Competing Photocyclization and Photoenolization of Phenyl α-Diketones

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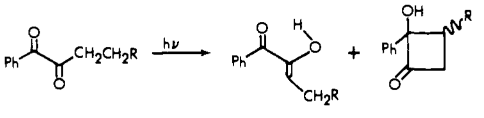
Abstract: The photochemistry of several phenyl alkyl α-diketones has been studied in solution. Photocyclization of 2-phenyl-2-hydroxycyclobutanones competes with photoenolization to 1-phenyl-2-hydroxy-2-alken-1-ones. Both processes compete with phosphorescence, whereas fluorescence quantum yields are independent of the alkyl group. Quantum yields of cyclization are higher in wet acetonitrile than in benzene and increase as the C–H bonds γ to the 1-keto group are made more labile. Cyclization apparently proceeds by the expected γ-hydrogen atom abstraction, exclusively by the 1-keto group, to yield a 1-hydroxy-2-keto-1,4-biradical which cyclizes in high efficiency even in hydrocarbon solvents. Relative reactivities of primary:secondary:tertiary C–H bonds are 1:60:390. Quantum yields and rates of enolization are strongly dependent on the type of C–H bonds α to the 2-keto group, the relative reactivities of primary:secondary:tertiary being 1:1000:300 000. In α-ketovalerophenone, the rate ratio for γ-hydrogen abstraction/enolization is 2.3/1. There is no evidence that photoenolization of these phenyl diketones involves an upper triplet. Photoenolization may involve β-hydrogen abstraction by the 1-keto group to yield an oxyallyl intermediate. It is suggested that the lowest n,π* triplet of these α-diketones has significant zwitterionic character.

Spectroscopists and photochemists have been intrigued by the excited-state behavior of 1,2-diketones for some time. Energies of the long-wavelength n-π* transition of diketones have been correlated with ground-state conformations of the carbonyl groups.[2-5] Although biacetyl and other acyclic aliphatic α-diketones are most stable with trans, coplanar conformations,[5,6] the carbonyl groups of benzil and other phenyl α-diketones are presumably twisted.[2-5] The large Stokes loss observed with the twisted α-diketones has been attributed to major configurational differences between ground and excited states[5] and suggests planar excited states. By analogy to conjugated dienes,[7] diketone triplets have been suggested to exist as nonequilibrating mixtures of cis and trans stereoisomers.[8] The concept of stereoisomeric excited states is consistent with the simple LCAO-MO representation for the lowest excited state of biacetyl.[9] However, a detailed vibrational analysis of the spectra of solid biacetyl indicates that the predicted increase in bond order between the carbonyl carbons does not occur in either the singlet or triplet state.[10] Moreover, photoelectron spectra of α-diketones[11] are now interpreted as demonstrating a large splitting of n orbitals due to through-bond coupling,[12] such that the formally conjugated π orbitals may not interact very strongly.[13]

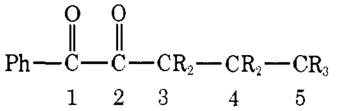
Despite the uncertainty about the nature of its excited states, biacetyl has played a key role in early spectroscopic studies of energy transfer because of its relatively intense phosphorescence in fluid solution.[14] Photoreactions of α-diketones are varied, often paralleling those of monoketones.[15,16] The most important photoreaction of biacetyl in the vapor phase is cleavage of the bond between the carbonyl carbons.[17] In solution, quantum yields for cleavage of biacetyl are considerably reduced.[18] Photoenolization has been observed of biacetyl in the vapor phase[19] and of biacetyl[20] and other aliphatic α-diketones[21] in solution. In a detailed study of the enolization, Lemaire found that the quantum yield is temperature and wavelength dependent.[20] The kinetics for quenching of biacetyl by a variety of substrates in solution have been investigated,[22,23] but quantitative studies of photoreactions of other α-diketones are surprisingly scarce. Aliphatic α-diketones with γ-hydrogens undergo photoinduced 1,5-hydrogen transfer to yield exclusively 2-hydroxycyclobutanones,[24] at the expense of their phosphorescence efficiencies.[25] A kinetic study of this photoreaction has been reported.[26] That suitably substituted aliphatic α-diketones fail to form acylcyclobutanols and do not undergo type II cleavage is one of the most intriguing aspects of their photochemistry.[21,24,27]

