

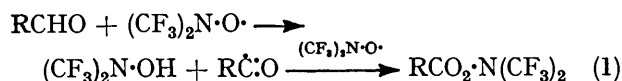
## Nitroxide Chemistry. Part IV.<sup>1</sup> Reaction of Bistrifluoromethyl Nitroxide with Aldehydes

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Bistrifluoromethyl nitroxide abstracts aldehydic hydrogen atoms from acetaldehyde, propionaldehyde, pivalaldehyde, benzaldehyde, *m*- and *p*-tolualdehyde, terephthalaldehyde, and pentafluorobenzaldehyde with great ease, to give *NN*-bistrifluoromethylhydroxylamine and the corresponding (bistrifluoromethylamino-oxy)carbonyl-alkane or -arene in almost quantitative yields. Basic hydrolysis of the carbonyl compounds  $\text{ArCO}_2\cdot\text{N}(\text{CF}_3)_2$  ( $\text{Ar} = \text{Ph}$  or  $\text{C}_6\text{F}_5$ ) yields the corresponding arenecarboxylic acids, and attack of bistrifluoromethyl nitroxide on the phenyl compound at elevated temperature leads to nuclear substitution with the formation of (bistrifluoromethylamino-oxy)[(bistrifluoromethylamino-oxy)carbonyl]benzenes.

ATTACK by bistrifluoromethyl nitroxide on several simple aldehydes has been studied as part of a methodical examination of the effect of this nitroxide on organic compounds of various types.<sup>2</sup>

Reactions between acetaldehyde, propionaldehyde, or pivalaldehyde and bistrifluoromethyl nitroxide (2 mol. equiv.) were found to set in at low temperatures and proceed rapidly, exothermically, and cleanly to completion as indicated by the equation:



Efficient scavenging of the presumed intermediate alkanoyl radicals by the nitroxide was revealed by the detection of carbon monoxide [traces, together with  $\text{Me}_3\text{C}\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ ] in only the products from pivalaldehyde. The (bistrifluoromethylamino-oxy)carbonyl-alkanes (I) ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Me}_3\text{C}$ ) thus obtained were produced previously either *via* reactions of the corresponding alkanoyl chlorides ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) with the reagents  $[(\text{CF}_3)_2\text{N}\cdot\text{O}]_2\text{Hg}$ ,<sup>3</sup>  $(\text{CF}_3)_2\text{N}\cdot\text{O}^-\text{Na}^+$ ,<sup>4</sup>  $(\text{CF}_3)_2\text{N}\cdot\text{OH}-\text{MF}$  ( $\text{M} = \text{K}$  or  $\text{Cs}$ ),<sup>5</sup> or  $(\text{CF}_3)_2\text{N}\cdot\text{OH}$ -pyridine,<sup>6</sup> or as by-product in the reaction between bistrifluoromethyl nitroxide and neopentane ( $\text{R} = \text{Me}_3\text{C}$ ).<sup>2a</sup>

Similarly, bistrifluoromethyl nitroxide reacts with

<sup>1</sup> Part III, R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, 1449.

<sup>2</sup> The results of work on alkanes (a), alkenes (a), alkynes (b), perfluoro-olefins (c), fluoroalkynes (b), tetrafluoroallene (d), isocyanides (e), and pentafluoropyridine (f) have been published [(a) R. E. Banks, B. Justin, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1971, 2777; (b) R. E. Banks, R. N. Haszeldine, and T. Myerscough, *ibid.*, p. 1951; (c) R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *ibid.*, 1966, 901; (d) R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, 2336; (e) R. E. Banks, R. N. Haszeldine, and C. W. Stephens, *Tetrahedron Letters*, 1972, 3699; (f) R. E. Banks, W. M. Cheng, R. N. Haszeldine, and G. Shaw, *J. Chem. Soc. (C)*, 1970, 55]. Papers dealing with ketones, alkylbenzenes [see also ref. (c)], cycloalkanes, halogenoalkanes, and perfluoro-dienes are being prepared.

