Nitroxide Chemistry. Part V.[1] Reactions Between Bistrifluoromethyl Nitroxide and Alkylbenzenes; Mechanism of Formation of Carbonyl Compounds

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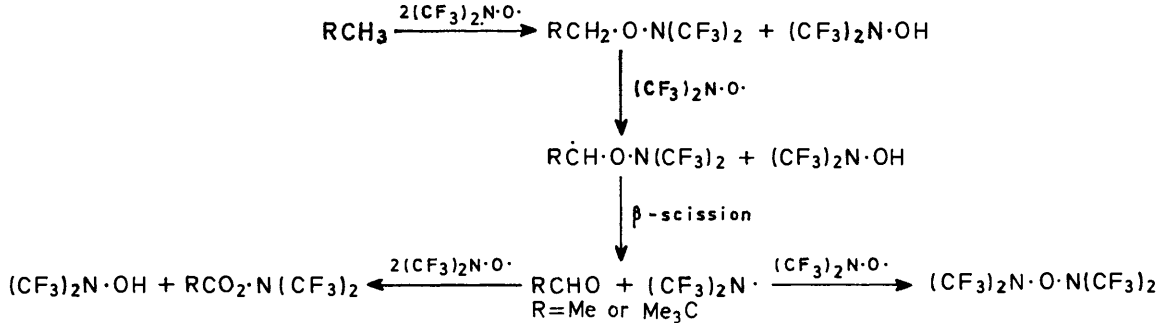
The reaction sequence $ArCH_3 \xrightarrow{X\cdot} XH + ArCH_2X \xrightarrow{X\cdot} XH$, $ArCHX_2$, $(CF_3)_2NX$, ArCOX [Ar = Ph, *p*-ClC_6H_4, C_6F_5; X = $(CF_3)_2N{\cdot}O$] has been established, and evidence adduced for the formation of aldehydes, ArCHO, as precursors of the carbonyl compounds ArCOX. The compounds $PhCH_2X$, $PhCHX_2$, and $PhCX_3$ have been synthesised by treatment of benzyl bromide, benzylidene dichloride, and benzylidyne trichloride, respectively, with the mercurial HgX_2 [X = $(CF_3)_2N{\cdot}O$]; the first of these undergoes C–O bond cleavage when heated with hydrobromic or hydriodic acid, with liberation of the hydroxylamine $(CF_3)_2N{\cdot}OH$; the last decomposes thermally into $PhCO_2N(CF_3)_2$ and two compounds believed to be isomers of $(CF_3)_2N{\cdot}C_6H_4{\cdot}CO_2{\cdot}N(CF_3)_2$.

CARBONYL compounds often occur as by-products in reactions involving the formation of materials containing the grouping $>CH{\cdot}O{\cdot}N(CF_3)_2$ from alkanes and bistrifluoromethyl nitroxide.[2] The suggestion[3] that aldehydic intermediates might be involved (*e.g.* see Scheme 1) led to the present investigation and thereby to the discovery[1] of the extreme ease with which the reaction $RCHO + 2(CF_3)_2N{\cdot}O{\cdot} \longrightarrow RCO_2{\cdot}N(CF_3)_2 + (CF_3)_2N{\cdot}OH$ (R = alkyl or aryl) takes place. Methylbenzenes were chosen as substrates to eliminate complications arising from the formation of *vic*-bis(bistrifluoromethylamino-oxy) derivatives (*cf.* ref. 2 and the work with ethylbenzene discussed later) and to extend the preliminary observations that bistrifluoromethyl nitroxide much prefers to abstract benzylic hydrogen from toluene[4] or its 2,3,4,5,6-pentafluoro-derivative[5] rather than attack their ring systems.



SCHEME 1

Reactions of Bistrifluoromethyl Nitroxide with Toluene and with (Bistrifluoromethylamino-oxymethyl)benzene (1).—A rapid exothermic reaction occurred when a 2 : 1 molar mixture of bistrifluoromethyl nitroxide and toluene was warmed from −196 °C to room temperature; the major products were *NN*-bistrifluoromethylhydroxylamine and (bistrifluoromethylamino-oxymethyl)benzene (1) (65% based on 93% consumption of toluene), as reported earlier,[4] and only small amounts of (bistrifluoromethylamino-oxy)carbonylbenzene (2) (3%) and the oxadiazapentane (4), not detected previously, were formed. With a 6 : 1 molar ratio of reactants, however, the yield of the carbonyl compound (2) increased to 64%, no monosubstituted derivative (1) was detected, and the disubstituted derivative (3) (10%) appeared; almost half of the nitroxide consumed was converted into *NN*-bistrifluoromethylhydroxylamine, and the molar ratio of (2) to (4) was *ca.* 0·9. Both reactions also yielded a high-boiling, multicomponent, yellow oil which presumably arose *via*

$PhCH_2{\cdot}O{\cdot}N(CF_3)_2$ (1) $\quad$ $PhCO_2{\cdot}N(CF_3)_2$ (2)

$PhCH[O{\cdot}N(CF_3)_2]_2$ (3) $\quad$ $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (4)

$PhĊH{\cdot}O{\cdot}N(CF_3)_2$ (5) $\quad$ $PhC[O{\cdot}N(CF_3)_2]_3$ (6)

