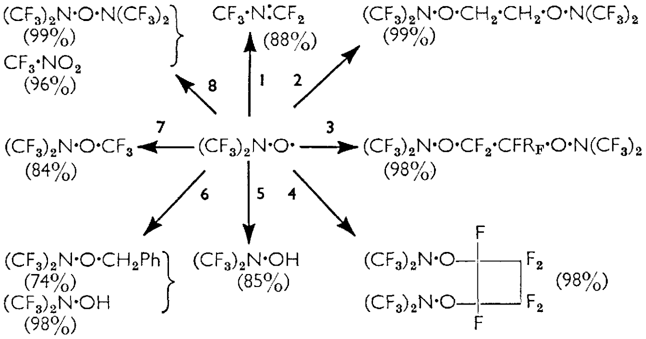
Perfluoroalkyl Derivatives of Nitrogen. Part XXI.[1] Some Reactions of Bistrifluoromethylnitroxide

By R. E. Banks, R. N. Haszeldine, and M. J. Stevenson

Bistrifluoromethylnitroxide combines readily with ethylene, tetrafluoroethylene, hexafluoropropene, or hexafluorocyclobutene to give almost quantitative yields of the compounds 1,2-bis(*NN*-bistrifluoromethylnitroxy)-ethane, perfluoro-[1,2-bis(*NN*-dimethylnitroxy)ethane], perfluoro-[1,2-bis(*NN*-dimethylnitroxy)propane], and perfluoro-[1,2-bis(*NN*-dimethylnitroxy)cyclobutane], severally. It reacts with trifluoronitrosomethane to form perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), and with trifluoroiodomethane to yield tristrifluoromethylhydroxylamine. Catalytic reduction of bistrifluoromethylnitroxide affords bistrifluoromethylhydroxylamine, and hot iron converts it into perfluoro(methylenemethylamine). Bistrifluoromethylnitroxide and toluene interact readily to yield *O*-benzyl-*NN*-bistrifluoromethylhydroxylamine and bistrifluoromethylhydroxylamine.

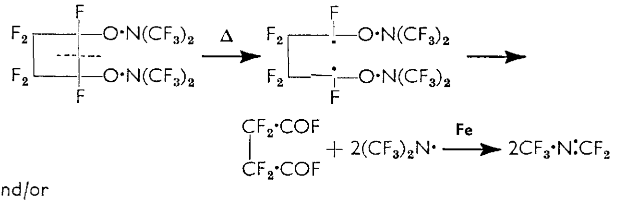
BISTRIFLUOROMETHYLNITROXIDE, $(CF_3)_2N\cdot O\cdot$, a stable purple gas,[2,3] prepared by reaction of bistrifluoromethylhydroxylamine with silver oxide,[2] potassium permanganate,[3] or sodium fluoride, has now been shown to react as in the annexed Scheme. Previously [2,3] it has been shown to undergo no reaction with air, water, 10% aqueous sodium hydroxide, trichlorofluoromethane, glass, mercury, copper, or stainless steel (all, presumably, at room temperature), to combine rapidly at 25° with nitric oxide or nitrogen dioxide to give *O*-nitrosobistrifluoromethylhydroxylamine and a product thought to be *O*-nitrobistrifluoromethylhydroxylamine, respectively, and to react with aqueous potassium iodide to yield iodine and bistrifluoromethylhydroxylamine.



1. Fe, 225°; 2. $CH_2{:}CH_2$, room temp.; 3. $CF_2{:}CFR_F$ (R_F = F or CF_3), room temp.; 4. $\overline{CF_2\cdot CF{:}CF\cdot CF_2}$, 85°; 5. H_2/Pd–Al_2O_3, room temp.; 6. $PhCH_3$, 23°; 7. CF_3I, u.v. light; 8. $CF_3\cdot NO$, room temp., dark.

