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Spectroscopic Studies on Enols

II.* Proton Magnetic Resonance and Infrared Spectra of Diacetoacetic and Cinnamoylacetoacetic Esters

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Proton magnetic resonance (PMR) data and infrared spectra of methyl and ethyl diacetoacetate confirm the complete enolisation of these compounds and also show that the intramolecular hydrogen bonds are stronger than in the enol of triacetylmethane. The spectra of ethyl cinnamoylacetoacetate and 3-cinnamoylpentane-2,4-dione are also discussed. The PMR spectrum of the latter compound shows the presence of two different chelate enols.

In the first part of these studies the extremely low infrared chelate carbonyl frequency and enol proton resonance field of a complex natural product, ceroptene [1], successively led to the investigation of simple β-triketones. It was found that even the first member of this series, triacetylmethane, was completely enolised in solution. The PMR and IR spectra indicated that the intramolecular hydrogen bond in the enol was very strong.

As β-triketones constitute a special case of α-substituted β-diketones it seemed desirable to investigate the influence of α-substituents other than acyl groups on the properties of the conjugated chelate system.

The esters of diacetoacetic acid are easily prepared and are almost completely enolised, as indicated by bromine titration experiments [2]. Methyl and ethyl diacetoacetate were chosen for comparison with triacetylmethane and cinnamoylacetoacetic ester and 3-cinnamoylpentane-2,4-dione for comparison with the cinnamoyl derivatives investigated in Part I.

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* Part I. Forsén, S. and Nilsson, M., Proton Magnetic Resonance Studies of Enolised β-Triketones, *Acta Chem. Scand.* 13 (1959) 1383.

EXPERIMENTAL

Methods. The PMR measurements were made on dilute carbon tetrachloride solutions at 40 Mc/s and 22 ± 1°C. The resonance shifts are given in *p.p.m.* against an external water standard and are indicated by δ_{aq}*; a positive sign denotes a shift towards higher field. The infrared spectra were recorded for *ca.* 0.1 M solutions in carbon tetrachloride. For further details the reader is referred to Part I.

Materials. Methyl and ethyl diacetoacetate were prepared according to a standard procedure [3] and were purified *via* the copper salts and distilled through a short Vigreux column. Methyl diacetoacetate,b.p. 84.5–85.0°/12 mm (Lit. b.p. 101–102°/20 mm.[3]) Ethyl diacetoacetate, b.p. 93.0–93.5°/11 mm (Lit. b.p. 95–97°/11 mm [4]).

Ethyl cinnamoylacetoacetate was prepared from sodioacetoacetic ester and cinnamoyl chloride in ether and was recrystallised from methanol and sublimed, m.p. 53–54° (Lit. m.p. 44° [5]). (Found: C 69.0; H 6.4. Calc. for $C_{15}H_{16}O_4$: C 69.2; H 6.2.)

3-Cinnamoylpentane-2,4-dione: Acetylacetone (0.1 mole) in dry ether (100 ml) was treated with powdered sodium or sodium hydride (0.1 mole) at 0° to give the sodium salt. Cinnamoyl chloride (0.1 mole) in ether solution was added with stirring at 0° during 1 h. The colour of the mixture at first became deep yellow but turned to pale yellow towards the end of the addition. The mixture was stirred at room temperature for another hour and water was then added. The ether solution was washed with water and with sodium hydrogen carbonate solution and was then extracted with sodium carbonate (10 %). The extract was acidified and the product recovered by ether extraction. The crude product was recrystallised from *cyclo*hexane to afford 3-cinnamoylpentane-2,4-dione in a 40 % yield. The melting point was, however, unsharp and varied somewhat. The freshly collected material had m.p. 58–62°, but on aging the m.p. range broadened. This as well as the general appearance of the crystals seemed to indicate the presence of two interconvertible forms. A sample was dried at room temperature over paraffin and phosphorus(V)oxide and analysed, m.p. 54–59°. (Found: C 73.2; H 6.1. Calc. for $C_{14}H_{14}O_3$: C 73.0; H 6.1.) 3-Cinnamoylpentane-2,4-dione gave a strong red colour with iron(III)chloride and a green colour with copper(II)acetate.

