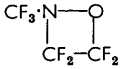
# **260.** *Perfluoroalkyl Derivatives of Nitrogen. Part IX.* The Reaction of Trifluoronitrosomethane with Some Unsymmetrical Olefins.*†

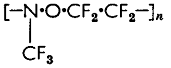
By D. A. Barr, R. N. Haszeldine, and C. J. Willis.

Trifluoronitrosomethane reacts with an olefin $CF_2{:}CXY$ ($CF_2{:}CFCl$, $CF_2{:}CCl_2$, $CF_2{:}CF\cdot CF_3$) to give an oxazetidine $CF_3\cdot N\cdot O\cdot CXY\cdot CF_2$ and a viscous or elastomeric 1 : 1 copolymer $[\cdot N(CF_3)\cdot O\cdot CF_2\cdot CXY\cdot]_n$. The direction of addition to the olefin in formation of oxazetidine is opposite to that involved in copolymer formation. Pyrolysis of oxazetidine and of polymer yields compounds such as $CF_3\cdot N{:}CF_2$, $CF_3\cdot N{:}CF\cdot CF_3$, $CF_3\cdot N{:}CFCl$, and $CF_3\cdot N{:}CCl_2$; initial cleavage of the N–O bond in oxazetidine or polymer is followed by degradation of the polyhalogeno-alkoxy-radical by acyl halide formation. The elastomer from tetrafluoroethylene and trifluoronitrosomethane, the first reported with the –N–O–C–C– backbone, retains its flexibility at −30°. Reaction schemes are advanced for the formation of 1 : 1 copolymer by a low-temperature free-radical process, and for oxazetidine formation involving an initial 1 : 1 molecular complex of the Diels–Alder type. Trifluoronitrosomethane is considered as a free-radical source through its rapid reaction with nitric oxide, even at temperatures below −100°, to give ultimately the compounds $CF_3\cdot NO_2$, $(CF_3)_2N\cdot O\cdot NO$, and $CO_2$.

Trifluoronitrosomethane reacts readily with tetrafluoroethylene to give two products,[1] an oxazetidine (I) and a 1 : 1 copolymer (II); the polymer predominates in reactions

(I)





(II)

at room temperature, and the oxazetidine at higher temperatures (*ca.* 100°). When pyrolysed, each of these compounds gives, quantitatively, an equimolar mixture of perfluoro(methylenemethylamine), $CF_3\cdot N{:}CF_2$, and carbonyl fluoride. Both radical and ionic intermediates could explain the effects of varying reaction conditions, with the former slightly favoured.[1]

The reaction of trifluoronitrosomethane with some unsymmetrical fluoro-olefins has now been studied in order to throw further light on the mechanism of formation of the unusual compounds (I) and (II). The olefins $CF_2{:}CXY$, where (i) X = F, Y = Cl, (ii) X = Y = Cl, and (iii) X = F, Y = $CF_3$, all yield an oxazetidine and a 1 : 1 copolymer.[2] In each case two structures are clearly possible for the oxazetidine and for the polymer,

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

depending on the direction of addition of trifluoronitrosomethane to the olefin. This direction of addition has been established by pyrolysis and identification of the products.

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* Part VIII, Griffin and Haszeldine, *J.*, 1960, 1398.

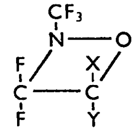
† Presented at the American Chemical Society, Atlantic City, 1956, Abs. 13M; Symposium on Fluorine Chemistry, Birmingham, 1959; see also *Proc. Chem. Soc.*, 1959, 230.

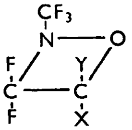
[1] Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

[2] Barr, Haszeldine, and Willis, *Proc. Chem. Soc.*, 1959, 230.

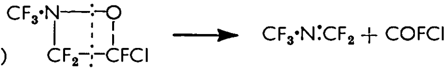
The results are summarised in the annexed Table, from which two notable features emerge: (i) the direction of addition is specific both for the formation of oxazetidine ($\overline{CF_3{\cdot}N{\cdot}O{\cdot}CFX{\cdot}CF_2}$) and for formation of the copolymer ($[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY-]_n$), and (ii) the direction of addition involved in formation of the oxazetidine is opposite to that involved in formation of the copolymer.

Whether the oxazetidine $CF_3{\cdot}\overline{N{\cdot}O{\cdot}CXY{\cdot}CF_2}$ is capable of existence in two forms (as shown) has yet to be determined.





Chlorotrifluoroethylene reacted with trifluoronitrosomethane under the mild conditions previously used for tetrafluoroethylene, *i.e.*, in sealed glass or silica tubes under 5—10 atm. pressure and in absence of light or air; formation of the oxazetidine was favoured at 70°, and at 20° the 1 : 1 copolymer predominated. Pyrolysis of the oxazetidine at 550° gave only equimolar amounts of the compounds $CF_3{\cdot}N{:}CF_2$ and COFCl, thus suggesting structure (III) rather than (IV):

(III)


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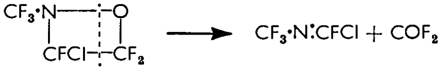
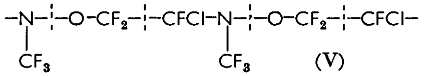
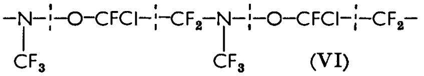


By contrast, pyrolysis of the polymer gave equimolar amounts of the compounds $CF_3{\cdot}N{:}CFCl$ and $COF_2$, with only traces of the compound $CF_3{\cdot}N{:}CF_2$; structure (V) thus predominates considerably over (VI).

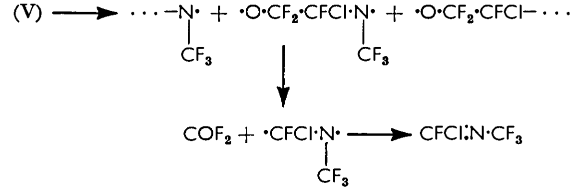


$-N(CF_3)-O-CF_2-CFCl-N(CF_3)-O-CF_2-CFCl-$ (V)

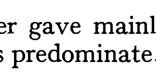


$-N(CF_3)-O-CFCl-CF_2-N(CF_3)-O-CFCl-CF_2-$ (VI)

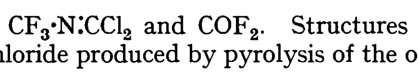
Breakdown of oxazetidine and polymer is believed to be initiated by N–O cleavage, followed by elimination of carbonyl halide from the polyhalogeno-alkoxy-radical[1,3] so produced, *e.g.*:



1,1-Dichlorodifluoroethylene reacted with trifluoronitrosomethane under similar conditions. The oxazetidine yielded the compounds $CF_3{\cdot}N{:}CF_2$ and $COCl_2$ on pyrolysis, whereas



(VII)



$-N(CF_3)-O-CF_2-CCl_2-N(CF_3)-O-CF_2-CCl_2-$ (VIII)

the polymer gave mainly the compounds $CF_3{\cdot}N{:}CCl_2$ and $COF_2$. Structures (VII) and (VIII) thus predominate. The carbonyl chloride produced by pyrolysis of the oxazetidine dissociated to some extent into carbon monoxide and chlorine. Cleavage of compound

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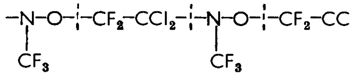
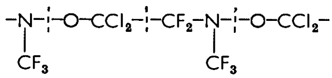
[3] Francis and Haszeldine, *J.*, 1955, 2151; Haszeldine and Nyman, *J.*, 1959, 387, 420, 1084.

