

25. *Some Derivatives of tert.*-Butylbenzene.

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Space-filling atomic models can represent only with difficulty 2 : 6-di-substituted *tert.*-butylbenzenes, particularly if the substituents are halogen atoms. In the present paper a number of such compounds, *e.g.*, (V)—(VII), are described and their ready formation reflects clearly on the limitations of these models.

Further examples are provided of the displacement of a *tert.*-butyl group from the benzene nucleus during substitution experiments.

MANY have directed attention to steric hindrance effects associated with a *tert.*-butyl group in the benzene nucleus but little regard has been paid to the surprising *ease* with which substituents can be introduced into both of the positions *ortho* to this group. The papers of Carpenter, Easter, and Wood are rich in illustrations of this type of reaction. They have shown that a nitro-group can be introduced into position 6 of a *tert.*-butylbenzene with NO<sub>2</sub>, Me, Pr<sup>i</sup>, NH<sub>2</sub>, CN, OMe, or CHO already in position 2. With some types of space-filling models it is just possible to construct these molecules, but such models are unable to represent compound (I), which has been prepared both by Carpenter and Easter<sup>1</sup> and by Burgoyne, Klose, and Watson.<sup>2</sup> The aim of the present research was to prepare further examples of this stereochemically interesting type of compound.

First, use was made of the readily available 4-*tert.*-butyl-2 : 6-dinitrotoluene<sup>3</sup> to prepare 2-amino-6-nitro- and 2 : 6-diamino-4-*tert.*-butyltoluenes and their acetyl and toluene-*p*-sulphonyl derivatives. It was found that 3-*tert.*-butyl-6-methyl-5-nitro-*N*-toluene-*p*-sulphonylaniline (II) could be only monochlorinated and monobrominated; the diamide (III), also, could be only monobrominated but both the diamides (III) and (IV) were readily dichlorinated at the vacant positions.

Next it was found that 1 : 4-dibromo-2 : 5-di-*tert.*-butylbenzene<sup>4</sup> could be mononitrated. The product (V) is a compound of the desired type. Attempts to convert it into the amine were unsuccessful. 1 : 4-Di-*tert.*-butyl-2 : 5-di-iodobenzene, prepared from

<sup>1</sup> Carpenter and Easter, *J. Org. Chem.*, 1954, **19**, 77.

<sup>2</sup> Burgoyne, Klose, and Watson, *ibid.*, 1955, **20**, 1508.

<sup>3</sup> Brady and Lahiri, *J.*, 1934, 1954.

<sup>4</sup> Kofod, Kumar, and Sutton, *J.*, 1951, 1793.

1 : 4-diamino-2 : 5-di-*tert.*-butylbenzene, with nitric acid gave in fairly good yield 2 : 5-di-*tert.*-butyl-4-iodonitrobenzene, an iodine atom and not, as is usual in this series, a *tert.*-butyl group having undergone displacement. 1 : 4-Diamino-2 : 5-di-*tert.*-butylbenzene was converted by bromine in acetic acid into 2 : 5-di-*tert.*-butylbenzoquinone, but with *N*-bromosuccinimide in pyridine gave 2 : 5-di-*tert.*-butylbenzoquinone dibromodi-imide.

4-*tert.*-Butyl-3 : 5-dinitrobenzoic acid<sup>5</sup> was reduced to 3-amino-4-*tert.*-butyl-5-nitrobenzoic acid in good yield and from this diazo-reactions smoothly gave acids (VI) and (VII), which formed soluble sodium salts. Both these halogenated acids rapidly became red on exposure to light. An attempt was made to prepare the acid (VI) from 3-bromo-4-*tert.*-butylbenzoic acid (VIII), obtained by the bromination of 4-*tert.*-butylbenzoic acid; since this bromo-acid was not easily decarboxylated, it was oriented by conversion by the Hofmann reaction into the amine, whose acetyl derivative<sup>6</sup> (IX) is readily distinguished from the isomer (X) obtained in almost quantitative yield by bromination of 4-*tert.*-butylacetanilide.<sup>7</sup> The bromo-acid (VIII), on treatment with fuming nitric acid, gave two mononitro-derivatives, neither identical with (VI). Both yielded sparingly soluble sodium salts and were not particularly sensitive to light. Attempts to brominate 2- and 3-nitro-4-*tert.*-butylbenzoic acid either by bromine and an iron catalyst or by Derbyshire and Waters's method<sup>8</sup> were unsuccessful. The *tert.*-butyl-nitrobenzoic acids offer a ready source of *tert.*-butyl-nitrobenzenes and *tert.*-butyl-2 : 5- and -2 : 6-dinitrobenzenes are described in the Experimental part.

