*Journal of Fluorine Chemistry*, 55 (1991) 179–187

# Decomposition of perfluoro-(2,4,4,7,7,9-hexamethyl-3,8-dioxa-2,5,6,9-tetra-azadec-5-ene) in the presence of fluoroalkenes, ethyne, benzene and nitroso compounds

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(Received June 17, 1991; accepted September 3, 1991)

## Abstract

Thermolysis of the azo compound $(CF_3)_2NOC(CF_3)_2N{=}NC(CF_3)_2ON(CF_3)_2$ (**1**) alone at 140 °C gives nitrogen, hexafluoroacetone and the hydrazine $(CF_3)_2NN(CF_3)_2$ via $(CF_3)_2N\cdot$ radical coupling in quantitative yield, while from decomposition in the presence of the alkenes $CF_2{=}CCl_2$, $CF_2{=}CFCl$ and $CF_2{=}CHF$ (*ca.* 1:1 molar ratio) the major products are the dimer $[(CF_3)_2NCF_2CCl_2]_2$, trimer $(CF_3)_2N(CF_2CFCl)_2CFClCF_2N(CF_3)_2$ and a mixture of tetramers $(CF_3)_2N(C_2HF_3)_4N(CF_3)_2$, respectively. The $(CF_3)_2N\cdot$ radicals generated from **1** can also be trapped with bromine $[\rightarrow (CF_3)_2NBr]$ and nitroso compounds $[\rightarrow (CF_3)_2NNRO\cdot$ $(R{=}CF_3$ and Ph)], but with ethyne or benzene near-quantitative yields of the amine $(CF_3)_2NH$ are obtained.

## Introduction

The $(CF_3)_2N\cdot$ radical has been generated from precursors of the type $(CF_3)_2NX$ where X=Cl, Br or I [1], $X{=}OCF_3$ [2], $X{=}ON(CF_3)_2$ [3] and $X{=}HgN(CF_3)_2$ [4]. Only in the latter case was the radical produced in the absence of other radicals, but the mercurial decomposition was slow.

The azo compound **1** [5] was considered to be a further possible precursor of the $(CF_3)_2N\cdot$ radical and the results of a preliminary investigation carried out in 1980–81 [6] into the decomposition of **1** both alone and in the presence of compounds containing multiple bonds are now reported.

## Experimental

### *Starting material*

Perfluoro-(2,4,4,7,7,9-hexamethyl-3,8-dioxa-2,5,6,9-tetra-azadec-5-ene) (**1**) was prepared in quantitative yield by reaction of *N,N*-bis(trifluoromethyl)amino-oxyl with hexafluoroacetone azine (2:1 molar ratio) *in vacuo* at 25 °C (3 d) [5].

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### *General techniques*

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture.

Reactions were carried out *in vacuo* in sealed Pyrex tubes (*ca.* 300 $cm^3$), unless stated otherwise, and volatile products were separated by fractional condensation *in vacuo* followed by distillation (20 cm, Vigreux column) where necessary. Products were examined by molecular weight determination (Regnault's method), IR spectroscopy (Perkin–Elmer 257 spectrometer), $^{19}F$ NMR spectroscopy (Perkin–Elmer R10 or Varian HA100 spectrometers operating at 56.46 and 94.1 MHz, respectively, reference external $CF_3CO_2H$; chemical shifts to low field of reference are designated positive), mass spectrometry (A.E.I. MS 902 instrument) and GLC [6 m methyl silicone (OV 1) gum or 3 m silicone SE30 oil (30%) on Celite]. Boiling points were determined by Siwoloboff's method.

Thermal gravimetric analysis (TGA) was carried out on DuPont 950 and 900 thermal analysers in series and ESR experiments employed a Varian E9 spectrometer in the dual cavity mode ('strong pitch' as reference) with a mercury vapour lamp (1 kW) behind a quartz window used to irradiate the samples.

