

Photodecomposition of Acetoins

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The photodecomposition of α -substituted acetoins (1a—e), both by direct irradiation and by α -diketone sensitization, has been studied. Direct irradiation at 313 nm gives acetyl derivatives (2a—e) in good yield. The reactions are not quenched by triplet quenchers. Quantum yields for the formation of 2-acetyl-1-methylpyrrole (2a) are low relative to those for acetophenone (2e) and markedly decrease as solvent polarity increases. α -Diketones such as biacetyl and benzil photosensitize the decomposition of acetoins (1a—d) to (2a—d), and are thereby converted into reduction products. The decomposition of α -phenylacetoin (1e) is not sensitized by the α -diketones. The sensitized decomposition of acetoins (1a—d) can be completely quenched by triplet quenchers. Quantum yields for disappearance of biacetyl in the reaction with (1a) and rate constants for biacetyl phosphorescence quenching by (1a) are both enhanced on going from benzene to acetonitrile as solvent. Mechanisms are discussed on the basis of kinetic and deuterium-labelling experiments.

MUCH attention has been paid recently to the photochemical behaviour of the α -phenylphenacyl (desyl) system. This system undergoes primary photochemical α -fission¹ in competition with β -fission (elimination of the α -substituent),² γ -fission,³ photorearrangement,⁴ photo-reduction,⁵ and photocyclization (benzofuran formation).⁶ The nature of these competitive reactions depends upon both substituents and solvent.

In spite of widespread investigations of the photochemical reactivity of various alkanones,⁷ much less is known about the photochemistry of acetoins derivatives.⁸ As part of a study designated to provide information about the photochemistry of α -substituted aliphatic ketones, the photodecomposition of acetoins α -substitu-

ted by heterocycles (1a—d) has been investigated and compared with that of α -phenylacetoin (1e). We report here the results of mechanistic studies on these photodecompositions and describe the effects of α -substituents on reactivity.⁹

The condensation of pyrroles with ketones and aldehydes is a useful method for the synthesis of dipyrrolyl-methanes.¹⁰ Accordingly, we prepared the acetoins (1a—d) by treatment of biacetyl with pyrroles and indoles under mild conditions. The reactions (Table 1) were carried out at room temperature in the presence of

⁶ (a) J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, 1964, **86**, 5277; (b) J. C. Sheehan, R. M. Wilson, and A. W. Oxford, *ibid.*, 1971, **93**, 7222.

⁷ N. J. Turro, J. C. Dalton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 1972, **5**, 92.

⁸ For photochemistry of acetoins, see (a) E. J. Baum, L. D. Hess, J. R. Wyatt, and J. N. Pitts, jun., *J. Amer. Chem. Soc.*, 1964, **91**, 2461. Photochemical 1,3-acetyl shifts of α -hydroxyketones have been reported recently; see (b) T. Sasaki, K. Kanematsu, K. Hayadawa, and A. Kondo, *J. Org. Chem.*, 1973, **38**, 4100; (c) R. G. Carlson and A. V. Prabhu, *J. Org. Chem.*, 1974, **39**, 1753; (d) K. G. Hancock, J. T. Lau, and P. L. Wylie, *Tetrahedron Letters*, 1974, 4149.

⁹ For preliminary accounts see H.-S. Ryang and H. Sakurai, *J.C.S. Chem. Comm.*, (a) 1972, 77; (b) 1973, 824.

¹⁰ (a) A. H. Corvin and W. M. Quattlebaum, jun., *J. Amer. Chem. Soc.*, 1936, **58**, 1081; (b) A. Treibsam and F. Reitsam, *Chem. Ber.*, 1957, **90**, 777; (c) M. Scholtz, *Ber.*, 1913, **46**, 1082, 2138.

¹ (a) W. D. Cohen, *Chem. Weekblad*, 1916, **13**, 902; (b) E. Paterno, G. Chieffi, and G. Perret, *Gazzetta*, 1914, **44**, 1, 151; (c) J. Kenyon, A. Rassoul, and G. Soliman, *J. Chem. Soc.*, 1956, 1774; (d) G. Kornis and P. De Mayo, *Canad. J. Chem.*, 1964, **42**, 2822; (e) H.-G. Heine, H.-J. Rosenkranz, and H. Rudolph, *Angew. Chem. Internat. Edn.*, 1972, **11**, 974; (f) H.-G. Heine, *Tetrahedron Letters*, 1972, 3411, 4755; (g) S. P. Pappas and A. Chattopadhyay, *J. Amer. Chem. Soc.*, 1973, **95**, 6484; (h) H.-G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *J. Org. Chem.*, 1974, **39**, 691.

