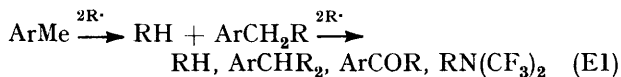


## Nitroxide Chemistry. Part 15.<sup>1</sup> Reactions between Bistrifluoromethyl Nitroxide and Benzyl Alcohol, Azide, Chloride, and Cyanide

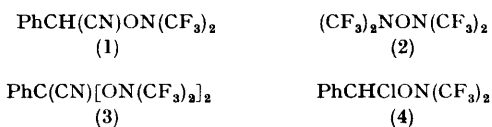
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Bistrifluoromethyl nitroxide readily attacks benzyl cyanide and benzyl chloride at room temperature to give the  $\alpha$ -bistrifluoromethylamino-oxy-derivatives PhCHRCN and PhCHRCl [R = -ON(CF<sub>3</sub>)<sub>2</sub>] respectively; treatment of the former product with the nitroxide yields benzoyl cyanide and the di-substituted derivative PhCR<sub>2</sub>CN. Abstraction of a benzylic hydrogen atom by the nitroxide from benzyl alcohol and benzyl azide leads, respectively, to the formation of benzaldehyde (and hence PhCOR) and benzonitrile.

REACTION of bistrifluoromethyl nitroxide [(CF<sub>3</sub>)<sub>2</sub>NO· = R·] with methylbenzenes ArMe (Ar = Ph, *p*-ClC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>F<sub>5</sub>) involves the sequence shown in equation (E1).

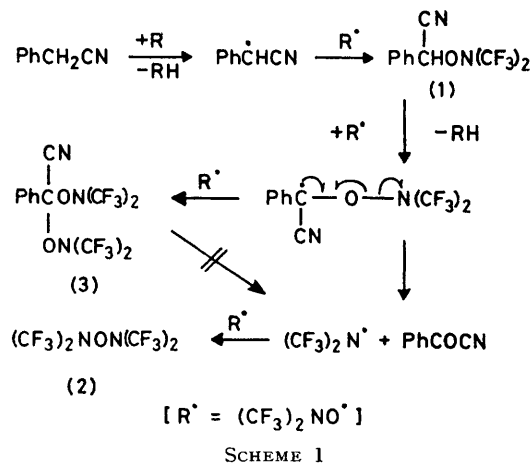


The formation of the carbonyl compounds is ascribed to rapid,<sup>2</sup> 100%-efficient scavenging of aldehydes produced in the second stage *via* fission of  $\beta$ -N-O bonds in benzylic radicals generated initially: R· + ArCH<sub>2</sub>R → RH + ArCHR → ArCHO [→ (with 2R·) ArCOR + RH] + (CF<sub>3</sub>)<sub>2</sub>N· [→ (with R·) RN(CF<sub>3</sub>)<sub>2</sub>].<sup>3</sup> Support for this mechanistic proposal has now been obtained through study of the reaction between bistrifluoromethyl nitroxide and benzyl cyanide. This occurs less readily than the corresponding one involving toluene [presumably owing to a polar effect (*cf.* ref. 3)] to give, at room temperature with a 2 : 1 (R· : PhCH<sub>2</sub>CN) molar mixture of reactants,  $\alpha$ -(bistrifluoromethylamino-oxy)-benzyl cyanide (1) almost quantitatively, together with *NN*-bistrifluoromethylhydroxylamine and small amounts of benzoyl cyanide and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (2). In a separate experiment, the monosubstituted product (1) was found to react relatively slowly with the nitroxide (1 : 2 molar ratio) at room temperature to give *NN*-bistrifluoromethylhydroxylamine,  $\alpha\alpha$ -bis(bistrifluoromethylamino-oxy)-benzyl cyanide (3) [28.5% based on 98% consumption of (1)], benzoyl cyanide (67%), and the oxadiazapentane (2) [molar ratio PhCOCN : (2) = *ca.* 1 : 1]. Since the  $\alpha\alpha$ -disubstituted derivative (3) is apparently stable at its boiling point (170 °C), formation of benzoyl cyanide clearly points to a '  $\beta$ -scission mechanism ' (Scheme 1).



