Tetrahedron Vol. 33, pp 1013 to 1015 Pergamon Press 1977 Printed in Great Britain

ON THE PHOTOSENSITIVITY OF DIBENZOYLMETHANE, BENZOYLACETONE AND ETHYL BENZOYLACETATE IN SOLUTION

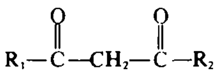
P. MARKOV* and I. PETKOV
Department of Organic Chemistry, University of Sofia, Sofia, Bulgaria

(*Received in UK* 2 *August* 1976; *Accepted for publication* 11 *October* 1976)

Abstract—The influence of sunlight on the keto-enol ratio of dibenzoylmethane, benzoylacetone and ethyl benzoylacetate in heptane solution was examined. It was shown that the tautomeric equilibrium is strongly displaced to the keto form. Important differences in the photosensitivity of β-diketones and β-ketoesters depending on the structural features and the nature of irradiation have been established.

In an earlier investigation[1] it was shown that the ratio keto/enol in hexane solutions of acetylacetone and hexadione-2,4 was not affected by UV irradiation. More recently, the influence of UV light on the keto-enol equilibrium in solutions of some β-diketones has been studied by Veierov *et al.*[2]

The present study was undertaken to gain further insight into the influence of some structural features and the nature of the irradiation on the process of photoketonization. For this purpose the action of sunlight and UV irradiation on heptane (0.5×10^{-4} mol × l^{-1}) solutions of compounds 1–5 has been examined.



$$R_1\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R_2$$

1: $R_1 = Me$, $R_2 = Me$; 2: $R_1 = Ph$, $R_2 = Me$; 3: $R_1 = Ph$, $R_2 = Ph$ 4: $R_1 = Ph$, $R_2 = OEt$ 5: $R_1 = Me$, $R_2 = OEt$

It was established that the enol forms of benzoylacetone (**2**), dibenzoylmethane (**3**) and ethyl benzoylacetate (**4**) are sensitive toward sunlight. The observed changes in their UV spectra, which appear after a successive expositions of the solutions are presented in Figs. 1–3.

The spectral change in the 280–340 nm region is accompanied by the appearance of a new absorption maxima (240–250 nm). According to Morton *et al.*,[3] the high intensity bands (280–340 nm) are associated with the π → π* transition in the CO conjugated ethylene system (enol form). Newly formed bands (240–250 nm) belong to the benzoyl group of the ketonic form. The spectrophotometric assay of the irradiated solutions, kept in dark shows a gradual restoration of their original spectral characteristics.

The action of sunlight on the keto-enol ratio of **4** was studied by IR spectra. The absorption bands in the 6 μm region found for this compound before, after and at varying intervals after irradiation are shown in Fig. 4.

As expected, the strong IR absorption near 1630–1660 cm^{-1}, attributed to the enol form (Fig. 4a), decreases in intensity during irradiation while the absorption bands related with the ketonic form (1700–1760 cm^{-1}) increase their intensities (Fig. 4b).

These results reveal that the keto-enol equilibrium in heptane solutions of compounds **2**–**4** is strongly displaced to the ketonic form under the influence of sunlight. As it has already been shown[1,4,5] in the case of ethylacetoacetate (**5**) and its analogues, such a process can be provoked by UV irradiation only.

Irradiation of heptane solutions of compounds **1**–**3** with a UV monochromatic (313 nm) light does not lead to a change in their spectral characteristics. But for **4** such a change take place in the both cases by an action with sunlight or ultraviolet irradiation.

The data, presented in Table 1 give reasons for some conclusions concerning the relation between the structure of β-dicarbonyl compounds into consideration and the possibility of photoketonization.

Previously[6,7] we used the Pariser-Parr-Pople SCF-CI

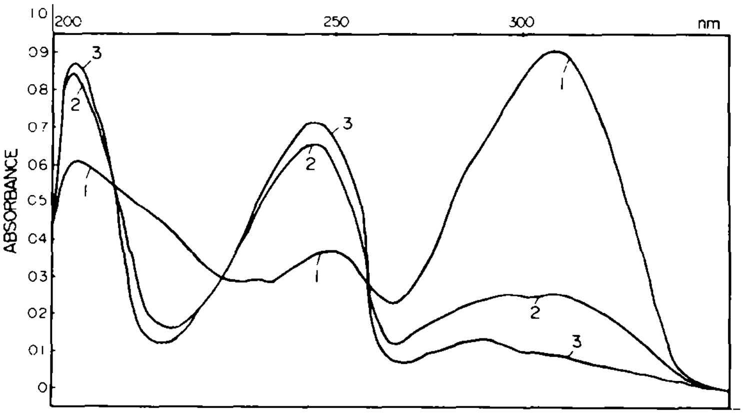


Fig. 1. UV absorption spectrum of dibenzoylmethane in heptane (*ca.* 0.25×10^{-4} M curve 1, before exposition to sunlight; curve 2, after a 60 min exposition; curve 3, after 120 min exposition.

