176. *Polyhalogeno-allenes. Part I. Tetrafluoroallene, its Dimer, and the Reaction of the Dimer with Trifluoronitrosomethane.*

By R. E. Banks, R. N. Haszeldine, and D. R. Taylor.

Tetrafluoroallene, prepared in improved yield, reacts readily with hydrogen halides and with sources of fluoride ion, probably *via* nucleophilic attack. Tetrafluoroallene dimer, shown to be perfluoro-(1,2-dimethylenecyclobutane), reacts with trifluoronitrosomethane to give perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene}. Formation of the homopolymer of tetrafluoroallene, considered to be $[-CF_2\cdot C(:CF_2)-]_n$, has been reinvestigated.

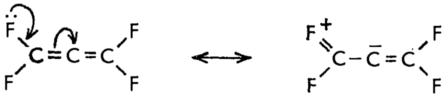
Earlier workers[1] found that tetrafluoroallene was best prepared by dehydrobromination of 1,3-dibromo-1,1,3,3-tetrafluoropropane in two stages; modification of the dehydrobromination conditions has now enabled better yields of tetrafluoroallene to be obtained:

$$CF_2Br_2 + CH_2{:}CF_2 \xrightarrow{(Ph\cdot CO)_2O_2} CF_2Br\cdot CH_2\cdot CF_2Br\ (51\%) \xrightarrow{KOH} CF_2Br\cdot CH{:}CF_2\ (89\%) \xrightarrow{KOH} CF_2{:}C{:}CF_2\ (33\%)$$

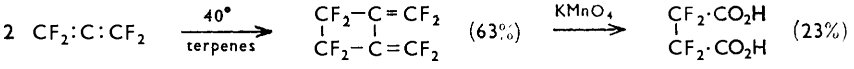
Tetrafluoroallene, b. p. —37·6° (cf. allene, b. p. —34·3°), is a colourless monomeric gas with a distinctive fluorocarbon-type odour that is quite different from the garlic-like smell associated with allenic hydrocarbons. It polymerises readily, especially under pressure when the liquid phase is present, and must thus be stored at —196° *in vacuo*.

The infrared (i.r.) spectrum of tetrafluoroallene vapour shows two intense bands, at 2070 and 1250 cm.$^{-1}$, and an intense doublet at 1034—1044 cm.$^{-1}$. The very characteristic band at 2070 cm.$^{-1}$ can be assigned to the asymmetric stretching vibration of the allenic system, which appears in the spectrum of allene[2] at 1980 cm.$^{-1}$ and in that of 1,1-difluoroallene[3] at 2020 cm.$^{-1}$; the symmetric stretching vibration of the allenic system in tetrafluoroallene will occur only in the Raman spectrum, which has not been examined. The band at 1250 cm.$^{-1}$ is assigned to the C–F stretching vibration.

The ultraviolet (u.v.) spectrum of tetrafluoroallene vapour shows a single broad maximum at 208—210 mμ (ε 230). The position of this maximum, at longer wavelength than for allene[4] (171 mμ) or its simple homologues (*e.g.*, $Et\cdot CH{:}C{:}CH_2$,[5] 170 mμ) suggests the occurrence of mesomerism of the type



Earlier workers[1] investigated only three reactions of tetrafluoroallene: (a) chlorination to yield 1,2,2,3-tetrachlorotetrafluoropropane; (b) dimerisation in the presence of free-radical scavengers to yield a compound thought to be perfluoro-(1,2-dimethylenecyclobutane) (I), since permanganate oxidation converted it into perfluorosuccinic acid:



(I)

and (c) polymerisation under autogenous pressure to give a white solid to which was assigned, mainly on the basis of *X*-ray-diffraction data, the structure $[-C(:CF_2)\cdot CF_2-]_n$.

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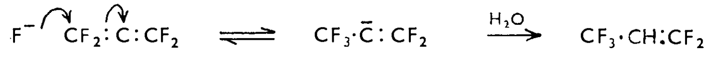
[1] Jacobs and Bauer, *J. Amer. Chem. Soc.*, 1959, **81**, 606.
[2] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1.
[3] Blomquist and Longone, *J. Amer. Chem. Soc.*, 1957, **79**, 4981.
[4] Sutcliffe and Walsh, *J.*, 1952, 899.
[5] Burr and Miller, *Chem. Rev.*, 1941, **29**, 419.

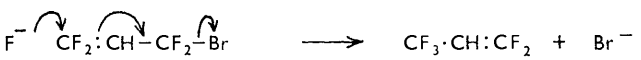
Studies are now reported of the chemical properties of tetrafluoroallene, involving addition, dimerisation, and polymerisation.

Ionic Reactions of Tetrafluoroallene.[6]—Perfluoro-olefins such as tetrafluoroethylene or hexafluoropropene characteristically resist attack by hydrogen halides and other reagents normally classed as electrophilic. In sharp contrast, tetrafluoroallene reacts rapidly with an excess of hydrogen bromide, chloride, or fluoride at —45, 20, and 20°, respectively, to give the compounds $CF_2X{\cdot}CH{:}CF_2$ (X = Br, Cl, F) in 89, 99, and 99% yield, respectively. The compounds $CF_2X{\cdot}CH{:}CF_2$ display typical fluoro-olefin resistance to electrophilic attack and do not react further with the hydrogen halides, under these conditions, to give the compounds $CF_2X{\cdot}CH_2{\cdot}CF_2X$.

Tetrafluoroallene is particularly sensitive to nucleophilic attack, more so than most other perfluoro-olefins; with neutral methanol at —24—20° it yields methyl 1,1,3,3-tetrafluoroprop-2-enyl ether,[7] and moist cæsium fluoride at 100° quantitatively converts it into 2*H*-pentafluoropropene:



The 2*H*-pentafluoropropene detected as a by-product (4% yield) during the preparation of tetrafluoroallene from 3-bromo-1,1,3,3-tetrafluoropropene probably arises in a similar manner *via* nucleophilic attack by fluoride ion; an alternative route is by S_N2' substitution [8] of the allylic bromine:



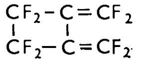
although, in a separate experiment, 2*H*-pentafluoropropene was formed in only 2% yield by reaction of the bromo-compound with potassium fluoride in dimethylformamide.

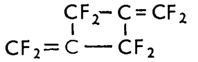
The susceptibility of tetrafluoroallene to nucleophilic attack suggests that its addition reactions with hydrogen halides involve nucleophilic attack by halide ion rather than electrophilic attack by proton.

Allene also reacts rapidly with an excess of hydrogen fluoride at low temperatures, presumably by electrophilic attack, to give 2,2-difluoropropane quantitatively.[9] Similarly, allene reacts with hydrogen chloride at —78° in the presence of bismuth trichloride to give a mixture of 2-chloropropene and 2,2-dichloropropane in which the former predominates when only one molar proportion of hydrogen chloride is used.[10] Addition of hydrogen halide to allene thus occurs in the opposite direction from that to tetrafluoroallene.

The reaction of tetrafluoroallene with an excess of chlorine, under conditions favouring ionic intermediates, yields 2,3-dichloro-1,1,3,3-tetrafluoropropene in 99% yield. Reaction under conditions favouring radical intermediates (in sunlight at 25° for 6 hours) gives 92% of 1,2,2,3-tetrachlorotetrafluoropropane and only 5% of the dichloropropene. The susceptibility of polyfluoro-olefins to chlorine-atom attack is well established.

