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THE FRIEDEL-CRAFTS t-BUTYLATION OF 2-NAPHTHOL

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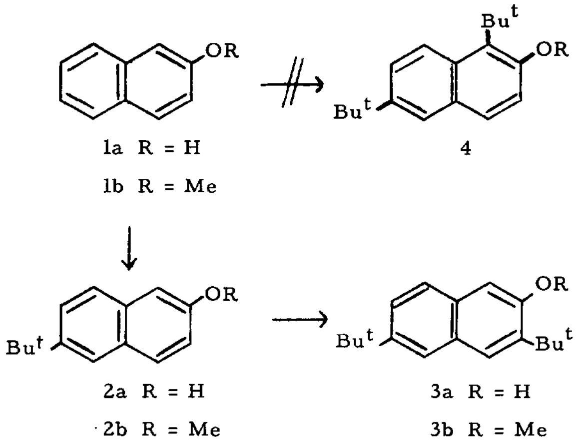
The history[1,2] of the Friedel-Crafts reaction of 2-naphthol and its methyl ether with t-butyl chloride or equivalent reagents is littered with misinterpretations. The situation was partly clarified in 1950 by Buu-Hoi[1] who showed that 2-naphthol gives a mono-t-butyl derivative m.p. 120° and a di-t-butyl derivative m.p. 139°, which are both C-alkyl derivatives. He proved that the monoalkyl derivative is 6-t-butyl-2-naphthol and that the di-t-butyl derivative can be made from the mono-derivative by further alkylation. The dialkyl derivative was shown to contain a hydroxyl group which was sterically hindered (insolubility in aqueous sodium hydroxide). Arguing by analogy with the alkylation of 2-naphthol with smaller alkyl groups, Buu-Hoi assigned to the substance the structure 1,6-di-t-butyl-2-naphthol which was in accord with its cryptophenolic nature and this structure assignment was "confirmed" by the failure of the compound to couple with diazonium salts. The possibility that this observation results from the known inability of the compound to give the phenoxide ion in aqueous media was ignored.

This structure assignment has been accepted[3] and even supported[4] by later workers on the basis of the long half life of a derived radical or radicals of unknown structure.

We find that the autoxidation of the di-t-butylnaphthol is very slow. This is not expected for a hindered 1-alkyl-2-naphthol.[5] One of the products from this autoxidation is a red solid m.p. 135°[6] to which we assign the structure 3,6-di-t-butyl-1,2-naphthaquinone (5) on the basis of the following spectral characteristics, $\lambda_{(max)}$ (EtOH) 225, 260 and 348 nm, $\nu_{(max)}$ 1690 and 1660 cm^{-1}, τ ($CDCl_3$) 8.60 and 8.65, singlets, 18H, 2 Bu^t, 1.90 - 2.80, multiplet, 4H, 3 aromatic protons and the β-proton of the enone system. In particular the NMR spectrum lacks the high field doublet characteristic of the olefinic proton at C-3 of 1,2-naphthaquinone.

The same quinone is obtained more readily from the di-t-butylnaphthol by oxidation with Fremy's salt or by oxidation with lead tetraacetate followed by hydrolysis. We conclude that the di-t-butyl naphthol is 3,6-di-t-butyl-2-naphthol. This assignment is supported by the NMR spectra of the phenol itself which show one aromatic proton at high field (τ 3.15 in $CDCl_3$) as a broad singlet. This broad singlet is preferentially shielded relative to the other aromatic protons when the spectrum is measured in C_6D_6 (compared to CCl_4) and when it is measured in dimethyl sulphoxide containing sodium hydride (compared to dimethyl sulphoxide).[7] There is, therefore, <u>ortho</u> to the hydroxyl group <u>one</u> proton which has no adjacent protons.

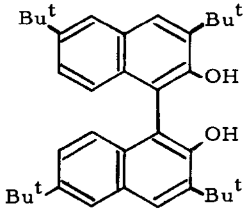


1a R = H
1b R = Me

4

2a R = H
2b R = Me

3a R = H
3b R = Me



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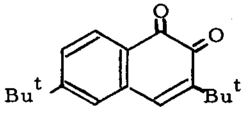

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Oxidation of the di-t-butylnaphthol with ferricyanide[3] or with cobalt (III) acetylacetonate gives a 'dimer' m.p. 332-334°. Its NMR spectrum shows it to be a symmetrical C-C coupled binaphthyl with a 1,3,6 trisubstituted 2-naphthol substitution pattern. We therefore now assign to it the structure (6).

The course of the Friedel-Crafts t-butylation of 2-methoxynapthalene has also been unclear. In a remarkable paper Ferris and Hamer[2] have claimed the preparation by this method of 1-t-butyl-2-methoxynaphthalene as a sharp melting solid. We find that this reaction gives a mixture of starting material plus 6-t-butyl-2-methoxynaphthalene (2b) m.p. 75.5-76.5°[6] and 3,6-di-t-butyl-2-methoxynaphthalene (3b), m.p. 81-82°[6] which were identified by comparison with authentic samples of these two compounds made by methylating the parent phenols discussed above (MeI/NaH in dimethylsulphoxide). The m.p. we find for the 6-t-butyl-2-methoxynaphthalene is different from that reported.[1]

The reported[2] preparation of 4-t-butyl-2-methoxynaphthalene by Friedel-Crafts t-butylation of 1-bromo-2-methoxynaphthalene followed by reductive removal of the bromine is also suspect. In our hands the only identified product from t-butylation of 1-bromo-2-methoxynaphthalene is 6-t-butyl-1-bromo-2-methoxynaphthalene, m.p. 136°, identical to material obtained by bromination of 2b.

It is well known that steric factors are important in Friedel-Crafts reactions with bulky reagent complexes. Although the order of reactivity of the positions in 2-naphthol on electronic grounds is $1>6>3>8$, the order of steric accessibility is found from inspection of models to be $6>3>8>1$. We conclude that in the Friedel-Crafts alkylation of 2-naphthol with small alkyl groups electronic factors are more important than steric ones, but that in the t-butylation the reverse is true.

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