

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

Raymond Fisher and Anthony E. Tipping*

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD (UK)

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Abstract

Thermolysis of the azo compound $(\text{CF}_3)_2\text{NOC}(\text{CF}_3)_2\text{N}=\text{NC}(\text{CF}_3)_2\text{ON}(\text{CF}_3)_2$ (**1**) alone at 140 °C gives nitrogen, hexafluoroacetone and the hydrazine $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ via $(\text{CF}_3)_2\text{N}\cdot$ radical coupling in quantitative yield, while from decomposition in the presence of the alkenes $\text{CF}_2=\text{CCl}_2$, $\text{CF}_2=\text{CFCl}$ and $\text{CF}_2=\text{CHF}$ (ca. 1:1 molar ratio) the major products are the dimer $[(\text{CF}_3)_2\text{NCF}_2\text{CCl}_2]_2$, trimer $(\text{CF}_3)_2\text{N}(\text{CF}_2\text{CFCl})_2\text{CFCICF}_2\text{N}(\text{CF}_3)_2$ and a mixture of tetramers $(\text{CF}_3)_2\text{N}(\text{C}_2\text{HF}_3)_4\text{N}(\text{CF}_3)_2$, respectively. The $(\text{CF}_3)_2\text{N}\cdot$ radicals generated from **1** can also be trapped with bromine [$\rightarrow (\text{CF}_3)_2\text{NBr}$] and nitroso compounds [$\rightarrow (\text{CF}_3)_2\text{NNRO}\cdot$ ($\text{R}=\text{CF}_3$ and Ph)], but with ethyne or benzene near-quantitative yields of the amine $(\text{CF}_3)_2\text{NH}$ are obtained.

Introduction

The $(\text{CF}_3)_2\text{N}\cdot$ radical has been generated from precursors of the type $(\text{CF}_3)_2\text{NX}$ where $\text{X}=\text{Cl}$, Br or I [1], $\text{X}=\text{OCF}_3$ [2], $\text{X}=\text{ON}(\text{CF}_3)_2$ [3] and $\text{X}=\text{HgN}(\text{CF}_3)_2$ [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 $(\text{CF}_3)_2\text{N}\cdot$ 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].

*To whom enquiries should be addressed.

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 cm³), 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), ¹⁹F NMR spectroscopy (Perkin–Elmer R10 or Varian HA100 spectrometers operating at 56.46 and 94.1 MHz, respectively, reference external CF₃CO₂H; 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 ¹⁹F 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 ¹⁹F NMR spectra with those of an authentic sample.

(b) With 1,1-dichlorodifluoroethylene

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%. C₈Cl₄F₁₆N₂ requires C, 16.9; Cl, 24.9; N, 4.9; F, 53.3%), b.p., 145–147 °C. ¹⁹F NMR: δ +24.5 [t, 2(CF₃)₂N, *J* = 19 Hz] and +2.5 (broad s, 2CF₂) ppm. Mass spectrum *m/z*: 502/500/498 [9.1%, (M – Cl₂)⁺], 350/348/346 (16.1%, C₆F₁₀NCl₂⁺), 288/286/284 [3.9%, (CF₃)₂NCF₂CCl₂⁺], 262/260/258 (20.7%,

