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The reaction of perfluoro-2,5-diazahexane 2,5-dioxyl with aromatic compounds and perfluoroiodoalkanes

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Abstract

Treatment of perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) with the fluoroarenes C_6F_5X (X = F or Br at *c.* 20 °C; X = CF_3 at 50 °C) and pentafluoropyridine (50 °C) gives 2:1 copolymers in high yield, but pentachloropyridine is unreactive at 50 °C. Copolymers are also formed between **1** and the arenes C_6F_5I, C_6F_5H and C_6H_6 which did not analyse correctly for 2:1 copolymers; in the latter case, hydrogen abstraction is taking place as shown by the presence of N–OH and C=O groups in the polymer. Hexafluorobenzene is not incorporated in the polymer formed by treatment of **1** with a mixture of vinylidene fluoride and hexafluorobenzene. Photochemical reaction of trifluoroiodomethane with **1** affords the bishydroxylamine $CF_3ON(CF_3)CF_2CF_2N(CF_3)OCF_3$ in quantitative yield, while the di-iodides $I(CF_2)_nI$ ($n = 2$ and 4) give copolymers of **1** and the units $(CF_2)_n$ ($n = 2$ and 4), which contain $(CF_2)_nI$ end-groups.

Introduction

The reactions of perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) which have been reported [1–6] are comparable in type to those of its monofunctional analogue bis(trifluoromethyl)nitroxide $(CF_3)_2NO\cdot$. With compounds which react with the nitroxide to give 1:2 adducts, the bifunctional dioxyl **1** affords heterocyclic compounds, e.g. with SO_2 [6], or copolymers or mixtures of copolymers and heterocycles, e.g. with alkenes [1, 2, 7]. The diol **2**, the bisnitrite **3** and the mercurial **4** have also been prepared by reaction of **1** with hydrogen bromide [1, 2], nitric oxide [1, 2] and mercury [8], respectively.

In a continuation of a study of the chemistry of dioxyl **1**, its reactions with arenes and perfluoroiodo- and perfluorodi-iodo-alkanes are now reported.

Experimental

Starting materials

Perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) was prepared by hydrolysis of the 2:1:1 adduct of trifluoronitrosomethane, tetrafluoroethene and phosphorus trichloride, followed by oxidation [$KMnO_4/H_2SO_4(aq)$] [2].

The perfluoroarenes, pentachloropyridine, pentafluoropyridine and vinylidene fluoride were commercial samples and the fluoroiodoalkanes CF_3I and $I(CF_2)_nI$ ($n = 2$, 4) were research samples available in this Department; the purity of each was checked (IR, ^{19}F NMR spectroscopy) before use.

General techniques

Reactions were carried out *in vacuo* in Rotaflo tubes (*c.* 100 cm^3) at room or elevated temperature in the dark (with the arenes) or irradiated at a distance of 10 cm from a Hanovia 500 W medium-pressure UV lamp (with the fluoroiodoalkanes) until the purple colour due to dioxyl **1** had disappeared. The volatile products were fractionated by passing the vapour at low pressure (1–2 mmHg) through traps cooled to an increasingly lower temperature, and polymeric materials were extracted from the tube with 1,1,2-trichlorotrifluoroethane followed by removal of the solvent *in vacuo* and pumping to constant weight.

The products were examined by IR spectroscopy (Perkin-Elmer 137 or 257 instruments), ^{19}F NMR spectroscopy [Perkin-Elmer R10 (56.46 MHz) or Varian Associates HA100 (94.12 MHz) instruments; external reference CF_3CO_2H] and mass spectrometry (A.E.I. MS 902 spectrometer with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions in $CF_2ClCFCl_2$ as stated in the text; chemical shifts to low field of reference are designated positive.

Boiling points were determined by Siwoloboff's method.