Our two laboratories, working independently, have both studied the photocyclization of 1-phenyl-1,2-diones in solution, discovered a competing photoenolization, and communicated our findings separately.[28] In this paper, we report our joint findings in full and attempt to correlate the chemistry with recent advances in the understanding of the spectroscopy of α-dicarbonyls.



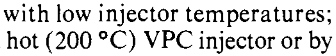
Results

Below is drawn a general structure for the diketones with the carbons numbered to facilitate discussion.



$$\underset{1}{\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}}}{-}\underset{2}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}}{-}\underset{3}{\mathrm{CR_2}}{-}\underset{4}{\mathrm{CR_2}}{-}\underset{5}{\mathrm{CR_3}}$$

Photoreaction. The phenyl diketones listed in Table I have been studied. Irradiation of diketones with hydrogens on carbon 4, which is γ to the 1-keto group, results in the formation of 2-phenyl-2-hydroxycyclobutanones, as expected.[24] However, the chemical yields vary markedly with structure, ranging from 100% for **8** to 3% for **7**. Although 1-phenyl-4,4-dimethyl-1,2-pentanedione (**6**) and 1,3-diphenyl-1,2-propanedione (**9**) possess no such γ-hydrogens, they also photoreact very efficiently. Vapor phase chromatographic (VPC) analysis of irradiated **6** indicated only one product, which by its spectroscopic and chemical behavior is the enol **10**. Reaction of **10** with bromine leads to formation of the α-bromodiketone **11** and HBr. Under the same conditions diketone **6** itself does not brominate. A brief look at the IR and NMR of the photoproduct from **9** suggests an enol structure. Enol **10** is stable for days at room temperature in dilute solutions and can be analyzed by VPC with low injector temperatures; but it is reconverted to **6** in a hot (200 °C) VPC injector or by treatment with aqueous acid or base.[29] Infrared and NMR analysis of the

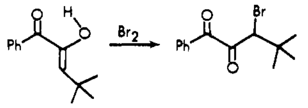


$$\mathbf{9} \xrightarrow{h\nu} \mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}CH{-}Ph}$$

Table I. Kinetic Parameters for Photoreactions of 1-Phenyl-1,2-diones PhCOCOR[a]

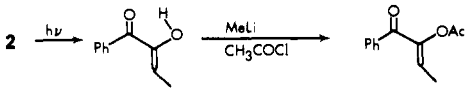
Diketone	R	Solvent	Φ_{CB}[b,c]	Φ_{-DK}[c,d]	$10^{-3}\,k_q\tau$, M^{-1}[c,e]	k_γ, $10^5\ s^{-1}$[f]	$(k_d + k_c)$, $10^5\ s^{-1}$[f]
1	CH_3	Benzene		<0.01	190 (1000)[g]		0.25 (0.05)
1-D	CD_3	Benzene			(1100)[g]		(0.045)
2	CH_2CH_3	Benzene	0.04 (0.043)	0.50 (0.23)	30 (19)[g-i]	0.10	1.6 (2.5)
		Wet CH_3CN	0.06	0.61	53[g,h]	0.11	1.8
2-D	CD_2CH_3	Benzene	(0.052)	(0.12)	(38)[h]		(1.2)[q]
3	$CH_2CH_2CH_3$	Benzene	0.52 (0.40)	0.73 (0.45)	9.1 (7.6)[h-j]	3.9	1.6 (2.7)
		Wet CH_3CN	0.71	0.87	16.8[h]	4.2	1.8
3-D	$CD_2CH_2CH_3$	Benzene	(0.37)	(0.38)	(9.0)[h,i]		(1.9)[q]
4	$CH_2CH(CH_3)_2$	Benzene	0.81[k] (0.60)	0.88 (0.65)	3.4 (1.7)[h-j]	13.0	1.8
		Wet CH_3CN	0.88	0.93	6.8[h]	13.0	1.7
5	$CH_2CHMeEt$	Benzene	0.80[l]	0.89 (0.63)	(1.7)		
		Wet CH_3CN	0.88[l]	0.94	*m*		
6	$CH_2C(CH_3)_3$	Benzene		0.62	22[g]		2.3
7	$CH(CH_2CH_3)_2$	Benzene	0.015	0.53	0.19[n]	5.0	260.0
8	$C(CH_3)_3$	Benzene	0.28	*m*	1.04[h,j]	36.0[o]	
		Wet CH_3CN	0.75	*m*	1.80[h]	41.0[o]	
o-Cl-**3**	$CH_2CH_2CH_3$	Benzene	0.29	0.67	6.5[h]	3.5	3.2
		Wet CH_3CN	0.45	*m*	*m*		
p-MeO-**3**	$CH_2CH_2CH_3$	Benzene	0.56	0.81	12.0[g,p]	3.3	0.9
		Wet CH_3CN	0.78	0.95	*m*		