Rapid exothermic reactions occur when mixtures of bistrifluoromethyl nitroxide and benzyl chloride or benzyl alcohol are allowed to warm from -196 °C to

room temperature. Initially, the chloride yields its  $\alpha$ -bistrifluoromethylamino-oxy-derivative (4) (91% based on 85% consumption of PhCH<sub>2</sub>Cl, with a nitroxide : substrate ratio of *ca.* 2 : 1) and the alcohol is oxidised to benzaldehyde, which rapidly<sup>2</sup> undergoes a secondary reaction with bistrifluoromethyl nitroxide to give the *O*-benzoylhydroxylamine PhC(O)ON(CF<sub>3</sub>)<sub>2</sub> (5). With a



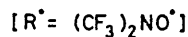
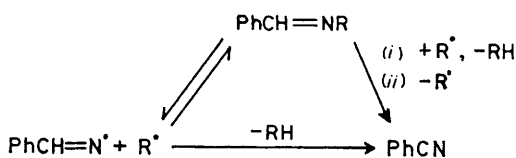
3 : 1 molar ratio of reactants [(CF<sub>3</sub>)<sub>2</sub>NO : PhCH<sub>2</sub>OH], virtually complete consumption of the nitroxide leads to 64% conversion of the alcohol into a *ca.* 2 : 1 molar mixture of the benzoyl compound (5) and its precursor, benzaldehyde. Slow passage of an excess of bistrifluoromethyl nitroxide into a stirred solution of benzyl alcohol in carbon tetrachloride at room temperature leads to complete conversion of the alcohol into (5).

In the presence of carbon tetrachloride, benzyl azide reacts smoothly with bistrifluoromethyl nitroxide at room temperature according to the equation PhCH<sub>2</sub>N<sub>3</sub> + 2(CF<sub>3</sub>)<sub>2</sub>NO· → PhCN + N<sub>2</sub> + 2(CF<sub>3</sub>)<sub>2</sub>NOH. Presumably this reaction is initiated by abstraction of benzylic hydrogen, accompanied or followed by loss of nitrogen to produce an iminyl radical (Scheme 2). An experiment in which no solvent was used resulted in a violent explosion.

Reactions between bistrifluoromethyl nitroxide and  $\alpha$ -substituted toluenes