### *Reactions of the azo compound 1*

#### *(a) Pyrolysis alone*

Compound **1** (3.50 g, 5.30 mmol), heated at 140 °C (1 d), gave (i) nitrogen (0.15 g, 5.30 mmol, 100%; mol. wt., 28), (ii) a −196 °C fraction identified as hexafluoroacetone (1.75 g, 10.54 mmol, 100%) by comparison of its IR and $^{19}F$ NMR spectra with those of an authentic sample and (iii) a −95 °C fraction identified as tetrakis(trifluoromethyl)hydrazine (**2**) (1.60 g, 5.30 mmol, 100%) by comparison of its IR and $^{19}F$ NMR spectra with those of an authentic sample.

#### *(b) With 1,1-dichorodifluoroethylene*

A mixture of the alkene (1.40 g, 10.5 mmol) and compound **1** (6.73 g, 10.1 mmol), heated at 140 °C (1 d), gave (i) nitrogen (0.28 g, 10.0 mmol, 99.5%; mol. wt., 28), (ii) hexafluoroacetone (3.30 g, 19.8 mmol, 98%), which condensed at −196 °C, (iii) unchanged alkene (0.04 g, 0.30 mmol, 3% recovered) (−120 °C fraction), (iv) a −95 °C fraction (1.79 g), which was shown to consist of hydrazine **2** (1.60 g, 4.80 mmol, 47%) contaminated with two minor unidentified components (*ca.* 0.19 g) by GLC (OV 1 at 30 °C) and (v) a −23 °C fraction identified as perfluoro(2,7-dimethyl-4,4,5,5-tetrachloro-2,7-diazaoctane) (**3**) (nc) [2.70 g, 4.70 mmol, 47% based on **1** 90% based on alkene] (Found: C, 17.2; Cl, 24.7; N, 5.0; F, 53.0%. $C_8Cl_4F_{16}N_2$ requires C, 16.9; Cl, 24.9; N, 4.9; F, 53.3%), b.p., 145–147 °C. $^{19}F$ NMR: $\delta$ +24.5 [t, $2(CF_3)_2N$, $J = 19$ Hz] and +2.5 (broad s, $2CF_2$) ppm. Mass spectrum *m/z*: 502/500/498 [9.1%, $(M-Cl_2)^+$], 350/348/346 (16.1%, $C_6F_{10}NCl_2^+$), 288/286/284 [3.9%, $(CF_3)_2NCF_2CCl_2^+$], 262/260/258 (20.7%,

$C_7F_4N_2Cl_2^+$), 202 [41.4%, $(CF_3)_2NCF_2^+$], 114 (39.4%, $C_2F_4N^+$) and 69 (100%, $CF_3^+$).

*(c) With chlorotrifluoroethylene (1:1 molar ratio)*

A mixture of **1** (6.59 g, 9.90 mmol) and the alkene (1.18 g, 10.1 mmol), heated at 140 °C (1 d), gave (i) nitrogen (0.27 g, 9.65 mmol, 97.5%; mol. wt., 28), (ii) hexafluoroacetone (3.22 g, 19.4 mmol, 98%) (−196 °C fraction), (iii) unchanged alkene (0.05 g, 0.42 mmol, 4% recovered) (−120 °C fraction), (iv) a −78 °C fraction (2.19 g), shown by GLC (OV 1 at 30 °C) to consist mainly of hydrazine **2** (1.98 g, 6.5 mmol, 65.5%) contaminated with small amounts of three higher-boiling compounds, and (v) a −23 °C fraction identified as perfluoro-(2,9-dimethyl-4,5,7-trichloro-2,9-diazadecane) (**4**) (nc) [2.03 g, 3.10 mmol, 31% based on **1**, 92% based on alkene] (Found: C, 18.4; Cl, 16.6; N, 4.3; F, 60.6%. $C_{10}Cl_3F_{21}N_2$ requires C, 18.4; Cl, 16.3; N, 4.3; F, 61.0%), b.p., 152–154 °C. $^{19}F$ NMR: $\delta$ +24.9 [two overlapping multiplets, 12F, $2(CF_3)_2N$] and +9 to −10 (many complex bands, 9F, $3CF_2$ and 3CFCl) ppm. Mass spectrum *m/z*: 617 [trace, $(M-Cl)^+$], 500 {0.2% $[M-(CF_3)_2N]^+$}, 300/298/296 (15.8%, $CF_2{=}NC_4F_6Cl_2^+$), 270/268 [6.4%, $(CF_3)_2NCF_2CFCl^+$] 202 [92.2%, $(CF_3)_2NCF_2^+$], 114 (59.7%, $C_2F_4N^+$) and 69 (100%, $CF_3^+$); GLC (OV 1 at 30 °C), showed only one peak.

