

### 196. 4-Nitro-2,6-di-*t*-butylphenol and its Thermal Decomposition.

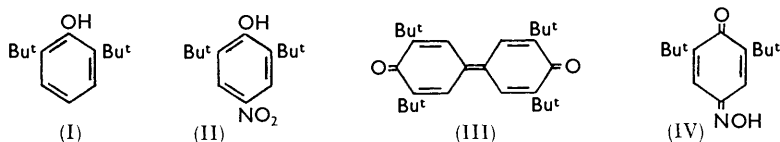
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2,6-Di-*t*-butylphenol can be nitrated at position 4 in acetic acid solution by nitric acid. Other products are 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone and 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl with some 2,6-di-*t*-butyl-1,4-benzoquinone.

When heated, the nitrophenol decomposes into nitric oxide, 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone, 2,6-di-*t*-butyl-1,4-benzoquinone 4-oxime, and water.

Other reactions resulting in the elimination of the nitro-group of the nitrophenol are reported.

PREVIOUS attempts to nitrate 2,6-di-*t*-butylphenol (I) resulted either in oxidation to 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone<sup>1</sup> (III) or in the expulsion of a *t*-butyl-group with the formation of 2,4-dinitro-6-*t*-butylphenol.<sup>2</sup> It is now shown that, by attention to detail, mononitration of the phenol can be achieved; \* the yield of 4-nitro-2,6-di-*t*-butylphenol (II) is about 30%, the remainder of the product being 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone (III) and 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl with some 2,6-di-*t*-butyl-1,4-benzoquinone.



The reactions of the nitrophenol (II) are unusual: it gives the Liebermann nitroso-test; it decomposes on being heated into the diphenoquinone (III), nitric oxide, and water; it is hydrolysed by sulphuric acid to 2,6-di-*t*-butyl-1,4-benzoquinone and its

\* After this paper had been completed we learnt that Dr. K. U. Ingold has also prepared 4-nitro-2,6-di-*t*-butylphenol by nitration of 2,6-di-*t*-butylphenol, and that he has hydrogenated it to the aminophenol.

<sup>1</sup> (a) Kharasch and Joshi, *J. Org. Chem.*, 1957, **22**, 1439; (b) Bachman and Dever, *J. Amer. Chem. Soc.*, 1958, **80**, 5871.

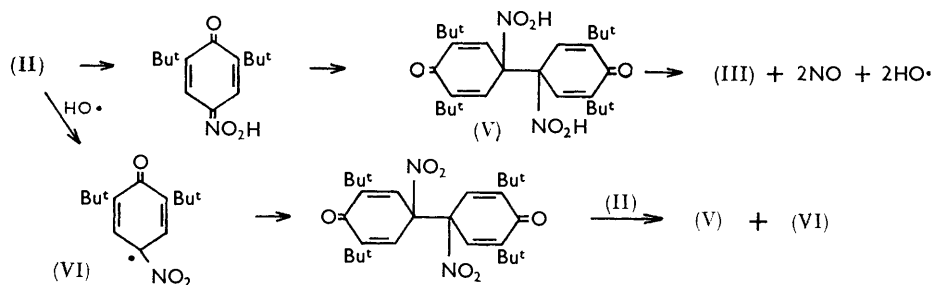
<sup>2</sup> Hart and Cassis, *J. Amer. Chem. Soc.*, 1951, **73**, 3179.

mono-oxime (IV), and is converted by zinc and acetic acid into 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl.

Nevertheless, the evidence in support of its nitrophenol structure is conclusive. (a) It is hydrogenated to an aminophenol and this can be diazotised or oxidised (to 2,6-di-*t*-butyl-1,4-benzoquinone), and has been characterised by its *N*-acetyl derivative. The structure assigned to this acetyl compound is supported by infrared bands at 2.77 (free phenolic OH), 3.03, 6.47, 7.64 (secondary amido-group), 6.03 ( $>C=O$ ), and 5.7  $\mu$  (aromatic nucleus having 1,2,3,5-substituents). (b) The infrared spectrum (potassium chloride disc) has strong bands at 6.62 and 7.55 ( $>C:NO_2$ ), a sharp band at 2.80 (free OH), and a pattern of two bands in the 5.5  $\mu$  region consistent with two non-adjacent ring hydrogen atoms. (c) The hydrogen resonance spectrum (in carbon disulphide) has three bands with  $\tau$  values of 8.54, 4.37, and 3.57, due to *t*-butyl, phenolic, and aromatic hydrogen respectively.