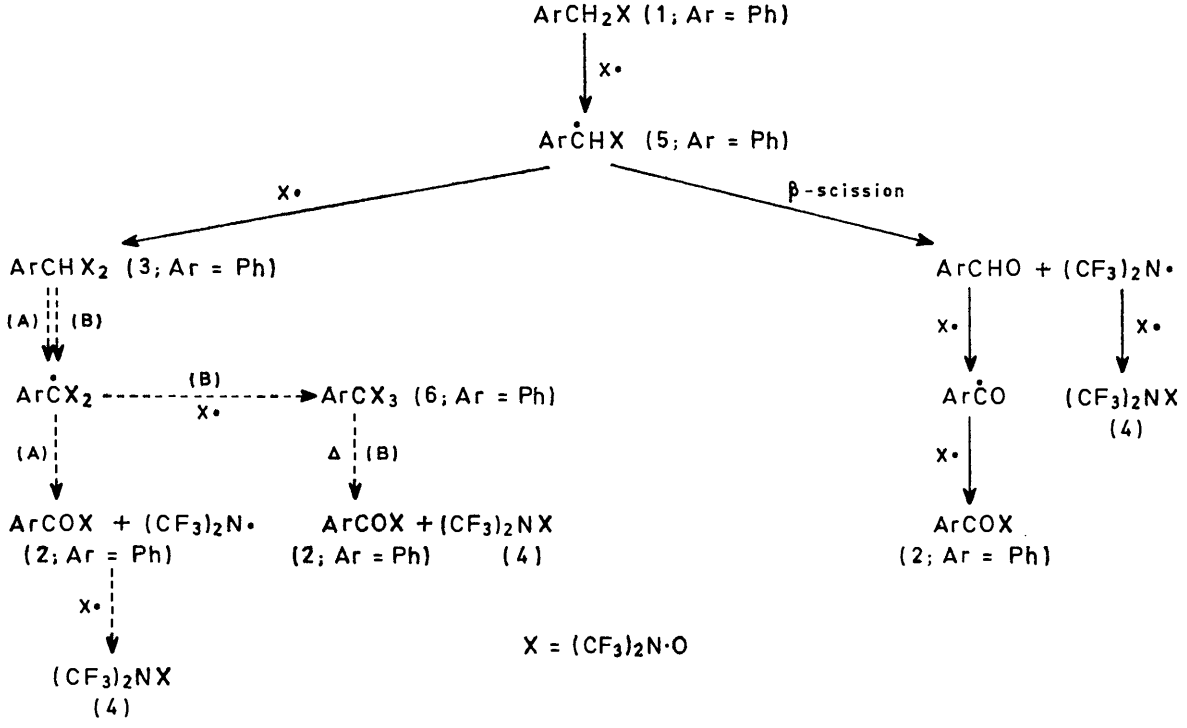
attack of bistrifluoromethyl nitroxide and/or the N–O–N compound (4) (a ready source of free radicals[6]) on a ring carbon atom.

A reaction between the nitroxide and (bistrifluoromethylamino-oxymethyl)benzene (1) (2 : 1 molar ratio) proceeded smoothly at room temperature, although it was slower and less exothermic than that between

[1] Part IV, R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 80.
[2] R. E. Banks, R. N. Haszeldine, and B. Justin, *J. Chem. Soc.* (*C*), 1971, 2777.
[3] B. Justin, Ph.D. Thesis, Manchester University, 1969.
[4] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.* (*C*), 1966, 901.
[5] G. Shaw, Ph.D. Thesis, Manchester University, 1968.
[6] R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, 1449.

the nitroxide and toluene. The major products were *NN*-bistrifluoromethylhydroxylamine, the carbonyl compound (2) [71% based on 60% consumption of starting material (1)], the disubstituted derivative (3) (14%), and the oxadiazapentane (4) [(2) : (4) = *ca.* 1·2]. With a four-molar proportion of the nitroxide, complete conversion of (bistrifluoromethylamino-oxymethyl)-benzene (1) into products (2) (78%) and (3) (18%) occurred.

only slowly at room temperature, 85% of (3) being recovered after 14 days. Abstraction of hydrogen occurred, as indicated by the formation of *NN*-bistrifluoromethylhydroxylamine, but the yield of the carbonyl compound (2) (the only identifiable non-volatile product) was only *ca.* 4%. Use of a higher concentration of bistrifluoromethyl nitroxide (4- or 8-molar proportion) and forcing reaction conditions (60—70 °C, 2—5 days) did not markedly change the



SCHEME 2

The most obvious initial step in the reaction between bistrifluoromethyl nitroxide and (bistrifluoromethyl-amino-oxymethyl)benzene is abstraction of a benzylic hydrogen atom and scavenging of the radical $PhC\dot{H}\cdot O\cdot N(CF_3)_2$ (5) thus produced by more nitroxide, giving the disubstituted derivative (3). β-Scission of radical (5) to give benzaldehyde provides an obvious means[1] for explaining the formation of the carbonyl compound (2), but two other mechanisms must also be considered [routes (A) and (B), Scheme 2 (Ar = Ph)].

To assess the viability of the alternative route (A), a reaction was carried out between the disubstituted derivative (3) and bistrifluoromethyl nitroxide. The starting material (3) was prepared in 91% yield from benzylidene dichloride and the mercurial $[(CF_3)_2N\cdot O]_2$-Hg—a superior alternative to the route $PhCH_3 \longrightarrow PhCH_2\cdot O\cdot N(CF_3)_2 \longrightarrow PhCH[O\cdot N(CF_3)_2]_2$ already described, and one which has been applied also to the preparation of $PhCH_2\cdot O\cdot N(CF_3)_2$ (from benzyl bromide, 96% yield) and $PhC[O\cdot N(CF_3)_2]_3$ (6) (from benzylidyne trichloride, 85% yield).

Reaction between the disubstituted derivative (3) and a two-molar equivalent of the nitroxide occurred

yield of the carbonyl compound (2), although the yields of *NN*-bistrifluoromethylhydroxylamine and of the unidentified high-boiling products increased. Clearly, route (A) cannot be responsible for the formation of the carbonyl compound (2) to any extent, if at all, in the $(CF_3)_2N\cdot O\cdot$–$PhCH_2\cdot O\cdot N(CF_3)_2$ reaction.

The trisubstituted derivative (6) was not detected in the high-boiling product from any of the reactions discussed so far, and the possibility of its loss through thermal decomposition to the carbonyl derivative (2) and the oxadiazapentane (4) [see Scheme 2 (Ar = Ph)] was eliminated by its recovery in 93 and 84% yield, respectively, after being heated at 120 °C for 15 h or 130 °C for 50 h. Route (B) is therefore eliminated, and the aldehyde route has been adopted to explain the formation of carbonyl compounds as by-products in reactions between bistrifluoromethyl nitroxide and methylbenzenes (Scheme 2) and certain alkanes (Scheme 1 and ref. 2). That no aldehydes have, as yet, been detected in reaction products is ascribed to the facility with which bistrifluoromethyl nitroxide abstracts an aldehydic hydrogen atom, as demonstrated, for example, by the formation of the carbonyl compound

p-$MeC_6H_4{\cdot}CO_2{\cdot}N(CF_3)_2$ in 98% yield when a 2 : 1 molar mixture of the nitroxide and *p*-tolualdehyde is allowed to warm from −196 to −24 °C.[1]