² A. Schonberg, A. K. Fatten, and S. Omran, *J. Amer. Chem. Soc.* 1956, **78**, 1224.

³ J. R. Collier and J. Hill, *Chem. Comm.*, 1969, 640.

⁴ H.-G. Heine, *Tetrahedron Letters*, 1971, 1473.

⁵ G. Giamician and P. Silber, *Ber.*, 1901, **34**, 1530.

a small amount of formic acid. Structures were established on the basis of elemental analysis and spectroscopic data (Experimental section). α -Phenylacetoin (1e) was prepared as described by Stocker *et al.*¹¹

TABLE 1

Products (1) from biacetyl with pyrroles and indoles

R	Solvent	Yield (%)	M.p. [B.p.]
1-Methylpyrrol-2-yl	(Neat)	55	[88—90° (5 mmHg)]
Pyrrol-2-yl	Benzene	60	[107° (6 mmHg)]
1-Methylindol-3-yl	(Neat)	92	99.5—100.5°
Indol-3-yl	(Neat)	91	136.5—137.5°

Irradiations on a preparative scale were carried out in a doughnut-shaped Pyrex vessel under nitrogen with a 350 W high-pressure mercury lamp at room temperature. Acetyl derivatives (2a—e) were obtained in good yield (Table 2). Structures were determined from spectro-

TABLE 2

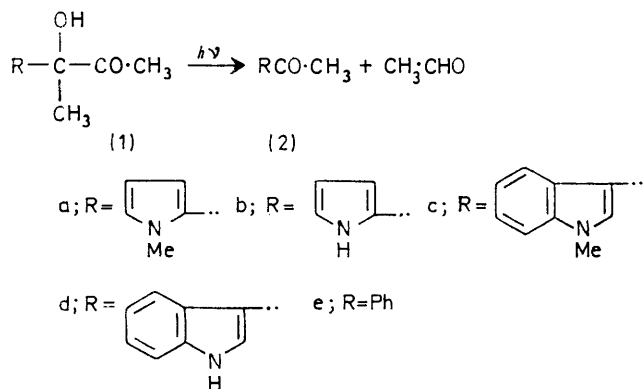
Product yields in the direct photolysis of acetoin^a

Substrate	Solvent	Yield of (2) (%) ^b
(1a)	Benzene	68
(1b)	Benzene	80
(1c)	Benzene	90
(1d)	Benzene-methanol (1 : 1)	78
(1e)	Benzene	70

^a Irradiations carried out in a Pyrex vessel with a 350 W high-pressure mercury lamp. ^b Isolated yield.

scopic data and comparison with authentic samples. The formation of acetaldehyde was confirmed by g.l.c.

To elucidate a general decomposition mode for these acetoin and to examine whether the presence of pyrroles or indoles as α -substituents favours this decomposition, quantitative data for the reactions of (1a and e) were



obtained and compared. Quantum yields for the formation of (2a) and (2e) were measured in various solvents. Degassed 0.03M-solutions of (1a) and (1e) in sealed Pyrex tubes were irradiated at room temperature on a 'merry-go-round' apparatus with 313 nm radiation transmitted by a potassium chromate filter. Light intensities were measured by potassium ferrioxalate actinometry. Product yields were determined by analytical g.l.c. for

¹¹ J. H. Stocker, P. Sidisunthorn, B. M. Benjamin, and C. J. Collins, *J. Amer. Chem. Soc.*, 1960, **82**, 3913.

conversions of <5%. The results are shown in Table 3. The quantum yields for the formation of (2a) are low

TABLE 3

Solvent effects on the direct photolysis of the acetoin (1a) and (1e)^a

Solvent	ϕ^b	
	(1a)	(1e)
Cyclohexane	0.083	
Benzene	0.076	0.150
Dichloromethane	0.047	
Ethanol	0.035	0.096
Acetonitrile	0.026	0.083
Methanol	0.021	

^a In degassed 0.03M-solutions of (1a) and (1e); irradiation at 313 nm. ^b Quantum yields for the formation of (2a) and (2e).

relative to those for (2e) and markedly decrease as solvent polarity increases.