Formulation of the 2 : 1 adducts from bistrifluoromethylnitroxide and the olefins ethylene, tetrafluoroethylene, perfluoropropene, and perfluorocyclobutene as nitroxyalkanes and not as amine oxides [*e.g.*, $(CF_3)_2N\cdot O\cdot CF_2\cdot CF_2\cdot O\cdot N(CF_3)_2$ *not* $(CF_3)_2\overset{+}{N}(\overset{-}{O})\cdot CF_2\cdot CF_2\cdot\overset{+}{N}(\overset{-}{O})(CF_3)_2$] is based on n.m.r. and mass spectroscopic measurements, and the failure to de-oxygenate them with hot iron; the adducts give mass spectra that do not show peaks due to $(P - 16)^+$ or $(P - 32)^+$ ions, contrary to what would be expected if they contained oxygen atoms co-ordinated to nitrogen.[4]

When heated at 210° for 3 hr. with iron powder, the adducts from bistrifluoromethylnitroxide and ethylene, tetrafluoroethylene, or perfluoropropene undergo no change and are recovered almost quantitatively; under these conditions, however, the adduct from perfluorocyclobutene is not de-oxygenated but breaks down to give high yields of perfluoro(methylenemethylamine) and perfluorosuccinyl fluoride, possibly as follows:



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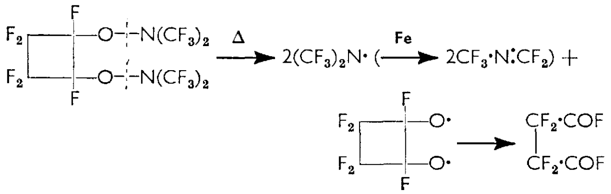

Hot iron de-oxyfluorinates bistrifluoromethylnitroxide to perfluoro(methylenemethylamine).

Since perfluoroamine *N*-oxides are unknown, no definite conclusions regarding structure can be drawn from the infrared (i.r.) spectra or boiling points of the bistrifluoromethylnitroxide–olefin adducts; their i.r. spectra show no bands in the 6—7 μ region where an N–O link in a perfluoroamine *N*-oxide might reasonably be expected to absorb [cf.[5] $CF_3\cdot\overset{+}{N}(\overset{-}{O}){:}N\cdot CF_3$ shows N–O str. (as.) at 6·37 μ].

The fact that only 2 : 1 nitroxide–olefin adducts were obtained shows that bistrifluoromethylnitroxide is an excellent free-radical scavenger, a conclusion that is underlined by the formation of only the compound $(CF_3)_2N\cdot O\cdot CF_2\cdot CF_2\cdot O\cdot N(CF_3)_2$ when the nitroxide and tetrafluoroethylene were mixed in the molar ratio of 1 : 10. When mixed with an excess of an equimolar mixture of ethylene and tetrafluoroethylene, bistrifluoromethylnitroxide combines almost exclusively

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[1] Part XX, R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe, *J. Chem. Soc.*, 1965, 7209.

[2] W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, 1965, **87**, 802.

[3] S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Doklady Akad. Nauk S.S.S.R.*, 1965, **160**, 1319.

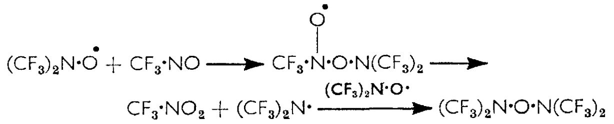
[4] T. A. Bryce and J. R. Maxwell, *Chem. Comm.*, 1965, 206.

[5] J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 919.

(98%) with the fluoro-olefin, indicating that it is a strongly nucleophilic radical $[(CF_3)_2\ddot{N}{\cdot}O{\cdot} \longleftrightarrow (CF_3)_2\overset{+\cdot}{N}{\cdot}O^-]$.

