# Polyhalogenoallenes. Part IX.[1] Reaction of Tetrafluoroallene with Bistrifluoromethyl Nitroxide and with Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane)

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Perfluoro-[1,3-bis(dimethylamino-oxy)propan-2-one], perfluoro-(2-dimethylamino-3-dimethylamino-oxyprop-1-ene), perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), and polymeric material can be obtained by treating tetrafluoroallene with bistrifluoromethyl nitroxide at room temperature or below. The propene arises from attack on tetrafluoroallene by perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane).

TETRAFLUOROALLENE readily undergoes free-radical homopolymerization, giving only high-molecular-weight polymer (1) even when telomer production might be expected, e.g. when a dilute solution of the allene in trifluoroiodomethane is irradiated with u.v. light.[2] The ease with which tetrafluoroallene polymerizes has thus forestalled attempts to determine the orientation of free-radical attack on its cumulene system; however, initiation and propagation steps involving attack on the central carbon atom seem the most likely, since only these can lead to the formation of allylic radicals.[2] The result of photochemical hydrobromination of the perfluoro-allene $C_2F_5 \cdot CF \colon C \colon CF_2$, which does not poly-

merize readily, indicates that bromine atom preferentially attacks the central carbon of the cumulene system.[3]

$$\left[\begin{array}{c} CF_2 \\ \| \\ C \cdot CF_2 \end{array}\right]_n \quad (1)$$
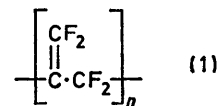
Work on the reaction between tetrafluoroallene and bistrifluoromethyl nitroxide was undertaken following the discovery [4] that the nitroxide converts the perfluoroacetylenes $R_FC \colon CR'_F$ (R_F, $R'_F = CF_3$, CF_3; CF_3, F; C_6F_5, C_6F_5) into the corresponding 1,2-dicarbonyl compounds $R_FCO \cdot COR'_F$. Attempts to prepare telomers

[1] Part VIII, R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine, and D. R. Taylor, J. Chem. Soc. (C), 1969, 1104.

[2] R. E. Banks, R. N. Haszeldine, and D. R. Taylor, J. Chem. Soc., 1965, 978.

[3] R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, J. Chem. Soc. (C), 1969, 454.

[4] R. E. Banks, R. N. Haszeldine, and T. Myerscough, J. Chem. Soc. (C), 1971, 1951.

of the type $(CF_3)_2N \cdot O[CF_2 \cdot CF_2]_xO \cdot N(CF_3)_2$ ($x = 2$, 3, 4, etc.) from the nitroxide and tetrafluoroethylene lead predominantly and often even exclusively to the formation of only the 2 : 1 adduct ($x = 1$),[5,6] so polymerization of the allene was not expected to prevent a comparison being drawn between the allene and its acetylenic isomer perfluoropropyne. This proved to be the case, since the allene reacted smoothly with 2 mol. equiv. of the nitroxide at room temperature to give perfluoro-[1,3-bis(dimethylamino-oxy)propan-2-one] (2) (ca. 31% yield), perfluoro-(2-dimethylamino-3-dimethyl-amino-oxyprop-1-ene) (3) (ca. 42%), polytetrafluoro-allene (ca. 16%), and the well-known N–O–N compound perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) [7,8] (4) (10%). Formation of the propene (3) was not observed when tetrafluoroallene was treated with 6 mol. equiv. of bistrifluoromethyl nitroxide; the product consisted almost entirely of the ketone (2) (89%), the diazapen-tane (4), and unchanged nitroxide (40%), the molar ratio of the first two products being 1 : 1 within the limits of experimental error.

These facts, taken in conjunction with the observation that perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) combines with tetrafluoroallene at room temperature to yield perfluoro-(2-dimethylamino-3-dimethylamino-oxyprop-1-ene) (3) and the work on reactions between bistrifluoromethyl nitroxide and acetylenes,[4] seem best interpreted in terms of the illustrated Scheme.
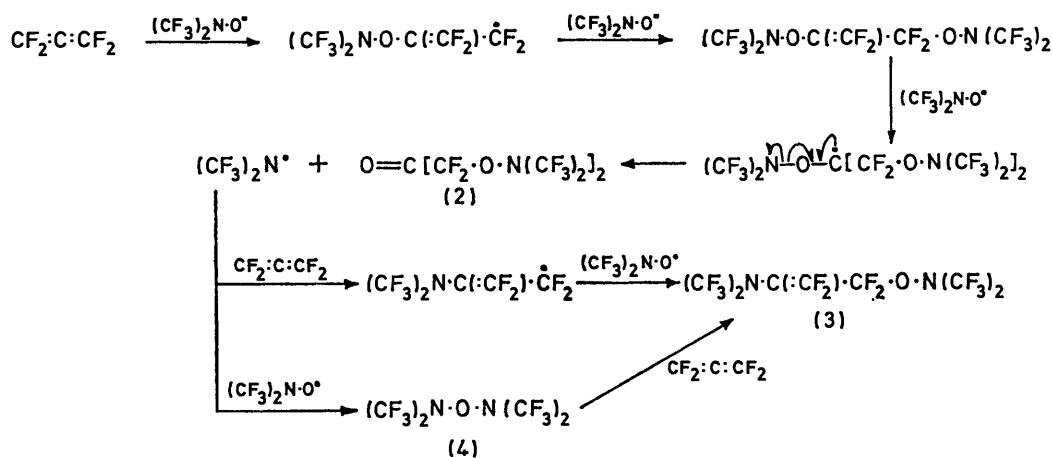
known to be the more susceptible towards free-radical attack.[8]