Dimerisation of Tetrafluoroallene.—Tetrafluoroallene at 5—10 atm. and 20—120° in the presence of a terpene mixture, yields 66% of a colourless liquid dimer, b. p. 62°, together with a higher oligomer, probably a trimer (34%), but no polytetrafluoroallene; the reaction is slow at room temperature and is essentially complete after 7 days at 70°. Two dimers, (I) and (II), are possible, and it appeared that the reported [1] low yield of perfluorosuccinic

(I)




(II)

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[6] Banks, Haszeldine, and Taylor, *Proc. Chem. Soc.*, 1964, 121.

[7] Taylor, unpublished results.

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

[9] Austin, U.S.P. 2,585,529/1952.

[10] Jacobs and Johnson, *J. Amer. Chem. Soc.*, 1960, **82**, 6397.

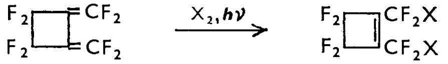
acid, obtained by permanganate oxidation of the dimer fraction, might be due to the presence of an appreciable amount of the head-to-tail dimer (II). Repetition of the oxidation provided evidence for the presence of only the head-to-head dimer (I); perfluorosuccinic acid was formed in not less than 32% yield, but no products were isolated that could have originated from isomer (II), *e.g.*, the unknown perfluorocyclobutane-1,3-dione or the known difluoromalonic acid.

The dimer fraction could not be resolved by gas–liquid chromatography and its ^{19}F nuclear magnetic resonance (n.m.r.) spectrum showed three absorption regions, as expected for isomer (I) but not for (II) which contains only two types of fluorine nucleus; however, the fine-structure of the three regions was too complicated to allow a detailed correlation with structure (I) to be made in the absence of data for related compounds.

The i.r. and u.v. spectra of the vapour of the dimer fraction were also consistent with structure (I): the i.r. spectrum contained two intense C=C stretching vibrations, at 1739 and 1789 cm.$^{-1}$, and strong u.v. absorption occurred at 232 mμ (ε 930). 1,2-Dimethylenecyclobutane similarly shows double-bond absorption at 1650—1750 cm.$^{-1}$ (doublet) and ultraviolet maxima at 237 and 246 mμ;[11] by contrast, 1,3-dimethylenecyclobutane has an i.r. spectrum containing a single olefinic absorption (1661 cm.$^{-1}$), and shows no u.v. maximum above 200 mμ.[12]

Photochemical bromination and chlorination of the dimer fraction provide good proof that it is entirely perfluoro-(1,2-dimethylenecyclobutane) (I): the ^{19}F n.m.r. spectra of the dihalides obtained are only compatible with compounds arising through 1,4-addition of halogen to the dienic system of (I), and no impurity bands are present:

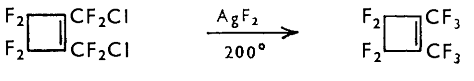
(I)



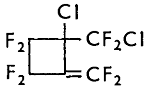
(IIIa: X = Cl) (86%)
(IIIb: X = Br) (92%)

The i.r. spectra of the dihalides are consistent with the cyclobutenes (IIIa) and (IIIb).

No reaction occurred when the dichloride (IIIa) was heated with antimony trifluoride activated with chlorine, and mercuric fluoride at 200° also proved ineffective. Silver difluoride gave a complex product from which a fluorocarbon C_6F_{10}, considered to be (IV), was isolated:



(IIIa) (IV) (25%)



(V)

Its b. p. (34·3°) and C=C i.r. absorption (1718 cm.$^{-1}$) are close to those reported[13] for perfluoro-(1,2-dimethylcyclobutene) (36°; 1715 cm.$^{-1}$), but the low yield, which impairs the value of the evidence for the structure of (IIIa), prevented the recording of its n.m.r. spectrum. A single attempt to convert the dibromide (IIIb) into (IV), by use of activated antimony trifluoride, was unsuccessful.

Zinc in dioxan at 100° converts the dichloride (IIIa) into perfluoro-(1,2-dimethylenecyclobutane). Since anhydrous zinc chloride in dioxan fails to cause isomerisation of (IIIa) into (V), it appears that dechlorination of (IIIa) does not proceed *via* isomerisation followed by a 1,2-elimination, but directly by 1,4-dechlorination. 1,4-Eliminations to give dienes are not unknown (*e.g.*, debromination of 1,4-dibromobut-2-ene to butadiene;[14] conversion of 1,4-dibromobut-2-yne into butatriene[15]), although 1,4-dichlorohexafluorobut-2-ene does not dechlorinate to hexafluorobutadiene under mild conditions.[16]

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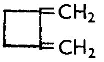
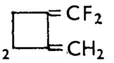
[11] Blomquist and Verdol, *J. Amer. Chem. Soc.*, 1955, **77**, 1806.
[12] Caserio, Parker, Piccolini, and Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5507.
[13] Mahler, *J. Amer. Chem. Soc.*, 1962, **84**, 4600.
[14] Thiele, *Annalen*, 1899, **308**, 333.
[15] Schubert, Liddicoet, and Lanka, *J. Amer. Chem. Soc.*, 1954, **76**, 1929, 1956.
[16] Haszeldine, *J.*, 1952, 4423.

Mechanism of the Dimerisation of Tetrafluoroallene.—The apparently exclusive formation of perfluoro-(1,2-dimethylenecyclobutane) from tetrafluoroallene is in accord with the preference shown by other allenes for head-to-head dimerisation; allene itself was originally reported to form only the head-to-head dimer (VI),[17] but recently it has been found that


(VI)

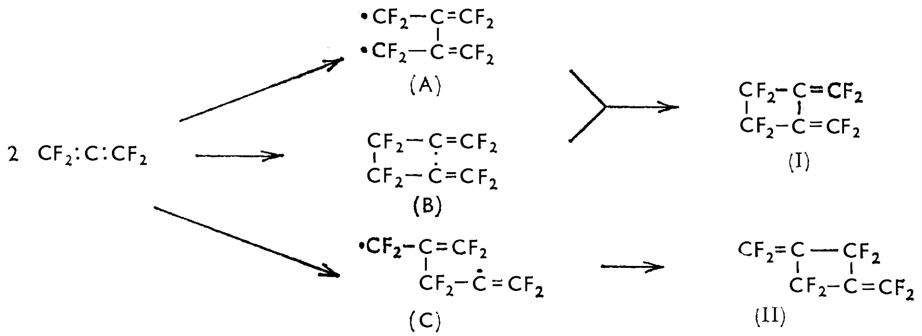

(VII)


(VIII)


(IXa: X = H; IXb: X = Br)

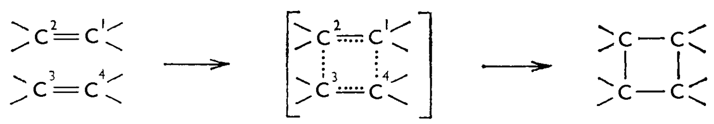
the dimerisation can yield an 85 : 15 mixture of (VI) and the head-to-tail dimer (VII);[18] 1,1-difluoroallene is believed to dimerise in only head-to-head fashion to give (VIII),[19] whereas both 1,1-dimethylallene and 3-bromo-1,1-dimethylallene afford a mixture of two of the three possible head-to-head dimers [(IXa) and (IXb), respectively].[20]

No accurate kinetic studies of the dimerisation of allenes have been reported, but the reaction appears to be analogous to the dimerisation of olefins to cyclobutanes.[21] The head-to-head dimerisation of tetrafluoroallene can be explained by considering the relative stabilities of the possible intermediate diradicals that can be formed. If there is time for rotation of the $\dot{\mathrm{C}}\mathrm{F}_2\text{—}\overset{|}{\mathrm{C}}=$ bond of the diradicals (A) or (C) before ring-closure occurs,[22] these radicals will be di- and mono-allylic, respectively.