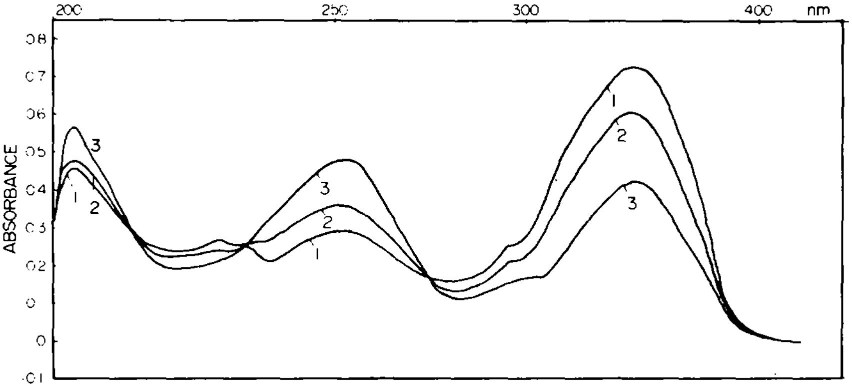


Fig. 2. UV absorption spectrum of benzoylacetone in heptane (*ca.* 0.5 × 10^{-4} M): curve 1, before exposition to sunlight; curve 2, after a 60 min exposition; curve 3, after a 120 min exposition.

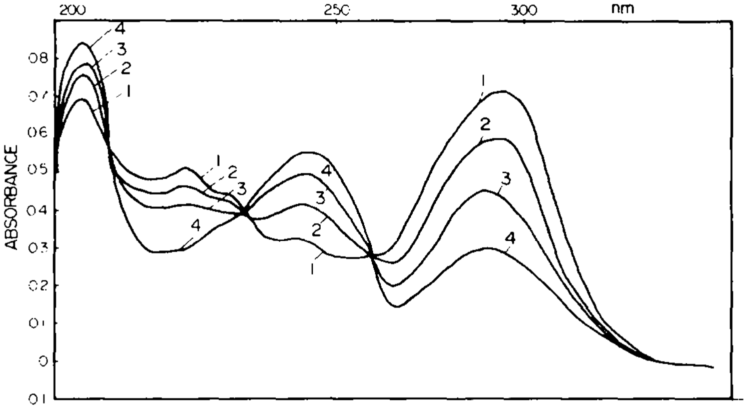


Fig. 3. UV absorption spectrum of ethyl benzoylacetate in heptane (*ca.* 0.5 × 10^{-4} M): curve 1, before exposition to sunlight; curve 2, after a 2 min exposition; curve 3, after a 4 min exposition; curve 4, after a 10 min exposition.

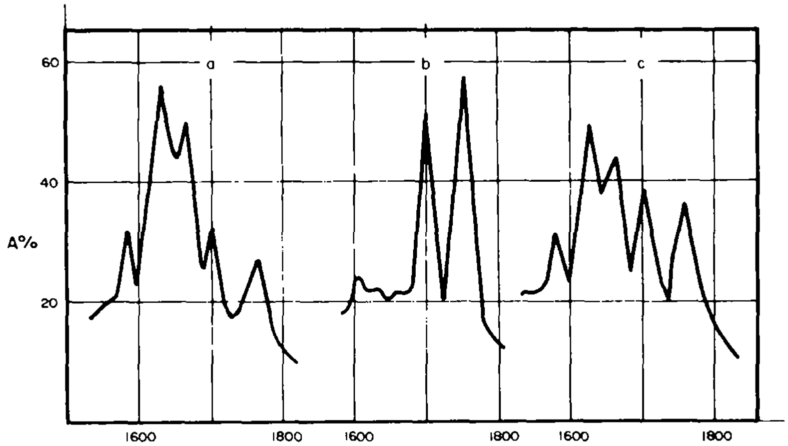
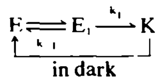


Fig. 4. IR spectrum of 1×10^{-2} mol × l^{-1} heptane solution of 4 before (a), after 8 hr exposition to sunlight (b) and 16 hr after the end of irradiation (c).

scheme and CNDO/S method in order to study theoretically the ground and excited states properties of the enol form of acetoacetic acid. It was suggested that photoinduced ketonization is preceded by the formation of an unstable non chelated rotamer of the enol form (E_1)



An experimental evidence for a formation of the transient enol has been reached by Veierov *et al.*[2] The transient could be simply the result of rotational possibilities about the single C–C bond

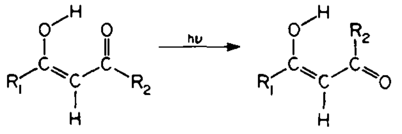


Table 1. Relative effects of sunlight and 313 nm irradiation on the keto-enol equilibrium of compounds 1-5.