aromatic aldehydes at sub-ambient temperatures to give (bistrifluoromethylamino-oxy)carbonylarenes in almost quantitative yields, attack at the aldehydic function taking preference over nuclear attack in the cases of benzaldehyde, terephthalaldehyde, and pentafluorobenzaldehyde and over nuclear or side-chain attack in the cases of *m*- and *p*-tolualdehyde. The formation of only *NN*-bistrifluoromethylhydroxylamine (100%) and the carbonyl compound  $\text{C}_6\text{F}_5\cdot\text{CO}_2\cdot\text{N}(\text{CF}_3)_2$  (96%) from pentafluorobenzaldehyde and *ca.* 2 mol. equiv. of bistrifluoromethyl nitroxide at room temperature is completely out of keeping with the claim<sup>7</sup> that the aldehydic group in this substrate resists attack by the nitroxide at 22–60 °C, the products being  $\text{C}_6\text{F}_5\text{X}_4\cdot\text{CHO}$  (two isomers) and  $\text{C}_6\text{F}_5\text{X}_6\cdot\text{CHO}$  [ $\text{X} = (\text{CF}_3)_2\text{N}\cdot\text{O}\cdot$ ]. The phenyl derivative  $\text{PhCO}_2\cdot\text{N}(\text{CF}_3)_2$ , which, like its fluoro-analogue  $\text{C}_6\text{F}_5\cdot\text{CO}_2\cdot\text{N}(\text{CF}_3)_2$ , readily undergoes basic hydrolysis to the corresponding aromatic carboxylic acid, is also obtainable *via* classical benzoylation of *NN*-bistrifluoromethylhydroxylamine.<sup>6</sup>

Reaction of  $\text{PhCO}_2\cdot\text{N}(\text{CF}_3)_2$  with 4 mol. equiv. of bistrifluoromethyl nitroxide at 70 °C does lead to nuclear substitution, the major products being *NN*-bistrifluoromethylhydroxylamine, the *para*-substituted derivative  $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{N}(\text{CF}_3)_2$ , and either the *ortho*- or *meta*-isomer of the latter [the complete absence in the literature of <sup>1</sup>H n.m.r. data on  $(\text{CF}_3)_2\text{N}\cdot\text{O}$  derivatives of benzene meant that no decision could be reached on this structural point].

<sup>3</sup> H. J. Emeléus, J. M. Shreeve, and P. M. Spaziant, *J. Chem. Soc. (A)*, 1969, 431.

<sup>4</sup> R. E. Banks, R. N. Haszeldine, and D. L. Hyde, *Chem. Comm.*, 1967, 413.

<sup>5</sup> L. L. Nash, D. P. Babb, J. J. Couville, and J. M. Shreeve, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3373.

<sup>6</sup> R. E. Banks, D. L. Connell, and R. N. Haszeldine, unpublished work.

<sup>7</sup> M. A. Englin and A. V. Mel'nikova, *Zhur. Vsesoyuz. Khim. obshch. im. D.T. Mendeleeva*, 1968, **13**, 594.

## EXPERIMENTAL

I.r., n.m.r., and mass spectra were measured with a Perkin-Elmer 257 spectrophotometer, a Perkin-Elmer R10 instrument ( $^1\text{H}$  at 60.0 and  $^{19}\text{F}$  at 56.46 MHz), and an A.E.I. MS902 spectrometer (ionising electron beam energy 70 eV), respectively. Fluorine chemical shifts ( $\delta_{\text{F}}$ ) are quoted relative to  $\text{CF}_3\text{-CO}_2\text{H}$  (interchange ref., positive values to high field) and proton chemical shifts relative to benzene ( $\delta_{\text{H}}$ ; interchange ref.) or  $\text{Me}_4\text{Si}$  ( $\tau$ ; internal ref.). G.l.c. was performed with a Pye 104 instrument.

