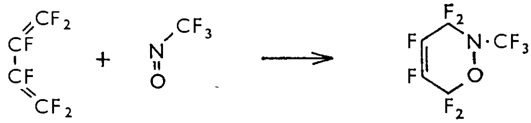
1146. *Perfluoroalkyl Derivatives of Nitrogen. Part XVIII.*[1] *Reaction of Trifluoronitrosomethane with Perfluorobutadiene and* 3,4-*Dichlorohexafluorobut*-1-*ene*

By R. E. Banks, M. G. Barlow, and R. N. Haszeldine

Trifluoronitrosomethane reacts with perfluorobutadiene to yield perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) and a 1 : 1 copolymer in which the predominant repeating unit is $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF{:}CF{\cdot}CF_2-]_n$. Oxidation of the oxazine yields a dibasic acid believed to be perfluoro-(3-methyl-2-oxa-3-azabutane)-1,4-dicarboxylic acid, whilst its chlorination provides perfluoro-(4,5-dichlorotetrahydro-2-methyl-2*H*-1,2-oxazine) which gives, *inter alia*, perfluoro-(2,3-dichloro-1-methylazetidine) when pyrolysed. Reaction of trifluoronitrosomethane with 3,4-dichlorohexafluorobut-1-ene yields the oxazetidines $CF_3{\cdot}N{\cdot}O{\cdot}CF(CFCl{\cdot}CF_2Cl){\cdot}CF_2$ and $CF_3{\cdot}N{\cdot}O{\cdot}CF_2{\cdot}CF{\cdot}CFCl{\cdot}CF_2Cl$ and a 1 : 1 copolymer, $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF(CFCl{\cdot}CF_2Cl)-]_n$. Pyrolysis of a mixture of the oxazetidines or of the copolymer gives 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine.

At temperatures above −78° the major product of the reaction between trifluoronitrosomethane and perfluorobutadiene is perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) (I). This is the first example of the participation of perfluorobutadiene in a Diels–Alder type of reaction:



(I)

Hitherto, it has been thought that perfluorobutadiene will act as neither the diene nor the

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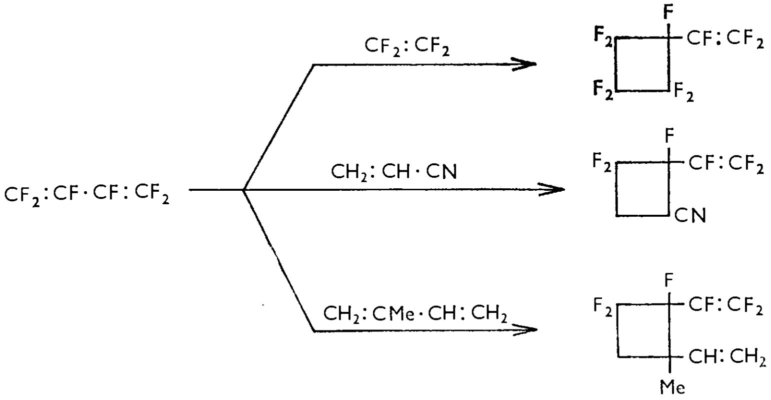
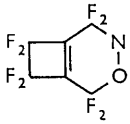
[1] Part XVII, preceding Paper.

dienophile in a Diels–Alder reaction, since it does not appear to combine with maleic anhydride, and reacts with certain electron-rich or electron-poor olefins to yield 1 : 1 adducts which are believed to be cyclobutane derivatives,[2,3] *e.g.*,

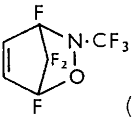


Participation of trifluoronitrosomethane in a Diels–Alder reaction is not restricted to that leading to (I): the nitroso-compound combines readily with perfluoro-(1,2-dimethylenecyclobutane),[4] perfluorocyclopentadiene,[5] or butadiene [6] to give quantitative yields of the 1 : 4-adducts (II), (III), and (IV), respectively.

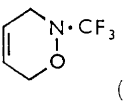
In addition to the oxazine (I), a 1 : 1 alternating copolymer, $[-\mathrm{N(CF_3){\cdot}O{\cdot}C_4F_6}-]_n$ is formed in the reactions between trifluoronitrosomethane and perfluorobutadiene, the ratio of the yields of these two products being 32, 6, 3, and *ca.* 1 at temperatures of 80, 20, —7, and —78°, respectively. Thus, a close similarity exists between this reaction and that involving trifluoronitrosomethane and a fluoro-olefin of type $\mathrm{CF_2{:}CXY}$ [where



(II)



(III)



(IV)

(i) X = Y = F; (ii) X = F, Y = H; (iii) X = F, Y = Cl; (iv) X = F, Y = $\mathrm{CF_3}$; (v) X = Y = Cl],[7] which yields a mixture of a 1 : 1 adduct (an oxazetidine, $\mathrm{CF_3{\cdot}\overline{N{\cdot}O{\cdot}CXY{\cdot}C}F_2}$) and a 1 : 1 alternating copolymer {predominantly $[-\mathrm{N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY}-]_n$} in which the former predominates at high reaction temperatures.

Perfluoro-(3,6-*dihydro*-2-*methyl*-2*H*-1,2-*oxazine*).—This product (I) is a colourless volatile liquid, b. p. 52·4°, which is obtained in 97% yield when an equimolar mixture of trifluoronitrosomethane and perfluorobutadiene is kept at 80° and a few atmospheres pressure for three hours. Its structure was deduced from the properties and reactions described below; these differentiate it from the unknown oxazetidines (V) and (VI), one or both of which might have been expected to arise from the above reaction in view of the apparent preference shown by perfluorobutadiene to yield four-membered ring compounds in cyclisation reactions (*vide ut supra*).

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[2] R. M. Ryazanova, I. M. Dolgopol'skii, and A. L. Klebanskii, *Zhur. Vsesoyuz. Khim. obshch. im D. I. Mendeleeva*, 1961, **6**, 356.

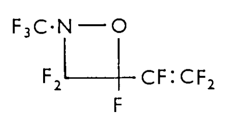
[3] R. E. Puntnam, J. L. Anderson, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1961, **83**, 386.

[4] R. E. Banks, R. N. Haszeldine, and D. R. Taylor, *J.*, 1965, 978.

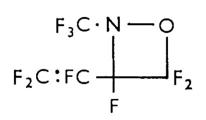
[5] R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, *Chem. Comm.*, 1965, 41.

[6] R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J.*, 1965, 4714.

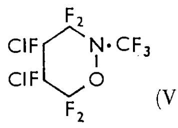
[7] D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J.*, 1961, 1351; R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis, *J.*, 1965, 2506.



(V)



(VI)

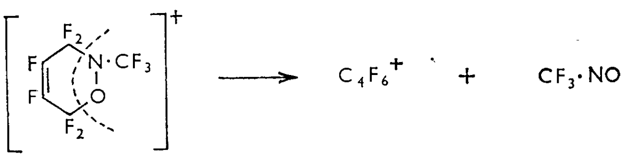


(VII)

The presence of a C⁚C bond in (I) is revealed by infrared spectroscopy (intense absorption at 1764 cm.$^{-1}$, vapour spectrum) and confirmed by mild photochemical chlorination, which gives perfluoro-(4,5-dichlorotetrahydro-2-methyl-2*H*-1,2-oxazine) (VII) in 98% yield. This C⁚C stretching frequency is closer to that for perfluorocyclohexene [8] (1749 cm.$^{-1}$) than for perfluorobut-1-ene [9] (1792 cm.$^{-1}$), and is unusually high for a *cis*- •CF⁚CF• bond.

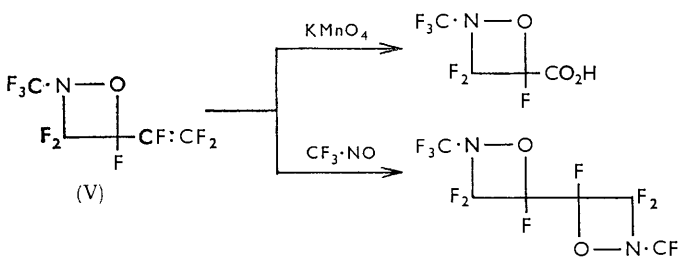
The ^{19}F n.m.r. spectrum of (I) shows the expected number (five) and type of bands, and is incompatible with either structure (V) or (VI). One feature of the spectrum that remains unexplained is the small spin–spin coupling constant between the vinylic fluorine nuclei (2·0 c./sec.); normally [10] such constants lie within the range 30—40 c./sec.

The base peak in the mass spectrum of (I) is provided by the CF_3^+ ion, which is followed in intensity by the $C_4F_6^+$ ion that probably arises from the retro Diels–Alder cleavage.