*(d) With chlorotrifluoroethylene (2:1 molar ratio)*

A mixture of **1** (6.60 g, 9.91 mmol) and the alkene (0.62 g, 5.3 mmol), heated at 160 °C (1 d), gave, (i) nitrogen (0.27 g, 9.65 mmol, 97.5%; mol. wt., 28), (ii) hexafluoroacetone (3.24 g, 19.5 mmol, 99%) which condensed at −196 °C and (iii) a −78 °C fraction (3.65 g) which was distilled to give hydrazine **2** (2.28 g, 7.50 mmol, 75%), b.p., 32 °C, lit. [7] b.p., 31 °C, and a colourless higher-boiling liquid (1.37 g), b.p., 62–154 °C. $^{19}F$ NMR: $\delta$ +24.0 to +25.0 [complex, $(CF_3)_2N$] and +9.5 to −11.0 (complex multiplets, $CF_2$ and CFCl) ppm. Examination of the liquid by coupled GLC (OV 1 at 70 °C) and mass spectrometry showed the presence of perfluoro-(2,5-dimethyl-3-chloro-2,5-diazahexane) (**6**) [*ca.* 0.22 g, 0.52 mmol, 5% based on **1**, 10% based on alkene]. Mass spectrum *m/z*: 385 [1.3%, $(M-Cl)^+$], 316 (1.2%, $C_5F_{12}N_2^+$), 270/268 [3.4%, $(M-C_2F_6Cl)^+$], 220/218 [3.4%, $(CF_3)_2NCFCl^+$], 202 [14.3%, $(CF_3)_2NCF_2^+$], 114 (30.3%, $C_2F_4N^+$) and 69 (100%, $CF_3^+$), the two diastereoisomers (*ca.* 1:1 ratio) of perfluoro-(2,7-dimethyl-4,5-dichloro-2,7-diazaoctane) (**5**) [*ca.* 0.60 g, 1.12 mmol, 11% based on **1**, 41% based on alkene]. Mass spectrum *m/z* (in order of retention time): 501 [0.1% (0.1%), $(M-Cl)^+$], 466 [0.5% (0.3%), $(M-Cl_2)^+$], 385 [3.1% (2.0%), $C_6F_{15}N_2^+$], 297 [7.2% (6.4%), $C_5F_{11}N_2^+$], 202 [26.8% (18.7%), $(CF_3)_2NCF_2^+$], 137/135 [25.8% (18.8%), $C_2F_4Cl^+/C_4F_2NCl^+$], 114 [36.9% (29.0%), $C_2F_4N^+$] and 69 [100% (100%), $CF_3^+$), and trimer **4** [*ca.* 0.57 g, 0.87 mmol, 9% based on **1**, 49% based on alkene].

