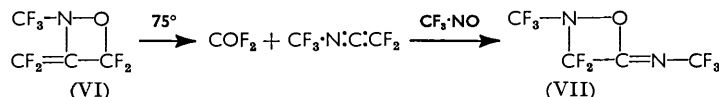
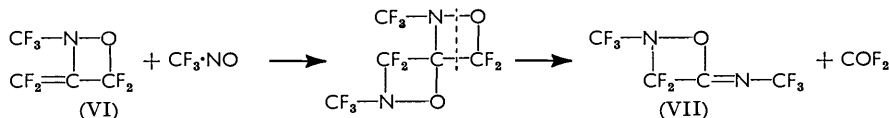


at 3425 and 1506 cm^{-1} [N-H stretching and bending vibrations, respectively; cf.⁹ bis-(trifluoromethyl)amine 3460 and 1504 cm^{-1}], was prevented by its instability.

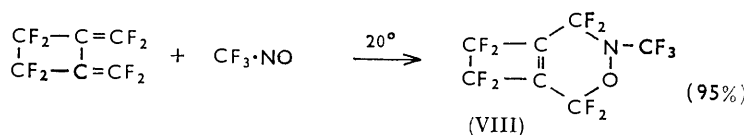
Perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) is also obtained (82% yield) when perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) is heated with trifluoronitrosomethane; its formation in this manner may involve either decomposition of the oxazetidine (VI) followed by combination of the perfluoro-(*N*-vinylidenemethylamine) thus formed with trifluoronitrosomethane,



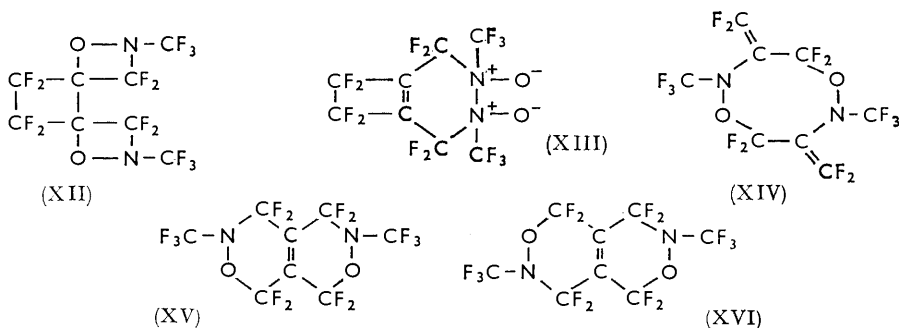
or formation of a spirocyclic compound, which decomposes under the reaction conditions:



Perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)ene} (VIII).—This product is formed (optimum yield: 22% at 145°/10 atm.) when tetrafluoroallene is heated with trifluoronitrosomethane under conditions favourable for dimerisation of tetrafluoroallene to perfluoro-(1,2-dimethylenecyclobutane). Reaction of this dimer with trifluoronitrosomethane at room temperature gives an almost quantitative yield of the perfluoro-compound (VIII), the properties of which have been reported.¹



The 2:2-Adduct, $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$.—The main product (up to 62%) of reactions between equimolar amounts of tetrafluoroallene and trifluoronitrosomethane at 56–145°/5–10 atm. is a colourless, liquid 2:2-adduct, $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$, b. p. 137–138°, which gives a single broad peak when examined by gas-liquid chromatography, indicating that it may be a mixture of isomers. This product gives a mass spectrum too complex to do more than confirm the molecular weight, and its ¹⁹F n.m.r. spectrum shows nine regions of absorption, some of which are broad and lack useful fine structure.



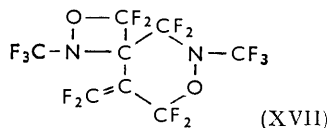
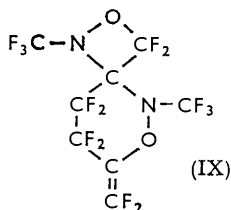
The possibility that the 2:2-adduct is either compound (XII) or (XIII), or a mixture of these two, produced by the reaction of trifluoronitrosomethane with perfluoro-(1,2-dimethylenecyclobutane) (tetrafluoroallene dimer, see above and ref. 1) is discounted, since this reaction is known to yield only the bicyclo-octene (VIII), and the infrared

⁹ D. A. Barr and R. N. Haszeldine, *J.*, 1955, 4169.

spectrum of the adduct contains a sharp intense absorption at 1760 cm^{-1} , which is best correlated with the presence of an exocyclic difluoromethylene group.