Formation of (A) should thus be preferred to (C) or to the di-vinylic radical (B), and hence only (I) should result. [Formation of (A) should thus be preferred to (C) or to the di-vinylic radical (B), and hence only (1) should result.] However, a four-centre mechanism cannot be excluded.

Successful prediction of the direction of addition in cyclobutane formation by a four-centre process can be made only if it is assumed that the bond between C^2 and C^3 is formed slightly in advance of that between C^1 and C^4, so that a certain degree of free-radical character can be associated with the C^1 and C^4 sites, despite the fact that the electrons remain paired and no rotation about the C^1–C^2 and C^3–C^4 bonds occurs:[21]



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[17] Lebedev *et al.*, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1359 (*Chem. Abs.*, 1915, **9**, 799).

[18] Williams and Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 4269.

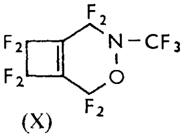
[19] Knoth and Coffman, *J. Amer. Chem. Soc.*, 1960, **82**, 3873.

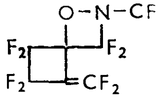
[20] Jacobs and Petty, *J. Org. Chem.*, 1963, **28**, 1360.

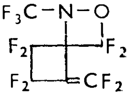
[21] Roberts and Sharts, *Org. Reactions*, 1962, **12**, 1.

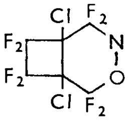
[22] Jacobs and Illingworth, *J. Org. Chem.*, 1963, **28**, 2692.

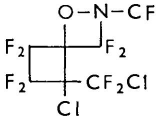
Reaction of Tetrafluoroallene Dimer with Trifluoronitrosomethane.—Perfluoro-(1,2-dimethylenecyclobutane) combines readily with trifluoronitrosomethane at room temperature to give a quantitative yield of a 1 : 1 adduct, which, on the basis of the evidence presented below, is probably perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene} (X).

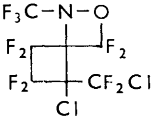

(X)


(XI)


(XII)


(XIII)


(XIV)


(XV)

It is a colourless liquid, b. p. 106°, with an acrid odour, and the presence of a C=C bond, indicated by a weak, sharp absorption at 1718 cm.$^{-1}$ in the i.r. spectrum of the vapour, is confirmed by the quantitative formation of the saturated dichloride $C_7Cl_2F_{11}NO$ when the adduct is chlorinated photochemically. Gas–liquid chromatography does not show the presence of more than one isomer in the 1 : 1 adduct or its dichloride.

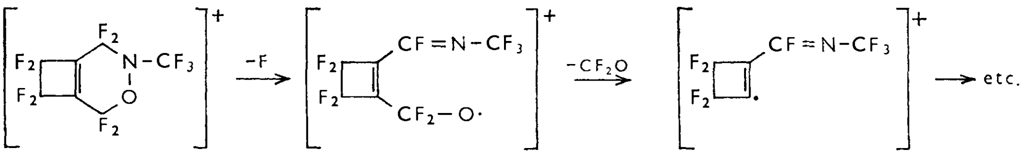
Three reasonable structures can be written for the 1 : 1 adduct (X—XII) and for its dichloride (XIII—XV). The ^{19}F n.m.r. spectrum of the adduct is compatible only with (X), and besides providing confirmation of molecular weight, the mass spectrum shows several features which reinforce the evidence for the structure (X). Two of the apparent modes of decomposition are:

$$C_7F_{11}NO^+ \xrightarrow{-F} C_7F_{10}NO^+ \xrightarrow{-CF_2O} C_6F_8N^+ \xrightarrow{-CF_3N} C_5F_5^+$$

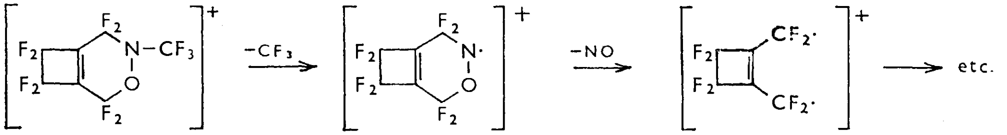
and

$$C_7F_{11}NO^+ \xrightarrow{-CF_3} C_6F_8NO^+ \xrightarrow{-N} C_6F_8O^+ \xrightarrow{-O} C_6F_8^+ \xrightarrow{-CF_2} C_5F_6^+$$

There is no indication of preliminary loss of a CF_2 fragment, which militates against (XI) and (XII) because these contain exocyclic $:CF_2$ groups; the mass spectrum of $C_6F_5{\cdot}N{:}CF_2$,[23] for example, shows a prominent peak at a mass number equivalent to C_6F_5N. The loss of CF_2O must have been preceded to some extent by loss of a fluorine atom or ion, since a metastable peak is observed at mass 188, corresponding to the transition $(188^+)\ 304^+ \longrightarrow 238^+ + 66$ $(C_7F_{10}NO^+ \longrightarrow C_6F_8N^+ + CF_2O)$. Loss of a CF_2O fragment cannot be reconciled with (XI) unless extensive rearrangement occurs, but both of the degradations shown above can be accommodated by (X):



(X)



(X)

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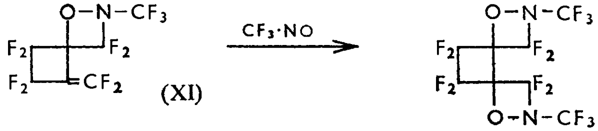
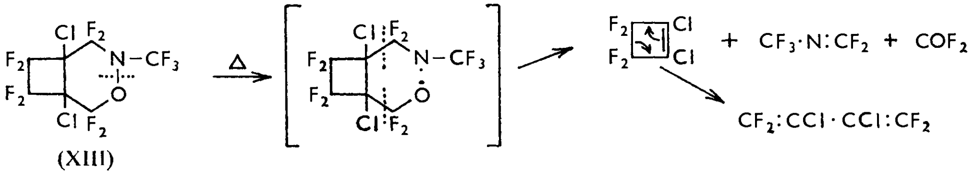
[23] Birchall, Haszeldine, and Umfreville, unpublished results.

Although the adduct combines smoothly with chlorine, it does not react with trifluoronitrosomethane, even under conditions vigorous enough to decompose the latter; this seems to be evidence against (XI) and (XII), since compounds with these structures might be expected to undergo further cyclo-addition reactions, *e.g.*,

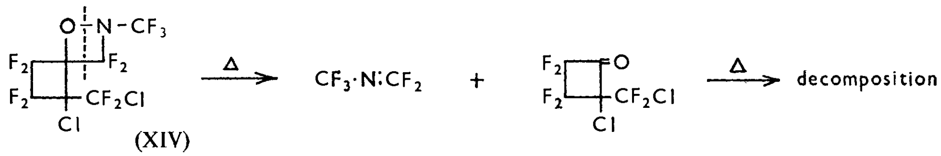

(XI)

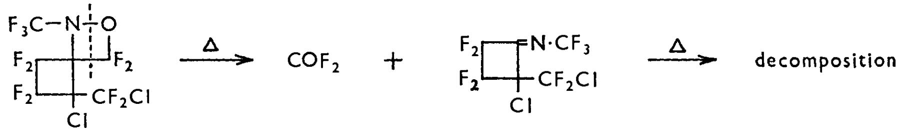
An unsuccessful attempt was made to prepare the unknown perfluoro(methylenecyclobutane) by heating tetrafluoroallene with tetrafluoroethylene; it is thus not yet known whether a spirocyclic oxazetidine analogous to (XI) and (XII) can be prepared from perfluoro(methylenecyclobutane).