Next were examined derivatives of 2 : 5-di-*tert.*-butylaniline. Both the acetyl and the toluene-*p*-sulphonyl derivative could be monochlorinated. Continued action of sulphuryl chloride on the toluene-*p*-sulphonyl derivative resulted in displacement of a *tert.*-butyl group by chlorine to give the dichloro-compound (XI), alternatively prepared by chlorination of 3-*tert.*-butyl-*N*-toluene-*p*-sulphonylaniline. Similarly 4-bromo-2 : 5-di-*tert.*-butyl-*N*-toluene-*p*-sulphonylaniline suffered loss of a *tert.*-butyl group to give the amide (XII), alternatively prepared by bromination of 5-*tert.*-butyl-2-chloro-*N*-toluene-*p*-sulphonylaniline (XIII). 2 : 4-Dibromo-5-*tert.*-butyl-*N*-toluene-*p*-sulphonylaniline suffered no change with sulphuryl chloride.

Many examples are now known of the removal of the *tert.*-butyl group from the benzene nucleus in the course of substitution experiments and, indeed, the poor yields obtained in many simple reactions, *e.g.*, the less than 40% yield now recorded for the conversion of 4-*tert.*-butyl-2-nitroacetanilide into the dinitro-derivative, is in the main occasioned by side reactions involving displacement of the *tert.*-butyl group. The examples fall into two classes: (a) removal under the action of a reagent such as aluminium chloride<sup>9</sup> or hydrogen fluoride,<sup>10</sup> leaving hydrogen in the vacated position; and (b) removal by nitric acid,<sup>11</sup> bromine,<sup>12</sup> or sulphuryl chloride with entry of NO<sub>2</sub>, Br, or Cl respectively. In class (b) the replacement is favoured by the presence of a powerfully *ortho-para*-directing group, such as OH, OMe, or NH·SO<sub>2</sub>·C<sub>7</sub>H<sub>7</sub>, in the *ortho*- or *para*-position to the *tert.*-butyl group, and various mechanisms are possible. Robertson<sup>13</sup> has suggested that the *tert.*-butyl group separates as a positive ion; in other examples it has been possible to isolate quinonoid intermediates, *e.g.*, (XIV), which readily pass into the final products by expulsion of butylene. In others, *e.g.*, (XV), it appears probable that the replacement involves

<sup>5</sup> Bell, *J.*, 1956, 3243.

<sup>6</sup> Shoesmith and Mackie, *J.*, 1928, 2339.

<sup>7</sup> Crawford and Stewart, *J.*, 1952, 4447; Cadogan, Hey, and Williams, *J.*, 1954, 3357; de la Mare and Harvey, *J.*, 1957, 131.

<sup>8</sup> Derbyshire and Waters, *J.*, 1950, 573.

<sup>9</sup> Kulka, *J. Amer. Chem. Soc.*, 1954, **76**, 5469.

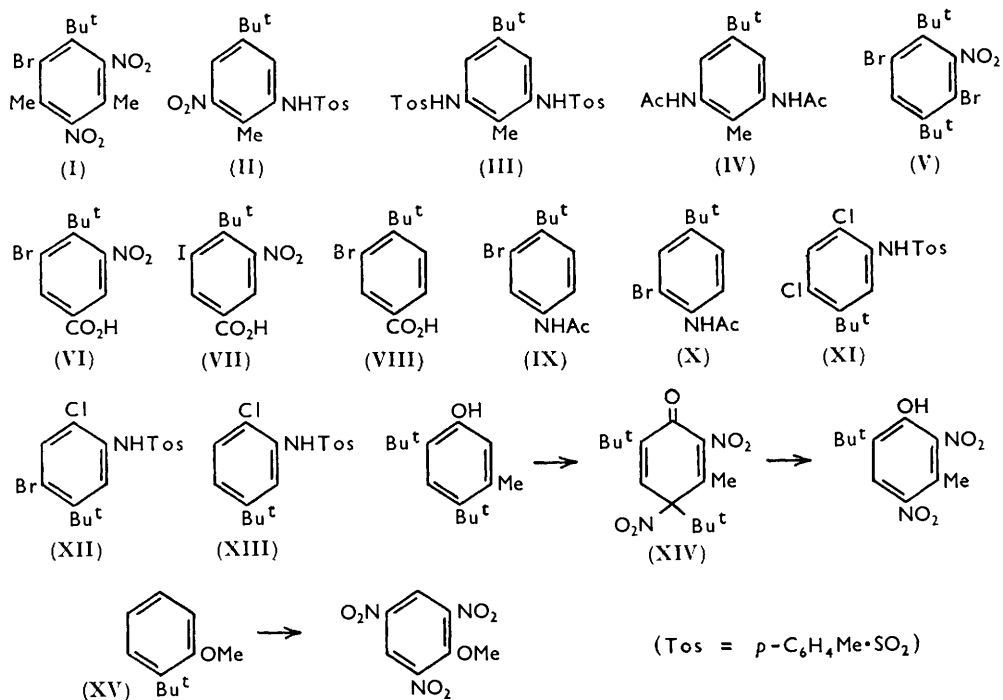
<sup>10</sup> Schlatter, *ibid.*, p. 4952.