The ability of bistrifluoromethylnitroxide to attack C–H bonds is demonstrated by its rapid reaction with toluene at room temperature, which yields bistrifluoromethylhydroxylamine and, by scavenging of benzyl radicals, the hydroxylamine $PhCH_2{\cdot}O{\cdot}N(CF_3)_2$; the last compound did not react with iron powder at 210° and showed a very weak (<1% abundance) $(P - 16)^+$ peak in its mass spectrum. Spectroscopic studies showed that only the hydroxylamine $PhCH_2{\cdot}O{\cdot}N(CF_3)_2$ was formed, and in particular that attack of bistrifluoromethylnitroxide on the aromatic nucleus, to give $CH_3{\cdot}C_6H_4{\cdot}O{\cdot}N(CF_3)_2$, had not occurred. The specificity of radical attack on the side-chain of toluene is noteworthy.

Formation of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) from bistrifluoromethylnitroxide and trifluoronitrosomethane can be explained by the free-radical sequence



EXPERIMENTAL

Products were identified by molecular weight determination (Regnault's method), elemental analysis, infrared spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), nuclear magnetic resonance spectroscopy (Perkin-Elmer R10 spectrometer operating at 14·09 kg and 35°), mass spectrometry (A.E.I. MS/2H instrument with a resolution of 1 in 700), and gas–liquid chromatography (Perkin-Elmer Fraktometer model 452).

Bistrifluoromethylhydroxylamine was prepared by reaction of *O*-nitrosobistrifluoromethylhydroxylamine with hydrochloric acid in the presence of mercury.[6]

Preparation of Bistrifluoromethylnitroxide.—(*a*) *Using silver oxide*. Bistrifluoromethylhydroxylamine (5·00 g., 29·6 mmoles) and dry silver oxide (10·0 g.), sealed in a 300-ml. Dreadnought ampoule, were heated at 85° for 18 hr. in a tumbler heater. Fractionation of the product gave bistrifluoromethylnitroxide (2·41 g., 14·4 mmoles; 90% yield) (Found: C, 14·3; N, 8·4. Calc. for C_2F_6NO: C, 14·3; N, 8·3%) and bistrifluoromethylhydroxylamine (2·30 g., 13·61 mmoles; 46% recovery). The i.r. spectrum of bistrifluoromethylnitroxide contains strong bands at 7·63, 7·88, 8·15, 10·08, and 13·73, 13·83, 13·93 μ (triplet); its mass spectrum shows peaks at m/e values (assignments and relative abundances in parentheses) of 168 ($C_2F_6NO^+$, 11·8), 152 ($C_2F_6N^+$, 12·7), 114 ($C_2F_4N^+$, 2·4), 85 (CF_3O^+, 5·9), 83 (CF_3N^+, 4·7), 81 ($C_2F_3^+$, 38·8), *69*(CF_3^+, *100·0*), 50 (CF_2^+, 5·6), 31 (CF^+, 4·7), and 30 (NO^+, 34·1).

(*b*) *Using sodium fluoride*. Bistrifluoromethylhydroxylamine (0·801 g., 4·74 mmoles) and anhydrous commercial sodium fluoride (5·0 g.), sealed in a 40-ml. Pyrex ampoule, were heated at 170° for 3 days. Fractionation of the product gave bistrifluoromethylnitroxide (0·121 g., 0·720 mmoles; 36% based on 42% conversion of the hydroxylamine), bistrifluoromethylhydroxylamine (0·466 g., 2·75 mmoles; 58% recovery), carbon dioxide, and a trace of trifluoronitromethane.

Reactions of Bistrifluoromethylnitroxide.—(*a*) *With hydrogen*. Bistrifluoromethylnitroxide (0·149 g., 0·887 mmoles) mixed with an excess of hydrogen was passed slowly through a 15 × 1 cm. bed of palladium–alumina catalyst.[7] An exothermic reaction occurred, and fractionation of the product, trapped at −196°, gave bistrifluoromethylhydroxylamine (0·128 g., 0·757 mmoles; 85%).