This type of cleavage is commonplace during mass spectroscopy of unsaturated six-membered-ring compounds.[11] The other possible ion from such a cleavage, CF_3NO^+, also appears in the spectrum but is much less abundant than $C_4F_6^+$. Ions corresponding to loss of the fragments CF_3, CF_3N, and C_2F_3O from the parent ion are also prominent, and a moderately intense peak arises by loss of fluorine from the parent ion to give $C_5F_8NO^+$, which then appears to lose either the fragment CF_2O, to give $C_4F_6N^+$, or the fragment C_2F_5N, to give $C_3F_3O^+$. No peaks corresponding to the ions $C_4F_7NO^+$ and $C_3F_6NO^+$ are observed; this militates against structure (V) or (VI) for the 1 : 1 adduct of trifluoronitrosomethane with perfluorobutadiene, since the parent ions of these oxazetidines would be expected to lose readily the fragments CF_2 and C_2F_3.

Oxidation of (I) with acetonic permanganate at *ca.* —15° gives a dibasic acid, believed to have the structure $HO_2C{\cdot}CF_2{\cdot}O{\cdot}N(CF_3){\cdot}CF_2{\cdot}CO_2H$, in 42% yield; also, (I) does not react with trifluoronitrosomethane even under conditions vigorous enough to decompose the latter. This is evidence against structures (V) and (VI), since compounds with these structures would be expected to yield monobasic acids on oxidation and to undergo cyclo-addition reactions with trifluoronitrosomethane, *e.g.*,



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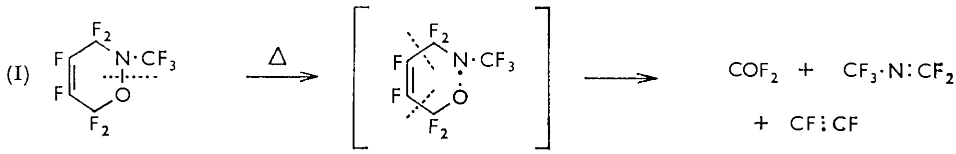
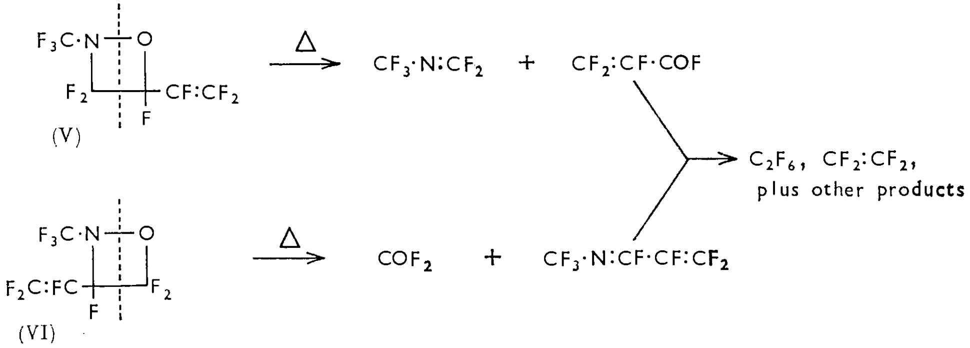
[8] J. Burdon and D. H. Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.
[9] T. J. Brice, J. D. Lazerte, L. J. Hals, and W. H. Pearlson, *J. Amer. Chem. Soc.*, 1953, **75**, 2698.
[10] H. H. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, 1956, **24**, 479.
[11] K. Biemann, " Mass Spectrometry," McGraw-Hill, New York, 1962, p. 103.

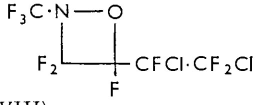
By analogy with the thermal decomposition of polyfluoro-oxazetidines,[7] it might be expected that thermal decomposition of a compound with structure (I) would be initiated by fission of the N–O bond and eventually give rise to carbonyl fluoride, perfluoro(methylenemethylamine), and difluoroacetylene or compounds derived from it, thus:



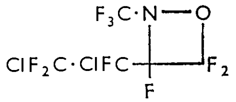
The oxazine was found to be more stable to heat than was expected: it was only 14% decomposed when pyrolysed in platinum at 600°/*ca.* 1 mm. with a contact time of *ca.* 5 seconds. This provides strong evidence against the oxazetidine structures (V) and (VI), which would be extensively decomposed under the above conditions. The pyrolysis product from (I) was complex, containing carbonyl fluoride (42% yield), perfluoro(methylenemethylamine) (49%), hexafluoroethane (the major product), tetrafluoroethylene, carbon dioxide, silicon tetrafluoride (these last two arose by attack on glass traps by the pyrolysate), and unidentified material that attacked glass and turned brown when it was allowed to warm up from −196° to room temperature. These products do not provide clear-cut evidence for structure (I); indeed, it could be argued that the 1 : 1 adduct was an almost equimolar mixture of (V) and (VI), and that under the pyrolysis conditions the perfluoroacrylyl fluoride and perfluoro-4-azapenta-1,3-diene formed concomitantly with the perfluoro(methylenemethylamine) and carbonyl fluoride, respectively, had undergone reaction to yield the other observed products:



In contrast to the above pyrolysis results, thermal degradation of the dichloride (VII) derived from (I) provided excellent confirmatory evidence for the oxazine structure so clearly indicated for the latter by the results of physical methods of analysis. In addition, the isomeric oxazetidines (VIII) and (IX) have been synthesised (*vide infra*) and found to be different from their oxazine isomer (VII).



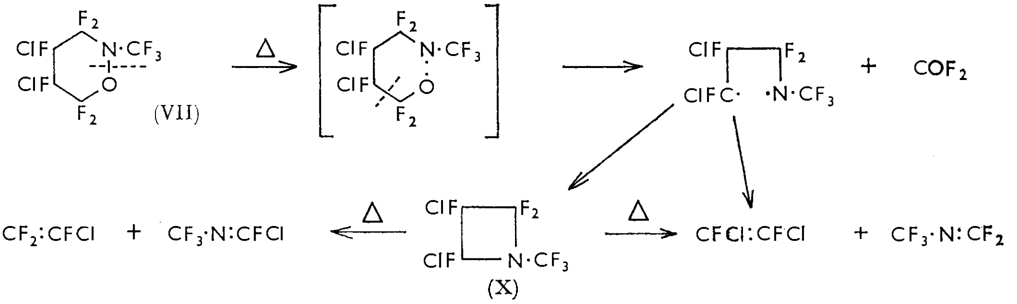
(VIII)



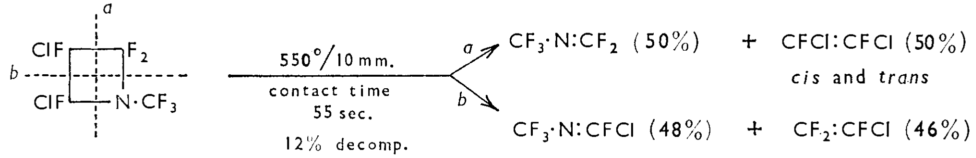
(IX)

Perfluoro-(2,3-*dichloro*-1-*methylazetidine*) (X).—Like its olefinic precursor (I), perfluoro-(4,5-dichlorotetrahydro-2-methyl-2*H*-1,2-oxazine) (VII) is more stable thermally than a polyfluoro-oxazetidine; thus, it is only 47 and 83% decomposed when pyrolysed in silica at 520°/4—5 mm. and 600°/4—5 mm., respectively, with a contact time of *ca.* 20 sec., whereas a mixture of oxazetidines (VIII) and (IX) is decomposed completely by pyrolysis at 500°/9 mm. with a contact time of *ca.* 15 sec.

The product from pyrolysis of (VII) at 600°/4—5 mm. is complex; it contains, besides unchanged starting material (17%), carbonyl fluoride (99%), perfluoro(methylenemethylamine) (65%), *cis*- and *trans*-1,2-dichlorodifluoroethylene (59%), perfluoro-(2,3-dichloro-1-methylazetidine) (X; 32%), chlorotrifluoroethylene (9%), chlorofluoromethylenetrifluoromethylamine (4%), dichlorodifluoromethane (3%), tetrafluoroethylene (1%), and traces of trifluoromethyl isocyanate, carbon dioxide, and silicon tetrafluoride; the same products in similar yield are obtained from pyrolysis of (VII) at 520°/4—5 mm. The following breakdown scheme accounts for the main products observed:

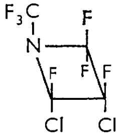


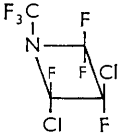
Perfluoro-(2,3-dichloro-1-methylazetidine) (X) was shown by separate experiment to undergo thermal breakdown in the manner used in the above scheme, thus:



Also formed in this separate pyrolysis are traces of dichlorodifluoromethane and chlorotrifluoromethane.