(VII) in the other direction also occurred to a very small extent, to give the original reactants $CF_3{\cdot}NO$ and $CF_2{:}CCl_2$. The last two compounds were also formed, to an extent of 5—10%, by pyrolysis of the polymer, revealing an alternative breakdown route:



$$-\underset{CF_3}{\underset{|}{N}}-O-\vdots-CF_2-CCl_2-\vdots-\underset{CF_3}{\underset{|}{N}}-O-\vdots-CF_2-CCl_2-$$

Although the copolymer has mainly structure (VIII), some of the copolymer (IX) is present, since its pyrolysis products $CF_3{\cdot}N{:}CF_2$ and $COCl_2$ were detected. An alternative,[3] though less likely, explanation is that the polymer is in fact entirely of structure (VIII),



$$-\underset{CF_3}{\underset{|}{N}}-\vdots-O-CCl_2-\vdots-CF_2-\underset{CF_3}{\underset{|}{N}}-\vdots-O-CCl_2-\vdots-CF_2-$$

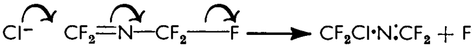
(IX)

and the pyrolysis by-products $CF_3{\cdot}N{:}CF_2$ and $COCl_2$ result from formation of the original reactants $CF_3{\cdot}NO$ and $CF_2{:}CCl_2$ which, under the pyrolysis conditions, react to give the oxazetidine (VII), breakdown of which would give $CF_3{\cdot}N{:}CF_2$ and $COCl_2$.

The compound $CF_3{\cdot}N{:}CCl_2$ was identical with that obtained by reaction of the compound $CF_3{\cdot}N{:}CF_2$ with an equimolar amount of anhydrous hydrogen chloride. The overall reaction may be represented:

$$3CF_3{\cdot}N{:}CF_2 + 2HCl \longrightarrow CF_3{\cdot}N{:}CCl_2 + 2(CF_3)_2NH$$

Much unchanged hydrogen chloride was recovered, but only traces of the compound $CF_3{\cdot}N{:}CF_2$ remained, and the compound $CF_3{\cdot}N{:}CFCl$ was only a minor ultimate product. The amine $CF_3{\cdot}NH{\cdot}CF_2Cl$ is probably the initial product, formed by a relatively slow addition, followed by rapid loss of hydrogen fluoride to give $CF_3{\cdot}N{:}CFCl$. It was known[4] that hydrogen fluoride forms the amine $(CF_3)_2NH$ from the compound $CF_3{\cdot}N{:}CF_2$ at higher temperatures, and the present result revealed that the high temperature previously employed was unnecessary; this was confirmed experimentally, since anhydrous hydrogen fluoride and perfluoro(methylenemethylamine) react rapidly and quantitatively at room temperature to give bistrifluoromethylamine. The compound $CF_3{\cdot}N{:}CFCl$ also reacts with anhydrous hydrogen chloride, but the amine $CF_3{\cdot}NH{\cdot}CFCl_2$ again loses hydrogen fluoride, to give the compound $CF_3{\cdot}N{:}CCl_2$. The reaction of the last compound with hydrogen chloride at room temperature is very slow. Loss of hydrogen fluoride from the amine $CF_3{\cdot}NH{\cdot}CF_2Cl$ or $CF_3{\cdot}NH{\cdot}CFCl_2$ does not involve the fluorine of the $CF_3$ group, since the compounds $CF_2Cl{\cdot}N{:}CF_2$ and $CFCl_2{\cdot}N{:}CF_2$ were not ultimate products, although the possibility that they were formed initially:



$$Cl^- \quad CF_2{=}N{-}CF_2{-}F \longrightarrow CF_2Cl{\cdot}N{:}CF_2 + F^-$$

and underwent rapid rearrangement of the allylic type:

$$CF_2Cl{\cdot}N{:}CF_2 \rightleftharpoons CFCl{:}N{\cdot}CF_3$$

cannot be excluded completely.

As expected, the $N{:}CF_2$ stretching vibration is markedly affected by replacement of fluorine by chlorine: $CF_3{\cdot}N{:}CF_2$ 5·53, $CF_3{\cdot}N{:}CFCl$ 5·74, $CF_3{\cdot}N{:}CCl_2$ 5·99 μ.

Examination was made of the possibility of the reactions,

$$CF_3{\cdot}N{:}CF_2 + COCl_2 \rightleftharpoons CF_3{\cdot}N{:}CFCl + COFCl \rightleftharpoons CF_3{\cdot}N{:}CCl_2 + COF_2$$

occurring at the high temperatures used in the pyrolyses, since such exchange reactions would vitiate structural assignments based on the pyrolysis products actually isolated; under the conditions used, the pairs of compounds $CF_3{\cdot}N{:}CF_2 + COCl_2$, $CF_3{\cdot}N{:}CFCl$ +

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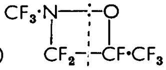
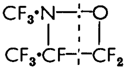
[4] Barr and Haszeldine, *J.*, 1955, 2532.

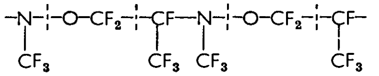
$COF_2$, or $CF_3{\cdot}N{:}CCl_2 + COF_2$ failed to react to give even traces of products resulting from an exchange reaction.

Hexafluoropropene failed to react with trifluoronitrosomethane under the conditions used for the other olefins; but at higher pressures and 100° reaction occurred, to give both oxazetidine and a 1 : 1 copolymer; the use of temperatures much above 100° is precluded

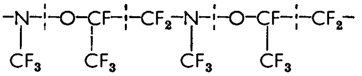
(X) 

 (XI)

by the self-decomposition of trifluoronitrosomethane. Pyrolysis of the oxazetidine gave the compounds $CF_3{\cdot}N{:}CF_2$ and $CF_3{\cdot}COF$ arising from (X) in 90% yield. The other possible oxazetidine (XI) was a minor constituent (10%) as measured by the amounts of the compounds $CF_3{\cdot}N{:}CF{\cdot}CF_3$ and $COF_2$ produced. The extent of these alternative modes of addition was reversed in the 1 : 1 copolymer, which yielded compounds $CF_3{\cdot}N{:}CF{\cdot}CF_3$ and $COF_2$ (90%) from (XII), and compounds $CF_3{\cdot}N{:}CF_2$ and $CF_3{\cdot}COF$ (10%) from (XIII).