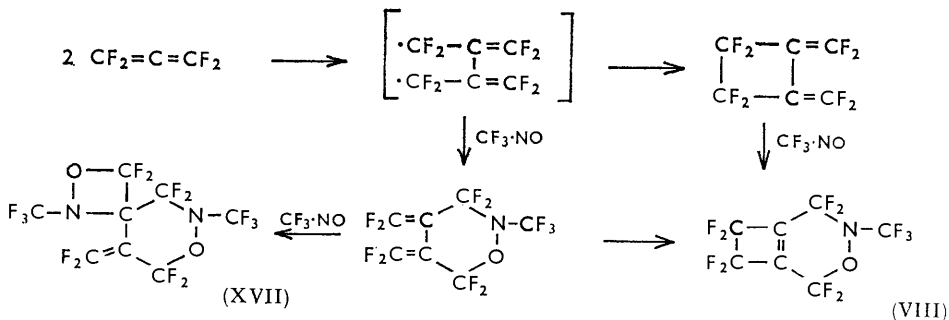
That the adduct contains only one C=C bond is supported by the fact that mild photochemical chlorination gives a saturated dichloride, $\text{C}_8\text{Cl}_2\text{F}_{14}\text{N}_2\text{O}_2$, in 90% yield, which militates against eight-membered ring structures with two exocyclic difluoromethylene groups of type (XIV). Pyrolysis of this dichloride yields, *inter alia*, perfluoro(methylene-methylamine), 2,3-dichlorotetrafluoropropene, chlorodifluoroacetyl chloride, and carbonyl fluoride.

By analogy with the structures of 2:2-adducts obtained from allene and a number of olefins,¹⁰ $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ might be expected to have structure (XV) or (XVI); however, the strong C=C absorption at 1760 cm^{-1} and the ^{19}F n.m.r. spectrum are not consistent with such symmetrical structures, and the formation of products containing the $\text{CF}_2\text{Cl}\cdot\text{CCl}<$ group on pyrolysis of the dichloride $\text{C}_8\text{Cl}_2\text{F}_{14}\text{N}_2\text{O}_2$ is not compatible with the dichlorides derived from structures (XV) and (XVI), but indicates that the 2:2-adduct contains an exocyclic difluoromethylene group. Several structures meeting the last requirement can be devised, and although it is impossible to relate simply and completely any one of them, *e.g.*, (IX) or (XVII), to the pyrolysis fragments obtained from the dichloride, it seems likely that compounds of these types are present in the 2:2-adduct.



Effect of Temperature on the Reaction between Tetrafluoroallene and Trifluoronitrosomethane.

—A series of reactions was carried out in which equimolar mixtures of tetrafluoroallene and trifluoronitrosomethane were kept under pressure (*ca.* 10 atm.) at temperatures in the range -10° to 145° . As in reactions between trifluoronitrosomethane and fluoro-olefins of the type CF_2CXY , the yield of 1:1-copolymer (V) falls off rapidly with increase in temperature, and becomes negligible at temperatures above 100° . This decrease in copolymer yield is accompanied by increases in the yields of the bicyclo-octene (VIII) and the 2:2-adduct (*e.g.*, IX), and not, as in reactions between trifluoronitrosomethane and fluoro-olefins, by an increase in the yield of oxazetidine (VI). Since the rate of dimerisation of tetrafluoroallene increases as the temperature is increased within the above range, the observed temperature-effect can be explained by postulating that both the bicyclo-octene (VIII) and the 2:2-adduct arise by interaction of trifluoronitrosomethane with tetrafluoroallene dimer or with an intermediate biradical in the formation of the dimer, *e.g.*,



¹⁰ H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 2723.

Support for the hypothesis that the bicyclo-octene is formed by reaction of tetrafluoroallene dimer with trifluoronitrosomethane is provided by the observation that the yield of the bicyclo-octene diminishes as the initial concentration of the allene is decreased. However, the yield of the 2:2-adduct is favoured by low initial concentrations of tetrafluoroallene, so some other factor apparently operates during its formation.

EXPERIMENTAL

Trifluoronitrosomethane¹¹ and tetrafluoroallene¹ were prepared as described previously.

Reaction of Tetrafluoroallene with Trifluoronitrosomethane.—The detailed description of the experiments carried out under various reaction conditions is preceded by a summary of the optimum yields obtained for the five major products (see Table 1).

TABLE 1

Optimum yields of products from the $\text{CF}_2\text{:C:CF}_2/\text{CF}_3\text{:NO}$ reaction

Product	Yield ^a (mole %)	Calc. initial [*] press. (atm.)	Temp.	Time	Initial allene conc. (molar)
1:1 Copolymer (V)	98	10	-10°	21 days	0.50
Perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI)	43 ^b	1	60	7 hr.	0.66
Perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII)	42	1	100	6 hr.	0.10
Perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene} (VIII)	22	10	145	7 hr.	0.50
2:2 Adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ (e.g., IX, XVII)	76	10	65	72 hr.	0.14

^a Based on tetrafluoroallene consumed. ^b Based on trifluoronitrosomethane consumed.

* Pressure calculated on the assumption that reactants were wholly in the gas phase. Observation showed that a liquid phase was present in reactions at pressures > 1 atm.

(A) Sealed tube reactions at a calculated initial pressure of 10 atm.

