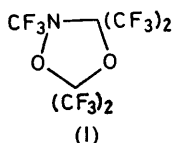


Perfluoroalkyl Derivatives of Nitrogen. Part 47.¹ Reaction of Trifluoronitrosomethane and Heptafluoro-1-nitrosopropane with Dimethyl- or Diphenyl-diazomethane: a Convenient Synthesis of Perfluorinated Azoxyalkanes²

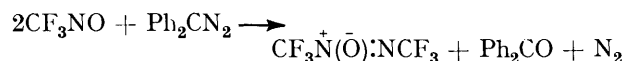
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Trifluoronitrosomethane and heptafluoro-1-nitrosopropane rapidly attack diphenyldiazomethane in diethyl ether at -78°C to yield, quantitatively, benzophenone and perfluoro-azoxymethane or -1,1'-azoxypropane respectively; an analogous reaction occurs between the former nitrosoalkane and dimethyldiazomethane. Use of an equimolar mixture of the nitrosoalkanes provides the azoxy-compounds $\text{CF}_3\ddot{\text{N}}(\ddot{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$ and $\text{n-C}_3\text{F}_7\ddot{\text{N}}(\ddot{\text{O}}):\text{NCF}_3$.

A RECENT brief report³ describes how treatment of trifluoronitrosomethane with bis(trifluoromethyl)diazomethane at 110°C for 24 h has enabled the first thermally stable 1,3,4-dioxazolidine (1) to be isolated; initial formation of hexafluoroacetone was suggested to occur *en route* to the dioxazolidine, apparently on the basis that addition of one molar proportion of this ketone to the reactants increased the yield of the heterocycle from 25 to 53%, but no mechanisms were formulated. Disclosure of these results prompts us to provide full details (*cf.* ref. 2) of an investigation, terminated more than 10 years ago,⁴ of reactions between lower perfluoronitrosoalkanes and dimethyl- or diphenyl-diazomethane.



Perfluoroazoxymethane and benzophenone can be isolated virtually quantitatively from the solution produced by passing trifluoronitrosomethane into cold (-120 to -78°C) diethyl ether containing diphenyldiazomethane [from the practical viewpoint (see Experimental section), di-*n*-butyl ether is the preferred solvent]. Even at -78°C , the nitroso-compound is consumed immediately, with concomitant evolution of nitrogen according to the equation:

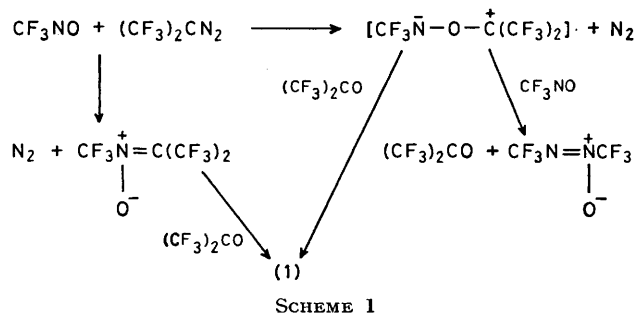


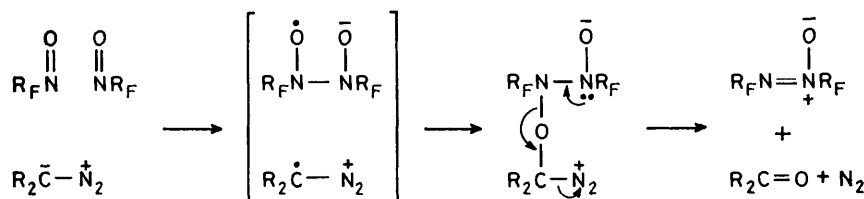
An analogous reaction occurs if dimethyldiazomethane is used instead of the diphenyl compound, and replacement of the nitrosoalkane by its higher homologue heptafluoro-1-nitrosopropane provides the corresponding azoxy-compound $\text{n-C}_3\text{F}_7\ddot{\text{N}}(\ddot{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$ and benzophenone in 97 and 99% yield, respectively. When an equimolar mixture of trifluoronitrosomethane and heptafluoro-1-nitrosopropane is passed into a solution of diphenyldiazomethane in di-*n*-butyl ether at -78°C , all four possible azoxyalkanes are obtained, *i.e.* $\text{CF}_3\ddot{\text{N}}(\ddot{\text{O}}):\text{NCF}_3$, $\text{CF}_3\ddot{\text{N}}(\ddot{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$, $\text{CF}_3\text{N}:\ddot{\text{N}}(\ddot{\text{O}})\text{C}_3\text{F}_7\text{-n}$, and $\text{n-C}_3\text{F}_7\ddot{\text{N}}(\ddot{\text{O}}):\text{NCF}_3$.

