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## ABNORMAL BASE CATALYSED REACTION OF FORMALDEHYDE AND BENZALDEHYDES WITH 1-(2-HYDROXYPHENYL)-3-PHENYL-1, 3-PROPANEDIONE

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Abstract . 1-(2-Hydroxyphenyl)-3-phenyl-1, 3-propanedione (1a) reacts with formaldehyde in the presence of different 1-arylpiperazines (2) to form (1:1) inclusion compounds (3) which on column chromatographic separation yield 4,5,11,12-dibenzo-7-hydroxymethyl-1,3-dioxa-6,10-dioxo-7,9-diphenylcyclododecane (4) and the corresponding 2 1 react with formaldehyde in the presence of triethylamine to form 3-aroyl-3-(2,3-dihydro-4H-1-benzopyran-4-one-3-ylmethyl)-2,3-dihydro-4H-1-benzopyran-4-one (5) along with benzoic acids and with benzaldehydes in the presence of a base to give 2-aryl-2,3-dihydro-4H-1-benzopyran-4-one (6)

It is well known that 1,3-diketones undergo a CO-C bond cleavage under basic conditions<sup>1</sup>. 1,3-Diphenyl-1,3-propanedione is reported to undergo dimerisation on reaction with formaldehyde<sup>2</sup>,<sup>3</sup> and to form 2-benzoyl-1,3,5-triphenyl-1,5-pentanedione<sup>4</sup> on reaction with benzaldehyde. Similarly, 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (1a) condenses with aryl aldehydes to form the corresponding arylidene derivatives<sup>5</sup> as well as 3-arylflavones<sup>6</sup>.

During our attempts to carry out the Mannich reaction on 1, when equimolar quantities of 1a, 1-arylpiperazines (2) and formaldehyde were stirred in ethanol at room temperature, 3 separated. On column chromatographic separation 3



Table I : Inclusion compounds 3

No	R	m.p.(°C)	yield (%)
3a	н	112-13	93
3Ъ	2-CH3	169-170	94
3c	3-CH3	135-36	91
3d	4-CH3	166-67	94



gave 4,5;11,12-dibenzo-7-hydroxymethyl-1,3-dioxa-6,10-dioxo-7,9-diphenylcyclododecane (4)? (m.p. : 97-98°C, yield : 91%) and the starting 2 in a 1:1 molar ratio The reaction was parallel to that of 1,3-diphenyl-1,3-propanedione with formaldehyde. Using different 1-arylpiperazines, a series of 3 was prepared (table I) 1 reacted with formaldehyde in the presence of other secondary amines, like morpholine, piperidine, pyrrolidine, etc., in the same manner. Hence, the reaction appeared to be a base catalysed reaction of formaldehyde with 1

When 1a was reacted with equimolar quantities of formaldehyde in ethanol in the presence of triethylamine, at room temperature, 3-benzoyl-3-(2,3-dihydro-4H-1-benzopyran-4-one-3-ylmethyl)-2,3-dihydro-4H-1-benzopyran-4-one (5a)<sup>8</sup> was obtained. From the mother liquor, benzoic acid was isolated in the equivalent amount. Similarly 1b-d reacted with formaldehyde in the same manner and a series of 5 was obtained (table II).





To extend the reaction, 1a was reacted with equivalent amounts of substituted benzaldehydes in the presence of morpholine in ethanol to obtain a series of 2-aryl-2,3-dihydro-4H-1-benzopyran-4-ones (6)<sup>9</sup> (table III) In each reaction benzoic acid was isolated as the side product.

The formations of 5 was believed to take place as shown in scheme II, while 4 could be formed by dimerisation of 1 through methylene bridges and the hydroxymethylation. The reaction of 1 with a benzaldehyde could proceed by the mechanism shown in scheme II, however, the initial hydroxychalcone (A) may undergo spontaneous cyclisation.

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## SCHEME II



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- 7 Spectral data of 4 : IR (KBr, cm-1) = 1670 & 1680 (C=O). 1H-NMR (CDCls) : 1.2 (s, 2H, -C-CH2-C-); 4.7 (s, 4H, -O-CH2-O); 5.0 (s, 1H, -CH2-OH); 6.8-8.0 (m, 19H, Ar-H and -CO-CH-CO). 13C-NMR (CDCls) : 27.63 (8C), 53.63 (9C), 66.64 (-CH2OH), 68.37 (2C), 102.72 (7C), 179.44, 182.58, 188.76 and 195.15 (C=O)

Spectral data of 5 ' IR (KBr, cm<sup>-1</sup>) = 1665 & 1690 (C=O).
<sup>1</sup>H-NMR (CDCls) : 2 16-2.4 (m, 1H, COCH); 2.67-3.0 (m, 2H, -C-CH2-C);
3 98-4 4 (m, 2H, OCHa Hb'); 4.43 (d, 1H, OCHa Hb, Jgen=12Hz); 5 15 (d, 1H, OCHa Hb, Jgen=12Hz); 6.84-7.93 (m, 13H, Ar-H).
<sup>1</sup>3C-NMR (CDCls) 26 76 (CH2), 42.04 (3C), 61.22 (3'C),71 08 and 72 38 (2C) and (2'C), 192.12, 193.10, 196.35 (C=O).

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9 Spectral data of 6a IR (KBr, cm<sup>-1</sup>) = 1690 (CO).
<sup>1</sup>H-NMR (CDCls) · 2.75-3.15 (m, 2H, -CO-CH<sub>2</sub>, Jgem=16Hz, Jvic=4Hz);
5 5 (q, 1H, -CO-CH, Jgem=16Hz, Jvic=4Hz); 7 0-8 0 (m, 9H, Ar-H).
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