Photochemical Reactions of Some 1-Aryl-1,2-propanediones[1)]

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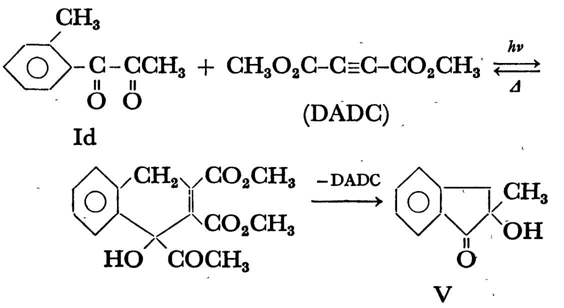
Irradiation of four 1-aryl-1,2-propanediones (Ia—Id) with over 300 nm light in 2-propanol gives reduction products identified to be the corresponding pinacols or hydrols formed by the reduction at the aroyl (but not acetyl) oxygen. The products from 1-(*o*-tolyl)-1,2-propanedione (Id) can also be accounted for by the initial hydrogen abstraction from *ortho* methyl by the aroyl carbonyl oxygen. Their photoreactivities are discussed as regards their electronic emission spectra and triplet configuration.

Sometimes one of the two carbonyls in unsymmetrical α-dicarbonyl compounds is selectively photoreduced,[2,3)] *e.g.*, unsymmetrical benzils are photoreduced at a carbonyl with a stronger electron-withdrawing group.[4)] The product is not always determined by the hydrogen abstraction with excited diketone, because the 1,2-hydrogen migration from the resulting ketyl radical being sometimes significant.[5,6)] Intramolecular H abstraction reactions might be utilized to see which of the two carbonyls really abstracts a H atom on the basis of sterically favorable proximity. The intramolecular H transfer is specific as revealed by the fact that the 1,5-shift predominates over the 1,6-shift, particularly in acyclic ketones which are photoreduced with 100% γ-H abstraction.[7)]

Cyclization of 1-(*o*-tolyl)-1,2-propanedione to 2-hydroxy-2-methylindanone (V) on irradiation has been reported by Bishop and Hamer.[8)] They preferred a mechanism *via* benzocyclobutanol to that *via* photoenol (VIII).[8b,c)] We have obtained some evidence for a six-membered transition state (1,5-shift) followed by 1,2-shift, *e.g.*, trapping of the intermediary enol(VII) with dimethyl acetylenedicarboxylate (DADC) as shown below.



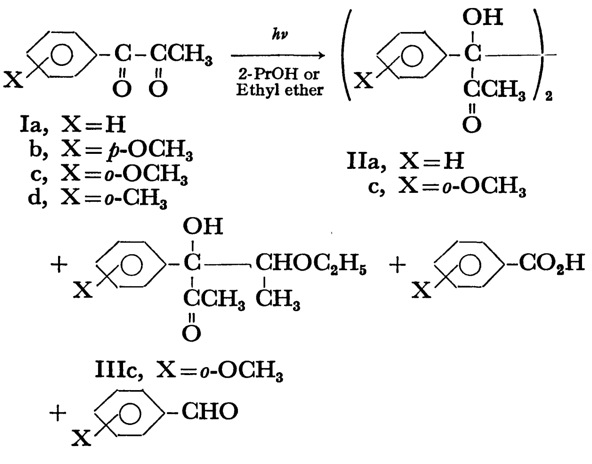
(1)

From their interest in the photoreduction behavior of alkyl aryl α-diketones, the authors present some results on the correlation of photoreactivity with electronic configuration.

Results and Discussion

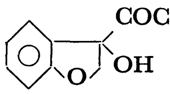
Irradiation of α-Diketones. 1-Aryl-1,2-propanediones (Ia—Id) were irradiated in dilute 2-propanol or ethyl ether with UV light filtered with Pyrex (>300 nm).