<sup>11</sup> Albert and Sears, *ibid.*, p. 4979; Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, **16**, 586; Bell and Wilson, *J.*, 1956, 2340.

<sup>12</sup> Muller, Ley, and Kiedaisch, *Chem. Ber.*, 1954, **87**, 1605; Forman and Sears, *J. Amer. Chem. Soc.*, 1954, **76**, 4977; Bartlett, Roha, and Stiles, *ibid.*, p. 2349.

<sup>13</sup> Robertson, *Science Progr.*, 1955, 431.

formation of a transition complex under the action of the *ortho-para*-directing group, followed by abstraction of a proton from the *tert.*-butyl group, which is then expelled as butylene.



Bartlett, Roha, and Stiles<sup>12</sup> obtained, by bromination of 2 : 5-di-*tert.*-butylaniline, a dibromo-derivative, which crystallised from ethanol in pale pink prisms, m. p. 256° (decomp.). This would of necessity be the 4 : 6-dibromo-compound, in which a *tert.*-butyl group is flanked by two bromine atoms. Repetition of this experiment gave the readily soluble monobromo-derivative, m. p. 90°, and its hydrobromide together with a very small yield of a compound which was only slightly soluble in the ordinary organic solvents even at the boiling point. After recrystallisation from *o*-dichlorobenzene it had m. p. 266° and sublimed with only slight decomposition. It appears to be isomeric with the monobromo-base, but is not attacked by acetic anhydride even in the presence of sulphuric acid and is characterised by a splendid crimson colour in concentrated sulphuric acid.

A somewhat similar behaviour is shown by 3-*tert.*-butylaniline, which can be smoothly monobrominated but on dibromination yields an oily dibromo-base together with a very small amount of another dibromo-compound, which crystallises from *o*-dichlorobenzene in pale red prisms, m. p. 222—226°. This compound also is not attacked by acetic anhydride and gives a crimson solution in concentrated sulphuric acid.

#### EXPERIMENTAL

Chlorination, unless otherwise stated, was brought about by heating the compound with excess of sulphuryl chloride, removing the excess, and recrystallising the residue from acetic acid.

*2-Amino-4-tert.-butyl-6-nitrotoluene.*—Sodium sulphide (25 g.) in water (50 c.c.) was added to a boiling solution of 4-*tert.*-butyl-2 : 6-dinitrotoluene (10 g.) in ethanol (60 c.c.). The resultant solution was poured into water, and the precipitate extracted with boiling dilute hydrochloric

acid to yield a crude hydrochloride, which was used to prepare 2-acetamido-4-*tert.*-butyl-6-nitrotoluene, which crystallised from ethanol in straw-coloured needles, m. p. 139° (Found: C, 62.3; H, 6.7.  $C_{13}H_{18}O_3N_2$  requires C, 62.4; H, 7.2%), and 3-*tert.*-butyl-6-methyl-5-nitro-N-toluene-*p*-sulphonylaniline (II), which crystallised from acetic acid in prisms, m. p. 176° (Found: C, 60.0; H, 6.0.  $C_{18}H_{22}O_4N_2S$  requires C, 59.6; H, 6.1%).

*Bromination of 3-tert.-Butyl-6-methyl-5-nitro-N-toluene-p-sulphonylaniline.*—Excess of *N*-bromosuccinimide was added to the compound dissolved in pyridine and, after a short time, the mixture was decomposed by dilute hydrochloric acid. The precipitate on crystallisation from acetic acid gave a *monobromo-derivative* as prisms, m. p. 199° (Found: C, 49.1; H, 4.7.  $C_{18}H_{21}O_4N_2SBr$  requires C, 49.0; H, 4.8%).