Except for the formation of a trace of bistrifluoromethylamine in the reaction between toluene and a two-molar proportion of bistrifluoromethyl nitroxide, no direct evidence [*e.g.*, formation of $PhCH_2{\cdot}N(CF_3)_2$ or $PhCO{\cdot}N(CF_3)_2$] for the formation of bistrifluoromethylamino-radicals *via* β-scission of the radical (5) (Scheme 2) was obtained in the foregoing work except the formation of the oxadiazapentane (4). It seems that the last compound must have arisen *via* scavenging of $(CF_3)_2N{\cdot}$ radicals from the β-scission by the nitroxide, since the latter does not react with bistrifluoromethylamine under the conditions of the foregoing experiments [$(CF_3)_2N{\cdot}O{\cdot} + (CF_3)_2NH \not\longrightarrow (CF_3)_2N{\cdot}OH + (CF_3)_2N{\cdot}$].[7]

The reactivity order $PhCH_3 > PhCH_2{\cdot}O{\cdot}(CF_3)_2 \gg PhCH[O{\cdot}N(CF_3)_2]_2$ with respect to abstraction of a benzylic hydrogen atom by bistrifluoromethyl nitroxide may be ascribed primarily to a polar effect,[8] the transition state for the reactions being represented by $[(CF_3)_2N{\cdot}O{\cdot}\ H{:}CX_2Ph \longleftrightarrow (CF_3)_2N{\cdot}\bar{O}{:}\ \overset{+}{H}CX_2Ph]$, where X = H or $(CF_3)_2N{\cdot}O$.

Reactions of Bistrifluoromethyl Nitroxide with p-*Chlorotoluene, 2,3,4,5,6-Pentafluorotoluene, and the Derived (Bistrifluoromethylamino-oxymethyl)benzenes.*—The introduction of a *para*-chlorine substituent into toluene does not affect the reaction pattern (Scheme 2, full arrows): with a two-molar equivalent of the nitroxide an exothermic change occurs rapidly at room temperature, giving the products (7), $(CF_3)_2N{\cdot}OH$, and (8) in 95, 49, and 3% yield, respectively, based on 85% consumption of *p*-chlorotoluene; the monosubstituted compound (7) is attacked by an excess of the nitroxide at room temperature with the production of the carbonyl derivative (8) (67%), the oxadiazapentane (4), the disubstituted compound *p*-$ClC_6H_4{\cdot}CH[O{\cdot}N(CF_3)_2]_2$ (26%), and the hydroxylamine $(CF_3)_2N{\cdot}OH$.

2,3,4,5,6-Pentafluorotoluene is noticeably more resistant to attack by bistrifluoromethyl nitroxide than either toluene or *p*-chlorotoluene, presumably owing

p-$ClC_6H_4{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$ (7)

p-$ClC_6H_4{\cdot}CO_2{\cdot}N(CF_3)_2$ (8)

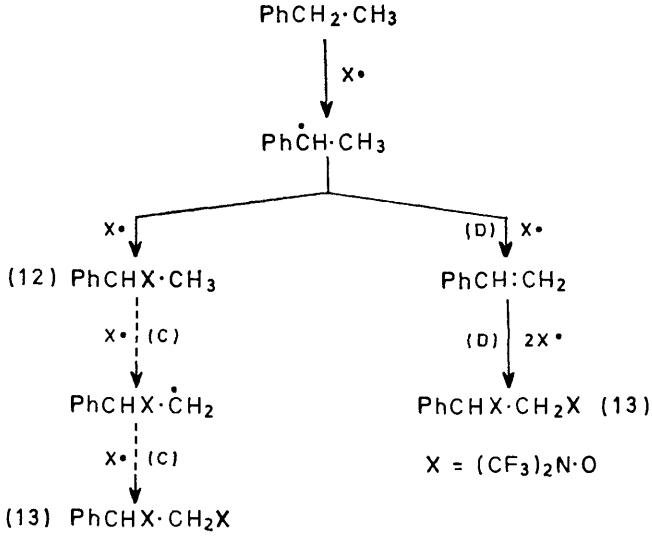
$C_6F_5{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$ (9)

$ArCH[O{\cdot}N(CF_3)_2]_2$ (10)

$ArCO_2{\cdot}N(CF_3)_2$ (11)

to the relatively powerful polar effect of the C_6F_5 group (*cf.* the previous section and ref. 8). Thus, when stored at room temperature for *ca.* 3 h, a 2 : 1 molar mixture of the nitroxide and the pentafluoro-compound gives 1-(bistrifluoromethylamino-oxymethyl)-2,3,4,5,6-pentafluorobenzene, (9) (76% based on 82% consumption of $C_6F_5{\cdot}CH_3$), *NN*-bistrifluoromethylhydroxylamine (44%), a trace of the disubstituted derivative $C_6F_5{\cdot}CH[O{\cdot}N(CF_3)_2]_2$, a small amount of the oxadiazapentane (4), and a complex high-boiling oil showing i.r. absorption consistent with the presence of olefinic (5·70 and 5·85 μm; *cf.*[9] C=C str. for cyclo-C_6F_{10} 5·70 μm) and $(CF_3)_2N{\cdot}O$ [2] groups [presumably formed by attack of the nitroxide on a nuclear carbon atom (*cf.* ref. 10)]. Despite the formation of the N–O–N compound (4), no carbonyl derivative, $C_6F_5{\cdot}CO_2{\cdot}N(CF_3)_2$, was detected in the product; but this compound (3% based on 94% consumption of starting material) was obtained, together with the oxadiazapentane (4), the disubstituted derivative $C_6F_5{\cdot}CH[O{\cdot}N(CF_3)_2]_2$ (39%), the hydroxylamine $(CF_3)_2N{\cdot}OH$, and unsaturated multi-component high-boiling material when the monosubstituted compound (9) was left in contact with bistrifluoromethyl nitroxide at room temperature for *ca.* 2 days. The formation of both the compounds $C_6F_5{\cdot}CO_2{\cdot}N(CF_3)_2$ and $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$, albeit in small amounts, and the swiftness of the reaction $C_6F_5{\cdot}CHO + 2(CF_3)_2N{\cdot}O{\cdot} \longrightarrow C_6F_5{\cdot}CO_2{\cdot}N(CF_3)_2 + (CF_3)_2N{\cdot}OH$ at room temperature,[1] implicates pentafluorobenzaldehyde as an intermediate, so the mechanism shown in Scheme 2 (full arrows) seems quite general. On this basis, the tendency for a disubstituted product (10) to be formed at the expense of the corresponding carbonyl compound (11) along the series $C_6H_5{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$, *p*-$ClC_6H_4{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$, $C_6F_5{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$ [relative ratios of (10) : (11) = *ca.* 1, 2, and 60] is ascribed to the relative stabilities of the intermediates $ArCH{\cdot}O{\cdot}N(CF_3)_2$, increase in stability favouring scavenging by bistrifluoromethyl nitroxide.