Bistrifluoromethyl nitroxide was prepared by oxidation of *NN*-bistrifluoromethylhydroxylamine with silver(I) <sup>20</sup> or, preferably, silver(II) oxide,<sup>8</sup> and was stored at room temperature in a Pyrex bulb fitted with a Springham's greaseless stopcock (Viton diaphragm) and painted black. The hydroxylamine, which is highly toxic, was obtained by treatment of trifluoronitrosomethane with ammonia.<sup>6,9</sup>

*Reactions of Bistrifluoromethyl Nitroxide.*—(a) *With aliphatic aldehydes.* The nitroxide and the aldehyde under examination were condensed separately, *in vacuo*, into a cold ( $-196^\circ\text{C}$ ) Pyrex tube (20 ml) fitted with a 4 mm

TABLE 1

Reactions between bistrifluoromethyl nitroxide and aliphatic aldehydes

Aldehyde (g, mmol)	( $\text{CF}_3$ ) <sub>2</sub> N·O· (g, mmol)	Reaction temp. (°C)	Products (g, mmol)
MeCHO 0.11, 2.50	0.84, 5.00	-78 <sup>a</sup>	( $\text{CF}_3$ ) <sub>2</sub> N·O· (trace) ( $\text{CF}_3$ ) <sub>2</sub> N·OH (0.41, 2.43) $\text{MeCO}_2\text{·N}(\text{CF}_3)_2$ (0.52, 2.46) <sup>b</sup>
EtCHO 0.185, 3.19	1.075, 6.40	-78 <sup>c</sup>	( $\text{CF}_3$ ) <sub>2</sub> N·O· (trace) ( $\text{CF}_3$ ) <sub>2</sub> N·OH (0.53, 3.14) $\text{EtCO}_2\text{·N}(\text{CF}_3)_2$ (0.70, 3.11) <sup>d</sup>
$\text{Me}_3\text{C·CHO}$ 0.60, 6.98	2.34, 13.9	ca. -45 <sup>e</sup>	( $\text{CF}_3$ ) <sub>2</sub> N·OH (1.17, 6.92) $\text{Me}_3\text{C·CO}_2\text{·N}(\text{CF}_3)_2$ (1.73, 6.84) <sup>e</sup> $\text{Me}_3\text{C·O·N}(\text{CF}_3)_2$ (trace) $\text{Me}_3\text{C·CHO}$ (trace) CO (trace)

<sup>a</sup> The reaction was exothermic and complete in *ca.* 2 min.  
<sup>b</sup> Co-condensed with ( $\text{CF}_3$ )<sub>2</sub>N·OH in  $-78$  and  $-45^\circ\text{C}$  traps; identified by comparison of the i.r. spectrum of the mixture with those of analytically pure samples of ( $\text{CF}_3$ )<sub>2</sub>N·OH and  $\text{MeCO}_2\text{·N}(\text{CF}_3)_2$ .<sup>20</sup> <sup>c</sup> The reaction proceeded rapidly and exothermically to completion. <sup>d</sup> Isolated by g.l.c. (4 m PEGA; 70–160 °C), b.p. 94 °C at 751 mmHg (Siwoloboff) (lit.,<sup>5</sup> 93 °C at 760 mmHg),  $\lambda_{\text{max}}$  (vapour) 5.42 (C=O str.), 9.52 (N–O str.), 10.38 (C–N str.), 13.98 ( $\text{CF}_3$  def.)  $\mu\text{m}$ ,  $\delta_{\text{F}}$  (50% w/w in  $\text{CCl}_4$ )  $-9.4$  (s) p.p.m.,  $\tau$  (50% w/w in  $\text{CCl}_4$ ) 8.79 ( $\text{CH}_3$ , t,  $J$  7.9 Hz), 7.53 ( $\text{CH}_2$ , q) (rel. int. 3:2), top mass peak  $m/e$  150 [ $\text{CF}_2\text{-N}(\text{OH})\text{·CF}_3^+$ , 4%]; *cf.* ref. 2a], base peak  $m/e$  57 [ $\text{M}^+ - (\text{CF}_3)_2\text{N·O·}$ ]. <sup>e</sup> Isolated by g.l.c. (2 m SE30, 50 °C), identified by comparison of its i.r., n.m.r. ( $^{19}\text{F}$  and  $^1\text{H}$ ), and mass spectra with those of an analytically pure sample.<sup>2a</sup>