RESULTS

The PMR spectrum of ethyl diacetoacetate in carbon tetrachloride solution and the chemical shifts are given in Fig. 1. The assignments are obvious. The enol proton signal (1) occurs at δ_{aq}—13.35, markedly lower than for triacetylmethane (δ_{aq}—12.60). The signals from the protons of the acetyl groups (3) coalesce and the ethoxyl group shows up clearly (signal groups 2 and 4). The spectrum of the pure liquid was practically the same as that of the solution and no signals due to the presence of the non-enolised ester were detected.

In methyl diacetoacetate (spectrum not shown) the enol proton gives a signal at even lower field, δ_{aq}—13.43, the acetyl protons absorb at δ_{aq} 2.53 and the methoxyl protons at δ_{aq} 1.07.

The carbonyl region of the infrared spectrum of the ethyl ester is shown in Fig. 2. The peak at 1 710 cm^{-1} was assigned to the ester carbonyl group and the broad band at 1 560 cm^{-1} to the chelate carbonyl group. In the *O-H* region there is a very broad and weak absorption between 3 000 and 2 000 cm^{-1}. The relevant absorptions of the methyl ester are identical with those of the ethyl ester.

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* For conversion to τ-values [Tiers, G. V. D. *J. Phys. Chem.* **62** (1958) 1151] the following relation is valid at 22°C: $\tau = \delta_{aq} + 5.19$.

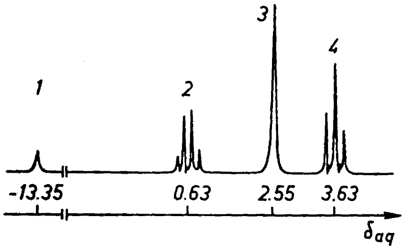


Fig. 1. PMR spectrum of ethyl diacetoacetate (carbon tetrachloride solution, mole fraction, $x = 0.08$).

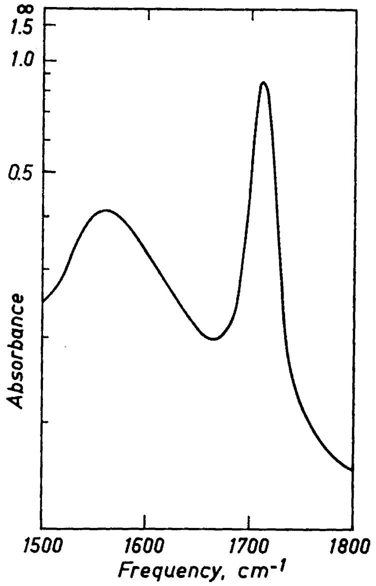
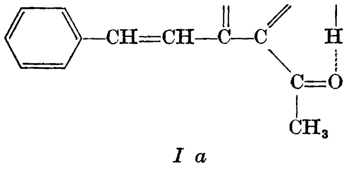


Fig. 2. The carbonyl region of the infrared spectrum of ethyl diacetoacetate (0.1 M solution in carbon tetrachloride, 0.1 mm cell, the absorption of the solvent is compensated)

The PMR spectrum of ethyl cinnamoylacetoacetate, presented in Fig. 3, is more complicated but still easy to interpret. Signal 1 is due to the enol proton and signal group 2 is made up by contributions from the protons of the benzene ring and from the protons at the *trans* ethylenic double bond (conventional coupling constant, $J = 15$ c/s). Signal groups 4 and 6 are due to the ethoxyl protons and signal 5 to the acetyl protons. Signal 3 may be due to the presence of a small amount (less than 5 %) of non-enolised material.

The IR spectrum contains bands due to the ester carbonyl group (1 710 cm^{-1}), to the ethylenic double bond (1 630 cm^{-1}) and to the conjugated benzene ring (1 580 cm^{-1}). A broad band at 1 530 cm^{-1} is tentatively assigned to the chelated carbonyl group.



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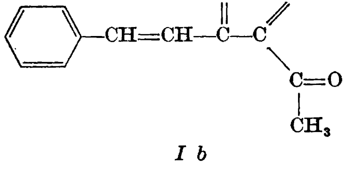

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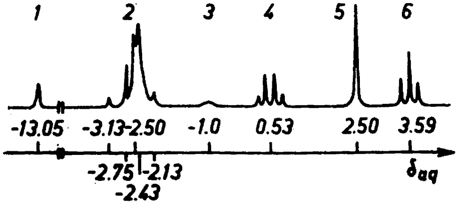

Fig. 3. PMR spectrum of ethyl cinnamoylacetoacetate (carbon tetrachloride solution, $x = 0.08$).

