70. *The Chlorination of the Aceto*-o-*xylidides.*

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THE chlorination of aceto-*o*-3- and 4-xylidide has been fully examined (compare Crossley, J., 1904, **85**, 277; Hinkel, J., 1920, **117**, 1301; Hinkel, Collins, and Ayling, J., 1923, **123**, 2972) and all the chloro-derivatives anticipated in view of the work of Orton and his co-workers (compare *inter alia*, J., 1927, 986) on the chlorination of anilides have been isolated, *viz.*, the 4- and the 6-chloro- and the 4 : 6-dichloro-derivative of aceto-*o*-3-xylidide and the 3- and the 5-chloro- and the 3 : 5-dichloro-derivative of the *o*-4-xylidide.

The extent of chlorination of aceto-*o*-3-xylidide depended mainly on the temperature; the yield of monochloroaceto-*o*-3-xylidides varied with the strength of the acetic acid employed and was greatest (65%) in glacial acetic acid at 10—12°, chloroamine formation being practically eliminated. 4-*Chloroaceto*-o-3-*xylidide* was also formed, but its ready solubility in organic solvents rendered its isolation difficult. The monochloroaceto-*o*-3-xylidides were most conveniently prepared by chlorination with "dichloramine T" (compare Orton and Bradfield, J., 1927, 993), the 4- and the 6-chloro-derivative being obtained in yields of 17 and 65% respectively.

With two molecules of chlorine in glacial acetic acid above 40°, aceto-*o*-3-xylidide yielded 4 : 6-*dichloroaceto*-o-3-*xylidide*; at lower temperatures the 6-monochloro-derivative also was formed. With excess of chlorine and an increase of temperature, a mixture of chloroaceto-*o*-3-xylidides resulted, from which 4 : 6-*dichloro*- and 4 : 5 : 6-*trichloro*-o-3-*xylidine* were isolated.

When treated with hypochlorous acid, according to the method of Chattaway and Orton (J., 1899, **75**, 1046), aceto-*o*-3-xylidide yielded a crystalline *chloroamine*, which was readily transformed into a mixture of 4- and 6-chloroaceto-*o*-3-xylidide. 6-Chloroaceto-*o*-3-xylidide also formed a *chloroamine*, which could be converted into 4 : 6-dichloroaceto-*o*-3-xylidide, but sufficient 4-chloro-derivative was not available for a similar conversion to be realised. 4 : 6-Dichloroaceto-*o*-3-xylidide, in which both *o*- and *p*-positions are occupied, similarly formed a chloroamine, but attempts at isomerisation led only to the regeneration of the dichloroacetoxylidide.

Chlorination of aceto-*o*-4-xylidide in glacial acetic acid with one molecule of chlorine or with "dichloramine T" in chloroform gave a mixture of 5-chloroaceto-*o*-4-xylidide (Claus, *J. pr. Chem.*, 1892, **46**, 30) and 3-*chloroaceto*-o-4-*xylidide.*

When treated with hypochlorous acid, aceto-*o*-4-xylidide yielded the crystalline *chloroamine*, which only partly isomerised into a mixture of 3- and 5-chloroaceto-*o*-4-xylidide, some aceto-*o*-4-xylidide being recovered. 5-Chloroaceto-*o*-4-xylidide also formed a *chloroamine*, which could be partly transformed into 3 : 5-dichloroaceto-*o*-4-xylidide, but the similar preparation and transformation of the chloroamine of 3-chloroaceto-*o*-4-xylidide could not be attempted owing to lack of material.

The ease with which chlorine can be directly introduced into the aceto-*o*-xylidides corresponds completely to the ease with which the transformation of the corresponding chloroamines can be effected (compare Chattaway and Orton, J., 1900, **77**, 789). Aceto-*o*-3-xylidide can be readily chlorinated and the corresponding chloroamines can also be transformed almost quantitatively. The action of chlorine on aceto-*o*-4-xylidide, however, does not proceed so readily and, in dichlorination, 3 : 5-dichloroaceto-*o*-4-xylidide is formed only in very small amount (compare Crossley, *loc. cit.*). Corresponding to this, the chloroamines of aceto-*o*-4-xylidide and 5-chloroaceto-*o*-4-xylidide are only partly transformed, appreciable hydrolysis occurring during the reaction.