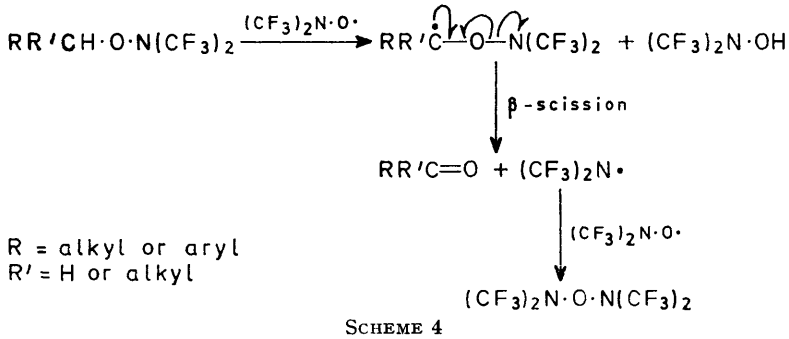
Reaction of Bistrifluoromethyl Nitroxide with Ethylbenzene.—A rapid exothermic reaction occurs between



SCHEME 3

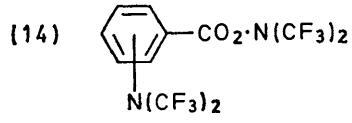
[7] T. Myerscough, Ph.D. Thesis, Manchester University, 1970.
[8] W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, ch. 12.
[9] R. N. Haszeldine, *Nature*, 1951, **168**, 1028.
[10] M. A. Englin and A. V. Melnikova, *Zhur. Vsesoyuz. Khim. obshch. im. D. T. Mendeleeva*, 1968, **13**, 594 (*Chem. Abs.*, 1969, **70**, 28,503k).

a two-molar proportion of the nitroxide and ethylbenzene at room temperature, giving mainly the products (12) (75%), (13) (6%), and $(CF_3)_2N{\cdot}OH$ (49%). Formation of the product (13) can be explained in two ways [routes (C) and (D), Scheme 3], but since the monosubstituted derivative (12) was found to react only relatively slowly with bistrifluoromethyl nitroxide at room temperature to give mainly acetophenone (76%) together with (13) (19%), $(CF_3)_2N{\cdot}OH$, and (4) [molar ratio of this product to PhCOMe = *ca.* 1·0], it seems that



SCHEME 4

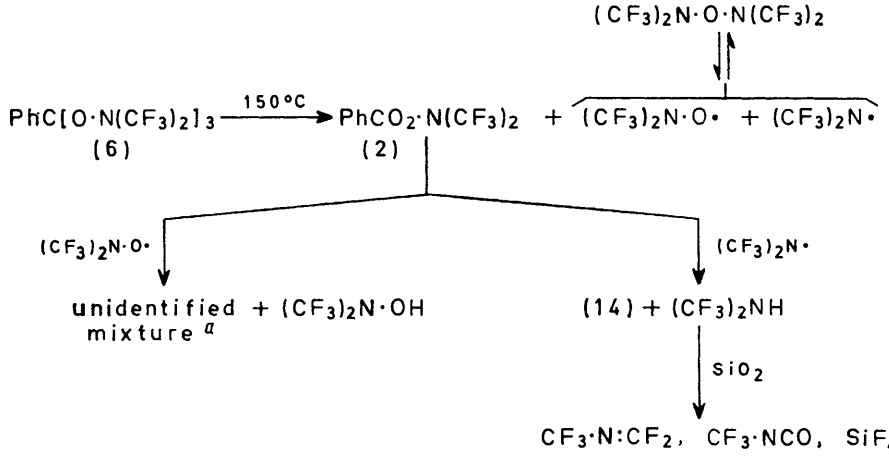
route (C) plays little or no part in the reaction. The preferred route, (D), is analogous to the mechanism adopted for the formation of αβ-bis(bistrifluoromethylamino-oxy)alkanes from certain alkanes and bistrifluoromethyl nitroxide.[2] Formation of acetophenone



from the monosubstituted derivative (12) can be explained by the type of mechanism believed to be involved in the formation of carbonyl compounds from methylbenzenes (Scheme 2) and certain alkanes (Scheme 1), a generalised version of which is shown in Scheme 4.

Reactions of Some (Bistrifluoromethylamino-oxymethyl)benzenes.—The monosubstituted compound (1) resists attack by hot aqueous potassium hydroxide or hydrochloric acid, but its C–O bond is cleaved by hydrogen bromide in acetic acid at 120 °C, giving benzyl bromide, *NN*-bistrifluoromethylhydroxylamine, and, through reaction of the latter with acetic acid, (bistrifluoromethylamino-oxy)carbonylmethane. Hot hydroiodic acid acts similarly, the products being *NN*-bistrifluoromethylhydroxylamine and toluene, which presumably arises *via* benzyl iodide.

As stated earlier, the trisubstituted derivative of toluene (6) can be recovered substantially unchanged after storage at 130 °C in Pyrex for 50 h. After 70 h at 150 °C, however, it has decomposed almost completely, giving a mixture of the volatile compounds $(CF_3)_2N{\cdot}OH$, $(CF_3)_2NH$, $CF_3{\cdot}N{:}CF_2$, $CF_3{\cdot}NCO$, $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$, and SiF_4, and a multicomponent oil which contains, *inter alia*, the carbonyl compound (2) (*ca.* 25% yield) and two products (estimated total yield 30%) believed on the basis of n.m.r. and g.l.c.–mass spectrometry to be (bistrifluoromethylamino)[(bistrifluoromethylamino-oxy)carbonyl]benzenes (14). These two products possess very similar mass spectra, each showing a top mass peak corresponding to the molecular ion of (14) and containing a base peak corresponding to the ion $(CF_3)_2N{\cdot}C_6H_4{\cdot}CO^+$; the ^{19}F n.m.r. spectrum of the



SCHEME 5

[a] No (bistrifluoromethylamino-oxy)[(bistrifluoromethylamino-oxy)carbonyl]benzenes, $(CF_3)_2N{\cdot}O{\cdot}C_6H_4{\cdot}CO_2{\cdot}N(CF_3)_2$ [formed at 70 °C from $(CF_3)_2N{\cdot}O{\cdot}$ and (2) [1]] were detected by g.l.c.