For comparison, 2,6-di-*t*-butyl-4-nitrosophenol was prepared by the action of nitrous acid on 2,6-di-*t*-butylphenol under conditions controlled to minimise oxidation. Oxidation of the nitrosophenol by alkaline ferricyanide gives the nitrophenol (II), in poor yield, with considerable amounts of diphenoquinone (III) and the monoquinone. The nitrophenol (II) is oxidised by hot alkaline ferricyanide to the diquinone (III).

The unusual reactions of the nitrophenol (II) may be ascribed to the presence of 2,6-substituents: a number of 2,6-disubstituted 4-nitrophenols decompose when heated.<sup>3</sup> The only serious investigation is by Jones and Kenner<sup>3a</sup> who established that nitric oxide is evolved when a number of 2,6-disubstituted 4-nitrophenols are heated alone or in acetic acid. The identification of the non-gaseous products of the decomposition was less satisfactory; a 2,6-disubstituted 1,4-benzoquinone was recognised as a product of the decomposition of some nitrophenols and it was suggested that a diphenoquinone was also formed from two of these.



In this paper it is shown that 4-nitro-2,6-di-*t*-butylphenol (II) decomposes thermally in dodecane to give nitric oxide, water, the diphenoquinone (III), and a small amount of the mono-oxime of 2,6-di-*t*-butyl-1,4-benzoquinone (IV). The formation of the diphenoquinone strongly suggests a free-radical mechanism and this view is supported by the behaviour of the nitrophenol (II) in acid solution: 2,6-di-*t*-butyl-1,4-benzoquinone and its mono-oxime are formed under these conditions. The above scheme based on a free-radical mechanism provides a satisfactory explanation of the course of the decomposition.

#### EXPERIMENTAL

*Nitration of 2,6-Di-t-butylphenol.*—A mixture of nitric acid (*d* 1.5; 4.71 g.) and acetic acid (15 c.c.) was added dropwise during 15 min. to a stirred solution of 2,6-di-*t*-butylphenol (15.45 g.) in acetic acid (100 c.c.) at 0–5°. A brown solid began to separate in the later stages of the nitration. The mixture was poured into an excess of water (1 l.) about 20 min. after all the nitric acid had been added, and the resulting suspension was made alkaline by the gradual

<sup>3</sup> (a) Armstrong and Brown, *Ber.*, 1874, **7**, 926; (b) Post, *Annalen*, 1880, **205**, 91; (c) Perkin and Mackenzie, *J.*, 1892, **61**, 869; (d) Fries and Oehmke, *Annalen*, 1928, **462**, 1; (e) Jones and Kenner, *J.*, 1931, 1842.

addition of solid sodium hydroxide. There remained undissolved a brown solid (A). The greenish-yellow aqueous alkaline solution (B) contained the nitrophenol (II).

2,3',5,5'-Tetra-*t*-butyl-4,4'-diphenoquinone (III) was obtained from the solid (A) by crystallisation from alcohol. From the more soluble fractions of this crystallisation 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl (VII) and 2,6-di-*t*-butyl-1,4-benzoquinone were isolated by fractional precipitation with water and then further crystallisation.

The benzoquinone was isolated more conveniently by steam-distillation of material (A).

4-Nitro-2,6-di-*t*-butylphenol (II), precipitated from solution (B) by careful addition of an excess of hydrochloric acid, crystallises from alcohol or light petroleum (b. p. 100—120°) as pale yellow plates or needles, m. p. 157.5° (decomp.) (Found: C, 66.9; H, 8.2; N, 5.5.  $C_{14}H_{21}NO_3$  requires C, 66.9; H, 8.4; N, 5.6%). The  $\alpha$ -naphthylurethane was prepared by heating the compound at 100° with  $\alpha$ -naphthyl isocyanate and a little pyridine; it had m. p. 200° (decomp.) (Found: C, 71.7; H, 6.6; N, 6.7.  $C_{25}H_{28}N_2O_4$  requires C, 71.4; H, 6.7; N, 6.7%).