Perfluoro-(2,3-dichloro-1-methylazetidine), apparently the first polyfluoroazetidine to be reported, is a colourless liquid, b. p. 67·5° (isoteniscope), which, according to limited studies, is best obtained (64% yield) by pyrolysis of the oxazine (VII) at 575°/20 mm. with a contact time of *ca.* 10 seconds. Its structure was established by elemental analysis, by its thermal degradation referred to above, and by infrared, n.m.r., and mass spectroscopy. Its infrared spectrum shows only very weak bands at frequencies higher than 1353 cm.$^{-1}$, indicating that no C:C or C:N bonds are present, and the absence of the latter type of linkage is confirmed by the failure of the compound to react with water (both cyclic and acyclic polyfluoro-compounds containing the N:C link are rapidly degraded by water [12]). The n.m.r. spectrum of the azetidine reveals that it is a 45 : 55 mixture of *cis*- and *trans*-isomers (Xa, Xb); the spectrum consists of thirteen bands (see Experimental section), and for each isomer an AB-type pattern of bands is observed (coupling constant = 125 c./sec.) due to the non-equivalence of the fluorine nuclei of the CF_2 groups caused by the rigidity of the azetidine ring.


(Xa)


(Xb)

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[12] D. A. Barr and R. N. Haszeldine, *J.*, 1955, 1881; *J.*, 1956, 3416; R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J.*, 1962, 3407.

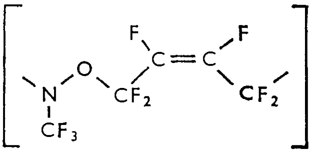
The mass spectrum of (X) is fully consistent with its structure. The parent ion, $C_4Cl_2F_7N^+$, is vanishingly small, but the presence of peaks due to the ions $C_4Cl_2F_6N^+$ and $C_4ClF_7N^+$ arising by loss of fluorine and chlorine, respectively, from the parent ion enables the molecular formula to be deduced. The base peak has a mass number corresponding to CF_3^+, and peaks corresponding to the ions $C_2ClF_3^+$ and $C_2Cl_2F_2^+$, ascribed to cleavage of the azetidine ring in direction *a* and *b* as on pyrolysis (*vide ut supra*), are also very prominent. The ratio of abundances of the last two ions is 5 : 1, indicating that either the ion $C_2ClF_3^+$ is the more stable of the two, or the compound $CF_3{\cdot}N{:}CFCl$ is more stable than $CF_3{\cdot}N{:}CF_2$.

The Copolymer of Trifluoronitrosomethane with Perfluorobutadiene.—The 1 : 1 copolymer formed from trifluoronitrosomethane and perfluorobutadiene at 20° is a weakly elastomeric, transparent gel, but if the carefully purified monomers are allowed to interact at —78° the product is a tough white crêpe rubber. The latter form is insoluble in common hydrocarbon solvents, although it is swollen slightly by light petroleum (b. p. 100—120°), and by diethyl ether; however, it is soluble in fluorinated solvents such as perfluoro-n-pentane and 1,1,2-trichlorotrifluoroethane. It resists attack by hot concentrated mineral acids, but is slowly degraded by hot ethanolic potassium hydroxide with the formation of fluoride ions. Thermal degradation of the copolymer occurs when it is heated at temperatures above 200° in air. Thus, the properties of the copolymer follow closely those of the nitroso-rubber $[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF_2-]_n$.[7,13]

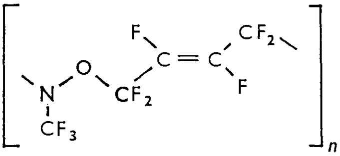
By analogy with the structures of other nitroso-rubbers,[7] three plausible structures (XI), (XII), and (XIII) can be written for the copolymer, and one of these can exist in *cis*- and *trans*-forms (XIIIa and XIIIb, respectively).

$[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF(CF{:}CF_2)-]_n$
(XI)

$[-N(CF_3){\cdot}O{\cdot}CF(CF{:}CF_2){\cdot}CF_2-]_n$
(XII)



(XIIIa)



(XIIIb)

The infrared spectrum of the copolymer (natural film) varied slightly according to its temperature of formation. Thus, the copolymer prepared at —78° gave a strong band at 1786 cm.$^{-1}$ and two weaker bands at 1721 and 1698 cm.$^{-1}$, together with a possible shoulder at 1770 cm.$^{-1}$; whereas that obtained at 0° showed the same bands except for that at 1698 cm.$^{-1}$, and the 1721 cm.$^{-1}$ band was more intense. The band at 1786 cm.$^{-1}$ is close to that expected for a $CF{:}CF_2$ group and may be ascribed to the presence of repeating units (XI) and (XII), while the 1721 cm.$^{-1}$ band can be accounted for by the presence of unit (XIIIa) (*cis*-$CF_3{\cdot}CF{:}CF{\cdot}CF_3$ shows [9] C:C absorption at 1724 cm.$^{-1}$). It is possible that the weak band at 1698 cm.$^{-1}$ in the spectrum of the copolymer prepared at —78° is due to the presence of unit (XIIIb); the C:C stretching frequency of the *trans*-$CF_2{\cdot}CF{:}CF{\cdot}CF_2$ group does not appear to be known, but it should be weak on symmetry grounds. Photochemical chlorination of a solution of the copolymer in 1,1,2-trichlorotrifluoroethane confirmed the presence of one olefinic bond in each repeating unit: a brittle white resin of empirical formula $C_5Cl_2F_9NO$ that contained no C:C bonds by infrared spectroscopy was obtained in 97% yield; this new polymer softened and became elastomeric at 100°.

In an attempt to obtain further information about the structure of the copolymer of trifluoronitrosomethane with perfluorobutadiene, a sample, prepared at —78°, was pyrolysed at 550° *in vacuo*. By analogy with the mode of thermal decomposition now well established

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[13] R. E. Banks, J. M. Birchall, and R. N. Haszeldine, in " High Temperature Resistance and Thermal Degradation of Polymers," Society of Chemical Industry (London) Monograph, **1961**, No. **13**, p. 283.

for a nitroso-rubber,[7,13] polymer chains composed of unit (XI), (XII), or (XIII) might be expected to unzip to give initially the products shown below:

$$\text{(XI)}\ -N(CF_3)-\vdots-O-CF_2-\vdots-CF(CF{:}CF_2)-N(CF_3)-\vdots-O-CF_2-\vdots-CF(CF{:}CF_2)- \xrightarrow{\Delta} CF_2{:}CF{\cdot}CF{:}N{\cdot}CF_3 + COF_2$$

$$\text{XII)}\ -N(CF_3)-\vdots-O-CF(CF{:}CF_2)-\vdots-CF_2-N(CF_3)-\vdots-O-CF(CF{:}CF_2)-\vdots-CF_2- \xrightarrow{\Delta} CF_3{\cdot}N{:}CF_2 + CF_2{:}CF{\cdot}COF$$

$$\text{(XIII)}\ -N(CF_3)-\vdots-O-CF_2-\vdots-CF{:}CF-\vdots-CF_2-N(CF_3)-\vdots-O-CF_2-\vdots-CF{:}CF-\vdots-CF_2- \xrightarrow{\Delta} CF_3{\cdot}N{:}CF_2 + COF_2 + CF{\vdots}CF$$

However, the only products that were identified in the very complex mixture (at least fifteen components) were carbonyl fluoride (55% yield), perfluoro(methylenemethylamine) (41%), trifluoromethyl isocyanate (3%; presumably this arose from reaction of the previous compound with traces of moisture in the apparatus[14]), hexafluoroethane (7%), and tetrafluoroethylene (11%). No definite conclusions can thus be drawn from this result, although it seems reasonable to assume that all three structures (XI—XIII) are present in view of the occurrence of carbonyl fluoride and perfluoro(methylenemethylamine) as the major products.

$$-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF(CFCl{\cdot}CF_2Cl)-]_n \quad \text{(XIV)} \qquad [-N(CF_3){\cdot}O{\cdot}CF(CFCl{\cdot}CF_2Cl){\cdot}CF_2-]_n \quad \text{(XV)}$$

$$[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CFCl{\cdot}CFCl{\cdot}CF_2-]_n \quad \text{(XVI)}$$

