Tetrahedron. Vol. 26, pp. 4443 to 4447. Pergamon Press 1970. Printed in Great Britain

SPECTROSCOPIC STUDIES OF TAUTOMERIC SYSTEMS—II[1]

DIACYLACETATES

D. C. NONHEBEL

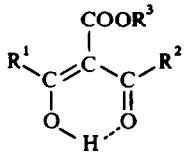
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1.

(*Received in the UK 5 May* 1970; *Accepted for publication* 14 *May* 1970)

Abstract—The structures of the enol tautomers of alkyl aroylacetoacetates and aroylbenzoyl-acetates have been determined by NMR and IR spectroscopy as have the structures of their copper chelates. The enol tautomers of alkyl aroylbenzoylacetates have different structures from their copper chelates.

STERIC considerations have been shown to be important in controlling the direction of enolization of triacylmethanes, whereas electronic effects were found to be relatively unimportant.[1] Thus in both diacylbenzoylmethanes and acyldibenzoylmethanes a benzoyl group is not involved in the H-bonded chelate ring even though benzoylacetone is more highly enolized than acetylacetone. The present work extends this to an examination of benzoylacetoacetates and dibenzoylacetates using IR and NMR spectroscopy.

Diacylacetates with different acyl groups could exist in three isomeric intramolecularly H-bonded forms (**1–3**), in each of which one CO group is not involved in



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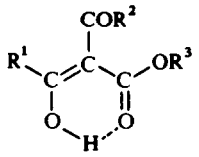

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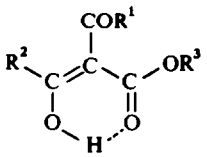

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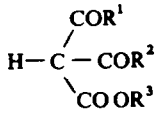
the H-bonded chelate ring. Each of these isomers may exist in either or both of two tautomeric forms. In addition these compounds may exist in the ketonic form (**4**).



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Forsen and Nilsson[2] have shown that diacetoacetic esters exist in the form **1** ($R^1 = R^2 =$ Me, $R^3 =$ Me or Et) in which the ester grouping is not involved in enolization. This is consistent with the fact that Me and Et acetoacetates are less enolized than acetylacetone,[3] i.e. the enol tautomer in the alkyl acetoacetates is less stable with respect to the keto tautomer than is the case with acetylacetone.

The NMR spectrum of methyl benzoylacetoacetate shows two low-field peaks at τ −3·08 and −7·25 of relative intensities 2:3 indicative of two H-bonded chelate forms. There is also a small peak at τ 4·51 due to the methine proton of the tricarbonyl

form. Consistent with this, treatment with deuterium oxide resulted in the rapid disappearance of the two low-field peaks and the slow disappearance (after 24 hr) of the methine proton signal. The IR spectrum shows strong bands at 1710 cm^{-1} attributable to a conjugated but non-chelated ester CO group and at 1650 cm^{-1} characteristic of a conjugated non-chelated benzoyl group. This suggests that the two enolic forms present in methyl benzoylacetoacetate are **1** and **2** (R^1 = Me, R^2 = Ph, R^3 = Me) which have respectively an ester group and a benzoyl group not involved in the H-bonded chelate ring. The NMR spectrum has three Me signals at τ 7·62, 7·68 and 8·01. The small signal at τ 7·68 is assigned to the Me of the acetyl group in the non-enolized form **4**. The relative intensities of the signals at τ 7·62 and 8·01 are 3:2. That at τ 7·62 is due to the Me group in the form **1** and is fairly similar to the position of the Me signals in benzoylacetone (τ 7·85). The enolic proton signal of this form occurs at τ −7·25 on the basis of the relative intensities of the enolic peaks, which is where the enolic proton signal of this form would be expected to appear. Thus the enolic proton signal of acetyldibenzoylmethane is at τ −7·29. The Me signal at τ 8·01 is assigned to the Me of structure **2**. The Me signal of methyl acetoacetate is at τ 8·04. The enolic proton signal of this isomer is at τ −3·08. This is consistent with the fact that the enolic proton signal in methyl acetoacetate (τ −1·95) is very much less downfield than that of benzoylacetone (τ −6·1). There is an appreciable downfield shift of the enolic proton in form **2** compared to methyl acetoacetate as would be expected from comparison of the positions at which the enolic signals occurs in acetylacetone (τ −5·0)[5] and diacetylbenzoylmethane (τ −7·29). The OMe protons of the forms **1** and **2** occur respectively at τ 6·53 and 6·42 while that of the diketoester **4** occurs at τ 6·26. The work of Elguero *et al.* on the NMR spectrum of methyl α,β-dioxobutyrate-α-phenylhydrazone indicates that the Me protons of a carbomethoxy group involved in a H-bonded chelate ring occur at lower field than when it is not involved in the chelate ring.[6] The OMe protons of the carbomethoxy group of the ketonic tautomer occur at τ 6·26.