Ia was photoreduced at the benzoyl oxygen but not the acetyl oxygen. A reduction dimer, 1,2-diacetyl-1,2-diphenylethanediol (IIa, 10%) was obtained. The major product was benzoic acid (23%) which seems



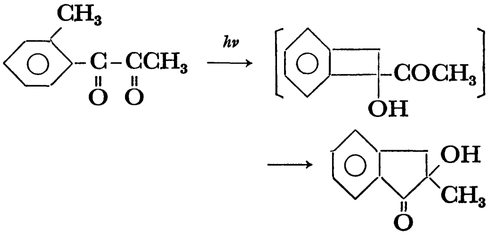
(2)

to be derived from benzoyl radical *via* photodecomposition. In the case of *p*-methoxy derivative (Ib), a complex mixture consisting of more than five components was obtained. The major product was *p*-anisaldehyde (*ca.* 40%) along with a small amount of *p*-anisic acid, all attempts for isolation of other components in a pure form being unsuccessful. The photodecomposition rate was *ca.* 5 times as slow as that of Ia. Photochemical behavior of Ic (*o*-OCH$_3$) is quite different from that of Ia and Ib. It is smoothly reduced in ether to a dimer (IIc, 550 mg) and a 1 : 1 adduct of ether (IIIc, 100 mg) along with a trace of *o*-anisic acid. The yield including all recovered materials becomes 90%. There is no product which is reduced at the acetyl oxygen or cyclized by the intramolecular reduction to benzofuran derivative (IV).



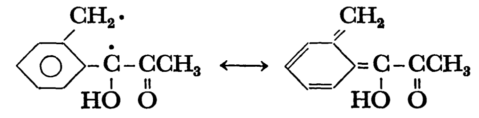
IV

*Photolysis of 1-(*o*-Tolyl)-1,2-propanedione (Id).* The photocyclization of Id to indanone (V) was reported by Bishop and Hamer, who assumed either a mechanism involving hydrogen abstraction of *o*-CH$_3$ hydrogen by acetyl oxygen or a presumed intermediate (VI) which then expanded to V.[8b)]



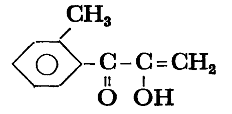
(3)

We postulated an alternative mechanism involving an enol intermediate for the photocyclization of Id on the basis of trapping of intermediary enol, VII.[9]



VII

The change of UV spectrum of Id in degassed cyclohexane on irradiation with 366 nm light (Fig. 1) illustrates the gradual disappearance of Id (λ_{max} 257 nm) with a simultaneous increase in V (λ_{max} 242 and 250 nm). The two isosbestic points at 253 and 297 nm indicate the stoichiometry for the conversion Id→V without accumulation of intermediates such as enols (VII and VIII).



VIII

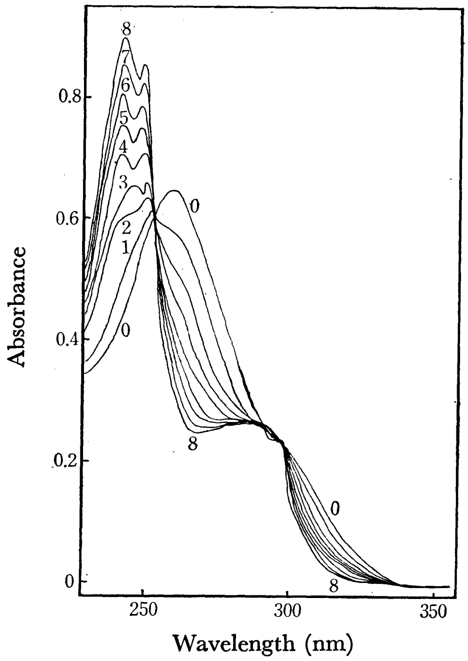


Fig. 1. UV absorption of 1-(*o*-tolyl)-1,2-propanedione in cyclohexane in a 1 cm square cell, degassed and sealed, followed by successive irradiation.
(0) Before irradiation, (1) after 30 s of irradiation, (2) after 60 s, (3) after 90 s, (4) after 135 s, (5) after 160 s, (6) after 200 s, (7) after 250 s, (8) after 300 s.