(*b*) *With iron*. Bistrifluoromethylnitroxide (0·133 g., 0·792 mmoles) and freshly-reduced iron powder (*ca.* 3 g.), contained in a 20-ml. Pyrex ampoule, were heated at 225° for 4 hr. Fractionation of the product gave perfluoro-(methylenemethylamine) (0·07 g., 0·526 mmoles; 88%) contaminated with trifluoromethyl isocyanate, and silicon tetrafluoride.

(*c*) *With trifluoroiodomethane*. Bistrifluoromethylnitroxide (0·149 g., 0·887 mmoles) and trifluoroiodomethane (0·175 g., 0·895 mmoles), sealed in a 30-ml. Pyrex ampoule, were exposed for 4 hr. to ultraviolet light from a Hanovia 250-w lamp placed 10 cm. distant. Fractionation of the product gave tristrifluoromethylhydroxylamine (0·178 g., 0·751 mmoles; 84% based on the nitroxide).

No reaction occurred when an equimolar mixture of bistrifluoromethylnitroxide (0·225 g., 1·34 mmoles) and trifluoroiodomethane (0·262 g., 1·34 mmoles) was kept in a 30-ml. Pyrex tube at room temperature in the dark for 3 days.

(*d*) *With trifluoronitrosomethane*. Bistrifluoromethylnitroxide (0·081 g., 0·482 mmoles) and trifluoronitrosomethane (0·470 g., 0·475 mmoles), sealed in a 20-ml. Pyrex ampoule, were kept in the dark at room temperature for 3 days. Fractionation of the product gave trifluoronitrosomethane (0·024 g., 0·237 mmoles; 50% recovery), trifluoronitromethane (0·027 g., 0·230 mmoles; 96% based on $CF_3{\cdot}NO$ consumed), and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0·076 g., 0·238 mmoles; 99% based on the nitroxide) which was spectroscopically (i.r. and mass spec.) identical with an authentic sample prepared by photolysis of tristrifluoromethylhydroxylamine.[8]

(*e*) *With tetrafluoroethylene*. Bistrifluoromethylnitroxide (0·250 g., 1·49 mmoles) and tetrafluoroethylene (0·149 g., 1·49 mmoles) were condensed separately, *in vacuo*, into a 98-ml. Pyrex tube cooled to −196°, which was then sealed. By the time the tube had warmed up to room temperature the purple colour of the nitroxide had disappeared, and fractionation of the product gave tetrafluoroethylene (0·075 g., 0·754 mmoles; 50% recovery) and *perfluoro-*[1,2-*bis*(NN-*dimethylnitroxy*)*ethane*] (0·320 g., 0·734 mmoles; 99%) (Found: C, 16·7; N, 6·6%; *M*, 435. $C_6F_{16}N_2O_2$ requires C, 16·5; N, 6·4%; *M*, 436), b. p. 89°/748 mm. (Siwoloboff), n_D^{12} 1·2650.

When the above experiment was repeated using 0·225 g. (1·34 mmoles) of bistrifluoromethylnitroxide and an excess of tetrafluoroethylene (1·340 g., 13·40 mmoles), the product was a mixture of perfluoro-[1,2-bis(*NN*-dimethylnitroxy)ethane] (0·288 g., 0·661 mmoles; 99% based on the nitroxide) and tetrafluoroethylene (1·273 g., 12·73 mmoles; 95% recovery).

The i.r. spectrum of perfluoro-[1,2-bis(dimethylnitroxy)ethane] contains strong bands in the 7·58—8·59 μ region

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[6] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1957, 1741.

[7] I. L. Knunyants, M. P. Krasuskaya, and E. I. Mysov, *Izvest. Akad. Nauk S.S.S.R.*, 1960, 1412.

[8] R. N. Haszeldine and A. E. Tipping, in the press.