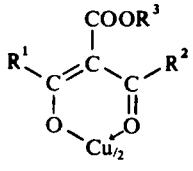
The IR and NMR spectra of ethyl benzoylacetoacetate and methyl *p*-methylbenzoylacetoacetate also indicate the presence of the same two enolic forms together with a lesser amount of the ketonic tautomer (Table 1). The proportions of the two enolic isomers are much the same in all three compounds. The enolic proton signals in methyl *p*-methylbenzoylacetoacetate are at τ −7·30 and −3·04 for the forms (**1** and **2**; R^1 = *p*-Me C_6H_4, R^2 = R^3 = Me), i.e. the enolic proton signal of the enol **1** is shifted slightly downfield whereas that of the enol **1** is shifted upfield. This is in accord with what is known of the influence of electron-donating substituents in *p*-substituted acylbenzoylmethanes in which the enolic signal is shifted slightly downfield.[5] Electron-donating substituents in *p*-substituted diacylbenzoylmethanes, in which the aroyl group is not involved in the chelate ring, are known to result in the enolic proton signal being less downfield.[1] The assignments made for these compounds are thus fully consistent with these facts.

The greater resonance stabilization of the enol tautomer compared to the keto tautomer in benzoylacetone (99% enolized) as compared to ethyl benzoylacetate (21% enolized) and this in turn compared to ethyl acetoacetate (8% enolized) would lead one to predict that the favoured enolic tautomer of benzoylacetoacetates (R^1 = Me, R^2 = Ph) would have the structure **1**. As was true for diacetylbenzoylmethane steric hindrance between the acetyl group and the phenyl ring in the tautomer **1**

would prevent the latter from lying in the plane of the chelate ring hence reducing the resonance stabilization of this form. Steric hindrance would also be significant, though to a smaller extent, in the tautomer **2** between the phenyl and carbomethoxy groups. This results in these compounds existing as a mixture of the two enol tautomers (**1** and **2**). That ethyl cinnamoylacetoacetate (R^1 = Me, R^2 = PhCH=CH, R^3 = Et), in contrast, exists solely as the tautomer **1** can be readily explained on the basis of the smaller steric requirements of the cinnamoyl group.[2] That steric hindrance does occur in these aroylacetoacetates is indicated by the fact that the keto tautomer is present in the extent of 10–15% though there is less than 5% of this tautomer in ethyl cinnamoylacetoacetate.

The NMR spectrum of ethyl dibenzoylacetate was characterized by a single enolic signal at τ −3·50 (Table 1) attributable to the enol tautomer **2** ($R^1 = R^2$ = Ph, R^3 = Et). The existence of this as the sole enol tautomer can again be rationalized on steric considerations. Models indicate that there would be severe steric interaction in the enol tautomer **1** were the phenyl groups to lie in the plane of the H-bonded chelate ring. This would be reduced in the tautomer **2** but is presumably still considerable in that the compound is only enolized to the extent of 50%. The greater proportion of the keto tautomer for ethyl dibenzoylacetate as compared to ethyl benzoylacetoacetate is paralleled by the observation that triaroylmethanes are only partially enolized whilst acyldiaroylmethanes are very extensively if not completely enolized.[8, 9] The IR spectrum of ethyl dibenzoylacetate was too complex to enable any deductions to be made as to the nature of the enol tautomer because of the presence of a large proportion of the keto tautomer. The NMR spectrum of ethyl benzoyl-*p*-methylbenzoyl acetate (R^1 = Ph, R^2 = *p*-MeC_6H_4, R^3 = Et) was similar to that of ethyl dibenzoylacetate though there were two enolic signals at τ − 3·43 and −3·47 due to the enol tautomers **1** and **2**.

The IR spectra of the copper chelates of both the aroylacetoacetates and aroylbenzoylacetates are characterized by a CO absorption at 1703–1705 cm^{-1} diagnostic of a conjugated but non-chelated ester group (Table 2). This indicates that the chelates of both series of compounds have the general structure **5**. There was no



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evidence of absorption at 1680 or 1650 cm^{-1} typical of a non-chelated acetyl and benzoyl group respectively. The structure of the copper chelate of aroylbenzoylacetates is thus different from that of the enol tautomer of these compounds while for the aroylacetoacetates the copper chelate has the structure corresponding to the major component of the mixture of the tautomers. These results are in marked contrast to those for triacylmethanes for which the enol and the copper chelate had the same structures.[1] The structures of the chelates of the diacylacetates correspond to what would be the most highly resonance-stabilized form *if* the phenyl group could lie comfortably in the plane of the chelate ring. It is, however, difficult to see how

