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HYDROGEN BONDING AND AUTOXIDATION BEHAVIOUR OF HINDERED 1-ALKYL-2-NAPHTHOLS WITH ARYL SUBSTITUENTS

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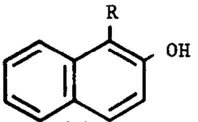
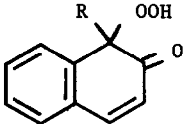
We have reported the clean autoxidation of 1-isopropyl-2-naphthol (1, R = iPr) in benzene at room temperature over a few hours to yield a hydroperoxynaphthalenone (2, R = iPr)[1] and the much faster autoxidation under the same conditions of 1-t-butyl- and 1-t-pentyl-2-naphthol to analogous hydroperoxides.[2] Since 1-methyl-2-naphthol did not react with oxygen over several days we concluded that the rate of autoxidation of this series of alkylnaphthols was influenced by the bulk of the alkyl groups which, in those cases where the congestion between peri substituents is severe, causes marked in-plane distortion of the carbon skeleton of the naphthalene nucleus.[3]



(1)



(2)

It was therefore intriguing that 1-phenyl-2-naphthol,[4,5,6] 1-benzyl-2-naphthol[1] and particularly 1-triphenylmethyl-2-naphthol,[7] all of which have been known for some time, have not been reported to be unstable in air. There is evidence from A values of cyclohexanes,[8] from conformations of the tetrasubstituted ethanes[9] and from distortions of the 1,8-disubstituted naphthalenes[10] that the steric requirements of a phenyl group are greater than for a methyl group. It is known that tri- and tetra-arylmethanes adopt propeller-like conformations in which the ortho protons of each phenyl group lie opposite the face of the adjacent phenyl group;[11] however calculations of the energy of such molecules, particularly those with substituents in ortho positions, as in 1-triphenylmethyl-2-naphthol, show there is considerable strain and attempts to construct a model of this substance with space-filling models support this view.

We have therefore prepared the series of compounds (1) where R = Ph, CH_2Ph, $CHPh_2$, $CMePh_2$, CPh_3 and examined their autoxidation behaviour. We find that 1-phenyl-2-naphthol is conveniently prepared in 42% yield by photolysis of a benzene solution of 1-iodo-2-naphthol[12] for 21 hours with a medium pressure mercury lamp and chromatographic separation from a small amount of 2,2'-dihydroxy-1,1'-binaphthyl.[13] 1-Benzyl-2-naphthol was made as before.[1] The other compounds were made from 1-diphenylmethylenenaphthalen-2(1H)-one (o-naphthofuchsone)[14] by reaction with sodium borohydride, methyl magnesium iodide[15] and phenyl magnesium bromide[7] respectively.

We find that none of this series of aryl and aralkylnaphthols will react with oxygen over a period of two days under the conditions used previously. While this may be due to the relatively small bulk of the groups R = Ph and R = CH_2Ph, it seemed likely that some other factor was inhibiting autoxidation of the more strained members of the series. The infra-red spectra of all of these compounds show that the phenolic OH group is hydrogen-bonded to an aryl group. In the case of the benzylnaphthol only about a third of the molecules show this H-bonding but in all the other cases there is no band for free OH. We conclude that even in the more strained cases, this H-bonding so stabilises the phenol as to prevent totally the hydrogen atom abstraction necessary to the autoxidation.[16]

Compound	R = Ph	CH_2Ph	$CHPh_2$	$CMePh_2$	CPh_3	Me
ν_{max} (CCl_4)	3550	3605 and 3540	3505	3505	3500	3635cm^{-1}

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