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OXIDATIVE REARRANGEMENT OF *o*-HYDROXYDIARYLCARBINOLS

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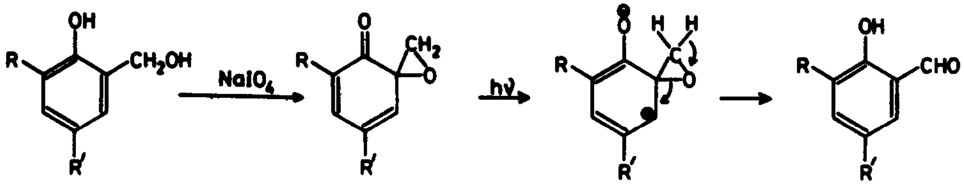
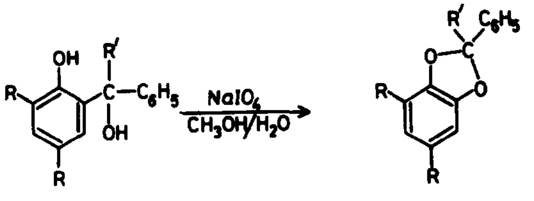
Monomeric spiro-epoxy-2,4-cyclohexadienones of structure **2** can be prepared in good yields by periodate oxidation of *o*-hydroxymethylphenols **1** having at least one bulky substituent.[1] Though spiro-epoxy-2,4-cyclohexadienones **2** rapidly isomerize photochemically to give salicylaldehydes **4** (conceivably *via* a dipolar intermediate of structure **3** as indicated), they are thermally rather stable, giving salicylaldehydes only slowly even at 120°.



1 **2** **3** **4**

In attempting to apply the oxidation-photochemical isomerization sequence to the synthesis of *o*-hydroxybenzophenones we observed the apparently novel oxidative rearrangement of *o*-hydroxy-substituted diaryl-carbinols and triaryl-carbinols to 2-aryl-substituted benzo-1,3-dioxols under mild conditions.

For example, addition of sodium periodate (1.07 g; 5 mmol) in water (15 ml) to 2-hydroxy-3,5-di-tert.-butyldiphenyl-carbinol[2] (**5a**; 1.25 g; 4 mmol) in methanol (75 ml) at room temperature gives a pale yellow solution from which sodium iodate and a colorless crystalline organic material rapidly start precipitating. Filtration after 7 hours and treatment of the residue with water gives, in 60 % yield, a colorless crystalline compound, m.p. 84-85° (from CH_3OH/H_2O), for which elemental analysis, molecular weight (by MS) and the following spectroscopic data are in agreement with the benzo-1,3-dioxol 6a, *i.e.* benzaldehyde acetal of 3,5-di-*tert*.-butylcatechol. The IR spectrum indicates the absence of hydroxy and carbonyl groups. The UV spectrum in isoöctane shows a longest-wavelength absorption maximum at 283 nm (ε 3,900). In its 60 MHz NMR spectrum (in $CDCl_3$) the oxidation product shows the protons of the phenyl substituent as a broad multiplet around δ 7.4. A downfield singlet at δ 6.88 is assigned to the methine proton, while the closely spaced AB system (J_{AB} 1.9 Hz) centered at δ 6.78 is attributed to the *meta* protons of the catechol moiety. The *tert*.-butyl groups give rise to singlets at δ 1.29 and δ 1.38, respectively.

