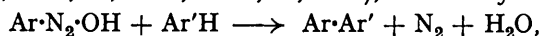


242. Union of Aryl Nuclei. Part V. A Modification of the Gomberg Reaction.

By J. ELKS, J. W. HAWORTH, and D. H. HEY.

The addition of aqueous sodium acetate in place of aqueous sodium hydroxide to a mixture of diazotised *o*-, *m*-, or *p*-nitroaniline and benzene results in an increase in the yield of the nitrodiphenyl from 21, 18, and 26% to 45, 45, and 60% respectively. A less marked increase in the yield of biaryl is also found with diazotised *o*-chloroaniline and diazotised β -naphthylamine, but with a number of other diazotised amines the yields are less satisfactory when sodium acetate replaces sodium hydroxide.

THE method for the union of aryl nuclei introduced by Gomberg and his co-workers (*J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372), which may be represented thus,



is carried out (*a*) by adding an aqueous diazotised amine to a cold well-stirred mixture of the second component Ar'H (a neutral aromatic liquid immiscible with water) and sufficient aqueous sodium hydroxide to make the mixture alkaline on completion of the addition, or (*b*) by adding slowly the appropriate quantity of aqueous sodium hydroxide to the stirred mixture of the aqueous diazonium solution and the second component. Grieve and Hey (*J.*, 1938, 108) attempted to improve the yields obtained in this reaction by introducing variations in the experimental procedure, using diazotised aniline and benzene, but in no case was any marked improvement noted. One of the modifications thus attempted was the substitution of aqueous sodium acetate for aqueous sodium hydroxide in the process (*b*) of Gomberg, but the result was a decrease in the yield of diphenyl from 24 to 5%.

It is now found that in the reaction with the nitroanilines the replacement of sodium hydroxide by sodium acetate, coupled with an extension of the time of the reaction, results in a very marked increase in the yield of the nitrodiphenyl. Comparative experiments with various diazotised amines and benzene in presence of aqueous sodium hydroxide on the one hand and aqueous sodium acetate on the other showed that, although in the cases of all three nitroanilines the yield of the nitrodiphenyl was more than doubled in the sodium acetate modification, when other bases were used, with the sole exceptions of *o*-chloroaniline and β -naphthylamine, the yields of biaryls were inferior to those normally obtained by Gomberg's original method.

Using diazotised β -naphthylamine with nitrobenzene in place of benzene, Dr. S. E.

The 4-nitrodiphenyl, which separated in fairly pure form on removal of the benzene, did not require distillation before crystallisation. The 2-phenylnaphthalene was isolated by distillation with superheated steam.

Action of Diazotised β -Naphthylamine on Nitrobenzene (with S. E. LAWTON).—The product from the reaction between diazotised β -naphthylamine ($\frac{1}{2}$ mol.) and nitrobenzene (1000 c.c.) in presence of aqueous sodium acetate (160 g. of trihydrate in 300 c.c.), carried out as in the preceding examples, was subjected to distillation with steam to remove the excess of nitrobenzene and the residue was distilled with superheated steam. The 2'-nitro-2-phenylnaphthalene (18 g.) was collected as a red solid, which after repeated crystallisation from glacial acetic acid (with charcoal) was obtained in yellow needles, m. p. 101°. The tarry non-volatile residue gave 4'-nitro-2-phenylnaphthalene (32 g.), which after purification by sublimation in a vacuum separated from glacial acetic acid in red needles, m. p. 174° (cf. Hey and Lawton, *loc. cit.*).

THE UNIVERSITY, MANCHESTER.
ROYAL COLLEGE OF SCIENCE, LONDON, S.W. 7.

[Received, July 10th, 1940.]
