# **162.** *Replacement of the Diazonium by the Azido Group in Acid Solution.*

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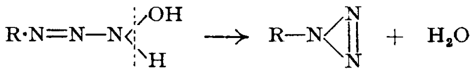
A rapid method is described for obtaining steam-volatile aryl azides in excellent yields from aryldiazonium sulphates by reaction with hydroxylamine sulphate in sulphuric-acetic acid medium.

ARYL azides had been prepared in major yield by the action of ammonia on aryldiazonium perbromides (Griess, *Annalen*, 1866, **137**, 81), and also by reaction of aryldiazonium salts with hydroxylamine (Mai, *Ber.*, 1892, **25**, 373; 1893, **26**, 1271; cf. also Forster and Fierz, *J.*, 1907, **91**, 1350). Both processes involve an alkaline medium, and, in the latter case, the course of the reaction varies according to the procedure (Mai, *loc. cit.*), for when the solution of the diazonium salt is added to the alkaline hydroxylamine, high yields of the parent amine can be recovered, whereas if the diazonium solution is first mixed with the hydroxylamine salt and then made alkaline, the aryl azide (azoimide) becomes the chief product. The mechanism of the process would appear to be a type of Lossen reaction in which the stages are: the initial formation of a diazoamino-compound with the hydroxylamine, subsequent fission of water, and rearrangement of the residue to the azide:



A rapid method is now described for the preparation of aryl azides in excellent yield by treatment of aryldiazonium sulphates in sulphuric–glacial acetic acid medium (Hodgson and Walker, *J.*, 1933, 1620) with excess of hydroxylamine sulphate, followed by steam-distillation, whereupon the relevant azide (if steam-volatile) passes over. By this means yields exceeding 70% of *m*-nitrophenyl azide have been obtained from *m*-nitroaniline, and β-azidonaphthalene (β-naphthyl azoimide), stated by Forster and Fierz (*J.*, 1907, **91**, 1942) to have been successfully prepared by them only by the direct action of diazotised β-naphthylamine on hydrazoic acid, was also isolated. Similarly, azides have also been prepared from *o*- and *p*-nitroaniline, *p*-chloroaniline, *p*-nitro-*o*-toluidine, *o*- and *m*-nitro-*p*-toluidine, α-naphthylamine, and *m*- and *p*-phenylenediamine.

## EXPERIMENTAL.

*General procedure.* A solution of the amine (0·02 g.-mol.) in glacial acetic acid (25 c.c.) is stirred into one of sodium nitrite (1·5 g.) in sulphuric acid (10 c.c., *d* 1·84) at 0°, the mixture kept at room temperature for 30 minutes to ensure complete diazotisation, and then poured on finely powdered hydroxylamine sulphate (15 g.) contained in a flask fitted for steam-distillation; after vigorous shaking to secure admixture, steam is passed through, and the aryl azide distils over. A by-product may be the corresponding phenol, which, when volatile in steam, may contaminate the azide, but is readily removed from it by digestion with cold dilute alkali. Most of the phenol formed, however, appears to react with unchanged diazo-compound to produce more complex non-steam volatile products; *e.g.*, only traces of *o*-nitrophenol passed over with the *o*-nitroazidobenzene.

*Examples.* *o*-Nitroazidobenzene (1·0 g., 31% yield) from *o*-nitroaniline (2·76 g.), crystallised from light petroleum in pale yellow, almost colourless needles, m. p. 52° (Noelting, Grandmougin, and Michael, *Ber.*, 1892, **25**, 3338, give m. p. 51—52°) (Found: N, 34·2. Calc. for $C_6H_4O_2N_4$: N, 34·1%). *m*-Nitroazidobenzene (5·2 g., 71% yield) from *m*-nitroaniline (5·5 g.), crystallised from light petroleum in almost colourless needles, m. p. 56° (Noelting *et al.*, *loc. cit.*, give m. p. 55°) (Found: N, 34·3. Calc. for $C_6H_4O_2N_4$: N, 34·1%). *p*-Nitroazidobenzene (1·5 g., 44·5% yield) from *p*-nitroaniline (2·76 g.) crystallised from light petroleum in yellow needles, m. p. 74° (Noelting *et al.*, *loc. cit.*, give m. p. 74°) (Found: N, 34·3%). *o*-Nitro-*p*-azidotoluene (2·5 g., 70%) from *o*-nitro-*p*-toluidine (3 g.) crystallised from light petroleum in very pale almost colourless needles, m. p. 70° (Noelting *et al.*, *loc. cit.*, give m. p. 69—70°) (Found: N, 31·6. Calc. for $C_7H_6O_2N_4$: N, 31·4%). *m*-Nitro-*p*-azidotoluene (1·9 g., 53%) from *m*-nitro-*p*-toluidine (3 g.) crystallised from light petroleum in pale yellow needles, m. p. 36° (Zincke and Schwarz, *Annalen*, 1899, **307**, 41, give m. p. 35°) (Found: N, 31·5%). *p*-Nitro-*o*-azidotoluene (2·0 g., 50%) from *p*-nitro-*o*-toluidine (3·0 g.), crystallised from light petroleum in needles, m. p. 69° (Noelting *et al.*, *loc. cit.*, give m. p. 68°) (Found: N, 31·6%). *p*-Chloroazidobenzene was obtained from *p*-chloroaniline and had the properties described by Griess (*Jahresber.*, 1866, 453) and Forster (*J.*, 1906, **89**, 236), *viz.*, easy fusibility and m. p. 20°. *m*-Diazidobenzene (small yield) was steam-distilled over as an oil which solidified at 0° in pale yellow needles, m. p. *ca.* 5° (Forster and Fierz, *J.*, 1907, **91**, 1953, give m. p. *ca.* 5°) (Found: N, 52·7. Calc. for $C_6H_4N_6$: N, 52·5%). *p*-Diazidobenzene (small yield), crystallised in bright yellow crystals from ether, m. p. 83° (Griess, *Ber.*, 1888, **21**, 1560, gives m. p. 83°) (Found: N, 52·6%). α-Azidonaphthalene steam-distilled over as a pale yellow oil which solidified to a crystalline mass, m. p. *ca.* 12° (Forster and Fierz, *loc. cit.*, give m. p. 12°). β-Azidonaphthalene passed over very slowly in steam, and the small amount obtained crystallised from light petroleum in needles, m. p. 33° (Forster and Fierz, *loc. cit.*, give m. p. 33°) (Found : N, 25·1. Calc. for $C_{10}H_7N_3$ : N, 24·8%).

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