The quantum yields in various solvents for the disappearance of Id and the formation of V determined independently by glc and UV are given in Table 1.

If there is accumulation of enols (VII and/or VIII) liable to return to the starting diketone as evidenced with 1-phenyl-1,2-alkanedione,[10,11] quantum yields for the disappearance of Id estimated by means of glc at 180 °C (the injection temperature) would be lower than those by UV spectrometry at an ambient temperature. No appreciable difference can be seen between the yields from glc and UV (Table 1), suggesting no accumulation of enol although there may be the enol of short life. The stoichiometry of the photocyclization of Id to V was also confirmed by similar quantum yields for the disappearance of Id to those for the formation of V. However, the value of the quantum yield (0.57 in cyclohexane) is small in view of the quantum efficiency of over 0.9 for the population of α-diketones at its lowest triplet. Thus, the efficiency for the intersystem crossing of S→T with benzil is known to be 0.92[12] and other aliphatic α-diketones have values 0.95—0.98.[13] Photoenolization might be expected to play a role for the triplet energy dissipation, since the emissive efficiency is generally *ca.* 0.1.[14]

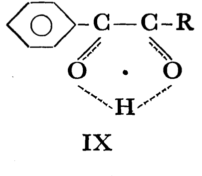
TABLE 1. QUANTUM YIELDS FOR DISAPPEARANCE OF Id AND FORMATION OF V IN VARIOUS SOLVENTS[a]

Solvent	Quantum yield for disappearance of Id	Quantum yield for formation of V
Ethyl ether	0.46 (0.44)	0.25
Cyclohexane	0.57 (0.57)	0.51
Benzene	0.62 (0.61)	0.54
Acetonitrile	0.53 (0.51)	0.42
Ethanol	0.66 (0.51)	0.43

a) Degassed solutions of *ca.* 10^{-2}M diketone were irradiated to 50—70% conversion by 366 nm light. Ferrioxalate actinometry was used. Estimation by glc technique using propiophenone as an internal standard. Values in brackets are estimated from the measurement of disappearance of α-diketone $n\pi^*$ absorption around 400 nm.

α-Diketons with α-hydrogen undergo facile photoenolization followed by thermal decomposition, which tends to lower apparent yields. Variation in solvent polarity does not affect the efficiency of disappearance of Id and formation of V (Table 1). The solvent effect was also observed with 1-phenyl-1,2-alkanediones,[10,11] *i.e.*, quantum yields for disappearance of diketones tends to be slightly higher in wet acetonitrile than in benzene.

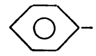
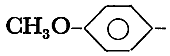
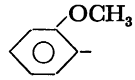
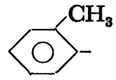
This is contrast to the Type II photoenolization and photocyclization of aromatic monoketones,[15] which are influenced by solvent polarity, especially by a hydrogen bonding on account of the suppression of reversal hydrogen shift from 1,4-biradical to the original ketone. However, since the hydrogen exchange with solvent is difficult for semidione radical IX, as judged by no incorporation of deuterium into V,[8a] the reformation of Id and formation of product V should be too fast to exchange the proton of the hydroxy group with solvent.



IX

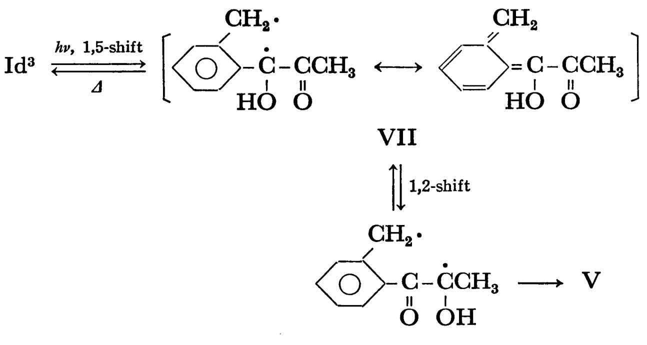
The biradical seems to resist the hydrogen exchange by the intramolecular hydrogen bonding (IX).

