Perfluoro-2,5-diazahexane-2,5-dioxyl and its Use in Polymer Chemistry and in Polymer Cross-linking

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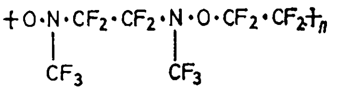
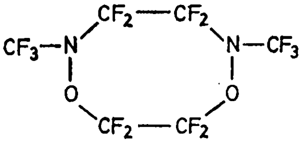
Summary Perfluoro-2,5-diazahexane-2,5-dioxyl has been synthesised; it reacts with nitric oxide to give $CF_3\cdot N(O\cdot NO)\cdot CF_2\cdot CF_2\cdot N(O\cdot NO)\cdot CF_3$, with hydrogen bromide, toluene, triphenylmethane, or hydrogen–Pd–$BaSO_4$ to give $CF_3\cdot N(OH)\cdot CF_2\cdot CF_2\cdot N(OH)\cdot CF_3$, and with perfluorinated olefins or dienes to give nitroso-rubbers and heterocycles, the latter type of reaction finding application in the cross-linking of trifluoronitrosomethane–tetrafluoroethylene–hexafluorobutadiene terpolymers.

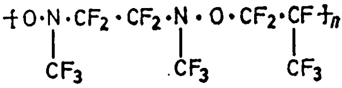
PERFLUORO-2,5-DIAZAHEXANE-2,5-DIOXYL, apparently the first perfluorinated bis-nitroxide to be isolated,‡ has been prepared (43% based on $CF_3\cdot NO$) by treatment with cold water of the $CF_3\cdot NO$–C_2F_4–PCl_3 adduct (2 : 1 : 1)[1] followed by dropwise addition of the hydrolysate§ to a solution (*ca.* 90 °C) of potassium permanganate in dilute sulphuric acid. The structure of the bis-nitroxide, a deep purple liquid, b.p. 55 °C at 769 mmHg, was established by elemental analysis, molecular weight determination (Regnault), and e.s.r. and mass spectroscopy.

Although apparently unaffected by storage for several days as a vapour in the dark at 21 °C in Pyrex, perfluoro-2,5-diazahexane-2,5-dioxyl decomposes at 350 °C in platinum (vacuum flow pyrolysis) to give COF_2, $CF_3\cdot N:CF_2$, $(CF_3)_2N\cdot O\cdot CF_3$, and $CF_3\cdot\overline{N\cdot O\cdot CF_2\cdot CF_2}$. Like its mono-functional analogue, bistrifluoromethyl nitroxide,[3] perfluoro-2,5-diazahexane-2,5-dioxyl readily attacks nitric oxide and hydrogen-atom donors (hydrogen bromide at ~ 0 °C is the preferred preparative reagent), giving $CF_3\cdot N(O\cdot NO)\cdot CF_2\cdot CF_2\cdot N(O\cdot NO)\cdot CF_3$ and $CF_3\cdot N(OH)\cdot CF_2\cdot CF_2\cdot N(OH)\cdot CF_3$, respectively. Attack by the bis-nitroxide on tetrafluoroethylene, hexafluoropropene, hexafluorobuta-1,3-diene, or hexafluorocyclopentadiene leads to the forma-

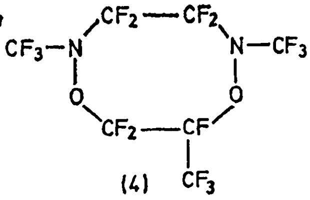

$\left[O\cdot\underset{CF_3}{N}\cdot CF_2\cdot CF_2\cdot\underset{CF_3}{N}\cdot O\cdot CF_2\cdot CF_2\right]_n$

(1)


(2)


$\left[O\cdot\underset{CF_3}{N}\cdot CF_2\cdot CF_2\cdot\underset{CF_3}{N}\cdot O\cdot CF_2\cdot\underset{CF_3}{CF}\right]_n$

(3)


(4)

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‡ U.v. irradiation of perfluoro-*NN'*-difluoropiperazine in the presence of oxygen and/or silica (*cf.* ref. 2) yielded a wax which changed into a nitroxide [possibly $\cdot O\cdot\overline{N\cdot CF_2\cdot CF_2\cdot N(\dot{O})\cdot CF_2\cdot CF_2}$] containing (e.s.r.) purple liquid when heated to *ca.* 200 °C. (R. E. Banks, P. A. Carson, and R. N. Haszeldine, unpublished results.)