*(e) With chlorotrifluoroethylene (polymerisation experiment)*

A mixture of **1** (0.025 g, $3.7\times10^{-2}$ mmol), the alkene (7.5 g, 56.5 mmol) and solvent 1,1,2-trichlorotrifluoroethane (*ca.* 50 cm$^3$), sealed *in* *vacuo* in a spherical glass vessel equipped with a cold finger (*ca.* 70 cm$^3$) and kept on a laboratory bench (28 d) gave a dense white precipitate identified as poly(chlorotrifluoroethylene) (5.40 g, 72%) [Found: C, 20.3; Cl, 30.1; F, 48.5%. Calc. for $(C_2F_3Cl)_n$: C, 20.6; Cl, 30.5; F, 48.9%]. TGA (total weight loss between 395 and 450 °C), m.p., 216 °C, glass transition temp., −4 °C.

Two control experiments, one utilising the same quantities of reactants but carried out in the dark, and the other with compound **1** absent, gave no polymer.

### (*f*) *With trifluorethylene*

A mixture of **1** (3.25 g, 4.90 mmol) and the alkene (0.40 g, 4.90 mmol), heated at 140 °C (1 d) gave (i) nitrogen (0.13 g, 4.64 mmol, 94.5%; mol. wt., 28), (ii) hexafluoroacetone (1.58 g, 9.5 mmol, 97%) (−196 °C fraction), (iii) a −78 °C fraction (1.28 g) shown by GLC (OV 1 at 30 °C) to consist of hydrazine **2** (*ca.* 1.21 g, 3.97 mmol, 81%) contaminated with minor amounts of components with longer retention times, (iv) a −23 °C fraction identified as a mixture of isomers of the 2,11-diazadodecane $(CF_3)_2N[C_2HF_3]_4N(CF_3)_2$ (**7**) (nc) [0.40 g, 0.65 mmol, 13.5% based on **1**, 54% based on alkene] (Found: C, 20.8; H, 0.6; N, 4.8; F, 72.1%. Calc. for $C_{12}H_4F_{24}N_2$: C, 20.5; H, 0.5; N, 4.4; F, 72.1%), b.p., 160–170 °C. $^1$H NMR: $\delta$ broad bands in range 4.5 to 5.7 ppm. $^{19}$F NMR: $\delta$ +24.5 [t, $(CF_3)_2NCF_2$, $J$=8 Hz] and +20.8 [mult., $(CF_3)_2NCHF$] ppm in the ratio 1:4 and complex multiplets in the range −8 to +3.5 ($CF_2$) and −48 to −65 (CHF) ppm. Mass spectrum *m/z*: 480 {0.6%, $[M-(CF_3)_2N]^+$}, 449 (3.7%, $C_9H_4F_{17}N^+$), 316 (4.7%, $C_6H_2F_{12}N^+$), 228 (16.2%, $C_5H_2F_8N^+$), 202 [13.9%, $(CF_3)_2NCF_2{}^+$], 184 [63.6%, $(CF_3)_2NCHF^+$], 114 (16.8%, $C_2F_4N^+$), 96 (41.1%, $C_2HF_3N^+$) and 69 (100%, $CF_3{}^+$), and (v) a waxy oil (0.18 g) which remained in the tube, mass spectrum *m/z*: 705 (1.2%, $C_{16}H_5F_{26}N^+$), 592 (2.0%, $C_{13}H_4F_{22}N^+$), 417 (2.5%, $C_8H_3F_{16}N^+$), 234 (5.7%, $C_4HF_9N^+$), 228 (5.0%, $C_5H_2F_8N^+$), 202 (22.0%, $(CF_3)_2NCF_2{}^+$], 184 [94.1%, $(CF_3)_2NCHF^+$], 146 (9.4%, $C_3HF_5N^+$), 114 (17.3%, $C_2F_4N^+$), 96 (43.4%, $C_2HF_3N^+$) and 69 (100%, $CF_3{}^+$).

