

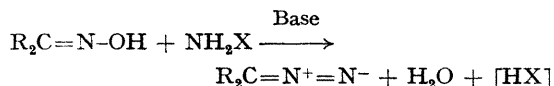
## Phenyl Azide from the Reaction of Nitrosobenzene with Hydroxylamine-*O*-sulphonic Acid

By J.-P. ANSELME\* and N. KOGA

(Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02116)

**Summary** Under the conditions of the Forster reaction, nitrosobenzene gives phenyl azide, presumably *via* the intermediate diazonium salt.

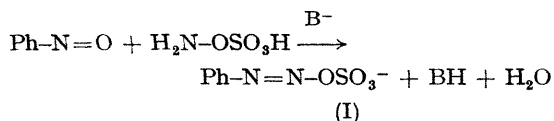
THE base-catalysed conversion of  $\alpha$ -ketoximes into  $\alpha$ -diazo-ketones by means of chloramine reported by Forster in 1915<sup>1</sup> has been shown by Meinwald, Gassman, and Miller<sup>2</sup> to be a general reaction of oximes. The failure of *p*-benzoquinone oxime<sup>1</sup> to undergo the Forster reaction was explained



by the assumption that it existed entirely as the nitroso-tautomer (*p*-nitrosophenol) under the reaction conditions.†

As part of our interest in the Forster reaction, we investigated the reaction of nitrosobenzene with hydroxylamine-*O*-sulphonic acid. Treatment of tetrahydrofuran solution of nitrosobenzene containing 4 equiv. of sodium methoxide (in methanol) with hydroxylamine-*O*-sulphonic acid (4 equiv.) at room temperature gave a 25% yield of a straw-coloured liquid, b.p. 28–29°/1 mm. It was identified as phenyl azide by its b.p. and by comparison of its i.r. spectrum with that of an authentic sample; this was further confirmed by the formation of *N*-phenyltriphenylphosphinimine, m.p. 131–132°, identical in all respects with an authentic sample.‡

The first step of the reaction may be viewed as a condensation of the nitroso-group with hydroxylamine-*O*-sulphonic acid to give the salt of the mixed anhydride (I) of benzenediazoic acid and of sulphuric acid.



† This view received apparent confirmation from Forster's failure to isolate the diazonium salt from the reaction of nitrosobenzene with chloramine (ref. 1).

‡ Phenyl azide is also formed in comparable yield with aqueous sodium hydroxide as the base. It could also be detected (by i.r.), in very small quantities, when nitrosobenzene was treated with chloramine, generated *in situ* from 5% sodium hypochlorite and ammonium hydroxide.

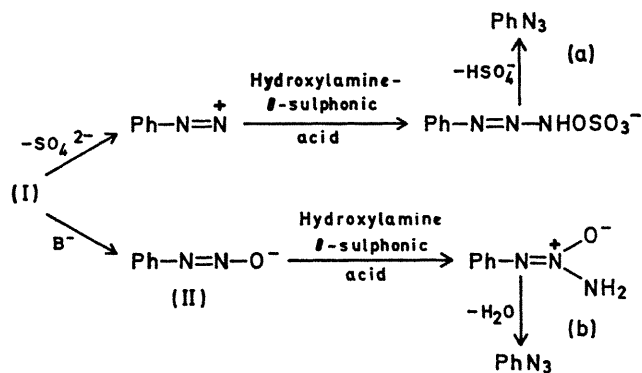
<sup>1</sup> M. O. Forster, *J. Chem. Soc.*, 1915, 107, 260.

<sup>2</sup> J. Meinwald, P. G. Gassman, and E. G. Miller, *J. Amer. Chem. Soc.*, 1959, 81, 4751.

<sup>3</sup> H. Bretschneider and H. Rager, *Monatsh.*, 1950, 81, 970; Forster (ref. 1) reported the formation of phenyl azide (24% of crude product) and of *p*-nitrophenyl azide (25%) from the reaction of the corresponding diazonium salts with chloramine in basic solution.

<sup>4</sup> A. Key and P. K. Dutt, *J. Chem. Soc.*, 1928, 2035.

The conversion of (I) into phenyl azide by hydroxylamine-*O*-sulphonic acid may proceed *via* the diazonium ion [path (a)] or the diazotate ion [path (b)]. Route (a) is reminiscent



of the reaction of diazonium salts with toluene-*p*-sulphonamide<sup>3</sup> to give the tosyl-triazenes which can be isolated. These triazenes are very prone to fragmentation to the azide and toluene-*p*-sulphonic acid.<sup>3,4</sup> Since diazoic acids (PhN=NOH) can be formally considered as the "aza" analogue of oximes, path (b) is similar to the Meinwald, Gassman, and Miller mechanism<sup>2</sup> of the Forster reaction.

Our results explain the failure of Forster to obtain the expected product from nitrosobenzene and make it likely that under the proper conditions, quinone oximes can be converted into diazo-oxides.

The partial support of this work by the Alfred P. Sloan Foundation is acknowledged.

(Received, January 29th, 1970; Com. 134.)