(1) At -10°. Tetrafluoroallene (2.09 g., 18.7 mmoles) and trifluoronitrosomethane (1.85 g., 18.7 mmoles), sealed in a 90 ml. Dreadnought tube and kept at -45° for 48 hr., then at -10° for 21 days, gave unchanged starting materials (18%), perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (<1%), traces of carbonyl fluoride and hexafluoroethane and an involatile residue, which was extracted with perfluoro-n-pentane to give, after evaporation of the solvent, a colourless, viscous, 1:1-copolymer (3.14 g., 98% based on $\text{CF}_2\text{:C:CF}_2$ consumed) [Found: C, 22.5; N, 6.6. A 1:1 copolymer, $(\text{C}_4\text{F}_7\text{NO})_n$, requires C, 22.8; N, 6.6%]. The copolymer was soluble in acetone; rapid evaporation of the acetone solution *in vacuo* gave a brittle glass of unchanged analytical composition, softening at 90–95°.

(2) At 90°. Tetrafluoroallene (47.1 mmoles) and trifluoronitrosomethane (47.1 mmoles), kept at 90° in a 300 ml. Dreadnought tube for 40 hr. gave (a) carbonyl fluoride (7.5 mmoles), (b) perfluoro(methylenemethylamine) (0.95 mmole), (c) a fraction (4.1 mmoles) (Found: *M*, 238) consisting of perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (0.1 mmole; 0.5% based on $\text{CF}_2\text{:C:CF}_2$), perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) (2.9 mmoles; 6% based on $\text{CF}_2\text{:C:CF}_2$), hexafluoroazoxymethane (0.1 mmole) and an unidentified substance (0.9 mmole), (d) a fraction (5.28 g.), and (e) traces of carbon dioxide, silicon tetrafluoride, trifluoromethyl isocyanate, and trifluoronitromethane. The liquid (2.43 g.) remaining in the reaction vessel was added to fraction (d) and distilled through a short Vigreux column under nitrogen, to give (i) a fraction (1.72 g.) b. p. 60–80°/160 mm., consisting of perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene} (VIII) (3.6 mmoles; 16% based on $\text{CF}_2\text{:C:CF}_2$) and the 2:2-adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ (1.4 mmoles), and (ii) a 2:2-adduct (e.g., IX, XVII) (13.3 mmoles; total yield 62%) [Found: C, 22.6; N, 6.6%; *M*, 433 (Victor Meyer), 422 (mass spectroscopy). $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ requires C, 22.8; N, 6.6%; *M*, 422], b. p. 137–138°/758 mm. (Siwoloboff), and (iii) an involatile residue, spectroscopically identified as the 1:1-copolymer of tetrafluoroallene with trifluoronitrosomethane (1.09 g.; 11% yield).

(3) At 56°. Tetrafluoroallene (61.0 mmoles) and trifluoronitrosomethane (61.0 mmoles) kept in a 320 ml. Dreadnought tube for 10 days at 56°, gave trifluoronitrosomethane (5% recovery),

¹¹ D. A. Barr and R. N. Haszeldine, *J.*, 1955, 1881; A. H. Dinwoodie and R. N. Haszeldine, *J.*, 1965, 1675.

carbonyl fluoride (2.0 mmoles), perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (0.1 mmole), perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) (2.3 mmoles; 4% based on $\text{CF}_2\text{:C:CF}_2$), perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene} (VIII) (4.8 mmoles; 8% based on trifluoronitrosomethane consumed), the 2:2 adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ (13.4 mmoles; 44% based on $\text{CF}_2\text{:C:CF}_2$), the 1:1-copolymer (3.8 g.; 30% based on $\text{CF}_2\text{:C:CF}_2$), and traces of silicon tetrafluoride, trifluoromethyl isocyanate, perfluoro(methylenemethylamine) and carbon dioxide.

(4) *At 145°.* On one occasion a violent explosion occurred when the reactants were rapidly heated from -196° to 140° in a 300 ml. Dreadnought tube (calculated initial pressure 10 atm.); the tube was completely shattered, and carbon was formed. Therefore, tetrafluoroallene (50.8 mmoles) and trifluoronitrosomethane (50.8 mmoles) were sealed *in vacuo* in a 430 ml. Dreadnought tube and slowly heated (2 hr.) to 145° . After a further 5 hr. at 145° , fractional condensation *in vacuo* gave carbonyl fluoride (8.9 mmoles, mixed with traces of hexafluoroethane, carbon dioxide, and silicon tetrafluoride), a mixture (6.1 mmoles) of perfluoro(methylenemethylamine) and trifluoromethyl isocyanate, perfluoro(2-methyl-4-methylimino-1,2-oxazetidine) (VII) (2.8 mmoles; 6% based on $\text{CF}_2\text{:C:CF}_2$), an unidentified substance (1.2 mmoles), perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene} (VIII) (5.6 mmoles; 22% based on tetrafluoroallene), and the 2:2 adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ (14.5 mmoles; 57% yield).

