

## Solvent Effects on Intersystem Crossing in the Photocyclization of Methyl *o*-Benzyloxyphenylglyoxylate

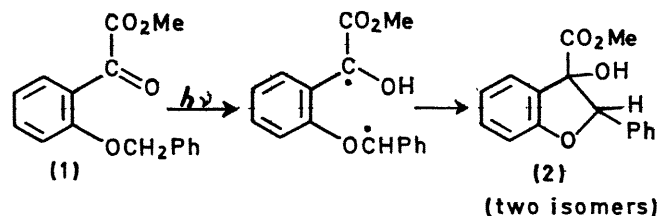
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**Summary** Solvent effects on the quantum yield of the phototransformation (1)  $\rightarrow$  (2) may be attributed, in part, to diminished intersystem crossing efficiency with increasing solvent polarity.

THE quantum yield of Type II photoelimination of aralkyl ketones increases with increasing solvent polarity.<sup>1</sup> In contrast, Type II photoelimination and 3-oxetanol formation from  $\alpha$ -alkoxyacetophenones exhibit a reverse solvent effect.<sup>2</sup> Both results have been attributed to inefficiency in the cyclization step following H-abstraction. By analogy with  $\alpha$ -alkoxyacetophenones, the quantum yield of formation of dihydrobenzofurans (2) from methyl *o*-benzyloxyphenylglyoxylate (1) decreases with increasing solvent polarity.<sup>3</sup> We report a solvent effect on the intersystem crossing efficiency (1)  $\rightarrow$  (2), which parallels the overall quantum yields.

The phototransformation (1)  $\rightarrow$  (2) has been shown to proceed *via* a reactive  $n,\pi^*$  triplet state which undergoes intramolecular H-abstraction from the benzyloxy carbon followed by cyclization to the isomeric products.<sup>3</sup> In



polar media, sensitization with benzophenone, which absorbed greater than 90% of the light, resulted in significantly larger quantum yields ( $\phi_{sens}$ ) of formation of (2) relative to the direct yields ( $\phi_{dir}$ ) under conditions of equal

light utilization (Table). The possibility that the increased yields resulted from "chemical sensitization" involving H-abstraction by benzophenone<sup>4</sup> was rendered unlikely by parallel studies with *m*- and *p*-methoxyacetophenone, both poor H-abstracters,<sup>5</sup> which provided equivalent quantum yields of sensitization in acetonitrile.†

Solvent effects on the photoreactivity of (1)

Solvent	$\phi_{dir}^{a,b}$	$\phi_{sens}^{b,c}$	$\phi_{isc}^d$
Benzene .. ..	0.89	0.86	1.03
Acetonitrile .. ..	0.56	0.71	0.79
t-Butyl alcohol .. ..	0.47	0.67	0.70

<sup>a</sup> Ferrioxalate actinometry; 366 nm. <sup>b</sup> Average of two or more determinations; range of experimental values  $\pm 5\%$ ; conversions less than 15%. <sup>c</sup> 0.17–1.5 M-Benzophenone; 0.03–0.1 M-(1); 366 nm. <sup>d</sup> See text.

Assuming unit efficiency in the intersystem crossing of the sensitizer and in the energy transfer step, the quantum yields of intersystem crossing (<sup>1</sup>1)  $\rightarrow$  (<sup>3</sup>1) ( $\phi_{isc}$ ) may be

equated to the ratio  $\phi_{dir}/\phi_{sens}$ . In the sense that these assumptions may not be strictly valid, the calculated intersystem crossing efficiencies represent maximum values.

Since fluorescence was not observed in any of the solvents, the effect is attributed to a re-ordering of the energy levels in polar media which enhances the importance of thermal deactivation possibly by necessitating crossover (a) between states of like orbital configuration,<sup>7</sup> or (b) to a non-abstracting triplet state. Additional information may be obtained from studies on sensitized olefin isomerization.<sup>8</sup> Evidence for inefficient intersystem crossing of aminobenzophenones in polar media has been acquired by the latter method.<sup>9</sup>

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† These results were obtained at 313 nm due to the low extinction coefficients of *m*- and *p*-methoxyacetophenone at 366 nm. The concentrations utilized were low enough to ensure efficient energy transfer.<sup>6</sup>

<sup>1</sup> (a) P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 5398; (b) P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 94.

<sup>2</sup> F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 311.

<sup>3</sup> S. P. Pappas, J. E. Alexander, and R. D. Zehr, *J. Amer. Chem. Soc.*, 1970, **92**, 6927.

<sup>4</sup> B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, 1969, **91**, 450.

<sup>5</sup> (a) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Amer. Chem. Soc.*, 1967, **89**, 5466; (b) P. J. Wagner, A. E. Kempainen, H. N. Schott, *ibid.*, 1970, **92**, 5280.

<sup>6</sup> O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, 1969, **91**, 5391.

<sup>7</sup> (a) M. A. El-Sayed, *Accounts Chem. Res.*, 1968, **1**, 8; (b) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, 1969, **7**, 149.

<sup>8</sup> A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, **43**, 2129.

<sup>9</sup> S. G. Cohen, M. D. Saltzman, and J. B. Guttenplan, *Tetrahedron Letters*, 1969, 4321.