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Reactions of dioxyl 1

(a) With benzene (general procedure)

A mixture of **1** (1.38 g, 4.63 mmol) and benzene (0.50 g, 6.41 mmol), stored (14 d), gave a mixture of the compounds CF_3NCO, $CF_3N{=}CF_2$ and SiF_4 (0.07 g, 0.56 mmol), unchanged benzene (0.36 g, 4.62 mmol, 72% recovered) and a dioxyl **1**/benzene copolymer (1.45 g, 95%) [Analysis: Found: C, 22.9; H, 0.5; F. 57.4; N, 8.3%. Calc. for copolymer of **1** and C_6H_6 in the ratio 2.6:1 $(C_{16.4}H_6F_{26}N_{5.2}O_{5.2})_n$: C, 23.1; H, 0.7; F, 57.9; N, 8.5%]. IR $\nu_{max.}$ (cm^{-1}): 3440 (br., O−H str.); 2907 (w, C−H str.); 1773 (w, C=O str.); 1271–1179 (vs, C−F str.); 1089 (s, C−O str.); 1044 (s, N−O str.); 717 (m, CF_3 str.). MS *m/z*: 688 (0.1%); 389 (0.8); 295 (1.3, $C_5HF_{10}N_2O^+$); 282 (1.3, $C_4F_{10}N_2O^+$); 181 (6.7, $C_3HF_6NO^+$); 150 (16.1, $C_2HF_5NO^+$); 149 (16.5, $C_2F_5NO^+$); 114 (21.2, $C_2F_4N^+$); 69 (100.0, CF_3^+); 47 (6.3, CFO^+).

(b) With polyfluoroaromatic compounds

Reactions of dioxyl **1** with the polyfluoroarenes C_6F_5X (X=F, Br, I, CF_3 and H) and with pentafluoropyridine are summarised in Table 1. Elemental analysis data on the product copolymers (**6a–f**) are given in Table 2 and IR and MS data in Table 3.

TABLE 1. Reaction of dioxyl **1** with polyfluoroaromatic compounds

Arene	Reaction conditions		Ratio arene/**1**	Recovered arene (%)	Products	(%)
	Temp. (°C)	Time (d)				
C_6F_6	20	21	1.5:1	67	**6a**	(98)
C_6F_5Br	20	14	1.1:1	55	**6b**	(97.5)
$C_6F_5CF_3$	50	6	0.82:1	36.5	**6c**	(100)
C_5F_5N	50	4	1.8:1	71.5	**6d**	(100)
C_6F_5I	20	19	1.3:1	*	**6e**	(88.5)
C_6F_5H	20	16	2.7:1	80	**6f**	(100)

*Not determined because recovered C_6F_5I was heavily contaminated with iodine.

(c) With pentachloropyridine

A mixture of **1** (0.85 g, 2.85 mmol) and pentachloropyridine (0.55 g, 2.19 mmol) in tetrachloromethane (10.0 g) heated at 50 °C (28 d) gave unchanged pentachloropyridine (0.55 g, 2.19 mmol, 100% recovered) and a mixture of unchanged dioxyl **1** and tetrachloromethane.

(d) With a mixture of vinylidene fluoride and hexafluorobenzene

A mixture of **1** (0.90 g, 3.02 mmol), the alkene (0.22 g, 3.44 mmol) and hexafluorobenzene (0.02 g, 0.11 mmol), stored (13 d), gave unchanged vinylidene fluoride (0.035 g, 0.55 mmol, 16% recovered), unchanged hexafluorobenzene (0.02 g, 0.11 mmol, 100% recovered) and a 1:1 dioxyl **1**/vinylidene fluoride copolymer (1.05 g, 96%) [Analysis: Found: C, 19.6; H, 0.6; N, 7.3%. Calc. for $(C_6H_2F_{12}N_2O_2)_n$: C, 19.9; H, 0.6; N, 7.7%].

A second experiment using a mixture of **1** (0.77 g, 2.58 mmol), the alkene (0.18 g, 2.81 mmol) and hexafluorobenzene (0.24 g, 1.29 mmol), stored (7 d), gave unchanged hexafluorobenzene (0.23 g, 1.24 mmol, 96% recovered) and a 1:1 dioxyl **1**/vinylidene fluoride copolymer (0.89 g, 95.5%) (Analysis: Found: C, 20.0; H, 0.7; N, 7.4%).

