Autoxidation of 1-Alkyl-2-naphthols

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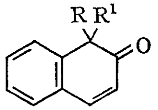
WE have observed that 1-isopropyl-2-naphthol, as the solid or in solution in benzene, is converted on standing in air into a crystalline material, $C_{13}H_{14}O_3$, which contains two atoms of oxygen more than the phenol. It is reported[1] that 1-cyclohexyl-2-naphthol behaves analogously but the structure of the product has not been established. We have shown that these autoxidation products are the hydroperoxynaphthalenones (Ia) and (Ib).

Both phenols when shaken in benzene at room temperature with oxygen in diffuse daylight absorb only one mole of oxygen. The product (Ia)† from 1-isopropyl-2-naphthol (75% yield) crystallises from benzene as pale yellow needles, m.p. 135—137°, which can be sublimed unchanged at 100°/0·05 mm. Its u.v. spectrum, λ_{max} (ethanol) 234, 240, and 313 mμ (log ϵ 4·17, 4·19 and 3·92), resembles those of known 1,1-disubstituted-2(1*H*)-naphthalenones,[2] and this structure type is confirmed by its i.r. spectrum, ν_{max} (Nujol) 3300 (H-bonded OH) and 1660 (H-bonded conjugated C=O) cm.$^{-1}$ and its n.m.r. spectrum (60 Mc./sec., $CDCl_3$), two doublets each with J = 7 c./sec. centred at τ 9·15 and 9·18 (total 6H, CH_3·CH·CH_3, the methyl groups are magnetically non-equivalent) a septuplet J = 7 c./sec. at τ 7·87 (1H, CH_3·C*H*·CH_3), a doublet, J = 10 c./sec., at τ 3·86 (1H, CH=C*H*·CO), a multiplet at τ 2·2—2·8 (5H, C*H*=CHCO, and aromatics) and a singlet at τ 0·43 (1H, H-bonded OH). The presence of the hydroperoxy-group is confirmed by the rapid reduction of (Ia) by iodide ion or ferrous thiocyanate. Catalytic hydrogenolysis of (Ia) very rapidly reduces it to the hydroxynaphthalenone (IIa),† m.p. 88—89°, λ_{max} (ethanol) 236·5 and 312·5 mμ (log ϵ 4·09 and 3·82), ν_{max} (Nujol) 3400 (OH), 1660 (C=O) cm.$^{-1}$, n.m.r. ($CDCl_3$) two doublets each with J = 7 c./sec. at τ 9·15 and 9·18 (CH_3·CH·CH_3), a septuplet with J = 7 c./sec. at τ 7·95 (CH_3·C*H*·CH_3) a singlet at τ 6·20 (OH), a doublet with J = 10 c./sec. at τ 3·86 (CH=C*H*·CO) and a multiplet at τ 2·3—2·8 (C*H*=CH·CO and aromatics).



(Ia) R = OOH, R^1 = isopropyl
(Ib) R = OOH, R^1 = cyclohexyl
(IIa) R = OH, R^1 = isopropyl
(IIb) R = OH, R^1 = cyclohexyl
(IIIa) R = OAc, R^1 = isopropyl

Oxidation of 1-isopropyl-2-naphthol with lead tetra-acetate[3] gives the expected acetoxynpahthalenone (IIIa),† m.p. 77—77·5°, λ_{max} (ethonal) 233, 238·5, and 309 mμ (log ϵ 4·11, 4·14, and 3·93) ν_{max} (Nujol) 1740 (OAc), 1680 (C=O) cm.$^{-1}$, n.m.r. (CCl_4) two doublets each with J = 7 c./sec. centred at τ 9·15 and 9·20 (CH_3·CH·CH_3), a singlet at τ 8·00 (O·CO·CH_3), a multiplet at τ 7·95 (CH_3·CH·CH_3), a doublet with J = 10 c./sec. at τ 3·98 (CH=CH·CO), a doublet with J = 10 c./sec. at τ 2·78 (CH=CH·CO) and a singlet at τ 2·80 (aromatics). The spectra of (Ia), (IIa), and (IIIa) are thus very similar. Their structural relationship is confirmed by the fact that alkaline hydrolysis of (IIIa) gives (IIa).

Oxygenation of 1-cyclohexyl-2-naphthol in benzene gives the hydroperoxynaphthalenone (Ib)† (77% yield), m.p. 179—181°, λ_{max} (ethanol) 236, 241, and 316 mμ (log ϵ 4·12, 4·14, and 3·89), ν_{max} (Nujol) 3200 (OH), 1660 (C=O) cm.$^{-1}$, n.m.r. ($CDCl_3$) broad multiplet at τ 8—9 (cyclohexyl), a doublet with J = 10 c./sec. at τ 3·92 (CH=CH·CO), a multiplet at τ 2·2—2·8 (CH=CH·CO and aromatics) and a singlet at τ 1·18 (OH). Reduction of (Ib) with iodide gives the hydroxynaphthalenone (IIb)†, m.p. 92—94°, λ_{max} (ethanol) 235 and 312·5 mμ (log ϵ 4·29 and 3·73), ν_{max} (Nujol) 3400 (OH) and 1665 (C=O) cm.$^{-1}$, n.m.r. ($CDCl_3$) broad multiplet at τ 8—9 (cyclohexyl), a singlet at τ 6·18 (OH), a doublet with J = 10 c./sec. at τ 3·87 (CH=CH·CO) and a multiplet at τ 2·2—2·8 (CH=CH·CO and aromatics).

The analyses and spectra are compatible only with the assigned structures.

Very few cases of ready autoxidation of phenols to hydroperoxides are known.[4] The behaviour of other 1-alkyl-2-naphthols under these conditions is being investigated.

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† Satisfactory analytical data have been obtained.

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