

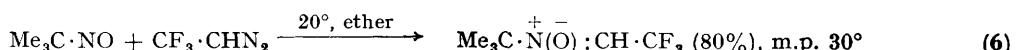
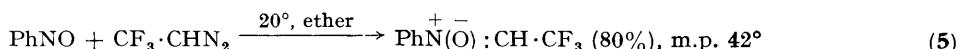
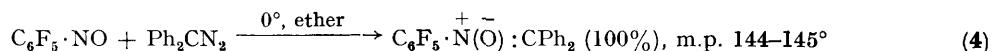
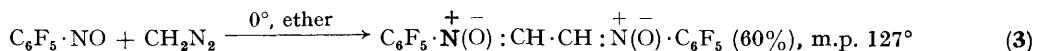
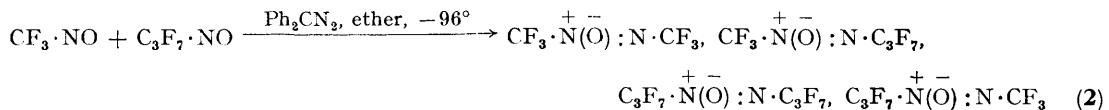
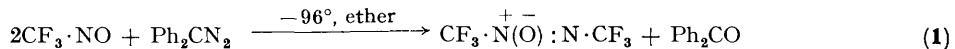
## Fluoro-nitrones and Polymers Containing the $-N-O-C-$ Repeating Unit

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RAPID evolution of nitrogen occurs when trifluoronoitrosomethane is passed into an ethereal solution of diazomethane at  $-96^\circ$  or 2,2,2-trifluorodiazooethane at  $-72^\circ$ , 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.*  $95^\circ$  and *ca.*  $120^\circ$ , 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 review<sup>1</sup> published since our isolation of (I), that reaction of trifluoronoitrosomethane with ethereal diazomethane at  $-70^\circ$  yields an oligomeric nitrone, m.p.  $95^\circ$ , 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 trifluoronoitrosomethane 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  $R_F^+ N(O) : NR'_F^-$ , e.g., equation (2)

N-Perfluoroalkyl nitrones of the type  $R_F^+ N(O) : CPh_2^-$  may be transient intermediates in reactions between perfluoronitrosoalkanes and diphenyldiazomethane, since benzophenone is formed in good yields when the nitrones  $PhN(O) : CPh_2^-$  or  $C_6F_5 \cdot N(O) : CPh_2^-$  are treated with trifluoronoitrosomethane 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 pentafluoronoitrosobenzene with 2,2,2-trifluorodiazooethane in ethereal solution at  $20^\circ$  gives an unstable crystalline solid which may be the nitrone  $C_6F_5 \cdot N(O) : CH \cdot CF_3$ .

<sup>1</sup> S. P. Makarov, V. A. Shpanskii, V. A. Ginsburg, A. I. Shchekotikhin, A. S. Filatov, L. L. Martynova, I. V. Pavlovskaya, A. F. Golovaneva, and A. Ya. Yakubovich, *Doklady Akad. Nauk 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,<sup>2</sup> but the formation of a polymer or of an azoxy-compound is novel.

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<sup>2</sup> J. Hamer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 473.