*Chlorination of 3-tert.-Butyl-6-methyl-5-nitro-N-toluene-p-sulphonylaniline.*—Boiling for 1 hour with sulphuryl chloride gave the *monochloro-derivative*, which formed prisms, m. p. 193° (Found: C, 55.2; H, 5.2.  $C_{18}H_{21}O_4N_2SCl$  requires C, 54.5; H, 5.3%).

2 : 6-Diamino-4-*tert.*-butyltoluene.—Stannous chloride (33 g.) in concentrated hydrochloric acid (35 c.c.) was added slowly to a boiling solution of 4-*tert.*-butyl-2 : 6-dinitrotoluene (5 g.) in ethanol (50 c.c.). After  $\frac{1}{2}$  hr. the ethanol was distilled off, and the residue made strongly alkaline and extracted with ether. The semisolid residue left after evaporation of the ether was recrystallised from aqueous methanol, to yield the *diamine* in plates, m. p. 98° (Found: C, 73.7; H, 10.2.  $C_{11}H_{18}N_2$  requires C, 74.2; H, 10.1%). This gave with acetic anhydride 2 : 6-diacetamido-4-*tert.*-butyltoluene (IV), which crystallised from ethanol in needles, m. p. 302—304° (Found: C, 68.6; H, 8.2.  $C_{15}H_{22}O_2N_2$  requires C, 68.7; H, 8.4%), and with toluene-*p*-sulphonyl chloride 4-*tert.*-butyl-2 : 6-ditoluene-*p*-sulphonamidotoluene (III), which crystallised from acetic acid in prisms, m. p. 212° (Found: C, 62.1; H, 6.4.  $C_{25}H_{30}O_4N_2S_2$  requires C, 61.7; H, 6.2%). The latter with excess of *N*-bromosuccinimide in pyridine gave a *monobromo-derivative*, which crystallised from acetic acid in prisms, m. p. 217—220° (Found: C, 52.9; H, 5.3; Br, 14.8.  $C_{25}H_{29}O_4N_2S_2Br$  requires C, 53.1; H, 5.1; Br, 14.2%).

2 : 6-Diacetamido-4-*tert.*-butyltoluene gave a *dichloro-derivative*, prisms, m. p. 267° (Found: C, 54.3; H, 6.0.  $C_{15}H_{20}O_2N_2Cl_2$  requires C, 54.4; H, 6.0%), which with acetic anhydride and sulphuric acid gave the *tetra-acetyl derivative*, which formed needles, m. p. 216°, from acetic acid (Found: Cl, 17.6.  $C_{19}H_{24}O_4N_2Cl_2$  requires Cl, 17.1%).

4-*tert.*-Butyl-2 : 6-ditoluene-*p*-sulphonamidotoluene gave a *dichloro-derivative*, needles, m. p. 220—222° (Found: C, 54.1; H, 5.1.  $C_{25}H_{28}O_4N_2S_2Cl_2$  requires C, 54.1; H, 5.1%). This was hydrolysed by solution in cold sulphuric acid to the base, which with acetic anhydride and sulphuric acid gave the tetra-acetyl derivative, m. p. 216° (see above). The mother-liquor from the chlorination gave a *trichloro-derivative*, which formed prisms, m. p. 169—171° (Found: C, 50.5; H, 4.3.  $C_{25}H_{27}O_4N_2S_2Cl_3$  requires C, 50.9; H, 4.6%), and contained reactive chlorine. It was readily converted by zinc dust in acetic acid into an impure *monochloro-derivative*, which formed prisms, m. p. 220—222°, from acetic acid (Found: C, 58.4; H, 5.6; Cl, 6.1.  $C_{22}H_{29}O_4N_2S_2Cl$  requires C, 57.6; H, 5.6; Cl, 6.8%). This was alternatively prepared by the addition of sulphuryl chloride (1 mol.) to a suspension of 4-*tert.*-butyl-2 : 6-ditoluene-*p*-sulphonamidotoluene in warm chloroform and concentration of the resultant solution.