[a] Irradiated at 365 nm in sealed, degassed tubes. [b] Quantum yield for cyclobutanol formation, extrapolated to zero diketone concentration (ref 28a). [c] Values in parentheses are those obtained at 0.2 M diketone for **3** and **4**, 0.06 M for **2** (ref 28b). [d] Quantum yield for diketone disappearance, extrapolated to zero diketone. [e] Pyrene quencher, 365 nm, unless otherwise indicated. [f] From eq 1 and 2, Φ_{CB} in wet CH_3CN; $k_q = 5 \times 10^9\ M^{-1}$ in benzene, $1 \times 10^{10}\ m^{-1}\ s^{-1}$ in CH_3CN. [g] Phosphorescence quenching, 0.005–0.01 M diketone. [h] Quenching of cyclobutanol formation, extrapolated to zero diketone. [i] Same value observed at 436 nm. [j] Same value observed with anthracene as quencher. [k] Same value observed with benzophenone sensitizer. [l] Measured at 436 nm relative to diketone **4** as actinometer. [m] Not measured. [n] Quenching of 0.05 M diketone disappearance. [o] Minimum values, may be as much as 33% higher. [p] Acridine as quencher. [q] Calculated on basis that there is no isotope effect or k_γ.



10 **11**

photosylates of phenyl diketones **2**–**4** indicated that photoenolization competes to varying degrees with cyclobutanol formation. Enolization predominates in **2** and **7**; isolated enol **12** displays spectral properties very similar to those of **10**. Moreover, treatment of **12** at −80 °C with methyllithium followed by acetyl chloride yields the enol acetate of **2**.



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Only when C-4 is tertiary, as in **4** and **5**, does cyclization predominate. After 100% disappearance (by UV) of **4**, preparative VPC with the injector set at 200 °C regenerated 8% **4**, presumably via its enol. In excellent agreement, NMR analysis of irradiated **4** indicated a 95:5 ratio of hydroxycyclobutanone:enol. Extensive irradiation of **1** in benzene does not produce enol but does produce, very slowly, several products of undetermined structure. We looked for and could find no products such a benzoylcyclobutanols, or diketone **1** and olefin, which might arise from γ-hydrogen abstraction by the 2-keto group of diketone **6**. A small amount of type I cleavage to give isobutylene and benzaldehyde was observed for diketone **8**.