Quenching studies were also carried out (Table 4). In the presence of cyclohexa-1,3-diene or penta-1,3-diene, which are known effective triplet quenchers, the quantum

TABLE 4

Quenching studies on the direct photolysis of the acetoin (1a) and (1e)^a

Additive	ϕ^b	
	(1a)	(1e)
None ^c	0.076	0.150
Cyclohexa-1,3-diene (0.05M) ^c	0.079	
Penta-1,3-diene (neat)	0.083	0.153

^a In degassed 0.03M solution; irradiation at 313 nm. ^b Quantum yields for the formation of (2a) and (2e). ^c In benzene.

yields were unaffected. These results suggest that the reaction proceeds from either an $n-\pi^*$ singlet state or an extremely short-lived $n-\pi^*$ triplet state within about 10^{-10} s. The quantum yield for the formation of (1a) in the presence of biacetyl or benzil was abnormally enhanced relative to that in the absence of α -diketone. Irradiation under conditions which allowed absorption by the α -diketone alone afforded the same decomposition product. However, the presence of the α -diketones did not influence the decomposition of (1e). This α -diketone-photosensitized decomposition was studied in detail.

Preparative-scale irradiation at 436 nm (tetra-ammine-copper sulphate filter)¹² of solution of (1a) and biacetyl in acetonitrile resulted in quantitative formation of (2a) and reduction products of biacetyl, *i.e.* acetoin (3), 3-hydroxy-3-methylpentane-2,4-dione (4), and 3,4-dihydroxy-3,4-dimethylhexane-2,5-dione (5). Similarly, irradiation of a solution containing (1a) and benzil gave (2a) and benzoin (6) (as major reduction product). Similar results were obtained in the cases of (1b—d), although irradiation of the α -diketones in the presence of (1e) resulted in no reaction. The α -diketone-sensitized decomposition of (1a—d) can be completely quenched by pyrene (0.01M) or cyclohexa-1,3-diene (0.1M).

Quantum yields for biacetyl disappearance in the reaction with (1a) and rate constants for biacetyl

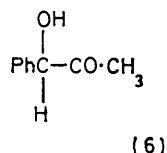
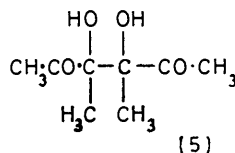
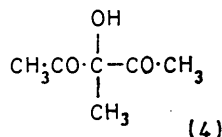
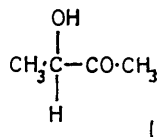
¹² N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, 1969, **91**, 7113.

phosphorescence quenching (k_q^p) by (1a) and (1e) were measured in degassed benzene and acetonitrile (Table 5).

TABLE 5
Quantitative data for biacetyl-photosensitized decomposition

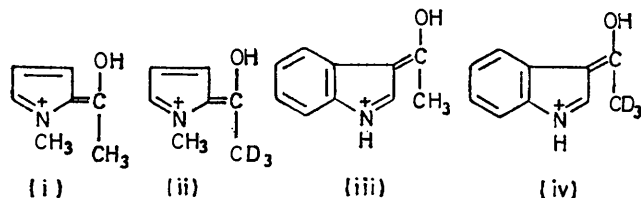
Acetoin	Solvent	ϕ^a	k_q^p ($l \text{ mol}^{-1} \text{ s}^{-1}$) ^b
(1a)	Benzene	0.16	7.4×10^7
(1a)	Acetonitrile	0.41	2.2×10^8
(1e)	Benzene		2.0×10^8

^a Quantum yields for biacetyl disappearance; irradiation at 436 nm, in degassed solution of biacetyl (0.05M) and (1a) (0.05M). ^b Rate constants for biacetyl phosphorescence quenching calculated from experimental $k_q^p \tau_p$ values and assumption that $\tau_p = 0.46 \times 10^{-2}$ s, in degassed 0.05M-solutions of biacetyl; excitation at 430 nm.



The quantum yields were determined by ferrioxalate actinometry. Both the quantum yields for biacetyl disappearance and k_q^p were enhanced on going from benzene to acetonitrile. This solvent dependence is the reverse of that in direct photolysis. The low k_q^p value for (1e) relative to (1a) is consistent with the lack of photosensitized decomposition of (1e). The complete quenching of the reaction by the triplet quenchers and the measured k_q^p values unambiguously show that the reaction goes through the $n-\pi^*$ triplet of biacetyl.

In studying the mechanism, it was thought that the low quantum efficiency for (1a) relative to that for (1e) in direct photolysis might be due to a competitive quenching process leading to a bicyclic oxetan (7). Sheehan and his co-workers have investigated the interaction between the excited carbonyl group and the nonconjugated aryl