Fischer–Porter PTFE needle valve. The tube was sealed and placed in a bath at a predetermined temperature in the dark, and the product was worked up when the purple colour of the nitroxide had virtually disappeared. Work-up involved trap-to-trap fractional condensation of volatile product at 1–2 mmHg pressure and analysis of fractions by i.r. spectroscopy, g.l.c., and molecular weight determination.

<sup>8</sup> H. G. Ang, *Chem. Comm.*, 1968, 1320.

<sup>9</sup> S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Doklady Akad. Nauk S.S.S.R.*, 1965, **160**, 1319.

ation (Regnault's method); some (bistrifluoromethylamino-oxy)carbonyl compounds were subsequently isolated by g.l.c. and characterised spectroscopically. Details are in Table 1.

(b) *With aromatic aldehydes.* These reactions were carried out as described in (a) except that the aldehyde under investigation was placed in the reaction vessel before it was freed from air and cooled, and in some cases carbon tetrachloride (inert solvent) was introduced by condensation techniques. Volatile products were worked up as in (a). In every case except that of the reaction involving benzaldehyde, the (bistrifluoromethylamino-oxy)carbonyl derivative was isolated from the non-volatile product by standard techniques; all such derivatives were characterised by elemental analysis and/or spectroscopic methods (i.r., n.m.r., and mass). Details are in Table 2.

*Reactions of (Bistrifluoromethylamino-oxy)carbonylbenzene.*—(a) *Hydrolysis.* The carbonyl compound (0.15 g, 0.55 mmol) was heated (95 °C) for 10 h with 2M-potassium hydroxide (2 ml) in a Pyrex ampoule (20 ml). The volatile product was dried ( $\text{P}_2\text{O}_5$ ) and shown by i.r. spectroscopy and molecular weight determination (Regnault's method) to be carbon dioxide (0.022 g, 0.50 mmol, 91%) (Found:  $M$ , 45.6. Calc. for  $\text{CO}_2$ :  $M$ , 44) contaminated with traces of unknown material. The aqueous product, which contained fluoride ions, was acidified ( $\text{H}_2\text{SO}_4$ ) and extracted with ether ( $4 \times 10$  ml); evaporation of the dried ( $\text{MgSO}_4$ ) extract gave benzoic acid (0.06 g, 0.49 mmol, 89%), m.p. 118 °C (from water).

