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PHOTOCHEMICAL OXIDATIVE ESTERIFICATION OF BENZALDEHYDE IN ALCOHOLIC SOLUTIONS UNDER OXYGEN ATMOSPHERE

Hirochika SAKURAGI and Katsumi TOKUMARU
Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113

Irradiation of benzaldehyde in methanol, ethanol, and 2-propanol under oxygen atmosphere gave methyl, ethyl, and isopropyl benzoate, respectively, and their yields were increased when a catalytic amount of hydrochloric acid was present.

Photo-oxygenation of benzaldehyde is well-known to give benzoic acid through peroxybenzoic acid.[1] We have found that the use of alcoholic solvents completely alters the course of the reaction to result in a new photochemical oxidative esterification of benzaldehyde yielding the corresponding alkyl benzoates. Bradshaw's recent anomalous finding[2] that photolysis of benzophenone in a 2% hydrochloric acid solution in methanol afforded methyl benzoate has prompted us to report here the above finding, to which attention should be paid in experimental works using benzaldehyde.

Irradiation of benzaldehyde in methanol (ca. 0.1 M) under oxygen stream with a high pressure mercury lamp gave methyl benzoate and, in the presence of a catalytic amount of hydrochloric acid, its yield was increased to 90% based on the aldehyde consumed,[3] but without oxygen the irradiation in acidified methanol gave no methyl benzoate. Similar irradiation of p-methylbenzaldehyde afforded methyl p-methylbenzoate in 65% yield. In control experiments, decomposition of peroxybenzoic acid in methanol[4] in the dark and under illumination gave no detectable amount of methyl benzoate, and irradiation of benzoic acid in methanol in the presence of a catalytic amount of hydrochloric acid under oxygen or nitrogen afforded only a trace of the ester. The above results eliminate the possibility that methyl benzoate would be produced through the reaction with methanol of peroxyben-

zoic acid or benzoic acid which would result from photooxidation of benzaldehyde.

Irradiation of benzaldehyde in acidified ethanol and 2-propanol under oxygen also afforded the corresponding benzoate esters in 90 and 45% yields, respectively, based on the aldehyde consumed. These results are in striking contrast with the reported results for benzophenone which, on irradiation under nitrogen in acidified methanol, gives methyl benzoate but does not afford benzoate esters in ethanol and 2-propanol.[2)]

Mechanism for this new reaction is not certain and now being investigated. The presence of oxygen under irradiation is necessary for the reaction.

References

1) For example, C. Walling, "Free Radicals in Solution", John Wiley & Sons, New York, 1957, p. 397; L. Horner, "Autoxidation and Antioxidants", W. O. Lundberg, ed., Interscience Publishers, New York, 1961, Vol. I, p. 197.

2) J. S. Bradshaw, J. C. S. Chem. Comm., 1973, 504.

3) In a typical run, benzaldehyde (3 mmol) in methanol (25 ml) in the presence of a catalytic amount of hydrochloric acid was irradiated under a stream of oxygen with a Riko 100 w immersion-type high pressure mercury lamp at 5°C for 5 hours, during which 25% of benzaldehyde was consumed and methyl benzoate was produced in 90% yield based on the aldehyde consumed.

4) K. Tokumaru, O. Simamura and M. Fukuyama, Bull. Chem. Soc. Japan, 35, 1673 (1962).

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