



to air and is rapidly converted into the hydroperoxide (**2**; R = Bu<sup>t</sup>). 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

	Time for absorption of 0.5 mol of O <sub>2</sub> per mol	Yield (%) of hydro- peroxide	δ (H-8)
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

qualitatively with the strain due to congestion between the *peri*-substituents. The increasing congestion in the series of 1-alkyl-2-naphthols is indicated<sup>5</sup> by the progressive deshielding of the *peri* proton (H-8) in the <sup>1</sup>H n.m.r. spectra (see Table). The strain in 1,8-dimethylnaphthalene has been estimated as *ca.* 8 kcal mol<sup>-1</sup> and is evident from the distorted bond angles revealed in X-ray studies.<sup>6</sup> Although the different alkyl groups (Me, Pr<sup>i</sup>, Bu<sup>t</sup>), 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-naphthol are inert.

9-Alkyl-10-anthranols are reported<sup>7</sup> 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, PhCH<sub>2</sub>, 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.<sup>8</sup>

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.

We thank the S.R.C. for a studentship.

(Received, 23rd July 1974; Com. 923.)

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<sup>2</sup> K. Fries, *Ber.*, 1914, **47**, 1193.

<sup>3</sup> See P. A. Brady, J. Carnduff, and D. G. Leppard, *Tetrahedron Letters*, 1972, 4183.

<sup>4</sup> For analogous reactions see J. Kahovec and J. Pospisil, *Chem. and Ind.*, 1969, 489.

<sup>5</sup> H. van Bekkum, T. J. Nieuwstad, J. van Barneveld, P. Klapwijk, and B. M. Wepster, *Rec. trav. Chim.*, 1969, **88**, 1028.

<sup>6</sup> D. Bright, I. E. Maxwell, and J. de Boer, *J.C.S. Perkin II*, 1973, 2101.

<sup>7</sup> C. Dufraisse, A. Etienne, and J. Rigandy, *Bull. Soc. chim. France*, 1948, 804 and references therein.

<sup>8</sup> R. Caputo, L. Previtera, P. Monaco, and L. Mangoni, *Tetrahedron*, 1974, **30**, 963.