By analogy with the thermal decomposition of polyfluoro-oxazetidines,[24] it might be expected that thermal decomposition of (XIII) would be initiated by fission of the N–O bond and would eventually give rise to carbonyl fluoride, perfluoro(methylenemethylamine), and 1,2-dichlorotetrafluorocyclobutene and/or 2,3-dichlorotetrafluorobutadiene:


(XIII)

The dichloride was found to be considerably more stable to heat than expected; it was only 73% decomposed when pyrolysed in platinum at 605°/1 mm. with a contact time of *ca.* 17 sec. This is strong evidence against the spirocyclic oxazetidine structures (XIV) and (XV); all the polyfluoro-oxazetidines so far examined are completely decomposed at 400—500°/3 mm. with much shorter contact times.[24,25] The pyrolysis of the dichloride gave a complex product containing carbonyl fluoride (77%), perfluoro(methylenemethylamine) (56%), tetrafluoroethylene, hexafluoroethane, chlorotrifluoroethylene, trifluoromethyl isocyanate, and unidentified material; neither 1,2-dichlorotetrafluorocyclobutene nor 2,3-dichlorotetrafluorobutadiene was detected. These products do not provide clear-cut evidence for the structure of the dichloride, since the formation of carbonyl fluoride and perfluoro(methylenemethylamine) as major products can be interpreted in three ways: (i) the dichloride is (XIII) and it decomposes partly according to the scheme predicted; (ii) the dichloride is a mixture of the oxazetidines (XIV) and (XV), each of which would almost certainly decompose thermally to yield one of the major products:


(XIV)


(XV)

and (iii) the dichloride is a mixture of all three isomers (XIII—XV).

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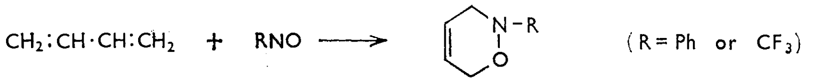
[24] Barr, Haszeldine, and Willis, *J.*, 1961, 1351.

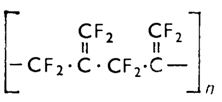
[25] Banks, Bennett, Haszeldine, and Sutcliffe, unpublished results.

Summarising, the 1 : 1 adduct of tetrafluoroallene dimer with trifluoronitrosomethane is considered to be (X), mainly on the basis of spectroscopic evidence, this being supported by chemical evidence which rules out the presence of (XI) or (XII) in any quantity.

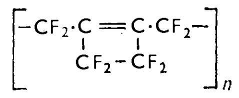
It may be noted that 1,4-addition reactions of the type which gives rise to (X) are known for butadiene, *e.g.*,[26,27] and for hexafluorobutadiene.[27]



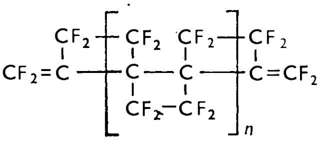
Homopolymerisation of Tetrafluoroallene.—The facile homopolymerisation of tetrafluoroallene at ambient temperatures under moderate pressure [1] has been confirmed; the monomer is converted, in 80% yield, into an involatile, waxy, white solid when kept at 15—20°/10 atm. (initial pressure) for 44 hours. By contrast, allene is converted into a mixture of dimers (5%), oligomers (trimers to hexamers, 70%), and polymer (25%) when kept at 140° for 3 days.[17,28] The polymerisation of tetrafluoroallene is accelerated by ultraviolet light and, to a greater extent, by free-radical initiators; this indicates that the polymerisation is a free-radical chain reaction, which is confirmed by the complete inhibition of polymerisation by free-radical scavengers.



(XVI)

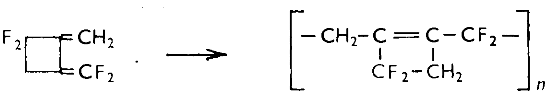


(XVII)

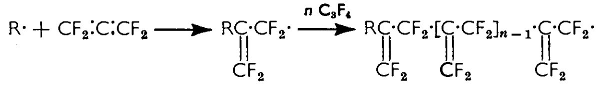


(XVIII)

The acylic structure (XVI) has been suggested for polytetrafluoroallene on the basis of *X*-ray-diffraction data,[29] and it has also been argued [1,29] that the intense i.r. band at 1721 cm.$^{-1}$ is consistent with the presence of only exocyclic unsaturation. However, the position of C=C absorption in the i.r. spectrum of the polymer is close to that assigned to the olefinic bond in perfluoro-(1,2-dimethylcyclobutene) (1715 cm.$^{-1}$),[13] which has a structure analogous to the repeating unit of (XVII), a possible structure for polytetrafluoroallene. A third possible structure for polytetrafluoroallene, (XVIII), appears to be ruled out, since a polymer of this type with high molecular weight and only terminal unsaturation would not be expected to show such strong i.r. absorption at 1721 cm.$^{-1}$. Support for (XVI), and against (XVII), is provided by the fact that the dimer of tetrafluoroallene fails to polymerise at 100° under pressure and in the absence of air, unlike the dimer of 1,1-difluoroallene, which polymerises spontaneously under normal conditions to a product thought to have a structure similar to that of (XVII): [19]



The direction of free-radical attack on tetrafluoroallene is not yet known; irradiation of a dilute solution of tetrafluoroallene in trifluoroiodomethane gave only polytetrafluoroallene and neither the 1 : 1 adduct [$CF_3{\cdot}C(\dot{:}CF_2){\cdot}CF_2I$ or $CF_3{\cdot}CF_2{\cdot}C(\dot{:}CF_2)I$] nor telomer iodides. However, the initiation and propagation steps



$$R\cdot + CF_2{:}C{:}CF_2 \longrightarrow R\underset{\substack{\| \\ CF_2}}{C}{\cdot}CF_2\cdot \xrightarrow{n\ C_3F_4} R\underset{\substack{\| \\ CF_2}}{C}{\cdot}CF_2{\cdot}[\underset{\substack{\| \\ CF_2}}{C}{\cdot}CF_2]_{n-1}{\cdot}\underset{\substack{\| \\ CF_2}}{C}{\cdot}CF_2\cdot$$

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[26] McKee, " The Chemistry of Heterocyclic Compounds," ed. Wiley, Interscience, New York, 1962, p. 332.

[27] Banks, Barlow, and Haszeldine, in the press.

[28] Weinstein and Fenselau, *Tetrahedron Letters*, 1963, 1463.

[29] McCullough, Jacobs, and Bauer, *Chem. and Ind.*, 1957, 706.

seem the most likely for the polymerisation of the tetrafluoroallene, since only these involve allylic radicals.

In the absence of light and impurities that might provide free radicals, tetrafluoroallene polymerises at an average rate of *ca.* 2%/hours during 40 hours at 20°; under these conditions, a small amount of dimer is also formed. The radicals for initiation of polymerisation could be (A) or (B), postulated as intermediates in the formation of perfluoro-(1,2-dimethylenecyclobutane) from tetrafluoroallene, or radicals produced by disproportionation of the monomer:

$$2\mathrm{CF_2{:}C{:}CF_2} \rightleftharpoons \mathrm{CF_2{:}CF{\cdot}CF_2{\cdot}} + \mathrm{CF{\vdots}C{\cdot}CF_2{\cdot}}$$

(cf. the initiation step suggested for the thermal homopolymerisation of styrene[30]).