### (*g*) *With ethyne*

A mixture of **1** (3.30 g, 4.97 mmol) and ethyne (0.13 g, 5.0 mmol), heated at 140 °C (1 d), gave (i) nitrogen (0.13 g, 4.64 mmol, 94%), (ii) hexafluoroacetone (1.62 g, 9.7 mmol, 98%) (−196 °C fraction), (iii) a mixture of *N,N*-bis(trifluoromethylamine (1.48 g, 9.7 mmol, 98%) and hydrazine **2** (0.02 g, 0.07 mmol, 1.5%) as shown by its $^{19}$F NMR spectrum and which condensed at −120 °C, and (iv) a black solid (0.18 g) which remained in the tube.

### (*h*) *With benzene*

A mixture of benzene (0.38 g, 4.90 mmol) and **1** (3.27 g, 4.90 mmol), heated at 140 °C (1 d), gave (i) nitrogen (0.13 g, 4.6 mmol, 95%), (ii) hexafluoroacetone (1.61 g, 9.7 mmol, 98% (−196 °C fraction), (iii) a mixture of the amine $(CF_3)_2NH$ (1.30 g, 8.5 mmol, 87%) and hydrazine **2** (0.06 g, 0.20 mmol, 4%) as shown by its $^{19}$F NMR spectrum (−120 °C fraction), (iv) a mixture (0.16 g) which condensed at −45 °C and was shown by IR and $^1$H and $^{19}$F NMR spectroscopy and GLC (OV 1 at 100 °C) to consist of unchanged benzene (*ca.* 0.04 g, 0.50 mmol, 10% recovered) and unidentified compounds (*ca.* 0.12 g) containing $(CF_3)_2N$ groups ($\delta_F$ +20 to +25 ppm) and (v) a colorless solid, which remained in the tube and was identified as biphenyl (0.29 g, 1.91 mmol, 78%), m.p. and mixed m.p., 70 °C; lit. [8] m.p., 70.5 °C.

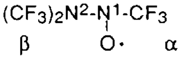
*(j) With bromine*

A mixture of **1** (3.30 g, 4.94 mmol) and bromine (0.80 g, 5.0 mmol) placed in a stoppered flask (*ca.* 50 cm$^3$) and kept at 30 °C in light (6 d) gave an orange yellow liquid (2.09 g) and residual unchanged bromine (0.27 g, 1.69 mmol, 34% recovered). The liquid was shown by IR and $^{19}$F NMR spectroscopy to consist of *N*-bromobis(trifluoromethyl)amine (1.58 g, 6.81 mmol, 69%) ($\delta_F$ +16.5 ppm; lit. [9] +16.2 ppm), hydrazine **2** (0.44 g, 1.45 mmol, 29.5%) and hexafluoroacetone (0.07 g).

*(k) With nitroso compounds*

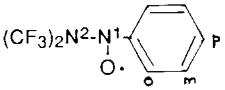
A mixture of compound **1** (0.01 g), trifluoronitrosomethane or nitrosobenzene (0.01 g) and tetrachloromethane (0.5 g) was sealed *in vacuo* in a thick-walled Pyrex tube (3 mm i.d.) which was vigorously shaken at room temperature for 2 min. The tube was then placed in the cavity of an ESR spectrometer at −40 °C and on continuous UV irradiation the ESR spectrum was recorded.

The parameters obtained for the hydrazino-oxyls are as follows.



$(\underset{\beta}{CF_3})_2N^2\text{-}\underset{O\cdot}{N^1}\text{-}\underset{\alpha}{CF_3}$

*g*, 2.0065; *a*(α-CF$_3$), 9.26 G; *a*(N$^1$), 9.60 G; *a*(N$^2$), 3.23 G; *a*(β-CF$_3$), 1.53 G.



*g*, 2.0065; a(*m*-H), 0.8 G; *a*(*o*, *p*-H), 1.6 G; *a*(N$^1$), 11.7 G; *a*(N$^2$), 2.4 G.