From a synthetic viewpoint, the conversion of tri-

fluoronitrosomethane and heptafluoro-1-nitrosopropane into the corresponding 'symmetrical' azoxyalkanes *via* treatment with diphenyldiazomethane is superior to methods employed previously;⁵⁻⁷ and the modification of this new method as described above seems to be the only route to the 'unsymmetrical' azoxyalkanes reported yet. Clearly, both versions of the reaction should be widely applicable to polyfluorinated nitrosoalkanes. No attempt was made to probe the mechanism of azoxyalkane formation, except that reaction of trifluoronitrosomethane with nitrones of the type $\text{Ar}\ddot{\text{N}}(\ddot{\text{O}}):\text{CXPh}$ ($\text{Ar} = \text{Ph}$, $\text{X} = \text{H}$ or Ph ; $\text{Ar} = \text{C}_6\text{F}_5$, $\text{X} = \text{Ph}$) in chloroform at 20 – 40°C was shown to occur only slowly (complete in 24 h) with formation of the corresponding carbonyl compounds PhCXO and fluorine-containing tars; in the case of *N*-phenylbenzylideneamine *N*-oxide, the only compound studied quantitatively, the yield of benzaldehyde was 86%. This militates against initial nitrene formation (von Pechmann–Staudinger reaction⁸) in the $\text{R}_F\text{NO-R}_2\text{CN}_2$ ($\text{R}_F = \text{CF}_3$ or $\text{n-C}_3\text{F}_7$; $\text{R}_2 = \text{Me}_2$ or Ph_2) reaction at, or below, -78°C .

Regarding formation of the 1,3,4-dioxazolidine (1) from trifluoronitrosomethane (b.p. -85°C) and bis(trifluoromethyl)diazomethane (b.p. 13°C) in the absence of solvent,³ formation of some hexafluoroacetone while both reactants were still in the liquid phase (presumably the autoclave used was loaded by a condensation technique), overtaken, as the temperature rose, by formation of the unknown nitrene $\text{CF}_3\ddot{\text{N}}(\ddot{\text{O}}):\text{C}(\text{CF}_3)_2$, followed by the occurrence of a 1,3-dipolar cycloaddition involving the ketone (see Scheme 1), seems plausible.





SCHEME 2

The production of hexafluoroacetone would result in concomitant generation of hexafluoroazoxymethane, not mentioned in the brief literature report.³ The fact that nitrone formation seems not to be involved in the cases of dimethyl- and diphenyl-diazomethane suggests the possibility of an electron-transfer mechanism (see Scheme 2) related to routes proposed⁹ for other low-temperature condensed-phase conversions of trifluoronitrosomethane.

EXPERIMENTAL

Reactions of Diphenyldiazomethane.—(a) *With trifluoronitrosomethane.* Diphenyldiazomethane (18.9 g, 0.0974 mol) was dissolved in diethyl ether (200 cm³) in a two-necked flask cooled to -78°C . The inlet tube to the flask led under the surface of the solution and was connected to a stainless steel cyclinder (20 cm³) containing trifluoronitrosomethane (*ca.* 0.2 mol) and equipped with a fine-control valve; the outlet from the flask was attached to a vacuum system *via* two traps cooled to -196°C . Initially, the apparatus was filled with dry nitrogen and the pressure was adjusted to 60 cmHg; this value was maintained during the experiment, the nitrogen evolved during the reaction being bled into a large (20 l) evacuated bulb connected to the exit from the last cold trap.

Trifluoronitrosomethane (19.0 g, 0.192 mol) was bubbled slowly through the cold (-78°C), deep red solution of diphenyldiazomethane in diethyl ether until it became colourless; this end-point coincided with cessation of the evolution of nitrogen (amount collected 2.66 g, 0.095 mol). Precise low-temperature distillation of the product recovered from the -196°C traps provided perfluoroazoxymethane (16.9 g, 0.0928 mol, 97%), b.p. $6.5\text{--}7.5^{\circ}\text{C}$ (lit.,⁵ 6.9°C) with the expected spectroscopic (i.r. and ¹⁹F n.m.r.¹⁰) parameters. Benzophenone (17.5 g, 0.0962 mol, 100%) was isolated from the distillation residue by standard techniques and identified in conventional ways (m.p., i.r. analysis, and conversion into its 2,4-dinitrophenylhydrazone derivative). Distillation of the product requires much less care if di-*n*-butyl ether is used as the solvent for the diphenyldiazomethane, and the yield of perfluoroazoxymethane is unaffected.