EXPERIMENTAL

I.r. spectra were measured with a Perkin-Elmer spectrophotometer model 257, [19]F n.m.r. spectra with a Perkin-Elmer R10 instrument operating at 56·46 MHz and 35 °C, mass spectra with an A.E.I. MS902 spectrometer, and u.v. spectra with a Unicam SP 700 spectrophotometer. G.l.c. techniques were as described in earlier papers.

Reaction of Tetrafluoroallene with Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane).—Tetrafluoroallene (0·634 g, 5·66 mmol) and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (4) [8] (1·83 g, 5·72 mmol) were condensed separately into a cold (−196 °C), evacuated, Pyrex tube (50 ml). The tube was sealed and stored in the dark at room temperature for 24 h. The volatile product was subjected to trap-to-trap fractional condensation, *in vacuo*, to yield *perfluoro-(2-dimethylamino-3-dimethylamino-oxyprop-1-ene)* (3) (−46 °C trap) (0·650 g, 1·50 mmol; 27%), b.p. 101 °C at 746 mmHg (Siwoloboff), $\lambda_{max.}$ (vapour) 5·74 μm (C : C str.) (Found: C, 20·4; N, 6·6%; *M*, 432. $C_7F_{16}N_2O$ requires C, 19·5; N, 6·5%; *M*, 432), apparently pure by g.l.c. and [19]F n.m.r. analysis {$(CF_3)_2\overset{1}{N}\cdot O\cdot \overset{2}{CF_2}\cdot \overset{3}{C}[N(CF_3)_2]\overset{4,5}{:CF_2}$, δ_1 −8·7br [$(CF_3)_2N\cdot O$, t showing signs of further splitting, $J_{1,2}$ 8·5 Hz], δ_2 −0·9vbr ($CF_2 \cdot C \vdots C$, complex m), δ_3 −19·0br [$(CF_3)_2N$, unresolved m], δ_4 −7·2 [*cis*-$(CF_3)_2N\cdot C \vdots CF$; complex m], δ_5 −6·2 [*cis*-$CF_2 \cdot C \vdots CF$, 1 : 3 : 3 : 1 q showing further splitting, $J_{2.5} = J_{4.5} = 15·8$ Hz] p.p.m. rel. to ext.

CF$_3$·CO$_2$H (rel. int. 6 : 2 : 6 : 1 : 1)}, perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (4) (−72 °C trap) (1·04 g, 3·25 mmol), and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) contaminated with a small amount of material showing i.r. absorptions at 5·45 (C : O str.) and 5·81 μm (C : C str.) (−96 °C trap) [0·057 g; total recovery of the diazapentane (4) = *ca.* 3·44 mmol, 60%]. A colourless, viscous, involatile residue (0·33 g) believed to be essentially the oligomer $(CF_3)_2N[C(\vdots CF_2)\cdot CF_2]O\cdot N(CF_3)_2$ {$\lambda_{max.}$(film) 5·78vs μm [C$\vdots$CF$_2$ str.; *cf.* ﹏CF$_2$·C($\vdots$CF$_2$)·CF$_2$·C($\vdots$CF$_2$)﹏,[3] 5·81 μm]} was recovered from the reaction vessel.

Initial attack by bistrifluoromethyl nitroxide or bistrifluoromethylamino-radical on tetrafluoroallene is postulated to occur at the central carbon atom, since in reactions between the diazapentane and an unsymmetrical per- or poly-fluoro-olefin the $(CF_3)_2N$ group becomes attached preferentially to the olefinic carbon atom

[5] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)*, 1966, 901.
[6] R. E. Banks, R. N. Haszeldine, and T. Myerscough, unpublished results.
[7] See, *e.g.*, R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. (C)*, 1966, 1236; R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)*, 1966, 901.

[8] R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, 1449.

