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EFFECT OF UV IRRADIATION ON SOME β-DICARBONYL COMPOUNDS IN SOLUTION

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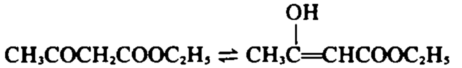
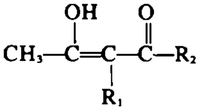
Abstract—The pronounced effect of UV-polychromatic irradiation in shifting the position of keto-enol equilibrium has been described and in particular the influence of UV irradiation on the keto-enol ratio of ethylacetoacetate in cyclohexane solutions was examined. It was shown that the equilibrium



$$CH_3COCH_2COOC_2H_5 \rightleftharpoons CH_3\overset{\overset{\displaystyle OH}{|}}{C}{=}CHCOOC_2H_5$$

is strongly displaced to the keto form. The results indicate clearly that the effect of the UV-irradiation on the keto-enol equilibrium is reversible.

We have now extended this study to some other β-dicarbonyl compounds as α-alkylacetoacetates and β-diketones. The influence of UV irradiation on these compounds was established by their UV and IR spectra.



$$CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}\underset{\underset{\displaystyle R_1}{|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_2$$

1: $R_1 = H$; $R_2 = OEt$ 4: $R_1 = iso\text{-}C_5H_{11}$; $R_2 = OEt$
2: $R_1 = H$; $R_2 = OMe5$: $R_1 = H$; $R_2 = Me$
3: $R_1 = Pr$; $R_2 = OEt6$; $R_1 = H$; $R_2 = Et$

Calvin *et al*[2] measured the UV spectra of β-diketones and β-ketoesters in chloroform and reported maxima at 246 nm. According to Kabachnik *et al*[3] the enolizable β-ketoesters of the type 3 and 4 in different solutions show maxima in the region 233–240 nm associated with the high intensity K band of the chelated enolic tautomer. The low intensity band of the keto form (280–300 nm) which is related with the $n \rightarrow \pi^*$ transition is completely masked by the high intensity band in β-ketoesters of appreciable enol content even in ethanol which shifts the equilibrium towards the keto form.

We examined the UV spectra of compounds 1–6 in cyclohexane. The data obtained (Table 1) are in essential agreement with those previously reported.

Fig 1 shows the change of the intensity of the characteristic absorption bands for enolic forms of the compounds 1, 2 and 4 during the equilibration process. We found that the UV spectrum of ethyl-iso-pentylacetoacetate (4) differs greatly from those of compounds 1 and 2. During the equilibration process a new strong absorption maxi at 240 nm appears (curve 1 compared with curve 4).

Irradiation of cyclohexane solutions of compounds 1–6 with Hanau-SRU 300 W lamp in quartz glass apparatus under standard conditions led to the diminuation of the intensity of the characteristic bands in their UV spectra. In all cases a good linear relation corresponding to formula

$$A = k\tau + n$$

where A is the absorbance and τ is the time of irradiation was observed. A statistical analysis of each set of data was carried out. The calculated values of coefficients k and n are given in Table 2.

As the intensity of the irradiation was constant in all experiments the results presented strongly indicate that the introduction of α-alkyl substituents in ethylacetoacetate leads to an important decrease in the slope of the respective straight line. These differences probably can be traced to the lower enol content in the initial equilibration solutions of the α-substituted β-keto-esters. On the other hand this behaviour is also characteristic of compounds (5 and 6) possessing a high enol content.

It was proved unequivocally that the spectral changes in the 220–280 nm region during the time of irradiation do not lead to the appearance of a new absorption maxima in the UV spectra of the investigated compounds. It is apparent that if UV irradia-

Table 1. UV absorption data for enolizable β-dicarbonyl compounds[a]

Compound	max (nm)
$CH_3COCH_2COOC_2H_5$ (1)	245
$CH_3COCH_2COOCH_3$ (2)	246
$CH_3COCH(n\text{-}C_3H_7)COOC_2H_5$ (3)	227
$CH_3COCH(iso\text{-}C_5H_{11})COOC_2H_5$ (4)	227, 240
$CH_3COCH_2COCH_3$ (5)	273

[a] Average equilibration time, 8 days.