(e) With trifluoroiodomethane

A mixture of **1** (0.62 g, 2.08 mmol) and trifluoroiodomethane (1.35 g, 6.89 mmol), irradiated (24 h) and the products then shaken *in vacuo* with mercury (3.0 g) to remove the iodine formed (10 min), gave unchanged trifluoroiodomethane (0.53 g, 2.71 mmol, 39.5%) which condensed at −196 °C and a −23 °C fraction identified as perfluoro-(3,6-dimethyl-2,7-dioxa-2,6-diaza-octane) (**12**) (nc) (0.91 g, 2.08 mmol, 100%) (Analysis: Found: C, 16.5; F, 69.9; N, 6.4%. $C_6F_{16}N_2O_2$ requires: C, 16.5; F, 69.7; N, 6.4%), b.p. 104 °C. IR $\nu_{max.}$ (cm^{-1}): 1287–1174 (vs, C−F str.); 1101 and 1082 (s, C−O str.); 1059 and 1043 (s, N−O str.); 722s and 710 (m, CF_3 def.). ^{19}F NMR (neat) δ: +11.0 (br., 12F, $2NCF_3$ and $2OCF_3$); −23.1 (s, 4F, CF_2CF_2) ppm. MS *m/z*: 417 [0.6%, $(M-F)^+$]; 329 (1.0, $C_5F_{11}N_2O_2^+$); 218 (47.5, $C_3F_8NO^+$);

TABLE 2. Elemental analysis data for dioxyl **1**/arene copolymers

Compound	Analysis						Compound	Analysis					
	Found (%)			Calc. (%)[a]				Found (%)			Calc. (%)[a]		
	C	F	N	C	F	N		C	F	N	C	F	N
6a	21.3	63.1	7.2	21.5	63.2	7.2	**6d**	20.6	61.7	9.1	20.4	62.1	9.2
6b	19.9	56.4	6.7	19.9	56.3	6.6	**6e**	18.8	53.6	6.4[b]	18.9	53.4	6.3[b]
6c	21.6	63.4	7.1	21.6	63.9	6.7	**6f**	21.4	60.4		22.0	62.2	

[a] Calc. for 2:1 copolymers of dioxyl **1** and the arene.
[b] % I (Found: 12.0. Calc. 14.3).

TABLE 3. Summary of IR and MS data for dioxyl **1**/arene copolymers

Compound	IR (cm^{-1})	MS *m/z* (%)[a]
6a	1736 (C=C); 1282–1170 (C–F); 1031 (C–O–N); 713 (CF_3 def.).	798 (7, $C_{14}F_{26}N_4O_5$); 782 (3); 763 (3); 298 (3); 199 (95); 186 (9, C_6F_6); 153 (49); 151 (73); 114 (23); 103 (55); 101 (100); 100 (26); 85 (37); 69 (92); 47 (16).
6b	1757 and 1692 (C=C); 1280 (C–F); 1105 (C–O); 1040 (C–O–N); 708 (CF_3 def.).	842/844 (8, $C_{14}BrF_{25}N_4O_4$); 823/825 (2); 544/546 (3); 298 (16); 246/248 (12, C_6BrF_5); 199 (53); 153 (13); 151 (20); 114 (33); 103 (20); 101 (30); 69 (100); 47 (14).
6c	1698 (C=C); 1274–1164 (C–F); 1107 (C–O); 1030 (C–O–N); 710 (CF_3 def.).	832 (1, $C_{15}F_{28}N_4O_4$); 813 (2); 263 (5); 236 (4, C_7F_8); 199 (41); 164 (18); 149 (8); 114 (39); 100 (14); 69 (100); 47 (13); 44 (11).
6d	1761 (C=N); 1280–1163 (C–F); 1098 (C–O); 1029 (C–O–N); 711 (CF_3 def.).	746 (2, $C_{13}F_{24}N_5O_4$); 249 (12); 199 (46); 153 (48); 114 (20); 103 (64); 101 (100); 100 (22); 85 (42); 69 (76); 47 (17); 44 (36); 31 (18).
6e	1751 and 1667 (C=C); 1279–1164 (C–F); 1107 (C–O); 1033 (C–O–N); 713 (CF_3 def.).	893 (0.3, $C_{16}F_{29}N_5O_5$); 294 (100, C_6F_5I); 167 (52); 151 (18); 117 (58); 103 (14); 101 (22); 93 (14); 69 (24); 44 (17).
6f	1715 (C=C); 1282–1170 (C–F); 1031 (C–O–N); 713 (CF_3 def.).	764 (5, $C_{14}HF_{25}N_4O_4$); 745 (3); 298 (19); 199 (100); 16.8 (13.3, C_6HF_5); 164 (11); 149 (12); 114 (24); 100 (32); 99 (20); 69 (91); 47 (8); 44 (21).