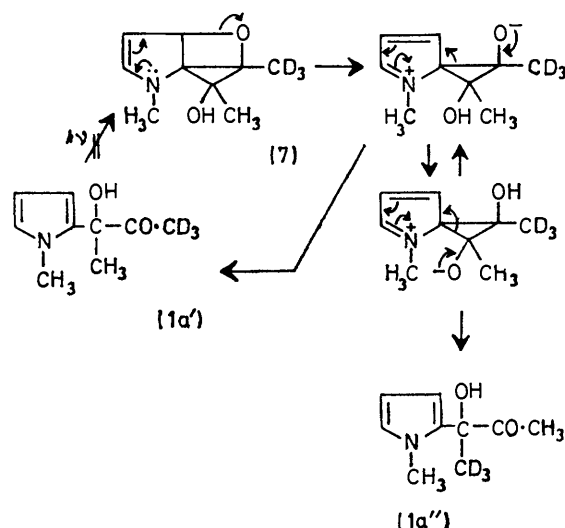
unit on the reaction of benzoin acetate and proposed that the low cyclization efficiency of 4-methoxybenzoin acetate relative to that of 3-methoxybenzoin acetate is

* The mass spectrum of (1a') shows significant peaks at m/e 124 and 127 [probably (i) and (ii) respectively], whereas (1a) shows no peak at m/e 127. Similarly the mass spectrum of [1,1,1-³H₃](1d) shows prominent peaks at m/e 160 and 163, probably due to fragments (iii) and (iv), respectively. These results suggest that the decomposition of (1a) and (1d) under electron impact involves rearrangement.

due to reconversion into starting material *via* a bicyclic oxetan.^{6b} In order to examine whether such a quenching process is involved in this case, deuterium-labelling experiments were carried out.*

The [²H₃] derivative (1a') (98% ²H) derived from deuteration of (1a) under mild basic conditions was irradiated in methanol and acetonitrile. The resulting 2-acetyl-1-methylpyrrole (2a') contained no deuterium, and the deuterium content of the recovered (1a') was the same as that of the starting acetoin. These results indicate that the quenching process leading to (7) probably does not occur in this case, because irradiation of (1a') should then have led to the introduction of deuterium into (2a') and production of a mixture of (1a') and (1a''). With regard to the biacetyl-sensitized decomposition, the absence of the above photoisomerization was confirmed by similar deuterium-labelling experiments.

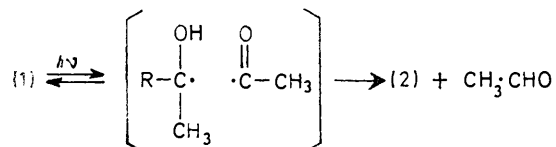
The results of these experiments allow us to suggest a mechanism. It is reasonable that the direct photolysis of



the acetoin involves first homolytic α -fission with formation of acyl and alkyl radicals, followed by disproportionation of the two radicals in a solvent cage. Hine has reported that the photolysis of benzoin ethers gives benzaldehyde and benzil from the benzoyl radicals, and the dimerization product from the alkoxybenzyl radicals.¹⁷ The absence of radical dimerization product in this case is consistent with cage disproportionation. An explanation of the observed inefficiency is that cage recombination of the α -cleavage radicals occurs. The decrease in quantum efficiency in polar solvents may be due in part to hydrogen bonding between the hydroxy-proton of the alkyl radical and the polar solvent, which impedes the disproportionation. The importance of hydrogen bonding with regard to hydrogen transfer has also been discussed for Type II photoelimination of phenyl ketones. Wagner and Kempainen have proposed that quantum yields of Type II processes are enhanced in polar solvents because hydrogen bonding between the

hydroxy-proton of the diradical intermediate and solvents prevents back-transfer of hydrogen to the γ -carbon atom.¹³

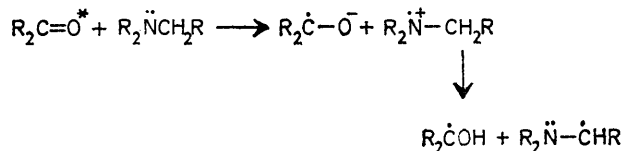
It is unlikely that the inefficiency is entirely due to cage recombination. We consider the low quantum efficiency for (1a) relative to that for (1e) to indicate another quenching path, attributable to the α -heterocycle. However, the results of the deuterium-labelling experiments indicate that a quenching process leading to (7) is not involved. Wagner and Kemppainen have demonstrated that the Type II processes of amino-ketones are competitively quenched by charge-transfer interaction between the remote amino-group and the



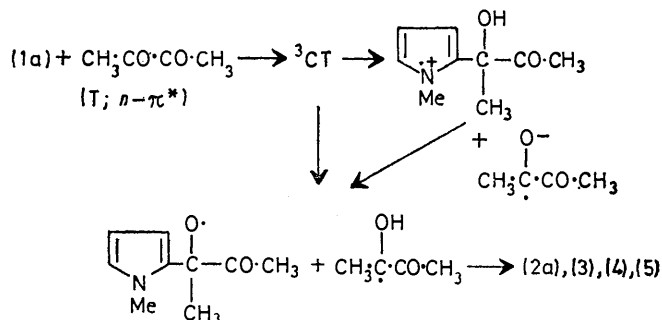
excited carbonyl.¹⁴ Rapid intramolecular charge-transfer interaction between the electrophilic excited carbonyl group and the α -heterocycle in the acetoin may well be an important quenching process.