Pyrolysis at 550° *in vacuo* of the chlorinated copolymer of trifluoronitrosomethane with perfluorobutadiene, expected to be composed of one or more of the units (XIV), (XV), and (XVI) derived from (XI), (XII), and (XIII), respectively, gave more useful structural information than that of its unsaturated precursor. The products were: carbonyl fluoride (58% yield), perfluoro(methylenemethylamine) (78%), trifluoromethyl isocyanate (1%), chlorotrifluoroethylene (14%), *cis*- and *trans*-1,2-dichlorodifluoroethylene (12%), αβ-dichlorotrifluoropropionyl fluoride (11%), 1,3-dichlorotetrafluoropropene (23%), 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (6%), and nitrogen (4%), together with small quantities of hexafluoroethane, tetrafluoroethylene, chlorotrifluoromethane, dichlorodifluoromethane, carbon, unidentified compounds, silicon tetrafluoride (a silica pyrolysis tube was used), and a compound believed to be a chloropentafluoropropene (13%). The major products, except chlorotrifluoroethylene and the chloropentafluoropropene, can be accounted for by postulating that the chlorinated copolymer is composed of repeating units (XIV), (XV), and (XVI), and that they degrade only according to the schemes shown. On this basis, the combined yields of the olefins 1,2-dichlorodifluoroethylene and 1,3-dichlorotetrafluoropropene [derived from (XVI) *via* decomposition modes A and B, respectively] places a minimum value of 35% upon the contribution of unit (XVI) to the structure of the chlorinated copolymer and hence of that of unit (XIII) to the structure of the copolymer of trifluoronitrosomethane with perfluorobutadiene. Using this value for the proportion of (XVI) present, it follows from the yield of carbonyl fluoride [formed from (XIV) and (XVI)] that the contribution of unit (XIV) to the structure of the chlorinated copolymer, and hence of (XI) to the trifluoronitrosomethane–perfluorobutadiene copolymer, is not less than 20%; however, this value is not confirmed by the yield of 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (6%), and, furthermore, the contribution of structure (XV) to the polymer, as indicated by the yield of αβ-dichlorotrifluoropropionyl fluoride (11%), does not coincide with that (66%) calculated by subtracting the yield of the olefin 1,2-dichlorodifluoroethylene [from (XVI; mode A)] from the total yield of perfluoro(methylenemethylamine) [formed from (XV) and (XVI; mode A)]. Part of the last discrepancy could be due to the fact that (XVI) is the source of chlorotrifluoroethylene and the chloropentafluoropropene. Summarising,

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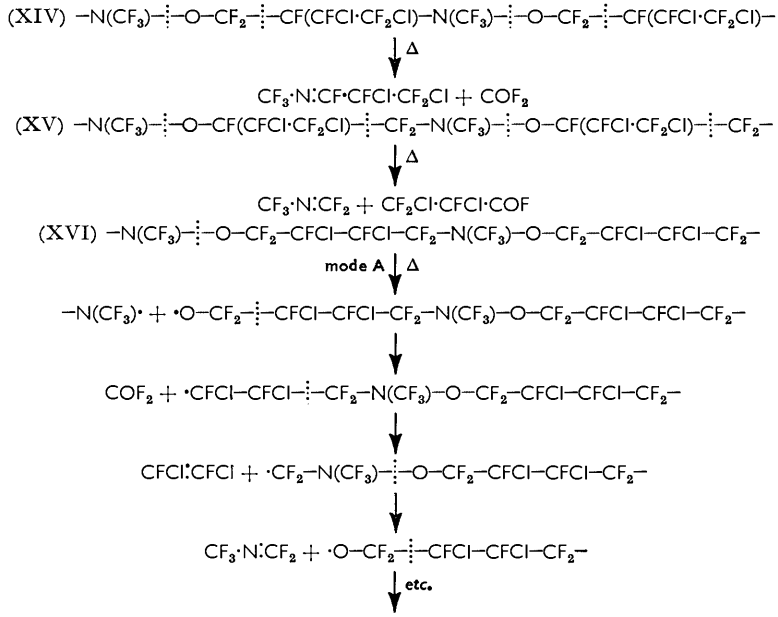
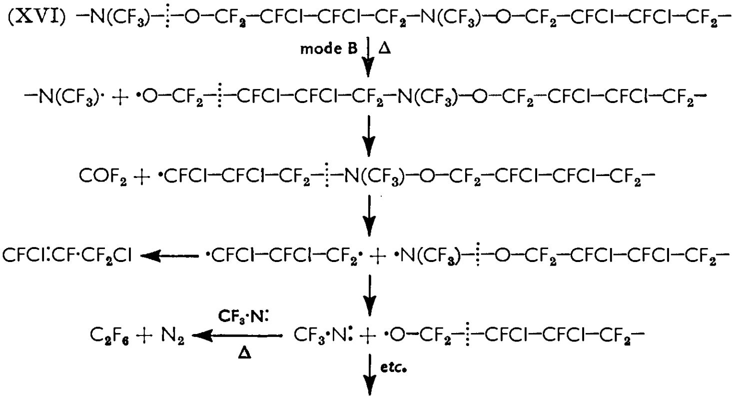
[14] D. A. Barr and R. N. Haszeldine, *J.*, 1956, 3428.



Scheme 1



Scheme 2

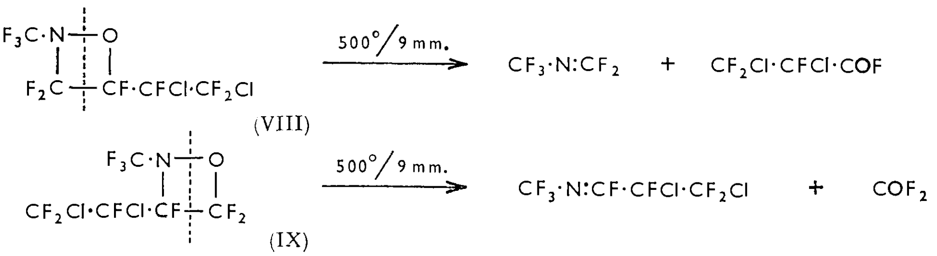
the pyrolysis data show that all three of the units (XIV), (XV), and (XVI) contribute to the structure of the chlorinated copolymer of trifluoronitrosomethane with perfluorobutadiene, possibly with unit (XVI) predominating, and hence the same conclusion is reached regarding the corresponding units [(XI), (XII), and (XIII), respectively] believed to be present in the parent unsaturated copolymer.

Reaction of Trifluoronitrosomethane with 3,4-*Dichlorohexafluorobut*-1-*ene*.—The objectives of this investigation were (i) to obtain an oxazetidine isomeric with the dichloride (VII) obtained from the 1 : 1 adduct of trifluoronitrosomethane and perfluorobutadiene (I), and thus provide further evidence for the structures of the last two compounds, and (ii) to prepare a copolymer containing repeating units thought to be present in the chlorinated copolymer of trifluoronitrosomethane with perfluorobutadiene, and through study of the pyrolytic breakdown of the former attempt to provide a more satisfactory understanding of the results of thermal degradation of the latter.

Reaction of trifluoronitrosomethane with 3,4-dichlorohexafluorobut-1-ene at 100°

(initial pressure *ca.* 10 atm.) gave, after 21 days, an oxazetidine fraction (83% yield based on conversion of 53% of the butene) and a 1 : 1 copolymer (8%); in a similar reaction at 20° during 10 weeks, these products were obtained in 25 and 75% yield, respectively, the conversion of reactants being only 8%. Thus, the variation with temperature of the ratio oxazetidine : copolymer is similar to that observed with other trifluoronitrosomethane–polyfluoro-olefin reactions, although the rate of the reaction is much slower than those in which polyfluoroethylenes are employed, and approaches that of the reaction between trifluoronitrosomethane and perfluoropropene.[7,15]

The oxazetidine fraction prepared at 100°, b. p. 104·9° (isoteniscope), showed a characteristic [7] strong polyfluoro-oxazetidine absorption at 1351 cm.$^{-1}$ in the infrared spectrum of its vapour, and was shown by gas–liquid chromatography to contain two isomers with a peak area ratio of 80 : 20. These isomers could not be separated, and the mixture was pyrolysed to provide structural information; the product was a complex mixture containing perfluoro(methylenemethylamine) (91% yield), carbonyl fluoride (16%), 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (8%), αβ-dichlorotrifluoropropionyl fluoride (65%), chlorotrifluoroethylene (4%), chlorotrifluoromethane (2%), dichlorodifluoromethane (2%), and traces of trifluoromethyl isocyanate and unidentified material. This result established that the oxazetidines have structures (VIII) and (IX), and that the former predominated:



The ratio of (VIII) : (IX), calculated from the yields of the two polyfluoro-imines, was 91 : 8.

The mass spectrum of the oxazetidine mixture showed only weak parent ions, isotopic analysis of which confirmed the molecular formula. The base peak was provided by the CF_3^+ ion, and was followed in intensity by a peak due to the CF_2Cl^+ ion. Peaks corresponding to loss of the fragments CF_2Cl and $CF_2Cl{\cdot}CFCl$ from the parent ions were prominent, indicating strongly the presence of the $CF_2Cl{\cdot}CFCl$ side-chain; the rearrangement ions $CFCl_2^+$ and $C_2F_4Cl^+$ were also fairly prominent, but this was not unexpected, since this type of rearrangement occurs in other chlorofluoro-compounds (*e.g.*, 1,2-dichlorotetrafluoroethane gives a prominent peak due to the ion $CFCl_2^+$).[16] In general, the spectrum did not contain many peaks that could be traced with certainty to either (VIII) or (IX) individually.