[a] Intensities expressed as percentage of the base peak.

130 (56.1, $C_2F_4NO^+$); 119 (22.5, $C_2F_5^+$); 114 (14.0, $C_2F_4N^+$); 69 (100.0, CF_3^+); 64 (4.7, CF_2N^+).

A mixture of **1** (0.62 g, 2.08 mmol) and trifluoroiodomethane (0.86 g, 4.39 mmol), stored (14d), gave a quantitative recovery of unchanged reactants.

(f) With 1,2-di-iodotetrafluoroethane

A mixture of **1** (1.01 g, 3.39 mmol) and 1,2-di-iodotetrafluoroethane (1.28 g, 3.62 mmol), irradiated (20 h) and the products shaken with mercury (3 g) to remove iodine (0.5 h), gave a mixture (0.49 mmol) of the compounds $CF_3N{=}CF_2$, COF_2 and SiF_4 (IR spectroscopy), and a viscous liquid identified as a dioxyl **1**/tetrafluoroethene copolymer (**14**) (1.16 g) (Analysis: Found: C, 17.0; F, 58.7%). ^{19}F NMR ($CF_2ClCFCl_2$) δ: +12.3 (mult., 6F, $2CF_3N$); −13.9 (br., 4F, OCF_2CF_2O); −21.5 (br., 4F, NCF_2CF_2N) ppm. MS *m/z*: 860 (2.5%, $C_{13}F_{30}N_5O_4^+$); 856 (1.8, $C_{12}F_{28}N_6O_6^+$); 758 (3.3, $C_{12}F_{26}N_4O_4^+$); 749 (4.2, $C_{11}F_{27}N_4O_3^+$); 562 (3.1, $C_9F_{20}N_3O_2^+$); 426 (5.6, $C_7F_{14}N_2O_3^+$); 363 (7.7, $C_6F_{13}N_2O^+$); 227 (51.8, $C_4F_7NO_2^+$ and $C_2F_4I^+$); 180 (7.3, $C_3F_6NO^+$); 177 (14.5, $C_3F_5NO_2^+$ and CF_2I^+); 127 (30.5, $C_2F_3NO_2^+$ and I^+); 114 (35.5, $C_2F_4N^+$); 100 (15.6, $C_2F_4^+$); 69 (100.0, CF_3^+); 47 (14.6, CFO^+).

(g) With 1,4-di-iodo-octafluorobutane

A mixture of **1** (0.87 g, 2.92 mmol) and the di-iodoalkane (1.38 g, 3.04 mmol), irradiated (5d) and the products shaken with mercury (5 g) to remove iodine (10 min), gave a mixture (0.09 g, 0.92 mmol) of the compounds CF_3NO, CF_3NCO, $CF_3N{=}CF_2$, COF_2 and SiF_4 (IR spectroscopy) and a dioxyl **1**/perfluoro(tetramethylene) copolymer (**15**) (1.22 g) (Analysis: Found: C, 17.6; F, 60.5%). ^{19}F NMR ($CF_2ClCFCl_2$) δ: +18.9 (mult., 1F, CF_2I); +12.2 (mult., 16F, $2CF_3N$); −10.9 (s, 8F, $2CF_2O$); −14.0 (s, 1F, CF_2O); −21.2 (s, 9F, NCF_2CF_2N); −36.1 (s, 2F, CCF_2CF_2C); −47.1 (br., 8F, CCF_2CF_2C) ppm. MS *m/z*: 821 (0.7%); 716 (1.7); 526 (0.6, $C_9F_{18}N_2O_3^+$); 476 (13.7, $C_8F_{16}N_2O_3^+$); 327 (5.4, $C_4F_8I^+$); 181 (7.9, $C_4F_7^+$); 177 (19.2, $C_3F_5NO_2^+$ and CF_2I^+); 169 (10.0, $C_3F_7^+$); 131 (10.1, $C_3F_5^+$); 130 (11.1, $C_2F_4NO^+$); 127 (21.6, $C_2F_3NO_2^+$ and I^+); 114 (22.2, $C_2F_4N^+$); 100 (21.0, $C_2F_4^+$); 69 (100.0, CF_3^+).