(C–F str.) at 9·26 μ (N–O str.), 10·32 μ (C–N str.), and 14·01 μ (CF_3 def.). Its 56·46 Mc./sec. ^{19}F n.m.r. spectrum shows two absorption systems at +0·86 p.p.m. (rel. to external $CF_3{\cdot}CO_2H$) and +1·55 p.p.m., of relative intensities 3·0 : 1·0, which are assigned to the fluorine nuclei of the CF_3 and CF_2 groups, respectively. The low-field absorption is a triplet (splitting = 7·7 c./sec.) with fairly broad components, the inner member being broader than the outer members (widths at half-height 2·0 and 1·4 c./sec., respectively). The absorption at 1·55 p.p.m. is a broadened septet (splitting = 7·7 c./sec.), the individual bands of which have widths at half-heights within the range 2·6—3·3 c./sec. The spectrum should be of the $A_6A_6'X_2X_2'$ type, and the comparatively simple form of the observed spectrum (approx. A_6X_2) means that J_{AX} or $J_{AX'}$, and $J_{XX'}$, and $J_{AA'}$ are very small; since $J_{FF} = 5{\cdot}2$ c./sec. for tristrifluoromethylhydroxylamine, the non-zero coupling constant is probably J_{AX}. The mass spectrum of perfluoro-[1,2-bis(dimethylnitroxy)-ethane] shows peaks at *m/e* values (assignments and relative abundances in parentheses) of 436 ($C_6F_{16}N_2O_2^+$, 3·2), 337 ($C_5F_{13}NO^+$, 5·4), 268 ($C_4F_{10}NO^+$, 5·3), 237 ($C_3F_9NO^+$, 1·3), 218 ($C_3F_8NO^+$, 1·2), 180 ($C_3F_6NO^+$, 8·3), 168 ($C_2F_6NO^+$, 0·5), 130 ($C_2F_4NO^+$, 7·3), 114 ($C_2F_4N^+$, 1·8), *69* (CF_3^+, *100·0*), 64 (CF_2N^+, 1·3), 47 (CFO^+, 2·8), 50 (CF_2^+, 2·8), 31 (CF^+, 0·8), and 30 (NO^+, 1·9).

(*f*) *With ethylene.* Bistrifluoromethylnitroxide (0·327 g., 1·946 mmoles) and ethylene (0·055 g., 1·946 mmoles), sealed in a 55-ml. Dreadnought ampoule, kept at room temperature for 18 hr., gave ethylene (0·027 g., 0·975 mmoles; 50% recovery) and 1,2-*bis*(NN-*bistrifluoromethylnitroxy*)-*ethane* (0·350 g., 0·962 mmoles; 99%) (Found: C, 20·1; H, 1·3; N, 7·7. $C_6H_4F_{12}N_2O_2$ requires C, 19·8; H, 1·1; N, 7·7%), b. p. 113·5°/757 mm. (Siwoloboff), n_D^{12} 1·2921.

The i.r. spectrum of 1,2-bis(*NN*-bistrifluoromethylnitroxy)ethane shows weak bands at 3·37, 3·44 (C–H str.), and 6·83 μ (C–H def.), very strong bands in the region 7·66—8·13 μ (C–F str.), and strong bands at 9·25 (N–O str.), 10·32 (C–N str.), and 14·10 μ (CF_3 def.). Its mass spectrum shows peaks at *m/e* values (relative abundances in parentheses) of 350 (<1), 334 (1·9), 322 (<1), 212 (1·1), 196 (36·6), 182 (24·4), 180 (3·7), 169 (1·6), 168 (4·8), 166 (3·7), 150 (5·9), 134 (1·9), 130 (2·6), 114 (3·8), 112 (6·5), 94 (17·2), 92 (2·3), 91 (1·6), 81 (1·7), 78 (3·5), 77 (3·7), 69 (81; CF_3^+), 65 (1·2), 51 (1·7), 50 (2·1), 47 (4·9), 45 (1·8), 44 (61·4), *43* (*100·0*; $CHNO^+$), 33 (1·4), 31 (3·4), 30 (16·3; NO^+), 27 (6·7), 15 (9·8). The 56·46 Mc./sec. ^{19}F n.m.r. spectrum of 1,2-bis(*NN*-bistrifluoromethylnitroxy)ethane consists of a fairly broad singlet (width at half-height 3 c./sec.) at 7·75 p.p.m. to low field of external $CF_3{\cdot}CO_2H$, while its 60 Mc./sec. ^1H spectrum consists of a sharp singlet at τ 5·71 (width at half-height *ca.* 1 c./sec.); these spectra are fully consistent with the proposed structure, the broadness of the ^{19}F resonance presumably being due to the presence of the ^{14}N quadrupolar nucleus.

