Condensation of Cyclohexane-1,3-diones with *o*-Hydroxybenzyl Alcohol. Synthesis of 3,4-Dihydro-1(2*H*)-xanthenones

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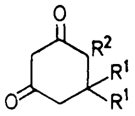
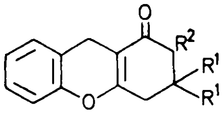
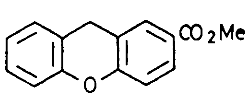
Summary The condensation of cyclohexane-1,3-diones with *o*-hydroxybenzyl alcohol provides a synthesis of 3,4-dihydro-1(2*H*)-xanthenones.



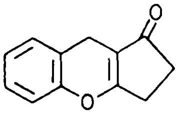
(2) $R^1 = R^2 = H$
(4) $R^1 = Me, R^2 = H$
(6) $R^1 = H, R^2 = CO_2Me$
(9) $R^1 = H, R^2 = CONH_2$



(3) $R^1 = R^2 = H$
(5) $R^1 = Me, R^2 = H$
(7) $R^1 = H, R^2 = CO_2Me$
(10) $R = H, R = CONH_2$



(8)



(11)

Previous work by Molho[1] and Quagliaro, Moreau, and Dreux[2] on the reaction of *o*-hydroxybenzyl alcohol (**1**) with ketones suggested to us that the reaction of (**1**) with cyclohexane-1,3-diones (**2**) might provide a general synthesis of 3,4-dihydro-1(2*H*)-xanthenones (**3**),[3] compounds that are potential sources of the hitherto unknown 3,4-dihydroxanthens.[3]

In the event, heating of (**1**) and (**2**) in hexamethylphosphoramide (HMPA) at 185° for 30 min gave (**3**)† (45%), m.p. 90·5—91·5°. U.v. and n.m.r. spectral data did not completely exclude the alternative formulation, 1,2-dihydro-4(3*H*)-xanthenone, but the structural assignment (**3**) is favoured on mechanistic grounds and corroborated by the conversion of the product *via* its toluene-*p*-sulphonylhydrazone into 3,4-dihydroxanthen.[4]

Similar condensation of dimedone (**4**) with (**1**) gave (**5**) (82%), m.p. 96—97·5°.‡

Reaction of (**6**) with (**1**) in the absence of solvent at 100° (15 mm) for 42 h gave (**7**) (51%), m.p. 126—127·5°.‡ The structure of (**7**) was established by hydrolysis and decarboxylation in aqueous acid to give (**3**), and reduction with sodium borohydride followed by dehydration with phosphorus oxychloride–pyridine and dehydrogenation with 5% palladium–charcoal to give methyl xanthen-2-carboxylate (**8**), m.p. 130—131°.‡

Reaction of (**9**) with (**1**) in HMPA–1,5-diazabicyclo[5,4,0]undec-5-ene at 185° (100 mm) for 30 min gave (**10**) (67%), m.p. 217—218°, whose structure was established by its conversion into (**8**).

Thus, the condensation of (**1**) with cyclohexane-1,3-diones to give compounds of type (**3**) has been effected under a variety of conditions.§ A preliminary investigation of the extension of this reaction to other cyclic *β*-diketones has been made. No analogous product could be obtained from cycloheptane-1,3-dione; however, reaction of (**1**) with cyclopentane-1,3-dione in HMPA at 75° for 66 h gave (**11**) (11%), m.p. 195–197°.‡

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† Acceptable elemental analyses have been obtained for all compounds characterized by melting point; parent peaks for these compounds have been observed in their low resolution mass spectra.

‡ U.v. and n.m.r. spectral data in accord with the structure assignment.

§ The reaction of (**1**) with (**9**) to give (**10**) was also effected in the presence of toluene-*p*-sulphonic acid; the yield (40%) was lower than that obtained under the conditions cited above.

[1] D. Molho, *Bull. Soc. chim. France*, 1961, **1417**.

[2] R. Quagliaro, M. Moreau, and J. Dreux, *Compt. rend.*, 1963, **257**, 2843.

[3] *Cf.*, also L. Jurd, *J. Org. Chem.*, 1966, **31**, 1639; T. Rios, *Bol. Inst. Quím. Univ. nac. auton. México*, 1966, **18**, 78 (*Chem. Abs.*, 1967, **67**, 82,037).

[4] D. J. Bichan and P. Yates, in the press.