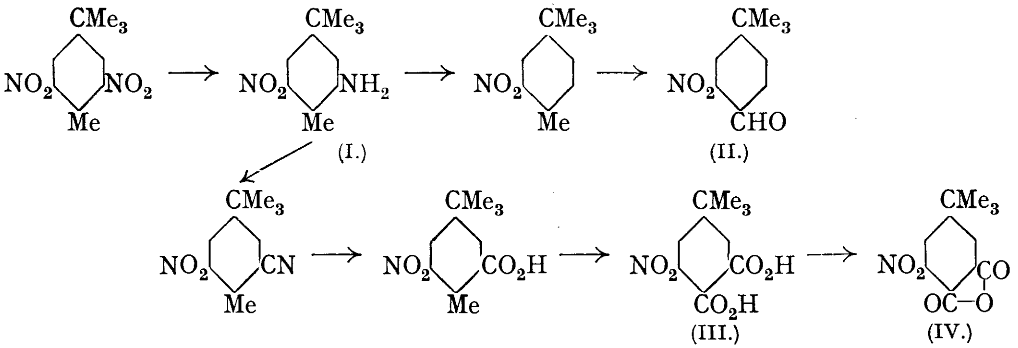
430. *The Nitration of Alkyl Benzenes. Part III. The Orientation of Dinitro*-p-tert.-*butyltoluene.*

By O. L. Brady and J. K. Lahiri.

A convenient starting point for the preparation of pure 2- and 3-nitro-*p*-*tert*.-butyltoluenes is the dinitro-*p*-*tert*.-butyltoluene described first by Bialobrzeski (*Ber.*, 1897, **30**, 1773) and later by Verley (*Bull. Soc. chim.*, 1898, **19**, 68) and by Auwers (*Ber.*, 1916, **49**, 2403). The constitution of this compound has, however, not been clearly established. Verley without experimental evidence regarded it as the 2:5-dinitro-derivative. The view outlined in Part I (this vol., p. 116) made it more likely that substitution would take place in the two ortho-positions with respect to the methyl group, although Senkowski (*Ber.*, 1890, **23**, 2414) obtained some ortho-substitution in the nitration of *tert.*-butylbenzene (compare Shoesmith and Mackie, J., 1928, 2334). Malherbe's failure (*Ber.*, 1919, **52**, 319) to detect ortho-substitution in this reaction was due to his relying on the absence of *o*-nitrobenzoic acid in the oxidation products he obtained, although Senkowski had pointed out that his *o*-nitro-*tert.*-butylbenzene could not be oxidised to this compound : the danger of such assumptions has been emphasised in Part I. Battegay and Haeffely (*Bull. Soc. chim.*, 1924, **35**, 981) have shown that the main product of the mononitration of *p*-*tert.*-butyltoluene has the nitro-group in the ortho-position to the methyl and, from the resemblance of the product obtained by the reduction of Bialobrzeski's dinitro-compound to a *m*-diamine, conclude that this dinitro-compound contains both nitro-groups ortho to the methyl.

Dinitro-*p*-*tert.*-butyltoluene cannot be oxidised to a dinitroterephthalic acid or to a dinitro-*p*-*tert.*-butylbenzoic acid. The resistance of the methyl group to oxidation suggests that it is di-ortho-substituted, and proof of this has been obtained by the following series of reactions :



The nitro-aldehyde (II) gives Baeyer and Drewson's indigo test for *o*-nitrobenzaldehydes (*Ber.*, 1883, **16**, 2205) very satisfactorily, showing that the unreduced nitro-group in (I) is ortho to the methyl. The dicarboxylic acid (III) yields an anhydride (IV) on heating, showing that the reduced nitro-group in (I) is also ortho to the methyl.

EXPERIMENTAL.

2 : 6-*Dinitro*-4-tert.-*butyltoluene.*—*p*-*tert.*-Butyltoluene (15 g.), prepared by Verley's method (*loc. cit.*), was cooled in ice and salt, and a mixture of nitric acid (30 c.c., *d* 1·5) and fuming sulphuric acid (60 g., 20% SO_3) added during 30 minutes. The mixture was heated for 3 hours on a water-bath and poured into water ; the solid on crystallisation from dilute alcohol gave 12 g. of 2 : 6-dinitro-4-*tert.*-butyltoluene, m. p. 96°. Bialobrzeski gives m. p. 94—95°, Verley, 87—88°, and Auwers, 96°.

