

## PHOTOCHEMISTRY OF ENOLIZABLE $\beta$ -DICARBONYL COMPOUNDS: STUDY ON THE PHOTOKETONIZATION OF SOME ESTERS OF AROYLACETIC ACIDS

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### Summary

A detailed experimental study of the reversible photochemistry of some esters of aroylacetic acids indicates the photoformation of the respective ketonic forms as a result of the shift of the keto-enol equilibrium. The rate constants and quantum yields of the process under consideration have been determined. Important differences in the photosensitivity of  $\beta$ -ketoesters depending on the structural features have been established.

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### Introduction

The concept of photo-induced hydrogen migration was originally put forward in order to explain the photochemical behaviour of *ortho*-substituted acetophenones and benzophenones [1, 2]. During the last few years interest has been growing in the field of light-induced enolization and related transformations [3 - 8]. Special attention has been given to the question of the excited enol. Its understanding has further increased the significance of this area of photochemistry [9, 10]. It is instructive, however, to note that, although the process of photoenolization has been the object of a considerable number of investigations of various degrees of sophistication, the effect is open to several interpretations [11, 12].

Guided by the desire to discover new pathways based on the idea of photo-activated hydrogen transfer, we have examined experimentally the photochemical behaviour of several  $\beta$ -dicarbonyl compounds. It was found [13] that irradiation of the highly enolic species gives high concentrations of  $\beta$ -dicarbonyl systems. Reversion to the enolic form occurs to some extent photochemically as well as in a dark reaction. Our current interest is concerned with the study of the influence of some structural features and the nature of irradiation on the rate and quantum yield of the photoketonization process.

This paper is a logical extension of earlier work in this field [14 - 17]. It was our aim to establish the effect of substituents on the photochemical properties of the ethyl esters of aroylacetic acids.

## 2. Experimental

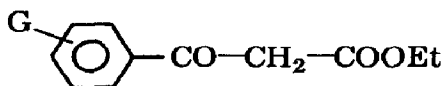
Compounds 1 - 9 were produced by acylating sodium ethylacetoacetate with suitable acyl halides in ether solution and a subsequent cleavage of the esters of the respective acids [18]. Final purification was accomplished by fractionation in a spinning band column.

Heptane (Merck, spectroscopic grade) was used as solvent. Heptane solutions with concentrations  $0.25 \times 10^{-4}$ ,  $0.50 \times 10^{-4}$  and  $1.00 \times 10^{-4}$  mol l<sup>-1</sup> were prepared and kept in the dark until thermodynamic equilibrium between two tautomeric forms was established. The samples (2 ml of these solutions) were thermostated at 20 °C in a quartz-glass vessel and exposed to direct sunlight or 313 nm UV irradiation under standard conditions. UV irradiation was obtained from a Hanau medium pressure mercury arc lamp, using filters for 313 nm wavelength. In the last case, the light quanta falling onto the quartz cell (1 cm) were determined by using a uranyl oxalate actinometer. The value obtained was  $1.06 \times 10^{16}$  quanta ml<sup>-1</sup> s<sup>-1</sup>. Heptane solutions of compounds 2 - 4 were irradiated by a beam from a nitrogen laser of wavelength  $\lambda = 337$  nm, possessing 200 kW pulse power with pulse duration 5 s and a frequency of 10 Hz.

The UV absorption spectra were measured on a Specord-UV-VIS spectrophotometer using quartz cells 0.5, 1.0 and 2.0 cm long. The data obtained were recalculated for a cell width of 1.0 cm. The IR spectra were measured on a UR-10 double beam spectrophotometer produced by Carl Zeiss - Jena. The NMR spectra were recorded on a Tesla BS 487C 80 MHz spectrometer for 3% cyclohexane solutions of compounds 1 - 9. Tetramethylsilane was used as the internal standard and the resonance fields are reported in  $\delta$  values. The sample temperature was 20 °C. Determinations of the enol fraction were made in non-irradiated samples and in samples irradiated with UV light for 12 h on the basis of the ratio of intensities for the respective signals of the  $=C-$  and  $>CH_2$  groups. The quantum yields were determined following the procedure given by Masson *et al.* [19].