(B) *Vapour-phase reactions.* The reaction vessel consisted of a 5-l. Pyrex bulb with a drawn-down neck and a cold-finger side arm, which was washed out with boiling alcoholic potassium hydroxide, repeatedly rinsed with water, and dried thoroughly before each experiment.

(1) *At 0°.* Negligible reaction occurred when a mixture of tetrafluoroallene (52.5 mmoles) and trifluoronitrosomethane (52.5 mmoles) was kept at 0° for 24 hr., but after a further 3 weeks at 0° a product was obtained, which consisted of unchanged starting materials (87% recovery), perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (0.52 g., 2.5 mmoles; 37% based on $\text{CF}_2\text{:C:CF}_2$ consumed) (Found: *M*, 212. Calc. for $\text{C}_4\text{F}_7\text{NO}$: *M*, 211), and a fraction (-45° trap) which consisted mainly of the 2:2-adduct (*ca.* 1.0 mmole; 30% based on reactants consumed). Colourless 1:1-copolymer remained in the reaction vessel.

(2) *At 60° with an excess of tetrafluoroallene.* Tetrafluoroallene (10.1 g., 90.0 mmoles) and trifluoronitrosomethane (4.45 g., 45.0 mmoles) were sealed in the 5-l. reactor and brought rapidly to 60° in a preheated oven. The products were removed by fractional condensation *in vacuo* after 3.5 hr., and the recovered reactants (93 mmoles) were reheated at 60° for a further 3.5 hr.; in this way side-reactions between products and trifluoronitrosomethane were minimised. The total product so obtained consisted of trifluoronitrosomethane (50% recovery), tetrafluoroallene (68% recovery), carbonyl fluoride (*ca.* 1.9 mmoles), perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI), (10.0 mmoles; 43% based on trifluoronitrosomethane consumed), perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) (1.0 mmole; 2%), perfluoro(1,2-dimethylenecyclobutane) (0.3 mmole), the bicyclo-octene (VIII) (2.9 mmoles; 13% based on trifluoronitrosomethane consumed), the 2:2-adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ (4.1 mmoles; 36% based on trifluoronitrosomethane consumed), and the 1:1-copolymer that remained in the reactor. Perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) was isolated by gas chromatography (8 m. \times 9 mm. 25% w/w Kel-F oil/Celite column at 20°) as a colourless liquid (Found: C, 23.0; N, 6.6%; *M*, 210. $\text{C}_4\text{F}_7\text{NO}$ requires C, 22.8; N, 6.6%; *M*, 211).

The vapour pressure of perfluoro-(2-methyl-3-methylene-1,2-oxazetidine), over the range -35° to 10° , is given by $\log_{10} p$ (cm.) = $7.29 - 1625/T$, whence the calculated b. p. is 27.4° , Trouton's constant is 25, and the latent heat of vaporisation is 7440 cal.mole $^{-1}$.

(3) *At 100° with an excess of trifluoronitrosomethane.* Tetrafluoroallene (13.5 mmoles) and trifluoronitrosomethane (120 mmoles), kept at 100° for 6 hr. in the 5-l. reactor, gave (a) trifluoronitrosomethane (105 mmoles), (b) tetrafluoroallene (0.135 mmole), (c) carbonyl fluoride, (d) perfluoro(methylenemethylamine), (e) a fraction (1.45 g., 6.45 mmoles) (Found: *M*, 224) consisting of perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (0.1 mmole), an unidentified substance (1.4 mmoles), and perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) (5.0 mmoles; 42% based on tetrafluoroallene consumed), and (f) a fraction (1.20 g.) consisting mainly of the 2:2 adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ (45% based on tetrafluoroallene consumed). Colourless 1:1-copolymer remained in the reaction vessel.

Gas chromatography (8 m. \times 9 mm. 25% w/w Kel-F oil/Celite column at 20°) gave perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) as a colourless, unstable liquid (Found: C, 21.2; N, 11.7%; *M*, 242. $\text{C}_4\text{F}_8\text{N}_2\text{O}$ requires C, 19.7; N, 11.5%; *M*, 244), b. p. -69.5°

101.2 mm. An attempt to determine the boiling point by isoteniscope failed; an irregular vapour-pressure plot resulted, and a solid formed in the isoteniscope.

(C) *Sealed-tube reactions at 65–70° at various initial concentrations of tetrafluoroallene.* To determine the general effect of the initial concentration of tetrafluoroallene on the products, three experiments were carried out at 65–70° in sealed Dreadnought tubes (initial pressure calculated at 10 atm.). The less abundant reactant was in each case entirely consumed; the products were distilled *in vacuo*, and the resulting fractions were analysed by gas-liquid chromatography (g.l.c.), infrared spectroscopy, and molecular-weight determination. The results are summarised in Table 2.