(b) *With bistrifluoromethyl nitroxide.* The nitroxide (5.10 g, 30.4 mmol) was condensed, *in vacuo*, into a cold ( $-196^\circ\text{C}$ ) Pyrex ampoule (70 ml) containing (bistrifluoromethylamino-oxy)carbonylbenzene (2.05 g, 7.51 mmol) and carbon tetrachloride (4.77 g). The ampoule was sealed, *in vacuo*, warmed to room temperature, and heated at 70 °C until the intensity of the purple colour of the radical had diminished considerably (48 h) (the liquid product in the ampoule was then present as two immiscible layers). Trap-to-trap vacuum fractionation of the volatile product gave bistrifluoromethyl nitroxide (1.18 g, 7.02 mmol, 23% recovery) contaminated with bistrifluoromethylamine (0.10 g, 0.65 mmol, 3%), a mixture of *NN*-bistrifluoromethylhydroxylamine (0.81 g, 4.79 mmol, 20%) and carbon tetrachloride (4.77 g), and a trace of a colourless liquid ( $-24^\circ\text{C}$  trap) which was added to the involatile, viscous, golden-yellow, liquid residue remaining in the ampoule. This involatile product contained five major components and several minor ones of longer retention times (g.l.c. analysis, 2 m APL at 110 °C); extraction with carbon tetrachloride mainly removed three of the major constituents, which were isolated from the extract by g.l.c. (4 m APL; 120 °C) and shown to be (bistrifluoromethylamino-oxy)carbonylbenzene (0.18 g, 0.66 mmol, 9% recovery), 1-(bistrifluoromethylamino-oxy)-4-[(bistrifluoromethylamino-oxy)carbonyl]benzene (0.69 g, 1.57 mmol, 23%) [Found: C, 30.1; H, 1.0; N, 6.4%;  $M$  (mass spec.), 440.  $\text{C}_{11}\text{H}_4\text{F}_{12}\text{N}_2\text{O}_3$  requires C, 30.0; H, 0.9; N, 6.4%;  $M$ , 440],  $\lambda_{\text{max}}$  (film) 5.55  $\mu\text{m}$  (C=O str.),  $\delta_{\text{F}}$  (*ca.* 15% w/w in  $\text{CCl}_4$ )  $-9.45$  (s) and  $-9.98$  (s) p.p.m. (rel. int. 1:1),  $\delta_{\text{H}}$  (same soln.)  $-0.7$  and  $-1.5$  p.p.m. (9 Hz 'doublets' of symmetrical AA'BB' splitting pattern) (rel. int. 1:1), and another liquid (bistrifluoromethylamino-oxy)[(bistrifluoromethylamino-oxy)carbonyl]benzene (0.51 g, 1.16 mmol, 17%) [Found: C, 30.0; H, 1.0; N, 6.3%;  $M$  (mass spec.), 440],  $\lambda_{\text{max}}$  (film) 5.53  $\mu\text{m}$  (C=O str.),  $\delta_{\text{F}}$  (*ca.* 15% w/w in  $\text{CCl}_4$ )  $-10.0$  (s) and  $-10.53$  (s) p.p.m.

TABLE 2  
Reactions between bistrifluoromethyl nitroxide and aromatic aldehydes

Aldehyde (g, mmol)	$(CF_3)_2N\cdot O\cdot$ (g, mmol)	Bath temp. ( $^{\circ}C$ ) (tube size, ml)	Products (g, mmol)	Elemental analyses (%) *			
				C	H	F	N
PhCHO 1.20, 11.3	3.81, 22.7	20 <sup>a</sup> (25)	$(CF_3)_2N\cdot O\cdot$ (trace) $(CF_3)_2N\cdot OH$ (1.90, 11.24) $PhCO_2\cdot N(CF_3)_2$ <sup>b</sup> (3.08, 11.3)	39.8 39.5	1.9 1.8	41.4 41.8	5.2 5.1
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·CHO 0.56, 4.67	1.58, 9.40	20 <sup>a,c</sup> (60)	$(CF_3)_2N\cdot OH$ (0.79, 4.67) <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·CHO (0.05, 0.42) Unidentified (0.15, —) <sup>e</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> ·N(CF <sub>3</sub> ) <sub>2</sub> <sup>d</sup> (1.12, 3.90)	40.6 41.8	2.2 2.4		
<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> ·CHO 0.47, 3.91	1.31, 7.80	—24 <sup>e</sup> (60)	$(CF_3)_2N\cdot O\cdot$ (0.06, 0.36) $(CF_3)_2N\cdot OH$ (0.62, 3.67) <i>m</i> -MeC <sub>6</sub> H <sub>4</sub> ·CHO (0.02, 0.17) <i>m</i> -MeC <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> ·N(CF <sub>3</sub> ) <sub>2</sub> <sup>f</sup> (1.05, 3.66)	41.5 41.8	2.1 2.4		5.0 4.9
1,4-C <sub>6</sub> H <sub>4</sub> (CHO) <sub>2</sub> 0.67, 5.00	3.36, 20.0	20 <sup>g</sup> (25)	$(CF_3)_2N\cdot O\cdot$ (0.34, 2.00) $(CF_3)_2N\cdot OH$ (1.51, 8.94) CCl <sub>4</sub> (1.0, —) 1,4-C <sub>6</sub> H <sub>4</sub> [CO <sub>2</sub> ·N(CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> <sup>h</sup> (2.27, 4.85)	30.8 30.8	0.8 0.85	48.7 48.8	6.3 6.0
C <sub>6</sub> F <sub>5</sub> ·CHO 1.93, 9.85	3.50, 20.8	20 <sup>a,i</sup> (40)	$(CF_3)_2N\cdot O\cdot$ (0.18, 1.07) $(CF_3)_2N\cdot OH$ (1.66, 9.82) CCl <sub>4</sub> (3.2, —) C <sub>6</sub> F <sub>5</sub> ·CO <sub>2</sub> ·N(CF <sub>3</sub> ) <sub>2</sub> <sup>j</sup> (3.43, 9.45)	30.6 29.8		56.2 57.6	4.0 3.9

