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RADICAL TYPE SUBSTITUTION REACTIONS OF 2-CYCLOPROPYLPHENOL

by

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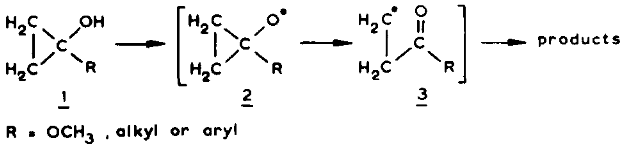
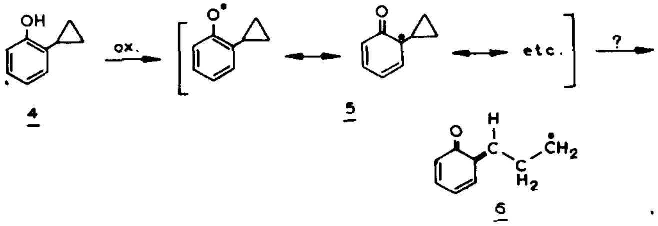
Previously we reported on the oxidation of cyclopropanols 1 by metal ions (1). It can be deduced from the reaction products and ESR studies that the ring-opened carbon radical 3 is a more stable intermediate than the strained



cyclopropyloxy radical 2.

We now wish to describe the results of radical type reactions of 2-cyclopropylphenol 4, which can in a sense be considered a vinylogue of 1.

In principle the phenoxy radical 5 can give rise (by formal analogy) to ring-

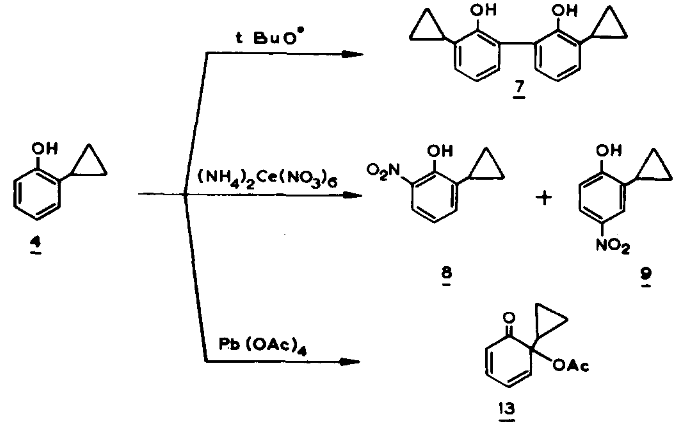


-opened reaction products derived from 6 or to products with the unbroken cyclopropyl ring derived from radical 5.

The phenol 4 was synthesized in 17 % yield from phenylcyclopropane (2) according to Levina et al. (3).

The reaction of tert. butylperoxide and a threefold excess of 4 at 150°C for 25 hours resulted in a mixture (total yield 65 %), containing mainly 3,3'-dicyclopropyl-biphenyl-2,2'-diol 7 (4). No ring-opened products could be detected.

The NMR spectrum ($CDCl_3$) showed broad absorptions between δ = 5.6 - 7.5 ppm



(phenyl H + HO), δ = 1.5 - 2.5 ppm and δ = 0.3 - 1.4 ppm (cyclopropyl H) in a ratio of 8 : 2 : 8.

The UV spectrum (EtOH) showed maxima at 207 nm (ϵ = 30.400), 247 nm (sh, ϵ = 8100) and 285 nm (ϵ = 5400). These data are very similar to those of biphenyl-2,2'-diol (5).

The phenol 4 reacted with an equivalent amount of cerium ammonium nitrate in acetonitrile at room temperature to form within half an hour a mixture of 2-cyclopropyl-6-nitrophenol 8 (yield 29 %) and 2-cyclopropyl-4-nitrophenol 9 (yield 23 %), which were separated as their silyl ethers by preparative gaschromatography. The NMR spectrum ($CDCl_3$) of 8 displayed a singlet at δ = 11.0 ppm (OH), two doublets centred at δ = 7.9 ppm ($-CH=\overset{|}{C}-NO_2$) and multiplets between $\delta = 6.7 - 7.3$ ppm (2 H phenyl), $\delta = 2.0 - 2.6$ ppm and $\delta = 0.5 - 1.25$ ppm (cyclopropyl H).

The NMR spectrum ($CDCl_3$) of 9 showed a singlet at $\delta = 10.9$ ppm (OH), a multiplet between $\delta = 7.6 - 8.1$ ppm (2 H, $-CH=\overset{|}{C}-NO_2$), a doublet at $\delta = 6.8$ ppm (1 H) and two multiplets between $\delta = 2.0 - 2.5$ ppm and $\delta = 0.5 - 1.2$ ppm (cyclopropyl H). The IR spectrum of both isomers had the characteristic NO_2 and OH absorptions. The molecular weight determination (mass spec.) confirmed the elemental composition.

On carrying out the reaction with e.g. o-cresol and cerium ammonium nitrate or ferric nitrate, a similar mixture of nitro isomers was obtained (6).

In contrast to these findings Young obtained ring-opened dinitrates from phenyl- and 1,2-diphenylcyclopropane and ceric ammonium nitrate (7).

It is known from the studies of Ouellette et al. (8) that phenylcyclopropanes gives with an acetic acid solution of Pb^{4+}-, Tl^{3+}- and Hg^{2+}-acetate ring--opened products. The first step in these reactions appears to be an electrophilic attack of the metal acetate as shown by the negative ρ-value.

Surprisingly we find that 2-cyclopropylphenol 4 and $Pb(OAc)_4$ (1.5 eq.) in dry chloroform yields within half an hour at least 50 % of purified 2-acetoxy-2--cyclopropyl-3,5-cyclohexadien-1-one 13 as the main product. The IR spectrum (liq.) shows bands at 1735 cm^{-1} ($CH_3C=O$), 1675 and 1635 cm^{-1} (conjugated C=O and C=C) and 1240 cm^{-1} (acetate C-O). The NMR spectrum (100 MHz, $CDCl_3$) displays multiplets between $\delta = 6.7 - 7.1$ ppm ($-\overset{|}{C}=CH-\underset{|}{\overset{|}{C}}-O-$) and $\delta = 5.95 - 6.4$ ppm (-CH=CH-CH=), a singlet at $\delta = 2.05$ ppm ($CH_3C=O$) and multiplets between $\delta = 0.95 - 1.3$ ppm (1 H) and $\delta = 0.3 - 0.7$ ppm (4 H, cyclopropyl). The molecular weight (mass spec.) amounts to M = 192.08004. Calc. for $C_{11}H_{12}O_3$: 192.07854. The preparation of a 3,5-cyclohexadien-1-one (yield 30 %) from o-cresol and $Pb(OAc)_4$ has also been mentioned by Wessely et al. (9).

It can be concluded that 2-cyclopropylphenol 4 behaves typically like a phenol in all these oxidative processes, and that the spin delocalisation in intermediary radicals produces so little spin density at the carbon atom carrying the cyclopropyl ring, that this is insufficient to break the cyclopropyl ring.

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