These results provide confirmatory evidence for the structures of both (VII) and (I).

The 1 : 1 copolymer of trifluoronitrosomethane with 3,4-dichlorohexafluorobut-1-ene, a colourless viscous oil when prepared at 100° but a brittle glass when prepared at 20°, was expected, by analogy with other nitroso-polymers,[7,17] to contain both units (XIV) and (XV), with the former predominating. This appears to be the case, because pyrolysis of the polymer yielded the products carbonyl fluoride (85% yield), 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (59%), perfluoro(methylenemethylamine) (12%), chlorotrifluoroethylene (30%), chlorofluoromethylenetrifluoromethylamine (11%), chlorotrifluoromethane (5%), and small amounts of hexafluoroethane, trifluoromethyl isocyanate,

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[15] R. E. Banks, R. N. Haszeldine, and H. Sutcliffe, unpublished results.
[16] J. R. Majer, *Adv. Fluorine Chem.*, 1961, **2**, 55.
[17] R. E. Banks, F. Bennett, and R. N. Haszeldine, unpublished results.

1,2-dichlorodifluoroethylene, and unidentified compounds. The high yield of carbonyl fluoride indicates that structure (XIV) greatly predominates over (XV), although the yield of 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine does not confirm this; it may be that modes of decomposition of the polymer chains occur which lead to formation of chlorotrifluoroethylene and chlorofluoromethylenetrifluoromethylamine instead of 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine. In addition to this, αβ-dichlorotrifluoropropionyl fluoride, which if formed ought to have survived the pyrolytic conditions, judging from its appearance in the pyrolysate from the oxazetidine mixture (VIII + IX), was not detected, although perfluoro(methylenemethylamine) occurred in 12% yield; thus, some doubt exists about the presence of units of type (XV) in the polymer, since the last fragment might have arisen in other ways.

This result, taken in conjunction with the results of pyrolysis of the chlorinated copolymer of trifluoronitrosomethane with perfluorobutadiene, provides sound evidence for the presence of the three repeating units (XI), (XII), and (XIII) in the trifluoronitrosomethane–perfluorobutadiene copolymer.

EXPERIMENTAL

Products were separated by trap-to-trap fractional condensation *in vacuo* or by precise distillation, and were identified by molecular-weight determination (Regnault's method), elemental analysis, physical properties, infrared (i.r.) spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), nuclear magnetic resonance (n.m.r.) spectroscopy (A.E.I. RS2 spectrometer operating at 60 Mc./sec.), mass spectrometry (A.E.I. MS/2H instrument), and gas–liquid chromatography (Perkin-Elmer " Vapor Fraktometer " model 116). Molar % compositions of mixtures were calculated from gas-chromatographic peak areas by triangulation, and the columns used (these were mainly packed with 30% w/w Kel-F No. 1 oil/Celite) were calibrated with known mixtures. Thermal gravimetric analysis of polymers was effected with a Stanton Thermal Balance.

Trifluoronitrosomethane was prepared by photolysis of a trifluoroiodomethane–nitric oxide mixture,[18] and by pyrolysis of trifluoroacetyl nitrite.[19] 3,4-Dichlorohexafluorobut-1-ene was obtained by dehydroiodination of the adduct $CF_2Cl{\cdot}CFCl{\cdot}CHF{\cdot}CF_2I$, formed by free-radical addition of 1,2-dichlorotrifluoroiodoethane across the olefinic bond of trifluoroethylene.[20] Perfluorobutadiene was prepared by dechlorination of 1,2,3,4-tetrachlorohexafluorobutane obtained by coupling of 1,2-dichlorotrifluoroiodoethane.[21,22]

Reaction of Trifluoronitrosomethane with Perfluorobutadiene.—Trifluoronitrosomethane (0·988 g., 9·98 mmoles) and perfluorobutadiene (1·583 g., 9·77 mmoles), kept in a 50 ml. Dreadnought ampoule at 20° overnight, gave unchanged nitroso-compound (0·28 mmole), *perfluoro*-(3,6-*dihydro*-2-*methyl*-2H-1,2-*oxazine*) (2·193 g., 8·40 mmoles; 86% yield based on reactants consumed) (Found: C, 23·1; N, 5·6%; *M*, 260. C_5F_9NO requires C, 23·0; N, 5·4%; *M*, 261), b. p. 52·4° (isoteniscope), and a 1 : 1 *copolymer* (0·311 g.; 13%) (Found: C, 23·1; N, 5·9. $[C_5F_9NO]_n$ requires C, 23·0; N, 5·4%).

TABLE 1

Product distribution in the $CF_3{\cdot}NO$–C_4F_6 reaction

Temp. (°c)	Time (hr.)	Reactants (mmoles of each)	Product composition (g.; mmoles; % yield) Oxazine	Copolymer
−78°	1000	27·2	3·27; 12·5; 46	3·81; —; 54
−7	72	14·3	2·87; 11·0; 77	0·85; —; 23
20	8	9·8	2·11; 8·4; 86	0·34; —; 14
80	3	8·8	2·22; 8·5; 97	0·07; —; 3

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[18] A. H. Dinwoodie and R. N. Haszeldine, *J.*, 1965, 1675.

[19] R. E. Banks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 1961, 64; R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, publication in preparation.

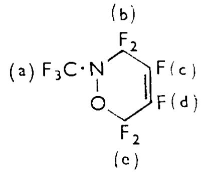
[20] P. Tarrant and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 3640.

[21] R. E. Banks, M. G. Barlow, R. N. Haszeldine, C. H. Thompson, and A. E. Tipping, publication in preparation.

[22] R. N. Haszeldine, *J.*, 1952, 4423.

The distribution of products in reactions carried out at other temperatures is shown in Table 1.

Properties and Reactions of Perfluoro-(3,6-*dihydro-*2-*methyl-*2H-1,2-*oxazine*).—(*a*) *Physical properties.* The vapour pressure of the oxazine, measured over the range −10° to 50°, is given by the equation $\log_{10}p$ (mm.) = 7·9108 − 1638/T. The calculated b. p. is 52·4°, Trouton's constant is 23·1, and the latent heat of vaporisation is 7530 cal. mole^{-1}.



(XVII)

The i.r. spectrum of perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) shows a strong C⁚C absorption at 1764 cm.$^{-1}$.

The ^{19}F n.m.r. spectrum of the oxazine showed five regions of absorption, an analysis of which is presented in Table 2; the chemical shifts and coupling constants were obtained by the standard techniques, with trifluoroacetic acid as external reference.

Mass-spectral data for the oxazine are listed in Table 3.

TABLE 2

Nuclear magnetic resonance of perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) (XVII)

Chemical shift (p.p.m.)	Multiplet structure	Assignment to F nuclei	Spin–spin coupling constants (c./sec.)
−8·83	1 : 2 : 1 Triplet	a	J_{ab} = 11·7
+11·13	Broad doublet of doublets	e	J_{ce} = 11·4 J_{de} = 18·4
+23·60	34 Bands (doublet of quartets of doublets of triplets)	b	J_{bc} = 16·5 J_{bd} = 10·1 J_{be} = 1·6
+80·13	Triplet of triplets of doublets	d	J_{cd} = 2·0
+82·05	63 Resolved bands (triplet of triplets of doublets of quartets)	c	J_{ac} = 0·8

TABLE 3

Mass spectrum of perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine)

m/e	Relative intensity (%)	*m/e*	Relative intensity (%)	*m/e*	Relative intensity (%)
261	2·0	131	4·5	85	0·4
242	2·5	128	0·7	81	2·1
223	0·2	126	2·3	76	4·5
214	0·2	124	0·5	74	2·0
195	0·4	123	0·2	71	0·3
192	1·1	119	0·2	*69*	*100·0*
181	0·3	114	7·8	64	0·4
178	3·6	112	7·7	62	6·2
176	0·3	109	4·4	57	0·4
164	4·7	107	1·1	55	0·6
162	85·1	100	4·2	50	3·9
159	0·2	99	0·3	47	3·7
154	7·7	95	1·4	43	0·7
150	2·7	93	42·0	31	20·5
145	0·7	92	0·4	30	7·1
143	1·5	88	0·4		

(*b*) *Oxidation.* Potassium permanganate (4·1 g., 25·6 mmoles) in AnalaR acetone (250 ml.) was added to a stirred, cooled (−15°) solution of perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) (6·70 g., 25·6 mmoles) in acetone (50 ml.) during 2·5 hr. The reaction mixture was stirred for 30 min., and then treated with water (100 ml.). Acetone was evaporated *in vacuo* and the aqueous residue was decolourised with aqueous sodium hydrogen sulphite, acidified (H_2SO_4), and extracted with ether. The ethereal extract was dried ($MgSO_4$) and evaporated *in vacuo*, leaving an oil which solidified when left *in vacuo* over phosphoric anhydride. The solid was sublimed twice at 70—75° (bath temp.) *in vacuo*, to give *perfluoro-*(3-*methyl-*2-*oxa-*3-*azabutane*)-1,4-*dicarboxylic acid* (3·1 g., 10·8 mmoles, 42%) (Found: C, 20·6; H, 0·8; N, 4·9%; Equiv., 146. $C_5H_2F_6NO_5$ requires C, 20·8; H, 0·7; N, 4·9%; Equiv., 144), m. p. 80—82°. This acid, a white deliquescent crystalline solid, reacted with aniline in ethereal solution, to give a *dianilinium salt* (Found: C, 43·2; H, 3·5; N, 8·8. $C_{17}H_{16}F_7N_3O_5$ requires C, 43·0; H, 3·4; N, 8·9%), m. p. 85·5—86·0°.

