An Anomalous Product in the Photolysis of Benzophenone in Acidified Methanol

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Summary Benzophenone when irradiated in a 2% solution of hydrochloric acid in methanol, gave methyl benzoate as the only isolable product, whereas in neutral methanol, benzopinacol and 1,1-diphenylethane-1,2-diol were formed.

METHYL BENZOATE was the only isolable product when benzophenone was irradiated in a 2% hydrochloric acid solution in methanol. The reaction was carried out in a Pyrex tube under a nitrogen atmosphere using 350 nm lamps in a Rayonet photochemical reactor. After 45 h, 52% of benzophenone was converted, yielding 60% of methyl benzoate. The product was isolated by g.l.c. and verified by spectral comparison with an authentic sample.

When irradiated in methanol acidified by sulphuric acid (5 ml concentrated H_2SO_4 in 300 ml methanol), benzophenone yielded methyl benzoate, benzopinacol, and 1,1-diphenylethane-1,2-diol. In neutral methanol, benzopinacol (75%) and 1,1-diphenylethane-1,2-diol (20%) were formed together with three minor products. No benzoate esters were isolated when benzophenone was irradiated in 2% hydrochloric acid solutions in both ethanol and isopropyl alcohol. These latter two reactions gave only benzopinacol in quantitative yields.

The photoreaction of benzophenone in a variety of solvents to form benzopinacol has been studied in great detail.[1] In methanol, the reaction has been reported to yield 1,1-diphenylethane-1,2-diol and 4-benzoyltriphenyl methanol.[2] The photoreaction of benzophenone in acid media has not previously been reported.

We do not believe that our reaction is a Norrish Type I α-cleavage resulting in the formation of benzoyl radical. There have been a number of recent reports of α-cleavage reactions yielding the benzoyl radical.[3] In every case, benzaldehyde was the only isolated aromatic product.[3] No trace of benzaldehyde was found in our reaction, nor was benzene or biphenyl, which presumably would be companion products of an α-cleavage.

Another possible mechanism—the photodecomposition of benzopinacol in acid media—was eliminated since pinacol was stable under the conditions used.

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[1] See D. C. Neckers, 'Mechanistic Organic Photochemistry,' Reinhold, New York, 1967, ch. 7 for a review of hydrogen abstraction reactions.

[2] H. Mauser, B. Nickel, U. Sproesser, and V. Bihl, *Z. Naturforsch.*, 1967, **22b**, 903.

[3] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 1972, **94**, 3852; P. J. Wagner and J. M. McGrath, *ibid.*, 3849; J. S. Bradshaw, R. D Knudsen, and W. W. Parish, *J.C.S. Chem. Comm.*, 1972, 1321.