In the α -diketone sensitized decomposition, the observed solvent effects and the quenching experiments clearly indicate that this decomposition is preceded by a mechanism different from that of direct photolysis. Sensitization *via* triplet energy transfer from the α -diketones to the acetoin is not likely because of the low triplet energies of the α -diketones ($E_T = 55 \text{ kcal mol}^{-1}$) relative to those of aliphatic ketones ($78\text{--}80 \text{ kcal mol}^{-1}$).^{7a,15} The formation of reduction products of the α -diketones suggests that hydrogen-atom transfer is involved. The photoreduction of α -diketones in the presence of known hydrogen donors has been widely investigated.¹⁶ The lack of decomposition in the case of (1e) suggests that this reduction is not similar to the generally postulated free-radical hydrogen abstraction from hydrocarbons, and that the presence of the α -heterocycle is a dominant factor. Cohen has proposed that photoreduction of carbonyl compounds by amines proceeds *via* charge-transfer followed by α -proton transfer from amines.¹⁷ In view of the low ionization potentials of these heterocycles,¹⁸ it is reasonable that charge transfer or electron transfer is involved. However, proton transfer from $\text{N}\cdot\text{CH}_3$ or NH is not likely, since

irradiation of a solution of biacetyl and 1-methylpyrrole in acetonitrile resulted in no reaction.



These results can be explained if charge-transfer or electron transfer from the heterocycle to the triplet biacetyl followed by transfer of a hydroxy-proton gives a radical pair, which affords both decomposition and reduction products. Transfer of an acidic proton to excited molecules involving charge transfer has been similarly argued for the decarboxylation of carboxylic acids containing heteroatoms.^{16b,19} The observed solvent effects are consistent with a charge-transfer mechanism. Turro and Engel have shown that the rate constants for biacetyl phosphorescence quenching (k_q^P) by aliphatic amines are $2\text{--}8 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, which are enhanced as solvent polarity is increased, and have proposed that biacetyl phosphorescence quenching by amines accompanying photoreduction proceeds *via* charge transfer.¹² The observed k_q^P values for (1a) are close to those for the amines. The effective increase in quantum yield for biacetyl disappearance in acetonitrile is probably attributable to the enhancement of a polarized or ionic character in the charge-transfer complex in acetonitrile.



The low quantum efficiency of decomposition of (1a) relative to that of (1e) in direct photolysis may be reasonably interpreted in an analogous manner as

¹³ (a) P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 5898; (b) P. J. Wagner and A. E. Kemppainen, *ibid.*, 1968, **90**, 5896.

¹⁴ P. J. Wagner, A. E. Kemppainen, and T. Jellinek, *J. Amer. Chem. Soc.*, 1972, **94**, 7512.

¹⁵ R. F. Borkmann and D. R. Kearns, *J. Chem. Phys.*, 1966, **44**, 945.

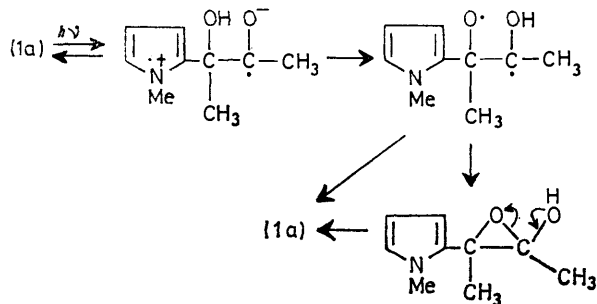
¹⁶ (a) P. W. Jolly and P. De Mayo, *Canad. J. Chem.*, 1964, **42**, 170; (b) W. H. Bentrude and D. R. Darnall, *Chem. Comm.*, 1968, 810; (c) G. E. Gream, J. C. Paice, and C. C. Ramsay, *Austral. J. Chem.*, 1967, **20**, 1671; (d) G. E. Gream, J. C. Paice, and B. S. J. Uszynski, *Chem. Comm.*, 1970, 895; (e) G. E. Gream, M. Mular, and J. C. Paice, *Tetrahedron Letters*, 1970, 3479; (f) N. J. Turro and T.-J. Lee, *J. Amer. Chem. Soc.*, 1969, **91**, 5651; (g) E. J. Baum and R. O. C. Norman, *J. Chem. Soc.*, (B), 1968, 227; (h) R. S. Davidson and P. R. Steiner, *J. Chem. Soc.* (C), 1971, 1682.

