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

By R. E. BANKS, W. T. FLOWERS, R. N. HASZELDINE, and P. E. JACKSON
(*The Chemistry Department, Faculty of Technology, University of Manchester, Manchester*, 1)

RAPID evolution of nitrogen occurs when trifluoronitrosomethane is passed into an ethereal solution of diazomethane at −96° or 2,2,2-trifluorodiazoethane 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 review[1] 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 $[-\overset{+}{N}(O)\overset{-}{}(CF_3)\cdot CH_2-]_5$).

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 $R_F\overset{+}{N}(O)\overset{-}{}:NR'_F$, *e.g.*, equation (**2**)

N-Perfluoroalkyl nitrones of the type $R_F\overset{+}{N}(O)\overset{-}{}:CPh_2$ may be transient intermediates in reactions between perfluoronitrosoalkanes and diphenyldiazomethane, since benzophenone is formed in good yields when the nitrones $Ph\overset{+}{N}(O)\overset{-}{}:CPh_2$ or $C_6F_5\cdot\overset{+}{N}(O)\overset{-}{}:CPh_2$ are treated with trifluoronitrosomethane in chloroform solution at 20–40°, 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-trifluorodiazoethane in ethereal solution at 20° gives an unstable crystalline solid which may be the nitrone $C_6F_5\cdot\overset{+}{N}(O)\overset{-}{}:CH\cdot CF_3$.

$$2CF_3\cdot NO + Ph_2CN_2 \xrightarrow{-96°,\ \text{ether}} CF_3\cdot\overset{+}{N}(O)\overset{-}{}:N\cdot CF_3 + Ph_2CO \quad (1)$$

$$CF_3\cdot NO + C_3F_7\cdot NO \xrightarrow{Ph_2CN_2,\ \text{ether},\ -96°} CF_3\cdot\overset{+}{N}(O)\overset{-}{}:N\cdot CF_3,\ CF_3\cdot\overset{+}{N}(O)\overset{-}{}:N\cdot C_3F_7,$$
$$C_3F_7\cdot\overset{+}{N}(O)\overset{-}{}:N\cdot C_3F_7,\ C_3F_7\cdot\overset{+}{N}(O)\overset{-}{}:N\cdot CF_3 \quad (2)$$

$$C_6F_5\cdot NO + CH_2N_2 \xrightarrow{0°,\ \text{ether}} C_6F_5\cdot\overset{+}{N}(O)\overset{-}{}:CH\cdot CH:\overset{+}{N}(O)\overset{-}{}\cdot C_6F_5\ (60\%),\ \text{m.p. } 127° \quad (3)$$

$$C_6F_5\cdot NO + Ph_2CN_2 \xrightarrow{0°,\ \text{ether}} C_6F_5\cdot\overset{+}{N}(O)\overset{-}{}:CPh_2\ (100\%),\ \text{m.p. } 144\text{–}145° \quad (4)$$

$$PhNO + CF_3\cdot CHN_2 \xrightarrow{20°,\ \text{ether}} Ph\overset{+}{N}(O)\overset{-}{}:CH\cdot CF_3\ (80\%),\ \text{m.p. } 42° \quad (5)$$

$$Me_3C\cdot NO + CF_3\cdot CHN_2 \xrightarrow{20°,\ \text{ether}} Me_3C\cdot\overset{+}{N}(O)\overset{-}{}:CH\cdot CF_3\ (80\%),\ \text{m.p. } 30° \quad (6)$$

[1] 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.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.

(*Received, March 19th*, 1965.)

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