*Nitration of 1 : 4-Dibromo-2 : 5-di-tert.-butylbenzene.*—(a) The compound (10 g.) was added to a mixture of fuming nitric acid (10 c.c.) and sulphuric acid (40 c.c.) and left for 2 days. The product was filtered off, washed with water and dilute aqueous ammonia, and recrystallised from acetone and then ethanol to yield the *mononitro-derivative* (V) (6 g.) as prisms, m. p. 129° (Found: C, 43.0; H, 4.8; N, 3.7.  $C_{14}H_{19}O_2NBr_2$  requires C, 42.7; H, 4.8; N, 3.6%). (b) The compound (1 g.) was introduced into fuming nitric acid (4 c.c.) and after a short time the mixture was poured on ice. The above mononitro-compound was obtained in inferior yield together with much material, m. p. 87—90°, easily soluble in cold light petroleum.

Attempted reduction of this nitro-compound by addition of stannous chloride in hydrochloric acid to a boiling ethanolic solution was unsuccessful. Long boiling in ethanol with iron powder or treatment in ethanol with sodium amalgam led to no definite products.

3-Amino-4-*tert.*-butyl-5-nitrobenzoic Acid.—4-*tert.*-Butyl-3 : 5-dinitrobenzoic acid (18 g.) was dissolved in water (120 c.c.) containing concentrated ammonia solution (18 c.c.), warmed to 50°, and saturated with hydrogen sulphide. The solution was evaporated to half-bulk, then filtered from sulphur, and the filtrate was faintly acidified with acetic acid. The crystalline crop (12 g.) was recrystallised from aqueous ethanol, to give 3-amino-4-*tert.*-butyl-5-nitrobenzoic acid as prisms, m. p. 230° (slight decomp.) (Found: C, 56.0; H, 5.7.  $C_{11}H_{14}O_4N_2$  requires

C, 55.5; H, 5.9%). With acetic anhydride and sulphuric acid it gave an *acetyl derivative*, which crystallised from acetic acid in needles, m. p. 253—255° (Found: C, 55.6; H, 5.9.  $C_{13}H_{16}O_6N_2$  requires C, 55.7; H, 5.7%).

*3-Bromo-4-tert.-butyl-5-nitrobenzoic Acid.*—The diazonium solution prepared by pouring 3-amino-4-*tert.*-butyl-5-nitrobenzoic acid (5 g.) mixed with sulphuric acid (15 c.c.) and sodium nitrite (1.5 g.) on ice was filtered into a solution of cuprous bromide in hydrobromic acid. The resultant precipitate was dissolved in dilute aqueous sodium hydroxide, reprecipitated by hydrochloric acid, and crystallised from acetic acid. *3-Bromo-4-tert.-butyl-5-nitrobenzoic acid* was obtained as almost colourless prisms, m. p. 238—241°, which rapidly became red on exposure to light (Found: C, 43.6; H, 4.0.  $C_{11}H_{12}O_4NBr$  requires C, 43.7; H, 4.0%). The m. p. was considerably depressed on admixture with the acid, m. p. 240—242°, obtained by nitration of 3-bromo-4-*tert.*-butylbenzoic acid (cf. below). By treatment with thionyl chloride followed by aniline the acid was converted into *3-bromo-4-tert.-butyl-5-nitrobenzanilide*, which formed plates, m. p. 193—194°, from acetic acid (Found: C, 54.9; H, 4.4.  $C_{17}H_{17}O_3N_2Br$  requires C, 54.1; H, 4.5%).

*4-tert.-Butyl-3-iodo-5-nitrobenzoic acid*, obtained by pouring the diazonium solution prepared as for the corresponding bromo-acid into potassium iodide solution, it crystallised from acetic acid in prisms, m. p. 229—232°, which rapidly became red on exposure to light (Found: C, 38.3; H, 3.6.  $C_{11}H_{12}O_4NI$  requires C, 37.8; H, 3.4%).

*3-Bromo-4-tert.-butylbenzoic Acid.*—(a) Silver nitrate (27 g.) in water (90 c.c.) was added to a well-stirred mixture of 4-*tert.*-butylbenzoic acid (27 g.), acetic acid (600 c.c.), concentrated nitric acid (90 c.c.), and bromine (7.8 c.c.). Then stirring was continued for  $\frac{1}{2}$  hr., and the mixture heated almost to boiling, filtered hot, and diluted until crystals began to appear. The crop (about 16 g.; m. p. *ca.* 170°) was recrystallised from a small bulk of acetic acid to give *3-bromo-4-tert.-butylbenzoic acid* as needles, m. p. 179° (Found: C, 51.6; H, 5.0%; equiv., 258.  $C_{11}H_{13}O_2Br$  requires C, 51.4; H, 5.1%; equiv., 257). (b) A mixture of *p-tert.*-butylbenzoic acid (20 g.), bromine (12 c.c.) and iron powder (1.5 g.) was gently warmed for 6 hr. and the product suspended in boiling water (300 c.c.) and treated with excess of aqueous ammonia. Ferric hydroxide was filtered off and the bromo-acid, recovered from the filtrate by precipitation with hydrochloric acid, was purified by recrystallisation from acetic acid.