3,3,5,5-Tetra-*t*-butyl-4,4'-diphenoquinone, red needles (from alcohol), m. p. 246—247.5° (Hart and Cassis<sup>2</sup> give m. p. 245—247°) (Found: C, 82.1; H, 9.8. Calc. for  $C_{28}H_{40}O_2$ : C, 82.3; H, 9.9%) was identified by comparison (infrared and mixed m. p.) with a sample from another source. It is reduced by zinc dust in hot acetic acid to 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl, m. p. 185—185.5° (Kharasch and Joshi<sup>1a</sup> give m. p. 185°) (Found: C, 81.7; H, 10.25. Calc. for  $C_{28}H_{42}O_2$ : C, 81.9; H, 10.3%), identical (infrared and mixed m. p.) with that isolated directly after nitration of 2,6-di-*t*-butylphenol (Found: C, 82.2; H, 10.1%). This phenol is readily oxidised to the diphenoquinone, even when boiled with decolorising charcoal in alcohol.

2,6-Di-*t*-butyl-1,4-benzoquinone formed deep yellow needles (from aqueous alcohol), m. p. 66—67° (Metro<sup>4</sup> gives m. p. 65—66°) (Found: C, 76.2; H, 9.2. Calc. for  $C_{14}H_{20}O_2$ : C, 76.3; H, 9.15%) [2,4-dinitrophenylhydrazone, yellow needles (from alcohol), m. p. 201° (Metro<sup>4</sup> gives m. p. 198—200°)]. Yields from the nitration were: (II) 36, (III) 42, (VII) 20, and the benzoquinone 2%.

*Reactions of 4-Nitro-2,6-di-t-butylphenol.*—(a) *Various.* The nitrophenol in concentrated sulphuric acid gives a bright green solution which slowly becomes brown, with evolution of sulphur dioxide. From this brown solution, 2,6-di-*t*-butyl-1,4-benzoquinone oxime (IV) was isolated by dilution with water and extraction with ether. It was identified by its infrared spectrum and mixed m. p.

The nitrophenol (0.1 g.) was boiled in acetic acid (3 c.c.) containing aqueous (60%) sulphuric acid; 2,6-di-*t*-butyl-1,4-benzoquinone was then isolated by neutralisation with sodium carbonate and extraction with ether, forming yellow needles, m. p. and mixed m. p. 67° (yield 68%) (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 200.5°).

When the nitrophenol is heated in acetic acid with nitric acid (*d* 1.5) at 65—70° the solution becomes paler and nitrous fumes are evolved; picric acid, m. p. and mixed m. p. 122°, is formed.

The nitrophenol was recovered unchanged on acidification after its alkaline solution had been boiled for 10 min.

(b) *Reduction.* (i) Hydrogenation of the nitrophenol (2 g.) at 3½ atm. in ethyl acetate (150 c.c.) containing platonic oxide (0.3 g.) gave a colourless solution after 10 hr. On exposure to air, it changed through olive-green to red. A portion of this solution, evaporated to dryness, left a red tar out of which grew yellow needles during 2 months. These were identified as 2,6-di-*t*-butyl-1,4-benzoquinone (mixed, m. p. and infrared spectrum) (Found: C, 76.4; H, 9.25. Calc. for  $C_{14}H_{20}O_2$ : C, 76.3; H, 9.15%).

Another portion of the hydrogenated product, diluted with acetic acid, was added to nitrosylsulphuric acid in sulphuric acid. On treatment with alkaline  $\beta$ -naphthol a red-brown precipitate was obtained having the character of an azo-compound; it gave a purple colour with sulphuric acid, discharged by dilution with water.

The remainder of the hydrogenated solution (45 c.c.) was mixed with acetic anhydride (10 c.c.) and kept overnight. The dark tar resulting on evaporation was extracted with light petroleum (b. p. 60—80°), to give 4-acetamido-2,6-di-*t*-butylphenol, pale cream prisms, m. p. 170—170.5° (from aqueous alcohol) (Found: C, 72.75; H, 9.7; N, 5.4.  $C_{16}H_{25}NO_2$  requires C, 73.0; H, 9.6; N, 5.3%).

<sup>4</sup> Metro, *J. Amer. Chem. Soc.*, 1955, **77**, 2901.