Whilst in aceto-*o*-3-xylidide one ortho- and one para-position are vacant, in aceto-*o*-4-xylidide the two substituting positions are ortho to the acetamido-group and the formation of 3-chloroaceto-*o*-4-xylidide might be retarded by the proximity of the neighbouring methyl and acetamido-groups. That such an effect does operate to some extent is shown by our results, since complete monochlorination of aceto-*o*-4-xylidide is never achieved and the yield of 3-chloro-derivative never exceeds 20%.

The constitutions of 6-chloroaceto-*o*-3-xylidide (Hinkel, Collins, and Ayling, *loc. cit.*)

and 3 : 5-dichloroaceto-*o*-4-xylidide (Crossley, *loc. cit.*) have already been established and 5-chloroaceto-*o*-4-xylidide has been prepared by Claus (*loc. cit.*). The constitutions of the remaining chloro-compounds have been determined partly from the various interconversions, both by direct chlorination and through the chloroamines, and partly by the synthesis of some of them.

The 4-chloroaceto-*o*-3-xylidide described above was identical with a sample prepared from 3-nitro-*o*-4-xylidine (Crossley and Wren, J., 1911, **99**, 2342) through *4-chloro-3-nitro-*o*-xylene* and *4-chloro-*o*-3-xylidine*. Nitration of 6-chloroaceto-*o*-3-xylidide yielded *6-chloro-4-nitroaceto-*o*-3-xylidide*, the orientation of which was established by de-acetylation and reduction to an *o*-diamine. The constitution of 4 : 6-dichloroaceto-*o*-3-xylidide is shown by its preparation from 6-chloroaceto-*o*-3-xylidide and by the fact that on hydrolysis and de-amination it yielded 3 : 5-dichloro-*o*-xylene. 4 : 5 : 6-Trichloro-*o*-3-xylidine was prepared by the reduction of 3 : 4 : 5-trichloro-6-nitro-*o*-xylene (Hinkel, *loc. cit.*).

The 5-chloroaceto-*o*-4-xylidide mentioned above was identical with a specimen prepared from 5-nitro-*o*-4-xylidine (Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2248) through 4-chloro-5-nitro-*o*-xylene and 5-chloro-*o*-4-xylidine (compare Claus, *loc. cit.*). The constitution of 3-chloroaceto-*o*-4-xylidide was established by a similar synthesis from 4-nitro-*o*-3-xylidine (Noelting, Braun, and Thesmar, *loc. cit.*).

EXPERIMENTAL.

*Monochlorination of Aceto-*o*-3-xylidide.*—(1) *In acetic acid containing* 4—5% *of water at* 0°. The chlorination of aceto-*o*-3-xylidide (3 g.) was carried out as described by Hinkel, Collins, and Ayling (*loc. cit.*), but the white solid which separated was immediately collected and crystallised from aqueous alcohol, yielding 6-chloroaceto-*o*-3-xylidide (1·44 g.; 40%).

The acetic acid filtrate on dilution with water deposited a yellow sticky substance, which liberated iodine from potassium iodide and was converted on standing into a pink solid. This solid was hydrolysed under reflux with 10% sulphuric acid for 2 hours, and the acid solution diluted until the acid content was *ca.* 1%. Steam-distillation yielded an oil. This was suspended in water, an equal weight of sulphuric acid added, and the mixture steam-distilled; practically pure 4-chloro-*o*-3-xylidine collected in the distillate. A dried ethereal extract of the distillate yielded an oil which, on acetylation, yielded *4-chloroaceto-*o*-3-xylidide*, which crystallised from aqueous alcohol or hot water in clusters of fine needles, m. p. 169° (Found : Cl, 18·2. $C_{10}H_{12}ONCl$ requires Cl, 18·0%).

4-Chloroaceto-*o*-3-xylidide, hydrolysed with 10% sulphuric acid as described above, gave 4-chloro-*o*-3-xylidine as a colourless oil, which rapidly became coloured in the air.

The acid residues after steam-distillation were basified and steam-distilled and the oil collected was acetylated, a further small yield (0·2 g.; 5%) of 6-chloroaceto-*o*-3-xylidide being obtained.

(2) *In glacial acetic acid at* 10—12°. The chlorination of aceto-*o*-3-xylidide (3 g.) was repeated in glacial acetic acid (30 c.c.), which was kept partly frozen throughout the experiment. A white solid separated, and one crystallisation yielded 6-chloroaceto-*o*-3-xylidide (2·2 g.; 61%); a further small amount (0·15 g.; 4%) was obtained from the acetic acid filtrate on dilution with water. The residue, treated as described above, yielded a small quantity of 4-chloroaceto-*o*-3-xylidide.