\* Found, upper figures; required, lower figures.

<sup>a</sup> A rapid exothermic reaction occurred. <sup>b</sup> B.p. 182  $^{\circ}C$  at 755 mmHg (Siwoloboff),  $\lambda_{max}$  (film) 3.25, 3.29, 3.31 $\mu$ v (t; mono-substituted benzene C-H str.), 5.56s (C=O str.), 6.24m, 6.29w, 6.68vw, 6.87m (aromatic C=C vib., ring conjugated to side chain), 7.66s, 7.92s, 8.14s, 8.28s (C-F str.), 9.28w (in-plane C-H bend), 9.56s (N-O str.), 10.06s, 10.28 (C-N str.), 11.62w, 12.45, 12.58w (dblt.; out-of-plane C-H bend), and 14.03, 14.30 $\mu$ m (dblt.; CF<sub>3</sub> def.),  $\delta_F$  (20% w/w in CCl<sub>4</sub>) —10.82 (s) p.p.m.,  $\tau$  (20% in CCl<sub>4</sub>) 1.87 (v. complex; *o*-H), 2.43 (v. complex; *m*-, *p*-H) (rel. int. 2 : 3), *M* (mass spec.) 273 [C<sub>9</sub>H<sub>5</sub>F<sub>6</sub>NO<sub>2</sub><sup>+</sup>, 1%; base peak *m/e* 105 (C<sub>6</sub>H<sub>5</sub>·CO<sup>+</sup>)]. <sup>c</sup> A reaction in which the tube was placed in a —24  $^{\circ}C$  bath was complete after 3 min and the yield of *p*-MeC<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>·N(CF<sub>3</sub>)<sub>2</sub> increased to 98% at the expense of the unidentified material, the i.r. spectrum of which was not inconsistent with the product of side-chain attack, *p*-(CF<sub>3</sub>)<sub>2</sub>N·O·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>·N(CF<sub>3</sub>)<sub>2</sub>. <sup>d</sup> Isolated by g.l.c. (2 m SE30; 155  $^{\circ}C$ ), b.p. 198  $^{\circ}C$  at 750 mmHg (Siwoloboff),  $n_D^{20}$  1.4329,  $\lambda_{max}$  (film) 5.57s  $\mu$ m (C=O str.),  $\delta_F$  (neat liq.) —9.53 (s) p.p.m.,  $\tau$  (neat liq.) 7.71 (s, CH<sub>3</sub>), and 2.91, 2.11 (8.6 Hz 'doublet' components of AA'BB' pattern) (rel. int. 3 : 2 : 2), top mass peak *m/e* 133 (C<sub>2</sub>F<sub>5</sub>N<sup>+</sup>, 2%), base peak *m/e* 119 (MeC<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>). <sup>e</sup> The reaction was complete after 4 min. <sup>f</sup> Isolated by g.l.c. (2 m SE30; 155  $^{\circ}C$ ),  $\lambda_{max}$  (film) 5.55s  $\mu$ m (C=O str.),  $\delta_F$  (neat liq.) —9.42 (s) p.p.m.,  $\tau$  (neat liq.) 7.72 (s, CH<sub>3</sub>), 2.7 (complex), and 2.2 (complex) (rel. int. 3 : 2 : 2), *M* (mass spec.) 287 [C<sub>10</sub>H<sub>7</sub>F<sub>6</sub>NO<sub>2</sub><sup>+</sup>, 1.5%; base peak *m/e* 119 (MeC<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>)]. <sup>g</sup> A