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,

$$\mathrm{Ar{\cdot}N_2{\cdot}OH + Ar'H \longrightarrow Ar{\cdot}Ar' + N_2 + H_2O},$$

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.

Lawton found that a mixture of 2′- and 4′-nitro-2-phenylnaphthalene could be obtained in a total yield of 40% by the sodium acetate method. The former isomeride was readily separated from the latter, since it was volatile in superheated steam (cf. Hey and Lawton, this vol., p. 374).

In the processes (*a*) and (*b*) referred to above, one entails an alkaline medium throughout, whereas in the other complete alkalinity is developed only towards the close of the reaction. The former method was described as being more suited to amines such as aniline and the toluidines and the latter more suited to the halogeno- and nitro-anilines. In the examples now studied it will be noted that, in general, it is with the amines of the latter type, which might be expected to yield relatively strong diazoic acids, that the sodium acetate modification works best. This is in conformity with the views put forward by Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1373) with regard to the mechanism of the reaction. The improvement in yield shown in the reaction with β-naphthylamine, however, is somewhat unexpected.

Subsequent to the completion of this work, Hodgson and Marsden (this vol., p. 208) reported improved yields in the preparation of biaryl derivatives from the action of stabilised diazonium salts on benzene and nitrobenzene. In particular they record that yields up to 70% can be obtained when the stabilised diazonium salt is used in presence of sodium acetate and either glacial acetic acid or acetic anhydride. This process is closely allied to the sodium acetate modification of the Gomberg reaction now reported and it is significant that the highest yields recorded by Hodgson and Marsden were obtained with the nitroanilines, particularly the *p*-isomeride. The remarkable facility with which derivatives of the nitroanilines can be converted into nitrodiphenyls has also been demonstrated by France, Heilbron, and Hey (this vol., p. 369), who obtained 2-, 3-, and 4-nitrodiphenyl in yields of 60, 64, and 60% from *o*-, *m*-, and *p*-nitronitrosoacetanilide respectively and benzene. It seems probable that the reactive agent common to all these reactions is the acetyl derivative of the diazohydroxide (I), which can be in tautomeric equilibrium both with the diazonium acetate (II) and with the nitrosoacetylarylamine (III), thus:

$$\begin{tikzcd}
\mathrm{Ar{\cdot}N{\vdots}N\}Cl + CH_3{\cdot}CO_2Na} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Ar{\cdot}N{\vdots}N\}O{\cdot}CO{\cdot}CH_3 + NaCl} \arrow[d, phantom, "\upharpoonleft\downharpoonright", "\text{(II.)}"'] \\
\text{(III.)}\ \mathrm{Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Ar{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}CH_3}\ \text{(I.)}
\end{tikzcd}$$

EXPERIMENTAL.

The amine (½ mol.) in presence of hydrochloric acid (*d* 1·16, 160 c.c.) and water (90 c.c.) was diazotised in the normal manner with aqueous sodium nitrite. The filtered diazonium solution was divided into two equal parts and each was added to benzene (500 c.c.) vigorously stirred at 5—10°. To the one mixture aqueous sodium hydroxide (30 g. in 150 c.c.) was gradually added, whereas into the second a solution of sodium acetate (80 g. of trihydrate) in water (200 c.c.) was dropped. Stirring was continued for 48 hours, the reaction being allowed to proceed at room temperature after the first 3 hours. The benzene layers were then separated, washed with water, and distilled. After removal of the excess of benzene the product was collected under reduced pressure, except where otherwise stated. The results obtained are shown in the following table:

				Yield with NaOH.		Yield with NaOAc.	
Amine.	Product.	M. p.	Collected at	Wt., g.	%.	Wt., g.	%.
Aniline	Diphenyl	70°*	160—170°/30—40 mm.	8·5	22	6·0	16
o-Nitroaniline	2-Nitrodiphenyl	37 §	185—195 /20—30 mm.	10·5	21	22·5	45
m-Nitroaniline	3-Nitrodiphenyl	61 §	190—210 /20—30 mm.	9·0	18	22·5	45
p-Nitroaniline	4-Nitrodiphenyl	113 *	—	13·0	26	30·0	60
o-Chloroaniline	2-Chlorodiphenyl	34 †	150—155 /10 mm.	12·0	25	18·0	38
m-Chloroaniline	3-Chlorodiphenyl	—	150—160 /6 mm.	12·0	25	6·0	13
p-Chloroaniline	4-Chlorodiphenyl	77 *	180—195 /20—30 mm.	19·0	40	16·5	35
p-Bromoaniline	4-Bromodiphenyl	90 *	170—175 /8 mm.	25·0	44	7·0	12
p-Toluidine	4-Methyldiphenyl	46 *	175—185 /20—30 mm.	9·0	22	4·5	11
p-Anisidine	4-Methoxydiphenyl	89 *	170—190 /20—30 mm.	11·5	25	2·0	4
p-Phenetidine	4-Ethoxydiphenyl	72 *	170—175 /10—15 mm.	14·5	29	5·5	11
β-Naphthylamine	2-Phenylnaphthalene	101 *	—	8·0	16	13·0	25

* From ethyl alcohol. † From aqueous ethyl alcohol. § From light petroleum (b. p. 40—60°).

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.*).

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