TABLE 1. NMR AND IR SPECTRA OF DIACYCACETATES

Compound	R^1	R^2	R^3	NMR Data (τ) Enolic or methine proton	Methyl protons	OCH_3 protons	IR ν_{co} (cm^{-1})
Ethyl benzoylacetoacetate	Me	Ph	Et				
Enol tautomer 1				−7·15	7·62	6·05	1706
Enol tautomer 2				−3·25	7·97	5·93	1660
Keto tautomer 4				4·33	7·68		
Methyl benzoylacetoacetate	Me	Ph	Me				
Enol tautomer 1				−7·25	7·62	6·53	1710
Enol tautomer 2				−3·08	8·01	6·42	1660
Keto tautomer 4				4·52	7·68	6·26	
Methyl *p*-methylbenzoylacetoacetate	Me	*p*-MeC_6H_4	Me	−7·30		6·51	1710
				−3·04	8·04	6·42	1660
				4·53		6·29	
Ethyl dibenzoylacetate	Ph	Ph	Et				
Enol tautomer 2				−3·50			
Keto tautomer 4				3·78			
Ethyl benzoyl-*p*-methylbenzoylacetate	Ph	*p*-MeC_6H_4	Et				
Enol tautomers 2 and 3				−3·43, −3·47			
Keto tautomer 4				3·83			

TABLE 2. COPPER CHELATES OF DIACYLACETATES

Compound	M.p.	Form	Analysis Found % C	H	Formulae	Calc. % C	H	IR ν_{co} (cm^{-1})
Bis(ethyl benzoylacetoacetato)copper	232° dec.	Blue powder	59·3	4·8	$C_{26}H_{26}CuO_8$	58·9	5·0	1705
Bis(methyl benzoylacetoacetato)copper	235° dec.	Blue powder	57·2	4·7	$C_{24}H_{22}CuO_8$	57·4	4·4	1705
Bis(methyl *p*-methylbenzoylacetoacetato)copper	233° dec.	Blue powder	58·6	5·2	$C_{26}H_{26}CuO_8$	58·9	5·0	1703
Bis(ethyl dibenzoylacetato)copper	195° dec.	Green needles	66·2	4·6	$C_{36}H_{30}CuO_8$	66·1	4·6	1705
Bis(ethyl benzoyl-*p*-methylbenzoylacetato)copper	190° dec.	Green needles	66·9	5·1	$C_{38}H_{34}CuO_8$	66·9	5·0	1705

replacement of hydrogen by copper would ease this steric interaction. Indeed it might be expected to make it more severe because of the greater size of the copper pushing the groups attached to the carbons in the chelate ring closer together. That the metal has such a profound effect on the structure might have implications in biosynthesis, e.g. in alkylations of polyketides.[10] It is conceivable that the structure of metal chelates of a polyketide might vary with the nature of the metal, and this in turn would be expected to alter the position of alkylation. This topic is being currently examined.

EXPERIMENTAL

IR spectra were determined on a Perkin–Elmer 125 spectrophotometer as solns in CCl_4 for the diacylacetates and as solns in $CHCl_3$ for the copper chelates; NMR spectra for $CDCl_3$ solns on a Perkin–Elmer R10 spectrometer operating at 40 MHz using TMS as an internal standard.

Ethyl benzoylacetoacetate. This was prepared by benzoylation of ethyl acetoacetate following the procedure of Shriner *et al.*[11] It was obtained as a colourless oil, b.p. 115–117°/1 mm.

Methyl benzoylacetacetate. This was similarly obtained from methyl acetoacetate as a *colourless oil*, b.p. 110–115/0·65 mm. (Found: C, 65·4; H, 5·3. $C_{12}H_{12}O_2$ requires: C, 65·4; H, 5·5%).

Methyl p-methylbenzoylacetate. This was obtained as above using *p*-methylbenzoyl chloride as a *colourless* oil, b.p. 137–139°/1·5 mm. (Found: C, 66·7; H, 5·6. $C_{13}H_{14}O_4$ requires: C, 66·65; H, 6·0%).

Ethyl dibenzoylacetate. This was prepared by benzoylation of ethyl benzoylacetate following the procedure of Perkin and Stenhouse.[12] It was isolated as white crystals, m.p. 112–114° (lit.[12] 112°).

Ethyl benzoyl-p-methylbenzoylacetate. This was similarly obtained from *p*-methylbenzoyl chloride and ethyl benzoylacetate as *white needles*, m.p. 119–120°. (Found: C, 73·0; H, 5·6. $C_{17}H_{18}O_4$ requires: C, 73·5; H, 5·85%).

Copper chelates of diacylacetates. An aqueous alcoholic soln of copper acetate was added to an alcoholic soln of the diacylacetate. The precipitated copper chelate was filtered off, and crystallized from benzene (Table 2).

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