TABLE 2

Initial tetrafluoroallene concentration (M)	0.143	0.500	0.833
Temp.	65°	70°	65°
Time	72 hr.	7 days	18 hr.
Product yields (moles-% based on $\text{CF}_2\text{:C:CF}_2$ consumed, unless otherwise stated):			
1:1-Copolymer [$\text{C}_4\text{F}_2\text{NO}]_n$ (V)	14	20	8 ^a
Perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI)	1	1	6 ^a
Perfluoro-{4-methyl-3-oxa-4-azabicyclo[4,2,0]oct-1(6)-ene} (VIII) ...	0.5	17	27 ^a
2:2-Adduct $\text{C}_8\text{F}_{14}\text{N}_2\text{O}_2$ [e.g. (IX), (XVII)]	76	50	35 ^a
$(\text{C}_3\text{F}_4)_n$ ($n \geq 2$)	—	—	64

^a Yields based on trifluoronitrosomethane consumed.

Properties of the 1:1-Copolymer.—(a) *Physical properties.* The infrared spectrum exhibits medium absorptions at 1757 and 1724 cm^{-1} assigned to C:C vibrations, and a diffuse pattern in the 1000–1400 cm^{-1} region, attributed to C-F vibrations. Solid samples of the copolymer softened at 90–95°. When a sample of the copolymer was subjected to thermogravimetric analysis in air with a heating rate of 2°/min., it lost 97% of its weight below 330° (85% in the range 130–300°). When a sample of the yellow solid obtained by treating the copolymer (0.26 g.) with hexamethylenediamine (0.10 g.) in the cold was subjected to thermogravimetric analysis under these conditions, it lost 95% of its weight below 620° (42% in the range 130–300°).

(b) *Chlorination.* The copolymer (0.5 g.), in perfluoro-n-pentane (25 ml.), was treated continuously with chlorine whilst being irradiated by light from tungsten lamps (400 w) for 15 hr. No reaction was apparent, and unchanged copolymer (80% recovery; identified by i.r. spectroscopy) was obtained on evaporating the solution.

(c) *Pyrolysis.* (i) *At 500°.* The copolymer (0.423 g.) was pyrolysed at 500°/<1 mm. during ca. 1 hr. in a platinum tube (1 cm. internal diam., heated over 50 cm.); volatile products were passed through a cooled (–78°) zone (5 cm.) of the platinum tube and were collected in traps (–196°) attached to the vacuum system; no uncondensable gases were detected. Fractionation of the condensate gave carbonyl fluoride (1.18 mmoles; 59%), a mixture (0.56 mmole; 28%) of perfluoro(methylenemethylamine) and trifluoromethyl isocyanate, and a mixture (0.26 mmole) of numerous unidentified substances. An involatile oil (0.2 g.) was poured out of the cold pyrolysis tube, leaving a tarry residue, which was washed out with acetone, dried, and weighed (0.1 g.).

(ii) *At 160–300°.* When the copolymer (0.546 g.) was rapidly heated to 160° in an evacuated sublimation apparatus, volatile products began to condense on the cold finger (–196°) (4.5 cm. external diam.). After 45 min. the temperature was raised to 300° during 1 hr.; pyrolysis appeared to be complete after a further 2 hr. The product trapped on the cold finger consisted of carbonyl fluoride (ca. 1.40 mmoles, mixed with silicon tetrafluoride, carbon dioxide, and hexafluoroethane), perfluoro(methylenemethylamine) (less than 0.05 mmole), and a mixture (–96° trap; 0.32 mmole) of numerous unidentified substances. A brown residue (0.235 g.) remained in the apparatus.

Properties of Perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI).—(a) *Chlorination.* The oxazetidine (4.90 mmoles) and chlorine (6.0 mmoles) were shaken *in vacuo* in a silica tube (120 ml.) and irradiated (vapour phase only) by light from tungsten lamps (400 w) for 4 hr., and then, after removal of material condensing *in vacuo* at > –67°, for a further 6 hr. The excess of chlorine was removed with dry mercury, and the residue was fractionated to give carbonyl fluoride (3.0 mmoles) and a mixture (–67° trap; 1.16 g., 4.80 mmoles. Found: *M*, 240) of 3-chloro-

3-chlorodifluoromethyl-4,4-difluoro-2-trifluoromethyl-1,2-oxazetidine, (X) (1.70 mmoles; 34% yield based on oxazetidine consumed), and *N*-(1,2-dichlorodifluoroethylidene)trifluoromethylamine, $\text{CF}_3\text{N}:\text{CCl}-\text{CF}_2\text{Cl}$ (3.10 mmoles; 63% yield based on oxazetidine consumed), both identified by g.l.c. and infrared spectroscopy. A sample (3.0 mmoles) of the -67° fraction was pyrolysed in a silica tube (9 mm. internal diam. heated over 50 cm.) at $550^\circ/\text{ca. } 4 \text{ mm.}$, during 5 min. with a contact time of 0.2 sec.; the products were condensed at -196° , freed from chlorine with dry mercury, and found to consist of carbonyl fluoride [1.0 mmole; 95% yield based on compound (X)] a trace of 2,3-dichlorotetrafluoropropene, which was removed by treatment with bromine, and *N*-(1,2-dichlorodifluoroethylidene)trifluoromethylamine [0.63 g. 93% yield based on compound (X),] (Found: C, 16.9; N, 6.4; Cl, 32.9%; *M*, 216. $\text{C}_3\text{Cl}_2\text{F}_5\text{N}$ requires C, 16.7; N, 6.4; Cl, 32.9%; *M*, 216), b. p. 55.6° (isotenoscope). The vapour pressure of *N*-(1,2-dichlorodifluoroethylidene)trifluoromethylamine over the range $10-45^\circ$ is given by the equation $\log_{10} p(\text{cm.}) = 6.83 - 1629/T$. The calculated b. p. is 55.6° , Trouton's constant is 23, and the latent heat of vaporisation is $7450 \text{ cal.mole}^{-1}$.