vigorous exothermic reaction (lasting ca. 2 min) set in soon after the carbon tetrachloride (1.01 g) used as inert solvent melted, and the temperature of the tube rose to at least 50  $^{\circ}C$ . <sup>h</sup> Left behind as a white solid after removal of the volatiles and recrystallised (twice) from acetone to yield white rods, m.p. 94  $^{\circ}C$ ,  $\lambda_{max}$  (mull) 5.56s  $\mu$ m (C=O str.),  $\delta_F$  (ca. 20% w/w in CDCl<sub>3</sub>) —11.28 (s) p.p.m.,  $\tau$  (ca. 20% w/w in CCl<sub>4</sub>) 1.83 (s), *M* (mass spec.) 468 [C<sub>12</sub>H<sub>4</sub>F<sub>12</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>, 7%; base peak *m/e* 300, (CF<sub>3</sub>)<sub>2</sub>N·O·CO·C<sub>6</sub>H<sub>4</sub>·CO<sup>+</sup>]. <sup>i</sup> Carbon tetrachloride (3.22 g) was used as a solvent and diluent. <sup>j</sup> The majority of this compound (>99% pure by g.l.c.) was left behind in the tube after removal of the volatile products, but some did transfer with the latter and was recovered from the —24  $^{\circ}C$  trap; b.p. 187  $^{\circ}C$  at 750 mmHg,  $n_D^{20}$  1.3729,  $\lambda_{max}$  (film) 5.47s  $\mu$ m (C=O str.),  $\delta_F$  (neat liq.) —8.57 (t,  $J_{OF_1, F_2}$  0.96 Hz), +60.93 (complex, 2-, 6-F), +70.52 (t of t, 4-F,  $J_{2-F, 4-F}$  6.8,  $J_{3-F, 4-F}$  19.8 Hz), and +85.57 p.p.m. (complex, 3-, 5-F) (rel. int. 6 : 2 : 1 : 2), *M* (mass spec.) 363 [C<sub>9</sub>F<sub>11</sub>NO<sub>2</sub><sup>+</sup>, 1%; base peak *m/e* 195 (C<sub>6</sub>F<sub>5</sub>·CO<sup>+</sup>)].

(rel. int. 1 : 1),  $\delta_H$  (same soln.) —0.98br (complex) and —1.23br p.p.m. (complex) (rel. int. 1 : 1).

*Hydrolysis of (Bistrifluoromethylamino-oxy)carbonyl-2,3,4,5,6-pentafluorobenzene.*—A curdy white precipitate appeared immediately when a sample of the carbonyl compound (0.32 g, 0.88 mmol) was shaken with ethanolic potassium hydroxide (10% w/v; 1.5 ml) at 20  $^{\circ}C$ . After

being shaken for 10 min, the mixture was acidified (H<sub>2</sub>SO<sub>4</sub>) and extracted with ether. Work-up of the extract gave pentafluorobenzoic acid (0.18 g, 0.85 mmol, 96%), m.p. 104  $^{\circ}C$  [from light petroleum (b.p. 80—100  $^{\circ}C$ )—toluene] (lit.<sup>10</sup> 103—104  $^{\circ}C$ ).

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<sup>10</sup> E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1959, 166.