Compound	cis-enol	ketonic form	Photoketonization	
	nm		UV light	sunlight
1	273	275	-[a]	-
2	306(294)[b]	242(250)	-[a]	+
3	337(294)	250(245)	-[a]	+
4	288	240	+	+
5	245	275	+[c]	-

[a] See also[2]

[b] Absorption bands which appear in the irradiated solutions

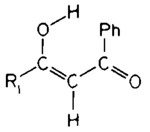
[c] See[1]

With compounds **1-3**, the rate of enol–enol interconversion

$$E_1 \xrightarrow[k_{-1}]{} E$$

is higher than that of ketonization ($k_{-1} \gg k_1$), while in the case of **4** the opposite relation is observed. This important difference can be explained by the stabilization of the transient enol by H-bond involving the carbethoxy group.[2]

Our data (Table 1) show that sunlight irradiation of solutions of **2** and **3** causes a very strong displacement of the keto-enol equilibrium. Apparently under these conditions, the photoinduced shift proceeds faster than enol–enol interconversion ($k_1 > k_{-1}$). It seems that there exist more possibilities for an intermediate stabilization of E_1. The distinguished fact that the presence of Ph group in the molecule of β-diketones appears to be by all means a necessary condition for a prototropic shift suggests that stabilization of the transient enol can be realized by a H-bond type interaction between the OH group and the π-electron system of the phenyl radical:



A considerable amount of work has been carried out to investigate such type interactions.[8,9]

An analysis of the electronic spectra of compounds **2–4** indicates that the change of intensity of the absorption bands, associated with the chelated enolic tautomer is connected with an additional change in the 220–230 nm region. The decrease in intensity of the 288 nm band leads to a lowering of the two maxima at 220 and 227 nm. The changes in UV spectrum of benzoylacetone permits us to establish that the absorption maximum at 306 nm consists of two different bands at 298 and 306 nm (Fig. 1, curve 2). A steady irradiation leads to complete disappearance of the maximum at 306 nm, the band at 298 nm remaining unchanged in the spectrum of the irradiated solution. It is noteworthy that a similar low intensity band could be observed in the UV spectrum of the irradiated heptane solution of dibenzoylmethane (Fig. 2). In any case it is probable that these intensities reflect an n → π^* transition in the keto group which is completely masked by the high intensity enolic form band. According to Morton *et al.*,[3] β-diketoform is characterized by a low intensity absorption band at 310 nm.

The newly obtained factor influencing keto-enol ratio gives rise to the question about the reliability of the available UV spectral data concerning keto-enol equilibrium of the compounds into consideration. It is evident that reliable data can be obtained only if the sample is not affected by sunlight.

EXPERIMENTAL

Acetylacetone, benzoylacetone and dibenzoylmethane were commercial products. Final purification of acetylacetone and benzoylacetone was accomplished by fractionation in a spinning band column. Ethyl benzoylacetate was produced according to[10] and rectified prior to use to a purity of 99% or higher. Heptane was spectroscopic grade. The concentration of solns investigated is given in the text.

The solns were prepared and kept in dark. The samples (2 ml) were thermostated at 20° in a quartz glass vessel and exposed to sunlight under standard conditions. Parallel experiments were carried out using a glass vessel. UV irradiation was made by a Hanau medium pressure mercury arc lamp, using filters for 313 nm wavelength.

UV absorption spectra were measured on a Specord UV-VIS spectrophotometer with quartz cells of 1 cm path length. The IR spectra were measured on a double beam spectrophotometer UR-10, produced by Carl Zeiss–Jena.

REFERENCES

[1] P. Markov, L. Shishkova and A. Radushev, *Tetrahedron* **29**, 3203 (1973).

[2] D. Veierov, T. Bercovici, E. Fischer, Y. Mazur and A. Yogev, *J. Am. Chem. Soc.* **95**, 8173 (1973).

[3] R. A. Morton, A. Hassan and T. C. Calloway, *J Chem. Soc.* 883 (1934).

[4] P. Markov, L. Shishkova and Z. Zdravkova, *Tetrahedron Letters* **39**, 4017 (1972).

[5] P. Markov and E. Radeva, *J. Photochem* **4**, 179 (1975).

[6] F Fratev, P. Markov and R. Vasileva, *Izv. Otd. Khim. Nauki, BAN* **7**, 737 (1974).

[7] P. Markov and F. Fratev, *Compt Rend. Acad. Bulg. Sci.* **28**, 771 (1975).

[8] W. F. Baitinger, P. R. Schleyer and K. Mislov, *J. Am. Chem. Soc.* **87**, 3168 (1965).

[9] A. W. Baker and A. T Shulgin, *J Am. Chem. Soc.* **80**, 5358 (1958).

[10] M. Viscontini and N Merchlung, *Helv. Chim. Acta* **35**, 2280 (1952).