(ii) The nitrophenol was also reduced when heated with an excess of cyclohexene and palladium-charcoal for 20 hr. under reflux.<sup>5</sup> The resulting aminophenol was identified by its *N*-acetyl derivative, m. p. and mixed m. p. 170-5°.

(iii) A solution of the nitrophenol (0.5 g.) in glacial acetic acid (15 c.c.) was refluxed for  $\frac{1}{2}$  hr. with zinc dust (0.1 g.). Nitrous fumes were evolved in the early stages and the colour, initially yellow, was rapidly discharged, then changed to red and again vanished. Dilution with water precipitated 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl (0.4 g.) (Found: C, 82.0; H, 10.15. Calc. for C<sub>28</sub>H<sub>42</sub>O<sub>2</sub>: C, 81.9; H, 10.3%), identical with that obtained by nitration of 2,6-di-*t*-butylphenol (mixed m. p. and infrared spectrum).

(b) *Thermal decomposition.* (i) In acetic anhydride. The nitrophenol (1 g.) in pyridine (3 c.c.) and acetic anhydride (15 c.c.) was heated under reflux. Soon there was evolution of nitrous fumes and the solution became dark with the separation of red-brown crystals having a bluish-purple sheen; pale yellow crystals sublimed into the condenser. These solids were combined (0.85 g.) and separated by sublimation into 2,6-di-*t*-butyl-1,4-benzoquinone, m. p. and mixed m. p. 67° (0.6 g.), and the diphenoquinone (III), m. p. and mixed m. p. 245-246° (0.15 g.).

(ii) In dodecane. The nitrophenol (2.5 g.) in dodecane (50 c.c.) was heated for 3 hr. in a slow stream of nitrogen at 215°. Gas was evolved as the solution changed in colour from deep amber to deep ruby-red. The gas was condensed in a liquid-nitrogen trap to a blue solid and was identified as nitric oxide. The dodecane solution was evaporated under reduced pressure to yield 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone, m. p. and mixed m. p. 247° (1.3 g.). Extraction of the final oily residue with aqueous alkali gave an intensely yellow aqueous solution, which on acidification gave a mixture (0.15 g.) of unchanged nitrophenol (II) and 2,6-di-*t*-butyl-1,4-benzoquinone 4-oxime (IV) in about equal amounts (estimated by infrared absorption).

*Preparation of 2,6-Di-t-butyl-1,4-benzoquinone 4-Oxime (IV).*—Dilute hydrochloric acid was added gradually to a stirred suspension of sodium nitrite (0.7 g.) and powdered sodium hydroxide in an alcoholic solution of 2,6-di-*t*-butylphenol (2 g.) until a slight excess of acid was present. Dilution with water precipitated 2,6-di-*t*-butyl-1,4-benzoquinone 4-oxime that was isolated by means of ether and crystallised from chloroform-light petroleum (b. p. 60-80°) and then twice from ethyl alcohol as pale yellow plates, m. p. 225-226° (decomp.) (Found: C, 71.2; H, 9.0; N, 6.1%; *M*, 237. Calc. for C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub>: C, 71.45; H, 9.0; N, 5.9%; *M*, 235) (Metro<sup>4</sup> gives m. p. 219-220°).

This oxime is also obtained, less satisfactorily, by adding sodium nitrite to a solution of 2,6-di-*t*-butylphenol in acetic acid. There are also formed the diphenoquinone (III) and 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl.

The oxime gives a bright yellow solution in aqueous alkali from which it is precipitated unchanged on acidification. In sulphuric acid a yellow solution is formed changing to brown, with slight evolution of sulphur dioxide. The oxime was recovered unchanged when such a solution was diluted with water after 9 days.

Oxidation of an alkaline solution of the oxime by ferricyanide<sup>6</sup> gave the diphenoquinone (III) and the benzoquinone in about equal amounts. If the oxidation mixture is acidified immediately after the reactants have been mixed, a poor yield of 4-nitro-2,6-di-*t*-butylphenol (identified by its infrared spectrum) is obtained together with a large amount of the oxime.

The oxime is oxidised by boiling alkaline permanganate to the diphenoquinone and a relatively small proportion of the benzoquinone.

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<sup>5</sup> Braude, Linstead, and Wooldridge, *J.*, 1954, 3590.

<sup>6</sup> Borsche and Berkhout, *Annalen*, 1904, 330, 95.