Substrate (g, mmol) (0.86, 7.35)	(CF <sub>3</sub> ) <sub>2</sub> NO <sup>•</sup> /g (mmol)	Reaction period and temperature (°C) (tube size in cm <sup>2</sup> )	Products [R = (CF <sub>3</sub> ) <sub>2</sub> NO <sup>•</sup> ] (g, mmol, %)
PhCH <sub>2</sub> CN (0.86, 7.35)	2.48 (14.8)	30 min, 20 (60)	PhCHRCN (1.70, 5.98, 81) <sup>a</sup> PhCOCN (0.04, 0.30, 4) <sup>b</sup> PhCH <sub>2</sub> CN (0.16, 1.33, 18) <sup>b</sup> RH (1.02, 6.04, 41) <sup>c</sup> RN(CF <sub>3</sub> ) <sub>2</sub> (0.12, 0.38, 5) <sup>c</sup> R <sup>•</sup> (0.25, 1.49, 10) <sup>c</sup>
PhCHRCN (0.82, 2.89)	1.01 (6.01)	5 h, 20 (60)	PhCR <sub>2</sub> CN (0.365, 0.81, 28) <sup>d</sup> PhCOCN (0.25, 1.91, 66) <sup>b,e</sup> PhCHRCN (0.015, 0.05, 2) <sup>b</sup> RH (0.46, 2.72, 45) <sup>c</sup> RN(CF <sub>3</sub> ) <sub>2</sub> (0.58, 1.81, 60) <sup>c</sup>
PhCH <sub>2</sub> Cl (1.44, 11.4)	3.92 (23.3)	j 20 (120)	PhCHRCN (2.59, 8.82, 77) <sup>f</sup> PhCH <sub>2</sub> Cl (0.21, 1.66, 15) <sup>b,e</sup> RH (1.89, 11.2, 48) <sup>c</sup> RN(CF <sub>3</sub> ) <sub>2</sub> <sup>c</sup> (CF <sub>3</sub> ) <sub>2</sub> NH <sup>•</sup> <sup>c</sup> Unidentified <sup>g</sup> } traces
PhCH <sub>2</sub> N <sub>3</sub> (0.87, 6.54)	2.36 (14.05) CCl <sub>4</sub> (10 cm <sup>3</sup> )	30 min, 20 (120)	PhCN (0.64, 6.21, 95) <sup>b,c</sup> N <sub>2</sub> (0.176, 6.30, 96) <sup>c,h</sup> RH (2.26, 13.35, 95) <sup>c</sup> Unidentified (ca. 0.02 g) <sup>i</sup>
PhCH <sub>2</sub> OH (0.55, 5.09)	2.55 (15.2)	2 min, <sup>j</sup> 20 (60)	PhC(O)R (0.57, 2.09, 64) <sup>c</sup> PhCHO (0.12, 1.15, 35) <sup>b,c</sup> PhCH <sub>2</sub> OH (0.20, 1.85, 36) <sup>b,c</sup> RH (0.75, 4.44, 59) <sup>c</sup> R <sup>•</sup> (trace) <sup>c</sup>

<sup>a</sup> Isolated (ca. 96% pure) by g.l.c. (3 m, APL, 170 °C) as an oil, b.p. 203 °C at 753 mmHg (Siwoloboff),  $\delta_F$  (ca. 60% solution in CCl<sub>4</sub>; 56.46 MHz) +10.2 (s);  $\delta_H$  (60 MHz; external C<sub>6</sub>H<sub>6</sub>) +0.69 (s, Ph) and -1.06 (s, CH);  $m/e$  284 ( $M^{+•}$ , <1%), 116 (C<sub>6</sub>H<sub>6</sub>N<sup>+</sup>, 100), and 89 (C<sub>7</sub>H<sub>5</sub><sup>+</sup>, 11) (metastable peak at  $m/e$  68.3 corresponding to C<sub>6</sub>H<sub>5</sub>CHCN<sup>+</sup>  $\rightarrow$  C<sub>7</sub>H<sub>5</sub><sup>+</sup> + HCN). <sup>b</sup> Identified by g.l.c. (using authentic samples). <sup>c</sup> Identified by i.r. spectroscopy. I.r. data for RN(CF<sub>3</sub>)<sub>2</sub> and (CF<sub>3</sub>)<sub>2</sub>NH can be found in refs. 6 and 7, respectively. <sup>d</sup> Isolated by g.l.c. (5 m, APL, 170 °C) as an oil, b.p. 170 °C at 753 mmHg (Siwoloboff) (Found: C, 32.9; H, 1.2; F, 49.3; N, 9.4%. C<sub>12</sub>H<sub>5</sub>F<sub>12</sub>N<sub>3</sub>O<sub>2</sub> requires C, 31.9; H, 1.1; F, 50.7; N, 9.3%;  $\delta_F$  (ca. 5% solution in CCl<sub>4</sub>; 94.12 MHz) -12.0 (s);  $\delta_H$  (100 MHz; external C<sub>6</sub>H<sub>6</sub>) +1.05 (complex);  $m/e$  283 ( $M^{+•}$  - R<sup>•</sup>, 100%; top-mass peak), 131 (C<sub>6</sub>H<sub>5</sub>NO<sup>+</sup>, 94), 105 (C<sub>7</sub>H<sub>5</sub>O<sup>+</sup>, 66), 35.9 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 36), and 69 (CF<sub>3</sub><sup>+</sup>, 66) [metastable peaks at  $m/e$  60.6 [C<sub>6</sub>H<sub>5</sub>C(CN)ON(CF<sub>3</sub>)<sub>2</sub><sup>+</sup>  $\rightarrow$  C<sub>6</sub>H<sub>5</sub>COCN<sup>+</sup> + (CF<sub>3</sub>)<sub>2</sub>N<sup>•</sup>] and 84.6 [C<sub>6</sub>H<sub>5</sub>COCN<sup>+</sup>  $\rightarrow$  C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup> + •CN]. <sup>e</sup> Isolated as crystals [m.p. 29 °C (lit.,<sup>8</sup> 32 °C)] when the involatile reaction product was cooled. <sup>f</sup> Colourless oil, b.p. 81-82 °C at 17 mmHg (Found: C, 37.1; H, 2.0; N, 4.7. C<sub>6</sub>H<sub>5</sub>ClF<sub>6</sub>NO requires C, 36.8; H, 2.0; N, 4.8%);  $\delta_F$  (neat liquid; 94.12 MHz, *p*-CF<sub>2</sub>ClC<sub>6</sub>H<sub>4</sub>Cl lock) +10.8 (s) and +9.5 (s) (relative intensity 1:1);  $\delta_H$  (100 MHz, external SiMe<sub>4</sub>) +6.93 (complex; Ph) and +6.16 (s, CH). <sup>g</sup> At least three compounds by g.l.c. (2 m, APL, 120 °C). <sup>h</sup> Found: *M* (Regnault), 28. <sup>i</sup> Shown by i.r. spectroscopy to contain material possessing -N<sub>3</sub> and -ON(CF<sub>3</sub>)<sub>2</sub> groups. <sup>j</sup> An exothermic reaction occurred soon after the reactants melted.