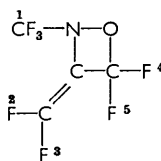
(b) *With trifluoronitrosomethane.* No reaction occurred when perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (1.96 mmoles) and trifluoronitrosomethane (2.0 mmoles) were kept at 20° for 24 hr. in a 40 ml. sealed Pyrex tube, but after 10 days at 75° the blue colour of trifluoronitrosomethane was nearly discharged. The product was fractionated to give unchanged oxazetidine (16% recovery), trifluoronitrosomethane (20% recovery), carbonyl fluoride (1.38 mmoles; 84% based on oxazetidine consumed), and perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII) (1.34 mmoles; 82% based on oxazetidine consumed), identified by g.l.c. and infrared spectroscopy.

(c) *With tetrafluoroallene.* No reaction occurred when perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (2.14 mmoles) was treated with tetrafluoroallene (5.0 mmoles) at 60° for 4 hr. in a 44-ml. sealed Pyrex tube; after a further 5 hr. at 110° fractionation *in vacuo* gave unchanged oxazetidine (20% recovery), tetrafluoroallene (3% recovery) carbonyl fluoride (1.44 mmoles; 86% based on oxazetidine consumed), perfluoro-(1,2-dimethylenecyclobutane) (1.34 mmoles), and higher polymers of tetrafluoroallene, together with unidentified substances.

(d) *Pyrolysis.* Perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) (VI) (3.52 mmoles) was pyrolysed at $300^\circ/1 \text{ mm.}$ with a contact time of 0.9 sec. in a continuously evacuated silica tube (0.9 cm. internal diam., heated over 10 cm.) fitted with a capillary inlet. Non-condensable gaseous products were not detected; volatile products were collected in traps (-196°) and finally fractionated *in vacuo* to give carbonyl fluoride (2.40 mmoles; 74%), small amounts of tetrafluoroethylene and a mixture (0.90 mmole) shown by infrared spectroscopy and g.l.c. to contain perfluoro(methylenemethylamine) and a compound that absorbed strongly at 2262 cm.^{-1} , thought to be perfluoro(*N*-vinylidenemethylamine). A further fraction (0.19 g.) which contained several unidentified compounds (g.l.c. analysis) but no unchanged oxazetidine, was obtained.

(e) *N.m.r. spectrum.* The ^{19}F n.m.r. spectrum of perfluoro-(2-methyl-3-methylene-1,2-oxazetidine) consists of three absorption regions (Table 3).

TABLE 3



Chemical shift (p.p.m. from trifluoroacetic acid)	Multiplet structure	Assignment to F nuclei	Spin-spin coupling constants (c./sec.)
-14.78, -11.87	Broad doublet	4 & 5	$J_{45} = 98.6$
0.07	1,2,2,2,1 Doublet of triplets	1	$J_{14} = J_{15} = 3.4$ $J_{12} \text{ OR } J_{13} = 7.0$
11.77, 15.14	Quartet of triplets & 1,2,1 triplet	2 & 3	$J_{23} = 45.0$ $J_{24} = J_{25} = 4.5$ $J_{34} = J_{35} = 5.3$

Reactions of Perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (VII).—(a) *Hydrolysis.* The methylimino-oxazetidine (VII) (0.40 mmole) and 10% aqueous sodium hydroxide solution

(2 ml.) were shaken for 3 hr. in a hydrolysis bulb at 20°. The solution became yellow; methylimino-oxazetidine (20%) was recovered, and the aqueous solution was found to contain fluoride ion.

(b) *With anhydrous hydrogen fluoride.* Perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (2.11 mmoles) and anhydrous hydrogen fluoride [obtained by heating anhydrous potassium hydrogen fluoride (0.221 g.) to redness *in vacuo*, for 15 min.] were sealed *in vacuo* in a 15-ml. stainless steel autoclave and kept at 20° for 72 hr. Volatile products were freed from hydrogen fluoride by treatment with anhydrous potassium fluoride, fractionated, and found to consist mainly of a colourless liquid component (Found: *M*, 291) absorbing at 2.92, 6.64, 7.42, and 8.03 μ , possibly a bis(polyfluoroalkyl)amine, which decomposed before analytical results could be obtained.

