Biacetyl Photosensitized Decomposition of Acetoin Derivatives

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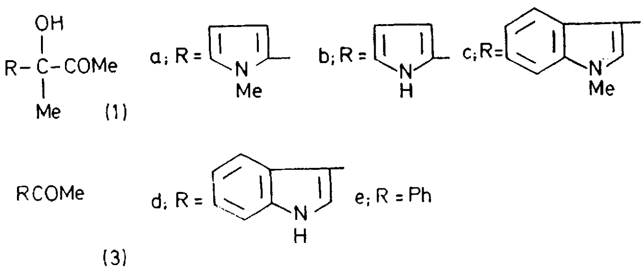
Summary Biacetyl photosensitizes the decomposition of the acetoin derivative (**1a**) to give (**3a**) and reduction products of biacetyl quantitatively; kinetic data suggest that the reaction occurs *via* charge-transfer interaction derived from *n*-π* triplet of biacetyl.

Photoreduction of carbonyl compounds by a charge-transfer mechanism has been the subject of recent debate.[1] In the course of mechanistic investigations on the photolysis of acetoin derivatives (**1a**—**d**)[2] in comparison with that of phenylacetoin (**1e**),† we have found that α-diketones, such as biacetyl (**2**) and benzil, photosensitize the decomposition of (**1a**—**d**), but do not effect the decomposition of (**1e**). We now present kinetic data for the photolysis of (**1a**) and (**1e**), and suggest that the photosensitized decomposition by (**2**) proceeds *via* charge-transfer interaction derived from the *n*-π* triplet of (**2**).

Irradiation on a preparative scale of a solution containing (**1a**) and (**2**) with light of 435 nm results in essentially quantitative formation of (**3a**) and reduction products, *i.e.*, acetoin (**4**), acetylacetoin (**5**), and 3,4-dihydroxy-3,4-dimethylhexane-2,5-dione, ($\pm$) and *meso*, (**6**).‡ On the other hand, irradiation of (**2**) in the presence of (**1e**) leads to



recovery of the starting materials. The reaction was completely quenched by pyrene (0·01 M) and cyclohexa-1,3-diene (0·1 M), which are expected to be diffusion-control quenchers of the biacetyl triplet.

† By analogy with (**1a**—**d**), irradiation of (**1e**) at 313 nm gave (**3e**) in good yield.

‡ Satisfactory spectroscopic and analytical data have been obtained.

The Table shows the quantum yields for the disappearance of (**2**) and the rate constants for quenching of biacetyl phosphorescence (k_q). Quantum yields were determined by ferrioxalate actinometry. The results suggest that the reactions are effectively influenced by solvent polarity. In biacetyl-sensitized decomposition, the quantum yields for the disappearance of (**2**) and k_q are effectively enhanced on going from benzene to acetonitrile. On direct photolysis, however, an effective decrease in quantum yields for the formation of (**3a**) and (**3e**) was found as the solvent polarity was increased.

TABLE

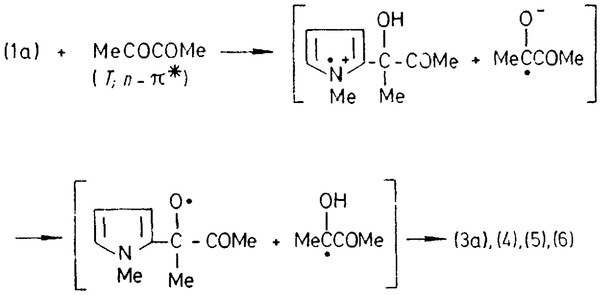
Acetoin	Solvent	ϕ^a	$k_q{}^b$ (M^{-1} s^{-1})
(**1a**)	C_6H_6	0·16	$7{\cdot}4 \times 10^7$
(**1a**)	MeCN	0·41	$2{\cdot}2 \times 10^8$
(**1e**)	C_6H_6	—	$2{\cdot}0 \times 10^6$

[a] Quantum yields for biacetyl disappearance by ferrioxalate actinometry with 435 nm irradiation, in degassed solution of biacetyl (0·05 M) and (**1a**) (0·05 M). [b] The rate constants for quenching of biacetyl phosphorescence calculated from experimental $k_q\tau$ values and assumption that $\tau = 0{\cdot}46 \times 10^{-3}$ s. (ref. 3g), in degassed 0·05 M (**3**), at 20°, excitation with 430 nm.

That the sensitized decomposition of (**1a**) occurs from the n–π^* triplet of (**2**) was confirmed by both the phosphorescence quenching of (**2**) by (**1a**) and the complete quenching of the reaction by triplet quenchers.

In terms of the absence of photosensitized decomposition of (**1e**) by (**2**), it has been unambiguously demonstrated that the presence of heterocycles with low ionization potentials, such as those containing a pyrrole or indole ring, greatly contributes to this sensitized reaction.

Photoreductions of α-diketones by known hydrogen donors have been widely investigated.[3] The absence of an abstractable hydrogen α to the hydroxy-group in this case suggests that this reduction is not similar to that generally postulated for the reduction by alcohols.



SCHEME.

A reasonable explanation for these results is that the radical ion pair produced by electron transfer from the heterocycle to excited biacetyl (n–π^* triplet) proceed to give a radical pair by the transference of a hydroxy-proton, which results in the formation of decomposed and reduced products (Scheme).§ Effective solvent dependency in this reaction should be reconciled with charge-transfer mechanism, in which the formation of the solvated ion pair is enhanced in a polar solvent. The low efficiency for the formation of (**3a**) relative to (**3e**) in direct photolysis, especially in polar solvents, can be explained on the basis of an intramolecular charge-transfer from the heterocycle to the excited carbonyl, which gives ground state starting materials.¶

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§ A charge-transfer mechanism has been suggested for the photosensitized decarboxylation of several carboxylic acids (ref. 3h and 3i) and the photoreduction of biacetyl by amines (ref. 3g).

¶ A detailed mechanism of the direct photolysis of acetoin derivatives will be described elsewhere.

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