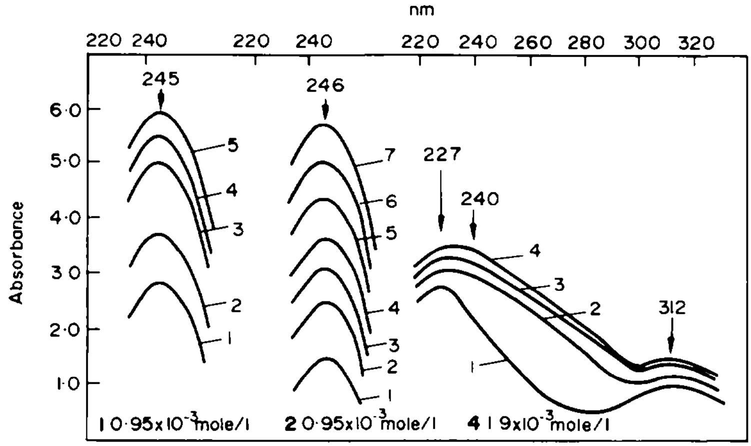


Fig 1. UV spectra of compounds, **1**, **2** and **4** measured at different times after solution (hr): (**1**), 1—0; 2—0·5; 3—2; 4—6; 5—20, (**2**), 1—0; 2—1; 3—2; 4—4; 5—6; 6—8; 7—17, (**4**), 1—0; 2—72; 3—144; 4—216. Solvent: cyclohexane.

Table 2[a]

Compound	C^b	k	n
1	0·95×10^{-3}	−0·075	6·01
2	0·95×10^{-3}	−0·050	5·39
3	0·95×10^{-3}	−0·006	1·14
	1·90×10^{-3}	−0·007	2·02
4	1·90×10^{-3}	−0·007	2·16
5	0·95×10^{-3}	−0·003	8·78
6	0·95×10^{-3}	−0·003	8·24

[a] Solvent: cyclohexane.
[b] Mole/l.

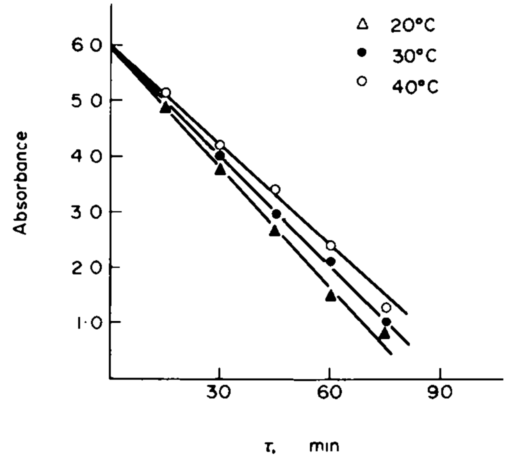


Fig 2. A plot of absorbances of enolic form of ethylacetoacetate against the time of UV irradiation at different temperatures.

tion causes only *cis–trans* isomerism of the enol, the appearance of a new absorption band related with the other conformation should be obtained. On the other hand the IR spectra of ethylacetoacetate in cyclohexane before and after irradiation show that as the enol form decreases (absorption bands in 1640–1660 cm^{-1} region) the keto form increases (absorption bands in 1720–1740 cm^{-1} region). After 24 hr the enol form is restored completely. Similarly, the UV irradiation affects the ratio of the absorbances of the two tautomeric forms in the IR spectrum of ethyl-*n*-propyl-acetoacetate in cyclohexane in the same way.

Data presented in Fig 2 are an attempt to find the influence of the temperature on the effect obtained. Variation of the rate of diminuation of the enol content during the irradiation shows the following order with respect to temperature

$$k_{20} > k_{30} > k_{40}.$$

The effect of solvent polarity on the position of equilibrium in tautomeric systems of the kind studied has been recognized for many years and has been attributed to the difference in polarity of the keto form and the chelated enol.[4] The implication is strong that the only important enolic variety is a *cis* enol.[5,6] Continuing our work on the influence of UV irradiation on enolizable β-dicarbonyl compounds we have now investigated a methanol solution (conc. 0·95×10^{-3} mole/l) of ethylacetoacetate. In contrast with the results obtained in non polar solvents the diminution of enol content does not follow a linear dependence on the time of irradiation (Fig 3).

The greatest change in enol content has been observed after 90 min. Further irradiation does not affect the keto/enol ratio.

