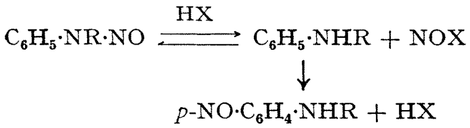
Rearrangement of *N*-Methyl-*N*-nitrosoaniline in the Presence of ^{15}N-Labelled Nitrite

By G. STEEL
(*Shell Research Limited, Thornton Research Centre, P.O. Box 1, Chester* CH1 3SH)
and D. L. H. WILLIAMS*
(*Chemistry Department, The University of Durham*)

Summary *p*-Nitroso-*N*-methylaniline obtained from the acid-catalysed rearrangement of *N*-methyl-*N*-nitrosoaniline in aqueous ethanol containing ^{15}N-labelled sodium nitrite showed no ^{15}N enrichment from the hydrochloric acid reaction and only very little when the acid was sulphuric acid.

THE Fischer–Hepp rearrangement of *N*-nitroso-amines has never been the subject of a detailed kinetic study. The assumption that the mechanism is intermolecular is based primarily on the observation[1] that hydrochloric acid is the most efficient catalyst and also on the occurrence of certain transnitrosation reactions. (For a review, see ref. 2). The mechanism is assumed to consist of a reversible denitrosation of the nitrosamine followed by the ring-nitrosation of the amine by NOX or by a species derived therefrom.



$$\begin{tikzcd} C_6H_5\cdot NR\cdot NO \arrow[r, shift left, "HX"] & C_6H_5\cdot NHR + NOX \arrow[l, shift left] \arrow[d] \\ & p\text{-}NO\cdot C_6H_4\cdot NHR + HX \end{tikzcd}$$

In order to test the intermolecularity of this rearrangement we have carried out the reaction with *N*-methyl-*N*-nitrosoaniline (in *ca.* 35% ethanol–water) in the presence of an equivalent amount of sodium nitrite (8% enriched in ^{15}N), (a) using *ca.* 3·5M-sulphuric acid and (b) using *ca.* 3·5M-hydrochloric acid. Reaction (a) was stopped after 6 hr. and reaction (b) after 12 hr. and a sample of *p*-nitroso-*N*-methylaniline extracted from an alkaline reaction mixture. The sample was separated from the excess of reactant by column chromatography. Both the reactant and the product were analysed for ^{15}N content by mass spectrometry but in the former case the parent ion peak was so low as to make intensity-ratio measurements unreliable. The results for *p*-nitroso-*N*-methylaniline are given in the Table.

Ratio of intensities of the peaks at m/e 136 *and* 137 *for samples of* p-*nitroso*-N-*methylaniline*

Sample	Ratios	Average ratios
Normal	0·085, 0·092, 0·082, 0·087, 0·083	0·086
Recovered from reaction (a)	0·098, 0·094, 0·097, 0·084, 0·083, 0·089, 0·103	0·093
Recovered from reaction (b)	0·087, 0·078, 0·085, 0·094, 0·087	0·086

The sample recovered from reaction (b) has a ratio representing exactly the natural abundance of ^{15}N (0·4%) whereas the ratio from reaction (a), if significantly different from the normal, corresponds to an abundance of *ca.* 0·7% *i.e.*

is equivalent to about 8% reaction proceeding by a completely intermolecular process.

It is hardly conceivable that a species NOX (NOCl or $NO{\cdot}OH_2^+$), should it become free during the rearrangement, would not exchange the ^{15}N label with the added nitrite (see ref. 3) at a rate far in excess of the rate of rearrangement. The nitroso-group does not then become detached from the ring either as NOCl or $NO{\cdot}OH_2^+$ as is required by the accepted intermolecular mechanism, and so it appears that the rearrangement takes place intramolecularly or, conceivably, by nitrosation of one molecule by another. Recently Russian workers[4] have found that the rearrangement takes place in sulphuric acid even in the presence of a large excess of urea (which would remove any free nitrous acid) and concluded that there must be an intramolecular pathway to the *p*-nitroso-isomer. The rearrangement is then similar to the acid-catalysed rearrangement of *N*-nitroanilines[5] rather than to the Orton rearrangement of *N*-chloroacetanilides where the intermolecularity has been demonstrated[6] by radiochlorine labelling. A detailed kinetic study of the rearrangement of *N*-nitrosoanilines is under way. It is hoped to establish the mechanism firmly.

(*Received, July 1st*, 1969; *Com.* 957.)

---

[1] P. W. Neber and H. Rauscher, *Annalen*, 1942, **550**, 182.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1953, p. 613; H. J. Shine, "Aromatic Rearrangements," Elsevier, 1967, p. 231.

[3] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

[4] T. I. Aslapovskaya, E. I. Belyaev, V. P. Kumarev, and B. A. Porai-Koshits, *Reakts. spos. org. Soedinenii*, 1968, **5**, 456.

[5] D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *J. Chem. Soc.*, 1964, 5349.

[6] A. R. Olson, R. S. Halford, and J. C. Hornel, *J. Amer. Chem. Soc.*, 1937, **59**, 1613.