Attempted reactions of the 2:1 dioxyl 1/ hexafluorobenzene copolymer 6a

(a) With bromine

A mixture of copolymer **6a** (0.20 g), bromine (0.12 g, 0.75 mmol) and solvent $CF_2ClCFCl_2$ (3.2 cm^3), stored (24 h) and the volatile products removed *in vacuo*, gave a solid shown (IR spectroscopy and mass spectrometry) to be unchanged copolymer **6a** (0.17 g, 85% recovered) [Analysis: Found: C, 21.2%. Calc. for $(C_{14}F_{26}N_4O_4)_n$: C, 21.5%].

A second experiment using copolymer **6a** (0.52 g), bromine (0.78 g, 4.87 mmol) and solvent $CF_2ClCFCl_2$

(3.1 cm^3), heated at 70 °C (10 d) and the volatile material removed *in vacuo*, gave a white solid which was shown (IR spectroscopy and mass spectrometry) to be unchanged copolymer **6a** (0.40 g, 77% recovered) [Analysis: Found: C, 21.8%. Calc. for $(C_{14}F_{26}N_4O_4)_n$: C, 21.5%].

(b) With bromine under photochemical conditions

A mixture of the copolymer **6a** (0.53 g), bromine (0.04 g, 0.25 mmol) and solvent $CF_2ClCFCl_2$ (3 cm^3), irradiated (6 d) and the volatile material removed *in vacuo*, gave a white solid which was shown (IR spectroscopy and mass spectrometry) to be unchanged copolymer **6a** (0.47 g, 89% recovered) [Analysis: Found: C, 21.3%. Calc. for $(C_{14}F_{26}N_4O_4)_n$: C, 21.5%].

(c) With N,N-*bis(trifluoromethyl)amino-oxyl*

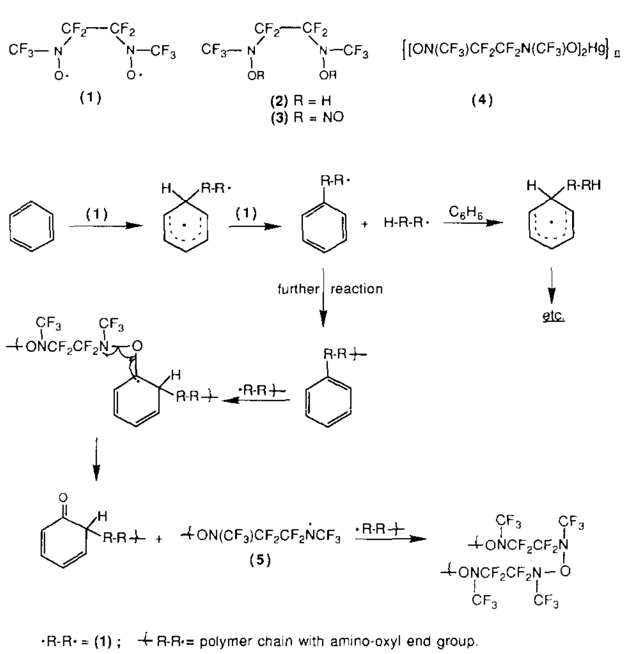
A mixture of the copolymer **6a** (0.51 g), the oxyl (0.34 g, 2.02 mmol) and solvent $CF_2ClCFCl_2$, heated at 70 °C (8 d) and the volatile material removed *in vacuo*, gave a white solid which was shown (IR spectroscopy and mass spectrometry) to be unchanged copolymer **6a** (0.51 g, 100% recovered) [Analysis: Found: C, 21.2; F, 63.4; N, 7.6%. Calc. for $(C_{14}F_{26}N_4O_4)_n$: C, 21.5; F, 63.2; N, 7.2%].

