XXXVIII.—*2-Substituted Derivatives of* p-*Cresol.*

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HOLLEMAN and HOEFLAKE (*Rec. trav. chim.*, 1916, **36**, 270) have shown that *p*-cresol is convertible into its 2-nitro-derivative [Me in position 1] by nitration of its carbonate and subsequent hydrolysis, but their procedure, as well as that described in D.R.-P. 206638 (Friedländer, "Fortschritte in der Teerfarbenfabrikation," IX, 151), is not entirely satisfactory, and the modifications now described enable much better yields to be obtained.

The methyl ether of 2-nitro-*p*-cresol was obtained in good yield by the action of methyl sulphate on (*a*) 2-nitro-*p*-cresol and (*b*) 2-nitro-*p*-tolyl carbonate in alkaline medium under atmospheric pressure. This compares well with Knecht's method (*Annalen*, 1882, **215**, 88; *Ber.*, 1882, **15**, 1072) of heating potassium 2-nitro-*p*-tolyloxide with methyl iodide *under pressure.* The methyl ether of 2-amino-*p*-cresol (*iso*cresidine) was obtained in 78—82% yield by reducing the methyl ether of 2-nitro-*p*-cresol with iron filings in an acid medium, instead of tin and hydrochloric acid (Knecht, *loc. cit.*).

2-Amino-*p*-cresol was obtained by the direct and simultaneous reduction and hydrolysis of 2-nitro-*p*-tolyl carbonate with (*a*) sodium sulphide and (*b*) less satisfactorily with iron filings in acid medium, a process entirely different from and simpler than those of Knecht (*Annalen*, 1882, **215**, 91; *Ber.*, 1882, **15**, 300), Wallach (*Ber.*, 1882, **15**, 2834), and Maasen (*Ber.*, 1884, **17**, 610), who obtained the substance by diazotisation of 2 : 4-tolylenediamine.

EXPERIMENTAL.

p-Tolyl carbonate, m. p. 113° after crystallising from alcohol, was obtained in 98% yield by passing carbonyl chloride into a stirred solution of *p*-cresol (108 g.) and sodium hydroxide (42 g.)

in water (500 c.c.) maintained at 40—50°; when the gas was no longer absorbed, the product was triturated with cold aqueous sodium hydroxide (3—5%), washed, and dried below 100°. Below 30°, *p*-tolyl chloroformate also was produced in the reaction, and above 60° hydrolysis of the *p*-tolyl carbonate took place.

A mixture of sulphuric acid (240 g. of 99—100% H_2SO_4) and nitric acid (2·12 mols. of 86—92% acid) at 10—12° was gradually added to a stirred solution of *p*-tolyl carbonate (240 g.) in 99—100% sulphuric acid (1200 g.) at 12—15°. The mixture, after being stirred for 2 hours at 18—20°, was poured on ice (2 kg.). The crude pressed material was boiled with aqueous sodium carbonate (200 g. in 2 l. of water) for 2 hours, the solution at once acidified at 35°, and the 3-nitro-*p*-cresol removed by distillation in steam. The residual 2-nitro-isomeride (yield, 79%), after being decolorised in benzene or alcohol with animal charcoal, was obtained in yellow odourless crystals, m. p. 76—77°.

A mixture of 2-nitro-*p*-cresol (153 g.), toluene (300 c.c.), methyl sulphate (140 g.), and anhydrous sodium carbonate (127 g.) was heated and stirred at 110—112° for 4—5 hours. On steam distillation the toluene came over, followed by 2-nitro-*p*-tolyl methyl ether as a pale yellow oil (yield, 77%).

A mixture of the crude 2-nitro-*p*-cresol from 120 g. of *p*-tolyl carbonate with toluene was dried by distilling off all but 300 c.c. of the latter. The residual solution was treated at 50—60° with methyl sulphate (140 g.) and sodium carbonate (160 g.), and the whole stirred and heated at 110—112° for 4—5 hours. The yield of methyl ether was 60% of the *p*-tolyl carbonate used. The ethyl ether was prepared in a similar manner.

2-Amino-*p*-cresol was obtained from a similar quantity of the above crude nitration product, after removal of traces of 3-nitro-*p*-cresol in steam, by the gradual addition of a solution of crystallised sodium sulphide (480 g.) in water (1600 c.c.) to a thin paste of the material in water (100 c.c.) at 40°. The reduction was completed in 4—5 hours at 90—95°, and the mixture was then acidified, boiled to remove hydrogen sulphide and sulphur dioxide, and neutralised. The total yield corresponded to 79% of the carbonate used, but one-fifth of this remained in solution. Recrystallised from ether, the product was obtained in colourless crystals, m. p. 157—159°.

*iso*Cresidine (2-amino-*p*-tolyl methyl ether) resulted from the reduction at 95—98°, in a reflux apparatus, of 2-nitro-*p*-tolyl methyl ether (167 g.) in water (600 c.c.) and glacial acetic acid (15—20 c.c.) by the gradual addition of iron filings (170 g.) during 2—3 hours. Isolation of the product by steam distillation gave a pure product but involved loss owing to the solubility of the base even in brine. Extraction of the reduction mixture with toluene and precipitation of the base in the form of its hydrochloride gave a better yield but a less pure product.

p-Tolyl chloroformate (compare Barrel and Morel, *Compt. rend.*, 1899, **128**, 1578; Pickard and Littlebury, J., 1907, **91**, 302) is best prepared by passing carbonyl chloride into a stirred solution of *p*-cresol (108 g.) and sodium hydroxide (42—44 g.) in water (500 c.c.), maintained below 10°. The oily product boils at 108°/30 mm. (yield, 78—80%).

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