## 3. Results and discussion

After equilibration in the dark, solutions of compounds 1 - 9



(1, G = H; 2, G = *p*-CH<sub>3</sub>; 3, G = *m*-CH<sub>3</sub>; 4, G = *o*-CH<sub>3</sub>; 5, G = *p*-NO<sub>2</sub>; 6, G =

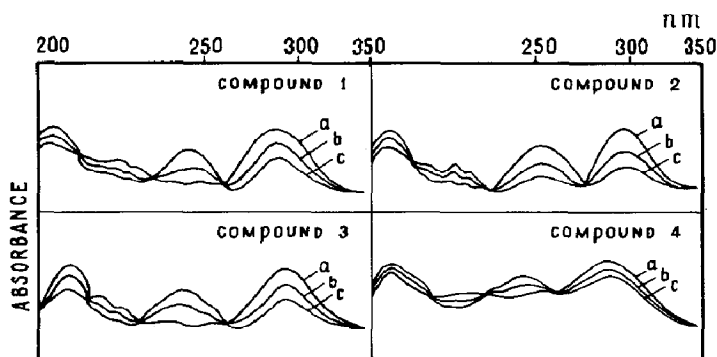


Fig. 1. UV spectra of compounds 1 - 4 measured at different times after the start of the UV 313 nm irradiation. Initial concentration,  $1.0 \times 10^{-4} \text{ mol l}^{-1}$ .

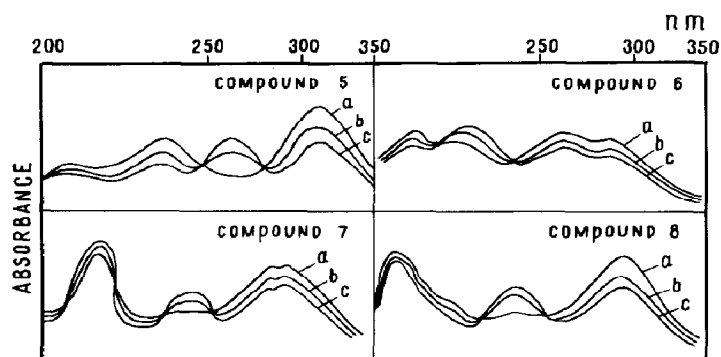


Fig. 2. UV spectra of compounds 5 - 8 measured at different times after the start of the UV 313 nm irradiation. Initial concentration,  $1.0 \times 10^{-4} \text{ mol l}^{-1}$ .

*m*-NO<sub>2</sub>; 7, G = *m*-OCH<sub>3</sub>; 8, G = *p*-Cl; 9, G = *p*-Br) in heptane were irradiated with 313 nm UV light, or with a 337 nm laser beam (compounds 2 - 4). In all cases, irradiation resulted in profound spectral changes (Figs. 1 and 2). Similar alterations in the UV spectra were obtained when direct sunlight was used. In this case it is noteworthy that sunlight does not cause any spectral change if the wavelengths up to 340 nm are eliminated by means of a proper set of filters. It was shown that the rate of the observed spectral changes in the 240 - 290 nm region during the irradiation was independent of the presence or absence of oxygen in the solutions of the  $\beta$ -ketoesters.

These changes are reversible, *i.e.* the original spectra of the solutions are restored in the dark at rates which vary widely with the compound, temperature and the presence of catalysts. The reverse process after the irradiation change is not too fast at room temperature and conventional spectrophotometric measurement may be used.

The action of sunlight or UV irradiation also causes changes in the IR spectral characteristics of compounds 1 - 9. The respective absorption bands in the 6  $\mu\text{m}$  region found for compound 2 ( $2 \times 10^{-2} \text{ mol l}^{-1}$ ) before (curve a), immediately after 8 h of sunlight irradiation (curve b) and 44 h after the end of irradiation (curve c) are shown in Fig. 3. The absorptions

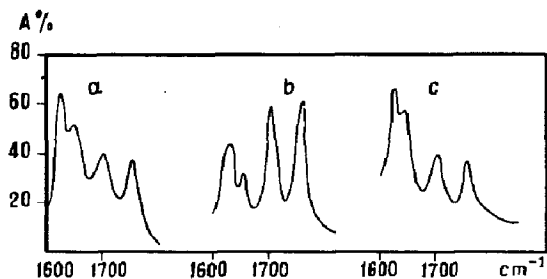


Fig. 3. IR spectra of a  $2 \times 10^{-2}$  mol  $l^{-1}$  heptane solution of compound 2: (a) before irradiation, (b) after 8 h sunlight irradiation and (c) 44 h after the end of the irradiation.

