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A NOVEL REACTION OF NITROSOBENZENE WITH BENZYLAMINE

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Nitrosobenzene has been reported to react readily with compounds containing a sufficiently activated methylene (1) or methyl (2) group and with aromatic amines (3). Photolysis of nitrosobenzene itself has led chiefly to azoxybenzene plus several other minor products (4). However, no references concerning its reaction with aliphatic amines have been found. It is the purpose of this communication to describe experiments which have a bearing on this issue.

Treating nitrosobenzene with benzylamine in benzene solution yielded benzaldehyde (76%), ammonia (59%) and azoxybenzene (57%) as the major products. Under identical conditions, α-methylbenzylamine and nitrosobenzene afforded 59% of ammonia, 54% of acetophenone, and 38% of azoxybenzene. The following sequence of steps has been proposed for the reaction:

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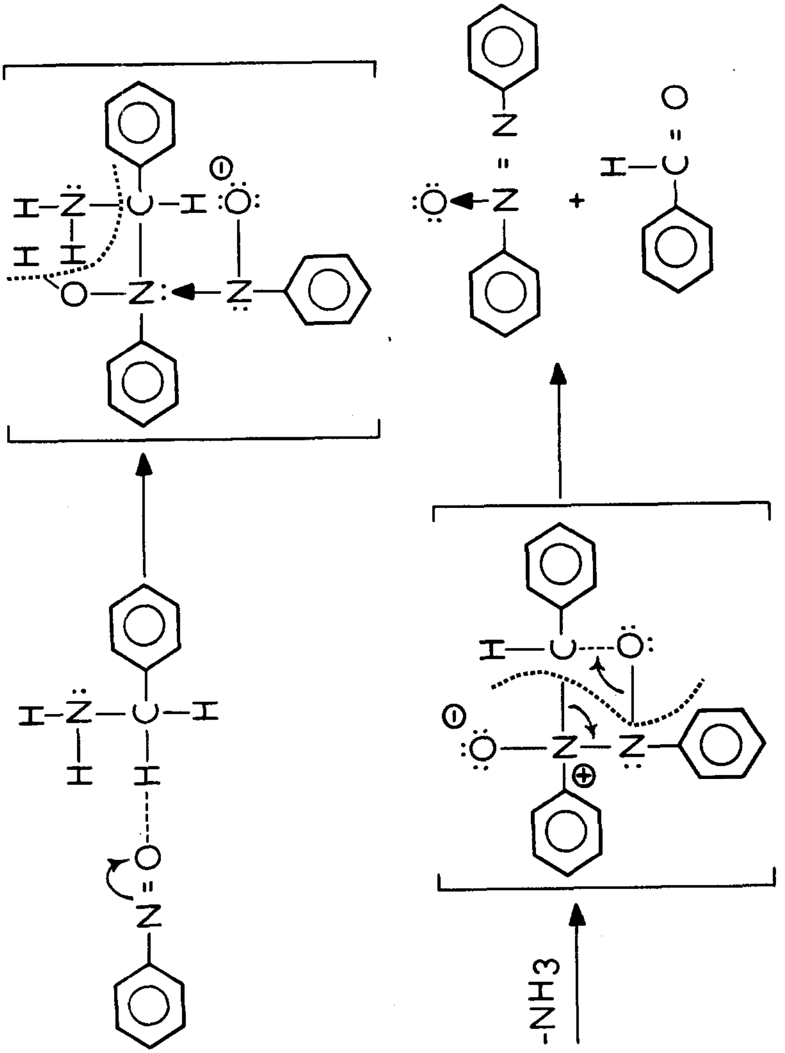
-NH3

As a first step, the abstraction of a hydrogen atom from the methylene group by the negatively charged oxygen atom in nitrosobenzene is relatively easy due to the neighboring aromatic ring participation. Ammonia and benzaldehyde are formed during the attack of the second nitrosobenzene molecule. Relief of strain in the system leads to azoxybenzene.

This is a new reaction involving the formation and cleavage of a carbon-nitrogen single bond between nitrosobenzene and benzylamine. Under the same conditions nitrosobenzene did not react appreciably with a primary aliphatic amine, such as n-propylamine.

In a typical run nitrosobenzene (100 mM) in benzene was refluxed gently for 12 hr. with benzylamine (50 mM). The ammonia gas formed was carried over in a gentle stream of nitrogen and absorbed in hydrochloric acid to yield 25 mM of ammonium chloride.

A portion of the reaction mixture was treated with 2,4-dinitrophenylhydrazine to yield benzaldehyde 2,4-dinitrophenylhydrazone, corresponding to 32 mM of benzaldehyde overall.

From the remainder of the reaction mixture benzylamine (8.1 mM) was recovered by extraction into dilute hydrochloric acid. Chromatography of the residual benzene solution on alumina followed by elution with benzene furnished 28.3 mM of azoxybenzene. A small amount (1.5 g) of an unidentified oily material was also recovered.

When chloroform was used as solvent in place of benzene, benzaldehyde (39%), ammonia (38%), azoxybenzene (65.2%), benzylamine hydrochloride (8%), sym-dibenzylurea (5) (1.5%, m.p. 167°C) and a brown oil were isolated as reaction products, while benzylamine (38%) was recovered.

All identifications were confirmed by elemental analyses, IR and UV spectra, or mixture melting points with authentic compounds.

It thus appears that nitrosobenzene acts as an oxidizing agent for arylalkylamines.

References

1. H. Nohira, K. Sato and T. Mukaiyama. *Bull. Chem. Soc. (Jap.)*. **36**, 870 (1963).
2. J. Hamer and A. Macoluso. *Chem. Rev*. **64**, 480 (1964).
3. G. E. Lewis and M. A. G. Osman. *Aust. J. Chem*. **17**, 498 (1964).
4. M. Shamma, J. K. Whitesell and P. L. Warner, Jr. *Tetrahedron Letters* ***No. 43***, 3869 (1965).
5. T. L. Davis and K. C. Blanchard. *J. Amer. Chem. Soc*. **45**, 1819 (1923).