Quantum Yields. In Table I are listed quantum yields for cyclobutanol formation (Φ_{CB}) and diketone disappearance (Φ_{-DK}), measured by VPC analysis at low conversions and UV analysis at moderate conversions, respectively. Actinometry is described in the Experimental Section. In all cases Φ values are higher in wet acetonitrile than in benzene, but only for **8** is the increase large. In the case of diketone **3** the quantum yield for cyclobutanol formation from 0.15 M diketone is the same at 35% conversion as at 5% conversion, indicating that the enol by-product is not a quencher. Quantum yields are slightly concentration dependent; the table lists values both at 0.2 M (in parentheses) and extrapolated to zero diketone concentration. The benzophenone-sensitized cyclization of **4** has the same quantum yield as the direct photoreaction. Diketone **4** was chosen for this experiment because studies of type II reactions have shown that aliphatic monoketones with tertiary γ C–H bonds exhibit the greatest singlet state reactivity.[30,31] Unlike the other diketones, **1** showed no decrease in UV absorption after 3 *days* of irradiation.

Quenching Studies. Oxygen, pyrene (E_T = 48.7 kcal),[32] acridine (E_T = 45 kcal),[33] and anthracene (E_T = 42 kcal)[34] completely quench the photoreactions of the diketones while having no measurable effect upon the fluorescence quantum yields. Degassed solutions of the diketones (0.05–0.20 M) in the presence of various amounts of triplet quenchers were irradiated in parallel at 365 or 436 nm. Relative quantum yields for cyclobutanol formation were measured by VPC analysis; diketone disappearance was measured by UV analysis. For those α-diketones which phosphoresce strongly enough (**1**, **2**, **6**, *p*-MeO-**3**), the effect of added quencher upon the phosphorescence intensity was also measured. Stern–Volmer plots of the data are linear out to Φ^0/Φ values of at least 10. The $k_q\tau$ values so obtained were extrapolated to zero diketone concentrations and are so listed in Table I. The same $k_q\tau$ values, within 20%, were obtained by analysis both of ketone disappearance and of cyclobutanol formation. The bimolecular rate constants for quenching, k_q, are assumed to be $5 \times 10^9\ M^{-1}\ s^{-1}$ for pyrene, anthracene, and acridine in benzene[35,36] and $1.0 \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile.[36,37] The $k_q\tau$ values obtained from quenching cyclobutanol formation agree with those found from phosphorescence quenching for **2** and are wavelength independent for **2**, **3**, **4**, and **8**. Since **7** produces such a low yield of cyclobutanol, only disappearance of diketone was monitored by Uv analysis for the quenching study. Diketone **1** displayed a significantly longer triplet lifetime in New York than in Michigan, the only significant difference between the results

Table II. Emission of 1-Phenyl-1,2-Alkanediones in Benzene at 25 °C

Ketone	λ^F_{max}, nm	λ^P_{max}, nm[a]	P/F[b]
1	488	540	2.9
2	495	544	0.43
3	498	—	0.1
4	500	—	<0.03
5	501	—	<0.03
6	505	561	0.39
7	502	—	<0.03
8	500	—	<0.03
o-Cl-**3**[c]	510	—	<0.03
p-MeO-**3**[d]	492	544	0.85

[a] Dashes indicate phosphorescence too weak to measure. [b] Phosphorescence/fluorescence ratio, roughly corrected for PM response; measured for 0.005 M diketone, invariant over 360–440 nm excitation. [c] o-Chlorophenyl. [d] *p*-Methoxyphenyl.

obtained in our two laboratories. Probably different levels of solvent impurities were responsible.

The unexpectedly low $k_q\tau$ value observed for pyrene quenching of nonenolizable diketone **8** suggested that energy transfer might be either reversible or sterically hindered. However, a more detailed study revealed no evidence for either effect. Identical Stern–Volmer slopes were found for both pyrene and anthracene. If energy transfer to pyrene were reversible, it would be much less so to anthracene.[38] The marked viscosity dependence of the $k_q\tau$ values[39] indicates that energy transfer is diffusion controlled.[36] The lack of detectable phosphorescence from **8** (see below) confirms that the low $k_q\tau$ value results from a short triplet lifetime.