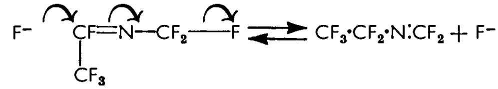


(XII)

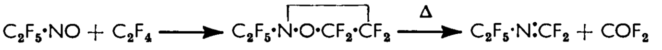


(XIII)

Perfluoro(ethylidenemethylamine) is the first compound of type $R_FN{:}CFR_F$ to be prepared unambiguously. The possibility that isomerisation by rearrangement of the allylic type might have occurred during pyrolysis:

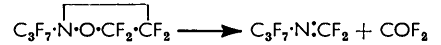


was eliminated by synthesis of its isomer as follows:



$$C_2F_5{\cdot}NO + C_2F_4 \longrightarrow C_2F_5{\cdot}N{\cdot}O{\cdot}CF_2{\cdot}CF_2 \xrightarrow{\Delta} C_2F_5{\cdot}N{:}CF_2 + COF_2$$

It can be safely assumed that no rearrangement will occur during the pyrolysis to give perfluoro(methylene-ethylamine), since the analogous reaction



$$C_3F_7{\cdot}N{\cdot}O{\cdot}CF_2{\cdot}CF_2 \longrightarrow C_3F_7{\cdot}N{:}CF_2 + COF_2$$

has been investigated[1] and the identity of the product confirmed by its hydrolysis to pentafluoropropionic acid. The isomers differ appreciably in infrared spectrum (*e.g.*, cf. C:N stretching vibrations: $CF_3{\cdot}N{:}CF_2$ 5·53; $C_2F_5{\cdot}N{:}CF_2$ 5·52; $C_3F_7{\cdot}N{:}CF_2$ 5·51; $CF_3{\cdot}N{:}CF{\cdot}CF_3$ 5·60 μ) and in boiling point ($C_2F_5{\cdot}N{:}CF_2$ −6°; $CF_3{\cdot}N{:}CF{\cdot}CF_3$ −15°).

It was suggested earlier[1] that the compound of b. p. 12·3° reported as perfluoro-(methylene-n-propylamine) $C_3F_7{\cdot}N{:}CF_2$ from pyrolysis of perfluorotripropylamine was in fact perfluoro(ethylidene-ethylamine) $C_2F_5{\cdot}N{:}CF{\cdot}CF_3$, or a mixture containing it, since the compound $C_3F_7{\cdot}N{:}CF_2$ of proved structure boiled at 25·6°. The new evidence supports this suggestion, and it is clear that a compound of type $R_FN{:}CF_2$ has a boiling point higher than that of its isomer $R'_FN{:}CFR''_F$.

*Elastomer Formation from Trifluoronitrosomethane and Tetrafluoroethylene.*—The first copolymer obtained from trifluoronitrosomethane and tetrafluoroethylene[1] was a viscous liquid, of molecular weight $\gg$7000 as far as could be determined ebullioscopically with perfluoromethylcyclohexane as solvent. Later samples were weak elastomers with gel-like appearance,[1] and the factors that affect formation of oil or of elastomer were therefore examined, particularly since dichlorodifluoroethylene also gave weak elastomers, whereas trifluoroethylene gave a strong elastomer[2] very readily. The main factors involved in formation of the elastomer $[-N(CF_3)\cdot O\cdot CF_2\cdot CF_2-]_n$ are purity of reactants, reactant ratio, and reaction temperature and pressure; proper control of these leads to polymer of greater chain length and to the transition from viscous oil to elastomer.

Purity of the reactants is vital. Trifluoronitrosomethane needs to be free from trifluoroiodomethane, trifluoronitromethane, dinitrogen tetroxide, and nitric oxide. Each of these can stop the growth of a polymer radical—by abstraction by the radical of iodine from trifluoroiodomethane, by addition of the radical to the $CF_2\cdot NO_2$ group, or by direct combination of the radical with the radical $NO_2$ or NO. Air or moisture, which decompose the nitroso-compound, must be excluded. The fluoro-olefin must be pure and free from peroxides. Use of a molar reactant ratio close to 1 : 1 gives the best results, and in this the copolymerisation resembles polycondensations. Finally, a temperature in the region $-20°$ to $+20°$, and conveniently 0°, leads to rapid combination of trifluoronitrosomethane and tetrafluoroethylene to give an elastomer. Use of a low temperature favours formation of polymer rather than oxazetidine, but is important in at least two other aspects: (*a*) provided that the pressure is high enough the reaction takes place mainly in the liquid phase; and (*b*) self-decomposition of trifluoronitrosomethane is minimised. As shown below, the self-decomposition of trifluoronitrosomethane yields, amongst other products, dinitrogen tetroxide and trifluoronitromethane, and these markedly affect the chain length of the polymer.

It is also possible to convert a viscous 1 : 1 copolymer of trifluoronitrosomethane and tetrafluoroethylene into an elastomer by heating the oil *in vacuo* at 50—150°; apparently polymer chains break and re-form under this ageing treatment, with possibly a small amount of cross-linking. The polymer system shows similarities to silicone or polyester polymers in this respect.

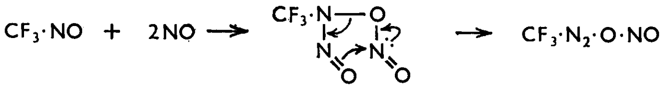
The elastomer from tetrafluoroethylene is a white translucent material reminiscent of a silicone rubber. It is the first to be reported with the $-N-O-C-C-$ backbone, has good thermal stability at 200° in presence of air, and is apparently unaffected over long periods at 180°. Pyrolysis at 550° yields equimolar amounts of the compounds $CF_3\cdot N\colon CF_2$ and $COF_2$ as reported earlier.[1] The new elastomer is of particular interest in two respects which should make it of value in a number of applications. It remains flexible at $-30°$, indicating that rotation of the chain about the N–O bond, and the size of the trifluoromethyl side-chain, effectively prevent crystallisation; by contrast polytetrafluoroethylene is highly crystalline. The elastomer is also insoluble in the common solvents, as is the shorter-chain oily polymer,[1] but dissolves in perfluoromethylcyclohexane, although less readily than the oily polymer. Solvent and chemical resistance are thus extremely good.

| | | | |
|---|---|---|---|
| $[\eta]$ | 1·0—2·0 | Tensile strength | 500 p.s.i. |
| Gehman $T_{10}$ | $-45°$ | Elongation at break | 500—1000% at 25° |
| $T_g$ | $-54°$ | | |

Other properties of the polymer are summarised in the annexed Table. Precise calculation of the molecular weight of the polymer from the equation $[\eta] = KM^{\alpha}$ cannot be carried out, since the value of $K$, the constant depending on the solvent, is not known for the fluorocarbon solvent used ($C_7F_{14}$), and $\alpha$ has not been determined for other fluoropolymers. However, $\alpha$ usually lies between 0·6 and 0·8 for linear flexible molecules, and is 0·65 for polydimethylsiloxane (a polymer not unlike the trifluoronitrosomethane–tetrafluoroethylene copolymer) in toluene solution ($K = 2{\cdot}0 \times 10^{-4}$). An approximate molecular weight for the elastomeric copolymer of 500,000—1,500,000 is obtained by assuming $K \approx 2{\cdot}0 \times 10^{-4}$ and $\alpha = 0{\cdot}65$.

