The Photochemical Reactions of Ethyl Benzoylformate in Solution

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In an earlier paper dealing with photoethyl oxallylation,[1] the present authors reported that the direct introduction of ethyl oxallyl radicals, generated by the photolysis of diethyl oxalate or ethyl phenyl oxalate, into several hydrogen-donating solvents was successful, and that ethoxycarbonyl derivatives, i. e., esters, were always found to be the second principal product in a series of the above reactions.

Concerning the formation of esters, it seems more likely that the esters would be formed by a recombination between ethoxycarbonyl and solvent radicals. However, as has been previously pointed out,[2] ethoxycarbonyl radicals decompose exothermically because of their remarkable unstability and give rise to only carbon dioxide and ethyl radicals (quantitatively).

Meanwhile, in our photoreactions of the above oxalates in a solvent, carbon monoxide was invariably isolated as a major gaseous product; the ratio of the formation of carbon monoxide to that of carbon dioxide was approximately 4.5. From the above results, it may be considered that the reaction path for ester formation involving free ethoxycarbonyl radicals produced through the photolysis of the oxalate is not very significant. Subsequently, it seems that the esters may be formed by the secondary photolysis of the corresponding α-keto esters.

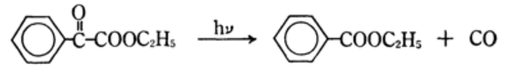
The photochemistry of α-keto esters in various media has been extensively studied recently by several investigators. Giving the photolysis of ethyl benzoylformate as an example, in an inert solvent such as benzene, ethyl benzoylformate is photodecarbonylated to afford benzaldehyde and acetaldehyde.[3] In alcoholic solvents at room temperature,[4,5] the formate is officiently photoreduced to the corresponding pinacol, while, on the other hand, at elevated temperature it undergoes intramolecular hydrogen abstraction, yielding acetaldehyde, the corresponding hydroxyketene, and the enol of phenylglyoxal. At any rate, the formation of esters from the α-keto esters by photodecarbonylation has not yet been reported.

In order to make sure of the feasibility of the formation of the ester from the α-keto ester, the photolysis of ethyl benzoylformate in solvents such as benzene and cyclohexane was undertaken.

The irradiation of a solution of ethyl benzoylformate (0.075 mole) in benzene (1.5 mole) with a light of approximately 3660 Å, provided by a 300 W. high-pressure mercury lamp through a suitable filter system, was carried out at 20°C for 7 days. As the photoproducts, ethyl benzoate (0.65 g.), ethyl mandelate (2.45 g.) and biphenyl (1.1 g.) were obtained, together with the products, such as benzaldehyde (0.5 g.) and acetaldehyde (0.1 g.), described above. Moreover, besides the above constituents, a small amount of a gaseous product consisting of carbon monoxide, carbon dioxide and ethane in the ratio of 19 : 6 : 1 was obtained.

In addition, the irradiation, at 20°C for 54 hr., of a solution of ethyl benzoylformate (0.1 mole) and cyclohexane (5.0 mole), using a 300 W. high-pressure mercury arc lamp, afforded the following various photoproducts: ethyl benzoate (1.0 g.), ethyl mandelate (1.6 g.), benzaldehyde (0.7 g.), biphenyl (0.4 g.), benzophenone (0.25 g.), ethyl cyclohexyl carboxylate (0.5 g.), and bicyclohexyl (1.8 g.), along with very small amounts of acetaldehyde, cyclohexyl methyl carbinol and cyclohexyl methyl ether. Most of the gaseous product obtained was composed of carbon monoxide. The conversion percentage of ethyl benzoylformate was 52%.

Although the present photochemical reaction is rather complex due to the many different radicals produced, the results show a plain demonstration of the possibility of ester formation from the α-keto ester by photodecarbonylation.



Details of this and further work will be reported shortly.

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