(*g*) *With an ethylene–tetrafluoroethylene mixture.* Bistrifluoromethylnitroxide (0·225 g., 1·34 mmoles) was expanded into a 100-ml. Pyrex bulb containing an equimolar mixture of ethylene (0·019 g., 0·68 mmoles) and tetrafluoroethylene (0·067 g., 0·67 mmoles). Reaction, complete after 2 hr. (as indicated by pressure change), gave perfluoro-[1,2-bis(*NN*-dimethylnitroxy)ethane] (0·286 g., 0·65 mmole; 98% based on the nitroxide), 1,2-bis(*NN*-bistrifluoromethylnitroxy)ethane (<1% by g.l.c. analysis), ethylene (0·0188 g., 0·67 mmoles; 99% recovery), and traces of tetrafluoroethylene.

(*h*) *With hexafluoropropene.* Bistrifluoromethylnitroxide (0·50 g., 2·98 mmoles) and hexafluoropropene (0·23 g., 1·50 mmoles), sealed in a 40-ml. Pyrex tube, reacted completely during 15 min. at room temperature to give *perfluoro*-[1,2-*bis*(NN-*dimethylnitroxy*)*propane*] (0·715 g., 1·471 mmoles; 98%) (Found: C, 17·5; N, 6·1%; *M*, 491. $C_7F_{18}N_2O_2$ requires C, 17·3; N, 5·8%; *M*, 486), b. p. 100·5°/767 mm. (Siwoloboff), n_D^{14} 1·2737.

The i.r. spectrum of perfluoro-[1,2-bis(*NN*-dimethylnitroxy)propane] shows very strong bands at 7·56, 7·84, and 8·09 μ (C–F str.), and strong bands at 9·10 (N–O str.), 10·33 (C–N str.), and 14·00 μ (CF_3 def.). Its 56·46 Mc./sec. ^{19}F n.m.r. spectrum ($CF_3{\cdot}CO_2H$ as external ref.) shows four absorption systems of relative intensity 12 : 3 : 2 : 1 at *ca.* −8·6, +0·45, +9·35, and +59·2 p.p.m. The absorption system at the lowest field value consists of a rather broad doublet at −8·8 p.p.m. (widths at half-height *ca.* 2·2 c./sec.) and a 1 : 2 : 1 triplet (widths at half-height *ca.* 2·2 c./sec.) at −8·5 p.p.m. of approximately equal intensity and splittings of 9·9 and 7·9 c./sec., respectively. These bands are assigned to the fluorine nuclei of the two $(CF_3)_2N$ groups. The bands at +0·45, + 9·35, and +59·2 p.p.m. are assigned to the fluorine nuclei of the CF_3, CF_2, and CF groups, severally, which belong to the perfluoropropene residue. The mass spectrum of perfluoro-[1,2-bis(*NN*-dimethylnitroxy) propane] shows peaks at *m/e* values (assignments and relative abundances in parentheses) of 486 ($C_7F_{18}N_2O_2^+$, 0·7), 380 ($C_7F_{14}NO^+$, 1·1), 334 ($C_5F_{12}NO_2^+$, 0·1), 318 ($C_5F_{12}NO^+$, 2·3), 292 ($C_6F_{10}NO^+$, 0·2), 268 ($C_4F_{10}NO^+$, 0·1), 246 ($C_4F_8NO_2^+$, 0·1), 230 ($C_4F_8NO^+$, 3·9), 218 ($C_3F_8NO^+$, 0·5), 211 ($C_4F_7NO^+$, 0·2), 180 ($C_3F_6NO^+$, 1·7), 169 ($C_3F_7^+$, 0·2), 168 ($C_2F_6NO^+$, 2·9), 147 ($C_3F_5O^+$, 0·4), 131 ($C_3F_5^+$, 0·5), 130 ($C_2F_4NO^+$, 4·5), 119 ($C_2F_5^+$, 1·0), 114 ($C_2F_4N^+$, 0·4), 100 ($C_2F_4^+$, 0·6), 97 ($C_2F_3O^+$, 3·4), *69* (CF_3^+, *100·0*), 66 (CF_2O^+, 0·2), 64 (CF_2N^+, 0·6), 50 (CF_2^+, 1·2), 47 (CFO^+, 2·3), 31 (CF^+, 1·0), and 30 (NO^+, 1·6).