*Reaction of Trifluoronitrosomethane with Nitric Oxide.*—Pure trifluoronitrosomethane reacts very rapidly with liquid nitric oxide at temperatures well below $-100°$, and yields nitrogen, trifluoronitromethane, *O*-nitrosobistrifluoromethylhydroxylamine, $(CF_3)_2N\cdot O\cdot NO$, silicon tetrafluoride, and carbon dioxide. These can arise by the annexed scheme. Addition of two molecules of nitric oxide to the nitroso-group is followed by formation of the diazonium nitrate, which decomposes to nitrogen and dinitrogen tetroxide with formation of a $CF_3$ radical. A similar scheme has been used to interpret the reaction of nitric oxide with tetrafluoroethylene to give the compound $NO_2{\cdot}CF_2{\cdot}CF_2{\cdot}NO$.[6]

The same products are formed, though much more slowly, when trifluoronitrosomethane reacts with nitric oxide in the vapour phase; the slowness of the reaction is revealed by the fact that the nitroso-compound is prepared in 80% yield by the photochemical vapour-phase reaction of trifluoroiodomethane with an excess of nitric oxide.



$$CF_3{\cdot}N_2{\cdot}O{\cdot}NO_2 \longrightarrow CF_3{\cdot} + N_2 + {\cdot}O{\cdot}NO_2 \xrightarrow{NO} N_2O_4 \longrightarrow 2NO_2$$

$$CF_3{\cdot} + NO \longrightarrow CF_3{\cdot}NO \xrightarrow{2NO} \text{Cycle repeats}$$

$$CF_3{\cdot} + NO_2 \longrightarrow CF_3{\cdot}NO_2 + CF_3{\cdot}O{\cdot}NO \longrightarrow NO + CF_3{\cdot}O{\cdot} \xrightarrow{\text{Glass}} CO_2 + SiF_4$$

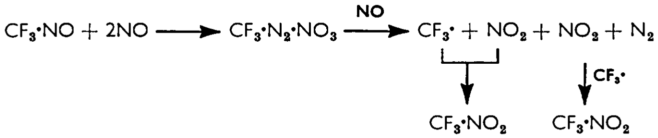
$$CF_3{\cdot} + CF_3{\cdot}NO \longrightarrow (CF_3)_2N{\cdot}O{\cdot} \xrightarrow{NO} (CF_3)_2N{\cdot}O{\cdot}NO$$

The formation of nitric oxide from trifluoronitrosomethane itself ($CF_3{\cdot}NO \rightleftharpoons CF_3{\cdot} + NO$) occurs to some extent at room temperature, since pure trifluoronitrosomethane very slowly decomposes in the dark, even at −20°, to give the same products as were noted from the liquid-phase reaction with nitric oxide. The self-decomposition of trifluoronitrosomethane thus follows the reaction path indicated in the equations above. Cleavage of the C–N bond in the nitroso-compound is accelerated by heat or light. Decomposition of trifluoronitrosomethane at temperatures above 100° is relatively rapid, and its photochemical dimerisation to give the compound $(CF_3)_2N{\cdot}O{\cdot}NO$ at room temperature is easily achieved.

Thus, trifluoronitrosomethane can act as a source of free radicals by direct dissociation, or by reaction with nitric oxide; radicals such as $CF_3{\cdot}$, $CF_3{\cdot}O{\cdot}$, $(CF_3)_2N{\cdot}O{\cdot}$, or $NO_2$, produced at temperatures well below those normally associated with free-radical formation, are thus available for initiation of the copolymerisation of trifluoronitrosomethane with fluoro-olefins.

*Thermal Decomposition of Trifluoronitrosomethane.*—The blue colour of trifluoronitrosomethane completely disappears when the compound is heated at 100° for 14 days in glass, and a 48% yield of trifluoronitromethane results; carbon dioxide, silicon tetrafluoride, and nitrogen are the only other products. The reaction scheme suggested is based on that for the trifluoronitrosomethane–nitric oxide reaction:

$$3CF_3{\cdot}NO \longrightarrow 3CF_3{\cdot} + 3NO$$



$$CF_3{\cdot}NO + 2NO \longrightarrow CF_3{\cdot}N_2{\cdot}NO_3 \xrightarrow{NO} \underbrace{CF_3{\cdot} + NO_2}_{CF_3{\cdot}NO_2} + \underbrace{NO_2}_{\xrightarrow{CF_3{\cdot}}\ CF_3{\cdot}NO_2} + N_2$$

$$2CF_3{\cdot} \xrightarrow{SiO_2} CO_2 + SiF_4$$

The overall reaction is thus

$$4CF_3{\cdot}NO \longrightarrow 2CF_3{\cdot}NO_2 + N_2 + 2CF_3{\cdot}\ (\text{as } CO_2 + SiF_4)$$

where a disproportionation-type reaction oxidises half of the trifluoronitrosomethane to trifluoronitromethane at the expense of the other half, which is converted into nitrogen

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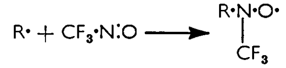
[5] Pearlson and Hals, U.S.P. 2,643,267; *Chem. Abs.*, 1954, **48**, 6461.

[6] Birchall, Bloom, Haszeldine, and Willis, *Proc. Chem. Soc.*, 1959, 367.

and trifluoromethyl radicals, these radicals decomposing on the wall, as often observed before, to give carbon dioxide and silicon tetrafluoride. The 48% yield of trifluoronitromethane obtained is close to that expected (50%) by the above scheme.

*Polymer Formation from Trifluoronitrosomethane and Olefins* $CF_2{:}CXY$.—Earlier studies[1] showed that addition of quinol halved the rate of the $C_3F_7\cdot NO{-}C_2F_4$ reaction and decreased the polymer : oxazetidine ratio eight-fold. By contrast, addition of t-butyl peroxide, or exposure to ultraviolet light, increased the rate of reaction and doubled the polymer : oxazetidine ratio; surface effects seemed relatively unimportant. This evidence points to a free-radical mechanism for copolymer formation, although the facts that polymerisation occurred without deliberate addition of an initiator, and at temperatures near 0° could be taken to indicate a carbanion ionic mechanism.

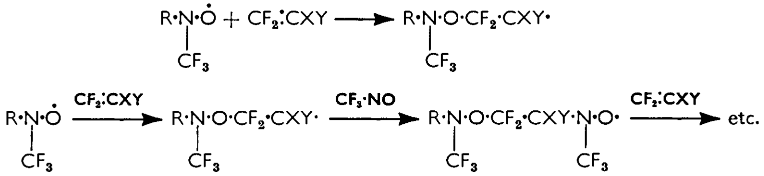
All the evidence now available is in favour of a radical mechanism. *Initiation* probably occurs by formation of $CF_3\cdot$, $CF_3\cdot O\cdot$, $(CF_3)_2N\cdot O\cdot$, or $NO_2$ radicals by the self-decomposition of trifluoronitrosomethane, this decomposition being accelerated by heat, light, or presence of oxygen. These radicals, R•, then attack the trifluoronitrosomethane nitrogen atom:



$$R\cdot + CF_3\cdot N{:}O \longrightarrow R\cdot\underset{CF_3}{N}\cdot O\cdot$$

The direction of addition of a free radical to a nitroso-group is known from the free-radical dimerisation of trifluoronitrosomethane to give the compound $(CF_3)_2N\cdot O\cdot NO$.[7]

