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

By THEODORA ELIZABETH DE KIEWIET and HENRY STEPHEN.

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,

$$C_6H_5{\cdot}NO_2 \longrightarrow C_6H_5{\cdot}NH_2 \longrightarrow C_6H_5{\cdot}NHAc \longrightarrow C_6H_4Cl{\cdot}NHAc.$$

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 *iso*nitroso-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	*p*-Chloroacetanilide
o-Nitrotoluene	4-Chloroaceto-*o*-toluidide
**m*- ,,	4- ,, -*m*- ,,
p- ,,	Aceto-*p*-toluidide
o-Chloronitrobenzene	2 : 4-Dichloroacetanilide
**m*- ,,	*m*-Chloroacetanilide
p- ,,	(*a*) *p*- ,,
	(*b*) 2 : 4-Dichloroacetanilide
o-Nitrobenzoic acid	Anthranilic acid
**m*- ,,	*m*-Aminobenzoic acid
p- ,,	*p*- ,,
**o*-Nitroanisole	5-Chloro-2-acetamidoanisole
p- ,,	Aceto-*p*-anisidide
**o*-Nitrophenetole	5-Chloro-2-acetamidophenetole
p- ,,	Phenacetin
o-Nitrophenol	*o*-Acetamidophenol
p- ,,	*p*-Acetamidophenyl acetate
3-Chloro-6-nitrophenol	3-Chloro-6-acetamidophenol
4- ,, -2- ,,	4-Chloro-2- ,,
3- ,, -4- ,,	3-Chloro-4-acetamidophenyl acetate
3-Nitro-*p*-cresol	3-Acetamido-*p*-cresol
α-Nitronaphthalene	4-Chloro-1-acetnaphthalide
β-Phenylhydroxylamine	*p*-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.

EXPERIMENTAL.

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 ½ 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 ($C_6H_4O_3NCl$ requires Cl, 20·5%).

3-Chloro-6-acetamidophenol crystallises from water in rhombic prisms, m. p. 186° (Found : Cl, 18·8. Calc. for $C_8H_8O_2NCl$: Cl, 19·1%).

3-*Chloro*-4-*acetamidophenyl acetate* crystallises from water in needles, m. p. 127° (Found : Cl, 15·35. $C_{10}H_{10}O_3NCl$ requires Cl, 15·6%).

The University of the Witwatersrand,
Johannesburg, South Africa. [*Received, November* 17*th*, 1930.]