TABLE 1

Reactions between bistrifluoromethyl nitroxide and monomethylbenzenes or their α-(bistrifluoromethylamino-oxy)-derivatives

Substrate (g, mmol)	$(CF_3)_2N{\cdot}O{\cdot}$ g, mmol	Reaction period and temp. (°C) (tube size in ml)	Products (g, mmol, %)	Elemental analyses
$PhCH_3$ (1·432, 15·56)	5·02, 29·9	5 min, 20 [a] (60)	$PhCH_3$ (0·105, 1·14, 7) $(CF_3)_2N{\cdot}OH$ (2·425, 14·3, 48) $(CF_3)_2N{\cdot}O{\cdot}$, $(CF_3)_2NH$, $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ } traces $PhCH_2{\cdot}O{\cdot}N(CF_3)_2$ (2·41, 9·31, 65) [b] $PhCO_2{\cdot}N(CF_3)_2$ (0·13, 0·48, 3) [b,c] Unidentified (0·58 g) [d]	
$PhCH_3$ (0·25, 2·7)	2·72, 16·2	45 min, 20 [a] (60)	$(CF_3)_2N{\cdot}OH$ (1·15, 6·8, 47) $(CF_3)_2N{\cdot}O{\cdot}$ (0·275, 1·64, 10) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (0·63, 1·96, 13·5) $PhCH[O{\cdot}N(CF_3)_2]_2$ (0·12, 0·28, 10) [b,e] $PhCO_2{\cdot}N(CF_3)_2$ (0·47, 1·72, 64) [b,c] Unidentified (*ca.* 0·2 g) [d]	
$PhCH_2{\cdot}O{\cdot}N(CF_3)_2$ (0·51, 1·98)	0·664, 3·95	15 min, 20 [f] (20)	$(CF_3)_2N{\cdot}OH$ (0·28, 1·66, 44) $(CF_3)_2N{\cdot}O{\cdot}$ (0·025, 0·15, 4) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (0·23, 0·72, 19) $PhCH_2{\cdot}O{\cdot}N(CF_3)_2$ (0·205, 0·79, 40) [b] $PhCH[O{\cdot}N(CF_3)_2]_2$ (0·07, 0·17, 14) [b,e] $PhCO_2{\cdot}N(CF_3)_2$ (0·23, 0·84, 71) [b,c] Unidentified (*ca.* 0·03 g) [d]	
$PhCH_2{\cdot}O{\cdot}N(CF_3)_2$ (0·51, 1·98)	1·32, 7·86	30 min, 20 [f] (60)	$(CF_3)_2N{\cdot}OH$ (0·57, 3·40, 77) $(CF_3)_2N{\cdot}O{\cdot}$ (0·12, 0·72, 9) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (0·48, 1·50, 21) $PhCH[O{\cdot}N(CF_3)_2]_2$ (0·15, 0·36, 18) [b,e] $PhCO_2{\cdot}N(CF_3)_2$ (0·42, 1·54, 78) [b,c] Unidentified (*ca.* 0·04 g) [d]	
$PhCH[O{\cdot}N(CF_3)_2]_2$ (0·86, 2·01)	0·69, 4·11	14 days, 20 (25)	$(CF_3)_2N{\cdot}OH$ (0·17, 1·01, 33) $(CF_3)_2N{\cdot}O{\cdot}$ (0·18, 1·05, 26) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (0·05, 0·16, 6) $PhCH[O{\cdot}N(CF_3)_2]_2$ (0·73, 1·70, 85) [b] $PhCO_2{\cdot}N(CF_3)_2$ (*ca.* 4% yield) [b,c] Unidentified (*ca.* 0·03 g)	
p-$ClC_6H_4{\cdot}CH_3$ (0·65, 5·13)	1·72, 10·24	3 min, 20 [a] (20)	$(CF_3)_2N{\cdot}OH$ (0·84, 4·98, 49) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (0·14, 0·45, 4) *p*-$ClC_6H_4{\cdot}CH_3$ (0·10, 0·79, 15) *p*-$ClC_6H_4{\cdot}CO_2{\cdot}N(CF_3)_2$ (0·04, 0·14, 3) [g] p-$ClC_6H_4{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$ (1·23, 4·18, 95) [g,h]	Found: C, 37·3; H, 2·1; F, 37·6; N, 4·8% Required: C, 36·8; H, 2·0; F, 38·8; N, 4·8%
p-$ClC_6H_4{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$ (1·63, 5·56)	2·80, 16·7	10 min, 20 [a] (20)	$(CF_3)_2N{\cdot}OH$ (1·34, 7·91, 51) $(CF_3)_2N{\cdot}O{\cdot}$ (0·18, 1·05, 6) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (1·02, 3·2, 20·5) p-$ClC_6H_4{\cdot}CO_2{\cdot}N(CF_3)_2$ (1·15, 3·73, 67) [i,j]	Found: C, 35·2; H, 1·4; N, 4·5% Required: C, 35·1; H, 1·3; N, 4·6%
			p-$ClC_6H_4{\cdot}CH[O{\cdot}N(CF_3)_2]_2$ (0·66, 1·43, 26) [i,k]	Found: C, 28·6; H, 1·2; N, 5·9% Required: C, 28·7; H, 1·1; N, 6·0%
$C_6F_5{\cdot}CH_3$ (3·62, 19·9	6·68, 39·8	*ca.* 3 h, 20 (80)	$(CF_3)_2N{\cdot}OH$ (2·92, 17·3, 44) $(CF_3)_2N{\cdot}O{\cdot}$ (trace) $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (not estimated) $C_6F_5{\cdot}CH_3$ (0·64, 3·51, 18) [m] $C_6F_5{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$ (4·37, 12·5, 76) [m,n]	Found: C, 30·6; H, 0·7; N, 4·2% Required: C, 30·9; H, 0·6; N, 4·0%
			$C_6F_5{\cdot}CH[O{\cdot}N(CF_3)_2]_2$ (trace) [m] Unidentified [o]	

TABLE 1 (*Continued*)