$\text{C}_7\text{F}_4\text{N}_2\text{Cl}_2^+$), 202 [41.4%, $(\text{CF}_3)_2\text{NCF}_2^+$], 114 (39.4%, $\text{C}_2\text{F}_4\text{N}^+$) 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%. $\text{C}_{10}\text{Cl}_3\text{F}_{21}\text{N}_2$ requires C, 18.4; Cl, 16.3; N, 4.3; F, 61.0%), b.p., 152–154 °C. ^{19}F NMR: δ +24.9 [two overlapping multiplets, 12F, $2(\text{CF}_3)_2\text{N}$] and +9 to −10 (many complex bands, 9F, 3CF_2 and 3CFCl) ppm. Mass spectrum m/z : 617 [trace, $(\text{M}-\text{Cl})^+$], 500 {0.2% [$\text{M}-(\text{CF}_3)_2\text{N}]^+$ }, 300/298/296 (15.8%, $\text{CF}_2=\text{NC}_4\text{F}_6\text{Cl}_2^+$), 270/268 [6.4%, $(\text{CF}_3)_2\text{NCF}_2\text{CFCl}^+$] 202 [92.2%, $(\text{CF}_3)_2\text{NCF}_2^+$], 114 (59.7%, $\text{C}_2\text{F}_4\text{N}^+$) 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: δ +24.0 to +25.0 [complex, $(\text{CF}_3)_2\text{N}$] 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%, $(\text{M}-\text{Cl})^+$], 316 (1.2%, $\text{C}_5\text{F}_{12}\text{N}_2^+$), 270/268 [3.4%, $(\text{M}-\text{C}_2\text{F}_6\text{Cl})^+$], 220/218 [3.4%, $(\text{CF}_3)_2\text{NCFCl}^+$], 202 [14.3%, $(\text{CF}_3)_2\text{NCF}_2^+$], 114 (30.3%, $\text{C}_2\text{F}_4\text{N}^+$) 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%), $(\text{M}-\text{Cl})^+$], 466 [0.5% (0.3%), $(\text{M}-\text{Cl}_2)^+$], 385 [3.1% (2.0%), $\text{C}_6\text{F}_{15}\text{N}_2^+$], 297 [7.2% (6.4%), $\text{C}_5\text{F}_{11}\text{N}_2^+$], 202 [26.8% (18.7%), $(\text{CF}_3)_2\text{NCF}_2^+$], 137/135 [25.8% (18.8%), $\text{C}_2\text{F}_4\text{Cl}^+/\text{C}_4\text{F}_2\text{NCl}^+$], 114 [36.9% (29.0%), $\text{C}_2\text{F}_4\text{N}^+$] 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, 3.7×10^{-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 cm³) 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 (C₂F₃Cl)_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 (CF₃)₂N[C₂HF₃]₄N(CF₃)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 C₁₂H₄F₂₄N₂: C, 20.5; H, 0.5; N, 4.4; F, 72.1%), b.p., 160–170 °C. ¹H NMR: δ broad bands in range 4.5 to 5.7 ppm. ¹⁹F NMR: δ +24.5 [t, (CF₃)₂NCF₂, *J* = 8 Hz] and +20.8 [mult., (CF₃)₂NCHF] ppm in the ratio 1:4 and complex multiplets in the range -8 to +3.5 (CF₂) and -48 to -65 (CHF) ppm. Mass spectrum *m/z*: 480 {0.6%, [M-(CF₃)₂N]⁺}, 449 (3.7%, C₉H₄F₁₇N⁺), 316 (4.7%, C₆H₂F₁₂N⁺), 228 (16.2%, C₅H₂F₈N⁺), 202 [13.9%, (CF₃)₂NCF₂⁺], 184 [63.6%, (CF₃)₂NCHF⁺], 114 (16.8%, C₂F₄N⁺), 96 (41.1%, C₂HF₃N⁺) and 69 (100%, CF₃⁺), and (v) a waxy oil (0.18 g) which remained in the tube, mass spectrum *m/z*: 705 (1.2%, C₁₆H₅F₂₆N⁺), 592 (2.0%, C₁₃H₄F₂₂N⁺), 417 (2.5%, C₈H₃F₁₆N⁺), 234 (5.7%, C₄HF₉N⁺), 228 (5.0%, C₅H₂F₈N⁺), 202 (22.0%, (CF₃)₂NCF₂⁺), 184 [94.1%, (CF₃)₂NCHF⁺], 146 (9.4%, C₃HF₅N⁺), 114 (17.3%, C₂F₄N⁺), 96 (43.4%, C₂HF₃N⁺) and 69 (100%, CF₃⁺).

(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 ¹⁹F 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 (CF₃)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 ^1H 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 $(\text{CF}_3)_2\text{N}$ groups (δ_{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 .

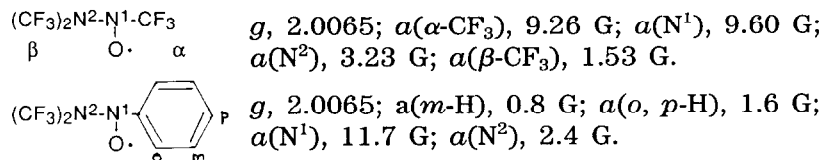
(j) *With bromine*

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 cm³) 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%) (δ_{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.

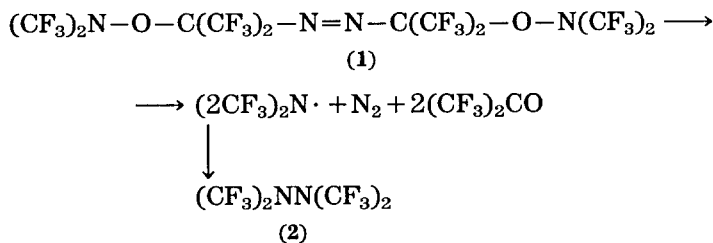
The parameters obtained for the hydrazino-oxyis are as follows.



