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FACILE OXIDATION OF o-HYDROXYPHENYL BENZYL KETONES TO UNSYMMETRICAL BENZILS WITH DIMETHYL SULPHOXIDE/POTASSIUM HYDROXIDE

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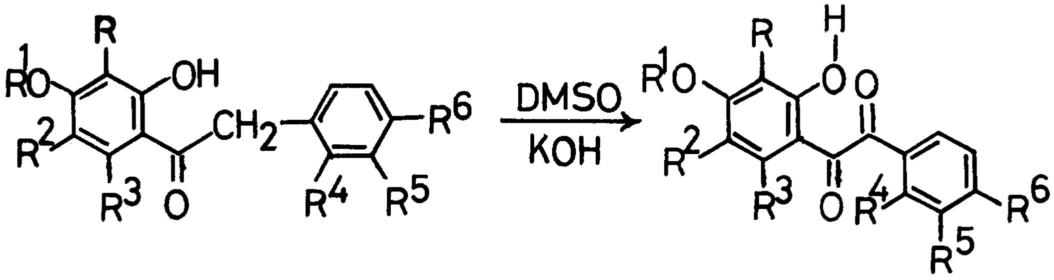
Abstract - o-Hydroxyphenyl benzyl ketones on treatment with dimethyl sulphoxide and powdered potassium hydroxide have been found to undergo facile oxidation to the corresponding benzils.

In a recent paper[1] from these laboratories o-hydroxyphenyl benzyl ketones derived from resorcinol and phloroglucinol units on reaction with dichloroacetic acid in aqueous alkaline medium were found to give the corresponding phenyl(α-carboxyvinyl)benzyl ketones and 2-carboxymethyl-2-phenyl-3(2H)-benzofuranone derivatives respectively; the target compounds, 2-carboxyisoflavanones were not formed under these conditions. In an attempted synthesis of target compounds, under alternative conditions, 2-hydroxy-4-methoxyphenyl benzyl ketone was vigorously stirred with dichloroacetic acid in dimethyl sulphoxide medium in the presence of powdered potassium hydroxide. After 30 minutes, the spot corresponding to the starting compound was found to be absent on TLC. The reaction mixture was acidified and extracted with ether. Ether residue on recrystallisation from light petroleum yielded a product A, mp 86-7°. In its NMR spectrum absence of the signal at δ 4.5 showed that the bridge methylene had been involved in the reaction. In mass spectrum, product A, showed $M^{\dot{+}}$ at m/e 256 (100%), 14 mu more than the starting material (molecular weight 242). On the basis of spectral studies and positive ferric reaction, product A was assigned the structure 2-hydroxy-4-methoxybenzil. This structure was finally confirmed by comparison (mmp, co-IR) with an authentic sample[2]. Interestingly when dichloroacetic acid was excluded from the above reaction mixture, 2-hydroxy-4-methoxybenzil was once again the product formed, proving thereby, that it had no role to play in the oxidation of the substrate. Next 2,4-dihydroxyphenyl benzyl ketone when treated similarly gave a product B, mp 126-7°. Marsh and Stephen[3] had earlier prepared 2,4-dihydroxybenzil by Hoesch reaction of resorcinol with benzoyl cyanide and reported mp 239°. To solve this ambiguity, product B was partially methylated using dimethyl sulphate, acetone and anhydrous potassium carbonate when the partial methylated product and product A, mentioned above, were found to be identical in all respects (mp, mmp, and co-IR). To prove the identity further, product B was converted into complete methyl ether (mp 103-4°, lit.[2] mp of 2,4-dimethoxybenzil 104°) and its diacetate (mp 141-2°). Moreover, NMR spectra of complete methyl ether and the diacetate were exactly those as predicted for

2,4-dimethoxybenzil and 2,4-diacetoxybenzil structures. This comprehensively proved the identity of product B to be 2,4-dihydroxybenzil. It is, therefore, likely that Marsh and Stephen did not isolate the target compound by condensing resorcinol with benzoyl cyanide but some other product to which they appear to have erroneously assigned the structure 2,4-dihydroxybenzil.

The scope of the present method has been studied in detail by subjecting phenyl benzyl ketones possessing different substitution patterns in rings A and B (Table), to the above reaction. In each case the corresponding benzil has been obtained in 55-80% yield, thus providing a convenient and simple procedure for the synthesis of these otherwise difficultly accessible synthetic intermediates. The structures of the different benzils have been confirmed by elemental analysis, colour reactions and spectral studies.



1,3,5,7,9,11,13,15 2,4,6,8,10,12,14,16

	R	R^1	R^2	R^3	R^4	R^5	R^6	mp (°C)		Yield %
								Found	Reported	
1,2	H	H	H	H	H	H	H	126-7	239[3]	55
3,4	H	CH_3	H	H	H	H	H	86-7	86[2]	65
5,6	H	CH_3	H	H	H	H	OCH_3	99-100	***	80
7,8	CH_3	CH_3	H	H	H	H	H	135	***	75
9,10	H	CH_3	CH_3	H	H	H	H	127-8	***	80
11,12	H	CH_3	H	OCH_3	H	H	H	109-10	***	65
13,14	H	CH_3	H	H	H	OCH_3	OCH_3	146-8	***	80
15,16	H	CH_3	H	H	OCH_3	H	H	154	***	55

*** New compounds

References

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