TABLE 2. ABSORPTION AND EMISSION SPECTRA OF α-DIKETONES[a]

Ar in Ar-COCOCH$_3$	abs λ_{max}^{EPA} (nm) (A)[b]	abs λ_{max}^{IP} (nm)	phos λ_{max}^{EPA} (nm) (P)[c]	phos λ_{max}^{IP} (nm)	$A-P$[d] (cm^{-1})	ΔE_{ST}[f] (cm^{-1})	E_T[e] (kcal/mol)
	396	537	525	537	6300	1800	54.4
	410	405, 410	520	527	5200	2100	55.0
	386	—	508	511	6200	300	56.3
	382	400	508	540	5800	900	56.3

a) Absorption spectra were measured at room temperature and emission spectra at 77 K in EPA (ether–isopentane–alcohol, 5: 5: 2, in vol.) and IP (isopentane). b) A: absorption maximum in EPA (cm^{-1}). c) P: phosphorescence maximum in EPA (cm^{-1}). d) The energy difference between the absorption and phosphorescence maxima. e) Value obtained from phosphorescence maxima. f) The energy difference between the fluorescence and phosphorescence maxima in EPA.

The formation of V can reasonably be explained by the following Scheme.[9]



Scheme 1.

However, an alternative direct 1,6-hydrogen shift can not completely be excluded.

Configuration of the Lowest Triplet State of α-Diketones. The configurational analysis of α-diketones in their excited states was performed in a similar way to that in our previous procedures.[4] The results are compiled in Table 2.

Phosphorescence spectra of α-diketones generally show a broad peak; hence we make use of their emission maxima at the lowest triplet energies instead of their 0-0 bands. Their energy diagrams are illustrated in Fig. 2.

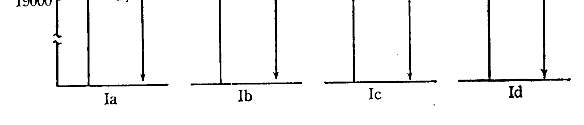


Fig. 2. Energy diagrams of α-diketones.

The nπ* absorption maximum shifts hypsochromically (below 400 nm) as the dihedral angle between the planes of two carbonyl groups of α-diketone increases from 0 to 90°, and bathochromically (over 400 nm) as the angle increases from 90 to 180°.[16]

Two carbonyls of 1-phenyl-1,2-propnedione (Ia) with its nπ* at 396 nm is orthogonally twisted.[17] The situation is the same with those for Ic and Id, since they have their nπ* absorptions at 386 and 382 nm, respectively. An aromatic ring and a carbonyl attached to it tend to be coplanar because of the resonance between the groups. The large energy difference between the absorption and phosphorescence maxima (A–P) in EPA is ascribed to the recovery of coplanarity at the excited triplet.[17] Judging from Table 2 and Fig. 2, the large value of (A–P) of Ic (6200 cm^{-1}) and Id (5800 cm^{-1}) similar to that of Ia (6300 cm^{-1}) seems to be due to the recovery of coplanarity of carbonyls. The coplanarity of carbonyls favors the hydrogen abstraction *via* a six-membered transition state in view of the proximity of *o*-methyl to benzoyl oxygen. α-(*o*-Tolyl)acetone, a monoketone analogue of Id, was found to yield the corresponding pinacol but not indenes.[9] The reduction to pinacol in spite of the proximity of *ortho*-methyl to the acetyl oxygen is explained by the small ability of intramolecular hydrogen abstraction of acetyl oxygen *via* 1,6-shift.