Results and discussion

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

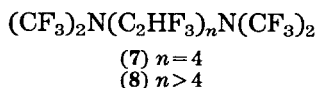
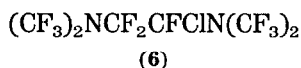
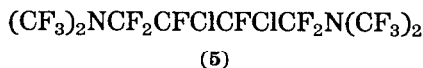
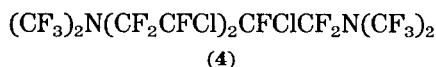
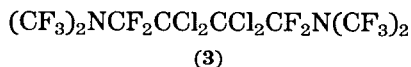
These products were formed via homolytic N–O bond fission, *i.e.*



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 $\{\delta_{\text{F}} +24.15$ [$2(\text{CF}_3)_2\text{N}$] and $+2.5$ (2CF_2) ppm} and mass spectrum $\{m/z$ 202 [41%, $(\text{CF}_3)_2\text{NCF}_2^+$] with an absence of peaks for $(\text{CF}_3)_2\text{NCCl}_2^+$ 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 [$(\text{CF}_3)_2\text{NCFCl}^+$]. 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 $(\text{CF}_3)_2\text{NCHF}$ and $(\text{CF}_3)_2\text{NCF}_2$ groupings {mass spectral bands at m/z 184 [63.6%, $(\text{CF}_3)_2\text{NCHF}^+$] and 202 [13.9%, $(\text{CF}_3)_2\text{NCF}_2^+$]}. Exclusive $(\text{CF}_3)_2\text{N}\cdot$ radical attack at the CF_2 groups of the alkenes $\text{CF}_2=\text{CCl}_2$ [10] and $\text{CF}_2=\text{CFCl}$ [1] has been observed previously, and it is therefore considered that products **3–6** are formed as shown in Scheme 1.



With trifluoroethylene, major $(\text{CF}_3)_2\text{N}\cdot$ radical attack (*ca.* 80%) has been found to occur at the CHF group [1, 3, 11] similar to $\dot{\text{C}}\text{F}_3$ attack [12], and

TABLE 1

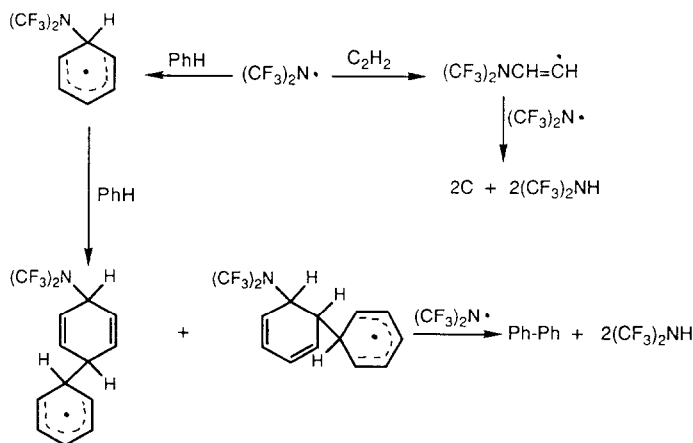
Decomposition of compound **1** in the presence of fluoroalkenes

Alkene	Molar ratio 1:alkene	Recovered alkene (%)	N_2	Products (%) ^a		
				2	$(\text{CF}_3)_2\text{CO}$	Others
$\text{CF}_2=\text{CCl}_2$	<i>ca.</i> 1:1	3	99.5	47	98	3 [47(90) ^b]
$\text{CF}_2=\text{CFCl}$	<i>ca.</i> 1:1	4	97.5	65.5	98	4 [31(92) ^b]
$\text{CF}_2=\text{CFCl}$	<i>ca.</i> 2:1		97.5	75	99	4 [9(49) ^b] 5 [11(41) ^b] 6 [5(10) ^b]
$\text{CF}_2=\text{CHF}$	1:1		94.5	<i>ca.</i> 80	97	7 [13.5(54) ^b] 8 ^c

^aYields based on reactant **1**.

^bYields based on alkene used, *i.e.* not recovered.

^cMixture of telomers of unknown molecular weight.



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 $(\text{CF}_3)_2\text{NCH}=\text{CHBr}$ [15] and of the compound $(\text{CF}_3)_2\text{NON}(\text{CF}_3)_2$ with benzene to afford the substituted benzene $(\text{CF}_3)_2\text{NC}_6\text{H}_5$ [16]; both reactions were considered to involve initial $(\text{CF}_3)_2\text{N}^\bullet$ 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 $(\text{CF}_3)_2\text{NBr}$ (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 ($\text{R}=\text{CF}_3$ or Ph) in the solvent tetrachloromethane in the cavity of an ESR spectrometer gave spectra consistent with those expected for the hydrazino-oxylys $(\text{CF}_3)_2\text{NNRO}^\bullet$ ($\text{R}=\text{CF}_3$ or Ph).

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