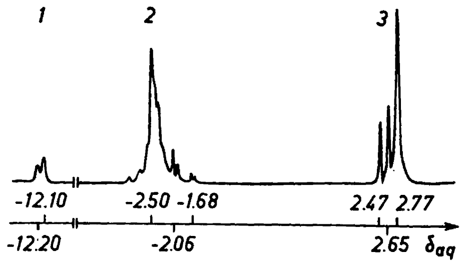

Fig. 4. PMR spectrum of 3-cinnamoylpentane-2,4-dione (carbon tetrachloride solution, $x = 0.08$).

The PMR spectrum of 3-cinnamoylpentane-2,4-dione can be interpreted in terms of the two enol forms I *a* and I *b*.

The spectrum of the enol I *a* should contain a single peak for the acetyl protons, whereas form I *b* should give two different acetyl peaks.

In the PMR spectrum, shown in Fig. 4, there are three peaks in signal group 3, which judged from the chemical shift should be due to acetyl protons. The relative intensities are 4:1:1. Signal group 1 must be due to the enol protons; the intensity ratio is 2:1. Signal group 2 consists of signals from the benzene ring protons and from the protons of the ethylenic double bond. The splitting of the latter indicates *trans* configuration ($J = 15$ c/s) as well as an effect similar to that found in signal groups 1 and 3 (internal intensity ratio 2:1). The spectrum is thus apparently made up by contributions from forms I *a* and I *b* in the proportion 2:1.

In benzene solution the splitting persists approximately unchanged, while the intensity ratio is somewhat lowered (1.8:1).

The infrared spectrum of the solution as well as of the solid compound (recorded on a potassium bromide disc) showed bands at 1 675 cm^{-1} (conjugated carbonyl group), 1 635 cm^{-1} (ethylenic double bond), 1 605 and 1 580 cm^{-1} (benzene ring) and also a broad band with the centre near 1 550 cm^{-1} due to the chelate carbonyl group.

DISCUSSION

The PMR data for the diacetoacetic esters indicate that the protons of the acetyl groups are equivalent. This is analogous to the findings for acetylacetone[6] and triacetylmethane and indicates a rapid transfer of the proton in the hydrogen bond. The equivalence of the acetyl protons and the "normal" infrared absorption of the ester carbonyl group indicates that the ester carbonyl, as expected, is not directly engaged in hydrogen bonding.

The data for the diacetoacetic esters fit well into the correlation of enol proton shifts and chelate carbonyl absorption frequencies for β-triketones in Part I and also indicate that the hydrogen bonds in these esters are stronger than in the enol of triacetylmethane and similar to that in acetyldimedone (δ_{aq}—13.30).

The carbalkoxy group thus has a larger effect than the acetyl group in increasing the strength of the hydrogen bond and stabilising the conjugated chelate system. As steric factors can be regarded as fairly constant the effect could be described in terms of the greater "inductive, electron-withdrawing power" of the carbalkoxy group.

The data for the cinnamoyl derivatives, however, deviate from this pattern. The comparison of cinnamoylacetoacetic ester and cinnamoylpentanedione indicates that the hydrogen bond is strongest in the former and thus confirms the larger effect of the carbethoxy group on the conjugated chelate system.

The infrared chelate carbonyl absorptions indicate that the hydrogen bond is more marked in the cinnamoyl derivatives than in the simple diacetoacetic esters and unconjugated β-triketones. The PMR enol proton shifts on the other hand indicate the opposite to be the case. For acyl-dimedones both PMR and IR data indicated the hydrogen bonds to be stronger in the conjugated compounds (Part I). The splitting of the enol proton signal from cinnamoylpentanedione also presents the unexpected fact that the isomer, which occurs in the least amount, has the largest negative enol proton shift.

The enol protons of the two forms of cinnamoylpentanedione are situated at different distances from the benzene ring as well as from the ethylenic double bond. Magnetic anisotropy effects from these sources [7,8] may therefore contribute to the observed splitting of the enol proton signal.

When judging the enol proton resonance frequency in cinnamoylacetoacetic ester and cinnamoylpentanedione it is to be noted that the olefinic protons of these compounds absorb around δ_{aq}—2.4, a significantly higher field than that for the corresponding resonance of ceroptene and cinnamoyldimedone (δ_{aq} *ca.*—3.1). For the present no attempt has been made to explain these phenomena, which probably are related to the larger flexibility of the molecules now investigated.

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