The observed difference of photochemical behavior between Ib (*p*-OCH$_3$) and Ic (*o*-OCH$_3$) remains obscure. The trend where the *p*-methoxy substrate is easily photodecomposed was observed in the photolysis of *p*-methoxybenzil and *p*-methoxyacetophenone, *i.e.*, *p*-methoxybenzil is photodecomposed as easily as unsubstituted benzil, but the yield of the reduction is much lower,[4] whereas, the *ortho*-substituted α-diketone, *o*-benzyloxyphenylglyoxalate, is photoreducible intramolecularly.[18a,b,c] This difference in behavior of *p*- and *o*-methoxy-substrates can be explained by the difference in their lowest triplets, *i.e.*, ππ* in the former and nπ* in the latter. The lowest triplet levels for all these α-diketones (Ia—Id) have nπ* character, since the phosphorescence maxima shift bathochromically with the change of solvent from EPA to isopentane (IP). Thus, the different behavior of Ic among Ia—Id should be explained by the mixing of $n\pi^*$ triplet level with $\pi\pi^*$ or CT.

The energy difference between the lowest singlet and the triplet (ΔE_{ST}), a measure of the behavior in the intersystem crossing for singlet to triplet,[18d] seems to reflect their photochemical behavior since this type of carbonyl reduction occurs by way of triplet; *i.e.*, Ia (H) and Ib (*p*-OCH_3), which are more easily photodecomposed to acid and aldehyde, exhibit higher values of ΔE_{ST} (>1800 cm^{-1}), while Ic (*o*-OCH_3) and Id (*o*-CH_3), which are mainly photoreduced, show a lower ΔE_{ST} (<900 cm^{-1}). However, all these ΔE_{ST} are estimated to be within several kcal/mol which is negligible for a discussion of the intersystem crossing.

Experimental

All NMR spectra were taken in CCl_4 solution with TMS as an internal standard on a JEOL, C 60 HL. Mass spectra were recorded on a Hitachi RMS-4 at 70 eV ionizing voltage.

Materials. 1-Phenyl-1,2-propanedione (Ia) was prepared by oxidation of α-phenylacetone with selenium oxide.[19] 1-(*p*-Anisyl)-1,2-propanedione (Ib) was prepared by the reaction of *trans*-anetole with a mixture of mercuric oxide and mercuric acetate in aqueous acetic acid.[20] 1-(*o*-Anisyl)-1,2-propanedione (Ic): *o*-Methoxyisonitrosopropiophenone was prepared by reacting *o*-methoxypropiophenone with *n*-butyl nitrite passing through dry HCl, mp 133—134 °C (lit,[21] 132 °C). The oxime was converted by heating with aqueous H_2SO_4 to give a yellow liquid. It has IR band at 2830 (OCH_3), 1710 (aliph. C=O), 1660 (arom, C=O), and 760 cm^{-1} (*ortho* substituent); NMR: τ 2.2—3.2 (m, 4H, phenyl), 6.28 (s, 3H, OCH_3), and 7.69 (s, 3H, $COCH_3$). 1-(*o*-Tolyl)-1,2-propanedione (Id) was obtained by nitrosation of *o*-methylpropiophenone similarly to Ic, mp 106—108 °C, followed by conversion into the diketone by heating with H_2SO_4, bp 128—137 °C/20 mmHg.

Quantum Yields. A cyclohexane solution of *ca.* 10^{-4} and 10^{-2} M α-diketone in 1 cm square cells were degassed by three freeze-pump-thaw-cycles. Irradiation was carried out with a 300 W high-pressure mercury vapor lamp using a Corning color filter (7—51) to isolate 366 nm light. Ferrioxalate actinometry was used. Total light intensity on the 9×25 mm unmasked area of a reaction cell was estimated to be 2.1×10^{15} quanta/s.