(c) *Chlorination.* No reaction occurred when the methylimino-oxazetidine and chlorine were irradiated for 6 hr. with light from tungsten lamps (400 w).

(d) *Photolysis.* The methylimino-oxazetidine (0.8 mmole) was irradiated *in vacuo* in a 10-ml. Pyrex tube with light from a 250 w. Hanovia mercury-vapour lamp placed 10 cm. away for 3 hr. Analysis by g.l.c. showed that no decomposition had occurred.

(e) *Pyrolysis.* Perfluoro-(2-methyl-4-methylimino-1,2-oxazetidine) (0.79 mmole) was pyrolysed at 500°/1 mm. in a continuously evacuated platinum tube (1.0 cm. internal diam., heated over 50 cm.) during 20 min. with a contact time of 1.2 sec.; effluent gases were passed through a 10 cm. length of the platinum tube cooled to -78°, and were collected in traps (-196°) attached to the vacuum system. The sole product was a mixture (0.180 g., 1.48 mmoles) (Found: *M*, 122. Calc. for a 50/50 mixture of C₂F₅N and C₂F₃NO: *M*, 122) of perfluoro(methylene-methylamine) (94%) and trifluoromethyl isocyanate (94%).

Properties of the 2:2-Adduct, C₈F₁₄N₂O₂.—(a) Physical properties. The compound C₈F₁₄N₂O₂ isolated from the reactions of tetrafluoroallene with trifluoronitrosomethane at 56—145° was a colourless liquid, b. p. 137—138°/758 mm. (Siwoloboff). Its infrared spectrum showed an intense absorption at 1760 cm.⁻¹. The ¹⁹F n.m.r. spectrum consists of several broad structureless bands, which gave no useful structural information.

Mass-spectral values for C₈F₁₄N₂O₂ are given in Table 4.

TABLE 4

Mass spectrum of the 2:2-adduct C₈F₁₄N₂O₂, obtained at 115° with an electron energy of 70 eV

<i>m/e</i>	422	403	337	315	273	249	242	223	204	188	182	174
Relative intensities (%)	0.5	0.5	0.5	1.0	1.0	0.5	0.5	0.5	2.0	0.5	0.5	0.5
<i>m/e</i>	164	157	155	145	143	138	130	124	114	112	100	93
Relative intensities (%)	0.5	1.5	1.0	0.5	1.0	2.5	1.0	2.0	3.0	2.0	0.5	2.5
<i>m/e</i>	88	85	76	74	69*	66	65	55	50	47	44	31
Relative intensities (%)	1.5	0.5	1.0	1.0	100.0	0.5	0.5	0.5	1.5	3.5	1.0	3.0

* CF₃ peak.

(b) *Chlorination.* The 2:2-adduct (1.01 g., 2.37 mmoles) was irradiated with chlorine (5.0 mmoles) in a 50-ml. Pyrex tube with light from a tungsten-filament lamp (400 w) for 72 hr., to give unchanged chlorine (2.6 mmoles) and a colourless, oily liquid (1.05 g.; 90%) (Found: C, 19.4; N, 5.8. C₈Cl₂F₁₄N₂O₂ requires C, 19.5; N, 5.8%), b. p. 191—192°/760 mm. (Siwoloboff). Unlike the 2:2-adduct, which reacted with cold acetic potassium permanganate, this dichloride failed to decolorise cold acetic potassium permanganate, and showed no C:C infrared vibrations.

(c) *Pyrolysis.* The dichloride of the 2:2-adduct was chosen for pyrolysis in the hope that a cleaner thermal breakdown would occur with the saturated structure. The dichloride was therefore pyrolysed in a continuously evacuated platinum tube (10 mm. internal diam., heated over 50 cm.), with contact times of 1—5 sec. at temperatures in the range 460—600°. Effluent gases were passed through cooled traps (-196°), the last of which contained activated charcoal to absorb nitrogen, carbon monoxide, etc. Products were separated by fractional condensation *in vacuo*; after examination in the usual way the most volatile fractions were shaken with 2N-aqueous sodium hydroxide to remove acyl fluorides, carbon dioxide, and silicon tetrafluoride, then dried (P₂O₅) and re-examined. Known compounds were identified and estimated by g.l.c. and infrared spectroscopy; a summary of the results of the four experiments is tabulated below.

Preparation of 2,3-Dichlorotetrafluoropropene.—Tetrafluoroallene (5.6 mmoles) and chlorine (11.5 mmoles) were sealed in a 45-ml. Dreadnought tube, and kept at 20° in the dark for 7 days. Unchanged chlorine was removed by shaking the mixture with dry mercury, and the residue was fractionated to give 2,3-dichlorotetrafluoropropene in 99% yield, as a colourless liquid (Found: C, 19.9; Cl, 38.7%; *M*, 184. Calc. for C₃Cl₂F₄: C, 19.7; Cl, 38.8%; *M*, 183), b. p. 44.9° (isoteniscope; lit.,¹² 46°). In the present work, the above method afforded a convenient alternative to the previously reported preparation.¹² For this purpose, equimolar amounts of chlorine and tetrafluoroallene (45 mmoles) were allowed to react in a sealed 350 ml. Dreadnought tube for 12 hr. at 20° in the dark; yields of ca. 95% were obtained.