Results and discussion

Reaction of dioxyl **1** with an excess of benzene (1:1.4 molar ratio) in the dark (14 d) gave unchanged benzene (72% recovered), a minor volatile mixture of breakdown products of **1** (CF_3NCO, $CF_3N{=}CF_2$ and SiF_4) and a copolymer of **1** and benzene (98.5%) in the approximate ratio 2.6:1 (elemental analysis). The copolymer showed IR bands at $\nu_{max.}$ 3440 (O–H str.) and 1773 (C=O str.) cm^{-1}, indicating that hydrogen abstraction had occurred to some extent.

Although the nitroxide $(CF_3)_2NO\cdot$ was reported originally not to react with benzene [9] and later work claimed that 1,2,4-tris[bis(trifluoromethyl)amino-oxy] benzene was formed [10], a study in this department showed that addition to the π-system took place to give a complex mixture of products, believed to consist of both cyclohexenyl and cyclohexadienyl compounds; analytical data indicated that the mixture contained on average four $(CF_3)_2NO$ groups per benzene molecule [11, 12]. The oxadiazapentane $(CF_3)_2NON(CF_3)_2$ was isolated from the reaction products and this indicated that carbonyl compounds were also formed, which was substantiated by UV spectral studies [12].

Clearly, analogous reactions are taking place in the reaction of dioxyl **1** with benzene to give carbonyl compounds and the amino radical **5** which is scavenged by any amino-oxy radical (including dioxyl **1**) present in the system as shown in Scheme 1.



·R-R· = (1) ; ⊣R-R· = polymer chain with amino-oxyl end group.

Scheme 1.

$[Ar(ON(CF_3)CF_2CF_2N(CF_3)O)_2]_n$

(6) a; Ar = C_6F_6
b; Ar = C_6F_5Br
c; Ar = $C_6F_5CF_3$
d; Ar = C_5F_5N
e; Ar = C_6F_5I
f; Ar = C_6F_5H

The reaction of dioxyl **1** with a series of polyfluoroarenes was next studied and the results obtained are summarised in Table 1.

The products from all the reactions were copolymers and those formed from the arenes C_6F_5X (X = F, Br and CF_3) and pentafluoropyridine gave correct elemental analyses for the 2:1 copolymers **6a–d**. In the reaction involving the arene C_6F_5I, a considerable amount of iodine was formed and the product did not analyse correctly for the 2:1 copolymer **6e**, being low in iodine content. Similarly, the copolymer derived from pentafluorobenzene did not give a correct elemental analysis for the 2:1 copolymer **6f**, but the ratio of **1**/ arene reacted (not recovered) was close to 2:1.

The IR spectra of all the copolymers formed from the benzenes showed weak absorptions in the range 1750–1660 cm^{-1}, which is the region associated with C=C stretch in fluoroalkenes, confirming the unsaturated nature of the products. However, the 2:1 copolymer **6a** did not react with the nitroxide $(CF_3)_2NO\cdot$ at 70 °C (8 d) nor did it react with bromine at 70 °C or under photochemical conditions, indicating steric protection of the double bonds in the copolymer.

It has been observed previously that reaction of the nitroxide $(CF_3)_2NO\cdot$ with hexafluorobenzene at 80 °C (14 d) afforded a mixture of the tetra- and hexa-addition products [11].

