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PHOTOLYSIS OF TRANS-β-BENZOYLACRYLIC ACID

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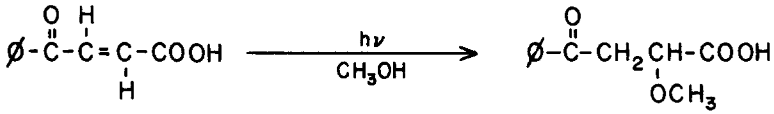
Several years ago Lutz reported (1) the photochemical behavior of trans-β-benzoylacrylic acid, namely, photodimerization and cis-trans isomerization We wish to report yet another photochemical reaction of benzoylacrylic acid.

When benzoylacrylic acid (I) was irradiated (2) in methanol for 3 days, a white crystalline product (II), m.p. 88.0-92.0°, was obtained in 81% yield. Elemental analysis gave; C, 63.38; H, 5.62 (calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81); ultraviolet (methanol): max 245.0 mμ (log ε, 4.10), 282.5 mμ (log ε, 3.07), and 290.0 mμ (shoulder) (log ε, 3.01); infrared ($CHCl_3$): 3.52μ (C-H stretch of OCH_3), 5.80μ (acid C=O), 5.92μ (ketone C=O) and 8.92μ (C-O- of $-O-CH_3$); nmr ($CDCl_3$): half buried doublet at 3.55δ (2H, $-CO-CH_2$), singlet at 3.58δ (3H, $-OCH_3$), triplet at 4.60δ (1H, -CH-O), multiplet between 7.33-8.41δ (5H, aromatic), and sharp singlet at 11.16δ (1H, $-CO_2H$). Based upon this data and its close resemblance to acetophenone in the uv spectrum, II was deduced to be β-benzoyl-α-methoxypropionic acid.



$$\underset{\text{I}}{\text{Ø}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\overset{\overset{\text{H}}{|}}{\text{C}}=\underset{\underset{\text{H}}{|}}{\text{C}}-\text{COOH}} \xrightarrow[\text{CH}_3\text{OH}]{h\nu} \underset{\text{II}}{\text{Ø}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_2\underset{\underset{\text{OCH}_3}{|}}{\text{CH}}-\text{COOH}}$$

Further confirmation of II was made by comparing a white crystalline solid obtained by treating I with sodium methoxide in methanol at room temperature, m.p. 90.5-92.5°, in 76% yield. Anal. calcd for $C_{11}H_{12}O_4$:C, 63.45; H, 5.81. Found: C, 63.42; H, 5.67. This product was found to be identical with II in all respects (mixed m.p., ir, uv and nmr).

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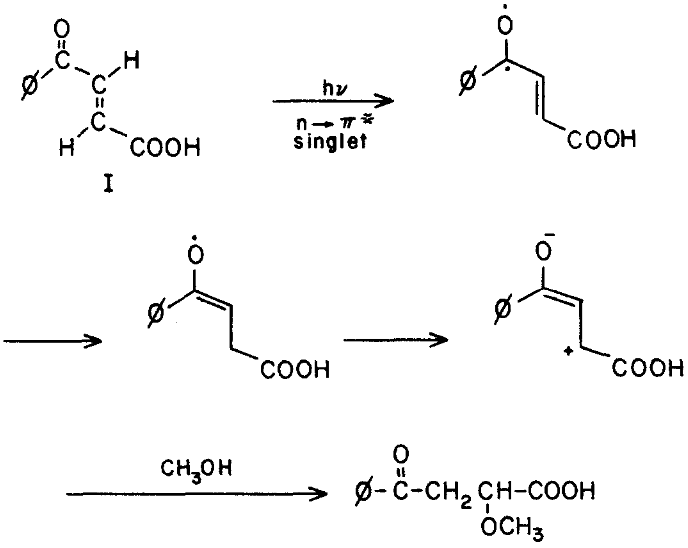
The possibility that II could have arisen from I nonphotochemically was eliminated by refluxing a methanolic solution of I in the dark for 3 days. Approximately 90% of benzoylacrylic acid was recovered unchanged and the rest was found to be the methyl ester (nmr and uv).

We do not have any experimental evidence to postulate the mechanism of this reaction. However, since no photoreduction of I was observed, a mechanism involving a Zwitter ion formed via an n → π* singlet seems reasonable (3):



I

II

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References

1. R. E. Lutz and G. W. Scott, J. Org. Chem. 13, 284 (1948).
2. The irradiation was performed using a 100-w Hanovia utility model (Type 30620) mercury lamp provided with Pyrex filter (Type 7740, No. 16223A). A 250 ml quartz flask provided with a water-cooled condenser and a nitrogen inlet tube was used.
3. N. J. Turro, Molecular Photochemistry, W. A. Benjamin Inc., pp. 169-172 New York, N. Y. (1967).