

Enol Benzoates of β -Diketones

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The structures of enol benzoates of substituted dibenzoylmethanes have been determined: in all cases benzoylation occurs at the carbonyl oxygen atom adjacent to the more electron-withdrawing aryl group. Benzoylacetone forms isomeric *E*- and *Z*-enol acetates and benzoates, reaction occurring at the oxygen atom of the acetyl group. A mechanism for the formation of enol benzoates of β -diketones is proposed.

ENOL esters of β -diketones are obtained by the reaction of β -diketones with acyl halides in pyridine^{1,2} and, together with triacylmethanes, from reactions of metal chelates of β -diketones with acyl halides.^{2,3-6} Acyl-benzoylmethanes invariably undergo acylation on the carbonyl oxygen atom adjacent to the alkyl group, irrespective of the size of the alkyl group in the diketone,

or of electronic or steric effects in the acyl chloride.^{2,5-7} The product from these reactions is thus the thermodynamically less stable of the two isomeric enol esters. There are no reports of acylation at more than one of the two carbonyl oxygen atoms of unsymmetrical β -diketones, though *O*-methylation of certain β -diketones has given mixtures of isomeric methyl ethers as a result of attack at both carbonyl oxygens.⁸ This work was

¹ L. Claisen, *Ber.*, 1903, **36**, 3674.

² H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc.*, 1962, 2153.

³ L. Claisen, *Ber.*, 1893, **26**, 1893.

⁴ D. C. Nonhebel and J. Smith, *J. Chem. Soc. (C)*, 1967, 1919.

⁵ H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc. (C)*, 1968, 2298.

⁶ M. G. Murray and D. C. Nonhebel, *J. Chem. Soc. (C)*, 1970, 1172.

⁷ L. J. Roll and R. Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 3469.

⁸ R. D. Campbell and H. M. Gilow, *J. Amer. Chem. Soc.*, 1960, **82**, 2389.

When benzylation of benzoylacetone was carried out at various temperatures it was found that the proportion of the *E*-isomer increased from 33% at 40 °C to

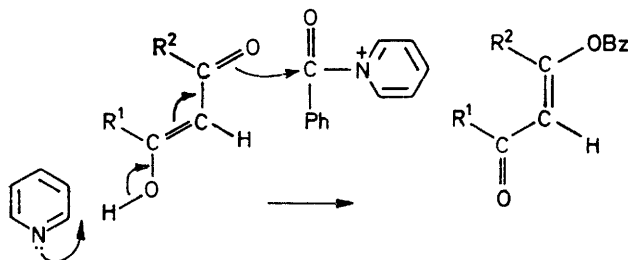
TABLE 3

N.m.r. data for *E*- and *Z*-enol esters (δ values; solvent CCl_4)

Structure	R ¹	R ²	H	Me	Ref.
(4)	Me	Me	5.98	2.25 (d, <i>J</i> 1.3 Hz)	9
(5)	Me	Me	5.72 (s)	2.13 (s)	9
(4)	Me	Ph	6.26 (q, <i>J</i> 1 Hz)	2.38 (d, <i>J</i> 1 Hz)	
(5)	Me	Ph	5.90 (s)	2.13 (s)	
(4)	Ph	Me	6.78 (q, <i>J</i> 1 Hz)	2.35 (d, <i>J</i> 1 Hz)	
(5)	Ph	Me	6.51 (s)	2.22 (s)	
(4)	Ph	Ph	6.90 (q, <i>J</i> 1 Hz)	2.46 (d, <i>J</i> 1 Hz)	
(5)	Ph	Ph	6.53 (s)	2.15 (s)	

66% at -10 °C, possibly indicating that this isomer is the kinetically preferred product.

A possible interpretation of the mechanism of the reaction is shown in the Scheme. The function of the



SCHEME

pyridine is to disrupt the intramolecularly hydrogen-bonded enolic system giving rise to a complexed *trans*-enol which then reacts with the benzoylpyridinium ion. Pyridine is an insufficiently strong base to effect the formation of an enolate anion though it clearly does interact with the β -diketone. The n.m.r. spectra of benzoylacetone and other β -diketones in pyridine showed immediate disappearance of the enolic proton signal on addition of deuterium oxide but the methine proton signal had not changed even after 5 days. When a trace of sodium deuterioxide was introduced the methine proton exchanged rapidly as the enolate ion was then present in the system.

The reaction is tentatively considered to involve the *trans*-enol, since the *E*-isomer appears to be the kinetically preferred product. The site of reaction is consistent with the proposed scheme in that the preferred *trans*-enol of benzoylacetone is undoubtedly that in which there is the more extended conjugated system. In substituted dibenzoylmethanes the more electron-rich carbonyl group is that which is preferentially enolized, thus giving rise to attack at the more electron-deficient carbonyl oxygen atom.