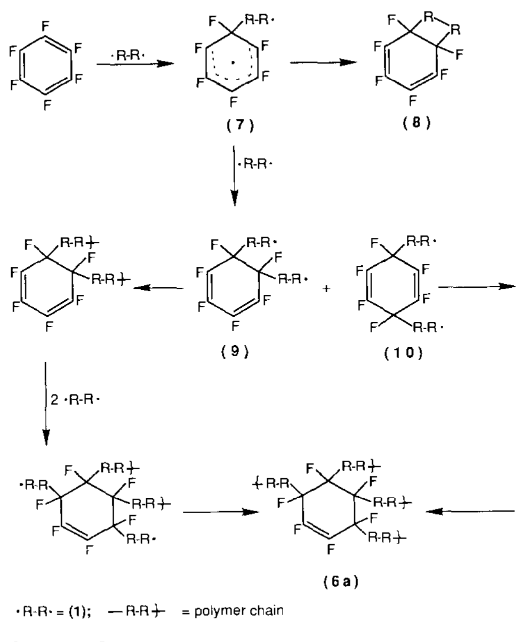
The strong IR absorption at 1760 cm^{-1} (C=N str.) observed for the copolymer **6d** formed from pentafluoropyridine showed the resistance of the C=N bond to attack by dioxyl **1**. Surprisingly, perhaps dioxyl **1** did not react with pentachloropyridine at 50 °C over an extended time period (28 d).

The products are considered to be formed as shown in Scheme 2 for hexafluorobenzene.

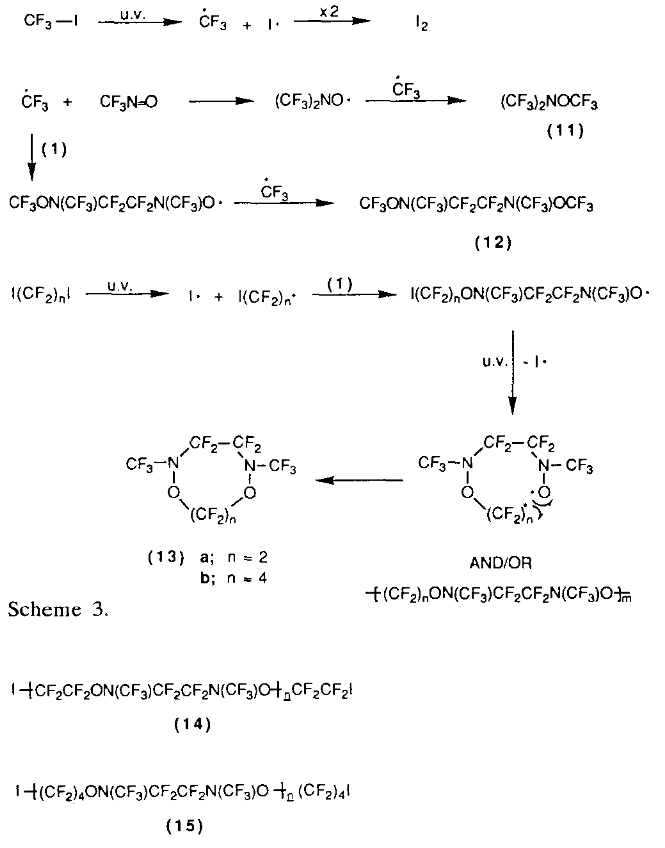
As expected, attack by dioxyl **1** on the polyfluoroarenes was slow leading to the formation of an intermediate radical **7** which could be scavenged by a second molecule of dioxyl **1** or undergo internal cyclisation. The latter reaction to give the bicyclo[6.4.0]dodecadiene system **8** is considered less likely, because in liquid-phase reactions of **1** with alkenes copolymer formation is favoured at the expense of cyclisation to afford 1:1 adducts [1, 2, 7]. Scavenging of the intermediate radical **7** by dioxyl **1** could occur at the 2- or 4-positions to give the dienes **9** and **10**, respectively; attack might be expected to be favoured at the 2-position, since this leads to a conjugated (and hence more stable) 1,3-diene. It has been reported [1] that reaction of dioxyl **1** with perfluoro-1,3-dienes is rapid at room temperature and affords copolymers in high yield.

