Photochemistry of *o*-Tolualdehyde: Photoenolization and Photobenzoin Condensation

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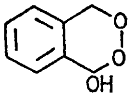
Summary Photolysis of *o*-tolualdehyde results in the formation of dimeric hemiacetal *via* the photoenol, or the benzoin *via* intermolecular hydrogen abstraction.

TRAPPING experiments with maleic anhydride have demonstrated that *o*-tolualdehyde (**1**),[1] like 2-methylbenzophenone,[2] gives an enol isomer on photolysis. However, we have found that the photochemistry of the aldehyde is somewhat different from that of the benzophenone.

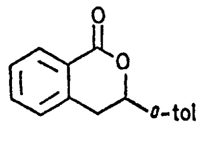
Photolysis† of a dilute ($0{\cdot}02$ M) aerated hexane solution of (**1**) results in the formation of the expected cyclic peroxide (**2**), m.p. 68—69°.‡ However, when the concentration was increased to $0{\cdot}2$ M the products isolated were *o*-toluic acid, phthalide, and the lactone (**3**), m.p. 100—102°.§ In the absence of oxygen the main product was the hemiacetal (**4**), m.p. 105—106°.

Flash photolysis of (**1**) in either hexane or ethanol solution results in transient absorption with λ_{max} 380 nm. The decay was first order but the rate increased with increasing concentrations of (**1**). For example, in ethanol the lifetime decreased from $1{\cdot}9$ to $0{\cdot}21$ s when the concentration of (**1**) was increased from $1{\cdot}6 \times 10^{-3}$ M to $3{\cdot}3 \times 10^{-3}$ M. A plot of the first-order decay constant *vs* concentration of (**1**) for dilute ($<10^{-2}$ M) hexane solutions gave a linear plot with a slope of $6{\cdot}9 \times 10^{3}$ M^{-1} s^{-1} and an intercept (lifetime at infinite dilution) of $1{\cdot}2$ s.

The transient observed in the flash experiments can be assigned an enol structure. On the basis of lifetime in the two solvents (at infinite dilution) and the reported lack of deuterium exchange[3] it is proposed that this is the (*Z*)-isomer (**5**). Unlike the benzophenones[4] there is no evidence for the formation of the (*E*)-isomer.[1] The kinetic data and the formation of (**4**) suggest that (**5**) reacts with (**1**) in a Diels–Alder reaction. We have re-examined 2-methylbenzophenone and find that no similar dimeric products are formed and that the enol lifetimes are independent of ketone concentration.



(2)



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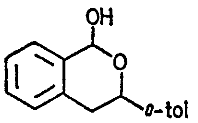

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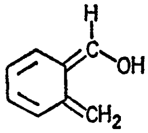

(5)

We have also photolysed the aldehyde under high concentration (>1 M) conditions and found that the main product is 2,2′-dimethylbenzoin, m.p. 77—78° (comparison

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† Hanovia 85 W mercury lamp, Pyrex filter, 25°.

‡ The peroxide reaction will be the subject of a separate paper.

§ The crystalline compounds described gave satisfactory elemental analyses and n.m.r., i.r., and mass spectral data consistent with the assigned structures.

with authentic material). Benzaldehyde gives benzoin under these conditions.[5] The formation of the benzoins can be rationalized as arising from intermolecular hydrogen abstraction followed by collapse of the radicals.[6]

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[1] S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.

[2] N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; M. Pfau, N. D. Heindel, and T. F. Lemke, *Compt. rend.*, 1965, **261**, 1071; F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398.

[3] B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 401.

[4] G. Porter and M. F. Tchir, *J. Chem. Soc.* (*A*), 1971, 3772.

[5] J. S. Bradshaw, R. D. Knudsen, and W. W. Parish, *J.S.C. Chem. Comm.*, 1972, 1321.

[6] M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, 1970, **92**, 1772; G. L. Closs and D. R. Paulson, *ibid.*, p. 7229.