The 1 : 1 copolymers obtained from the unsymmetrical olefin $CF_2{:}CXY$ ($X = F$, $Y = Cl$; $X = Y = Cl$; $X = F$, $Y = CF_3$) are predominantly of one structure $[-N(CF_3)\cdot O\cdot CF_2\cdot CXY-]_n$ and this is consistent with the following propagation steps:



$$R\cdot\underset{CF_3}{N}\cdot\dot{O} + CF_2{:}CXY \longrightarrow R\cdot\underset{CF_3}{N}\cdot O\cdot CF_2\cdot CXY\cdot$$

$$R\cdot\underset{CF_3}{N}\cdot\dot{O} \xrightarrow{CF_2:CXY} R\cdot\underset{CF_3}{N}\cdot O\cdot CF_2\cdot CXY\cdot \xrightarrow{CF_3\cdot NO} R\cdot\underset{CF_3}{N}\cdot O\cdot CF_2\cdot CXY\cdot\underset{CF_3}{N}\cdot O\cdot \xrightarrow{CF_2:CXY} \text{etc.}$$

Free-radical addition to the olefins $CF_2{:}CXY$ is known to be on the carbon indicated: $^*CF_2{:}CFCl$, $^*CF_2{:}CCl_2$, $^*CF_2{:}CF\cdot CF_3$.[8] The final polymer thus contains oxygen attached to the carbon atom of the olefin most susceptible to radical attack.

*Oxazetidine Formation.*—There is a similarity between oxazetidine ring formation and the Diels–Alder reaction. Both nitrogen and oxygen in the nitroso-compound contain unshared electrons, so that the N:O group is electron-rich and may be considered as equivalent to the diene of the Diels–Alder reaction; the fluoro-olefin has electron-withdrawing substituents and the double bond is electron-poor, thus being equivalent to the dienophile. Formation of a preliminary 1 : 1 molecular complex between the nitroso-compound and the fluoro-olefin would explain why the products contain equimolar amounts of the reactants as in the oxazetidine and the strictly 1 : 1 copolymer.

Formation of a 1 : 1 molecular complex in which (*a*) the nitrogen of trifluoronitrosomethane is vertically above the $CF_2$ carbon atom and at right angles to the plane of the F–C–F group of the olefin $CF_2{:}CXY$, and (*b*) the oxygen of trifluoronitrosomethane is vertically above the CXY carbon atom and at right angles to the plane of the X–C–Y group, could be assisted by overlap of an $sp^2$-orbital of nitrogen with that of fluorine in the $CF_2$ group. It should be noted that in all oxazetidines so far obtained from olefins of the $CF_2{:}CXY$ type, the nitrogen is attached to the $CF_2$ group.

When X and/or Y are bulky, *i.e.*, larger than fluorine, steric factors may also play a part, since models show that least steric interaction occurs between the $CF_3$ group of

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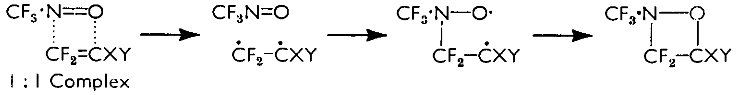
[7] Haszeldine and Mattinson, *J.*, 1957, 1741.

[8] Haszeldine, *Ann. Reports*, 1954, **51**, 291.

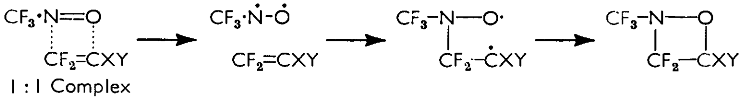
trifluoronitrosomethane and the atoms or groups X and Y when the nitrogen is vertically above the $CF_2$ group carbon atom, and the oxygen vertically above the CXY group carbon atom.

The step following complex formation may involve a molecular or four-centre process, but an argument based on radical intermediates will explain most of the observed facts. Thus, if complex formation involves, or is followed by, partial or complete diradical formation by the olefin to give $\dot{C}F_2\cdot\dot{C}XY$, then the more reactive of the species $-\dot{C}F_2$ or $-\dot{C}XY$ would attack the nitrogen of trifluoronitrosomethane to give the most stable diradical, ring closure in which affords the oxazetidine:

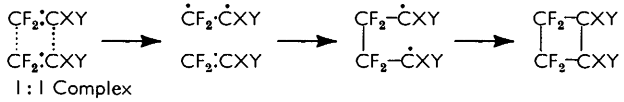


That a $-\dot{C}F_2$ radical is more reactive than a $-\dot{C}XY$ radical may be deduced from the fact that attack of a free radical Z (= $CF_3$, $CCl_3$, Br, etc.) on the olefins $CF_2\colon CXY$ (where X = F, Y = Cl; X = Y = Cl; X = F, Y = $CF_3$) yields $ZCF_2\cdot\dot{C}XY$ rather than the less stable radical $ZCFCl\cdot\dot{C}F_2$.[8] Trifluoronitrosomethane is particularly sensitive to radical attack, which takes place on nitrogen to give $Z\cdot N(CF_3)\cdot O\cdot$ rather than $(CF_3)(ZO)N\cdot$.[9]

A similar argument based on diradical formation from trifluoronitrosomethane, $CF_3\cdot\dot{N}\cdot\dot{O}$, followed by attack of the more reactive of the species $-\dot{N}-$ or $-\dot{O}$, *i.e.*, the nitrogen radical, on the olefin, would lead to the same result:



Diradical formation from the olefin is somewhat favoured, since it also explains formation of cyclobutane compounds on dimerisation of fluoroethylenes of type $CF_2\colon CXY$:



where head-to-head addition greatly predominates.

The above schemes lead to the predominance of an oxazetidine in which the nitrogen is attached to the carbon of the original olefin $CF_2\colon CXY$ most readily attacked by a free radical. This gives a direction of addition in oxazetidine formation opposite to that involved in polymer formation. Polymer formation involves attack on the trifluoronitrosomethane in the 1 : 1 complex by a free radical from *outside* the complex—the initiating radical R·, or the growing polymer $R\cdot N(CF_3)\cdot O\cdot CF_2\cdot CXY\cdot$. The new radical so formed $R\cdot N(CF_3)\cdot O\cdot$ or $R\cdot N(CF_3)\cdot O\cdot CF_2\cdot CXY\cdot N(CF_3)\cdot O\cdot$ then immediately attacks the $CF_2$ group of the nearby olefin $CF_2\colon CXY$ which had been present in the 1 : 1 complex.

Kinetic studies are in progress to throw further light on the mechanism of these novel reactions.

## EXPERIMENTAL

Trifluoronitrosomethane was prepared by irradiation of a mixture of trifluoroiodomethane and nitric oxide in the presence of mercury. Chlorotrifluoroethylene and 1,1-dichlorodifluoroethylene were commercial samples purified by distillation with particular care to remove traces of peroxides. Hexafluoropropene was obtained by pyrolysis of anhydrous sodium heptafluorobutyrate and was purified by distillation *in vacuo*. All the olefins had correct molecular weights and were spectroscopically pure.

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[9] Haszeldine and Steele, *J.*, 1957, 2800.

Products were identified by physical properties, by spectroscopic examination, by vapour-phase chromatography, and by determination of molecular weight (Regnault's method). Mixtures were analysed by infrared spectroscopy or by vapour-phase chromatography. Distillations were carried out in a vacuum-apparatus for manipulation of volatile compounds so that handling losses were usually negligible.