*3-Bromo-4-tert.-butylbenzoic acid* was dissolved by warming with a slight excess of thionyl chloride, and the product distilled. Almost the whole distilled at 170°/30 mm. and set to a mass of needles, m. p. 60—61°. This material was dissolved in a little dry ether and the solution stirred into ammonia solution (*d* 0.88), brisk reaction occurring with precipitation of the amide, m. p. 123°. This (8 g.), without further purification, was added to a solution of sodium hypobromite prepared from sodium hydroxide (12 g.) and bromine (3 c.c.). A clear solution was first obtained which soon became cloudy (evolution of nitrogen and rise in temperature). The resultant 3-bromo-4-*tert.*-butylaniline was removed in steam [alternatively it may be extracted with hot dilute hydrochloric acid, which on cooling deposits the hydrochloride in needles, m. p. 242° (decomp.)] and acetylated, to give 3-bromo-4-*tert.*-butylacetanilide, which crystallised from ethanol in fine needles, m. p. 144° (Shoosmith and Mackie<sup>6</sup> give m. p. 142—143°). The latter was quite different from 2-bromo-4-*tert.*-butylacetanilide, prepared by the addition of bromine (1 mol.) to *p-tert.*-butylacetanilide (12 g.) suspended in acetic acid (40 c.c.). After recrystallisation from ethanol it formed plates, m. p. 159° (Found: C, 53.7; H, 5.8. Calc. for  $C_{12}H_{16}ONBr$ : C, 53.3; H, 5.9%) (lit.,<sup>7</sup> m. p. 138.5°, 138°, 158°). The acetyl derivative was hydrolysed in ethanol with concentrated hydrochloric acid, and the resultant base, b. p. 150°/20 mm., reacylated, giving plates, m. p. 159°, and converted also into the *toluene-p-sulphonyl derivative*, which crystallised from acetic acid in needles, m. p. 111° (Found: C, 53.2; H, 5.3.  $C_{17}H_{20}O_2NSBr$  requires C, 53.4; H, 5.2%).

*Nitration of 3-Bromo-4-tert.-butylbenzoic Acid.*—The powdered acid (5 g.) was added slowly to fuming nitric acid (50 c.c.) cooled in ice, and the mixture poured into ice-cold water. The resultant plastic mass was induced to solidify by rubbing it with acetic acid, and the product (2.7 g.; m. p. *ca.* 150°) was purified by extraction with light petroleum, which left undissolved material (0.5 g.) of m. p. *ca.* 220°, and gave a crop, m. p. 157—168°. Both fractions were purified by recrystallisation from acetic acid and gave respectively needles, m. p. 240—242° (Found: C, 43.2; H, 3.7.  $C_{11}H_{12}O_4NBr$  requires C, 43.7; H, 4.0; N, 4.6%), and prisms, m. p. 170—172° (Found: C, 43.9; H, 3.6; N, 4.4%). Both of these *acids* formed sparingly soluble sodium salts, which could be readily recrystallised from boiling dilute sodium hydroxide solution.

The acid, m. p. 170—172°, gave an *anilide*, which crystallised from acetic acid in needles, m. p. 219—221° (Found: C, 54.5; H, 4.4.  $C_{17}H_{17}O_3N_2Br$  requires C, 54.1; H, 4.5%). The other acid gave an *anilide*, which crystallised from acetic acid in plates, m. p. 205° (Found: C, 53.9; H, 4.2%).

2 : 5-*Di-tert.-butylacetanilide*, prepared from 2 : 5-*di-tert.-butylaniline*, formed plates, m. p. 156°, from ethanol (Found: C, 77.7; H, 9.9.  $C_{16}H_{26}ON$  requires C, 77.8; H, 10.1%). It yielded a *monochloro-derivative*, which formed plates, m. p. 185°, from ethanol (Found: C, 68.4; H, 8.4.  $C_{16}H_{24}ONCl$  requires C, 68.2; H, 8.6%).