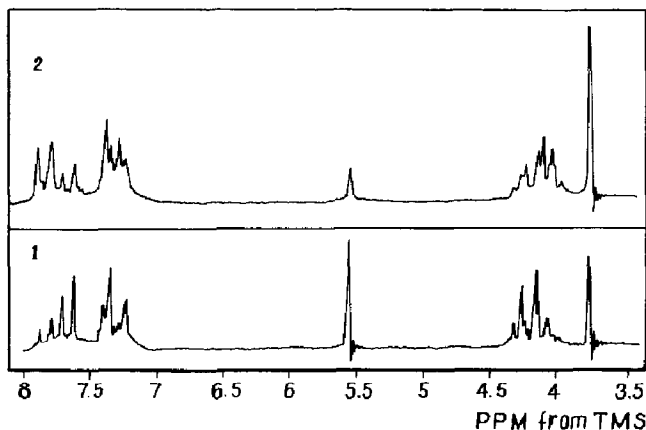
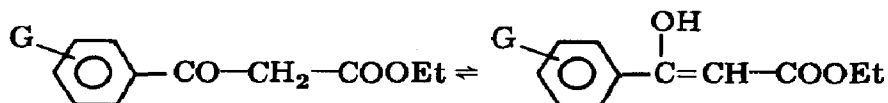


Fig. 4. NMR spectrum of compound 8 (3% solution) in heptane: 1, before exposure to UV irradiation; 2, after 12 h exposure.

due to the enolic form at 1630 and 1660  $cm^{-1}$  decreased with a parallel absorption increase at 1700 - 1740  $cm^{-1}$  due to the ketonic form of compound 2. The same spectroscopic behaviour was observed with other compounds.

The comparative NMR study of irradiated and non-irradiated cyclohexane solutions of compounds 1 - 9 (3% solutions) shows the existence of substantial differences. The decrease in the intensity of the methine proton signal leads to an increase in the intensity of the methylene proton signal (Fig. 4.).

It is seen that, as with the examples of photoketonization discussed previously [13 - 17], the keto-enol equilibrium in heptane solutions of compounds 1 - 9 is profoundly influenced by sunlight or UV 313 nm irradiation. The spectroscopic evidence is sufficient to decide that the keto-enol equilibrium



is shifted to the ketonic form under the influence of irradiation. The presence of isobestic points in the successive UV spectra (Figs. 1 and 2) implies that the irradiation affects only the ratio between two tautomeric forms.

The observed UV spectral data on the photoketonization were used to obtain the values of the molecular extinction coefficients  $\epsilon$  of the prototropic forms of compounds 1 - 9, following the method given by Vierord. The linear dependence between the absorbances  $A^e$  and  $A^k$  of enolic and ketonic forms, respectively, determined at different durations of the UV irradiation of the sample of compound 8 is given in Fig. 5. The point of

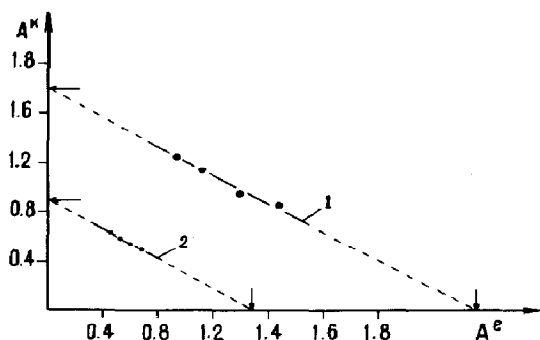


Fig. 5. Dependence between the absorbances  $A^e$  and  $A^k$  of enolic and ketonic forms of compound 8 measured at different times after the start of the UV irradiation. Initial concentrations: 1,  $1.00 \times 10^{-4}$ ; 2,  $0.50 \times 10^{-4} \text{ mol l}^{-1}$ .

TABLE 1

UV absorption data for compounds 1 - 9<sup>a</sup>

Compound	$\lambda_{\text{max}}^k$ (nm)	$\lambda_{\text{max}}^e$ (nm)	$\epsilon^k$	$\epsilon^e$	$f$	Enol percentage
1	242	290	11500	21400	0.49	70.2
2	251	294	17000	27800	0.64	72.8
3	245	290	12000	24300	0.49	65.7
4	245	284	8800	12000	0.28	51.3
5	257	313	16500	27800	0.60	72.4
6	225	290	21200	23800	0.53	66.6
7	251	286	6800	23400	0.52	57.4
8	252	293	15500	24200	0.54	66.7
9	258	294	16800	27600	0.61	62.0

<sup>a</sup>Average equilibrium time, 8 d.

intersection of the extrapolated straight line and the respective coordinate axis gives the numerical value of the extinction coefficient. The mean values determined on the basis of three independent experiments using solutions of different  $\beta$ -ketoester concentrations are presented in Table 1.