(*c*) *Chlorination.* A mixture of perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) (0·577 g., 2·13 mmoles) and chlorine (0·172 g., 2·42 mmoles), sealed in a 40 ml. Pyrex ampoule, was irradiated for 12 hr. with light from a tungsten-filament 100w lamp placed at a distance of 10 cm. The product was shaken with mercury to remove the excess of chlorine, and then fractionated, to yield *perfluoro-*(4,5-*dichlorotetrahydro-*2-*methyl-*2H-1,2-*oxazine*) (0·693 g., 2·09 mmoles, 98%) (Found: C, 18·2; N, 4·1%; *M*, 326. $C_5Cl_2F_9NO$ requires C, 18·1; N, 4·2%; *M*, 332), b. p. (Siwoloboff) 109°/753 mm., which showed no i.r. absorption in the C:C region.

The mass spectrum of perfluoro-(4,5-dichlorotetrahydro-2-methyl-2*H*-1,2-oxazine) exhibited the following ions (ions containing ^{37}Cl omitted; relative intensities % in parentheses): $C_5Cl_2F_9NO$ (0·7), $C_5Cl_2F_8NO$ (2·4), C_5ClF_9NO (0·5), C_5ClF_7NO (1·0), C_4ClF_7NO (5·1), $C_4Cl_2F_4NO$ (0·5), C_4ClF_6 (0·9), C_3ClF_5NO (3·0), C_3ClF_6 (0·5), C_3F_6NO (2·6), C_4ClF_5 (0·7), $C_3Cl_2F_4$ (5·2), C_4F_6 (3·0), C_3ClF_3NO (0·9), $C_2Cl_2F_3$ (1·1), C_2F_5NO (8·8), C_3ClF_4 (23·9), C_2ClF_3NO (1·1), C_2ClF_4 (4·3), $C_2Cl_2F_2$ (21·4), C_2F_5N (5·3), C_3F_7 (1·6), C_2F_4NO (11·9), C_2ClF_3 (20·2), C_2F_4N (4·3), C_2ClF_2O (3·3), C_3F_4 (1·6), C_3ClF_2 (2·0), CCl_2F (3·9), CF_3NO (1·6), C_2ClF_2 (6·0), C_2F_3N (0·7), C_3F_3 (7·1), C_2ClFN (1·1), $CClF_2$ (20·5), CCl_2 (3·6), C_2F_3 (0·5), C_2ClF (1·2), C_2F_2N (0·8), C_3F_2 (0·9), *CF_3 (100·0)*, CClF (10·7), CF_2N (1·5) CClO (1·0), C_2F_2 (1·3), CF_2 (2·0), CCl (4·2), CFO (1·3), CF (6·4), NO (4·4).

(*d*) *Pyrolysis.* Perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) (1·093 g., 4·19 mmoles) was passed at *ca.* 1 mm. pressure through a 100 × 1 cm. i.d. platinum tube heated to 600° over 55 cm. of its length (contact time *ca.* 15 sec.), to yield unchanged starting material (86% recovery), carbonyl fluoride (42% yield based on oxazine consumed), perfluoro(methylenemethylamine) (49% based on oxazine consumed), hexafluoroethane, tetrafluoroethylene, traces of carbon dioxide and silicon tetrafluoride (from attack on glass traps), and unidentified compounds, some of which were unstable at 20°.

(*e*) *Reaction with trifluoronitrosomethane.* A mixture of perfluoro-(3,6-dihydro-2-methyl-2*H*-1,2-oxazine) (0·320 g., 1·25 mmoles) and trifluoronitrosomethane (0·195 g., 1·97 mmole) was heated in a 4-ml. Dreadnought tube at 100° for 2 days, and then at 130° for 5 days. The product consisted of unchanged oxazine (0·298 g., 1·18 mmoles, 94% recovery), together with the compounds $CF_3{\cdot}NO_2$, $CF_3{\cdot}N{:}CF_2$, $CF_3{\cdot}NCO$, $(CF_3)_2NH$, $CF_3{\cdot}N{:}N{\cdot}CF_3$, CO_2, SiF_4, and nitrogen (products known to arise when trifluoronitrosomethane is decomposed thermally in glass vessels [23]).

Pyrolysis of Perfluoro-(4,5-*dichlorotetrahydro-*2-*methyl-*2*H*-1,2-*oxazine*).—(*a*) *At* 600°. Perfluoro-(4,5-dichlorotetrahydro-2-methyl-2*H*-1,2-oxazine) (1·472 g., 4·44 mmoles) was passed at 4—5 mm. through a 75 × 1 cm. i.d. silica tube heated to 600° over 55 cm. of its length (contact time *ca.* 20 sec.). The product contained unchanged starting material (17% recovery; all other yields quoted below are based on consumed oxazine), *perfluoro-*(2,3-*dichloro-*1-*methylazetidine*) (0·319 g., 1·20 mmoles, 32%) (Found: C, 18·0; N, 5·4%; *M*, 266. $C_4Cl_2F_7N$ requires C, 18·0; N, 5·3%; *M*, 266), perfluoro(methylenemethylamine) (65%), *cis-* and *trans-*1,2-dichlorodifluoroethylene (59%), chlorotrifluoroethylene (9%), chlorofluoromethylenetrifluoromethylamine (4%), carbonyl fluoride (99%), and traces of trifluoromethyl isocyanate, tetrafluorethylene, dichlorodifluoromethane, carbon dioxide, and silicon tetrafluoride.

The perfluoro-(2,3-dichloro-1-methylazetidine) was separated from the above product by gas–liquid chromatography (2 m., trixylyl phosphate–Celite at 50°) or by repeated trap-to-trap fractional condensation *in vacuo* (it condensed at −78°).

(*b*) *At* 575°. Using the silica tube described in the last experiment, the oxazine (8·700 g., 26·20 mmoles) was pyrolysed at 575°/20 mm. with a contact time of *ca.* 10 sec.; the product was fractionated, and the recovered starting material was passed through the pyrolysis tube. This recycling procedure was carried out five times, and the combined product was found to contain unchanged starting material (0·660 g.; 8% recovery), perfluoro-(2,3-dichloro-1-methylazetidine) (64%), *cis-* and *trans-*1,2-dichlorodifluoroethylene (35%), perfluoro(methylenemethylamine) (54%), chlorofluoromethylenetrifluoromethylamine (1%), chlorotrifluoroethylene (1%), carbonyl fluoride (100%), and traces of trifluoromethyl isocyanate, carbon dioxide, and silicon tetrafluoride.

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[23] R. E. Banks, M. G. Barlow, R. N. Haszeldine, and H. Sutcliffe, unpublished results.

(*c*) *At* 520°. The oxazine (0·873 g., 2·70 mmoles), pyrolysed as in experiment (*a*) but at 520°/4—5 mm. with *ca.* 20 sec. contact time, gave unchanged starting material (0·477 g., 53% recovery), perfluoro-(2,3-dichloro-1-methylazetidine) (39%), *cis*- and *trans*-1,2-dichlorodifluoroethylene (50%), perfluoro(methylenemethylamine) (54%), chlorofluoromethylenetrifluoromethylamine (7%), chlorotrifluoroethylene (8%), carbonyl fluoride (98%), and traces of hexafluoroethane, tetrafluoroethylene, dichlorodifluoromethane, carbon dioxide, and silicon tetrafluoride.

Properties and Reactions of Perfluoro-(2,3-*dichloro*-1-*methylazetidine*).—(*a*) *Physical properties.* The vapour pressure of perfluoro-(2,3-dichloro-1-methylazetidine), measured over the range 0—60°, is given by the equation $\log_{10}p$ (mm.) = 7·877 − 1702/T. The calculated b. p. is 67·5°, Trouton's constant is 22·9, and the latent heat of vaporisation is 7790 cal. mole^{-1}.