*Chlorination of 2 : 5-Di-tert.-butyl-N-toluene-p-sulphonylaniline.*—(a) Chlorine (1 mol.) was passed into a solution of the compound in cold chloroform, and the solution concentrated and diluted with light petroleum. The crop on crystallisation from acetic acid gave the 4-*chloro-derivative* in fine needles, m. p. 170° (Found: C, 64.5; H, 7.2.  $C_{21}H_{28}O_2NSCl$  requires C, 64.0; H, 7.1%); it was unchanged after treatment with *N*-bromosuccinimide in pyridine solution. (b) Sulphuryl chloride gave 5-*tert.-butyl-2 : 4-dichloro-N-toluene-p-sulphonylaniline* (XI) as needles, m. p. 150° (Found: C, 55.0; H, 5.0; Cl, 19.2.  $C_{17}H_{19}O_2NSCl_2$  requires C, 54.8; H, 5.1; Cl, 19.1%), identical with the product of chlorination of 3-*tert.-butyl-N-toluene-p-sulphonylaniline*. After being kept overnight in concentrated sulphuric acid this compound gave an oily base, which with acetic anhydride gave 5-*tert.-butyl-2 : 4-dichloroacetanilide*, m. p. 120—122° (Found: C, 55.3; H, 5.3.  $C_{12}H_{15}ONCl_2$  requires C, 55.4; H, 5.8%).

4-Bromo-2 : 5-*di-tert.-butyl-N-toluene-p-sulphonylaniline* gave 4-*bromo-5-tert.-butyl-2-chloro-N-toluene-p-sulphonylaniline* (XII) as needles, m. p. 140° [Found: C, 49.7; H, 4.8.  $C_{17}H_{19}O_2NSBrCl$  requires C, 49.0; H, 4.6%; 5.179 mg. gave 4.146 mg. of silver halides (theor., 4.122 mg.)], identical with a sample synthesised in the following way. 4-*tert.-Butyl-2-nitroaniline* was diazotised in concentrated sulphuric acid and converted by the Sandmeyer process into 4-*tert.-butyl-1-chloro-2-nitrobenzene*, which was distilled in steam. The resultant oil, without further purification, was reduced in boiling ethanol by stannous chloride in concentrated hydrochloric acid and the base, after distillation in steam, converted directly into 5-*tert.-butyl-2-chloro-N-toluene-p-sulphonylaniline*, which crystallised from acetic acid in flat needles, m. p. 143° (Found: C, 60.5; H, 5.7.  $C_{17}H_{20}O_2NClS$  requires C, 60.4; H, 5.9%). This with *N*-bromosuccinimide in pyridine was converted almost quantitatively into the 4-bromo-derivative, m. p. 140° (cf. above).

2-Bromo-5-*tert.-butyl-N-toluene-p-sulphonylaniline* gave a *monochloro-derivative* as needles, m. p. 158—160° (Found: C, 48.9; H, 4.5.  $C_{17}H_{19}O_2SBrCl$  requires C, 49.0; H, 4.6%).

4-*tert.-Butyl-3 : 5-dinitrobenzoic acid* with quinoline and copper at 200° gave in good yield 2-*tert.-butyl-1 : 3-dinitrobenzene*, readily volatile in steam and crystallising from ethanol in plates, m. p. 106° (Found: N, 12.8.  $C_{10}H_{12}O_4N_2$  requires N, 12.5%). Similarly, 4-*tert.-butyl-2 : 5-dinitrobenzoic acid* gave 2-*tert.-butyl-1 : 4-dinitrobenzene*, also easily volatile in steam and crystallising from ethanol in needles, m. p. 98° (Found: N, 12.6%). A mixture of the two isomerides melted below 80°.

4-*tert.-Butyl-2 : 6-dinitroaniline.*—4-*tert.-Butyl-2-nitroacetanilide* (11 g.) was introduced slowly into fuming nitric acid (50 c.c.) cooled in ice, and the resultant solution poured into iced water. The sticky precipitate, recrystallised from ethanol, gave 4-*tert.-butyl-2 : 6-dinitroacetanilide* as yellow needles, m. p. 132° (4.3 g.) (Found: N, 15.3.  $C_{12}H_{15}O_6N_3$  requires N, 14.9%). This was hydrolysed in ethanol by aqueous potassium hydroxide to give in poor yield the corresponding base; a considerable amount of alkali-soluble material was produced at the same time. The 4-*tert.-butyl-2 : 6-dinitroaniline* was purified by distillation in steam, followed by crystallisation from ethanol, and formed bright yellow, flat needles, m. p. 130° (Found: C, 49.5; H, 5.5; N, 17.1.  $C_{10}H_{13}O_4N_3$  requires C, 50.2; H, 5.4; N, 17.6%). The base was unchanged after treatment with toluene-*p*-sulphonyl chloride in pyridine but was readily acetylated by acetic anhydride in presence of sulphuric acid.