TABLE 5
Pyrolysis of C₃Cl₂F₁₄N₂O₂ at various temperatures

Temp.	460°	510°	550°	600°
Contact time (sec.)	1	3	5	3
% Decomp.	16	45	80	95
Yields (moles-%):				
COF ₂	95	135	174	148
CF ₃ ·N:CF ₂	51	100	115	116
CF ₂ :CCl·CF ₂ Cl	50	44	53	40
CF ₂ Cl·COCl	—	—	18	14
Other products formed	<i>a</i>	<i>a, b</i>	<i>a, b, c</i>	<i>a, b, c</i>

^a CClF₃, C₂F₆, CF₃·NCO, and C₈F₁₄N₂O₂. ^b CF₄, C₂F₄. ^c CO.

Reaction of 2,3-Dichlorotetrafluoropropene with Trifluoronitrosomethane.—Trifluoronitrosomethane (21.0 mmoles) and 2,3-dichlorotetrafluoropropene (21.0 mmoles), kept at 100° for 15 days in a 300-ml. sealed Dreadnought tube, gave trifluoronitrosomethane (3.93 mmoles) mixed with silicon tetrafluoride, hexafluoroethane, carbon dioxide, and carbonyl fluoride, trifluoronitromethane [2.53 mmoles, mixed with CF₃·N:CF₂, CF₃·NCO, and (CF₃)₂NH], unchanged 2,3-dichlorotetrafluoropropene (23% recovery), chlorodifluoroacetyl chloride (0.15 mmole), *N*-(1,2-dichlorodifluoroethylidene)trifluoromethylamine, CF₃·N:CCl·CF₂Cl (1.79 mmoles; 11% based on CF₂:CCl·CClF₂ consumed) and a mixture of isomeric oxazetidines C₄Cl₂F₇NO (7.41 mmoles; 46% based on CF₂:CCl·CF₂Cl) (Found: C, 17.2; N, 4.9; Cl, 24.9%; *M*, 281. C₄Cl₂F₇NO requires C, 17.0; N, 5.0; Cl, 25.1%; *M*, 282) as a colourless liquid. A viscous, involatile colourless oil (0.485 g.) remained in the reaction vessel; it was extracted with perfluoron-pentane and shown to be a 1:1-copolymer (13% based on CF₂:CCl·CF₂Cl consumed) (Found: C, 17.1; N, 5.2. A 1:1-copolymer [C₄Cl₂F₇NO]_n requires C, 17.0; N, 5.0%).

The vapour pressure of the mixture of oxazetidines C₄Cl₂F₇NO, over the range 14 to 54° is given by log₁₀ *p*(cm.) = 6.42 - 1661/*T*. The calculated b. p. is 92.3°, Trouton's constant is 21, and the latent heat of vaporisation is 7600 cal.mole⁻¹.

Pyrolysis of the Mixture of Oxazetidines C₄Cl₂F₇NO.—The oxazetidines C₄Cl₂F₇NO (0.316 g., 1.12 mmoles) were pyrolysed in a silica tube (9 mm. internal diam., heated over 50 cm.) at 555°/1 mm. during 33 min., with a contact time of 1.1 sec. The products were shaken with dry mercury to remove chlorine, and fractionated *in vacuo* to give carbonyl fluoride (0.86 mmole; 77%), perfluoro(methylenemethylamine) (0.34 mmole; 30%), chlorodifluoroacetyl chloride (0.06 mmole; 6%), *N*-(1,2-dichlorodifluoroethylidene)trifluoromethylamine (0.82 mmole; 73%), and traces of silicon tetrafluoride, tetrafluoroethylene, chlorotrifluoromethane and unidentified substances.

Preparation and Pyrolysis of Chlorodifluoroacetyl Chloride.—Sodium chlorodifluoroacetate (10.4 g.) was heated under reflux with phosphorous pentachloride (20.0 g.) for 2 hr., to give chlorodifluoroacetyl chloride (7.14 g., 70%) which was purified by fractional condensation *in vacuo*. A sample (1.50 g., 10.1 mmoles) was recovered unchanged after pyrolysis at 550°/1 mm. in a silica tube (9 mm., heated over 50 cm.) during 2 hr.

The authors are indebted to the Imperial Smelting Corporation Limited for a grant (to D. R. T.), and to Dr. K. G. Orrell for examination of, and report on, the n.m.r. spectra.

THE CHEMISTRY DEPARTMENT, FACULTY OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER.

[Received, December 10th, 1964.]

¹² A. L. Henne, A. M. Whaley, and J. K. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 3478.