Substrate (g, mmol)	$(CF_3)_2N\cdot O\cdot$ g, mmol	Reaction period and temp. (°C) (tube size in ml)	Products (g, mmol, %)	Elemental analyses
$C_6F_5\cdot CH_2\cdot O\cdot N(CF_3)_2$ (2·11, 6·06)	2·02, 12·0	47 h, 20 (20)	$(CF_3)_2N\cdot OH$ (0·87, 5·14, 50) $(CF_3)_2N\cdot O\cdot$ (0·29, 1·73, 14) $(CF_3)_2N\cdot O\cdot N(CF_3)_2$ (0·17, 0·54, 5) $C_6F_5\cdot CH_2\cdot O\cdot N(CF_3)_2$ (0·12, 0·34, 6) [p] $C_6F_5\cdot CH[O\cdot N(CF_3)_2]_2$ (1·16, 2·25, 39) [p,q] $C_6F_5\cdot CO_2\cdot N(CF_3)_2$ [p,r] (0·07, 0·19, 3) Unidentified (*ca.* 1·5 g)	

[a] The reaction was noticeably exothermic. [b] These products co-condensed in a −24 °C trap, and the mixture was analysed by i.r. spectroscopy and g.l.c. analysis. [c] An authentic sample was prepared from $(CF_3)_2N\cdot O\cdot$ and PhCHO.[1] [d] Involatile, multicomponent (by g.l.c. analysis), orange oil recovered from the reaction vessel and showing i.r. absorptions consistent with the presence of $(CF_3)_2N\cdot O$-substituted material. [e] An authentic sample was prepared from $[(CF_3)_2N\cdot O]_2Hg$ and $PhCHCl_2$ (see Table 2). [f] The reaction was slightly exothermic. [g] These two products and unchanged *p*-chlorotoluene co-condensed in a −24 °C trap and also comprised the non-volatile product; separation was achieved by g.l.c. (3 m SE30–Celite; 150 °C). [h] Gave top mass spectral peaks corresponding to the molecular ions $[C_9H_6{}^{37}ClF_6NO]^{+\cdot}$ and $[C_9H_6{}^{35}ClF_6NO]^{+\cdot}$; δ_F (neat liq.; ext. $CF_3\cdot CO_2H$) −8·94(s) p.p.m., τ 2·88(s) and 5·16(s) (rel. int. 2 : 1). [i] The involatile product, a pale yellow oil, comprised these two chlorobenzenes, which were isolated by g.l.c. (3 m SE30–Celite; 150 °C), plus several minor unknown components. [j] Liquid, $\lambda_{max.}$ (film) 5·55 μm (C=O str.), δ_F (*ca.* 50% w/w soln. in CCl_4; ext. $CF_3\cdot CO_2H$) −9·97(s) p.p.m., τ 2·32 (' AB '-type pattern). [k] Liquid, n_D^{20} 1·3794, δ_F (*ca.* 40% w/w soln. in CCl_4; ext. $CF_3\cdot CO_2H$) −10·23(s) p.p.m., τ 2·63(s) and 3·97(s) (rel. int. 4 : 1). [l] A preliminary investigation was carried out by G. Shaw.[5] [m] Co-condensed in a −24 °C trap together with several (g.l.c. analysis) unknown components. [n] Isolated by g.l.c. (3 m SE30–Celite; 105 °C); b.p. 164 °C at 753 mmHg (Siwoloboff), n_D^{20} 1·3971, *M* (mass spec.) 349 ($C_9H_2F_{11}NO$ requires *M*, 349), δ_F (neat liq.; ext. $CF_3\cdot CO_2H$) −7·85 [1·2 Hz triplet; $O\cdot N(CF_3)_2$], +67·0 (complex, 2- and 6-F), +76·6 (t of t, 4-F), and +87·5 (complex, 3- and 5-F) p.p.m. (rel. int. 6 : 2 : 1 : 2), τ 4·75(s). [o] Comprising 0·14 g of volatile material and 1·6 g of a colourless, multicomponent (g.l.c. analysis) oil. [p] Present in the −24 °C trap fraction and/or the involatile product (g.l.c. analysis; 3 m TXP–Celite; 110 °C). [q] A small impure sample was isolated by g.l.c. (4 m PEGA–Celite; 100 °C) and tentatively identified as principally $C_6F_5\cdot CH[O\cdot N(CF_3)_2]_2$ by i.r. and n.m.r. spectroscopy {δ_F (ext. $CF_3\cdot CO_2H$; 56·5 MHz) −8·5 p.p.m. [complex, $O\cdot N(CF_3)_2$], τ 3·74 (s; 100 MHz)}, and mass spectrometry [top mass peak at *m/e* 349 (11% rel. abund.), base peak at *m/e* 348 ($C_9HF_{11}NO^+$), and important peaks at *m/e* 196 ($C_7HF_5O^+$, 81%), 195 ($C_7F_5O^+$, 88%), 167 ($C_6F_5^+$, 16%), and 69 (CF_3^+, 55%)]. [r] An authentic sample was synthesised from $(CF_3)_2N\cdot O\cdot$ and $C_6F_5\cdot CHO$.[1]

TABLE 2

Reactions between bis(bistrifluoromethylamino-oxy)mercury and (halogenomethyl)benzenes

Substrate (g, mmol)	$[(CF_3)_2N\cdot O]_2Hg$ g, mmol	Reaction period (min) and temp. (°C) (tube size in ml)	Product (g, mmol, % yield)	Elemental analyses
$PhCH_2Br$ (1·37, 8·00)	2·69, 5·01	5, 20 (40)	$PhCH_2\cdot O\cdot N(CF_3)_2$ [a] (1·99, 7·67, 96)	
$PhCHCl_2$ (1·13, 7·02)	4·97, 9·26	20, 0 (60)	*PhCH*$[O\cdot N(CF_3)_2]_2$ [b] (2·45, 5·76, 91)	Found: C, 31·0; H, 1·6; F, 53·7; N, 6·5% Required: C, 31·2; H, 1·4; F, 35·5; N, 6·6%
$PhCCl_3$ [c] (0·868, 4·44)	3·27, 6·09	20, 0 (80)	*PhC*$[O\cdot N(CF_3)_2]_3$ [d] (2·24, 3·77, 85)	Found: C, 26·6; H, 0·9; N, 7·0% Required: C, 26·3; H, 0·8; N, 7·1%