6-*Nitro*-2-*amino*-4-tert.-*butyltoluene.*—Aqueous ammonium sulphide (60 g. of 16%) was added in small portions during 30 minutes to a solution of the pure dinitro-compound (10 g.) in boiling alcohol (100 c.c.), and the mixture heated under reflux for a further 90 minutes and filtered hot. After keeping overnight, a small quantity of unchanged dinitro-compound (1 g.) separated and was removed. The alcohol was evaporated on the water-bath, and the nitro-amino-derivative remained as an uncrystallisable oil, which, on treatment with concentrated hydrochloric acid, solidified as the hydrochloride ; this was dissolved in boiling 2*N*-hydrochloric acid, a small amount of insoluble material remaining. On cooling, 6-*nitro*-2-*amino*-4-tert.-*butyltoluene hydrochloride* was obtained as a felted mass of fawn-coloured needles which, if left in contact with the mother-liquor for some weeks, changed almost entirely to dense large transparent brown hexagonal crystals, m. p. 210° (decomp.) (Found : C, 54·1 ; H, 6·7. $C_{11}H_{17}O_2N_2Cl$ requires C, 54·0 ; H, 6·9%). Recrystallisation of the hexagonal crystals regenerated the light needles, which had the same m. p. (Found : C, 53·4 ; H, 7·0%).

The hydrochloride was dissolved in hot water, ammonia added, and the base extracted with ether, but on removal of the solvent an uncrystallisable oil was again obtained ; this oil was heated for a few minutes with acetic anhydride, cooled, and shaken with 2*N*-sodium carbonate, and the precipitated solid crystallised from alcohol, 6-*nitro*-2-*acetamido*-4-tert.-*butyltoluene* being obtained as yellow needles, m. p. 138—139° (Found : C, 62·3; H, 7·2. $C_{13}H_{18}O_3N_2$ requires C, 62·4; H, 7·2%).

2-*Nitro*-4-tert.-*butyltoluene*.—6-Nitro-2-amino-4-*tert*.-butyltoluene hydrochloride (15 g.) was warmed with concentrated sulphuric acid (30 c.c.) until all hydrogen chloride was evolved; the product was cooled and poured into absolute alcohol (200 c.c.). The mixture was heated under reflux, dry powdered sodium nitrite (30 g.) added in small portions, a mixture of concentrated sulphuric acid (10 c.c.) and absolute alcohol (50 c.c.) poured in, and more sodium nitrite (30 g.) added. The pasty mass was heated on the water-bath for 30 minutes, water added (100 c.c.), the alcohol distilled off, and the residue distilled in steam for 5 hours. The distillate was extracted with ether, and the extract washed with 2*N*-sodium hydroxide and water. After drying and removal of the ether, the residue on distillation under reduced pressure gave a 50% yield of 2-nitro-4-*tert*.-butyltoluene as a yellow oil of fruity odour, b. p. 140°/15 mm., $d^{21°}$ 1·0514, n_{5461} 1·52645 (Found : C, 68·0; H, 8·2; N, 7·3. Calc. : C, 68·4; H, 7·8; N, 7·3%). Battegay and Haeffely (*loc. cit.*) give b. p. 138—139°/13 mm.

The sodium hydroxide washings obtained above were acidified and extracted with ether. After removal of the ether and crystallisation of the residue from dilute alcohol, 6-*nitro*-2-*hydroxy*-4-tert.-*butyltoluene* (1 g.) was obtained as yellow leaflets, m. p. 128° (Found : C, 63·1; H, 7·2. $C_{11}H_{15}O_3N$ requires C, 63·1; H, 7·2%).

2-*Nitro*-4-tert.-*butylbenzaldehyde*.—A mixture of 2-nitro-4-*tert*.-butyltoluene (2 g.), glacial acetic acid (16 c.c.), acetic anhydride (20 c.c.), and concentrated sulphuric acid (3 c.c.) at 0° was treated with finely powdered chromium trioxide (4 g.) in small portions with thorough shaking, the temperature being kept below 10°. The solution was poured on ice and after 2 hours extracted with ether. The extract was washed with sodium carbonate solution and evaporated; the aldehyde diacetate remained as an uncrystallisable oil, which was hydrolysed by boiling for an hour with concentrated hydrochloric acid. The product was diluted and extracted with ether, and on removal of the solvent the aldehyde was obtained as a semi-solid mass. As the quantity did not admit of satisfactory purification, it was dissolved in alcohol and divided into two portions. One was treated with alcoholic 2 : 4-dinitrophenylhydrazine sulphate, giving a precipitate of 2-*nitro*-4-tert.-*butylbenzaldehyde*-2 : 4-*dinitrophenylhydrazone* as yellow needles, m. p. 228° after crystallisation from alcohol (Found: C, 52·5; H, 4·5. $C_{17}H_{17}O_6N_5$ requires C, 52·7; H, 4·4%). The second part was subdivided and warmed with a trace of acetone and sodium hydroxide; the characteristic colour changes of the Baeyer–Drewson indigo reaction then occurred and a finely divided, dark blue precipitate formed, which mounted the sides of the tube and could be seen as an indigo-blue stain by filtering the liquid through hardened filter paper and washing away the greenish solution. The test was obtained three or four times.