Dioxyl **1** was initially synthesised for use as a cross-linking agent for unsaturated nitroso rubbers [1, 3]. The polymers obtained from reaction between dioxyl **1** and alkenes are in general viscous oils of low molecular weight, and it was considered possible that reaction of **1** with an alkene in the presence of a polyfluoroarene would result in the arene being incorporated in the polymer chain and if higher molecular weight copolymers were formed these could exhibit improved physical properties. However, reaction between **1** and the alkene $CH_2{=}CF_2$ in the presence of hexafluorobenzene [*c.* 2:2:1 molar ratio (7 d) or *c.* 1:1:0.03 molar ratio (13 d)] at room temperature gave only a 1:1 dioxyl **1**/$CH_2{=}CF_2$ copolymer $[ON(CF_3)CF_2CF_2N(CF_3)OCH_2CF_2]_n$ and a near-quantitative recovery of the arene.

Tris(trifluoromethyl)hydroxylamine (**11**) was prepared originally by photochemical reaction of trifluoroiodomethane with trifluoronitrosomethane [13], and the proposed intermediate, the nitroxide $(CF_3)_2NO\cdot$, was later found to give **11** in high yield (84%) on reaction with trifluoroiodomethane under photochemical conditions [14]. It was therefore decided to investigate the photochemical reaction of trifluoroiodomethane with dioxyl **1** as a possible route to the perfluorobishydroxylamine **12**. If this was successful, an initial study of the corresponding reactions of the diiodoalkanes $I(CF_2)_nI$ ($n=2$ and 4) would then be undertaken as a possible synthesis of the corresponding 1:1 copolymers and also of the heterocycles **13a** and **13b** (Scheme 3). It was realised that liquid-phase reaction would favour polymer formation, while gas-phase reaction should favour heterocycle formation; low yields



Scheme 2.



Scheme 3.

of heterocycles have been observed in certain liquid-phase reactions of **1** with alkenes [2, 7].

The heterocycle **13a** has been made previously, together with a 1:1 copolymer (ratio 52:48), by the reaction of **1** with tetrafluoroethene in the gas phase [15].

Trifluoroiodomethane did not react with dioxyl **1** in the dark at room temperature (14 d), but on UV irradiation (1 d) of the mixture (3.3:1 molar ratio) followed by removal of the iodine formed with mercury, compound **12** (100%) was isolated together with unchanged iodoalkane (39.5% recovered). The high yield of compound **12** confirmed the effectiveness of **1** as a radical scavenger.

A mixture of dioxyl **1** and 1,2-di-iodotetrafluoroethane [a slight excess of the perhalogenoalkane was used to enable the completion of reaction to be judged (absence of colour due to **1** thus avoiding over-irradiation], irradiated (both liquid and gas phases, 20 h) gave (after removal of iodine) a small amount of a mixture of decomposition products ($CF_3N{=}CF_2$, COF_2 and SiF_4) and a copolymer of dioxyl **1** and tetrafluoroethene **14**, the IR and ^{19}F NMR spectra of which were almost identical to the IR [15] and ^{19}F NMR [2] spectra reported for the 1:1 copolymer formed by the liquid-phase reaction between dioxyl **1** and tetrafluoroethene. However, the mass spectrum of the polymer formed in the present work showed peaks at *m/z* 227 ($CF_2CF_2I^+$); 177 (CF_2I^+); 127 (I^+), indicating that CF_2CF_2I groups terminated the polymer chain. The heterocycle **13a** was not detected in the products.

Irradiation (liquid and gas phases) of a mixture of **1** and 1,4-di-iodo-octafluorobutane (1.0:1.04 molar ratio, 5 d) gave (after removal of iodine) a volatile mixture (*c*. 4%) of decomposition products (CF_3NCO, CF_3NO, $CF_3N{=}CF_2$, COF_2 and SiF_4) and a dioxyl **1**/perfluorotetramethylene copolymer (**15**). The ^{19}F NMR spectrum of **15** showed absorptions for the $-CF_2CF_2CF_2CF_2ON(CF_3)CF_2CF_2N(CF_3)O-$ chain and also for $-CF_2CF_2CF_2CF_2I$ end-groups in the ratio *c*. 4:1. No evidence was obtained for the formation of heterocycle **13b**.

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