(*i*) *With hexafluorocyclobutene.* Bistrifluoromethylnitroxide (0·250 g., 1·488 mmoles) and hexafluorocyclobutene (0·240 g., 1·481 mmoles), sealed in a 20-ml. Dreadnought ampoule, were heated at 85° for 7 days. Fractionation of the product gave hexafluorocyclobutene (0·120 g., 0·741 mmoles; 50% recovery) and *perfluoro*-[1,2-*bis*(NN-*dimethylnitroxy*)*cyclobutane*] (0·360 g., 0·723 mmoles; 98%) (Found: C, 19·5; N, 5·6. $C_8F_{18}N_2O_2$ requires C, 19·3; N, 5·6%), b. p. 112°/762 mm. (Siwoloboff), n_D^{12} 1·2919.

The i.r. spectrum of perfluoro-[1,2-bis(*NN*-dimethylnitroxy)cyclobutane] contains very strong bands in the 7·58—8·50 μ region (C–F str.), and strong bands at 9·76 (N–O str.), 10·35 (C–N str.), and 14·03 μ (CF_3 def.). Its 56·46 Mc./sec. ^{19}F n.m.r. spectrum ($CF_3{\cdot}CO_2H$ as external ref.) shows three main poorly-resolved absorption systems at (relative intensities and assignments in parentheses) +0·95 p.p.m. (6·0, CF_3 groups), +5·61 p.p.m. (2·0, ring CF_2 groups), and +5·77 p.p.m. (1·0, ring CF groups). The mass spectrum of perfluoro-[1,2-bis(*NN*-dimethylnitroxy)-cyclobutane] shows peaks at *m/e* values (relative abundances in parentheses) of 479 (<1; parent-ion minus F), 415 (<1), 327 (<1), 315 (2·2), 277 (1·0), 246 (3·5), 230 (14·1), 218 (<1), 180 (<1), 178 (<1), 169 (<1), 168 (1·4), 162 (<1), 159 (1·7), 158 (1·0), 147 (1·3), 131 (<1), 130 (5·4), 128 (2·6), 119 (18·8), 114 (1·2), 109 (4·0), 100 (7·6), 97 (6·8), 93 (1·4), 85 (1·1), 83 (1·0), 78 (1·1), 75 (3·0), *69* (*100·0*; CF_3^+), 64 (1·0), 50 (2·4), 47 (15·2), 31 (1·0), 30 (1·2; NO^+).

(*j*) *With toluene.* Bistrifluoromethylnitroxide (0·50 g., 2·98 mmoles) and sodium-dried toluene (0·274 g., 2·98 mmoles) were condensed into a 50-ml. Pyrex tube at −196° *in vacuo*. The tube was sealed and left to warm up to room temperature, when a rapid reaction occurred, as indicated by the disappearance of the purple colour of the nitroxide, to give a product that was fractionated to provide bistrifluoromethylhydroxylamine (0·247 g., 1·461 mmoles; 98%), toluene (0·104 g., 1·130 mmoles; 38% recovery), and *O-benzyl-NN-bistrifluoromethylhydroxylamine* (0·284 g., 1·096 mmoles; 74%) (Found: C, 41·7; H, 2·9; N, 5·5. $C_9H_7F_6NO$ requires C, 41·7; H, 2·7; N, 5·4%), b. p. 138°/756 mm. (Siwoloboff), n_D^{12} 1·3977. A small amount (*ca.* 0·1 g.) of unidentified yellow oil was also formed.