2-*Amino*-4-tert.-*butyltoluene*.—2-Nitro-4-*tert*.-butyltoluene (8 g.) was reduced with tin (10 g.) and concentrated hydrochloric acid (25 c.c.), sodium hydroxide (25 g. in 50 c.c. of water) added, and 2-amino-4-*tert*.-butyltoluene distilled in steam, extracted in ether, and obtained as a red oil, b. p. 121°/20 mm. (Found : C, 79·6; H, 10·2. Calc. : C, 81·0; H, 10·4%). Battegay and Haeffely (*loc. cit.*) give b. p. 128—129°/13 mm.

6-*Nitro*-2-*cyano*-4-tert.-*butyltoluene*.—6-Nitro-2-amino-4-*tert*.-butyltoluene hydrochloride (5 g.) was warmed with concentrated sulphuric acid (6 c.c.) to convert it into sulphate; the mixture was poured into water (50 c.c.) and diazotised between 0° and 5°, and the solution almost neutralised with sodium carbonate and added drop by drop to a solution prepared by adding warm sodium cyanide (4 g. in 16 c.c. of water) to copper sulphate (4 g. in 20 c.c. of water), heating on the water-bath for a few minutes, and cooling to 0°. Nitrogen was evolved with considerable frothing, and the reaction was completed by heating for 30 minutes. The mixture was extracted with ether, and after being washed with dilute sodium hydroxide solution the solvent was removed; the residual oil solidified slowly in a refrigerator and then crystallised from light petroleum as yellow-brown crystals of (25% yield) 6-*nitro*-2-*cyano*-4-tert.-*butyltoluene*, m. p. 83° (Found : C, 65·9; H, 6·5. $C_{12}H_{14}O_2N_2$ requires C, 66·0; H, 6·4%).

6-*Nitro*-2-*carboxy*-4-tert.-*butyltoluene*.—The cyano-compound (2 g.) was boiled with sulphuric acid (10 c.c. of concentrated acid and 5 c.c. of water) under reflux for 2 hours, the cooled mixture diluted, and the solid extracted with 2*N*-sodium carbonate. The alkaline solution on acidification gave a 30% yield of 6-*nitro*-2-*carboxy*-4-tert.-*butyltoluene*, which separated from 25% alcohol in white needles, m. p. 219° (Found : C, 60·6; H, 6·3. $C_{12}H_{15}O_4N$ requires C, 60·7; H, 6·3%).

5-*Nitro*-3 : 4-*dicarboxy*-tert.-*butylbenzene*.—The above acid could not be oxidised by a boiling solution of chromium trioxide in acetic acid, by chromium trioxide and concentrated sulphuric acid, by boiling alkaline permanganate, or by dilute nitric acid, boiling or at 190° for 8 hours. Oxidation was finally achieved by heating the compound (0·1 g.) with nitric acid (3 c.c., *d* 1·5) and water (12 c.c.) for 8 hours at 200°; the clear solution obtained gave on evaporation a solid which was much more readily soluble in water than 6-nitro-2-carboxy-4-*tert.*-butyltoluene. By leaving a solution of the solid in water to evaporate spontaneously, 5-*nitro*-3 : 4-*dicarboxy*-tert.-*butylbenzene* was obtained in colourless crystals, m. p. 365° (decomp.) (Found : C, 54·2; H, 5·0. $C_{12}H_{13}O_6N$ requires C, 53·9; H, 4·9%).

The dicarboxylic acid when heated gave a crystalline sublimate of the *anhydride*, m. p. 147—149°, insoluble in cold 2*N*-sodium carbonate, but dissolving on warming (Found : C, 57·1; H, 4·7. $C_{12}H_{11}O_5N$ requires C, 57·8; H, 4·4%). Unfortunately the difficulty experienced in oxidation left insufficient material for a more complete examination of the anhydride, but there seems no doubt of its identity; any other probable decomposition products of the dicarboxylic acid would differ considerably in composition from the product obtained; *e.g.*, if loss of one molecule of carbon dioxide occurred, the compound would be soluble in cold sodium carbonate solution and would have the composition C, 59·2; H, 5·8%; if loss of a molecule of water occurred, between two molecules of acid, the composition would be C, 55·8; H, 4·6%.

UNIVERSITY COLLEGE, LONDON.

[*Received, October 5th,* 1934.]