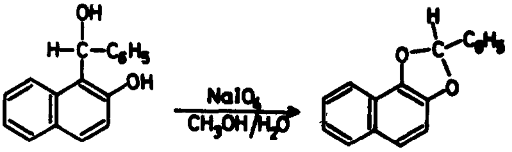


5a-d 6a-d

	R	R'
a)	t-C_4H_9	H
b)	H	H
c)	Br	H
d)	H	C_6H_5

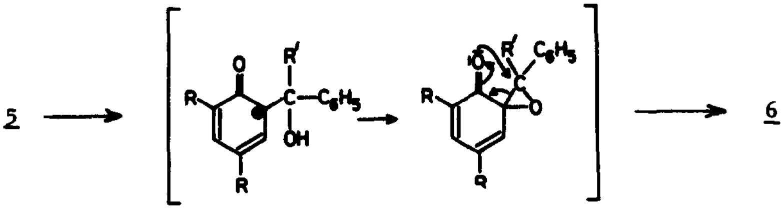
The oxidation of *o*-hydroxydiphenylcarbinols 5b[3] and 5c[4] with sodium periodate gave the catechol benzaldehyde acetals 6b (41 % yield; m.p. 49-51°; $\delta_{methine}$ 6.94) and 6c (44 % yield; m.p. 67-70°; $\delta_{methine}$ 7.06), respectively, though they were conveniently isolated by extraction with methylene chloride. Similar oxidation of 2-hydroxytriphenylcarbinol[5] (5d) and 2-hydroxynaphthyl--phenylcarbinol[6] (7) gave the corresponding catechol derivative 6d (67 % yield; m.p. 92-93°; lit.[7] m.p. 93°) and the 1,2-dihydroxynaphthalene derivative 8 (64 % yield; m.p. 78-80°; $\delta_{methine} > 7.1$), respectively. The odor of benzaldehyde is cognizable during the oxidation of 5a-c and 7, suggesting that a side reaction consists in the oxidative cleavage of the hydroxyaryl-carbinol bond.

The oxidative formation of a cyclic benzaldehyde acetal of catechol from



7 8

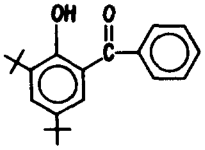
an o-hydroxydiphenylcarbinol may be rationalized by a mechanism involving the intermediacy of the phenoxonium ion 9 (or its equivalent) and the aryl-substituted spiro-epoxy-2,4-cyclohexadienone 10 which spontaneously rearranges as



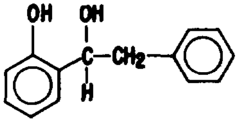
9 10

indicated. The driving force for the rearrangement apparently lies in the gain of energy associated with the aromatization and, more important, the stabilization of the conceivable dipolar precursor of 6 in which the phenoxy moiety bears the negative charge while the positive charge is located at the aryl-substituted carbon atom.

Significantly, we have found no UV-spectroscopic evidence for the presence of 3,5-di-*tert.*-butyl-2-hydroxybenzophenone (11) in the oxidative rearrangement of 5a. We expected 11 to be formed from the hypothetical intermediate 10 if, in analogy with the photochemical or thermal rearrangement of spiro-epoxy-2,4-cyclohexadienones 2, cleavage of the spiro-oxygen bond would be a mode of reaction. In contrast to the reaction with periodate, which involves attack at the phenolic site, the oxidation of 5a with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dioxane gave the benzophenone 11, most likely by attack at the benzylic carbon (yield 71 %; m.p. 60-62°; λ_{max} in isoöctane, 358 nm, ε 4,800; 273 nm, ε 12,100; 252 nm, ε 12,000).



11



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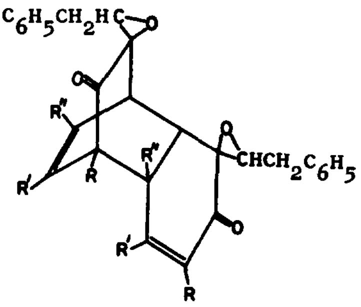

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Apparently, the oxidative rearrangement described above is limited to *o*-hydroxy-substituted diarylcarbinols and triarylcarbinols. Thus, the oxidation of benzyl-2-hydroxyphenylcarbinol (12) with sodium periodate did not give the phenylacetaldehyde acetal of catechol but the Diels-Alder dimer[8] 13 ($R=R'=R''=H$) of the intermediary benzyl-substituted spiro-epoxy-2,4-cyclohexadienone.

Satisfactory elemental analyses were obtained for all new compounds.

References and Footnotes

1. H.-D. Becker, T. Bremholt, and E. Adler, Tetrahedron Letters, 4205 (1972).
2. Compound 5a was prepared from 3,5-di-*tert*.-butylsalicylaldehyde and phenyllithium in ether; yield 71 %; m.p. 91-93°.
3. Carbinol 5b was prepared from salicylaldehyde and phenylmagnesium bromide; yield 87 %; m.p. 87-89°.
4. Carbinol 5c was prepared analogous to carbinol 5b; yield 84 %; m.p. 119-121°.
5. Carbinol 5d was prepared from 2-hydroxybenzophenone and phenylmagnesium bromide; yield 87 %; m.p. 137-139°.
6. Carbinol 7 was prepared from β-hydroxy-α-naphthaldehyde and phenylmagnesium bromide; yield 70 %; m.p. 117-118°.
7. R. Sachs and R. Thonet, Ber. 37, 3327 (1904).
8. Concerning the formation of similar Diels-Alder dimers of spiro-epoxy-2,4-cyclohexadienones, see E. Adler, S. Brasen, and H. Miyake, Acta Chem. Scand. 25, 2055 (1971).