EXPERIMENTAL

I.r. and u.v. spectra were measured with a Perkin-Elmer spectrophotometer model 21 (sodium chloride optics) and a Unicam S.P. 700 spectrophotometer, respectively. ^{19}F n.m.r. spectra were obtained with an A.E.I. RS2 spectrometer operating at 60 Mc./sec., chemical shifts and coupling constants being determined by the standard side-band techniques with trifluoroacetic acid as external reference. Mass spectra were obtained with an A.E.I. MS/2H instrument (single-focussing sector magnet) of resolution 1 in 700. Perkin-Elmer Fraktometers (models 116 and 451) were used for gas–liquid chromatography; molar % compositions were estimated from peak areas by triangulation, and columns were usually calibrated with known mixtures. Thermal gravimetric analysis of polymers was effected with a Stanton Thermal Balance.

Trifluoronitrosomethane[31] was purified by precise distillation in a semi-automatic low-temperature still.

1,3-*Dibromo*-1,1,3,3-*tetrafluoropropane*.—Dibromodifluoromethane (955 g., 4·55 moles), 1,1-difluoroethylene (66·1 g., 1·03 moles), and benzoyl peroxide (10·0 g.), heated in a 1·4-l. stainless-steel rocking autoclave at 110° for 5 hr., gave 1,1-difluoroethylene (21·2 g., 0·33 mole, 32%), dibromodifluoromethane (758 g., 3·61 moles, 79%), 1,3-dibromo-1,1,3,3-tetrafluoropropane (98·9 g., 0·36 mole, 51% yield based on $\mathrm{CH_2{:}CF_2}$ consumed) (Found: C, 13·1; H, 0·8; Br, 58·5; F, 27·8. Calc. for $\mathrm{C_3H_2Br_2F_4}$: C, 13·1; H, 0·7; Br, 58·4; F, 27·7%), b. p. 72°/300 mm., n_D^{25} 1·3977 (lit.,[32] 42·5°/85 mm. and 1·3974), and a residue (90·5 g.) presumably consisting of telomers, $\mathrm{CF_2Br{\cdot}[CH_2{\cdot}CF_2]_{\mathit{x}}{\cdot}Br}$.

3-*Bromo*-1,1,3,3-*tetrafluoropropene*.—The literature method[1] was adopted, with minor alterations, which led to improved yields. 1,3-Dibromo-1,1,3,3-tetrafluoropropane (220 g., 0·80 moles) was added drop-wise to potassium hydroxide pellets (112 g., 2·0 moles) in a wide-mouthed 750-ml. Pyrex flask fitted with a stainless-steel anchor-stirrer driven by a high-torque motor; the mixture was heated to 50—60° and the products were swept into traps at −72° and −196° with a slow stream of oxygen-free nitrogen at 30—35 cm. pressure. When half of the dibromotetrafluoropropane had been added, the nitrogen pressure was increased to atmospheric and more potassium hydroxide pellets (112 g.) were placed in the flask; the experiment was then continued as before. Distillation of the contents of the cold traps gave tetrafluoroallene (0·75 g., 6·7 mmoles, 1% yield based on $\mathrm{CF_2Br{\cdot}CH_2{\cdot}CF_2Br}$ consumed), 3-bromo-1,1,3,3-tetrafluoropropene (114 g., 0·59 mole, 89% based on $\mathrm{CF_2Br{\cdot}CH_2{\cdot}CF_2Br}$ consumed) (Found: Br, 41·0%; *M*, 192. Calc. for $\mathrm{C_3HBrF_4}$: Br, 41·4%; *M*, 193), b. p. 34°/760 mm. (lit.,[32] 35°), and 1,3-dibromo-1,1,3,3-tetrafluoropropane (38 g., 17% recovery).

An experiment at 100—120°/1 atm. gave 3-bromo-1,1,3,3-tetrafluoropropene (30%) and tetrafluoroallene (12%). Jacobs and Bauer[1] effected the dehydrobromination of 1,3-dibromo-1,1,3,3-tetrafluoropropane with potassium hydroxide pellets at 100°/1 atm. and obtained 3-bromo-1,1,3,3-tetrafluoropropene (51%) and tetrafluoroallene (5%).

Tetrafluoroallene.—Pelleted potassium hydroxide (112 g., 2 moles) was heated to 110°, under a slow stream of oxygen-free nitrogen, in a wide-mouthed, flanged, 750-ml. Pyrex flask equipped with a nichrome high-torque stirrer and a double-surface water-cooled reflux condenser topped with a cold finger (−23°) condenser. 3-Bromo-1,1,3,3-tetrafluoropropene (131·0 g., 0·68 mole) was added drop-wise to the potassium hydroxide, and fresh potassium

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[30] Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 183.

[31] Barr and Haszeldine, *J.*, 1955, 1881; Dinwoodie and Haszeldine, *J.*, 1965, in the press.

[32] Tarrant, Lovelace, and Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 2783.

hydroxide pellets were added (total, 224 g.) as discoloration occurred. Distillation of the product, collected in traps at −72 and −196°, gave tetrafluoroallene (25·1 g., 0·224 mole, 34% yield based on $CF_2{:}CH{\cdot}CF_2Br$ consumed) (Found: C, 32·1%; *M*, 112. Calc. for C_3F_1: C, 32·1%; *M*, 112), b. p. −37·6° (lit.,[1] −38°), 1,1,3,3,3-pentafluoropropene (3·7 g., 28 mmoles, 4%) (Found: C, 27·1; H, 0·6%; *M*, 133. Calc. for C_3HF_5: C, 27·3; H, 0·8%; *M*, 132), b. p. −23 to −24°/755 mm. (lit.,[33] −21°), with correct i.r. spectrum, and 3-bromo-1,1,3,3-tetrafluoropropene (3·9 g., 3% recovery).

Reaction of Tetrafluoroallene with Hydrogen Halides.—(a) *With hydrogen fluoride.* Tetrafluoroallene (1·18 g., 10·5 mmoles) and anhydrous hydrogen fluoride [obtained by heating, *in vacuo*, anhydrous potassium bifluoride (1·0 g., 12·8 mmoles)] were kept in a 17-ml. stainless-steel autoclave at −72° for 12 hr., and then at 20° for 2 hr., to give, after removal of the excess of hydrogen fluoride with potassium fluoride, 2*H*-pentafluoropropene (1·34 g., 10·2 mmoles, 99% yield) (Found: *M*, 131. Calc. for C_3HF_5: *M*, 132), which was spectroscopically and chromatographically identical with an authentic sample.

(b) *With hydrogen chloride.* Tetrafluoroallene (1·15 g., 10·3 mmoles) and anhydrous hydrogen chloride (0·37 g., 10·3 mmoles), kept in a 54-ml. Pyrex ampoule at 20° for 12 hr., gave 3-chloro-1,1,3,3-tetrafluoropropene (1·51 g., 99% yield) (Found: C, 24·2; H, 0·9; Cl, 24·0%; *M*, 150. Calc. for C_3HClF_4: C, 24·2; H, 0·7; Cl, 23·8%; *M*, 149), b. p. 13·9° (isoteniscope) (lit.,[34] 14·5°), which showed C=C i.r. absorption at 1757 cm.$^{-1}$.

The vapour pressure of 3-chloro-1,1,3,3-tetrafluoropropene, measured over the range −50—10°, is given by the equation $\log_{10}p$ (cm.) $= 6{\cdot}45 - 1314/T$, whence Trouton's constant is 21·0, and the latent heat of vaporisation is 6010 cal. mole^{-1}.