§ On one occasion a volatile yellow liquid (possibly Cl_2O) was also produced in the oxidation stage, and this exploded violently during an attempt to separate it from perfluoro-2,5-diazahexane-2,5-dioxyl by trap-to-trap fractional condensation *in vacuo*. Removal of chloride from the hydrolysate as silver chloride appears to eliminate this hazard.

tion of 1 : 1 copolymers and novel heterocycles, production of the former being much favoured by the use of low temperatures and condensed phase systems. Thus, the nitroso-rubber (**1**) (93%) and the diazacyclo-octane (**2**) (3%) are obtained by condensing perfluoro-2,5-diazahexane-2,5-dioxyl onto an equimolar proportion of C_2F_4 at −196 °C and allowing the mixture to warm to room temperature; a similar reaction between the bis-nitroxide and hexafluoropropene gives a copolymer mainly of structure (**3**) (86%) and the heterocycle (**4**) (7%), whereas insignificant polymer formation occurs and the yield of (**4**) rises to 63% if the reactants are mixed at room temperature and *ca.* 25 mmHg pressure. The structures (**1**)—(**4**) were established by elemental analysis and spectroscopy (i.r., ^{19}F n.m.r., and mass); as expected for compounds containing the N–O–C–C unit,[4] pyrolysis of (**1**) at 400 °C *in vacuo* gave an equimolar mixture of carbonyl fluoride and perfluoro-2-azapropene.

The ability of perfluoro-2,5-diazahexane-2,5-dioxyl to add to olefins, and its bifunctionality, suggested its use as a cross-linking agent for elastomers; *e.g.*, it has been found possible to vulcanise nitroso-rubbers[5] of the type prepared by the copolymerisation of trifluoronitrosomethane with perfluoro-olefins; hitherto cross-linking has involved reactions (*e.g.*, with diamines) which have markedly reduced the thermal stability and chemical resistance of the elastomer. An elastomer containing the units $-CF_2\cdot CF : CF\cdot CF_2-$ and $-CF_2\cdot CF(CF : CF_2)-$ as well as $-N(CF_3)\cdot O\cdot CF_2\cdot CF_2-$ in the main chain, prepared from $CF_3\cdot NO$, C_2F_4, and a small proportion of hexafluorobuta-1,3-diene,[6] was vulcanised by the bis-nitroxide to give products with essentially the same thermal stabilities as the raw terpolymers. Thus, a gum-like terpolymer $\{[n] = 0{\cdot}19\ \mathrm{dl\ g^{-1}}$ in $(C_4F_9)_3N$ at 25 °C$\}$ containing monomer residues in the ratio of $1{\cdot}00(CF_3\cdot NO) : 0{\cdot}75(C_2F_4) : 0{\cdot}25(C_4F_6)$ reaches a useful level of cure [V_r = 0·34¶ ($CF_2Cl\cdot CFCl_2$, 28 °C, 3 days equilibration time)] after being mixed with perfluoro-2,5-diazahexane-2,5-dioxyl (*ca.* 7% by wt.) and heated in a press (1000 p.s.i.) at 125 °C for 0·5 h. A vulcanisate with a V_r value of 0·29 can be obtained by keeping a mixture of terpolymer and bis-nitroxide (10 : 1 w/w) in the press (1000 p.s.i.) at ambient temperature for 4 h. The cross-links in the vulcanisates are of the same chemical type as the main chain of the $CF_3\cdot NO–C_2F_4$ copolymer.

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¶ V_r = ratio of the volume of the dry vulcanisate to that of the swollen network.

[1] A. Ya. Yakubovich, P. O. Gitel', Z. N. Lagutina, and F. N. Chelobov, *Zhur. obshchei Khim.*, 1966, **36**, 163, have proposed the structure $CF_3\cdot\overline{N\cdot O\cdot PCl_3\cdot O\cdot N(CF_3)_2\cdot CF_2\cdot C}F_2$ for this adduct; the alternative structure $CF_3\cdot\overline{\overset{+}{N}(\overset{-}{O})\cdot PCl_3\cdot \overset{+}{N}(\overset{-}{O})(CF_3)\cdot CF_2\cdot C}F_2$ is favoured by others (V. A. Ginsburg, L. L. Martynova, M. F. Lebedeva, S. S. Dubov, A. N. Medvedev, and B. I. Tetel'baum, *Zhur. obshchei Khim.*, 1967, **37**, 1073).

[2] R. E. Banks, K. Mullen, and G. E. Williamson, *J. Chem. Soc.* (*C*), 1968, 2608; R. E. Banks and G. F. Smith, paper on the preparation of perfluoromorpholine-*N*-oxyl presented at the 6th International Symposium on Fluorine Chemistry, Durham, England, July, 1971.

[3] For a recent review of the chemistry of $(CF_3)_2N\cdot O\cdot$ see D. P. Babb and J. M. Shreeve, *Intra-Science Chemistry Reports*, 1971, **5**, 55.

[4] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881.

[5] D. A. Barr and R. N. Haszeldine, *Nature*, 1955, **175**, 991; D. A. Barr, R. N. Haszeldine, and C. J. Willis, *Proc. Chem. Soc.*, 1959, 230; *J. Chem. Soc.*, 1961, 1351.

[6] R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 6149.