SCHEME 2

## EXPERIMENTAL

<sup>19</sup>F N.m.r. chemical shifts are quoted in p.p.m. relative to external trifluoroacetic acid, absorptions to low field being assigned positive values.

*Reactions of Bistrifluoromethyl Nitroxide with the Benzyl Derivatives PhCH<sub>2</sub>X (X = CN, Cl, N<sub>3</sub>, and OH) and with the  $\alpha$ -(Bistrifluoromethylamino-oxy)-derivative of Benzyl Cyanide.*—The nitroxide (synthesised from commercial trifluoroacetic acid as described previously<sup>5</sup>) was condensed, *in vacuo*, into a cold (-196 °C) Pyrex ampoule containing the substrate under examination; the ampoule was then sealed,

either by fusion of the neck or by means of a Fischer-Porter or Rotaflo PTFE needle valve, placed in a steel guard, and allowed to warm slowly to room temperature. Reaction progress was easily followed by periodic observation of diminution in the intensity of the purple colour caused by uptake of the nitroxide. Volatile product was transferred to a Pyrex vacuum system and examined by standard techniques; material too involatile for transfer was examined by g.l.c. Results are listed in the Table.

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## REFERENCES

- Part 14, M. G. Barlow, R. N. Haszeldine, and K. W. Murray, *J. Fluorine Chem.*, 1979, **14**, 373.
- R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 80.
- R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 1092.
- J. W. Cooper, B. P. Roberts, and J. N. Winter, *J.C.S. Chem. Comm.*, 1977, 320; B. P. Roberts and J. N. Winter, *J.C.S. Perkin II*, 1979, 1353.
- R. E. Banks, K. C. Eapen, R. N. Haszeldine, A. V. Holt, T. Myerscough, and S. Smith, *J.C.S. Perkin I*, 1974, 2532; R. E. Banks and C. Oppenheim, *J. Fluorine Chem.*, 1978, **12**, 27.
- R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. (C)*, 1966, 1236.
- D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 4169.
- 'Handbook of Chemistry and Physics,' 48th edn., The Chemical Rubber Co., Ohio, 1967-68.