(3) *By means of "dichloramine T."* Aceto-*o*-3-xylidide (5 g.) in chloroform was treated with "dichloramine T" (see Orton and Bradfield, *loc. cit.*). The chloro-*o*-xylidines obtained after hydrolysis and steam-distillation were collected in ether, dried, and acetylated with the requisite amount of acetic anhydride, also in ether. Evaporation of the ether and crystallisation from aqueous alcohol yielded 6-chloroaceto-*o*-3-xylidide, the mother-liquor yielding a mixture of 6- and 4-chloroaceto-*o*-3-xylidide, which was separated by the method described above. Total yield : 6-chloro-, 3·9 g. (65%) : 4-chloro-, 1·0 g. (17%).

*Dichlorination of Aceto-*o*-3-xylidide.*—Chlorine was passed into a solution of aceto-*o*-3-xylidide (5 g.) in glacial acetic acid (50 c.c.) at 40—50° until the gain in weight corresponded to the substitution of two chlorine atoms. The yellow solution, poured into much water, yielded *4 : 6-dichloroaceto-*o*-3-xylidide* (6·75 g.; 96%), which crystallised from acetone, aqueous alcohol, or hot water in clusters of fine white needles, m. p. 188° (Found : Cl, 30·4. $C_{10}H_{11}ONCl_2$ requires Cl, 30·6%).

When this xylidide (10 g.) was hydrolysed by heating under reflux with hydrochloric acid

(200 c.c.) for 4 hours, and the product basified and distilled in steam, 4 : 6-*dichloro*-o-3-*xylidine* was obtained; it crystallised from aqueous alcohol in clusters of radiating needles, m. p. 44° (Found : Cl, 37·4. $C_8H_9NCl_2$ requires Cl, 37·3%).

Chlorination of Aceto-o-3-*xylidide with Excess of Chlorine.*—Excess of chlorine was passed into a solution of aceto-*o*-3-xylidide (5 g.) in glacial acetic acid (50 c.c.) at 70°. The yellow solution, poured into water, yielded a solid, which was hydrolysed under reflux with 40% sulphuric acid for 4 hours; the product was basified and distilled in steam, two fractions being collected : (1) 4 : 6-dichloro-*o*-3-xylidine, which distilled fairly rapidly; (2) a second solid, which distilled slowly, and after crystallisation from light petroleum (b. p. 40—60°) and then several times from hot alcohol, gave 4 : 5 : 6-*trichloro*-o-3-*xylidine* as fine hair-like needles, m. p. 207° (Found : Cl, 47·2. $C_8H_8NCl_3$ requires Cl, 47·3%).

Chlorination of 6-*Chloroaceto*-o-3-*xylidide.*—Into the xylidide (2 g.) in glacial acetic acid (20 c.c.) at 50°, chlorine was passed until the gain in weight corresponded to the substitution of one chlorine atom. The mixture was poured into water, and the precipitated solid recrystallised from acetone, yielding 4 : 6-dichloroaceto-*o*-3-xylidide, m. p. 188° (2·1 g.; 90%).

Nitration of 6-*Chloroaceto*-o-3-*xylidide.*—The xylidide (4 g.) in glacial acetic acid (4 c.c.) was gradually added to a mixture of nitric acid (*d* 1·5; 9 c.c.) and glacial acetic acid (3 c.c.), and the whole heated on a steam-bath for 30 minutes and poured into water. The precipitated 6-*chloro*-4-*nitroaceto*-o-3-*xylidide* (4·6 g.; 95%) crystallised from alcohol in felted needles, m. p. 196·5° (Found : Cl, 14·9. $C_{10}H_{11}O_3N_2Cl$ requires Cl, 14·6%).

6-Chloro-4-nitroaceto-*o*-3-xylidide (4 g.) was heated under reflux for 1 hour with 40% sulphuric acid (200 c.c.), and the product cooled, diluted, and rendered alkaline with ammonia. The orange precipitate (3·2 g.; 98%) crystallised from alcohol in long fine needles, m. p. 143°, of 6-*chloro*-4-*nitro*-o-3-*xylidine* (Found : Cl, 17·7. $C_8H_9O_2N_2Cl$ requires Cl, 17·7%). This nitro-compound, reduced in alcoholic solution with sodium hydrosulphite, yielded an *o*-diamine (phenanthraquinone test).

