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SYNTHESIS AND PROPERTIES OF 3,4-DI-*t*-BUTYLPHENOL

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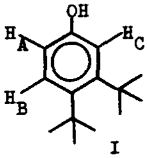
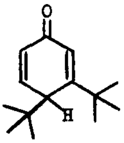
OWING to the strong steric repulsion which has been demonstrated[1] to exist between the *t*-butyl groups in an *o*-di-*t*-butylbenzene system, some degree of stabilization of the dienone tautomer (II) of 3,4-di-*t*-butylphenol (I) might be expected to occur.[2] We now wish to report the synthesis of this substance along with evidence which shows that it exists essentially as the phenol I.



I



II

Nitration of *o*-di-*t*-butylbenzene[3] with nitric acid (d. 1.42) in acetic anhydride at 0-5° afforded, in 90% yield, 3,4-di-*t*-butylnitrobenzene as a pale yellow oil with a musk-like odor, b.p. 114° (0.1 mm.), n_D^{25} 1.5431. (Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.16; H, 9.08; N, 6.12). Hydrogenation of this substance over palladium furnished 3,4-di-*t*-butylaniline in 91% yield as a faintly colored oil, b.p. 105° (0.2 mm.), n_D^{25} 1.5486. (Calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.78; H, 11.48; N, 6.69). The N-acetyl derivative of this amine crystallized as colorless prisms, m.p. 135.5-136°. (Calcd. for $C_{16}H_{25}NO$: N, 5.66. Found: N, 5.59).

Diazotization of the slightly soluble hydrochloride (m.p. 136-137°) of the amine at 0-5°, followed by treatment of the filtered solution with sodium fluoborate, gave the corresponding diazonium fluoborate in 30-50% yield as pale straw-colored plates, m.p. 74° (dec.). This diazonium salt underwent slow solvolysis in a mixture of acetic acid and acetic anhydride[4] at 25° with formation of the corresponding acetate; IR 5.65, 8.25 μ; NMR: two singlets at 8.47 τ (18 protons) and 7.80 τ (3 protons), a multiplet centered at 3.22 τ (1 proton) and two doublets at 2.82 τ (1 proton) and 2.52 τ (1 proton).

Hydrolysis of the acetate then gave the desired 3,4-di-*t*-butylphenol (I) as needle clusters (from petroleum ether), m.p. 97-97.5° (40% yield of purified product from the diazonium salt); IR: 2.8(m), 3.0(m), 3.4(s), 6.25(s), 7.1(m), 7.25(m), 7.4(m), 7.75(m), 8.05(s), 8.2(m), 8.4(s), 9.5(m), 9.8(w), 10.7(m), 11.5(m) and 12.35μ(s); λ_{max}^{EtOH} 277 mμ (ε 1640); $\lambda_{max}^{EtOH(KOH)}$ 294 mμ (ε 3160) [cf. *p*-*t*-butylphenol: λ_{max}^{EtOH} 277 mμ (ε 1900); $\lambda_{max}^{EtOH(KOH)}$ 294 mμ (ε 5000)].[5] Its NMR spectrum (in CCl_4) exhibits a singlet at 8.51 τ (18 protons), a multiplet essentially consisting of two doublets centered at 3.50 τ (H_A, J_{AB} 9 cps., J_{AC} 3 cps.) and two doublets at 3.02 τ (H_C, J_{AC} 3 cps.) and 2.62 τ (H_B, J_{AB} 9 cps.), in addition to a phenolic proton signal at 4.75 τ. (Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.63; H, 10.52).

The 3,5-dinitrobenzoate of I crystallized from petroleum ether as needles, m.p. 113-114°. (Calcd. for $C_{21}H_{24}N_2O_6$: C, 62.99; H, 6.04; N, 7.00. Found: C, 63.03; H, 6.14; N, 7.11). The phenol gave a yellowish-green solution with ferric chloride, but did not give a carbonyl derivative with 2,4-dinitrophenylhydrazine or semicarbazide hydrochloride. The IR spectrum shows no carbonyl absorption in the 6 μ region, nor does the NMR spectrum contain any detectable vinyl proton signal. From these data it is apparent that the steric repulsion of the ortho t-butyl groups in I is not sufficient to overcome the resonance stabilization of the benzenoid ring.[6]

The Friedel-Crafts acetylation of o-di-t-butylbenzene in the presence of aluminum chloride with subsequent Baeyer-Villiger oxidation and hydrolysis was found to yield p-t-butylphenol instead of the desired phenol (I). Acid hydrolysis of 3,4-di-t-butylaniline gave unidentified products.

With fuming nitric acid (d. 1.50) o-di-t-butylbenzene underwent nitration in acetic anhydride at -5° to give, in 50% yield, 1,2-di-t-butyl-4,5-dinitrobenzene as prisms, m.p. 139-140°; IR 7.40 μ(s); λ_{max}^{EtOH} 276 mμ (ε 7750), 220 mμ (ε 14,000). The structure of this compound was confirmed by its NMR spectrum which shows a single peak at 8.37 τ (18 protons) and another at 1.90 τ (2 protons). (Calcd. for $C_{14}H_{20}O_4N_2$: C, 59.98; H, 7.19; N, 9.99. Found: C, 59.83; H, 7.30; N, 10.11). The structure was further established by reduction to the corresponding diamine which with benzil gave a quinoxaline derivative, m.p. 194-195° (colorless needles from methanol); λ_{max}^{EtOH} 254 mμ (ε 50,700), 353 mμ (ε 17,700); NMR: singlet at 8.31 τ (18 protons) and a group of multiplets centered at 2.66 τ (12 protons). (Calcd. for $C_{28}H_{30}N_2$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.11; H, 7.57; N, 7.30). Several attempts to hydrolyze this ortho dinitro derivative to 2-nitro-4,5-di-t-butylphenol with hot aqueous alkali led largely to the recovery of starting material.

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REFERENCES

(1) For example, cf. the photochemical transformation of 1,2,4-tri-*t*-butylbenzene into a substituted Dewar benzene structure [E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.* **84**, 3789 (1962)].

(2) Cf. the tautomeric anthranol-anthrone equilibrium [K. H. Meyer, *Ann.* **379**, 37 (1911)].

(3) A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.* **85**, 173 (1963) and literature cited therein.

(4) Cf. H. L. Haller and P. S. Schaffer, *ibid.* **55**, 4954 (1933); L. E. Smith and H. L. Haller, *ibid.* **61**, 143 (1939).

(5) Cf. N. D. Coggenshall and A. S. Glessner, Jr., *ibid.* **71**, 3150 (1949).

(6) Augmented by two additional ortho substituents, this repulsion does appear to be sufficient to stabilize *trans*-5,6-di-*t*-butyl-2-hydroxy-2-cyclohexene-1,4-dione [G. R. Yohe, J. E. Dunbar, M. W. Lansford, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee and E. C. Smith, *J. Org. Chem.* **24**, 1251 (1959)].