Reactions were carried out in sealed, evacuated Pyrex or silica tubes, filled by condensation from the vacuum-apparatus; air, moisture, etc., were thus excluded.

*Reaction of Trifluoronitrosomethane with Chlorotrifluoroethylene.*—The nitroso-compound (0·200 g., 2·0 mmole) and chlorotrifluoroethylene (0·233 g., 2·0 mmole) were sealed in a 40 ml. Pyrex tube and heated at 70° for 24 hr.; the blue colour had almost disappeared. Removal of the volatile products from the small amount of polymer (15% based on $CF_3\cdot NO$ used), and fractionation, gave unchanged reactants (15%) and 4-*chloro*-3,3,4-*trifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine* (0·309 g., 1·43 mmole; 85% based on $CF_3\cdot NO$ used) as a colourless liquid (Found: C, 16·4; N, 6·6%; *M*, 217. $C_3ClF_6NO$ requires C, 16·6; N, 6·5%; *M*, 215·5), b. p. 30·0° (isoteniscope).

A similar reaction mixture kept at −45° (1 hr.), then allowed to warm to room temperature during 24 hr. and kept at room temperature for 6 days, yielded only 1% of the oxazetidine and mainly a very viscous colourless *copolymer* $[N(CF_3)\cdot O\cdot CF_2\cdot CFCl]_n$ (95% yield) (Found: C, 16·6; N, 6·7. $C_3ClF_6NO$ requires C, 16·6; N, 6·5%).

*Pyrolysis of the Oxazetidine* $\overline{N(CF_3)\cdot O\cdot CFCl\cdot CF_2}$.—The oxazetidine (0·950 g., 4·42 mmole) was passed at 5 mm. pressure through a Pyrex tube (10 mm. internal diameter) heated to 450° over 7 cm. Air was excluded. The pyrolysis was repeated. The yellow products that had condensed in a trap cooled to −183° were shaken with mercury to remove chlorine and fractionated to give unchanged oxazetidine (2·75 mmole, 60%), perfluoro(methylenemethylamine) (1·65 mole, 99% yield based on the oxazetidine decomposed), carbonyl chlorofluoride, and carbonyl fluoride. Identification of the products was confirmed by infrared spectroscopic examination, which also showed that not even traces of the compound $CF_3\cdot N{:}CFCl$ had been formed. Under these pyrolysis conditions the compound COFCl is partly decomposed into $COF_2$ and $COCl_2$, which in turn affords carbon monoxide and chlorine.

*Pyrolysis of the Polymer* $[N(CF_3)\cdot O\cdot CF_2\cdot CFCl]_n$.—The polymer (2·01 g.) contained in a Pyrex tube, closed at one end and with the other end attached to a vacuum-pump *via* a trap cooled in liquid oxygen, was slowly inserted into a furnace at 550°. Some of the polymer (0·40 g., 20%) distilled into the cooler part of the tube. The volatile products were distilled to give *chlorofluoromethylenetrifluoromethylamine*, $CF_3\cdot N{:}CFCl$ (6·6 mmole, 88% yield based on polymer decomposed) (Found: C, 16·3; N, 9·2%; *M*, 149·6. $C_2ClF_4N$ requires C, 16·1; N, 9·4%; *M*, 149·5), b. p. 5·5° (isoteniscope), carbonyl fluoride (90% yield based on polymer decomposed), perfluoro(methylenemethylamine) (<5% yield based on polymer decomposed), and silicon tetrafluoride.

*Attempted Reaction of Chlorofluoromethylenetrifluoromethylamine with Carbonyl Fluoride.*—The compound $CF_3\cdot N{:}CFCl$ (0·075 g., 0·50 mmole) and carbonyl fluoride (0·033 g., 0·50 mmole) were thoroughly mixed as gases in a 200-ml. trap fitted with a tap leading to a silica tube (15 mm. internal diameter) heated at 500° over 30 cm. and a receiving trap cooled in liquid oxygen. The tap was opened slightly so that the mixed gases passed through the heated tube into the receiver. This procedure was repeated. Fractionation gave unchanged chlorofluoromethylenetrifluoromethylamine (0·068 g., 0·45 mmole; 90%) and a mixture of carbonyl fluoride and silicon tetrafluoride (0·52 mmole). Infrared spectroscopic examination revealed no trace of the compounds $CF_3\cdot N{:}CF_2$, $COCl_2$, or COFCl.

Similar experiments were carried out with the compounds $CF_3\cdot N{:}CF_2$ and $COCl_2$, and $CF_3\cdot N{:}CCl_2$ and $COF_2$; halogen exchange was not detected.

*Reaction of Trifluoronitrosomethane with* 1,1-*Dichlorodifluoroethylene.*—(a) *At* 100°. Trifluoronitrosomethane (0·99 g., 10·0 mmole) and 1,1-dichlorodifluoroethylene (1·06 g., 7·9 mmole), sealed in a 100 ml. Pyrex tube and kept at 100° in the dark for 24 hr., gave unchanged nitroso-compound (0·23 g., 2·3 mmole), some polymer, and 4,4-*dichlorodifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine* (VII) (1·17 g., 65% based on nitroso-compound consumed) (Found: C, 15·8; N, 5·8%; *M*, 230. $C_3Cl_2F_5NO$ requires C, 15·5; N, 6·0%; *M*, 230), b. p. 63° (isoteniscope). (b) *At* 20°. Trifluoronitrosomethane (1·01 g., 10·2 mmole) and 1,1-dichlorodifluoroethylene (1·35 g., 10·2 mmole) were kept in a sealed 100 ml. Pyrex tube until the vapour phase was only faintly blue (5 days). Fractionation gave unchanged reactants (23%), the oxazetidine (0·058 g., 3%), and *the polymer* $[{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CCl_2{\cdot}]_n$ (1·75 g., 97% based on nitroso-compound consumed) [Found: C, 15·9; N, 6·3%. $(C_3F_5Cl_2NO)_n$ requires C, 15·5; N, 6·0%] as a viscous liquid or elastomeric gel.

*Reactions of the Oxazetidine* (VII).—(a) *Attempted hydrolysis.* The oxazetidine (0·085 g.) was recovered unchanged after being heated with 10% aqueous sodium hydroxide (2 ml.) at 100° for 4 hr. The aqueous solution gave a weak test for chloride and fluoride ions, indicating that hydrolysis was taking place, but very slowly. (b) *Pyrolysis.* The oxazetidine (0·510 g., 2·20 mmole) was passed four times, at *ca.* 5 mm. pressure and in absence of air, through a silica tube (15 mm. internal diameter) heated at 400° over a 30 cm. length, the reaction products being condensed in traps cooled by liquid oxygen. Non-condensable gas (carbon monoxide) was formed. The pale yellow condensate was shaken with mercury to remove chlorine, then fractionated to give perfluoro(methylenemethylamine), $CF_3{\cdot}N{:}CF_2$ (0·88 mmole, 98% based on oxazetidine consumed), unchanged oxazetidine, carbonyl chloride (0·24 mmole), and traces of the compounds $CF_3{\cdot}N{:}CCl_2$, $CF_2{:}CCl_2$, $COF_2$, and $CF_3NO$.

