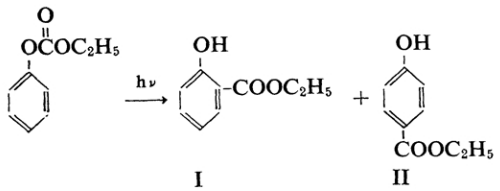
The Photochemical Rearrangement of Ethyl Phenyl Carbonate

By Chyongjin PAC and Shigeru TSUTSUMI

(Received July 31, 1964)

It has been reported that the migration of the acyl group in phenyl acetate occurs under the influence of ultraviolet light[1] in a manner similar to that of the Fries-reaction.[2] Such photochemical reactions of catechol acetate,[1] anilides,[3] phenyl benzoates[4] and *p-t*-butylphenyl benzoates[5] have been investigated and have supplied a convenient method for the preparation of a number of hydroxy or amino aromatic ketones.

The migration of the alkoxycarbonyl group, however, has been scarcely observed at all. In the course of the investigation of the reaction of ethoxycarbonyl radical in hydrocarbons,[6] it was found that the migration of the ethoxycarbonyl group took place in the photochemical reaction of ethyl phenyl carbonate (EPC), thus affording ethyl salicylate and ethyl *p*-oxybenzoate in fairly good yields.



I II

After the irradiation of EPC (13 g.) in 150 ml. of acetic acid for 120 hr. with a low pressure mercury arc (100 W.), the irradiated mixture was worked up as usual and gave ethyl salicylate, I (a 16% yield based on the EPC used), ethyl *p*-oxybenzoate, II (25%), and phenol (7~8%), while 26% of the EPC was recovered.

These products were identified by infrared spectroscopic and gas chromatographic measurements, mixed melting point tests with authentic samples, and elementary analyses.

In a similar way, the photochemical reaction of EPC in ethanol afforded I (17%), II (18%) and phenol (13%), while 23% of the EPC was recovered.

When ether was used as a solvent, a decrease in the yield was observed in I (8~10%) and II (10%), while phenol (13%) and EPC (39%) were also detected.

In non-polar solvents such as benzene or *n*-heptane, the wall of the light source was covered with polymeric products during the course of irradiation, and only trace amounts of the products or none at all were detected. However, it is not clear whether or not there were any solvent effects on the photochemical rearrangement of EPC.

On the basis of the results of mixed irradiation experiments,[7] it has been suggested that the migration of the acyl group is intramolecular, and Kobsa[5] showed that, upon the absorption of a light quantum, the ester decomposed into a pair of radicals in a solvent cage, which then underwent subsequent reactions.

Considering the above facts on the migration of the acyl group, the photochemical rearrangement of EPC may be expected to be intramolecular. The details of this reaction are now being investigated.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka

1) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, **1960**, 217.
2) A. H. Blatt, "Organic Reactions," Vol. 1, John Wiley & Sons, Inc., New York (1942), p. 342.
3) Dov Elad, *Tetrahedron Letters*, **1963**, 873.
4) C. H. Kuo, R. D. Hoffsommer, H. L. Slates, D. Taub and N. L. Wendler, *Chem. & Ind.*, **1960**, 1627.
5) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).
6) A preliminary report, This Bulletin, **36**, 234 (1963).
7) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, **1963**, 1781.