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α-KETOHYDROPEROXIDES FROM 2,4,6-TRI-t-BUTYLPHENOL

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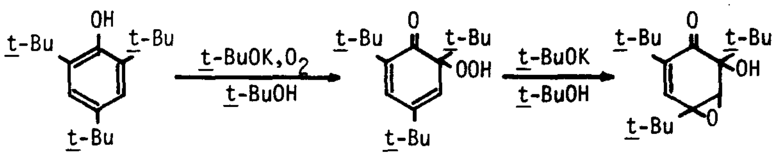
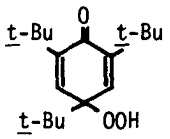
Although 6-hydroperoxy-2,4-cyclohexadienones have been considered to be intermediates in the reaction of dioxygenases which catalyze the oxidative cleavage of phenolic substances,[1] little has been reported on synthesis and reactions of such α-ketohydroperoxides derived from phenols.[2] We now wish to report the synthesis and some chemical behaviors of α-ketohydroperoxides derived from 2,4,6-tri-t-butylphenol (1) by base-catalyzed oxygenation. Spectral and analytical data of products are summarized in Table 1. The oxygen bubbling through a solution of 1 in a mixture of t-BuOH and petroleum ether (2:1) containing t-BuOK at 0°C for 2 hr and working up the reaction mixture (dilution with aqueous HCl, extraction with ether, and evaporation of the extract) gave 2,4,6-tri-t-butyl-6-hydroperoxy-2,4-cyclohexadienone (2) in 70% yield; mp 109-111°.





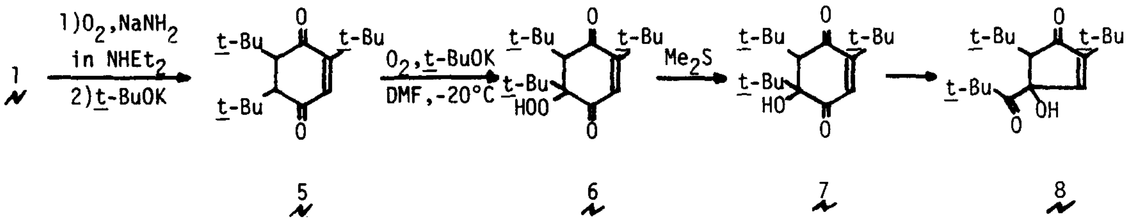
1 2 3 4

The hydroperoxide (2) liberated iodine from potassium iodide. The structure (2) was further confirmed by the facts that the treatment of 2 with CF_3COOH quantitatively gave 3,5-di-t-butyl-o-benzoquinone and the reduction of 2 with Me_2S afforded 3,5-di-t-butylcatechol formed by the de-t-butylation of the corresponding o-quinol, the primary reduced product. The treatments of 2 with t-BuOK gave epoxy-o-quinol (3)[3] in 90% yield in t-BuOH at 60°C for 3 min and gave 3 and the starting phenol (1) in 60 and 40 % yields, respectively, in DMF at room temperature for 5 min. The mechanism of this conversion envisaging intramolecular asymmetric cleavage of dioxetane intermediate by interaction with π-system has been suggested.[3] The NMR spectrum of a solution of 2 in CD_3OD containing CD_3ONa after being allowed to stand for 18 hr showed that 2 was partially converted to the isomeric hydroperoxide (4) where 2 : 4 = 1 : 1, suggesting an equilibrium between 2 and 4 being established under the conditions.[4]

Table 1. Spectral and Analytical Data

Compound	IR(Nujol)(cm^{-1})		^{1}H-NMR(CDCl$_3$), δ(ppm)				Elemental Analyses		
	ν_{OH}	ν_{CO}	*t*-Bu	CH-CO	CH=CO	OH(OOH)		C(%)	H(%)
2	3440	1650	0.92, 1.21, 1.24		6.13, 6.73	9.14	Calc.	73.43	10.27
							Found	73.28	10.55
6	3270	1660	1.11, 1.22, 1.32	2.76	6.08	6.39	Calc.	69.64	9.74
		1650					Found	69.43	10.04
7	3480	1690	0.98, 1.27, 1.30	2.63	6.66	4.48	Calc.	73.43	10.27
		1680					Found	73.60	10.54
8	3560	1730	1.07, 1.09, 1.29	2.49	6.77	3.41	Calc.	73.43	10.27
							Found	73.55	10.17

The similar base-catalyzed oxygenation of 2,5,6-tri-*t*-butyl-2-cyclohexene-1,4-dione (5), which was obtained by oxygenation of 1 in NHEt$_2$ with NaNH$_2$[5] followed by base-catalyzed rearrangement,[6] in DMF containing *t*-BuOK at -20°C for 6 hr quantitatively gave 2,5,6-tri-*t*-butyl-5-hydroperoxy-2-cyclohexene-1,4-dione (6); mp 192-194°. The structure was determined by comparison of the NMR data with that of 5 in which coupling between protons on C$_3$ and C$_5$ was seen.[6] The



compound 6 was reduced with KI or Me$_2$S quantitatively to give 2,5,6-tri-*t*-butyl-5-hydroxy-2-cyclohexene-1,4-dione (7); mp 43-44°, which was easily rearranged to ring contracted product (8); mp 171-172° by treating it with silica gel in contrast with the behavior of the *o*-quinol from 2.

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References and Notes

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