Optically Active Diketones. (*S*)-(+)-1-Phenyl-4-methylhexane-1,2-dione (**5**) $[\alpha]^{25}{}_{578}$ = 18.8° (benzene), 0.33 M in benzene, was irradiated at 438 nm to 74% conversion. Recovered unreacted diketone had undergone 10% racemization, $[\alpha]^{25}{}_{578}$ = 17.0°. At only 35% conversion, no such racemization is evident,[28b] nor is any at higher conversion in acetonitrile solvent. Hydroxycyclobutanone formed from (+)-5 displayed a simple *negative* curve in its ORD spectrum: $[\alpha]^{25}$ = −0.44° (578 nm); −0.66° (546 nm); −2.57° (436 nm). (*S*)-(−)-1-Phenyl-3-methylpentane-1,2-dione (**13**) was prepared. Its optical purity unfortunately was too low to allow monitoring of any photoracemization.

Spectroscopic Studies. All the phenyl diketones studied emit yellow to yellow-green light upon irradiation in fluid solutions. Fluorescence and phosphorescence maxima in benzene, as well as relative quantum yields, are recorded in Table II. Actual fluorescence quantum yields are almost independent of substitution and are comparable with that of benzil (~0.003),[14] while phosphorescence efficiencies vary markedly. Absorption maxima (in heptane) for the lowest energy UV transition range from 397 nm for diketone **1** to 379 nm for diketone **8**, with extinction coefficients ~30 cm²/mol. With increasing alkyl group substitution on the 3 and 4 carbons, shifts occur to shorter wavelength absorption and longer wavelength emission.

The only other discrete peak in the UV spectra of these phenyl diketones is the perturbed benzene L_a band, which occurs at 256 nm (ϵ 7600) for **1** and **2** and at 248 nm (ϵ 12 000) for **8**. The benzene L_b band is hidden by the L_a band in **1** and appears as a shoulder in **8**. No second n,π* transition, such as is prominent in biacetyl, is apparent. CD spectra for both (+)-**5** and (−)-**13** are displayed in Figure 1. Both show two bands of opposite ellipticities above 300 nm, presumably corresponding to two distinct n,π transitions as in other α-diketones.[40,41] In both cases, the lowest energy absorption band shows no evidence in CD for contributions from two differently polarized transitions.

Triplet excitation energies vary from 53 kcal for diketone **1** to 51 kcal for diketone **6**. In the polar solvent acetonitrile containing 2% water, the absorption maxima shift to shorter wavelengths, but the fluorescence and phosphorescence maxima remain at the same wavelength as in benzene.

The phosphorescence spectra of diketone **1** in benzene, carbon tetrachloride, and methylcyclohexane (MC) were measured at 77 °C; the phosphorescence maximum occurs at the same wavelength as at room temperature. The phosphorescence decay curves measured at the maxima are cleanly exponential, from which a solvent-independent triplet lifetime of 3 ms was calculated. No long-lived triplet was found in any of the three solvents.

The IR spectra of the diketones merit note. Two distinct carbonyl stretches are always present, one near 1675 cm⁻¹ and one at 1705–1710 cm⁻¹. The former corresponds closely to the C=O stretch found in phenyl ketones, the latter to that in acylic aliphatic ketones and in biacetyl.

Discussion

Our results indicate that certain aspects of α-diketone photochemistry parallel monoketone behavior whereas others are quite different. It is apparent that phosphorescence, cyclization, and enolization are competitive triplet state reactions in these phenyl α-diketones. The sensitization and quenching results combine with the structure-independent fluorescence yields to indicate quantum yields of intersystem crossing close to unity and negligible chemical reaction from the excited singlets. It is also evident that the fluorescence is prompt and not thermally activated, as has been suggested,[41] since its intensity is totally independent of triplet lifetime. The following simple scheme suffices to interpret our kinetic data. Relative phosphorescence yields are inversely proportional to triplet lifetimes, indicating a constant value for k_p near the 3×10^2 s⁻¹ measured for **1**.