The ^{19}F n.m.r. spectrum of perfluoro-(2,3-dichloro-1-methylazetidine) shows thirteen regions of absorption, analysis of which shows that the sample examined consisted of a 45 : 55 mixture of *cis*- and *trans*-isomers, (Xa) and (Xb).

The assignments (band number, p.p.m. from $CF_3{\cdot}CO_2H$, assignment) made for the *cis*-isomer (Xa) are as follows: 1, −19·6, CF_3; 3, −1·4, ·CFCl·N; 6—9, +10·1, +12·3, +13·5, +15·5, AB-type spectrum assigned to CF_2; 13, +52·3, C·CFCl·C; whilst those for the *trans*-isomer (Xb) are: 1, −19·6, CF_3; 2, −9·2, ·CFCl·N; 4, 5, 10, and 11, +5·9, +8·1, +19·3, and +21·3, AB-type spectrum due to the CF_2; 12, +43·6, C·CFCl·C.

The mass spectrum of perfluoro-(2,3-dichloro-1-methylazetidine) showed the following ions (relative intensities % in parentheses; ions containing ^{37}Cl omitted): $C_4Cl_2F_6N$ (0·9), C_4ClF_7N (18·8), C_3ClF_5N (0·7), C_4F_6N (0·6), C_3ClF_4N (0·9), $C_2Cl_2F_3$ (1·6), C_3ClF_4 (1·1), C_3F_5N (2·6), C_3ClF_3N (1·6), C_4ClF_2N (1·4), $C_2Cl_2F_2$ (14·2), C_2ClF_3N (3·1), C_3F_5 (0·6), C_2ClF_3 (96·2), C_2F_4N (27·5), C_3F_3N (0·6), CCl_2F (1·3), C_2F_4 (1·0), C_2ClF_2 (1·7), C_2F_3N (1·5), C_3F_3 (0·9), C_2ClFN (1·7), $CClF_2$ (8·7), CCl_2 (1·7), C_2F_3 (0·9), C_2ClF (1·0), C_2F_2N (2·6), *CF_3* (*100·0*), CClF (4·4), C_2F_2 (1·3), CF_2 (4·5) CCl (3·2), Cl (0·9), CF (3·1).

(*b*) *Attempted hydrolysis.* Perfluoro-(2,3-dichloro-1-methylazetidine) (0·025 g., 0·094 mmole) was left in contact with water (0·18 g.) overnight. The product was dried (P_2O_5) and found to be unchanged azetidine (0·024 g., 0·090 mmole; 96% recovery).

(*c*) *Pyrolysis.* Perfluoro-(2,3-dichloro-1-methylazetidine) (0·405 g., 1·52 mmoles) was passed at 10 mm. pressure through a 75 cm. × 1 cm. i.d. silica tube heated to 550° over 55 cm. of its length (contact time *ca.* 55 sec.). The product consisted of unchanged starting material (0·357 g., 1·34 mmoles; 88% recovery), together with (% yields based on azetidine consumed) perfluoro(methylenemethylamine) (50%), chlorofluoromethylenetrifluoromethylamine (48%), *cis*- and *trans*-1,2-dichlorodifluoroethylene (50%), chlorotrifluoroethylene (46%), and traces of bistrifluoromethylamine, trifluoromethyl isocyanate, chlorotrifluoromethane, dichlorodifluoromethane, and silicon tetrafluoride.

In a similar experiment at 680°/9–11 mm. with a contact time of *ca.* 120 sec., the azetidine (0·730 g., 2·74 mmoles) was recovered in 55% yield together with the compounds perfluoro-(methylenemethylamine) (19%), chlorofluoromethylenetrifluoromethylamine (57%), *cis*- and *trans*-1,2-dichlorodifluoroethylene (23%), chlorotrifluoroethylene (38%), trifluoromethyl isocyanate (10%), chlorotrifluoromethane, dichlorodifluoromethane, and silicon tetrafluoride and nitrogen.

Reactions of the 1 : 1 *Copolymer of Trifluoronitrosomethane with Perfluorobutadiene.*—(*a*) *Chlorination.* A solution of the copolymer (5·74 g., prepared at −78°) in 1,1,2-trichlorotrifluoroethane (25 ml.) was shaken with chlorine (2·00 g., 28·2 mmoles, 28% excess) in a 300-ml. Pyrex ampoule whilst being irradiated with light from a bank of three 100w tungsten-filament lamps placed at a distance of 10 cm. The 1,1,2-trichlorotrifluoroethane and the excess of chlorine were removed from the product, *in vacuo*, leaving a *fully chlorinated copolymer* (7·10 g.; 97%) (Found: C, 18·3; N, 4·4. $[C_5Cl_2F_9NO]_n$ requires C, 18·1; N, 4·2%) as a brittle white resin that became elastomeric when heated to 100°.

(*b*) *Pyrolysis.* A platinum boat containing the copolymer (0·751 g.) was placed at the closed end of a 100 cm. × 1 cm. i.d. silica tube heated to 550° over 55 cm. of its length; the end of the tube containing the platinum boat protruded for *ca.* 5 cm. from the furnace in which the main part of the tube was heated. Pyrolysis of the copolymer sample was effected by evacuating the apparatus and placing over the closed end of the silica tube a small furnace that was regulated to reach a temperature of 550° in 15 min. The volatile product was a mixture of the following compounds (mmoles, % yield calculated on the basis of 1 mole of product arising from 1 mole of the repeating unit C_5F_9NO): carbonyl fluoride (1·58, 55%), perfluoro(methylenemethylamine) (1·17, 41%), trifluoromethyl isocyanate (0·08, 3%), hexafluoroethane (0·20, 7%), tetrafluoroethylene (0·31, 11%), silicon tetrafluoride (trace), and unidentified material (2·07 mmoles; at least ten components detected by gas–liquid chromatography). A brown tar (*ca.* 0·02 g.) was recovered from the pyrolysis tube.

Thermal gravimetric analysis of the copolymer (in air) showed that it begins to lose weight at 200° and is completely destroyed at 350°. When heated at constant temperature at temperatures above 200°, a sample of the copolymer rapidly lost 25% of its weight before undergoing steady decomposition according to first-order kinetics (% wt. loss/min. = 0·15 at 210°, 0·46 at 230°, and 1·65 at 250°).

Pyrolysis of the Chlorinated Copolymer, $[C_5Cl_2F_9NO]_n$.—The chlorinated copolymer (1·199 g.) was pyrolysed at 550°, *in vacuo*, by the technique described above for the copolymer of trifluoronitrosomethane with perfluorobutadiene. A trace of carbon (*ca.* 0·02 g.) was left in the silica tube, and the volatile product was a mixture of the following compounds (mmoles, % yield): carbonyl fluoride (2·08, 58%), perfluoro(methylenemethylamine) (2·81, 78%), trifluoromethyl isocyanate (0·04, 1%), chlorotrifluoroethylene (0·51, 14%), *cis*- and *trans*-1,2-dichlorodifluoroethylene (0·42, 12%), αβ-dichlorotrifluoropropionyl fluoride (0·40, 11%), 1,3-dichlorotetrafluoropropene (0·82, 23%), and 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (0·20, 6%), together with nitrogen (0·15, 4%) and small quantities of hexafluoroethane, tetrafluoroethylene, chlorotrifluoromethane, dichlorodifluoromethane, unidentified compounds, silicon tetrafluoride, and a compound believed to be a chloropentafluoropropene (0·47, 13%) on the basis of its gas-chromatographic retention time and i.r. spectroscopy.

Reaction of Trifluoronitrosomethane with 3,4-*Dichlorohexafluorobut*-1-*ene*.—(*a*) *At* 100°. Trifluoronitrosomethane (1·75 g., 17·7 mmoles) and 3,4-dichlorohexafluorobut-1-ene (4·00 g., 17·2 mmoles), kept at 100° for 21 days in a 50-ml. Dreadnought ampoule, gave unchanged starting materials (CF_3·NO, 1·0 mmole; CF_2Cl·CFCl·CF:CF_2, 5·9 mmoles), a mixture of 3-(1,2-*dichloro*-1,2,2-*trifluoroethyl*)-3,4,4-*trifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine* and 4-(1,2-*dichloro*-1,2,2-*trifluoroethyl*)-3,3,4-*trifluoro*-2-*trifluoromethyl*-1,2-*oxazetidine* (2·50 g., 7·5 mmoles; 45% based on CF_3·NO consumed) (Found: C, 18·3; N, 4·1%; *M*, 327. $C_5Cl_2F_9NO$ requires C, 18·1; N, 4·2%; *M*, 332), a colourless viscous oily 1 : 1 *copolymer* (0·26 g., 5% based on CF_3·NO consumed) (Found: C, 18·3; N, 4·4. $[C_5Cl_2F_9NO]_n$ requires C, 18·1; N, 4·2%), and a mixture of the compounds carbonyl fluoride, perfluoro(methylenemethylamine), trifluoromethyl isocyanate, bistrifluoromethylamine, trifluoronitromethane, perfluoro(azomethane), perfluoro(azoxymethane), αβ-dichlorotrifluoropropionyl fluoride, 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine, carbon dioxide, silicon tetrafluoride, and nitrogen, which arose from the partial decomposition of the trifluoronitrosomethane, of the mixture of oxazetidines, and of the 1 : 1 copolymer.

