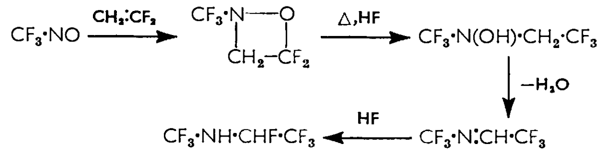
(a) *Pyrolysis at* 570°/3 mm. The copolymer (1·087 g.), pyrolysed at 570°/3 mm. during 10 min., left no residue in the platinum boat, and gave carbon monoxide (0·03 g., 1·07 mmole; 3% yield) and condensable material (0·966 g., 10·09 mmole; 89%), which was fractionated immediately to yield (i) carbonyl fluoride (0·27 g., 4·16 mmole), (ii) hexafluoroethane (0·01 g., 0·08 mmole), (iii) perfluoro(methylenemethylamine) (0·024 g., 0·18 mmole), and (iv) a mixture of perfluoro(methylenemethylamine) (0·24 g., 1·87 mmole), bistrifluoromethylamine (0·42 g., 2·78 mmole), and at least two unidentified compounds. The infrared spectrum of fraction (iv) contained bands at 3·29 and 5·8 μ attributed to the compound $CF_3\cdot N{:}CHF$.

Fraction (iv) decomposed after storage in glass for 4 days to yield carbon monoxide (0·043 g., 1·53 mmole), carbonyl fluoride (0·026 g., 0·39 mmole), silicon tetrafluoride (0·085 g., 0·82 mmole), perfluoro(methylenemethylamine), trifluoromethyl isocyanate (trace), and several unidentified compounds.

(b) *Pyrolysis at* 640°/3 *mm*. Pyrolysis of the copolymer (0·802 g.) gave carbon monoxide and a condensable product, which when stored (4 days in glass) decomposed to yield a further quantity of carbon monoxide (total CO formed = 0·054 g., 1·92 mmole), carbonyl fluoride (0·21 g., 3·15 mmole), perfluoro(methylenemethylamine) (0·16 g., 1·21 mmole), bistrifluoromethylamine (0·003 g., 0·02 mmole), trifluoromethyl isocyanate (0·013 g., 0·12 mmole), traces of carbon dioxide and hexafluoroethane, silicon tetrafluoride, and several unidentified compounds (*ca.* 1·39 mmole) which, on infrared evidence, might have contained N:C, C:C, COF, and >NH groups. The oxygen recovered as carbon monoxide and carbonyl fluoride was in excess of that present in the copolymer sample by 14%, implying that reaction of the pyrolysate had occurred with glass vessels to form products containing oxygen from the glass.

*Reaction of Trifluoronitrosomethane with Vinylidene Fluoride*.—(*a*) The nitroso-compound (0·60 g., 6·06 mmole) and vinylidene fluoride (0·43 g., 6·72 mmole) failed to react in a sealed 50-ml. Dreadnought tube at 70° during 1 week, and only small amounts of decomposition products arising from the nitroso-compound were produced.

(*b*) Trifluoronitrosomethane (20·64 g., 0·2086 mole) and vinylidene fluoride (13·36 g., 0·2087 mole), heated in a 100-ml. evacuated stainless steel autoclave at 100° for 17 weeks, gave 1,1,1-trifluoroethane (5·18 g., 61·7 mmole), trifluoronitrosomethane (2·82 g., 24·48 mmole), bistrifluoromethylamine (0·19 g., 1·26 mmole), hexafluoroazoxymethane (0·30 g., 1·63 mmole), hexafluoroazomethane, carbonyl fluoride, carbon dioxide, silicon tetrafluoride, and a *compound* (0·24 g., 1·3 mmole) (Found: C, 19·7; H, 0·8; N, 7·8%; *M*, 181. $C_3H_2F_7N$ requires C, 19·5; H, 1·1; N, 7·6%; *M*, 185), b. p. 24·2° (isoteniscope), which showed characteristic absorption in the infrared at 2·89 and 6·56 μ. The last compound may have been $(CF_3)(CF_3{\cdot}CHF)NH$ formed *via* an unstable oxazetidine:



