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A NOVEL OXIDATION REACTION[*]

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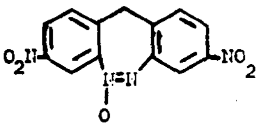
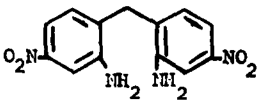
Payne and co-workers[1] have reported the oxidation of aniline to azoxybenzene, as the sole product,[2] in 62% yield by use of an excess of 50% hydrogen peroxide with acetonitrile as a coreactant in methanol at a pH of 8. In connection with other work that is being carried out in this laboratory, we wished to prepare the diazepine oxide I and felt that Payne's oxidation method[1] with 2,2'-diamino-4,4'-dinitrodiphenylmethane (II) would be a convenient route to I



I



II

We have found, however, that when II is oxidized, as described by Payne,[1] with 50% hydrogen peroxide and acetonitrile in methanol at pH 8

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[1] G.B. Payne, P.H. Deming and P.H. Williams, J. Org. Chem., 26, 659 (1961).

[2] Use of peroxyacetic acid gives a mixture of nitrobenzene and azoxybenzene: F.P. Greenspan, Ind. Eng. Chem., 39, 847 (1947).

and the excess hydrogen peroxide destroyed in 48 hours in the cold with palladium on charcoal, m-dinitrobenzene[3] is obtained in 67% yield. If the excess of hydrogen peroxide is destroyed over one hour, m-dinitrobenzene[3] and m-nitroaniline[3] are obtained in 50% and 11% yield respectively. When 30% hydrogen peroxide is used, m-nitroaniline[3] is obtained in 50% yield. In a few cases 3,3'-dinitroazoxybenzene[3] was also obtained depending upon the experimental conditions. Similar results were obtained using acetone or ethanol as the solvent. Absence of the acetonitrile resulted only in the recovery of starting material (II). Use of a smaller quantity of 50% hydrogen peroxide (0.1 mole per 0.005 mole of II as compared to 0.6 mole per 0.005 mole of II normally used) resulted in the recovery of II.

Reaction of m-nitroaniline with 50% hydrogen peroxide and acetonitrile at pH 8 gave a 60% yield of 3,3'-dinitroazoxybenzene,[3] while reaction of 3,3'-dinitroazoxybenzene in a similar manner led to its quantitative recovery thus arguing against one of these compounds being an intermediate in the formation of the m-dinitrobenzene. Preliminary experiments indicate that the isomeric 2,2'-dinitro-4,4'-diaminodiphenylmethane does not yield the above products when subjected to this reaction indicating that perhaps the formation of a compound such as I might be necessary for the reaction.

Other related compounds and possible intermediates as well as other reaction conditions are now under study to determine the scope and the mechanism of this reaction.

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[3] Correct m.p. and analysis; no depression on mixed m.p. with an authentic sample; and infrared spectra identical with authentic sample.