*Bromination of 2 : 5-Di-tert.-butylaniline.*—The method of Bartlett, Roha, and Stiles<sup>12</sup> gave a black oil, which was dissolved in ethanol and allowed to cool. The small reddish residue was very sparingly soluble in boiling ethanol or acetone but recrystallised from ethyl acetate or *o*-dichlorobenzene in pale red prisms, m. p. 262—266° (Found: C, 59.0; H, 7.1; N, 4.6; Br, 27.7.  $C_{14}H_{22}NBr$  requires C, 59.1; H, 7.7; N, 4.9; Br, 28.2%).

*Bromination of 3-tert.-Butylaniline.*—When bromine or *N*-bromosuccinimide (1—3 mols.) was added to the base in pyridine there was always produced in very small amount a compound which was readily isolated owing to its very small solubility. This after recrystallisation

from *o*-dichlorobenzene formed red prisms, m. p. 222—226° (Found: C, 40.1; H, 3.7; N, 4.6; Br, 51.8.  $C_{10}H_{13}NBr_2$  requires C, 39.1; H, 4.2; N, 4.6; Br, 52.1%).

1 : 4-Diamino-2 : 5-di-*tert*-butylbenzene.—Stannous chloride (49 g.) in hydrochloric acid (60 c.c.) was added to a boiling suspension of 2 : 5-di-*tert*-butyl-1 : 4-dinitrobenzene (11.4 g.) in ethanol (150 c.c.). The momentarily clear solution soon deposited crystals, which were filtered off and decomposed by aqueous sodium hydroxide, and the product was dried and extracted with boiling benzene. On cooling, the extract deposited the *diamine* as rosettes, m. p. 172—173° (Found: C, 76.0; H, 10.3.  $C_{14}H_{24}N_2$  requires C, 76.4; H, 10.9%). On addition of bromine (2 mols.) in acetic acid to a cold solution of the diamine in acetic acid there was obtained 2 : 5-di-*tert*-butylbenzoquinone, which crystallised from ethanol in yellow needles, m. p. 153° (Found: C, 76.5; H, 8.8. Calc. for  $C_{14}H_{20}O_2$ : C, 76.4; H, 9.1%). This quinone was unchanged after treatment with sulphur dioxide in boiling 80% ethanol.

By addition of *N*-bromosuccinimide (2 mols.) to the diamine in pyridine there was obtained 2 : 5-di-*tert*-butylbenzoquinone *dibromodi-imide* which crystallised from ethanol in yellow plates, m. p. 121° (Found: C, 45.4; H, 5.0; Br, 41.7.  $C_{14}H_{20}N_2Br_2$  requires C, 44.7; H, 5.3; Br, 42.5%).

The diamine was diazotised either in concentrated sulphuric acid or by Hodgson and Walker's method<sup>14</sup> and the diazonium solution, filtered from much 2 : 5-di-*tert*-butylbenzoquinone, poured into potassium iodide solution. 1 : 4-Di-*tert*-butyl-2 : 5-di-iodobenzene was precipitated and after repeated recrystallisation from ethanol formed needles, m. p. 138° (Found: C, 37.8; H, 4.7; I, 57.2.  $C_{14}H_{20}I_2$  requires C, 38.0; H, 4.5; I, 57.5%). The author is indebted to Dr. K. R. Buck for the following observation, "The dipole moment of this di-iodo-compound measured in dilute solution in benzene is, owing to the insensitivity of the method in the range 0—0.6 D, not clearly distinguishable from zero (cf. Kofod, Kumar, and Sutton<sup>4</sup>)."

A mixture of the di-iodo-compound (0.75 g.), fuming nitric acid (0.75 c.c.), and sulphuric acid (3 c.c.) was left for 2 days, then filtered (the filtrate on dilution deposited iodine). The sticky product was dissolved in a little acetone and the filtered solution diluted, giving a crop, m. p. 90—95°. This material after two recrystallisations from ethanol gave 1 : 4-di-*tert*-butyl-2-iodo-5-nitrobenzene as needles, m. p. 97° (Found: C, 46.4; H, 5.4.  $C_{14}H_{20}O_2NI$  requires C, 46.5; H, 5.5%).

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<sup>14</sup> Hodgson and Walker, *J.*, 1935, 530.