## Results and discussion

Pyrolysis of compound **1** at 140 °C gave nitrogen, hexafluoroacetone and tetrakis(trifluoromethyl)hydrazine (**2**) in quantitative yields.

These products were formed via homolytic N−O bond fission, *i.e.*

$$\underset{(\mathbf{1})}{(CF_3)_2N-O-C(CF_3)_2-N{=}N-C(CF_3)_2-O-N(CF_3)_2} \longrightarrow$$

$$\longrightarrow (2CF_3)_2N\cdot + N_2 + 2(CF_3)_2CO$$

$$\downarrow$$

$$\underset{(\mathbf{2})}{(CF_3)_2NN(CF_3)_2}$$

as shown by the results obtained (Table 1) from the thermal decomposition (140 °C, 24 h) of compound **1** in the presence of fluoroalkenes.

The dimeric product **3**, obtained from 1,1-dichlorodifluoroethylene, was identified by its $^{19}F$ NMR spectrum {$\delta_F$ +24.15 [2 $(CF_3)_2N$] and +2.5 (2 $CF_2$) ppm} and mass spectrum {*m/z* 202 [41%, $(CF_3)_2NCF_2^+$] with an absence of peaks for $(CF_3)_2NCCl_2^+$ at *m/z* 238/236/234}. The mass spectra of the chlorotrifluoroethylene dimer **5** and trimer **4**, formed as diastereomeric mixtures, each contained a strong band at *m/z* 202 but no bands at *m/z* 220/218 [$(CF_3)_2NCFCl^+$]. In contrast, the mass spectrum of compound **6** showed bands at both *m/z* 202 (14%) and 220/218 (3.5%).

The tetramer **7**, formed from trifluoroethylene, was a mixture of isomers and contained both $(CF_3)_2NCHF$ and $(CF_3)NCF_2$ groupings {mass spectral bands at *m/z* 184 [63.6%, $(CF_3)_2NCHF^+$] and 202 [13.9%, $(CF_3)_2NCF_2^+$]}.

Exclusive $(CF_3)_2N\cdot$ radical attack at the $CF_2$ groups of the alkenes $CF_2{=}CCl_2$ [10] and $CF_2{=}CFCl$ [1] has been observed previously, and it is therefore considered that products **3–6** are formed as shown in Scheme 1.

$(CF_3)_2NCF_2CCl_2CCl_2CF_2N(CF_3)_2$

(**3**)

$(CF_3)_2N(CF_2CFCl)_2CFClCF_2N(CF_3)_2$

(**4**)

$(CF_3)_2NCF_2CFClCFClCF_2N(CF_3)_2$

(**5**)

$(CF_3)_2NCF_2CFClN(CF_3)_2$

(**6**)

$(CF_3)_2N(C_2HF_3)_nN(CF_3)_2$

(**7**) $n=4$
(**8**) $n>4$

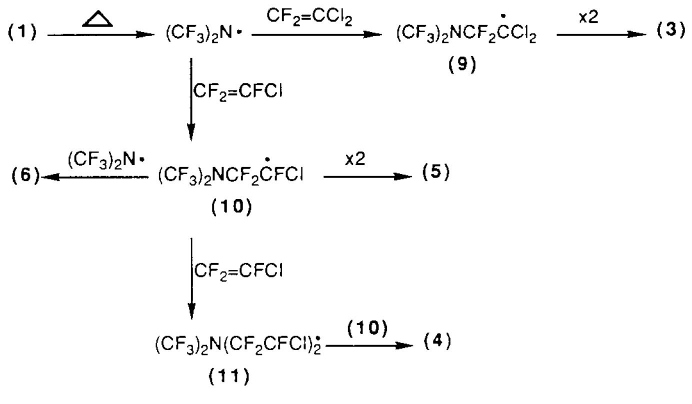
With trifluoroethylene, major $(CF_3)_2N\cdot$ radical attack (*ca.* 80%) has been found to occur at the CHF group [1, 3, 11] similar to $\dot{C}F_3$ attack [12], and

