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On the Photochemical Behaviour of Ethyl Acetoacetate in Water

Short Communication

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Irradiation of ethyl acetoacetate in water yielded acetic acid, ethyl acetate, acetonylacetone and diethyl succinate. The possible route of their formation is the recombination of the radicals resulting from the cleavage of the bonds between α-β and β-γ carbon atoms of the β-keto ester and/or their interaction with the solvent.

(Keywords: Ethyl acetoacetate; Homolytic photocleavage; Solvent effect)

Über das photochemische Verhalten von Acetessigester in wäßriger Lösung

(Kurze Mitteilung)

Bei der Bestrahlung wäßriger Lösungen von Acetessigester mit UV-Licht bilden sich Essigsäure, Ethylacetat, Acetonylaceton und Diethylsuccinat. Ein möglicher Weg zur Entstehung dieser Produkte ist die Rekombination der durch homolytische Trennung der Bindungen zwischen den α-β und β-γ-Kohlenstoffatomen des β-Ketoesters gebildeten Radikale, sowie ihre Wechselwirkung mit dem Lösungsmittel.

The effect of ultraviolet light on enolizable β-dicarbonyl compounds dissolved in aprotic solvents has been described in previous papers e.g. Refs.[1–5]). It was shown that one the channels of the dissipation of the electronic energy in such type molecules is the photo-induced ketonization and photo-activated metallotropy. In the meantime *Morizur* et al.[6,7] reported that the photolysis of 2-ethoxy-carbonyl-

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cyclopentanone results in an α-cleavage leading to the formation of aldehydes. Recently *Yoshioka* et al.[8] found that irradiation of ethyl 3-oxo-2,4-diphenylbutanoate causes its decarbonylation.

These data exclusively refer to solutions of β-dicarbonyls in nonpolar media. In the present communication we report the photolysis of ethyl acetoacetate in water.

Irradiation of ethyl acetoacetate (**1**) in water (volume ratio 1:30) with 400 W mercury arc (medium pressure) lamp for 50 hours under air atmosphere resulted in formation of four detectable products: acetic acid (**2**), ethyl acetate (**3**), acetonylacetone (**4**) and diethyl succinate (**5**). The experiments carried out under argon gave essentially the same final products. Their quantitative description was hindered because of their appreciable solubility in water.

Since the dicarbonyl tautomer is normally the predominating species in water[9] and because of photoketonization[1] it seems that in the case considered here the photoreactive forms is the keto tautomer:

$$\overset{4}{C}H_3—\overset{3}{C}O—\overset{2}{C}H_2—\overset{1}{C}OOC_2H_5$$

β-ketoesters with phenyl group in α-position to both carbonyls easily undergo α-cleavage and decarbonylation upon irradiation[8]. In this case the formation of the major reaction products may be explaned in terms of cleavage of the $C_2—C_3$ and $C_3—C_4$ bonds of the excited β-ketoester:

$$PhCH_2COCH(Ph)COOC_2H_5$$

In the case considered here the ultraviolet irradiation affords probably the formation of radical particles resulting from the cleavage of $C_1—C_2$ and $C_2—C_3$ bonds:

$$CH_3COCH_2COOC_2H_5$$

The favored cleavage of $C_2—C_3$ and $C_3—C_4$ bonds of ethyl-3-oxo-2,4-diphenylbutanoate is evidently due to the possibility of resonance stabilization of the radicals formed.

Experimental

The IR spectra were measured in Nujol mull or in $CHCl_3$ on IR-75 Specord (Carl Zeiss-Jena) spectrophotometer. Thin layer[3] chromatography (TLC) was made on Merck Silica Gel 60. Ethyl acetoacetate was a commercial product. Its final purification was accomplished by fraction in a spinning band column. Double distilled water was used as a solvent.

A mixture of 13.1 g (0.1 mol) ethyl acetoacetate in 300 cm^3 of water was irradiated under air atmosphere (50 h) with UV light from 400 W medium pressure mercury arc lamp in large scale immersionwell photochemical reactor (Applied Photophysics Ltd., 3325). Argon (99.999%) was bubbled into the solution when the experiment had to be carried out under inert atmosphere. The irradiation solutions were highly acidic (*pH* 3.5).

The reaction mixture was extracted throughly with ether (500 cm^3). The ether extract was dried (Na_2SO_4) and carefully fractionated with spinning band column. After elimination of the solvent the compounds **2** (0.6 g) and **3** (1.3 g) were isolated. These compounds showed the following data*, **2**: b.p. 118—119 °C, $n_D^{20} = 1.3707$ (Lit. 1.3698). **3**: b.p. 77—78 °C, $n_D^{20} = 1.3721$ (Lit. 1.3722). The IR spectrum and VPS data were identical with that of an autentic sample. The residue was distilled under reduced pressure to yield compound. **4** (3.3 g): b.p. 80—3 °C/5 Torr, $n_D^{20} = 1.4490$ (Lit. 1.4481). IR($CHCl_3$): 1 700 cm^{-1}. 2,4-Dinitrophenylhydrazone: m.p. 256—7 °C (Lit. 257 °C). **5**: b.p. 60—65 °C/1 Torr, $n_D^{20} = 1.4245$ (Lit. 1.4250). IR ($CHCl^3$): 1 730 cm^{-1}.

The blank experiment (without UV irradiation) gave unchanged ethyl acetoacetate.

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* All C,H-analyses agreed very well with the calculated values.

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