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A CONVENIENT NEW METHOD FOR REDUCTION OF QUINONES AND α-DIKETONES

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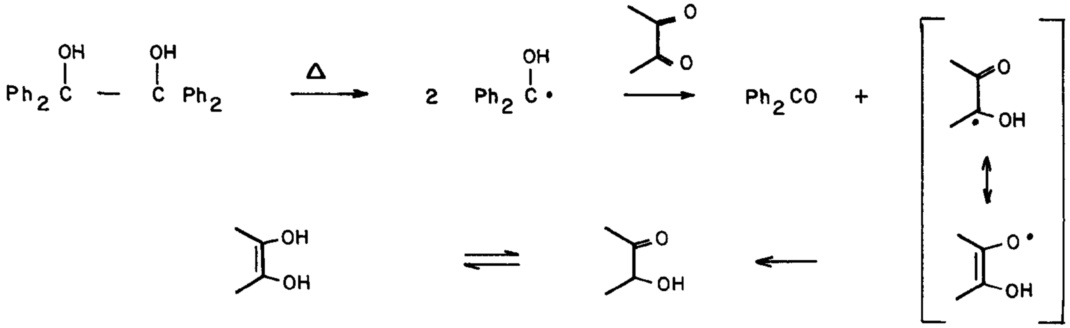
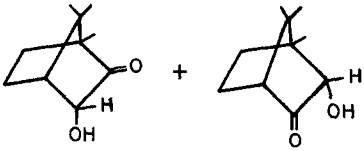
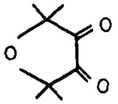
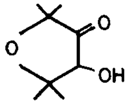
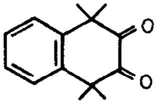
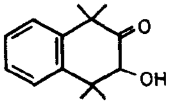
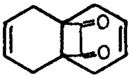
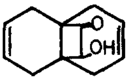
It has been shown recently[1,2] that photochemically generated benzophenone ketyl radicals can function efficiently as reducing agents for α-diketones. It has also been demonstrated[3] that such ketyl radicals can be formed by thermal cleavage of benzpinacol. Combination of these two observations has suggested a new method for reduction of α-diketones to α-hydroxyketones and of o- and p-quinones to hydroquinones which is remarkably simple and efficient. Further, replacement of the hydroxyl protons of benzpinacol by deuterium provides a means for synthesis of deuterium labelled α-hydroxyketones.



Thus, heating a solution of an α-diketone, such as camphorquinone, with a slight excess of benzpinacol for 2-3 minutes at 160-170° results in complete disappearance of the yellow color and nearly quantitative conversion (by GC analysis) to benzophenone and α-hydroxyketones[4]. Solvents used were decalin, dimethylformamide, ethylene glycol, and toluene. At the lower temperature, in refluxing toluene, about 1.5 hr were required for complete reduction. The solvent of choice was decalin since, in many cases, good yields of pure product crystallized upon cooling the reaction mixture. For example, a mixture of benzil (210 mg), benzpinacol (700 mg) and decalin (5 ml) in a test tube was immersed in an oil bath maintained at 165°. After 15 min, the solution was cooled; filtration afforded crystalline benzoin (176 mg, 85%).

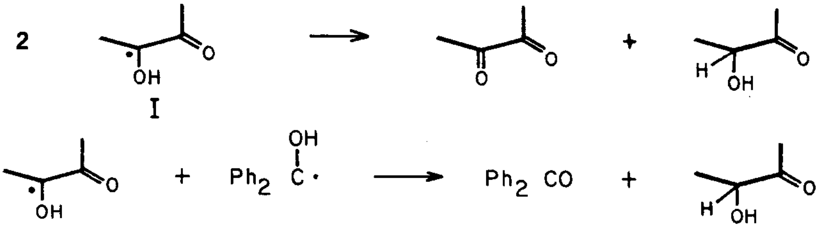
REDUCTIONS OF DIONES WITH BENZPINACOL

Dione	Product	Proc.[a]	Yield (%)
Benzil	Benzoin	A	85[b]
α-Furil	α-Furoin	B	64[b]
$PhCOCOCH_3$	$PhCHOHCOCH_3$ (65) $PhCOCHOHCH_3$ (35)	A	82[c,d]
Camphorquinone		A	75[c,e]
		A	73[c]
		A	63[b]
 II	 III	A	72[c,f]
p-Benzoquinone	Hydroquinone	B	87[b]
9,10-Phenanthrenequinone	9,10-Dihydroxyphenanthrene	B	91[b,g]

a. Procedure A involved heating a mixture of diketone and benzpinacol in decalin as described in the text. In procedure B, the dione was suspended in decalin, heated to reflux under nitrogen, and benzpinacol added in small portions over several minutes. b. Product crystallized from reaction mixture upon cooling. c. Product obtained by chromatography on Florisil. d. The ratio of isomeric products was close to that reported (ref. 6) for equilibrated mixtures of the two products. e. *cf.* ref. 4. f. The product was identical with a sample of II kindly supplied by Dr. J.J. Bloomfield. g. Product isolated as the diacetate.

The results obtained with a variety of compounds are summerized in the Table. Substances having low solubility in decalin could not be reduced by the test tube procedure (Procedure A) described above since decomposition of benzpinacol was faster than dissolution of the substance. In such cases, benzpinacol was added in portions to a hot stirred suspension of substance in decalin (Procedure B). The yields given are preparative yields and no special attempts were made to maximize them; GC analysis showed that significant amounts of by-products were not formed. In particular, further reduction to vic-diols was not detected.

Intermediacy of the semidione radical I is clearly involved in these reactions. The final step in the reduction might involve disproportionation of two semidione radicals as has been suggested in the photoreduction of camphorquinone[1] and phenanthraquinone[5] or hydrogen atom transfer from benzophenone ketyl radicals.



Since the hydroxyl protons of benzpinacol can readily be replaced by deuterium, a simple modification of the above procedure allows synthesis of deuterium labelled α-hydroxyketones. For example, a mixture of benzil (210 mg), benzpinacol (700 mg), decalin (8 ml), and deuterium oxide (2 ml) was heated until the decalin-water azeotrope had completely distilled over. The temperature of the remaining solution was raised rapidily to about 160° when the yellow color of the diketone disappeared. The solid (162 mg) obtained upon cooling was crystallized from methanol (to exchange the hydroxyl deuterium) and shown by mass spectral analysis to be benzoin-d_1 containing 92 ± 1% of one deuterium atom. Similar results were obtained using added benzene and a Cope separator; higher deuterium incorporation was readily achieved by several exchanges with deuterium oxide.

$$(Ph_2\overset{OD}{\overset{|}{C}}\!-\!)_2 + PhCOCOPh \longrightarrow Ph_2CO + Ph\overset{OD}{\overset{|}{C}}DCOPh$$

The convenience of the present method and its applicability to a wide variety of compounds should make it the method of choice[7] in cases where a brief period of heating is not undesirable.

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2. M.B. Rubin, Tetrahedron Letters, 3931 (1969).
3. D.C. Neckers and D.P. Colenbrander, ibid., 5045 (1968).
4. The product consisted of a mixture of two isomers identical with the mixture obtained[1] by photoreduction of camphorquinone in 2-propanol.
5. P.A. Carapellucci, H.P. Wolf, and K. Weiss, J. Amer. Chem. Soc., 91, 4635 (1969).
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7. For a summary of alternate methods for reduction of α-diketones to acyloins see W. Kreiser, Ann., 745, 164 (1971).