TABLE 1

Decomposition of compound **1** in the presence of fluoroalkenes

| Alkene | Molar ratio **1**:alkene | Recovered alkene (%) | $N_2$ | Products (%)[a] | | |
|---|---|---|---|---|---|---|
| | | | | **2** | $(CF_3)_2CO$ | Others |
| $CF_2{=}CCl_2$ | *ca.* 1:1 | 3 | 99.5 | 47 | 98 | **3** [47(90)[b]] |
| $CF_2{=}CFCl$ | *ca.* 1:1 | 4 | 97.5 | 65.5 | 98 | **4** [31(92)[b]] |
| $CF_2{=}CFCl$ | *ca.* 2:1 | | 97.5 | 75 | 99 | **4** [9(49)[b]]<br>**5** [11(41)[b]]<br>**6** [5(10)[b]] |
| $CF_2{=}CHF$ | 1:1 | | 94.5 | *ca.* 80 | 97 | **7** [13.5(54)[b]]<br>**8**[c] |

[a] Yields based on reactant **1**.
[b] Yields based on alkene used, *i.e.* not recovered.
[c] Mixture of telomers of unknown molecular weight.



Scheme 1.

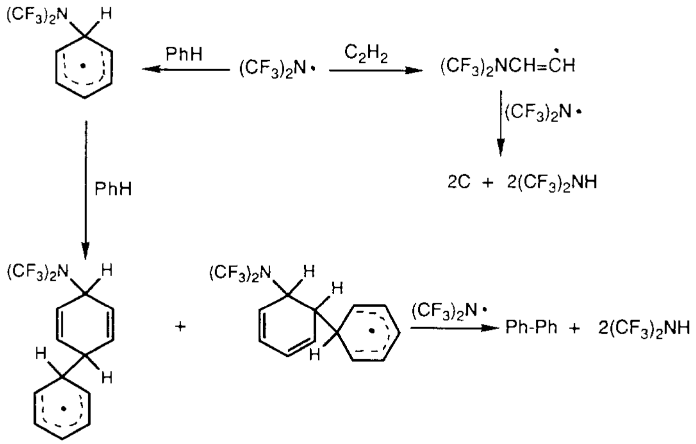
therefore the major intermediate radicals would be expected to be of the type $(CF_3)_2N(CHFCF_2)_n^{\bullet}$ $(n=1–3)$ leading to the tetramer $(CF_3)_2N(CHFCF_2)_m(CF_2CHF)_nN(CF_3)_2$ $(m=n=2;\ m=3,\ n=1)$ by coupling.

The photochemical reaction of the dibromide $CF_2BrCFClBr$ with chlorotrifluoroethylene has been reported recently [13] to give comparable products to those formed in the present work, *i.e.* $Br(CF_2CFCl)_m(CFClCF_2)_nBr$ $(m=n=1$, 38%; $m=2, n=1$, 19%; $m=n=2$ mainly + higher telomers, 43%).

Using the same reactant ratio (1:1), the telomer chain length increases as the intermediate radical stability $(-\dot{C}Cl_2 > -\dot{C}FCl > -\dot{C}F_2 > -\dot{C}HF)$ decreases, *i.e.* dimer with $CF_2{=}CCl_2$ (90%), trimer with $CF_2{=}CFCl$ (92%) and tetramer with $CHF{=}CF_2$ (54%). However, what is remarkable is the observed selectivity in the coupling of the intermediate radicals formed in the $CF_2{=}CFCl$ reaction, *i.e.* coupling between radicals **10** and **11** to give **4** is favoured, but dimerisation of radical **10** to give **5** and of radical **11** to give tetramer as well as coupling between intermediate radicals and $(CF_3)_2N\cdot$ radicals are not favoured. Even when a ratio of **1**:$CF_2{=}CFCl$ of 2:1 was used, trimer **4** was formed in a yield comparable to that of dimer **5**.

