

The Oxidation of 4-n-Propylphenol to 2-n-Propylquinol. **633**

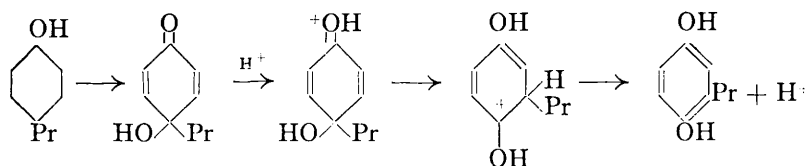
132. *The Oxidation of 4-n-Propylphenol to 2-n-Propylquinol.*

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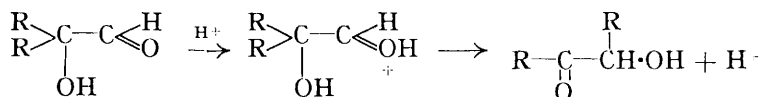
It was recently pointed out by one of us that the contrast between the tendency of kationoid normal alkyl groups to isomerise and the stability of such groups in the anionoid condition might offer a criterion as to the nature of reactions in which they participate (*J. Soc. Chem. Ind.*, 1933, **52**, 470). As a prelude to the study of the particular case which pro-

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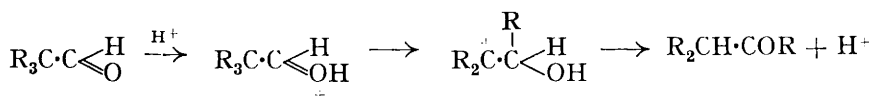
voked this suggestion, namely, the apparently anomalous meta-substitution of toluene by *tert.*-butyl chloride in presence of aluminium chloride, it was desirable to apply the method to a less obscure reaction. We have done this by subjecting 4-*n*-propylphenol to the conditions used by Kumagai and Wolfenstein for the well-known conversion of *p*-cresol into toluquinol (*Ber.*, 1908, **41**, 298). As would be anticipated from the following scheme, *n*-propylquinol was isolated; it was identified by comparison with a specimen of the same compound prepared from 3-*n*-propylphenol.



The reaction has the further interest that it is clearly a form, expanded by introduction of an ethylenic group, of the conversion by sulphuric acid of glycolaldehydes into α -hydroxy-ketones (Danilow and Danilowa, *Ber.*, 1927, **60**, 2390; 1929, **62**, 2653; 1930, **63**, 2765; 1934, **67**, 24). The following scheme appears to express the relationship of this reaction to the Wagner-Meerwein change adequately:—



Similarly the analogous isomerisation of aldehydes CR_3CHO (compare S. Danilow, *J. Russ. Phys. Chem. Soc.*, 1919, **51**, 97) may be written:



2-*n*-Propylquinol.—A mixture of nitric acid (*d* 1.42; 23.4 c.c.) with water (33.4 c.c.) was added gradually to a solution of *m*-propylphenol (50 g.) in benzene (80 g.). From the product a mixture of *o*-nitrophenols (25 g., b. p. 100–140°/0.5 mm.) was removed by steam distillation. 4-Nitro-3-*n*-propylphenol (25 g.) was then isolated from the residue by distillation at 157°/0.6 mm. and finally obtained in pale yellow needles, m. p. 58°, by crystallisation from light petroleum (Found: C, 60.0; H, 6.5; N, 7.9. $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$ requires C, 59.7; H, 6.1; N, 7.7%). The conditions prescribed by Schultz for the nitration of *m*-cresol (*Ber.*, 1907, **40**, 4322) would involve the use of 41 c.c. of nitric acid in the instance just recorded, but in these circumstances *dinitro-m*-propylphenol, b. p. 145°/0.5 mm., was obtained; it separated from light petroleum in pale yellow, prismatic crystals, m. p. 125° (Found: C, 48.1; H, 4.2; N, 12.5. $\text{C}_9\text{H}_{10}\text{O}_5\text{N}_2$ requires C, 47.8; H, 4.4; N, 12.4%). 4-Amino-3-*n*-propylphenol was isolated in the form of its hydrochloride after reduction of the nitro-compound with tin and hydrochloric acid, and characterised by its *acetyl* derivative. This crystallised from water in small white radiating prisms, m. p. 140° (Found: C, 68.0; H, 7.8; N, 7.4. $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}$ requires C, 68.4; H, 7.8; N, 7.3%). The corresponding quinone was obtained as an oil, which did not crystallise, when the amine hydrochloride was distilled in steam with a solution of ferric chloride. The distillate was shaken with sulphurous acid until the oil had disappeared, and *n*-propylquinol was finally isolated by extraction with ether (yield, 80%). It crystallised from benzene in fine white needles, m. p. 90° (Found: C, 70.8; H, 8.1. $\text{C}_9\text{H}_{12}\text{O}_2$ requires C, 71.1; H, 7.9%).

Oxidation of 4-*n*-Propylphenol.—The phenol (50 g.) was added to a solution of Caro's acid prepared from potassium persulphate (54 g.), sulphuric acid (7.3 c.c.), and water (142 c.c.), and the whole stirred at 70–80° for 4–5 hours. After extraction with ether, 4-*n*-propylphenol (38 g.) was recovered by distillation at 80–90°/0.5 mm. A later fraction (5 g.), b. p. 165–180°/0.5 mm., was further purified by steam distillation with ferric chloride, and subsequent reduction with sulphurous acid in the manner already described. After crystallisation from benzene, the product melted at 90° and did not depress the m. p. of *n*-propylquinol.