(*b*) *At* 20°. Trifluoronitrosomethane (0·309 g., 3·12 mmoles) and 3,4-dichlorohexafluorobut-1-ene (0·671 g., 2·89 mmoles), kept at 20° for 10 weeks in a 4-ml. Dreadnought ampoule, gave unchanged monomers (CF_3·NO; 2·89 mmoles; 93%. CF_2Cl·CFCl·CF:CF_2; 2·66 mmoles; 92%), the mixture of oxazetidines (0·05 mmole; 25% based on CF_3·NO consumed), and the 1 : 1 copolymer (0·058 g.; 75% based on CF_3·NO consumed) as a white brittle glass.

Properties and Reactions of the Mixture of Oxazetidines Obtained from Trifluoronitrosomethane and 3,4-*Dichlorohexafluorobut*-1-*ene*.—(*a*) *Physical properties*. The oxazetidine mixture prepared at 100° was shown by gas–liquid chromatography (2 m. di-2-ethylhexyl sebacate–Celite column at 50°) to contain the 3-(1,2-dichlorotrifluoroethyl) and 4-(1,2-dichlorotrifluoroethyl) isomers in the ratio 20 : 80. These isomers could not be separated by distillation or by preparative-scale gas–liquid chromatography. The vapour pressure of the oxazetidine mixture, measured over the range 40—100°, is given by the equation $\log_{10}p$ (mm.) = 7·393 − 1712/*T*, whence the b. p. is 104·9°, Trouton's constant is 20·7, and the latent heat of vaporisation is 7830 cal. mole^{-1}. The i.r. spectrum of the mixture shows a strong absorption at 1351 cm.$^{-1}$.

The mass spectrum of the oxazetidine mixture showed the following ions (relative intensities % in parentheses; ions containing ^{37}Cl omitted): $C_5Cl_2F_9NO$ (1·1), C_5ClF_9NO (3·3), C_4ClF_7NO (7·2), C_4ClF_5NO (1·0), C_4ClF_6 (1·9), C_3ClF_5NO (1·5), C_3F_6NO (12·8), C_2ClF_4NO (2·2), C_3ClF_4O (3·6), C_4F_6 (2·6), $C_2Cl_2F_3$ (3·8), C_2F_5NO (16·3), C_3ClF_4 (24·2), C_2ClF_4 (8·7), C_2F_5N (2·8), $C_2Cl_2F_2$ (4·3), C_3F_5 (1·4), C_2F_4NO (8·7), C_2ClF_3 (8·6), C_2F_4N (6·5), C_2ClF_2O (3·4), C_3F_4 (1·2), C_3ClF_2 (2·0), CCl_2F (9·3), C_2F_4 (2·2), CF_3NO (5·0), C_2ClF_2 (4·5), C_3F_3 (5·9), $CClF_2$ (69·9), C_2F_3 (1·4), *CF_3* (*100·0*), CClF (17·7), C_2F_2 (1·0), CF_2 (6·0), CCl (2·8), CFO (7·8), Cl (1·0), CF (14·8), NO (9·5).

(*b*) *Pyrolysis.* The oxazetidine mixture (0·484 g., 1·46 mmole) was completely decomposed by passage at 9 mm. through a 95 × 8 cm. i.d. platinum tube heated to 500° over 55 cm. of its length (contact time *ca.* 15 sec.). The product was fractionated, and found to be a mixture containing αβ-dichlorotrifluoropropionyl fluoride [65% yield; isolated by gas chromatography (2 m. Kel-F oil No. 3/Celite at 22°)] (Found: C, 18·3%; *M*, 198. Calc. for $C_3Cl_2F_4O$: C, 18·3; *M*, 199), b. p. (isoteniscope) 52°, perfluoro(methylenemethylamine) (91%), carbonyl fluoride (16%), 2,3-*dichlorotetrafluoropropylidenetrifluoromethylamine* (8%), chlorotrifluoroethylene (4%), chlorotrifluoromethane (2%), dichlorodifluoromethane (2%), small amounts of bistrifluoromethylamine, and trifluoromethyl isocyanate, and traces of unidentified compounds.

Pyrolysis of the 1 : 1 *Copolymer of Trifluoronitrosomethane with* 3,4-*Dichlorohexafluorobut*-1-*ene*.—The copolymer (0·220 g.) was pyrolysed at 480°, *in vacuo*, by the technique described above for the copolymer of trifluoronitrosomethane with perfluorobutadiene. A trace of carbon (*ca.* 0·02 g.) was left in the silica tube, and the volatile product was fractionated and shown by gas–liquid chromatography to be a mixture containing (mmoles, % yield) carbonyl fluoride (0·56, 85%), perfluoromethylenemethylamine (0·08 12%), chlorofluoromethylenetrifluoromethylamine (0·07, 11%), chlorotrifluoroethylene (0·20, 30%), 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (0·39, 59%), chlorotrifluoromethane (0·03, 5%), hexafluoroethane, dichlorodifluoromethane, trifluoromethyl isocyanate, silicon tetrafluoride, and traces of unidentified compounds.

The 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine (Found: C, 18·8%; *M*, 266. $C_4Cl_2F_7N$ requires C, 18·1%; *M*, 266) showed a strong $C{:}N$ stretching frequency at 1770 cm.$^{-1}$, and was identified by its mass spectrum, which showed the following ions (% relative abundance in parentheses; ions containing ^{37}Cl omitted): $C_4Cl_2F_6N$ (0·7), C_4ClF_7N (2·6), C_4F_7N (1·2), $C_3Cl_2F_4$ (2·1), C_3ClF_5N (1·6), C_4F_6N (1·8), C_3F_6N (4·1), $C_3Cl_2F_3$ (1·8), C_3ClF_4N (3·7), $C_2Cl_2F_3$ (10·2), C_3ClF_4 (19·4), C_3F_5N (2·4), C_3ClF_3N (3·4), C_2ClF_4 (1·2), $C_2Cl_2F_2$ (0·8), C_3F_5 (2·7), C_2ClF_3N (6·4), C_2Cl_2F (1·7), C_2ClF_3 (4·9), C_2F_4N (31·5), C_3F_4 (1·4), C_3ClF_2 (1·1), C_3F_3N (1·0), CCl_2F (13·2), C_2F_4 (1·4), C_2ClF_2 (1·4), C_2F_3N (2·0), C_3F_3 (5·9), C_2ClFN (3·4), $CClF_2$ (84·6), CF_3N (1·1), CCl_2 (1·2), C_2F_3 (2·7), C_2ClF (1·1), C_2F_2N (3·0), C_3F_2 (1·5), *CF_3* (*100·0*), CClF (3·9), C_2F_2 (2·0), CF_2 (6·2), CCl (5·0), Cl (2·7), CF (19·9). Although the parent ion is very weak, the molecular formula $C_4Cl_2F_7N$ is revealed by the occurrence of the ions $C_4ClF_7N^+$ and $C_4Cl_2F_6N^+$ by loss of chlorine and fluorine, respectively, from the parent. Formation of the pairs of ions $CClF_2^+$ and $C_3ClF_5N^+$, $C_2Cl_2F_3^+$ and $C_2F_4N^+$, and CF_3N^+ and $C_3Cl_2F_4^+$ by cleavages of the type

$$CF_3{\cdot}\overset{+}{N}{:}CF + C_2Cl_2F_3 \longleftarrow (CF_2Cl{\cdot}CFCl{-}\vdots{-}CF{:}N{\cdot}CF_3)^+ \longrightarrow CF_2Cl{\cdot}CFCl^+ + C_2F_4N$$

offers strong evidence for the structure $CF_2Cl{\cdot}CFCl{\cdot}CF{:}N{\cdot}CF_3$, with which the spectrum as a whole is fully consistent. Formation of the fairly prominent rearrangement ion CCl_2F^+ is not unexpected in view of the fact that such rearrangement processes are known to occur with polyfluorinated compounds.[16]

The vapour pressure of 2,3-dichlorotetrafluoropropylidenetrifluoromethylamine, measured over the range 10—70°, is given by the equation $\log_{10}p$ (mm.) = 6·950 − 1412/*T*, whence the b. p. is 73·5°, Trouton's constant is 18·6, and the latent heat of vaporisation is 6460 cal. mole.$^{-1}$.

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