(c) *With hydrogen bromide.* Tetrafluoroallene (1·23 g., 11·0 mmoles) and anhydrous hydrogen bromide (0·89 g., 11·0 mmoles), kept in the dark in a 50-ml. Pyrex ampoule at −45° for 1 hr., gave tetrafluoroallene (1·4 mmoles, 13%), hydrogen bromide (1·2 mmoles, 11%), and 3-bromo-1,1,3,3-tetrafluoropropene (1·65 g., 8·6 mmoles, 89% based on $CF_2{:}C{:}CF_2$ consumed) (Found: *M*, 193. Calc. for C_3HBrF_4: *M*, 193), which was spectroscopically and chromatographically identical with an authentic sample prepared by dehydrobromination of 1,3-dibromo-1,1,3,3-tetrafluoropropane.

Reaction of Tetrafluoroallene with Moist Cæsium Fluoride.—Tetrafluoroallene (1·28 g., 11·4 mmoles), an old, undried sample of cæsium fluoride (2·0 g.), and a 50 : 50 mixture (0·4 g.) of *p*-menthadiene with α-terpinolene were heated in a 350-ml. Dreadnought ampoule at 100° for 30 min. The volatile product (11·0 mmoles) was examined by gas–liquid chromatography and i.r. spectroscopy and was found to be a mixture of tetrafluoroallene (25%) and 1,1,3,3,3-pentafluoropropene (75%).

Reaction of 3-*Bromo*-1,1,3,3-*tetrafluoropropene with Potassium Fluoride.*—An exothermic reaction occurred when a mixture of 3-bromo-1,1,3,3-tetrafluoropropene (2·5 g., 13·0 mmoles), anhydrous potassium fluoride (5 g.), and dimethylformamide (20 ml.), sealed *in vacuo* in a 50-ml. Pyrex ampoule, was warmed from −196° to room temperature; the mixture became red. After 7 days, the product was distilled to yield carbon dioxide, 1,1,3,3,3-pentafluoropropene (0·24 mmole, 2%) and unidentified material.

Chlorination of Tetrafluoroallene.—(a) *In the dark.* A mixture of tetrafluoroallene (0·627 g., 5·6 mmoles) and chlorine (0·781 g., 11·5 mmoles), kept in the dark in a 45-ml. Dreadnought tube at −72° for 12 hr. and then at 20° for 7 days, gave unreacted chlorine (5·71 mmoles, 50%) and 2,3-dichloro-1,1,3,3-tetrafluoropropene (5·59 mmoles, 99%) (Found: C, 19·9; Cl, 38·7%; *M*, 184. Calc. for $C_3Cl_2F_4$: C, 19·7; Cl, 38·8%; *M*, 183), b. p. 44·9° (isoteniscope) (lit.,[35] 44·8°), which showed C=C i.r. absorption at 1736 cm.$^{-1}$.

The vapour pressure of 2,3-dichloro-1,1,3,3-tetrafluoropropene, measured over the range −25—30°, is given by the equation $\log_{10}p$ (cm.) $= 6{\cdot}73 - 1541/T$, whence Trouton's constant is 22·2, and the latent heat of vaporisation is 7060 cal. mole^{-1}.

(b) *In sunlight.* A mixture of tetrafluoroallene (0·694 g., 6·2 mmoles) and chlorine (0·875 g., 12·5 mmoles), sealed in a 45-ml. Pyrex ampoule, was exposed to sunlight for 6 hr., and gave chlorine (0·38 mmoles, 3%), 2,3-dichloro-1,1,3,3-tetrafluoropropene (0·27 mmoles, 5%), and 1,2,2,3-tetrachlorotetrafluoropropane (5·67 mmoles, 92%) (Found: C, 18·8; Cl, 55·6. Calc. for $C_3Cl_4F_4$: C, 18·9; Cl, 55·9%), b. p. 112—113° (lit.,[1] 111·8°).

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

[34] Ilgenfritz, U.S.P. 2,904,601/1959.

[35] Miller and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4164.

Dimerisation of Tetrafluoroallene.—(a) *At* 20°. Tetrafluoroallene (1·13 g., 10 mmoles) and a 50 : 50 mixture (0·5 g.) of *p*-menthadiene with α-terpinolene were kept, in the dark, in a sealed 45-ml. Dreadnought ampoule at 20° for 15 weeks. Fractionation of the product gave tetrafluoroallene (0·80 mmoles; 8% recovery) and perfluoro(1,2-dimethylenecyclobutane) (I) (0·97 g., 4·33 mmoles, 94% based on $CF_2{:}C{:}CF_2$ consumed) (Found: C, 32·4%; *M*, 224. Calc. for C_6F_8: C, 32·1%; *M*, 224).

(b) *At* 70°. Tetrafluoroallene (14·4 g., 0·128 mole) and the terpene mixture (1·0 g.), heated together, in the dark, in a sealed 350-ml. Dreadnought ampoule at 70° for 1 week, gave tetrafluoroallene (3·9 mmoles, 3% recovery), perfluoro-(1,2-dimethylenecyclobutane) (I) (8·95 g. 0·04 mole, 66% yield based on $CF_2{:}C{:}CF_2$ consumed), b. p. 62—63°/758 mm. (lit.,[1] 64°), which was spectroscopically identical with the material from (a), and a colourless liquid (4·06 g.), b. p. 55—58°/100 mm., which is probably a trimer of tetrafluoroallene (Found: *M*, 341. Calc. for C_9F_{12}: *M*, 336).

Properties and Reactions of Perfluoro-(1,2-*dimethylenecyclobutane*) (I).—(a) *Physical properties.* The vapour pressure, measured over the range 10—50°, is given by the equation $\log_{10}p$ (cm.) = 7·20 − 1783/*T*. The calculated b. p. is 62·0°, Trouton's constant is 24·0, and the latent heat of vaporisation is 8160 cal. mole^{-1}.

The n.m.r. spectrum of perfluoro-(1,2-dimethylenecyclobutane) shows three regions of ^{19}F absorption, each with complex fine-structure [band number, p.p.m. from $CF_3{\cdot}CO_2H$, multiplicity: (1) −2·34, complex; (2) 0·93, possibly a 1 : 2 : 1 triplet of quartets; (3) 38·20, complex). The proton absorption for 1,2-dimethylenecyclobutane has not been reported, but 1,3-dimethylenecyclobutane shows two regions of absorption, both of which are symmetrical quintets,[12] as expected from first-order theory. The ^{19}F n.m.r. spectrum of perfluoro-(1,3-dimethylenecyclobutane) should show an absorption pattern similar to that of its hydrocarbon analogue, but even a weak absorption of this type was not observed.

(b) *Oxidation.* The cyclobutane (3·45 g., 15·4 mmoles) was added drop-wise to a stirred, ice-cold solution of potassium permanganate (5·10 g., 32·2 mmoles) in AnalaR acetone (200 ml.). The reaction mixture was stirred at 0° for 2 hr., then at 20° for 2 hr., and then water (200 ml.) was added and the acetone was removed *in vacuo*. The aqueous solution was acidified (H_2SO_4), decolourised with sulphur dioxide, and extracted continuously with ether (24 hr.). The ethereal extract was dried ($CaSO_4$) and treated with aniline to yield dianilinium perfluorosuccinate (1·87 g., 4·97 mmoles, 32%, after recrystallisation from acetone–chloroform) (Found: C, 51·0; H, 4·4; N, 7·2. Calc. for $C_{16}H_{16}F_4O_4N_2$: C, 51·1; H, 4·3; N, 7·4%), m. p. 220° (lit.,[36] 224—225°), i.r. spectrum identical with that of an authentic sample.

Di-(*S*-benzylthiouronium) perfluorosuccinate was prepared by standard techniques from the product of a second oxidation experiment; it had m. p. and mixed m. p. 188—189° (lit.,[36] 189—190°).