[a] Identified by comparison of its i.r. spectrum with that of an authentic sample. [b] Purified finally by g.l.c. (2 m SE30–Celite; 130 °C), δ_F (*ca.* 50% w/w soln. in CCl_4; ext. $CF_3\cdot CO_2H$) −9·54(s) p.p.m., τ 2·63 (s, Ph) and 3·93 (s, PhC*H*), (rel. int. 5 : 1). [c] Diluted with carbon tetrachloride (2 g). [d] Isolated by g.l.c. (2 m SE30–Celite; 120 °C). B.p. 203 °C at 754 mmHg, *M* (mass spec.) 593 ($C_{13}H_5F_{18}N_3O_3$ requires *M*, 593), δ_F (neat liq.; ext. $CF_3\cdot CO_2H$) −10·95(s) p.p.m., τ 2·25 (complex, *o*-H) and 2·73 (complex, *m*-, *p*-H) (rel. int. 2 : 3).

oil shows two singlets at −21·9 and −21·7 p.p.m. (ext. $CF_3\cdot CO_2H$) attributable[11] to $(CF_3)_2N$ groups and a complex group of bands at −9·5 p.p.m. indicative[1] of the presence of $CO_2\cdot N(CF_3)_2$. The formation of isomers of type (14) can be explained as shown in Scheme 5; the oxadiazapentane (4) dissociates into bistrifluoromethyl nitroxide and bistrifluoromethylamino-radicals at temperatures above 85 °C.[6]

EXPERIMENTAL

For details of spectroscopic instrumentation and the preparation of bistrifluoromethyl nitroxide see Part IV.[1]

Reactions of Bistrifluoromethyl Nitroxide with Methylbenzenes and with their α-(Bistrifluoromethylamino-oxy)-derivatives.—The nitroxide 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 4 mm PTFE needle valve, and allowed to warm to the reaction temperature. Reaction progress was easily followed by observation of the diminution in the intensity of the purple colour caused by uptake of the nitroxide. Volatile product was transferred to a vacuum system and examined by trap-to-trap fractional condensation at 1—2 mmHg, fractions being analysed by i.r. spectroscopy, g.l.c., and molecular weight determination; involatile product was either discarded (if present in only small amount) or examined by g.l.c. and i.r. techniques. Results are listed in Table 1.

Synthesis of (Bistrifluoromethylamino-oxymethyl)benzenes.—Bis(bistrifluoromethylamino-oxy)mercury was prepared by condensing (*in vacuo*) an excess of bistrifluoromethyl

[11] F. S. Fawcett and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, **87**, 4341.

nitroxide onto carefully dried mercury contained in a cold (−196 °C) Pyrex ampoule fitted with a Fischer–Porter 4 mm PTFE needle valve. The ampoule was sealed, left at room temperature for 1 day, or sometimes more, evacuated to remove unchanged nitroxide, and then cooled (−196 °C) prior to introduction of a (halogenomethyl)benzene for reaction with the solid, cream-coloured mercurial. The ampoule was sealed, warmed to 0 °C or room temperature, and kept at that temperature for 5—20 min before volatile product was removed for trap-to-trap fractional condensation at 1—2 mmHg, leaving mercuric halide in the ampoule. Results are listed in Table 2.

Reaction of Bistrifluoromethyl Nitroxide with Ethylbenzene.—The nitroxide (1·55 g, 9·22 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex ampoule (60 ml) containing ethylbenzene (0·50 g, 4·71 mmol). The ampoule was sealed and allowed to warm slowly to room temperature. An exothermic reaction occurred immediately after the reactants had melted. Trap-to-trap fractional condensation of the volatile product, *in vacuo*, gave *NN*-bistrifluoromethylhydroxylamine (0·76 g, 4·51 mmol, 49%) contaminated with a trace of bistrifluoromethylamine (−196 and −72 °C traps), ethylbenzene (−45 °C trap), and a mixture (−24 °C trap) of ethylbenzene (total 0·07 g, 0·7 mmol, 15% recovery), [1-(*bistrifluoromethylamino-oxy*)*ethyl*]*benzene* (12) (0·82 g, 3·00 mmol; 75%) [Found: C, 43·75; H, 3·5; N, 5·1%; *M* (mass spec.), 273. $C_{10}H_9F_6NO$ requires: C, 43·9; H, 3·3; N, 5·1%; *M*, 273], b.p. 166 °C at 773 mmHg (Siwoloboff), δ_F (neat liq.; ext. $CF_3{\cdot}CO_2H$) −9·78(s) p.p.m., τ 2·77 (s, Ph), 5·04 (q, *J* 6·8 Hz, CH), and 8·58 (d, Me) (rel. int. 5 : 1 : 3) [isolated by g.l.c. (3 m SE30–Celite; 120 °C)], and [1,2-bis-(bistrifluoromethylamino-oxy)ethyl]benzene (13) (0·10 g, 0·23 mmol; 6%) (identified by comparison of its g.l.c. retention time with that of a sample obtained as described later). An involatile yellow oil (*ca.* 0·1 g) was recovered from the reaction vessel and shown by g.l.c. (2 m SE30–Celite; 130 °C) to contain at least six components, one or more of which was a $(CF_3)_2N{\cdot}O$-derivative (i.r. spectroscopic analysis).

Reaction of Bistrifluoromethyl Nitroxide with [1-(*Bistrifluoromethylamino-oxy*)*ethyl*]*benzene* (12).—The nitroxide (4·54 g, 27·03 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex ampoule (80 ml) containing the substrate (2·46 g, 9·01 mmol). The ampoule was sealed and stored at 20 °C for 1·75 h, by which time the purple colour of the nitroxide had faded considerably. Fractionation of the volatile product gave bistrifluoromethyl nitroxide (1·09 g, 6·50 mmol, 24% recovery), *NN*-bistrifluoromethylhydroxylamine (1·50 g, 8·87 mmol; 43%), and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (4) [2·21 g, 6·91 mmol, 34% based on $(CF_3)_2N{\cdot}O{\cdot}$ consumed]. The pale yellow involatile residue left in the vessel was shown by g.l.c. to be a multicomponent mixture from which were isolated by g.l.c. (6 m Apiezon L-Celite; 130—190 °C) acetophenone (0·82 g, 6·83 mmol, 76%) (identified by i.r. spectroscopy and g.l.c. retention time), [1-(bistrifluoromethylamino-oxy)ethyl]benzene (12) (trace), and [1,2-*bis*-(*bistrifluoromethylamino-oxy*)*ethyl*]*benzene* (13) (0·75 g, 1·70 mmol, 19%) (Found: C, 33·0; H, 1·9; N, 6·1. $C_{12}H_8F_{12}N_2O_2$ requires C, 32·7; H, 1·8; N, 6·3%), b.p. 197 °C at 758 mmHg (Siwoloboff), δ_F (neat liq.; 94·1 MHz, *p*-$CF_3{\cdot}S{\cdot}C_6H_4Cl$ lock) −9·99(s) and −8·81(s) p.p.m. downfield from $CF_3{\cdot}CO_2H$ (by calculation), τ (100 MHz) 3·12 (s, Ph), 5·25 (complex, PhC*H*), and 6·05 (complex, $PhCH{\cdot}CH_2$) (rel. int. 5 : 1 : 2), the mass spectrum of which showed no peak corresponding to a molecular ion but contained prominent peaks at *m/e* 272 {$C_{10}H_8F_6NO^+$ [$M^{+\cdot}$ − $(CF_3)_2N{\cdot}O{\cdot}$], 98%}, 120 ($C_8H_8O^+$, 75%), 104 ($C_8H_8^+$, 100%), and 69 (CF_3^+, 30%) and a peak at *m/e* 150 [$CF_2{:}N(OH){\cdot}$-CF_3^+, 7%] (*cf.* ref. 2).