An involatile tan-coloured oil (21·1 g.; 62%) recovered from the autoclave exhibited absorption in the infrared at 3·3 and 5·97 μ assigned to a $>C{:}CH-$ group; the elemental composition of the *oil* is consistent with the average structure $[-N(CF_3){\cdot}O{\cdot}CH_2{\cdot}CF_2{\cdot}N(CF_3){\cdot}O{\cdot}CH{:}CF-]_n$ (Found: C, 23·7; H, 0·9; F, 55·0%. $C_6H_3F_9N_2O_2$ requires C, 25·2; H, 0·7; F, 53·1%).

(*c*) A mixture of trifluoronitrosomethane (8·03 g., 0·811 mole) and vinylidene fluoride (5·74 g., 0·897 mole), heated at 150° (initial pressure 46 atm.) for 5 weeks, gave vinylidene fluoride (0·18 g., 2·86 mole), 1,1,1-trifluoroethane, trifluoronitromethane, bistrifluoromethylamine, hexafluoroazoxymethane, hexafluoroazomethane, carbonyl fluoride, silicon tetrafluoride, and an unknown, complex, liquid mixture (3·8 g.), boiling range 65—110°. An involatile tan-coloured oil (2·5 g., 18%) recovered from the autoclave had analysis close to that expected for a 1 : 1 *copolymer* of trifluoronitrosomethane with vinylidene fluoride (Found: C, 22·4; H, 1·3; N, 10·0. $C_3H_2F_5NO$ requires C, 22·1; H, 1·2; N, 8·6%). Vacuum distillation of this 1 : 1 copolymer gave hydrogen fluoride, a colourless oil, b. p. 50—60°/*ca.* 1 mm. (Found: C, 23·4; H, 0·8; N, 10·2%), and a brown solid (Found: C, 25·1; H, 0·9; N, 11·9%) as distillation residue.

*Pyrolysis of the* 1 : 1 *Copolymer from Trifluoronitrosomethane and Vinylidene Fluoride.*—The copolymer (1·54 g., 9·4 mmole) pyrolysed during 20 min. at 550°/3 mm. by the technique described earlier, gave carbon monoxide (0·057 g., 2·05 mmole; 4%), perfluoro(methylenemethylamine) (0·67 g., 0·50 mmole), bistrifluoromethylamine (0·06 g., 0·41 mmole), carbonyl fluoride (0·22 g., 3·26 mmole), hexafluoroethane (trace), hydrogen cyanide (trace), silicon tetrafluoride, and at least six unknown compounds (1·29 mmole). A residue of carbon was left in the platinum boat.

*Reaction of Trifluoronitrosomethane with Vinyl Fluoride.*—(a) *At* 20°/ca. 10 *atm.* A mixture of trifluoronitrosomethane (7·78 g., 78·6 mmole) and vinyl fluoride (3·35 g., 72·8 mmole), sealed in a 300-ml. Dreadnought tube and kept at 20° in the dark for 23 months, gave an equimolar mixture of unchanged reactants (10·93 g., 152 mmole), trifluoronitromethane, and hexafluoroazoxymethane.

(b) *At* 100°/ca. 10 *atm.* Trifluoronitrosomethane (4·30 g., 43·50 mmole) and vinyl fluoride (1·90 g., 41·30 mmole), sealed in a 300-ml. Dreadnought tube and kept at 100° in the dark for 6 months, gave unchanged starting materials contaminated with silicon tetrafluoride (3·81 g. 56·0 mmole), nitrogen (0·05 g., 1·88 mmole), trifluoronitromethane (0·75 g., 6·52 mmole), hexafluoroazomethane (0·32 g., 1·91 mmole), hexafluoroazoxymethane (0·11 g., 0·63 mmole), bistrifluoromethylamine (0·057 g., 0·37 mmole), carbon dioxide (trace), silicon tetrafluoride, four unidentified products, and a brown solid (1·09 g., 46% based on reactants consumed) of meaningless empirical formula ($C_{12}H_{21}F_{23}N_8O_{19}$) (Found: C, 13·8; H, 2·1; F, 42·9; N, 10·5%).