The azo compound **1** was also highly effective at polymerising chlorotrifluoroethylene, and the polymer formed in 72% yield from the reaction between the alkene and **1** [1500:1 molar ratio in the solvent $CF_2ClCFCl_2$ *in vacuo* in daylight (28 d)] had physical properties (glass transition temperature, melting point, etc.) almost identical to those reported for the polymer prepared using dicyclohexylperoxydicarbonate as initiator [14].

Surprisingly, reaction (1:1 molar) at 140 °C with ethyne and with benzene resulted in dehydrogenation. The former reaction gave nitrogen (94%), hexafluoroacetone (98%), hydrazine **2** (1.5%), the amine $(CF_3)_2NH$ (98%) and carbon, while the latter reaction afforded nitrogen (95%), hexafluoroacetone (99%), hydrazine **2** (4%), $(CF_3)_2NH$ (87%), unchanged benzene (10% recovered), a small amount of a liquid containing $(CF_3)_2N$-substituted compounds ($\delta_F$ +20 to +25 ppm) and biphenyl (78%). The products are considered to arise as shown in Scheme 2.



Scheme 2.

These results contrast those obtained from the light-initiated reaction at room temperature of the *N*-bromoamine with ethyne to give the adduct $(CF_3)_2NCH{=}CHBr$ [15] and of the compound $(CF_3)_2NON(CF_3)_2$ with benzene to afford the substituted benzene $(CF_3)_2NC_6H_5$ [16]; both reactions were considered to involve initial $(CF_3)_2N\cdot$ radical attack on the substrates.

Compound **1** also undergoes slow reaction at 30 °C in light with bromine (1:1 molar ratio) over 6 d to give the *N*-bromoamine $(CF_3)_2NBr$ (69%), hydrazine **2** (29.5%) and unchanged bromine (34% recovered).

Continuous UV irradiation at −40 °C of mixtures of the azo compound **1** and a nitroso compound RNO ($R = CF_3$ or Ph) in the solvent tetrachloromethane in the cavity of an ESR spectrometer gave spectra consistent with those expected for the hydrazino-oxyls $(CF_3)_2NNRO\cdot$ ($R = CF_3$ or Ph).

## Acknowledgement

We thank Professor R. N. Haszeldine for his interest in this work and for laboratory facilities.

## References

1 R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, (1965) 6141.
2 R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. C*, (1966) 1236.
3 R. E. Banks, R. N. Haszeldine and T. Myerscough, *J. Chem. Soc., Perkin Trans. 1*, (1972) 1449.
4 R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. C*, (1967) 1241.
5 R. Fisher, R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, (1980) 406.
6 R. Fischer, *Ph.D. Thesis*, University of Manchester, 1981.
7 R. C. Dobie and H. J. Emeléus, *J. Chem. Soc. A*, (1966) 933.

8 W. H. Zartman and H. Adkins, *J. Am. Chem. Soc.*, *54* (1932) 3398.
9 A. E. Tipping, *Ph.D. Thesis*, University of Manchester, 1963.
10 G. Newsholme, *Ph.D. Thesis*, University of Manchester, 1978.
11 G. L. Fleming, R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. C*, (1971) 3833.
12 R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, (1957) 2800.
13 V. Dědek and Z. Chvátal, *J. Fluorine Chem.*, *31* (1986) 363.
14 R. Storey, *Ph.D. Thesis*, University of Manchester, 1980.
15 H. J. Emeléus and B. W. Tattershall, *Z. Anorg. Chem.*, *327* (1964) 147; J. Freear and A. E. Tipping, *J. Chem. Soc. C*, (1968) 1096.
16 G. D. Connelly, R. N. Haszeldine, A. Kenny, C. M. Irvin and A. E. Tipping, *J. Fluorine Chem.*, *17* (1981) 191.