¹⁷ (a) S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, 1967, **89**, 3741; (b) S. G. Cohen and H. M. Chao, *ibid.*, 1968, **90**, 165; (c) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, 1968, **90**, 521; (d) S. G. Cohen and G. Parsons, *ibid.*, 1970, **92**, 7603; (e) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 1968, **72**, 3782; (f) S. G. Cohen, A. Parola, and G. H. Parsons, jun., *Chem. Rev.*, 1973, **73**, 141.

¹⁸ For the relationship between the ionization potentials and triplet carbonyl-donor complex, see (a) J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, 1972, **94**, 4040. For the ionization potentials of pyrroles and indoles (*ca.* 8.0 eV), see (b) J. H. D. Eland, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, **2**(3), 471; (c) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1970, **42**(9), 1064.

¹⁹ (a) R. S. Davidson and P. R. Steiner, *Chem. Comm.*, 1971, 1052; (b) R. S. Davidson, S. Korkut, and P. R. Steiner, *ibid.*, p. 1115.

follows. Intramolecular charge transfer from the heterocycle to the excited carbonyl group followed by hydroxy-proton transfer results in an epoxy-alcohol, which readily undergoes back-transfer of a proton to give the starting acetoin.



EXPERIMENTAL

N.m.r. spectra were determined on a Hitachi-Perkin-Elmer R-20 spectrometer or a JEOL JNM JS-100 spectrometer with tetramethylsilane as an internal standard. I.r. spectra were obtained on a Hitachi EPI-S2 spectrophotometer and mass spectra on a Hitachi-Perkin-Elmer RMU-60 spectrometer. G.l.c. analyses were run on a Shimadzu gas chromatograph (GC-3AF). Emission spectra were obtained with a Shimadzu MPF-2A spectrophotometer.

Organic Substrates.—1-Methylindole²⁰ and α -phenylacetoin¹¹ were prepared by reported procedures. Biacetyl, pyrrole, 1-methylpyrrole, indole, and benzil were obtained from commercial sources.

3-Hydroxy-3-(1-methylpyrrol-2-yl)butan-2-one (1a).—To a solution of 1-methylpyrrole (1.62 g, 20 mmol) and biacetyl (3.44 g, 40 mmol) were added several drops of formic acid by capillary. The solution was stirred at room temperature overnight. After recovery of the starting materials under reduced pressure, distillation afforded the acetoin (1a) (1.84 g, 11 mmol), b.p. 88–90° at 5 mmHg; m/e 167 (M^+), 159, 124, and 82; ν_{\max} (neat) 3 430, 1 700, and 715 cm^{-1} ; δ (CCl_4) 1.63 (3H, s), 1.98 (3H, s), 3.40 (3H, s), 3.95br (1H), 5.85 (1H, 2d, J 3.5 and 2.7 Hz), 6.08 (1H, 2d, J 3.5 and 1.7 Hz), and 6.39 (1H, 2d, J 2.7 and 1.7 Hz) (Found: C, 64.55; H, 8.0; N, 8.4. $\text{C}_9\text{H}_{13}\text{NO}_2$ requires C, 64.65; H, 7.85; N, 8.4%).

3-Hydroxy-3-(pyrrol-2-yl)butan-2-one (1b).—A solution of pyrrole (2.01 g, 30 mmol) and biacetyl (4.3 g, 50 mmol) in benzene (10 ml) was stirred at room temperature overnight after addition of several drops of formic acid by capillary. After recovery of the starting materials under reduced pressure, distillation gave the acetoin (1b) (2.7 g, 15 mmol), b.p. 105–107° at 6 mmHg; m/e 153 (M^+), 135, 110, and 92; ν_{\max} (neat) 3 370br, 1 700, and 727 cm^{-1} ; δ (CCl_4) 1.60 (3H, s), 2.07 (3H, s), 4.50br (1H), 6.00 (2H, m), 6.46 (1H, 2d, J 2.3 and 1.5 Hz), and 8.65br (1H) (Found: C, 62.8; H, 7.35; N, 8.95. $\text{C}_8\text{H}_{11}\text{NO}_2$ requires C, 62.7; H, 7.25; N, 9.15%).