(b) *With heptafluoro-1-nitrosopropane.* Using the technique employed for trifluoronitrosomethane (see above), heptafluoro-1-nitrosopropane (16.5 g, 0.0829 mol) was passed rapidly into a cold (-78°C) solution of diphenyldiazomethane (8.1 g, 0.042 mol) in diethyl ether (200 cm³). Nitrogen (1.15 g, 0.0411 mol) was evolved, and distillation of the liquid product through a vacuum-jacketed Vigreux column (100 \times 1 cm), using di-*n*-butyl ether as a 'chaser', gave perfluoro-1,1'-azoxypropane (15.3 g, 0.0401 mol, 97%), b.p. $93.5\text{--}94.5^{\circ}\text{C}$ (lit.,⁶ 94.5°C), with the expected i.r. spectrum, and benzophenone (7.5 g, 0.041 mol, 99%).

(c) *With an equimolar mixture of trifluoronitrosomethane and heptafluoro-1-nitrosopropane.* A gaseous mixture of

trifluoronitrosomethane (8.6 g, 0.087 mol) and heptafluoro-1-nitrosopropane (17.3 g, 0.087 mol) was drawn (at a pressure of 60 cmHg) through a cold (-78°C) solution of diphenyldiazomethane (17.1 g, 0.088 mol) in di-*n*-butyl ether (100 cm³). Nitrogen (2.41 g, 0.0861 mol) was collected, and the condensable product was distilled through an adiabatic Vigreux column (70 \times 1 cm) to give materials with the following boiling ranges (analytical methods stated in parentheses; *M* values were determined by Regnault's method): (i) $6\text{--}9^{\circ}\text{C}$, 3.2 g [$\text{CF}_3\text{N}(\bar{\text{O}}):\text{NCF}_3$; g.l.c., i.r., *M*]; (ii) $9\text{--}52^{\circ}\text{C}$, 1.2 g [$\text{CF}_3\text{N}(\bar{\text{O}}):\text{NCF}_3 + \text{CF}_3\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n} + \text{CF}_3\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$; g.l.c., i.r.]; (iii) $52\text{--}60^{\circ}\text{C}$, 9.3 g [$\text{CF}_3\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n} + \text{CF}_3\text{N}(\bar{\text{O}}):\text{C}_3\text{F}_7$; g.l.c.]; (iv) $60\text{--}89^{\circ}\text{C}$, 2.5 g [$\text{CF}_3\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n} + \text{CF}_3\text{N}(\bar{\text{O}}):\text{C}_3\text{F}_7\text{-n} + \text{n-C}_3\text{F}_7\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$; g.l.c., i.r.]; and (v) $89\text{--}95^{\circ}\text{C}$, 9.1 g [$\text{n-C}_3\text{F}_7\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$; g.l.c., i.r., and *M*]. Fraction (iii) was redistilled through a Podbielniak column [15 \times 1 cm packed with Heli-pak Hastelloy B wire coils (0.05 \times 0.10 \times 0.10 in)] to give a constant-boiling ($58\text{--}58.5^{\circ}\text{C}$) fraction (5.1 g) which exhibited only a single i.r. absorption near $6.4\ \mu\text{m}$ [$\text{N}(\bar{\text{O}})=\text{N}$ str.] and was shown by g.l.c. (10 m ditrityl phthalate-Celite) and ¹⁹F n.m.r.¹⁰ analysis to be a 15:85 mixture of the isomers $\text{CF}_3\text{N}(\bar{\text{O}}):\text{NC}_3\text{F}_7\text{-n}$ and $\text{CF}_3\text{N}(\bar{\text{O}}):\text{C}_3\text{F}_7\text{-n}$.

Reaction of Dimethyldiazomethane with Trifluoronitrosomethane.—Trifluoronitrosomethane (8.7 g, 0.088 mol) was bubbled slowly through a cold (-95°C) solution of dimethyldiazomethane in diethyl ether [prepared from acetone hydrazone (8.0 g, 0.11 mol)] until the colour changed from red to pale blue (showing that an excess of the nitroso-compound had been added). Fractionation of the ether solution provided perfluoroazoxymethane (6.57 g, 0.0361 mol, 82%), identified by i.r. spectroscopy, and diethyl ether containing acetone (detected by g.l.c. and isolated as its 2,4-dinitrophenylhydrazone derivative).

Reaction of Trifluoronitrosomethane with N-phenylbenzylideneamine N-Oxide.—Trifluoronitrosomethane (1.12 g, 0.011 mol) was condensed into a cold (-196°C), evacuated, Carius tube (50 cm³) containing a solution of the nitrone (0.98 g, 0.005 mol) in chloroform (5 cm³). The tube was sealed and stored at 20°C for 24 h, after which time the blue colour caused by the nitroso-compound had disappeared. Vacuum distillation of the product afforded benzaldehyde (0.45 g, 0.0043 mol, 86%) and a viscid brown residue which slowly evolved trifluoronitrosomethane, carbon dioxide, and silicon tetrafluoride (all identified by i.r. spectroscopy) when stored in glass at room temperature.

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