Products from 1-Phenyl-1,2-propanedione (Ia). A 2-propanol solution (100 ml) of the diketone (700 mg) was irradiated for 6 hr until its original yellow color had disappeared, and the two products were collected by a column packed with silica gel. The first eluted product, mp 131.5—132 °C (lit,[22] mp 118.5 °C) (10% yield) was 1,2-diacetyl-1,2-diphenylethanediol (IIa). It has the following spectral properties: IR peak at 3450 (OH) and at 1700 cm^{-1} (aliph. C=O); NMR: τ 2.90 (m, 10H, phenyl), 4.52 (s, 2H, OH), 7.77 (s, 6H, $COCH_3$); Mass *m/e* 149 ($M^+/2$); UV: $\lambda_{\max}^{\mathrm{MeOH}}$ 258—270 nm (an isolated phenyl ring). The second eluted product was identified to be benzoic acid (130 mg, 23%) from its IR data and mp.

*Products from 1-(*p*-Anisyl)-1,2-propanedione (Ib).* A 2-propanol solution (100 ml) of the diketone (1.01 g) was irradiated with over 300 nm light passing through a Pyrex filter; 64% of the starting diketone was recovered in spite of the long irradiation (24 hr). The glc analysis of the irradiated solution shows the presence of more than five products, in which *p*-anisaldehyde was a major product and confirmed by tlc, IR and UV. A small amount of *p*-anisic acid (5.4%) was detected.

*Products from 1-(*o*-Anisyl)-1,2-propanedione (Ic).* A dilute ethereal solution (120 ml) of the diketone (912 mg) was irradiated through a Pyrex filter to 90% conversion for 7 hr. Separation by column chromatography afforded three components. A major product was a pinacol (IIc, 550 mg); NMR: τ 3.0 (m, 8H, phenyl), 4.67 (s, 2H, OH), 6.34 (s, 6H, OCH_3), and 7.90 (s, 6H, $COCH_3$). The second product was a monoalcohol (IIIc, 100 mg); NMR: τ 3.0 (m, 7H, phenyl), 5.84 (s, 1H, OH), 6.25 (s, 3H, OCH_3), 6.74 (q, 2H, OCH_2CH_3), 8.00 (s, 3H, $COCH_3$), 8.78 (d, 3H, $OCHCH_3$) and 9.05 (t, 3H, OCH_2CH_3). The NMR spectrum, however, did not clearly show the signal of ethoxy methine proton expected to appear at τ *ca.* 6.0 hidden by the signal of methoxy methyl and ethoxy methylene protons. The third product in a small amount was *o*-anisaldehyde on the basis of NMR: τ 2—3 (m, 4H, phenyl), 7.40 (s, 3H, methyl), and 0.03 (s, H, aldehyde).

*Products from 1-(*o*-Tolyl)-1,2-propanedione (Id).* A 2-propanol solution (120 ml) of the diketone (862 mg) was irradiated for 3 hr to complete the conversion and the three products were collected by a column packed with silica gel. The first eluate was the starting diketone (1.6%). The second eluate (12.6%) (mp 97—99 °C) was identified to be *o*-toluic acid, since it has the same spectra (IR and UV) as those of the authentic sample. The third eluate (mp 53.0—54.5 °C) was 2-hydroxy-2-methylindanone (V, 75%).[8a]

All preparative scale irradiation was conducted using UV light (>300 nm) from a high pressure mercury lamp (Halos HIP 300 W) in a Pyrex tube (ϕ 35×150 mm) under N_2 for 30 min prior to and during the irradiation.

Emission Studies. Emission studies were performed on a Hitachi MPF-2A Fluorescence Spectrophotometer with phosphorescence attachments. Fluorescence spectra were recorded at an ambient temperature using EPA (ether–isopentane–ethanol, 5:5:2 in volume) as a solvent and phosphorescence spectra were recorded at 77 K using the same solvent.

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