(c) *Chlorination.* The cyclobutane (3·61 g., 16·1 mmoles) and chlorine (17 mmoles), in a 120-ml. silica ampoule, were irradiated for 10 hr. with light from three 150-w tungsten-filament lamps placed at a distance of 10 cm. The product was shaken with mercury, to remove the excess of chlorine, and then fractionated to yield 1,2-*bis*(*chlorodifluoromethyl*)*tetrafluorocyclobutene* (IIIa) (4·11 g., 13·9 mmoles, 86%) (Found: C, 24·5; Cl, 23·7%; *M*, 294. $C_6Cl_2F_8$ requires C, 24·4; Cl, 24·1%; *M*, 295), b. p. 91—92° (Siwoloboff), which showed weak C=C i.r. absorption at 1701 cm.$^{-1}$. Its ^{19}F n.m.r. spectrum consists of two bands: the first, at −24·5 p.p.m. from $CF_3{\cdot}CO_2H$, is a symmetrical 1 : 4 : 6 : 4 : 1 quintet (*J* 2·3 c./sec.), and is assigned to the fluorine nuclei of the CF_2Cl groups; the second, at 37·8 p.p.m., is of identical multiplicity (*J* 2·4 c./sec.), and is assigned to the fluorine nuclei of the ring CF_2 groups.

(d) *Bromination.* The cyclobutane (3·40 g., 15·2 mmoles) and bromine (2·38 g., 14·9 mmoles), in a 100-ml. Pyrex ampoule, showed no sign of reaction after 12 hr. in the dark. Irradiation for 15 min. with light from a 150-w tungsten-filament spotlight placed at a distance of 20 cm. caused the bromine colour to disappear, and the sole product was 1,2-*bis*(*bromodifluoromethyl*)*tetrafluorocyclobutene* (IIIb) (5·32 g., 13·8 mmoles, 92%) (Found: C, 18·6; Br, 41·2. $C_6Br_2F_8$ requires C, 18·7; Br, 41·7%), b. p. 123—124° (Siwoloboff), which showed weak C=C i.r. absorption at 1689 cm.$^{-1}$. Its ^{19}F n.m.r. spectrum consisted of two symmetrical 1 : 4 : 6 : 4 : 1 quintets (*J* 1·87 and 2·24 c./sec.) at −27·65 and 36·75 p.p.m., respectively; the first quintet is assigned to the fluorine nuclei of the CF_2Br groups, and the second to those of the ring CF_2 groups.

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[36] Evans and Tatlow, *J.*, 1954, 3779.

(e) *Reaction with trifluoronitrosomethane.* The cyclobutane (2·39 g., 10·7 mmoles) and trifluoronitrosomethane (1·07 g., 10·8 mmoles) were kept in a 90-ml. Dreadnought ampoule at 20° in the dark for 72 hr. Distillation of the product gave *perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene}* (X) (3·30 g., 10·2 mmoles, 95%) (Found: C, 25·9; N, 4·4%; *M*, 322. $C_7F_{11}NO$ requires C, 26·0; N, 4·3%; *M*, 323), b. p. 106° (Siwoloboff), which showed a weak C=C i.r. absorption at 1718 cm.$^{-1}$.

TABLE 1.

^{19}F Nuclear magnetic resonance spectrum of perfluoro-{4-methyl-3-oxa-4-azabicyclo-[4,2,0]oct-1(6)-ene}.

Chemical shift (p.p.m.)	Multiplet structure	Assignment to fluorine nuclei *	Spin–spin coupling constants (c./sec.)
−9·29	1 : 2 : 1 triplet	(1)	$J_{13} = 11·7$
7·78	Broad singlet (width at half-height = 6·4 c./sec.)	(2)	$J_{12} = J_{14} \approx 0$
23·17	Broad 1 : 3 : 3 : 1 quartet (width at half-height = 6·5 c./sec.)	(3)	$J_{24} = J_{34} = 1·95$
32·48	1 : 4 : 6 : 4 : 1 quintet	(4)	

* The assignment is as shown:

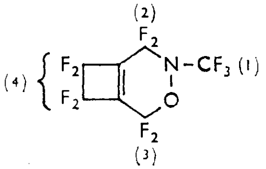

TABLE 2.

Mass spectrum of perfluoro-4-{methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene}, obtained at 130° with an electron energy of 70 ev.

m/e	Relative intensity (%)	*m/e*	Relative intensity (%)	*m/e*	Relative intensity (%)	*m/e*	Relative intensity (%)
323	0·5	193	4·0	131	0·5	71	1·0
304	6·0	188	6·0	124	23·0	*69* *	*100·0*
266	0·5	174	7·0	121	2·0	64	0·5
254	0·5	169	2·0	117	2·0	62	1·0
243	1·0	166	2·0	114	4·5	55	4·0
240	5·0	164	1·0	112	10·0	50	3·0
238	4·0	162	1·0	105	5·0	47	2·0
225	4·0	159	1·0	100	4·5	43	0·5
224	61·5	157	0·5	93	17·0	31	12·0
219	0·5	155	57·0	90	1·0	30	5·0
216	2·5	143	11·0	86	1·0		
212	7·0	138	4·0	81	0·5		
205	7·0	136	1·0	74	12·0		

* CF_3 peak.

The ^{19}F n.m.r. spectrum consists of four absorption regions, which are analysed in Table 1. Mass-spectral data for (X) are given in Table 2.

Reactions of 1,2-*Bis*(*chlorodifluoromethyl*)*tetrafluorocyclobutene* (IIIa).—(a) *Dechlorination.* The cyclobutene (1·829 g., 6·2 mmoles), acid-washed (with 2N-HCl) zinc dust (3·66 g.), and redistilled dioxan (50 ml.) were shaken in a 150-ml. Pyrex ampoule at 100° for 3 hr., to give perfluoro-(1,2-dimethylenecyclobutane) (I) (4·01 mmoles, 65%) and the original cyclobutene (0·19 mmoles, 3% recovery).

(b) *Reaction with zinc chloride.* A mixture of the cyclobutene (1·0 g., 3·39 mmoles), anhydrous zinc chloride (0·2 g.), and dioxan (25 ml.), heated in a 50-ml. Pyrex ampoule at 100° for 12 hr., gave a mixture (1·4 g.) that was shown by gas–liquid chromatography and i.r. analysis to contain the original cyclobutene (1·0 g., 100% recovery) and dioxan.

(c) *Reaction with silver difluoride.* The cyclobutene (1·20 g., 4·1 moles) was heated with freshly-prepared silver difluoride (1·75 g., 12 mmoles) in a 16-ml. stainless-steel autoclave at 200° for 7 days. Fractionation of the product *in vacuo*, followed by separation of the material which condensed at −67° and −72°, using gas–liquid chromatography (4 m. 30% w/w Kel-F 90 grease on Celite at 75°; N_2 flow-rate, 60 ml./min.), gave a compound believed to be perfluoro-(1,2-dimethylcyclobutene) (IV) (25% yield based on chromatographic-peak area measurements) (Found: C, 27·8%; *M*, 263. Calc. for C_6F_{10}: C, 27·5%; *M*, 262), b. p. 34·3° (isoteniscope) (lit.,[13] 36°). At least four other products were formed in the reaction.

The original cyclobutene was recovered in 94 and 86% yield, respectively, after treatment with SbF_3–Cl_2 at 200° for 4 hr. and with HgF_2 at 100° for 12 hr.