The influence of the type and the position of the substituent G (see earlier) on the spectral characteristics of esters 1 - 9 has not yet been an object of current interest. Recently, a number of widely scattered and isolated reports [20, 21] have appeared. One can see (Table 1) that the positions of two basic absorption maxima  $\lambda_{\max}^k$  and  $\lambda_{\max}^e$  are virtually independent of the type of substituent with the exception of compound 5. In this case, there is to some extent a bathochromic displacement of  $\lambda_{\max}^e$ . More important is the influence of the substituents on the oscillator strength  $f$ . The most striking feature in this respect is the low value of  $f$  for compound 4. This can be ascribed to the non-planarity of the molecule because of steric hindrance.

The enol content in deuterochloroform solutions of esters of some aroylacetic acids has recently been determined by NMR studies [22]. The data obtained substantially differ from the results [21] obtained by the use of bromine titration. This discrepancy may be connected with a newly discovered factor affecting the keto-enol equilibrium. It is evident that reliable data on the keto-enol ratio can be found only if the sample is not affected by sunlight. The enol content in heptane solutions of compounds 1 - 9 (equilibrated in the dark) has been determined spectroscopically. The data found are collected in Table 1. As seen the percentage of the enol form varies with the type and the position of the substituent in the benzene ring. There is no correlation between the respective  $+\sigma$  constants of the substituents and the quantity of the enol form.

The kinetics of photoketonization was studied using three different initial concentrations of the respective  $\beta$ -dicarbonyl compound:  $C_0 \approx 1.0 \times 10^{-4}$ ,  $0.5 \times 10^{-4}$  and  $0.25 \times 10^{-4}$  mol l<sup>-1</sup>. In all of the cases, the experimental data obtained satisfy the following equation which is the solution of the rate equation for a first order reaction:

$$\ln C_0^e - \ln C_t^e = kt \quad (1)$$

where  $C_0^e$  denote the initial concentration of the enol form and  $C_t^e$  is the concentration  $t$  s after starting the kinetic run. The observed rate constants  $k$  of the photoketonization which do not include the absorbed intensity (first order photoreaction) are presented in Table 2. The numerical values of  $k$  have been determined on the basis of a statistical analysis of each set of experimental data. The standard deviations are between 0.3 and 2%. It was shown that the nature of the irradiation does not influence the reaction kinetics. The quantum yields of the photoketonization of compounds 1 - 9 are collected in Table 3.

A comparison of the data presented in the tables shows the existence of a relation between the magnitudes of the rate constants  $k$ , quantum yields  $\phi$  and oscillator strengths  $f$ . As an example, the highest rate constant and quantum yield and a very high value of the oscillator strength were found for compound 9.

The results from the quantitative kinetic study have been used to determine the effect of the type and the position of the substituent in the ben-

TABLE 2

Rate constants  $k$  of the photoketonization in heptane solutions of compounds 1 - 9 measured by UV spectroscopy<sup>a</sup>

Compound	$k$ ( $s^{-1}$ ) $\times 10^4$		
	b	c	d
1	5.17	5.02	5.44
2	7.81	7.85	7.77
3	5.23	5.83	6.07
4	0.40	0.37	0.39
5	6.42	6.91	6.34
6	3.69	3.58	3.68
7	6.10	6.13	6.85
8	8.23	7.90	7.95
9	9.70	9.90	9.70

<sup>a</sup>Exciting irradiation, 313 nm.

Initial concentration of the  $\beta$ -ketoester in the irradiated solution: b,  $0.25 \times 10^{-4}$ ; c,  $0.50 \times 10^{-4}$ ; d,  $1.00 \times 10^{-4}$  mol l<sup>-1</sup>.

TABLE 3

Quantum yields  $\phi$  of the photoketonization in heptane solutions of compounds 1 - 9<sup>a</sup>

Compound	$\phi$
1	0.53
2	0.73
3	0.60
4	—
5	0.60
6	0.39
7	0.64
8	0.85
9	0.91

<sup>a</sup>Exciting irradiation, 313 nm.

zene ring of compounds 2 - 9 on the process under consideration. It is as yet difficult to rationalize the dependence of rate constants and quantum yields on the structure of the compounds under consideration. It seems, however, that the attachment of electron-releasing atoms or groups to the *para* position of the benzene ring tends to increase the oscillator strength because of an enlargement of the length of the conjugated system. In so far as the prototropic transformation can be regarded as an acid-base type of interaction, it is reasonable to consider that the increase in electron density at the methine carbon atom due to conjugation of the electron-releasing *p*-substituent will favour the ketonization process.

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