N-*Chloroaceto*-o-3-*xylidide.*—Aqueous potassium hypochlorite (prepared by addition of potassium bicarbonate, 12 g., to a saturated solution of bleaching powder, 200 c.c., at 30° and filtration) was added during 1 hour to an ice-cooled and well-shaken suspension of aceto-*o*-3-xylidide (2 g.) in water (120 c.c.). After 12 hours, the N-*chloroaceto*-o-3-*xylidide* (2·3 g.; 96%) was collected, dried, and crystallised from well-cooled chloroform, forming prismatic clusters, m. p. 94·5° (Found : Cl, iodometric, 18·0. $C_{10}H_{12}ONCl$ requires Cl, 18·0%).

The chloroamine (3·3 g.) was transformed by cautious warming on the water-bath. Crystallisation of the product from aqueous alcohol yielded 6-chloroaceto-*o*-3-xylidide (2·05 g.; 62%), and the residuum in solution, treated as described on p. 284, yielded 4-chloroaceto-*o*-3-xylidide and a further small amount of 6-chloroaceto-*o*-3-xylidide.

N : 6-*Dichloroaceto*-o-3-*xylidide*, prepared from 6-chloroaceto-*o*-3-xylidide in a manner similar to that described above, crystallised from well-cooled chloroform–light petroleum (b. p. 40—60°) in small prisms, m. p. 81° (Found : Cl, iodometric, 15·2. $C_{10}H_{11}ONCl_2$ requires Cl as :NCl, 15·3%). Transformation into 4 : 6-dichloroaceto-*o*-3-xylidide occurred vigorously when the chloroamine was heated with dilute acetic acid; the product contained a small amount of 6-chloroaceto-*o*-3-xylidide.

N : 4 : 6-*Trichloroaceto*-o-3-*xylidide.*—A solution of aceto-*o*-3-xylidide (2 g.) in glacial acetic acid (10 c.c.) was poured into a large excess (200 c.c.) of 0·5*N*-bleaching powder solution. The finely precipitated aceto-*o*-3-xylidide gradually clotted and melted to an oil on warming. The latter was dissolved in glacial acetic acid and re-precipitated by pouring into excess of bleaching powder solution. The oil, so obtained, after extraction with chloroform, only partly solidified. Boiling with dilute acetic acid slowly decomposed the compound to give 4 : 6-dichloroaceto-*o*-3-xylidide.

Chlorination of Aceto-o-4-*xylidide.*—(1) *In acetic acid with chlorine.* Chlorine was passed into an ice-cooled solution of aceto-*o*-4-xylidide (3 g.) in glacial acetic acid (15 c.c.) until the gain in weight corresponded to the substitution of one chlorine atom; a white solid separated. The mixture was poured into water, and the precipitated solid collected and hydrolysed under reflux with 20% sulphuric acid. The acid liquor was diluted to *ca.* 2% and distilled in steam, and the mixture of amines obtained extracted with ether. The dried ethereal solution, after acetylation, yielded a mixture of monochloroaceto-*o*-4-xylidides (1·7 g.; 56%), which, on fractional crystallisation from aqueous alcohol, was resolved into 5-chloroaceto-*o*-4-xylidide, glistening plates, m. p. 157° (Found : Cl, 17·8. Calc. : Cl, 18·0%) (Claus, *loc. cit.*, records m. p. 154°), and 3-*chloroaceto*-o-4-*xylidide*, clusters of radiating needles, m. p. 114° (Found :

Cl, 18·1. $C_{10}H_{12}ONCl$ requires Cl, 18·0%). The residual acid liquor, made alkaline and distilled in steam, yielded unchanged *o*-4-xylidine (0·3 g.; 10%).

3-Chloroaceto-*o*-4-xylidide (2 g.) was heated under reflux with 10% sulphuric acid (100 c.c.) for an hour. The product was made alkaline and distilled in steam. 3-*Chloro*-o-4-*xylidine*, isolated by means of ether, solidified at – 10° and then crystallised from light petroleum (b. p. 60—80°) in long felted needles, m. p. 26° (Found : Cl, 22·95. $C_8H_{10}NCl$ requires Cl, 22·8%).

5-Chloroaceto-*o*-4-xylidide, hydrolysed as described above, yielded 5-chloro-*o*-4-xylidine, which crystallised from well-cooled light petroleum (b. p. 40—60°) or aqueous alcohol in clusters of flat plates, m. p. 87·5° (Found : Cl, 22·8. Calc. : Cl, 22·8%) (Claus, *loc. cit.*, records m. p. 86°).