Reaction of Tetrafluoroallene with Tetrafluoroethylene.—Tetrafluoroallene (2·35 g., 21·0 mmoles), tetrafluoroethylene (10·5 g., 105 mmoles), and a 50 : 50 mixture (0·5 g.) of *p*-menthadiene and α-terpinolene, heated in a 350-ml. Dreadnought tube at 60° for 96 hr., gave tetrafluoroethylene (99·2 mmoles, 95% recovery), tetrafluoroallene (5·9 mmoles, 27% recovery), and perfluoro-(1,2-dimethylenecyclobutane) (I) (1·38 g., 6·2 mmoles, 82% based on $CF_2{:}C{:}CF_2$ consumed).

Reactions of Perfluoro-{*4-methyl-3-oxa-4-azabicyclo*[4,2,0]*oct-1*(6)*-ene*} (X).—(a) *With chlorine.* The bicyclo-octene (1·10 g., 3·4 mmoles) and chlorine (0·71 g., 10 mmoles) were sealed in a 63-ml. Pyrex ampoule and irradiated for 72 hr. with light from three 150-w tungsten-filament lamps placed at a distance of 10 cm. The product was fractionated, in the absence of grease or mercury, to yield chlorine (6·4 mmoles) and *perfluoro-*(*1,6-dichloro-4-methyl-3-oxa-4-azabicyclo*[4,2,0]*octane*) (XIII) (1·25 g., 94%) (Found: C, 21·3; Cl, 18·0; N, 3·6. $C_7Cl_2F_{11}NO$ requires C, 21·3; Cl, 18·0; N, 3·6%), b. p. 155—156° (Siwoloboff).

(b) *With trifluoronitrosomethane.* The bicyclo-octene (1·13 g., 3·5 mmoles) and trifluoronitrosomethane (2·56 g., 25·9 mmoles), kept in a 90-ml. Dreadnought tube at 20° for 7 days and then at 70° for 1 day, gave the bicyclo-octene (1·08 g., 95% recovery), trifluoronitrosomethane, trifluoronitromethane, perfluoro(methylenemethylamine), trifluoromethyl isocyanate, hexafluoroethane, carbonyl fluoride, silicon tetrafluoride, and carbon dioxide.

Pyrolysis of Perfluoro-(*1,6-dichloro-4-methyl-3-oxa-4-azabicyclo*[4,2,0]*octane*) (XIII).—(a) *With short contact time.* The bicyclo-octane (1·18 g., 3·00 mmoles) was pyrolysed at *ca.* 1 mm. pressure in a platinum tube (length 100 cm., i.d. 1 cm.) heated to 600° over 50 cm. of its length, with a contact time of *ca.* 3 sec. The product was separated into fractions by trap-to-trap condensation *in vacuo*, and each fraction was examined by gas–liquid chromatography and i.r. techniques; carbonyl fluoride and perfluoro(methylenemethylamine) (77 and 56%, respectively, based on starting material consumed) were found, together with starting material (54% recovery), the bicyclo-octene (X), hexafluoroethane, tetrafluoroethylene, chlorotrifluoromethane, carbon dioxide, and silicon tetrafluoride (the last two arising from attack on glass traps), and several unidentified volatile compounds.

In a similar pyrolysis with a contact time of *ca.* 0·2 sec., the bicyclo-octane was recovered unchanged.

(b) *With a long contact time.* The bicyclo-octane (1·33 g., 3·38 mmoles), pyrolysed as in (a) at 605°/1 mm., with a contact time of *ca.* 17 sec., gave carbonyl fluoride and perfluoro(methylenemethylamine) (51 and 37%, respectively, based on starting material consumed), together with starting material (27% recovery), the bicyclo-octene (X), trifluoromethyl isocyanate, hexafluoroethane, tetrafluoroethylene, chlorotrifluoromethane, carbon dioxide, silicon tetrafluoride, and several unidentified volatile compounds.

Polymerisation of Tetrafluoroallene.—(a) *In the dark.* Tetrafluoroallene was stored unchanged for several months at −196° *in vacuo*, or for shorter periods at 20° and sub-atmospheric pressure, in the dark. However, when tetrafluoroallene (2·11 g., 18·8 mmoles) was kept in a 45-ml. Dreadnought ampoule at 20° (calculated initial pressure, 10 atm.) for 44 hr., only 21% was recovered, the remainder having been converted into perfluoro-(1,2-dimethylenecyclobutane) (I) (0·11 g., 0·47 mmole, 3% based on C_3F_4 consumed) and polytetrafluoroallene (1·51 g., 93% based on C_3F_4 consumed) (Found: C, 32·1. Calc. for $[C_3F_4]_n$: C, 32·1%), m. p. 123—124° (lit.,[1] 103—106°).

In another experiment, tetrafluoroallene (1·12 g., 10 mmoles) was kept at 20° (calculated initial pressure, 5 atm.) in the dark for 4 months. No tetrafluoroallene was recovered, the product being a mixture of perfluoro-(1,2-dimethylenecyclobutane) (I) (0·06 g., 5%) and polytetrafluoroallene (1·06 g., 95%), m. p. 117—118°.

(b) *In ultraviolet light.* Tetrafluoroallene (1·61 g., 14·4 mmoles), contained in a 34-ml. Pyrex ampoule (calculated initial pressure 10 atm.), was irradiated for 44 hr. with light from a 250-w Hanovia lamp placed at a distance of 10 cm. The volatile product, a mixture of tetrafluoroallene (1·57 g., 1·4 mmoles, 10% recovery) and perfluoro-(1,2-dimethylenecyclobutane) (I)

(0·263 g., 1·2 mmoles, 9% based on C_3F_4 consumed), was removed from the ampoule, leaving the walls of the latter coated with polytetrafluoroallene.

(c) *In the presence of trifluoroiodomethane.* A mixture of tetrafluoroallene (0·283 g., 6·1 mmoles) and trifluoroiodomethane (24·0 g., 122 mmoles) was sealed in a 45-ml. Dreadnought ampoule and was shaken at 20° while the liquid phase was irradiated with light from a 250-w Hanovia lamp placed at a distance of 10 cm. A white solid (polytetrafluoroallene) separated immediately. At 45-min. intervals, two further quantities of tetrafluoroallene (making a total of 1·99 g., 18·3 mmoles) were introduced into the ampoule. The volatile product, a mixture of tetrafluoroallene (2·0 mmoles, 11% recovery) and trifluoroiodomethane (121 mmoles, 98% recovery), was removed from the ampoule, leaving a residue of polytetrafluoroallene (1·75 g., 100% based on C_3F_4 consumed) (Found: C, 32·0. Calc. for $[C_3F_4]_n$: C, 32·1%), m. p. 110—111°.

Properties of Polytetrafluoroallene.—The polymer is a white waxy solid when first formed, turning pale yellow on storage. All the samples mentioned above showed strong i.r. absorption at 1721 cm.$^{-1}$ (thin films), and were apparently insoluble in common solvents and in fluorinated solvents (*e.g.*, n-pentane, 1,1,2-trichloroethane), thus preventing determination of molecular weight by a solution method. Although i.r. analysis indicates the presence of a C=C bond, no reaction was detected when chlorine was bubbled through a slurry of finely divided polytetrafluoroallene in 1,1,2-trichloroethane in the presence of light from three tungsten-filament (total 400 w) lamps.

When a sample (70 mg.) of the polymer was subjected to thermal gravimetric analysis in air, with a heating rate of 2°/min., it began to lose weight at *ca.* 250° and lost 93% of its weight below 500° (75% in the range 330—400°).

The authors are indebted to the Imperial Smelting Corporation Ltd. for a grant (to D. R. T.), and to Drs. R. D. Sedgwick and J. Lee of this Department for the examination of, and report on, the n.m.r. and mass spectra.

CHEMISTRY DEPARTMENT, FACULTY OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER.

[*Received, May 6th,* 1964.]