The Addition of Alcohols to Ethyl Acetoacetate and a Photochemical Lactonization Reaction

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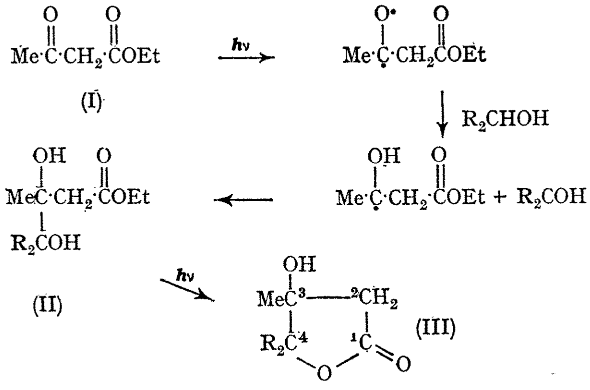
Summary The irradiation of ethyl acetoacetate in alcohol results in a dihydroxy-ester which lactonizes photochemically.

THE photopinacol reaction of ketones has been thoroughly investigated,[1] and work has also been done on the photochemistry of α-keto-acids and -esters.[2] We now describe a reaction of a β-keto-ester (I) whereby irradiation in a primary or secondary alcohol solution leads to a glycol (II), which further lactonizes to (III) photochemically. In a typical experiment, a solution of 10 g. of (I) in 150 ml. of methanol was irradiated under nitrogen with a 550 w Hanovia medium-pressure lamp, housed in a quartz immersion well. After 2 hr. irradiation, silica gel column chromatography gave (IIa) in 55% yield, as well as a small yield of (IIIa). The glycol was characterized chemically, by periodate oxidation to formaldehyde and (I), as well as spectroscopically. It showed i.r. peaks at 3500 (br, OH) and 1730 cm.$^{-1}$ (C=O), and n.m.r. signals in $(CD_3)_2SO$ solution at δ 1·12(s, 3H), 1·2 (tr, 3H), 2·4 (s, 2H) 3·28 (d, 2H), 4·05 (q, 2H), 4·32 (s, 1H), and 4·58 (t, 1H) p.p.m. Upon addition of D_2O, the hydroxy-signals at 4·32 and 4·58 disappeared and that at 3·28 became a singlet.

When the original irradiation was performed for 4 hr., (IIa) was no longer present in the reaction mixture. It was replaced by (IIIa), which could be isolated by silica gel column chromatography in 60% yield.[3] It was characterized by its mass spectrum (*M* 116), i.r. spectrum [3700 (OH), *ca.* 3400 cm.$^{-1}$, (br OH), and 1795 cm.$^{-1}$ (C=O)], and n.m.r. spectrum. The latter showed signals in $(CD_3)_2SO$ at δ 1·33 (s, CH_3), 2·27 and 2·66 (each a doublet, J 17 Hz., 2-H), 4·05 (s, 4-H), and 5·25 (s, OH) p.p.m., this last signal disappearing in presence of D_2O. The glycol (IIa) was quite stable in the absence of light, but it was quantitatively converted into (IIIa) upon further irradiation in chloroform or in alcohol.

When the irradiation of (I) was performed in propan-2-ol, the isolated yield of (IIIb) was 20%. No reaction took place when (I) was irradiated neat, in benzene or in t-butyl alcohol. It is therefore likely that the reaction is initiated by $n \rightarrow \pi^*$ excitation of the ketone and proceeds by hydrogen abstraction from the solvent. Since no symmetrical pinacol product was detected, the two radicals must react in a solvent cage to yield the glycol (II) which then lactonizes photochemically. The mechanistic path of this last step is under investigation.



a;. R=H, b; R=Me

We thank the National Science Foundation for financial support.

(*Received, July 28th,* 1969; *Com.* 1154.)

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[1] D. C. Neckers and D. P. Colenbrander, *Tetrahedron Letters*, 1968, 5045 and references therein cited.

[2] Discussed by D. C. Neckers in "Mechanistic Organic Photochemistry," Reinholt, New York, N.Y., 1967.

[3] The lactone (IIIa) was previously synthesized in about 33% yield *via* a Reformatski reaction by J. M. Stewart and D. W. Wooley, *J. Amer. Chem. Soc.*, 1959, **81**, 4951.