3-Hydroxy-3-(1-methylindol-3-yl)butan-2-one (1c).—A solution of 1-methylindole (1.31 g, 10 mmol) and biacetyl (1.72 g, 20 mmol) was stirred at room temperature overnight after addition of several drops of formic acid by capillary. Removal of biacetyl under reduced pressure and

washing with cold hexane gave the acetoin (1c) (2.00 g, 9.2 mmol). Recrystallization from benzene gave white crystals, m.p. 99.5–100.5°; m/e 217 (M^+), 199, 158, 156, and 115; ν_{\max} (KBr) 3 460, 3 050, 1 700, 835, and 750 cm^{-1} ; δ (CCl_4) 1.76 (3H, s), 2.08 (3H, s), 3.78 (3H, s), 4.15br (1H), 7.04 (1H, s), 7.08–7.28 (3H, m), and 7.47 (1H, 2d J 8.0 and 2.0 Hz) (Found: C, 71.85; H, 6.85; N, 6.45. $\text{C}_{13}\text{H}_{15}\text{N}_2$ requires C, 71.85; H, 6.95; N, 6.45%).

3-Hydroxy-3-(indol-3-yl)butan-2-one (1d).—A solution of indole (1.17 g, 10 mmol) and biacetyl (1.72 g, 20 mmol) was stirred overnight after addition of several drops of formic acid by capillary. Biacetyl was removed under reduced pressure and washing with cold benzene gave the acetoin (1d) (1.85 g, 9.1 mmol). Recrystallization from methanol gave white crystals, m.p. 137–137.5°; m/e 203 (M^+), 185, 160, 142, and 118; ν_{\max} (KBr) 3 420, 3 260, 1 700, and 740 cm^{-1} ; δ (CDCl_3) 1.72 (3H, s), 2.01 (3H, s), 4.56 (1H, s), 6.72 (1H, d, J 2.5 Hz), 6.9–7.5 (4H, m), and 8.20br (1H) (Found: C, 70.9; H, 6.7; N, 6.85. $\text{C}_{12}\text{H}_{13}\text{NO}_2$ requires C, 70.9; H, 6.45; N, 6.9%).

General Irradiation Procedure.—Irradiations were carried out in a doughnut-shaped Pyrex vessel with a 350 W high-pressure mercury lamp in a quartz immersion well with water-cooled jacket at room temperature. The solutions were flushed with nitrogen for several minutes before being irradiated.

The acetoin (1a). A solution of the acetoin (1.67 g, 10 mmol) in benzene (120 ml) was irradiated for 12 h at room temperature. Evaporation of low-boiling materials and distillation afforded 2-acetyl-1-methylpyrrole (2a) (0.84 g, 6.8 mmol), b.p. 88–90° at 23 mmHg (lit.,²¹ 88–93° at 22 mmHg), and (1a) (0.24 g) (residue 0.2 g).

The acetoin (1b). A solution of the acetoin (2.3 g, 15 mmol) in benzene (120 ml) was irradiated for 15 h. Evaporation of the volatile materials and distillation afforded 2-acetylpyrrole (2b) (1.3 g, 12 mmol), b.p. 95° at 15 mmHg, m.p. 90° (from *n*-hexane–benzene) (lit.,²² 90°).

The acetoin (1c). A solution of the acetoin (1.09 g, 5 mmol) in benzene (120 ml) was irradiated for 24 h. After evaporation of volatile material, sublimation at 150–160° and 5 mmHg (bath temperature) afforded white crystals (0.78 g, 4.5 mmol). The m.p. after recrystallization from benzene was 103–104°, which differed from the reported value (95°).²³ However spectroscopic data confirmed the identification of 3-acetyl-1-methylindole (2c): m/e 173 (M^+), 158, 130, 103, and 77; ν_{\max} (KBr) 1 640, 930, and 740 cm^{-1} ; (CCl_4) δ 2.34 (3H, s), 3.77 (3H, s), 7.10–7.36 (3H, m), 7.44 (1H, s), and 8.29 (1H, m) (Found: C, 76.15; H, 6.15; N, 8.05. Calc. for $\text{C}_{11}\text{H}_{11}\text{NO}$: C, 76.25; H, 6.4; N, 8.1%).

The acetoin (1d). A solution of the acetoin (1.02 g, 5 mmol) in benzene–methanol (1 : 1, 120 ml) was irradiated for 24 h. After evaporation of volatile material, sublimation at 170–180° and 5 mmHg (bath temperature) afforded 3-acetylindole (0.62 g, 3.9 mmol), m.p. 188–189° (from methanol) (lit.,²⁴ 190–191°), identical (spectroscopic data and mixed m.p.) with an authentic sample.

