PHOTOINDUCED KETONIZATION OF SOME CYCLIC β-KETOESTERS IN SOLUTION

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Summary

The influence of u.v. irradiation on the keto:enol ratio of 2-ethoxy-carbonylcyclopentanone, 2-ethoxycarbonylcyclohexanone and 2-ethoxy-carbonylcycloheptanone in hexane solution was examined. It was shown that the keto–enol equilibrium is displaced to the keto form. In all cases a good linear relation between the time of irradiation and the concentration of the enol form was established. The rate constants of the photoinduced ketonization have been calculated.

Introduction

In previous papers [1, 2], the effect of ultra-violet irradiation on open chain β-ketoesters has been discussed. This paper presents a study of the photoinduced ketonization of some cyclic β-ketoesters. Our choice stemmed from the hope that the peculiar steric requirements of medium ring compounds may influence the rate of the process of ketonization.

The enolizable cyclic β-ketoesters:

$$(CH_2)_{n-2} \overset{\displaystyle C=O}{\underset{\displaystyle CHCO_2C_2H_5}{|}}$$
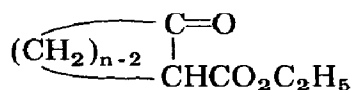
(I: $n = 5$; II: $n = 6$; III: $n = 7$)

show maxima in the region 255 - 263 nm, associated with the $\pi \rightarrow \pi^*$ transition in the carbonyl–conjugated ethylene system. Molar extinction coefficients of compounds (I) - (III) are in the region 11000 - 12000 and are nearly independent of the polarity of the solvent. Data on the i.r. absorption characteristics of the compounds in consideration were reported by Rhoads *et al.* [3]. Four bands appear in the double bond stretching region, a pair at higher frequency (1760 - 1710 cm^{-1}), related with the keto tautomer and a lower frequency pair (1665 - 1600 cm^{-1}), due to the

chelated enol. The relative intensities of these two sets of bands vary with the enol content.

We examined the u.v. and i.r. spectra of 2-ethoxycarbonylcyclopentanone (I), 2-ethoxycarbonylcyclohexanone (II) and 2-ethoxycarbonylcyclo-heptanone (III). The data obtained correspond closely to those reported in the literature [3].

Experimental

2-Ethoxycarbonylcyclopentanone was obtained from the diethyl ester of adipic acid and sodium [4], and compounds (II) and (III) through condensation of the corresponding cyclic monoketones with the diethyl ester of oxalic acid in the presence of sodium ethoxide [5]. Final purification was accomplished by fractionation in a spinning band column. Hexane (Merck, spectroscopic grade) was used as a solvent. The concentration of the investigated solutions was 0.95×10^{-3} mol/l.

The solutions (2 ml) were irradiated with a Hanau-SRU 300 W medium pressure mercury arc lamp in a quartz glass apparatus under standard conditions. The light quanta, falling into the quartz cell, were determined by using a uranyl oxalate actinometer. The value obtained was 1.06×10^{15} quanta $ml^{-1} s^{-1}$. The u.v. absorption spectra were measured on a Specord-UV-VIS spectrophotometer by using quartz cells with path lengths of 0.1, 0.2 and 0.5 cm. The data obtained were recalculated for a path length of 1 cm. The i.r. spectra were measured on a double beam spectrophotometer UR-10 produced by Carl Zeiss-Jena.

Results

The irradiation of hexane solutions of compounds (I) - (III) led to a decrease in the intensities of the absorption bands in the respective u.v. spectra, related to the enol form. The successive spectra of compounds investigated are presented in Fig. 1. The observed spectral change in the 240 - 270 nm region during the time of irradiation does not lead to the appearance of new absorption maxima. However, the possibility of the intermediate formation of unstable rotamers [6] in our experimental conditions remains uncertain.

The characteristic absorption bands in the 6 μm region found for compound III before, after and at different times after u.v. irradiation are shown in Fig. 2. As expected, the relative intensities of higher frequency $(1740 - 1710 cm^{-1})$ and lower frequency bands vary with the change of the enol content during the irradiation. The decreasing enol content leads to an increase in the keto form. The spectrophotometric assay of the irradiated solutions for a long period of time after the irradiation shows a gradual restoration of the enol content. It should be pointed out that 450 hours after the end of the irradiation, the enol concentration of compound (III) exceeds that in the starting solution.
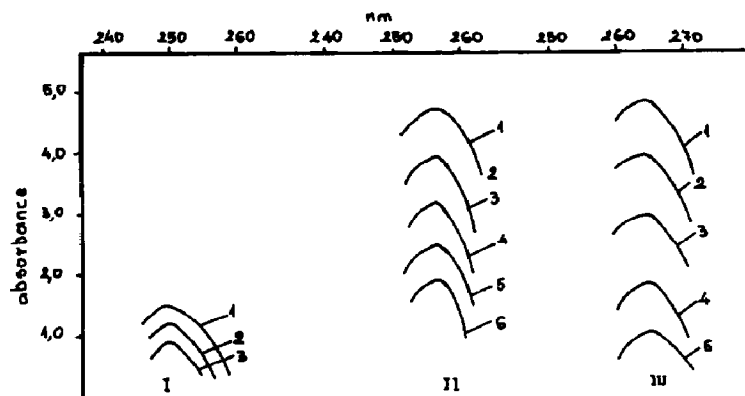
Fig. 1. U.v. spectra of compounds (I) - (III) measured at different times after the start of the u.v. irradiation (min). I: 1, 0; 2, 120; 3, 240. II: 1, 0; 2, 120; 3, 240; 4, 360; 5, 480. III: 1, 0; 2, 30; 3, 60; 4, 90; 5, 120.
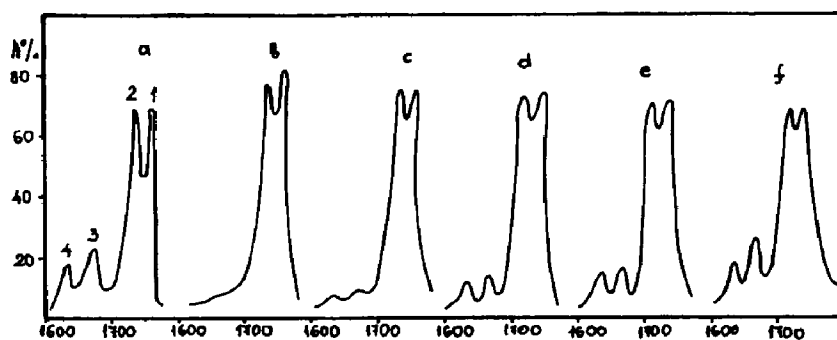