$$\mathrm{D_0} \xrightarrow{h\nu} {}^1\mathrm{D}^*$$

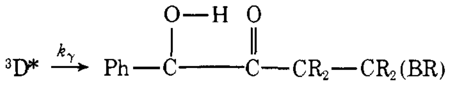
$${}^1\mathrm{D}^* \xrightarrow{>98\%} {}^3\mathrm{D}^*$$

$${}^1\mathrm{D}^* \xrightarrow{\sim 0.3\%} \mathrm{D_0} + h\nu_f$$

$${}^3\mathrm{D}^* \xrightarrow{k_p} \mathrm{D_0} + h\nu_p$$

$${}^3\mathrm{D}^* \xrightarrow{k_d} \mathrm{D_0} + \text{heat}$$

$${}^3\mathrm{D}^* \xrightarrow{k_e} \text{enol}$$



$${}^3\mathrm{D}^* \xrightarrow{k_\gamma} \mathrm{Ph{-}\overset{\overset{O-H}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}CR_2{-}CR_2}\ (\mathrm{BR})$$

$$\mathrm{BR} \xrightarrow{k_{-\gamma}} \mathrm{D_0}$$

$$\mathrm{BR} \xrightarrow{k_{cy}} \text{hydroxycyclobutanone}$$

$${}^3\mathrm{D} + \mathrm{Q} \xrightarrow{k_q} \mathrm{D_0} + {}^3\mathrm{Q}^*$$

Cyclization. Diketones **2–6** vary only at the 4 carbon. The steady increase in the ratio cyclization/(enolization + emission) as the C-4-H bond strength decreases indicates that cyclization involves γ-hydrogen abstraction by the 1-keto group. Cyclobutanol formation accompanying type II photoelimination from monoketones involves a 1,4-biradical intermediate.[31] A similar intermediate is apparently formed from diketones, but the behavior of the 2-keto-1-hydroxy-1,4-biradicals is quite different from that of simple 1-hydroxybiradicals. It has already been pointed out[31] that the failure of diketones to undergo elimination probably arises from the perpendicular orientation of the C-1 p orbital relative to the C-2–C-3 σ bond in the biradical. Such orientation would seem to be required for cleavage.[42] Although the polar-solvent-

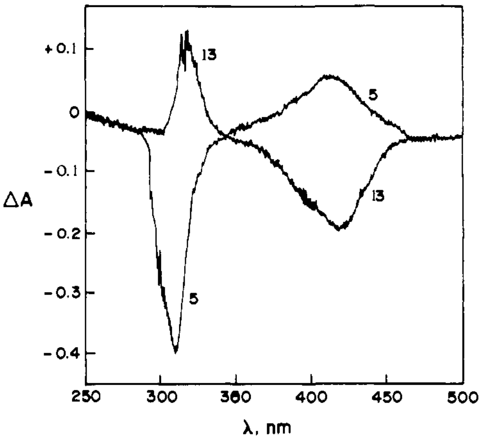
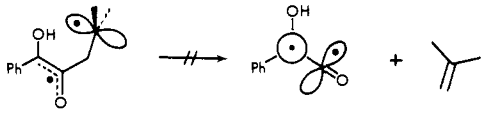
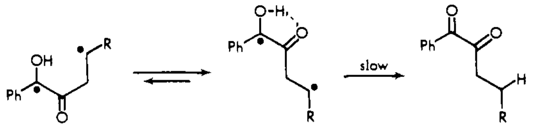


Figure 1. CD spectra of 0.0036 M (*S*)-(+)-**5** and of 0.018 M (*S*)-(−)-**13** in heptane, in 10-cm cells at 25 °C.



induced enhancement in cyclization quantum yields is small for diketones **2-6** and for several aliphatic α-diketones,[26] the effect is about as large for **8** as it is for many monoketones,[43] indicating the usual suppression of reverse hydrogen transfer by solvation of the hydroxylic proton. Relative to the biradicals derived from monoketones, the diketone-derived biradicals undergo appreciably less disproportionation back to ground state ketone, the $k_{cy}/k_{-\gamma}$ ratio changing from an average value of 1/10 for monoketones to 10/1 for diketones. We cannot definitely establish which competing biradical reaction the 2-keto group affects more, but intramolecular hydrogen bonding might well impede disproportionation substantially.[44] Such hydrogen bonding is certainly likely, given the rapid hydrogen transfer between oxygens in the semi-pinacol radicals derived from diketones.[15,16]