*Pyrolysis of the Polymer* $[{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CCl_2{\cdot}]_n$.—The polymer (2·35 g.), contained in a platinum tube closed at one end and attached through a trap cooled in liquid air to a vacuum pump, was heated to 550° *in vacuo.* Under these conditions, none of the polymer distilled unchanged to cooler parts of the tube. The blue condensate was distilled to give (i) *dichloromethylenetrifluoromethylamine,* $CF_3{\cdot}N{:}CCl_2$ (82% based on polymer taken) (Found: C, 14·2; N, 8·1%; *M*, 170. $C_2NCl_2F_3$ requires C, 14·4; N, 8·1%; *M*, 166), as a colourless liquid, b. p. 47° (isoteniscope), (ii) carbonyl fluoride (79%), (iii) perfluoro(methylenemethylamine) (8%), (iv) carbonyl chloride (6%), (v) 1,1-dichlorodifluoroethylene (5%), and (vi) trifluoronitrosomethane (3%). The compound $CF_3{\cdot}N{:}CFCl$ was not detected.

Pyrolysis of the polymer in a silica tube at *ca.* 450° *in vacuo* gave similar products, though in lower yield (*e.g.*, $CF_3{\cdot}N{:}CCl_2$ 65%), since part of the polymer distilled unchanged and condensed in cooler parts of the apparatus. Carbon monoxide was also detected.

*Reduction of Perfluoro(methylenemethylamine) with Hydrogen Chloride.*—Perfluoro(methylenemethylamine) (1·01 g., 7·5 mmole), and anhydrous hydrogen chloride (0·288 g., 7·9 mmole) sealed in a 50 ml. Pyrex tube at 20° for 44 hr. gave (i) dichloromethylenetrifluoromethylamine, $CF_3{\cdot}N{:}CCl_2$ (1·6 mmole, 26%) (Found: *M*, 164. Calc. for $C_2NF_3Cl_2$: *M*, 166), spectroscopically identical with the compound obtained by the pyrolysis of the polymer $[{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CCl_2{\cdot}]_n$, (ii) bistrifluoromethylamine (4·1 mmole, 54%) (Found: *M*, 152. Calc. for $C_2HNF_6$: *M*, 153) identified by means of its infrared spectrum, and (iii) unchanged hydrogen chloride (Found: *M*, 39. Calc. for HCl: *M*, 36·5), (iv) a small amount of chlorofluoromethylenetrifluoromethylamine, $CF_3{\cdot}N{:}CFCl$, spectroscopically identical with the compound obtained by the pyrolysis of the polymer $[{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CFCl{\cdot}]_n$.

*Reaction of Trifluoronitrosomethane with Hexafluoropropene.*—The nitroso-compound (0·60 g., 6·7 mmole) and hexafluoropropene (1·00 g., 6·7 mmole) failed to react in an evacuated 50 ml. Pyrex tube at 70° during 120 hr. The blue colour disappeared when the tube was kept at 100° for 120 hr., and fractionation gave a mixture of carbon dioxide and silicon tetrafluoride (0·23 g.), a mixture of hexafluoropropene and trifluoronitromethane (1·26 g.; *M*, 139), and a fraction (0·05 g.; *M*, 225) spectroscopic examination of which revealed the characteristic oxazetidine absorption at 7·3 μ.

Increase in pressure facilitated the reaction. In a second experiment, trifluoronitrosomethane (4·24 g., 43 mmole) and hexafluoropropene (6·43 g., 43 mmole) were kept in a 30 ml. evacuated stainless steel autoclave (initial pressure 25—30 atm.) at 100° for 14 days. Fractionation gave (*a*) *perfluoro-2,4-bis(trifluoromethyl)-1,2-oxazetidine* (0·7 g., 7%) (Found: C, 19·0; N, 5·4%; *M*, 248. $C_4F_9NO$ requires C, 19·3; N, 5·6%; *M*, 249) as a colourless liquid, b. p. (isoteniscope) 22·3°, (*b*) a small quantity (0·1 g., 1%) of a colourless liquid $(C_4F_9NO)_2$ (Found: C, 19·2; N, 5·8%; *M*, approx. 500) of vapour pressure approx. 20 mm. at 20°, and (*c*) *the polymer* $[{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF(CF_3){\cdot}]_n$ (3·94 g., 35%) (Found: C, 19·2; N, 5·6. $[C_4F_9NO]_n$ requires C, 19·3; N, 5·6%) as a colourless heavy oil.

The vapour pressure of the oxazetidine determined over the range −7° to 16° is given by the equation $\log_{10} p$ (mm.) = $7{\cdot}462 - 1353/T$, whence the latent heat of vaporisation is 6190 cal./mole, and Trouton's constant is 21·0.

*Pyrolysis of the Oxazetidine from Trifluoronitrosomethane and Hexafluoropropene.*—The method is as described above. The oxazetidine (0·70 g., 2·8 mmole) was passed at 2—3 mm.

pressure during 20 min. through the pyrolysis tube at 550°. Distillation gave a fraction (0·29 g.) consisting of trifluoroacetyl fluoride (Found: *M*, 108. Calc. for $C_2F_4O$: *M*, 116) contaminated by small amounts of carbonyl fluoride and silicon tetrafluoride, and a fraction (0·40 g.) consisting of perfluoro(methylenemethylamine) (Found: *M*, 130. Calc. for $C_2F_5N$: *M*, 133), and small amounts of trifluoroacetyl fluoride and perfluoro(ethylidenemethylamine). Spectroscopic analysis showed that the pyrolysis products and yields were $CF_3{\cdot}N{:}CF_2$ 90%, $CF_3{\cdot}COF$ 90%, $COF_2$ 10% and $CF_3{\cdot}N{:}CF{\cdot}CF_3$ 10%.

*Pyrolysis of the Copolymer from Trifluoronitrosomethane and Hexafluoropropene.*—The copolymer (0·868 g.), pyrolysed during 20 min. at 550° by the technique described earlier, gave perfluoro(ethylidenemethylamine), $CF_3{\cdot}N{:}CF{\cdot}CF_3$ (90% yield) (Found: C, 19·7; N, 7·3%; *M*, 183. $C_3F_7N$ requires C, 19·7; N, 7·6%; *M*, 183), b. p. (isoteniscope) −15°, carbonyl fluoride (90% yield), trifluoroacetyl fluoride (10% yield), and perfluoro(methylenemethylamine) (10% yield). The vapour pressure of perfluoro(ethylidenemethylamine) is given by $\log_{10} p$ (mm.) = $7{\cdot}221 - 1119/T$, whence the latent heat of vaporisation is 5125 cal./mole and Trouton's constant 19·9.

*Preparation of Perfluoro(methylene-ethylamine)* $C_2F_5{\cdot}N{:}CF_2$.—Perfluoro-(2-ethyl-1,2·oxazetidine) (0·231 g., 0·94 mmole), prepared by interaction of pentafluoronitrosoethane and tetrafluoroethylene, was pyrolysed at 550° under 2—3 mm. pressure during 10 min., to give *perfluoro(methylene-ethylamine)* (0·168 g., 0·92 mmole) (Found: C, 19·6; N, 7·6%; *M*, 182. $C_3F_7N$ requires C, 19·7; N, 7·6%; *M*, 183), b. p. (isoteniscope) −6°, and carbonyl fluoride (0·060 g., 0·92 mmole) (*M*, 66). The vapour pressure of perfluoro(methylene-ethylamine) is given by the equation $\log_{10} p$ (mm.) = $7{\cdot}903 - 1341/T$, whence the latent heat of vaporisation is 6110 cal./mole and Trouton's constant is 22·9.