Fig. 2. I.r. spectra of a 2×10^{-2} mol/l hexane solution of III before (a), after (b) and at different times after the end of u.v. irradiation (h): (c) 44; (d) 213; (e) 263; (f) 453. 1, C=O (ester); 2, C=O (keto); 3, C=O (conj); 4, C=C.

The existence of a linear relationship corresponding to:

$$C_\tau = k\tau + C_0$$

where C_τ is the concentration of the enol form τ seconds after the start of the irradiation, and C_0 is the initial concentration, has been firmly established;

The coefficient k could be regarded as a rate constant of the process of the photoinduced ketonization. The numerical values of k for compounds (I) - (III) and for some open chain β-ketoesters have been determined on the basis of statistical analysis of each set of experimental data (Table 1).

Discussion

It is noteworthy that in all cases, when the concentration of enol form in the irradiated hexane solutions is not below 1×10^{-4} mol/l, the photo-induced shift is a zero order reaction. This conclusion follows from the existing linear relationship between the enol content and the time of irradiation. It should be emphasized that such a linear dependence does not

TABLE 1

Rate constants (k) of the photoinduced ketonization of some enolizable β-ketoesters

Compound	C (mol/l)† $\times 10^{-3}$	k (s^{-1}) $\times 10^{-8}$
2-ethoxycarbonylcyclopentanone	0.11	0.04
2-ethoxycarbonylcyclohexanone	0.42	0.78
2-ethoxycarbonylcycloheptanone	0.39	3.92
ethylacetoacetate‡	0.53	11.17
methylacetoacetate‡	0.47	7.67
α-Pr-ethylacetoacetate‡	0.10	0.93

† Initial concentration of the enol form in the irradiated solution.

‡ Rate constant calculated on the basis of data, obtained in earlier investigations.

exist when methanol solutions of compounds (I) - (III) have been irradiated. In this case the initial enol concentrations are extremely low. Therefore, one concludes that for concentrations of the enol form approximately below 1×10^{-4} mol/l the photoinduced ketonization proceeds as a reaction whose order is different from zero. The implication is strong that in the chosen concentration range (1×10^{-3} to 1×10^{-4} mol/l) the important factor determining the degree of the photoinduced transformation is not the concentration of the enol form but the quantity of the light quanta which fall into the irradiated solution and the nature of the β-dicarbonyl compound. Following this line of reasoning it can be supposed that the structural features of the considered enolizable β-ketoesters are acting to determine the numerical values of the coefficient k in the linear equation.

The results of the theoretical [7, 8] and detailed experimental [6] investigation of the phenomenon observed suggest that the photoinduced ketonization is preceded by the formation of an unstable non-chelated rotamer of the enol form. In general two different pathways can be mentioned:
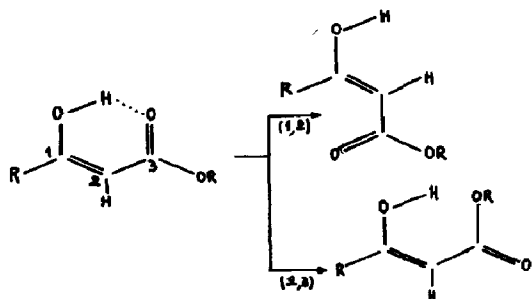

Fig. 3.

The transient could be simply the result of rotational possibilities about the single carbon–carbon bond (2–3). But as previously shown [7] the carbon–carbon double bond (1–2) in the excited enol of acetoacetic acid is

characterized by an extremely low value of the bond order. Accordingly, one might expect also, that in the excited state of the molecule, twisting around this bond is possible. Insofar as the planar rotamers *a* and *b* (Fig. 3) are characterized by nearly the same energies of the $\pi \rightarrow \pi^*$ transitions [8], it is not possible to distinguish between them only on the basis of the experimentally obtained data for this transition [6]. However, it is evident that in the cases considered in this study the twisting about carbon–carbon double bond has to be excluded completely even for the excited state of compounds (I) - (III). From this point of view, the experimentally obtained process of photoinduced ketonization in hexane solutions of cyclic β-keto-esters supports the conclusion that the preceding process of photoisomerization of *cis*-chelated enol to a non-chelated unstable rotamer is achieved probably *via* rotation around carbon–carbon single bond.

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