The u.m.r. assignments for perfluoro-(2-dimethylamino-3-dimethylamino-oxyprop-1-ene) (3), with respect to the $(CF_3)_2N$ and $(CF_3)_2N\cdot O$ groups, were made after reference to data for a range of compounds containing these groups.[4,5,9]

Reaction of Tetrafluoroallene with Bistrifluoromethyl Nitroxide.—(a) *With a reactant ratio of* 1:2. Tetrafluoroallene (0·462 g, 4·12 mmol) and bistrifluoromethyl nitroxide (1·38 g, 8·21 mmol) were condensed separately into a cold (−196 °C), evacuated, Pyrex tube (250 ml). The tube was sealed and allowed to warm to room temperature. After 2 h only a trace of the nitroxide remained (as indicated by the colour of the tube's content), but when the tube had been stored in the dark at room temperature for 2 weeks, the purple colour of the nitroxide had disappeared completely. The volatile product was subjected to trap-to-trap fractional condensation *in vacuo*, to give (i) (−72 °C trap) a colourless liquid (1·56 g) which was shown by g.l.c. and i.r. and n.m.r. spectroscopy to contain at least five components, including perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (4) (trace), perfluoro-(2-dimethylamino-3-di-methylamino-oxyprop-1-ene) (3) (estimated yield 1·74 mmol, 42%), and perfluoro-[1,3-bis(dimethylamino-oxy)propan-2-one] (2) (estimated yield 1·28 mmol, 31%), (ii) (−96 °C trap) perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (4) (0·137 g, 0·428 mmol; 10%), (iii) (−120 °C trap) a trace of bistrifluoromethylamine (0·007 g, 0·043 mmol), and (iv) (−196 °C trap) a trace of tetrafluoroallene contaminated with an unidentified compound. A colourless involatile oil (0·07 g) with an i.r. spectrum similar to that of poly-tetrafluoroallene [2] remained in the reaction vessel.

(b) *With a reactant ratio of* 1:6. Tetrafluoroallene (0·268 g, 2·39 mmol) and bistrifluoromethyl nitroxide (2·43 g, 14·5 mmol) were condensed separately into a cold (−196 °C), evacuated, Pyrex tube (50 ml). The tube was sealed and warmed to room temperature. A colourless liquid product formed rapidly and much nitroxide was still present. After storage at room temperature for 1 week, the tube was opened and the volatile product was fractionated, *in vacuo*, to give (i) (0 °C trap) a hydrate (presumably owing to contact of the reaction product with adventitious moisture) of perfluoro[1,3-bis(dimethylamino-oxy)propan-2-one] (0·348 g), as a hygroscopic white solid {v. broad O—H str. i.r. absorption centred at *ca.* 3·0 μm; δ −10·2br [$(CF_3)_2N\cdot O\cdot$, t, *J ca.* 8·4 Hz], +12·8vbr (CF_2, complex m) p.p.m. (ext. $CF_3\cdot CO_2H$; *ca.* 20% w/w soln. in ether) (rel. int. 3 : 1)]}, (ii) (−46 °C trap; 0·718 g) perfluoro-[1,3-bis(dimethylamino-oxy)propan-2-one] (2) {δ −8·5 [$(CF_3)_2$-$N\cdot O\cdot CF_2\cdot$; 8·8 Hz 'triplet' (A_4X_{12} spin system which approaches deceptive simplicity)] and +6·9br ($\cdot CF_2\cdot$, complex m) p.p.m. (ext. $CF_3\cdot CO_2H$) (rel. int. 3 : 1)}, shown by i.r. and n.m.r. spectroscopy to be contaminated by unknown material containing $(CF_3)_2N\cdot CF_2$ and $(CF_3)_2$-$N\cdot O\cdot CF_2$ groups, (iii) (−72 °C trap) perfluoro-(2,4-di-methyl-3-oxa-2,4-diazapentane) (4) (0·58 g, 1·82 mmol, 42% based on nitroxide consumed), (iv) (−120 °C trap) bistrifluoromethyl nitroxide (0·972 g, 5·78 mmol, 40% recovery), and (v) (−196 °C) a mixture (0·130 mmol) of silicon tetrafluoride and trifluoronitromethane. Fraction (ii) was shaken with a small amount of water then re-fractionated to give (−10 °C trap) a white solid, which was dehydrated with phosphorus pentoxide to yield perfluoro-[1,3-bis(dimethylamino-oxy)propan-2-one] (2) (0·649 g, 1·40 mmol, 59%), b.p. 116 °C at 753 mmHg (Siwoloboff), λ_{max} (vapour) 5·56m (C:O str.), 7·60vs, 7·81vs, 8·20vs, 8·46ms, 8·59ms, 8·77s (triplet) (C—F str.), 9·71ms (N—O str.), 10·32s (C—N str.), 10·57ms, 12·03w, and 14·05ms (CF_3 def.) μm, λ_{max} (vapour) 304 nm (ε 40; broad band covering the range 235—380 nm), *m/e* (major peaks) 296 ($C_5F_{10}NO_2^+$, 22%), 218 ($C_3F_8NO^+$, 36), 130 ($C_2F_4NO^+$, 44), 69 (CF_3^+, 100), 44 (CO_2^+, 24), 28 (CO^+, 13) [top mass peak 445 (M − F, $C_7F_{15}N_2O_3^+$, 1%)], which did not give satisfactory analytical figures [Found: C, 16·6; 19·8; N, 6·2%; *M* (Regnault), 464. $C_7F_{16}N_2O_3$ requires C, 18·1; N, 6·0%; *M*, 464].

[9] R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141; J. Freear and A. E. Tipping, *J. Chem. Soc.* (*C*), 1969, 1955, and earlier parts of this series.