Both 3- and 5-chloro-*o*-4-xylidine are much less basic than the monochloro-*o*-3-xylidines, their salts with hydrochloric and sulphuric acids being completed dissociated in dilute solution.

(2) *In chloroform with " dichloramine T."* Aceto-*o*-4-xylidide (10 g.) and " dichloramine T " (93%; 8·0 g.) were dissolved in chloroform (50 c.c.) and cooled, and hydrochloric acid (8 drops) added. Subsequent treatment as previously described gave a mixture of monochloroaceto-*o*-4-xylidides (6·25 g.; 67%), which was resolved by fractional crystallisation from aqueous alcohol into 5-chloroaceto-*o*-4-xylidide (4·5 g.; 48%) and 3-chloroaceto-*o*-4-xylidide (1·75 g.; 19%).

The acid residue from the steam-distillation of the monochloro-*o*-4-xylidines, on basification and distillation in steam, yielded unchanged *o*-4-xylidine (1·65 g.; 22%).

N-*Chloroaceto*-o-4-*xylidide*, prepared by the method previously described for the corresponding derivative of aceto-*o*-3-xylidide, was very soluble in chloroform and benzene and crystallised from light petroleum (b. p. 60—80°) in prisms, m. p. 55° (Found : Cl, iodometric, 17·9. $C_{10}H_{12}ONCl$ requires Cl, 18·0%). When pure, it can be kept for months in a dry atmosphere. If slightly impure or moist, however, it reddens rapidly and changes into a sticky liquid. When warmed with chloroform or acetic acid, it yielded a mixture of monochloroaceto-*o*-4-xylidides (50%) and aceto-*o*-4-xylidide (25%).

N : 5-*Dichloroaceto*-o-4-*xylidide* was best prepared by agitating finely powdered 5-chloroaceto-*o*-4-xylidide (2 g.) with a slight excess (200 c.c.) of warm *N*/2-bleaching powder solution made faintly acid with acetic acid (yield, 2·0 g.; 90%). It crystallised from well-cooled chloroform in prisms, m. p. 74° (Found : Cl, iodometric, 15·1. $C_{10}H_{11}ONCl_2$ requires Cl, as :NCl, 15·3%).

The chloroamine, dissolved in chloroform or acetic acid, is transformed slowly into 3 : 5-dichloroaceto-*o*-4-xylidide at the ordinary temperature. The transformation was accelerated by warming a solution of the chloroamine (2 g.) in acetic acid (10 c.c.), to which a few drops of sulphuric acid had been added, on the steam-bath for 2 days. The product was hydrolysed with 10% sulphuric acid, basified, and distilled in steam, a mixture of 3 : 5-dichloro-*o*-4-xylidine and 5-chloro-*o*-4-xylidine being obtained. The amines were acetylated and resolved by crystallisation from aqueous alcohol into 3 : 5-dichloroaceto-*o*-4-xylidide (0·86 g.; 48%) and 5-chloroaceto-*o*-4-xylidide (0·2 g.; 10%).

Synthesis of 4-*Chloroaceto*-o-3-*xylidide*.—Accumulated residues of dinitro-*o*-xylenes obtained from the nitration of *o*-xylene according to the several methods described by Crossley and Renouf (J., 1909, **95**, 206) were fractionally distilled under reduced pressure; the fraction, b. p. 185—200°/17 mm., after one crystallisation from sulphuric acid and one from alcohol, gave pure 3 : 4-dinitro-*o*-xylene, m. p. 82°.

3-Nitro-*o*-4-xylidine (Crossley and Wren, J., 1911, **99**, 2342) (4 g.) was suspended in hydrochloric acid (15 c.c.) and water (100 c.c.) and diazotised. Treatment with cuprous chloride, followed by steam-distillation, yielded 4-*chloro*-3-*nitro*-o-*xylene* (2·5 g.; 60%), which crystallised from aqueous alcohol in long, thin, pale yellow plates, m. p. 75° (Found : Cl, 18·2. $C_8H_8O_2NCl$ requires Cl, 19·1%).

The chloro-compound (1 g.), suspended in 5% acetic acid (200 c.c.), was warmed under reflux with iron filings (10 g.) for 4 hours. Basification and distillation in steam, followed by acetylation of the amine in ether, gave an acetyl derivative (1·0 g.; 93%), m. p. 169° (after crystallisation from aqueous alcohol), unchanged by admixture with the 4-chloroaceto-*o*-3-xylidide previously obtained.