Pyrolysis of [*Tris*(*bistrifluoromethylamino-oxy*)*methyl*]*benzene* (6).—Samples of compound (6) were recovered in 93 and 84% yield, respectively, after being heated at 120 °C (for 15 h) and 130 °C (for 50 h) in Pyrex ampoules (10 ml) in the absence of air; in both cases the recovered material was contaminated with (bistrifluoromethylamino-oxy)carbonylbenzene. When compound (6) (0·61 g, 1·03 mmol) was heated at 150 °C for 70 h in a Pyrex ampoule (10 ml), it slowly turned deep orange, and a small immiscible lower layer formed. The volatile product [0·104 g, 0·935 mmol. Found: *M* (Regnault), 111·5] was shown by i.r. spectroscopy to contain bistrifluoromethylamine, *NN*-bistrifluoromethylhydroxylamine, trifluoromethyl isocyanate, perfluoro-2-azapropene, perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (4), and silicon tetrafluoride. The reaction vessel, containing the relatively non-volatile product, was attached to a vacuum system *via* an external cold (−196 °C) trap and evacuated continuously for 10 h; a colourless oil (0·27 g) collected in the cold trap, leaving in the vessel an orange gum which was not examined. Examination of the oil by g.l.c. (2 m Apiezon L–Celite; 105 °C) and i.r. techniques showed it to be a multicomponent (nine g.l.c. peaks) mixture, the principal constituent being (bistrifluoromethylamino-oxy)carbonylbenzene (estimated yield 25%). The ^{19}F n.m.r. spectrum of the mixture showed bands at −21·9 (rel. int. 4) −21·7 (4), −11·2, −11·1, and −11·0 (total 4), a group of bands at −9·5 (17), and −7·5 (1) p.p.m. (ext. $CF_3{\cdot}CO_2H$) and several other very weak bands; its ^1H spectrum consisted mainly of two complex groups of bands centred at −1·3 (rel. int. 9) and −0·7 (13) p.p.m. (ext. C_6H_6). G.l.c.–mass spec. examination of the oily mixture indicated that the first five components to be eluted were highly substituted with $(CF_3)_2N{\cdot}O$ and/or $(CF_3)_2N$ groups (peaks were observed at *m/e* values >800); the materials giving rise to the sixth and seventh g.l.c. peaks each showed a top mass peak at *m/e* 424 ($C_{11}H_4F_{12}N_2O_2^{+\cdot}$, <1% rel. abund.), and prominent peaks at *m/e* 405 ($C_{11}H_4F_{11}N_2O_2^+$), 256 ($C_9H_4F_6NO^+$, base peak in each case), 159 ($C_3F_5N_2^+$, 13 and 18%), 140 ($C_3F_4N_2^+$, 26 and 37%), 95 ($C_2F_3N^+$, 11 and 19%), and 69 (CF_3^+, 32 and 49%). The eighth g.l.c. peak was of very low intensity, and the ninth peak was the most intense and caused by (bistrifluoromethylamino-oxy)carbonylbenzene.

Cleavage Reactions of (*Bistrifluoromethylamino-oxymethyl*)*benzene.*—Samples of (bistrifluoromethylamino-oxymethyl)benzene were recovered in 92 and 85% yield, respectively, after being heated with excess of aqueous 10% potassium hydroxide (under reflux; 6 h) or 4M-hydrochloric acid (80 °C; 18 days; 50 ml Pyrex ampoule).

A mixture of (bistrifluoromethylamino-oxymethyl)benzene (0·58 g, 2·24 mmol), anhydrous hydrogen bromide (0·405 g, 5·00 mmol), and glacial acetic acid (1·47 g) was heated at 120 °C for 31 h in a Pyrex ampoule (60 ml). The volatile product was subjected to trap-to-trap fractional condensation, *in vacuo*, fractions being analysed by g.l.c. and i.r. spectroscopy, and shown to comprise hydrogen bromide, carbon dioxide, silicon tetrafluoride, acetic acid, *NN*-bistrifluoromethylhydroxylamine, (bistrifluoromethylamino-oxy)carbonylmethane (the last two

totalled 0·42 mmol), benzyl bromide (0·28 g, 1·64 mmol; 52%), and (bistrifluoromethylamino-oxymethyl)benzene (0·06 g, 0·23 mmol; 10% recovery). An involatile, unidentified, pale yellow solid (0·07 g) (Found: C, 0·6; H, 3·8; ash, 2·2%), which partly melted at 250—260 °C, was recovered from the vessel.

When (bistrifluoromethylamino-oxymethyl)benzene (0·81 g, 3·13 mmol) was heated (120 °C for 42 h) with hydroiodic acid (s.g. 1·94; 2 ml) in a Pyrex ampoule (60 ml), the volatile product contained carbon dioxide, bistrifluoromethylamine (trace), *NN*-bistrifluoromethylhydroxylamine (0·05 g, 0·30 mmol, 12%), (bistrifluoromethylamino-oxymethyl)benzene (0·19 g, 0·73 mmol, 23% recovery), and toluene (0·20 g, 2·17 mmol, 91% based on substrate consumed). The involatile product, a brown slush, did not yield any benzyl alcohol when heated under reflux with 2M-potassium hydroxide.

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