The inefficient photoracemization of diketone **5** is clearly a result of inefficient disproportionation of the biradical. The quantum yield data in Table I indicate that, after 74% conversion, recovered **5** could have undergone *at most* 25% racemization. We find 10%. How much of the difference is due to combined experimental errors and how much is real cannot be assessed. However, that cyclization of optically active **5** involves some retention of optical activity does indicate that the biradical cyclizes before it establishes complete rotational equilibrium, a well-established facet of 1,4-biradical behavior.[31] Consequently, the diketone-derived biradicals cannot be much longer lived than the monoketone-derived biradicals and may even be shorter lived. The presence of the 2-keto group must enhance k_{cy} enough to offset any decrease in $k_{-\gamma}$. Decreased eclipsing about the C-2–C-3 bond may well allow the 2-keto biradical to reach the conformation necessary for cyclization more easily.

Rate constants for γ-hydrogen abstraction can be gleaned by application of eq 1 and 2 to the data (extrapolated to zero diketone concentration) and are listed in Table I. The calculation assumes that $\Phi_{isc} = 1$ and that biradical reversion is completely suppressed in wet acetonitrile. The rate constants vary with γ C–H bond strength as might be expected, showing a primary:secondary:tertiary selectivity (per C—H bond) of

$$k_\gamma = \frac{\Phi_{CB}{}^{max}}{\tau} \qquad (1)$$

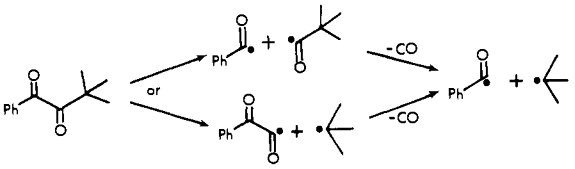
$$1/\tau = k_p + k_d + k_c + k_\gamma \qquad (2)$$

1:60:390, only slightly greater than the selectivity of 1:24:180 displayed by monoketone triplets.[31,45] The precision of our data is indicated by the very similar values of $(k_d + k_c)$ derived from the much different triplet lifetimes of ketones **2-6**, which vary only at the 4 carbon. Likewise, the analysis of **7** indicates a k_γ comparable with that of **3**, despite the much larger k_c value for **7**.

The effects of ring substituents on the photoreactivity of phenyl ketones is complex, because of the proximity of n,π* and π,π* triplets.[46] This particular problem does not beset α-diketones, so that one sees only small decreases in k_γ induced by *p*-methoxy and *o*-chloro substituents.

Diketone 8 shows unusual enough behavior to warrant separate discussion. The large polar solvent effect on its cyclization quantum yield resembles that found for the type II reaction of the analogous monoketone **14**.[43] Solvation of the intermediate biradicals is apparently so inefficient that in neither case is it clear that all the biradical disproportionation can be suppressed. Presumably the *gem*-dimethyl substitution impedes cyclization of both biradical intermediates, via 1,3-nonbonded interactions.

8 is the only diketone we studied which gives detectable α-cleavage products, benzaldehyde and isobutylene. We cannot distinguish between O=C–C=O and O=C–*t*-Bu cleavage as the primary photoprocess. The absence of such cleavage products from the other diketones including **9** suggests that the *tert*-butyl group so sterically crowds the triplet that the O=C–C=O cleavage known to occur in the gas phase[17] is promoted. The alternate process, with a CO–*t*-Bu bond energy on the order of 72 kcal,[47] could be a good 20 kcal endothermic.