Constitution of 4 : 6-*Dichloro*-o-3-*xylidine*.—The xylidine (1 g.) was dissolved in 50% sulphuric acid (10 c.c.) and diazotised at 0°, and the solution poured into boiling alcohol (20 c.c.) and heated for 30 minutes. Steam-distillation and extraction with ether yielded 3 : 5-dichloro-*o*-xylene as a pale yellow oil, which solidified in a freezing mixture (compare Crossley and Le Sueur, J., 1902, **81**, 1535; Crossley and Wren, J., 1910, **97**, 98) and yielded on nitration

3 : 5-dichloro-4 : 6-dinitro-*o*-xylene, m. p. 175°, unchanged by admixture with an authentic specimen (compare Crossley, *loc. cit.*).

4 : 5 : 6-*Trichloro*-o-3-*xylidine.*—3 : 4 : 5-Trichloro-6-nitro-*o*-xylene, m. p. 169° (Hinkel, J., 1920, **117**, 1301; the m. p. was previously recorded in error as 149°), was heated with iron filings and glacial acetic acid for 4 hours on a water-bath. Dilution, basification, and steam-distillation yielded a solid, which distilled slowly and crystallised from ethyl acetate in fine hair-like needles, m. p. 207°, unchanged by admixture with the above 4 : 5 : 6-trichloro-*o*-3-xylidine.

Synthesis of 5-*Chloroaceto*-o-4-*xylidide.*—5-Nitro-*o*-4-xylidine, prepared from *o*-4-xylidine (compare Noelting, Braun, and Thesmar, *loc. cit.*), was dissolved, 1 g. at a time, in hydrochloric acid (5 c.c.), and water (3 c.c.) added. The precipitated hydrochloride, diazotised at 20° and treated with cuprous chloride, yielded 5-*chloro*-4-*nitro*-o-*xylene* (0·7 g.; 64%), which crystallised from alcohol in long, fine, pale yellow needles, m. p. 63° (Claus and Groneweg, *J. pr. Chem.*, 1891, **43**, 257, record m. p. 73° for the compound, obtained by nitration of 4-chloro-*o*-xylene, which they considered to be 5-chloro-4-nitro-*o*-xylene, but which was probably a mixture) (Found: Cl, 19·3. $C_8H_8O_2NCl$ requires Cl, 19·1%).

5-Chloro-4-nitro-*o*-xylene was reduced with iron and 5% acetic acid, as described above, and the resulting amine acetylated. The acetyl derivative crystallised from dilute alcohol in glistening plates, m. p. 157°, unchanged by admixture with the 5-chloroaceto-*o*-4-xylidide described above (Found: Cl, 17·8. Calc.: Cl, 18·0%).

Synthesis of 3-*Chloroaceto*-o-4-*xylidide.*—4-Nitro-*o*-3-xylidine was prepared by a modification of the method of Noelting, Braun, and Thesmar (*loc. cit.*). Aceto-*o*-3-xylidide (2 g.) was added during 15 minutes to a mixture of nitric acid (*d* 1·5, 19 c.c.) and glacial acetic acid (5 c.c.) cooled to − 10°. After 15 minutes, the whole was poured into ice-water. The solid obtained (2·0 g.; 80%), consisting of the three isomeric nitroaceto-*o*-3-xylidides, was dissolved in hydrochloric acid mixed with an equal volume of water, and distilled in steam, yielding pure 4-nitro-*o*-3-xylidine, m. p. 119° (0·83 g.; 52%).

4-Nitro-*o*-3-xylidine, suspended, in quantities of 1 g., in hydrochloric acid (8 c.c.) and water (5 c.c.), was diazotised at 20°. Subsequent treatment as above yielded 3-chloro-4-nitro-*o*-xylene (0·9 g.; 80%), which crystallised from well-cooled alcohol in fine yellow needles, m. p, 46° (Found: Cl, 19·2. Calc.: Cl, 19·1%). This was reduced with iron and 5% acetic acid, and the resulting amine acetylated. The acetyl derivative crystallised from aqueous alcohol in clusters of radiating needles, m. p. 114°, unchanged by admixture with the above 3-chloroaceto-*o*-4-xylidide (Found: Cl, 18·1. Calc.: Cl, 18·0%)

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