The UV spectra of the irradiated solutions were investigated over a long period of time (500 hr). The data obtained for compound **2** (see Figs 1 and 4a) shows that the effect of irradiation on the keto–enol

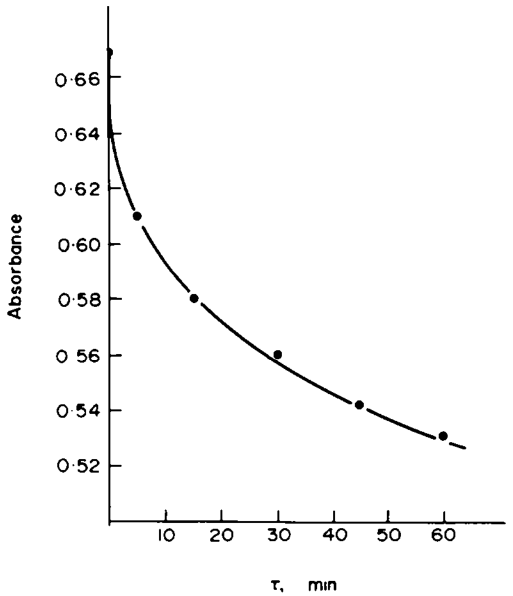


Fig 3. Dependence of the absorbance of enol form of ethylacetoacetate in methanol (conc. $0{\cdot}95\times10^{-3}$ mole/l) on the time of UV irradiation.

equilibrium is reversible. This result is analogous to our previous results[1] for compound **1**. The irradiated solutions of **4** were also investigated spectrophotometrically. The absorption curves (Fig 4b) of the UV spectrum of **4**, 500 hr after the irradiation show that the intensity of the absorption bands is very different from the initial spectrum of this compound. As can be seen from Figs 1 and 4b the maximum at 240 nm in UV spectrum of irradiated solutions of **4** corresponds closely to the band at 241 nm which appears in the process of equilibration. This band can reasonably be attributed to rotational isomerism. On this view the general intense absorption in 240 nm region of the enol form of **4** (Fig 1, curve 4) may well be masking relatively weak bands of significantly different frequencies.

It may be re-emphasized that after a long period of time the final absorbances of the enol form in the irradiated solutions of the α-alkyl substituted acetoacetates are much higher than those in the initial equilibrated solutions. The β-diketones **5** and **6** deserve special attention. It has been noted that there is no appreciable change of the enol content in investigated solutions during UV irradiation.

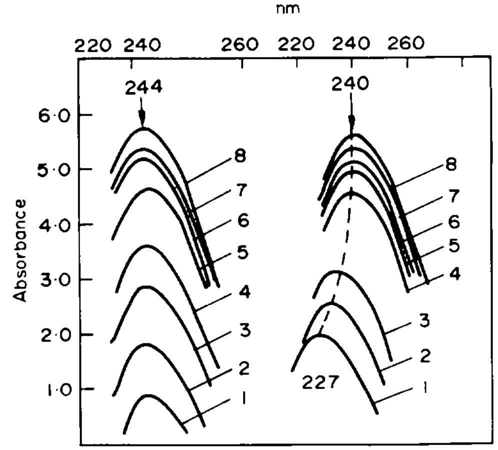


Fig 4. UV spectra of compounds **2**(a) and **4**(b) at different time after UV irradiation (hr); (a) 1—0; 2—24; 3—48; 4—72; 5—120; 6—168; 7—240; 8—504; (b) 1—0; 2—38; 3—62; 4—72; 5—199; 6—312; 7—408; 8—504. Solvent: cyclohexane, concentration—**2** $0{\cdot}95+10^{-3}$; **4** $1{\cdot}90\times10^{-3}$ mole/l.

EXPERIMENTAL

The α-substituted acetoacetates were produced by alkylating sodium ethylacetoacetate with suitable alkyl halides in ethanol solution. Final purification was accomplished by fractionation in a spinning band column. Ethylacetoacetate, methylacetoacetate, acetylacetone and propionylacetone were commercial products and were rectified prior to use to a purity 99% or better. Cyclohexane was Merck. Spectroscopic Grade. The concentration of solns investigated is given in the text.

The solns (2 ml) were irradiated with a Hanau-SRU 300 W high pressure mercury arc lamp in a quartz glass apparatus under standard conditions. The light quanta were determinated by using a uranyl oxalate actinometer. The value obtained was $6{\cdot}37\times10^{16}$ quanta ml^{-1} min^{-1}.

The UV absorption spectra were measured on a Specord UV-VIS spectrophotometer by using quartz cells with path lengths 0·1, 0·2 or 0·5 cm. The data obtained were recalculated for path length 1 cm. The IR spectra were measured on a double beam spectrophotometer UR-10 produced by Carl Zeiss-Jena.

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