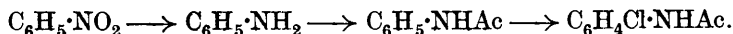


XII.—A New Method of reducing Aromatic Nitro-compounds.

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As anhydrous stannous chloride is now readily accessible (Stephen, J., 1930, 2786), its use for the reduction of aromatic nitro-compounds under anhydrous conditions has been investigated. The process to be described provides a simple means of reducing the nitro-compound, acetylating the base, and in many cases chlorinating the resulting anilide *in situ*; for instance,



All observations indicate that monochlorination takes place in the para-position to the original nitro-group. In *p*-substituted nitro-compounds no chlorination takes place except in the case of *p*-chloronitrobenzene which, only if hydrogen chloride is present during the reduction, gives 2 : 4-dichloroacetanilide (in the absence of hydrogen chloride, the product is *p*-chloroacetanilide).

The reduction of *p*-nitrophenetole by the present method does not yield any chlorophenetidine (compare Hurst and Thorpe, J., 1915, 107, 934).

It is probable that β -arylhydroxylamines may be concerned in the process, since β -phenylhydroxylamine on reduction by the present method gives only *p*-chloroacetanilide, which is also the product from the reduction of nitrobenzene. The reduction of β -phenylhydroxylamine derivatives and *isonitroso*-compounds is being investigated.

The reduction of *o*-nitrophenol and certain of its substitution products yielded in each case a *N*-monoacetyl derivative of the corresponding aminophenol, although sufficient acetic anhydride was present to acetylate the hydroxyl group. It is probable that the α -methylbenzoxazoles are intermediate products in the reduction of *o*-nitrophenolic compounds, since during the working up of the reaction mixture an oil was observed to form, which rapidly changed in acid solution to the *N*-monoacetyl derivative of the base (compare Upson, *Amer. Chem. J.*, 1904, 32, 40). No chlorination was

observed in these cases despite the fact that the para-position in the nitrophenol was unoccupied.

The following table summarises the experimental results of the present investigation :

Nitro-compound.	Reduction product isolated.
Nitrobenzene	<i>p</i> -Chloroacetanilide
<i>o</i> -Nitrotoluene	4-Chloroaceto- <i>o</i> -toluidide
* <i>m</i> - " "	4- " - <i>m</i> - "
<i>p</i> - " "	Aceto- <i>p</i> -toluidide
<i>o</i> -Chloronitrobenzene	2 : 4-Dichloroacetanilide
* <i>m</i> - " "	<i>m</i> -Chloroacetanilide
<i>p</i> - " "	(a) <i>p</i> - " "
<i>o</i> -Nitrobenzoic acid	(b) 2 : 4-Dichloroacetanilide
* <i>m</i> - " "	Anthranilic acid
<i>p</i> - " "	<i>m</i> -Aminobenzoic acid
* <i>o</i> -Nitroanisole	<i>p</i> - " "
<i>p</i> - " "	5-Chloro-2-acetamidoanisole
* <i>o</i> -Nitrophenetole	Aceto- <i>p</i> -anisidide
<i>p</i> - " "	5-Chloro-2-acetamidophenetole
<i>o</i> -Nitrophenol	Phenacetin
<i>p</i> - " "	<i>o</i> -Acetamidophenol
3-Chloro-6-nitrophenol	<i>p</i> -Acetamidophenyl acetate
4- " -2- " "	3-Chloro-6-acetamidophenol
3- " -4- " "	4-Chloro-2- " "
3-Nitro- <i>p</i> -cresol	3-Chloro-4-acetamidophenyl acetate
α -Nitronaphthalene	3-Acetamido- <i>p</i> -cresol
β -Phenylhydroxylamine	4-Chloro-1-acetnaphthalide
	<i>p</i> -Chloroacetanilide

The yields in all cases except those marked * were almost quantitative as acetyl derivatives; the average yield in the other cases was about 65%.

The authors are of the opinion that the mechanism of the chlorination taking place during the reduction is direct nuclear chlorination. A similar view has been expressed by Jones (*Brit. Assoc. Reports*, 1910, 85) in connexion with the action of chlorine on anilides.

E X P E R I M E N T A L.

The reduction of nitrobenzene is a typical example of the method.

Crystalline stannous chloride (3.5 g.; 3 mols.) was treated with acetic anhydride (4.6 g.; 9 mols.) in a 100 c.c. Claisen distilling flask; after dehydration was complete, nitrobenzene (0.6 g.; 1 mol.) was added, and the mixture heated for about $\frac{1}{2}$ hour until a clear yellow solution was obtained. The acetic acid was now removed under reduced pressure, and the residue treated with 10 c.c. of water and heated until a clear solution was obtained. On cooling, *p*-chloroacetanilide was obtained in almost theoretical yield, m. p. and mixed m. p. 173°.

Difficulty was experienced in isolating the anilides resulting from the reduction of *m*-substituted nitro-compounds, and it was found necessary in these cases to isolate the free bases by steam distillation in alkaline solution. A 30% yield of the anilides may be obtained

if the residue after removal of the acetic acid is extracted with hot benzene, and from the resulting solution a crystalline anilide can be isolated. A similar difficulty was experienced in isolating the anilides from the reduction of *o*-nitroanisole and *o*-nitrophenetole, and in these cases also it was found preferable to obtain the free bases.

3-Chloro-6-acetamidophenol and the *ON*-diacetyl derivative of 3-chloro-4-aminophenol have been prepared by the reduction of 3-chloro-6-nitrophenol and 3-chloro-4-nitrophenol, respectively, both of which were obtained (1.9 g. and 4 g., respectively) by the nitration of *m*-chlorophenol (6 g.) with nitric acid (d 1.42) (Uhlemann, *Ber.*, 1869, 2, 1161, isolated only 3-chloro-6-nitrophenol). These are readily separated, since the former is volatile in steam. The nitration of *m*-chlorophenol is also reported (Chem. Fabr. Griesheim Elektron, D.R.-P. 143449) as yielding 3-chloro-4-nitrophenol together with an isomeride volatile in steam, which was no doubt identical with 3-chloro-6-nitrophenol, although this is not definitely stated in the patent. The melting point, 38.9°, of the latter agrees with that stated by Uhlemann, but there is a discrepancy between the m. p. 120° found for 3-chloro-4-nitrophenol and 133° as stated in the patent referred to above. The non-volatile isomeride was repeatedly crystallised from hot water as pale yellow needles without affecting the melting point. Analysis for chlorine by Robertson's method (J., 1915, 107, 902) gave Cl, 20.0 (C₆H₄O₃NCl requires Cl, 20.5%).

3-Chloro-6-acetamidophenol crystallises from water in rhombic prisms, m. p. 186° (Found : Cl, 18.8. Calc. for C₈H₈O₂NCl: Cl, 19.1%).

3-Chloro-4-acetamidophenyl acetate crystallises from water in needles, m. p. 127° (Found : Cl, 15.35. C₁₀H₁₀O₃NCl requires Cl, 15.6%).

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