EXPERIMENTAL

3-Acetoxy-1-phenylbut-2-en-1-one.—A mixture of benzoylacetone (5.1 g, 0.03 mol), anhydrous pyridine (25 ml), and acetyl chloride (3.2 g, 0.04 mol) was shaken for 1 h at 25 °C. Cold water (100 ml) was added and shaking continued for a further 2 h. The mixture was extracted with

ether and the extract washed in turn with dilute hydrochloric acid, water, and sodium hydroxide solution until treatment of the organic layer with iron(III) chloride showed no trace of diketone. The ethereal extract was washed with cold water and dried (Na_2SO_4). Distillation gave the enol acetate of benzoylacetone (4 g, 65%), b.p. 125–130° at 2 mmHg (lit.,⁷ 120–122° at 2 mmHg).

T.l.c. of this enol acetate on silica gel in hexane-ether (6.5 : 1.5) showed the presence of two compounds in equal proportions. These were separated by t.l.c. and extracted with ether. Each solution was re-chromatographed as before. In both cases a fresh spot appeared corresponding to the other component. When the ether solutions were set aside for 3 h, 24 h, and 48 h and then re-chromatographed, increasing amounts of the other compound were found to be present. Chromatography on a column of alumina in hexane-ether (8.5 : 1.5) gave (*E*)-3-acetoxy-1-phenylbut-2-en-1-one. Further elution with the same solvent gave the (*Z*)-isomer.

O-Benzoyl Derivatives of β -Diketones.—The β -diketone (0.025 mol) and benzoyl chloride (0.0375 mol) in anhydrous pyridine (15 ml) were shaken at 25 °C for 1 h. Cold water (50 ml) was added and shaking continued for 2 h. The mixture was extracted with ether and the extract washed in turn with hydrochloric acid (1 : 1), water, and sodium hydroxide solution until the ether layer showed no trace of diketone (FeCl_3 test). The ether layer was washed with cold water, dried (Na_2SO_4), and passed through an alumina column (5 g) to remove tarry materials. Evaporation gave the crude enol benzoate, which was crystallised from the appropriate solvent (see Table 1).

3-Benzoyloxy-1-phenylbut-2-en-1-one.—This was prepared by the above method as a viscous oil; in order to avoid possible isomerisation it was not distilled. T.l.c. [hexane-ether (8.5 : 1.5)] showed the presence of two compounds and the same slow interconversion as found with the enol acetate. Chromatography on an alumina column [hexane-ether (8.5 : 1.5)] afforded (*E*)-3-benzoyloxy-1-phenylbut-2-en-1-one followed by the (*Z*)-isomer.

Hydrogenolysis of the Enol Acetate of Benzoylacetone.—Benzoylacetone enol acetate (5.0 g, 0.025 mol) in glacial acetic acid (25 ml) was hydrogenated at room temperature and atmospheric pressure over Adams catalyst (0.1 g) until absorption ceased (1200 ml; 2.25 mol per mol of enol acetate). The catalyst was filtered off and the filtrate stirred with 8N-chromic acid (5 ml). A solution of sodium hydrogen sulphite was added and the mixture was then extracted with ether. The ether layer was washed with dilute hydrochloric acid and then dried and evaporated, leaving butyrophenone (2.5 g, 68%).

Hydrogenolyses of Enol Benzoates.—These were carried out as described above. The enol benzoate of benzoyl- β -naphthoylethane gave β -naphthylmethyleneacetophenone, m.p. and mixed m.p. 164°, which on treatment with Brady's reagent gave β -naphthylmethyleneacetophenone 2,4-dinitrophenylhydrazone, m.p. 236° (Found: C, 68.2; H, 4.4; N, 12.3. $\text{C}_{25}\text{H}_{20}\text{N}_4\text{O}_4$ requires C, 68.2; H, 4.6; N, 12.7%).

Hydrogenations of Chalcones.—These were carried out in the same manner. Reduction of 4'-bromochalcone afforded β -phenyl-p-bromopropiophenone as plates (from petroleum), m.p. 101° (Found: C, 62.6; H, 4.8; Br, 27.8. $\text{C}_{15}\text{H}_{13}\text{BrO}$ requires C, 62.3; H, 4.5; Br, 27.6%).

The 2,4-dinitrophenylhydrazone of β -(*m*-bromophenyl)-propiophenone was obtained, by treatment of the reduction

product of 3-bromo-chalcone with Brady's reagent, as orange needles (from benzene-petroleum), m.p. 202—203° (Found: C, 53.2; H, 3.85; N, 11.95. $C_{21}H_{16}BrN_4O_4$ requires C, 53.7; H, 3.65; N, 11.95%). Reduction of 4'-methoxy-4-methylchalcone similarly gave, after treatment with Brady's reagent, the 2,4-dinitrophenylhydrazone of β -(p-tolyl)-p-methoxypropiophenone as orange needles

(benzene), m.p. 201—202° (Found: C, 63.5; H, 5.4; N, 12.8. $C_{23}H_{22}N_4O_4$ requires C, 63.6; H, 5.1; N, 12.9%). Reduction of 4-nitrochalcone gave β -(p-aminophenyl)-propiophenone as needles (from methanol), m.p. 78.5—80° (Found: C, 80.0; H, 6.8; N, 5.8. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%).

[5/1481 Received, 28th July, 1975]