Phenylacetoin (1e). A solution of phenylacetoin (0.82 g, 5 mmol) in benzene (120 ml) was irradiated for 10 h. Evaporation and distillation gave 0.27 g (2.3 mmol) of

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²³ Yu. A. Baskakov and N. N. Mel'nikov, *Obshchei Khim., Akad. Nauk S.S.S.R.*, 1963, **1**, 712 (*Chem. Abs.*, 1965, **49**, 1006c).

²⁴ R. Majima and M. Kotake, *Ber.*, 1922, **55**, 3865.

²⁰ D. A. Shirley and P. A. Roussil, *J. Amer. Chem. Soc.*, 1953, **75**, 375.

²¹ K. Hess and F. Wissing, *Ber.*, 1914, **47**, 1416.

acetophenone (0.27 g, 2.3 mmol) identified by g.l.c., and unchanged (1e) (0.29 g). Longer irradiation decreased the yield of (2e), probably owing to its further reaction.

Photolysis of the Acetoin (1a—d) in the Presence of α -Diketones.—A solution of the acetoin and the α -diketone (1.2 mol. equiv.) in acetonitrile (120 ml) was irradiated at room temperature under nitrogen with a 350 W high-pressure mercury lamp through a circulating solution prepared by dissolving copper sulphate (40 g) in concentrated ammonia (68 ml) and diluting to 1 l with water. The products were isolated and identified as described above. The formation of acetoin (3), 3-hydroxy-3-methylpentane-2,4-dione (4), 3,4-dihydroxy-3,4-dimethylhexane-2,5-dione (5), and benzoin (6) was confirmed by n.m.r. and mass spectral and g.l.c. analyses. Two reactions are described as examples.

The acetoin (1d) in the presence of biacetyl. A solution of the acetoin (2.03 g, 10 mmol) and biacetyl (1.03 g, 12 mmol) in acetonitrile (120 ml) was irradiated for 4 h. After evaporation of volatile material and removal of the reduction products of biacetyl by distillation at 50–80° and 15 mmHg (1.1 g), sublimation afforded the acetylidole (2d) (1.5 g, 9.4 mmol). The n.m.r. spectrum of the distillate mixture showed peaks due to compounds (3), (4), and (5) [(3) : (4) : (5) 9 : 3 : 7].

The acetoin (1a) in the presence of benzil. A solution of the acetoin (1.67 g, 10 mmol) and benzil (2.52 g, 12 mmol) in acetonitrile (120 ml) was irradiated for 4 h. After the removal of solvent two fractions boiling at 88–90° (23 mmHg) (1.20 g) and 190–194° (12 mmHg) (1.36 g) were collected (residue 1.3 g). The first distillate was identified as (2a). Dissolution of the second distillate in ether, cooling, and separation by suction filtration afforded pure benzoin (6), m.p. 137°. The residue was not studied further.

3-Hydroxy-3-(1-methylpyrrol-2-yl)[1,1,1-²H₃]butan-2-one

(1a').—A solution of the acetoin (1a) (1.66 g, 10 mmol) and potassium carbonate (0.08 g) in D₂O (20 ml) was heated at 70 °C for 24 h under nitrogen. After recovery of D₂O under reduced pressure, distillation gave the product (1a') (1.47 g; 98% ²H).

Quantum Yield Determinations.—Quantum yield determinations were conducted by using a 'merry-go-round' apparatus. The 313 nm line of a 350 W high-pressure mercury lamp was isolated by use of a 1 cm path of 0.002M-potassium chromate in aqueous 1% potassium carbonate. The 436 nm line was isolated with tetra-amminecopper sulphate solution (see above). Samples in 13 mm Pyrex tubes were degassed and sealed under vacuum. Potassium ferrioxalate actinometry was used for quantum yield determinations. The tubes were irradiated to <5% conversion at room temperature.

The extent of reaction was determined by u.v. spectroscopy for biacetyl disappearance and by g.l.c. (2 m 5% Ucon LB 550X on Shimalite W; 130 °C) for formation of (2a) and (2e).

Quenching of Biacetyl Phosphorescence.—The emission spectra of biacetyl were obtained in benzene and in acetonitrile at room temperature. 0.05M-Solutions of biacetyl and varying amounts of (1a) and (1e) were degassed and sealed under vacuum. Excitation was supplied by a 1 000 W xenon arc fitted to an excitation monochromator. Linear Stern–Volmer plots were obtained by plotting peak-height ratios of biacetyl phosphorescence in the absence and in the presence of quencher against quencher concentration. The slope of the Stern–Volmer plot is $k_q^p \tau_p$, where k_q^p is the rate constant for quenching of biacetyl phosphorescence and τ_p is the triplet lifetime of biacetyl in the presence of quencher; k_q^p is calculated from assumption of the value 0.46×10^{-3} s for τ_p .¹²

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