(c) *At* 20°/28 *atm.* Trifluoronitrosomethane (4·07 g., 41·2 mmole) and vinyl fluoride (1·94 g., 42·2 mmole) were kept in a 30-ml. stainless steel autoclave at 20° for 10 days; the pressure remained constant at 28 atm. The volatile products were fractionated and shown by infrared spectroscopy and gas-liquid chromatography to contain trifluoronitrosomethane (2·04 g., 20·59 mmole), vinyl fluoride (1·41 g., 30·76 mmole), trifluoronitromethane (0·29 g., 2·56 mmole) hexafluoroazoxymethane (0·50 g., 2·73 mmole), silicon tetrafluoride, and unidentified material (0·11 g., 0·71 mmole. Found: *M*, 154). The last product liberated hydrogen fluoride on exposure to air, and was destroyed when passed into gas-chromatography columns. A brown, viscous, involatile liquid (1·65 g., 65% based on reactants consumed) recovered from the autoclave liberated hydrogen fluoride when stored in glass and solidified to a black mass.

*Pyrolysis of the Solid formed from Trifluoronitrosomethane and Vinyl Fluoride at* 100°/10 *atm.*—The solid (0·181 g.), pyrolysed at 610°/3 mm. during 10 min., gave a residue of carbon (0·039 g., 22% based on solid pyrolysed), carbon monoxide (0·012 g., 0·41 mmole; 7%), bistrifluoromethylamine, trifluoromethyl isocyanate, carbon dioxide, hydrogen cyanide, and silicon tetrafluoride (by reaction of the pyrolysate with glass).

*Reaction of Trifluoronitrosomethane with Ethylene.*—(a) *At* 20°. Trifluoronitrosomethane (8·31 g., 83·9 mmole) and ethylene (2·35 g., 83·9 mmole), sealed in a 300-ml. Dreadnought tube and kept at 20° (initial pressure *ca.* 7 atm.), in the dark for 22 months, gave trifluoronitrosomethane (6·06 g., 61·25 mmole; 45%), ethylene (2·02 g., 72·1 mmole; 53%), trifluoronitromethane (0·46 g., 4·03 mmole), hexafluoroazomethane, hexafluoroazoxymethane (0·18 g., 0·99 mole), perfluoro(methylenemethylamine), and a colourless, elastomeric, *ca.* 1 : 1 *copolymer*, $[-N(CF_3)\cdot O\cdot CH_2\cdot CH_2-]_n$ (1·96 g., 75% based on reactants converted) (Found: C, 25·6; H, 2·1; N, 11·2%. $C_3H_4F_3NO$ requires C, 28·3; H, 3·1; N, 11·0%).

(b) *At* 100°. Trifluoronitrosomethane (3·93 g., 39·7 mmole) and ethylene (1·15 g., 41·1 mmole), sealed in a 300-ml. Dreadnought tube and kept at 100° (initial pressure *ca.* 8 atm.) in the dark for 6 months, gave nitrogen (0·027 g., 0·98 mmole), silicon tetrafluoride, bistrifluoromethylamine, unchanged reactants, trifluoronitromethane (0·90 g., 7·86 mmole), hexafluoroazomethane (0·56 g., 3·40 mmole), hexafluoroazoxymethane (0·05 g., 0·30 mmole), and a brown *solid* (1·6 g., 57% based on reactants consumed) (Found: C, 19·6; H, 2·2; N, 13·2. $C_4H_4F_6N_2O_2$ requires C, 21·2; H, 1·8; N, 12·4%).

*Warning.*—Trifluoronitrosomethane (4·89 g., 49·4 mmole) and ethylene (0·14 g., 50·0 mmole) were condensed into a 35-ml. stainless steel autoclave at −196°. When the autoclave had warmed to about room temperature (the pressure was 40 atm.), the contents detonated with such violence that the pressure gauge (Bourdon tube) was completely wrecked, despite the presence of a bursting disc designed to rupture at 150 atm.; the experiment was not repeated.

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