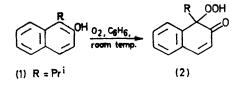
Autoxidation of Strained 1-Alkyl-2-naphthols: Steric Acceleration in a Radical Chain Reaction

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Summary The rate of autoxidation of certain 1-alkyl-2naphthols to hydroperoxides increases markedly with the degree of strain caused by *peri*-interactions.

WE have previously reported¹ that 1-isopropyl- (1) and 1-cyclohexyl-2-naphthol readily combine with oxygen to form stable hydroperoxides (2). The reactions show the characteristics of radical chain processes. It is reported² that 1-methyl-2-naphthol reacts with oxygen only \forall ery slowly and we find no reaction to occur over several days even if cobalt(III) acetylacetonate or (1) is added as a potential initiator.

It seemed that this marked difference in behaviour could be attributed to the greater steric congestion in the isopropylnaphthol than in the methylnaphthol and to relief of this congestion when C-1 becomes tetrahedral. To test this theory we have prepared a series of 2-naphthols and examined their autoxidation.



1-t-Butyl-2-naphthol³ was formed in the vigorous reaction of 1-methoxycarbonyl-2-naphthol with solvent-free MeMgI.⁴ It was purified as its methyl ether and recovered by quantitative ether cleavage using NaSEt. Its i.r. and ¹H n.m.r. spectra show the complete absence of the napththalen-2(1*H*)-one tautomer. The phenol is very sensitive to air and is rapidly converted into the hydroperoxide (2; $R = Bu^{t}$). 1,8-Dimethyl-2-naphthol was prepared by reduction of 2-methoxy-1,8-naphthalic anhydride and demethylation. It also reacts rapidly with air to give an analogous hydroperoxide. 1-Methyl-6-t-butyl-2-naphthol was found to be inert to oxygen.

TABLE

1	fime for absory of 0.5 mol of per mol	0 ₂ c	Tield (%) of hydro- peroxide
1-Methyl-2-naphthol	No reaction in 3 days	7.85	
1-Isopropyl-2-naphthol	4 h	8.08	90
1-t-Butyl-2-naphthol	10 min	8.41	85
1,8-Dimethyl-2-naphthol	3 h		94
1-Methyl-6-t-butyl-2-naphthol	No reaction in 3 days	7.84	

The uptake of oxygen by all these phenols was studied under identical conditions (3 mmol in 15 ml benzene; 1 atm. oxygen; standard stirring rate; dark). In each case where uptake occurs the reaction eventually goes to completion but for comparison the time taken for uptake of the first 0.5 mol per mol is recorded in the Table. The times are reproducible on different batches of phenol with relatively little variation $(\pm 10\%)$. It is clear that the very different reaction rates of the five naphthols correlate

- ¹ J. Carnduff and D. G. Leppard, Chem. Comm., 1967, 829.
- ² K. Fries, Ber., 1914, 47, 1193.
- ³ See P. A. Brady, J. Carnduff, and D. G. Leppard, *Tetrahedron Letters*, 1972, 4183. ⁴ For analogous reactions see J. Kahovec and J. Pospisil, *Chem. and Ind.*, 1969, 489.
- ⁶ H. van Bekkum, T. J. Nieuwstad, J. van Barneveld, P. Klapwijk, and B. M. Wepster, Rec. trav. Chim., 1969, 88, 1028.
- ⁶ D. Bright, I. E. Maxwell, and J. de Boer, J.C.S. Perkin II, 1973, 2101. ⁷ C. Dufraisse, A. Etienne, and J. Rigandy, Bull. Soc. chim. France, 1948, 804 and references therein.
- ⁸ R. Caputo, L. Previtera, P. Monaco, and L. Mangoni, Tetrahedron, 1974, 30, 963.

qualitatively with the strain due to congestion between the peri-substituents. The increasing congestion in the series of 1-alkyl-2-naphthols is indicated⁵ by the progressive deshielding of the *peri* proton (H-8) in the ¹H n.m.r. spectra (see Table). The strain in 1,8-dimethylnaphthalene has been estimated as ca. 8 kcal mol⁻¹ and is evident from the distorted bond angles revealed in X-ray studies.⁶ Although the different alkyl groups (Me, Pri, But), have different inductive effects, this cannot be the factor controlling reactivity since 1,8-dimethyl-2-naphthol reacts with oxygen while both 1-methyl-2-naphthol and 1-methyl-6-t-butyl-2-

9-Alkyl-10-anthranols are reported7 to take up oxygen rapidly to give hydroperoxides but the reported rates are about the same for all the alkyl groups studied (Me, Et, Ph, PhCH₂, vinyl). It has recently been reported that steric congestion, due to syn-axial groups, accelerates the autoxidation of certain cyclohexanecarboxaldehydes to yield various decarbonylated products.8

In the cases in which it occurs, autoxidation of the 1-alkyl-2-naphthols described here gives a single primary product in high yield and there is an unambiguous and pronounced effect of strain on the autoxidation rate.

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naphthol are inert.

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