

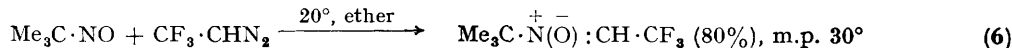
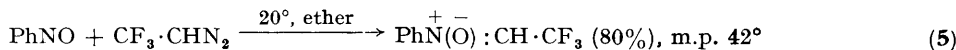
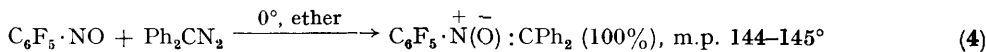
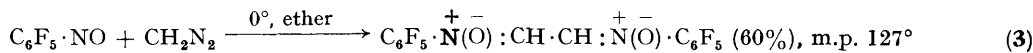
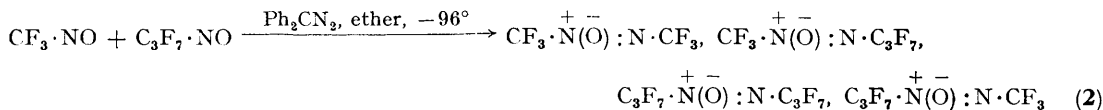
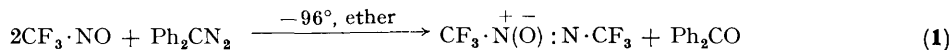
Fluoro-nitrones and Polymers Containing the $-N-O-C-$ Repeating Unit

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RAPID evolution of nitrogen occurs when trifluoronitrosomethane is passed into an ethereal solution of diazomethane at -96° or 2,2,2-trifluorodiazomethane at -72° , and the products, formed almost quantitatively, are polymers which are considered to have the structures $[-N(CF_3) \cdot O \cdot CH_2-]_n$ (I) and $[-N(CF_3) \cdot O \cdot CH(CF_3)-]_n$ (II), respectively. Both (I) and (II) are white resins of high molecular weight (softening points *ca.* 95° and *ca.* 120° , respectively), and appear to be the first polymers characterised by the $-N-O-C-$ backbone. The structure suggested for polymer (I), for which several plausible structures can be written, rests principally on the results of a detailed mass-spectrometric analysis; the structure of polymer (II) is suggested by analogy with the assignment for (I), and because both polymers have similar chemical properties. Russian workers have stated, in a review¹ published since our isolation of (I), that reaction of trifluoronitrosomethane with ethereal diazomethane at -70° yields an oligomeric nitrone, m.p. 95° , which they write as $[CF_3N(O)CH_2]_5$ (presumably they mean $[-N(O)(CF_3) \cdot CH_2-]_5$).

Polymer formation does not result from the reaction of trifluoronitrosomethane with diphenyldiazomethane, which occurs readily and quantitatively according to equation (1)



This reaction is general for perfluoronitrosoalkanes, and provides a convenient route to perfluoroazoxyalkanes; it can also be used to prepare perfluoroazoxyalkanes of the type $R_F \overset{+}{N}(\overset{-}{O}) : NR'_F$, *e.g.*, equation (2)

N-Perfluoroalkyl nitrones of the type $R_F \overset{+}{N}(\overset{-}{O}) : CPh_2$ may be transient intermediates in reactions between perfluoronitrosoalkanes and diphenyldiazomethane, since benzophenone is formed in good yields when the nitrones $Ph \overset{+}{N}(\overset{-}{O}) : CPh_2$ or $C_6F_5 \cdot \overset{+}{N}(\overset{-}{O}) : CPh_2$ are treated with trifluoronitrosomethane in chloroform solution at $20-40^\circ$, although only in the case of the reaction involving the last nitrone can the presence of an azoxy-compound be detected (i.r. spectroscopy) in the tarry product.

Fluoro-nitrones, hitherto unreported, are obtained in good yield either by the reaction of a fluoroaryl nitroso-compound with diazomethane or its derivatives, or by the reaction of an aryl- or alkyl-nitroso-compound with a fluoroalkyl diazo-compound, *e.g.*, equations (3-6)

Reaction of pentafluoronitrosobenzene with 2,2,2-trifluorodiazomethane in ethereal solution at 20° gives an unstable crystalline solid which may be the nitrone $C_6F_5 \cdot \overset{+}{N}(\overset{-}{O}) : CH \cdot CF_3$.

¹S. P. Makarov, V. A. Shpanskii, V. A. Ginsburg, A. I. Shechekotikhin, A. S. Filatov, L. L. Martynova, I. V. Pavlovskaya, A. F. Golovaneva, and A. Ya. Yakubovich, *Doklady Akad. Nauk S.S.S.R.*, 1962, **142**, 596.

The reaction of aryl nitroso-compounds with diazo-compounds to give nitrones has been known

for about seventy years,² but the formation of a polymer or of an azoxy-compound is novel.

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² J. Hamer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 473.