The i.r. spectrum of *O*-benzyl-*NN*-bistrifluoromethylhydroxylamine shows C–H bands at 2·48 (v. weak aromatic combination band), 3·27—3·45 (weak unsymmetrical triplet; C–H str.), and 13·5 and 14·65 μ (strong; C–H out-of-plane def.), aromatic C⁚C str. bands at 6·31, 6·76, and 6·91 μ (m. to s.), very strong C–F str. bands in the region 7·68—8·5 μ, and strong bands at 9·25 (N–O str.), 10·38 (C–N str.), and 14·16—14·37 μ (triplet ?). The 60 Mc./sec. ^1H n.m.r. spectrum of the hydroxylamine consists of an aromatic proton resonance at τ 2·77 (integrated intensity 5) and a methylene band (singlet) at τ 5·12 (integrated intensity 2); its 56·46 Mc./sec. ^{19}F n.mr. spectrum shows a broad singlet (width at half-height *ca.* 2·3 c./sec.) at 9·03 p.p.m. to low field of external $CF_3{\cdot}CO_2H$. The mass spectrum of *O*-benzyl-*NN*-bistrifluoromethylhydroxylamine shows peaks at *m/e* values (relative abundances in parentheses) of 259 (<1; parent ion), 243 (<1), 224 (<1), 210 (<1), 169 (<1), 168 (<1), 121 (1·6), 119 (5·4), 117 (5·3), 115 (2·0), 114 (31·6), 113 (6·6), 112 (97·3), 105 (1·7), 92 (7·7), *91* (*100·0*; $C_6H_5CH_2^+$), 90 (1·3), 89 (1·9), 85 (2·1), 83 (1·9), 78 (5·6), 77 (75·2), 76 (5·1), 75 (6·9), 74 (6·7), 69 (18·8; CF_3^+), 65 (13·5), 63 (2·9), 62 (1·7), 56 (5·3), 52 (2·9), 51 (25·0), 50 (17·8), 49 (2·9), 47 (1·5), 39 (6·4), 38 (10·3), 37 (3·3), 32 (2·6).

Reactions between Nitroxyalkanes and Iron.—The compounds $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$, $(CF_3)_2N{\cdot}O{\cdot}CH_2Ph$, $(CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}O{\cdot}N(CF_3)_2$, and $(CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot}CF(CF_3){\cdot}O{\cdot}N(CF_3)_2$ were recovered in 96—97% yield after being heated separately with an excess of clean iron powder (*ca.* 0·4 g. of nitroxyalkane; *ca.* 5 g. of iron) in 20-ml. Pyrex ampoules at 210° for 3 hr.

Perfluoro-[1,2-bis(*NN*-dimethylnitroxy)cyclobutane] (0·556 g., 1·116 mmoles) and iron powder (5·0 g.), heated at 210° for 3 hr. in a 20-ml. Pyrex vial, gave perfluoro-(methylenemethylamine) (0·261 g.; 1·963 mmoles; 88%) contaminated by a small amount of trifluoromethyl isocyanate, and perfluorosuccinyl fluoride (0·2134 g., 1·100 mmoles; 98%). The last compound was shaken with 2N-aqueous sodium hydroxide (3 ml.) to give a solution from which di-(*S*-benzylthiouronium) perfluorosuccinate (0·30 g., 51%), m. p. and mixed m. p. 187°, was isolated by standard techniques.

We are indebted to Dr. M. G. Barlow of this Department for reports on the n.m.r. spectra. Acknowledgement is made to the Ministry of Aviation who partly supported this work.

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[5/1191 *Received, November 5th*, 1965]