*Elastomer Formation from Trifluoronitrosomethane and Tetrafluoroethylene.*—A series of reactions was carried out with highly pure trifluoronitrosomethane and tetrafluoroethylene. The reactants were sealed *in vacuo* in 5—10 mm. (internal diameter), thick-walled Pyrex or silica tubing capable of withstanding high pressures, and precautions were taken against explosions. The rate of reaction could be followed visually by disappearance of the blue colour. After removal of volatile products the polymer was examined to see if it was a mobile or viscous oil or an elastomer.

(a) *Reactant purity.* Experiments in which reactants were deliberately contaminated by addition of trifluoroiodomethane, trifluoronitromethane, dinitrogen tetroxide, nitric oxide, air, or moisture, then allowed to react under near-optimum conditions of temperature, pressure, etc., showed clearly that oily polymers were produced rather than the elastomer.

(b) *Reactant ratio.* No major difference could be detected in the rate of reaction, the yield of polymer, or the quality of the polymer, when molar reactant ratios between 0·8 : 1 and 1·5 : 1 were used. Use of 1 : 5, 1 : 10, 5 : 1, or 10 : 1 ratios gave only oils, but the oils were still exclusively 1 : 1 copolymers, *i.e.*, neither of the monomers was incorporated in the copolymer in excess of the 50% molar ratio.

(c) *Temperature.* Polymerisation occurred at −65°, −20°, 0°, 20°, 40°, or 100°. At 100°, the oxazetidine was the main product, and the polymer was always a mobile oil, never an elastomer. Elastomer of long chain-length was produced at −65°, but only slowly. No difference was detected in the rate of reaction at −20°, 0°, or 20°, but a trend could be detected towards elastomer of shorter chain-length as the reaction temperature increased, and at 40° a very viscous oil, almost a glass, was produced of molecular weight 80,000—100,000.

(d) *Pressure.* Increase in pressure increased the rate of reaction and the chain-length of the polymer. The pressures could not be measured, but could be calculated when liquid phase was absent. Increase in initial pressure from 1 to 20 atm. at −20° gave a distinct increase in rate of reaction and in quality of the elastomer. At an initial pressure calculated as 80 atm. the elastomer was formed within 30 min. and was hard and tough with good " snap." In all cases the rate of reaction appeared to increase as soon as an appreciable liquid phase was present.

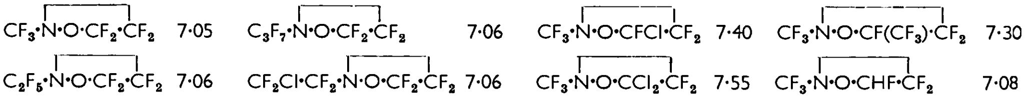
(e) *Time.* This varied from 30 min. when high pressure was used, to 7 days for reaction at low temperature or pressure, or with impure reactants.

(f) *Optimum conditions.* Pure reactants with a molar ratio of 1 : 1, or close to it, at a temperature of 0° and a calculated pressure of 20 atm. produced elastomeric 1 : 1 copolymer of molecular weight 500,000—1,500,000 in 95% yield after 24 hr. in the dark on a 2 g. scale in sealed evacuated glass or silica vessels.

(g) *Conversion of oil into elastomer.* The oil could often be converted into the elastomer in two ways. The simplest was to heat the oil at 50—150° *in vacuo* for 1—7 days. Alternatively, the oil could be sealed with fresh trifluoronitrosomethane and tetrafluoroethylene and kept under near-optimum conditions; then the final polymer was an elastomer. The molecular weight of elastomer obtained by either procedure never exceeded 500,000.

(h) *Pyrolysis of the elastomer.* The elastomer (1·00 g.), pyrolysed at 550° by the technique described above, gave only perfluoro(methylenemethylamine) (98% yield) and carbonyl fluoride (96% yield) contaminated by a small amount of silicon tetrafluoride; trifluoronitrosomethane and tetrafluoroethylene were absent.

*Characteristic Vibration of the Oxazetidine Ring.*—The infrared spectra of the oxazetidines described in this and earlier papers show the groups N:O, $NO_2$, $N\!:\!\overset{+}{N}(\overset{-}{O})$, ONO, $ONO_2$, C:C, C:N, etc., to be absent. A strong band at 7·0—7·5 μ appears to be characteristic of the perhalogenated oxazetidine ring system:



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CF_3\cdot N\cdot O\cdot CF_2\cdot CF_2$ | 7·05 | $C_3F_7\cdot N\cdot O\cdot CF_2\cdot CF_2$ | 7·06 | $CF_3\cdot N\cdot O\cdot CFCl\cdot CF_2$ | 7·40 | $CF_3\cdot N\cdot O\cdot CF(CF_3)\cdot CF_2$ | 7·30 |
| $C_2F_5\cdot N\cdot O\cdot CF_2\cdot CF_2$ | 7·06 | $CF_2Cl\cdot CF_2\cdot N\cdot O\cdot CF_2\cdot CF_2$ | 7·06 | $CF_3\cdot N\cdot O\cdot CCl_2\cdot CF_2$ | 7·55 | $CF_3\cdot N\cdot O\cdot CHF\cdot CF_2$ | 7·08 |

*Reaction of Trifluoronitrosomethane with Nitric Oxide.*—The nitroso-compound (0·125 g., 1·26 mmole), nitric oxide (0·60 g., 20 mmole), and mercury (10 ml.) in a sealed 85 ml. silica tube were allowed to warm from liquid-nitrogen temperature. Whilst liquid nitric oxide and nitroso-compound were still present a vigorous reaction ensued, and mercuric oxide began to coat the walls of the tube. Dinitrogen tetroxide caused the gas phase to change from blue to green, but the blue colour was regained later when the tube was shaken so that the mercury came into contact with the gas. After 5 min. the tube was opened and found to contain nitrogen, unchanged trifluoronitrosomethane (0·069 g., 0·70 mmole, 56%), trifluoronitromethane (0·040 g., 0·35 mmole, 63% based on $CF_3\cdot NO$ consumed), carbon dioxide (0·005 g., 0·10 mmole, 18% based on $CF_3\cdot NO$ consumed), and *O*-nitrosobistrifluoromethylhydroxylamine (0·010 g., 0·05 mmole, 18% based on $CF_3\cdot NO$ consumed).

When the reaction was repeated in absence of mercury, there was a similar vigorous decomposition at low temperature in the liquid phase, and the same products were obtained with the addition of dinitrogen tetroxide.

*Thermal Decomposition of Trifluoronitrosomethane.*—The nitroso-compound (150 ml. gas, 0·6 g.) was heated in a sealed 50 ml. Pyrex tube at 100° until the blue colour had disappeared (10 days). After a further 2 days the tube was opened and found to contain nitrogen, trifluoronitromethane (48% yield), carbon dioxide, and silicon tetrafluoride (40% yield).

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