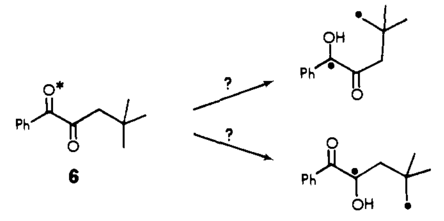


The most remarkable aspect of **8**'s photochemistry is its very rapid rate of γ-hydrogen abstraction. Whereas the other diketones average only 0.2% the triplet reactivity of the analogous monoketones, triplet **8** is 6–8% as reactive as triplet **14**. In other words, triplet **8** is 30–40 times more reactive than would be predicted by the behavior of the other diketones, even after correction for the inductive effect of β-methyls on the reactivity of γ C–H bonds. The enhanced reactivity of triplet **8** probably reflects conformational preferences and requirements as discussed below.

Comparison of Hydrogen Abstraction Rates by Diketone Triplets and Monoketone Triplets. The k_γ values displayed by monoketone triplets, both aliphatic and aromatic,[31] are some 500 times greater than the k_γ values of these phenyl diketones and some 1000 times greater than those of aliphatic α-diketones.[26] The most obvious explanation for the large rate difference between mono- and diketones is the decreased exothermicity of hydrogen abstraction by the much less energetic diketone triplet.[26] Since there is current interest in obtaining and correlating thermodynamic quantities for photochemical reactions,[48-50] the energetics of hydrogen abstraction by diketones deserve additional scrutiny.

The activation energy for the 20 kcal exothermic[51] γ-hydrogen abstraction by triplet valerophenone is ~3.5 kcal.[49] Calculations based on Benson's group additivities[52] suggest that γ-hydrogen abstraction is thermoneutral for triplet **3** and some 7 kcal *endothermic* for triplet 2,3-hexanedione. If the preexponential factor for triplet **3** is the same as for triplet valerophenone, the 500-fold difference in k_γ values suggests an E_a for triplet **3** of ~7.5 kcal. If the thermochemical calculations are correct, one would expect even larger activation energies, especially for the aliphatic diketone triplets. It has been suggested that intramolecular hydrogen abstraction by triplet α-diketones is facilitated by a more positive entropy of activation than obtains for monoketone triplets.[24] If that were the case, activation energies for diketone hydrogen abstraction could be higher than 7.5 kcal and more consistent with the thermodynamics. However, it is surprising that these presumed higher activation energies do not produce significantly greater sensitivity toward γ C–H bond strength. Moreover, triplet biacetyl averages 1/100 the reactivity of triplet benzophenone toward three good hydrogen donors.[23] It is contradictory to postulate a special entropy effect favoring intramolecular hydrogen abstraction by triplet diketones when the diketone/monoketone rate ratio for intramolecular reaction is no larger than, and in fact is apparently even smaller than, the corresponding rate ratio for intermolecular reactions. In short, thermodynamic analysis of α-diketone reactivity remains inconclusive.

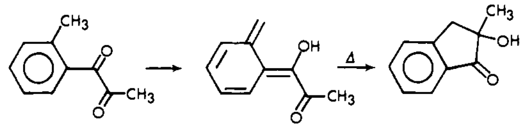
Apparent Isolation of Reactivity on the Carbonyl Next to Phenyl. Most diketones heretofore studied have been aliphatic and thus symmetric electronically. These phenyl diketones are not, so that it is reasonable to wonder whether one of the two carbonyls possesses greater intrinsic triplet state reactivity. Since the cross-conjugating phenyl group does lower the triplet excitation energy by 3-4 kcal/mol, it is readily conceivable that the lowest π* orbital is located primarily on the benzoyl carbonyl. The behavior of **6**, which possesses no C–H bonds γ to the 1-keto group, suggests that reactivity is in fact largely isolated on the 1-keto group. Very careful analysis of irradiated solutions of **6** revealed no products other than the enol. Two possible intramolecular hydrogen abstractions could have led to products: δ abstraction of a methyl hydrogen by the 1-keto group, and γ abstraction of a methyl hydrogen by the 2-keto group.



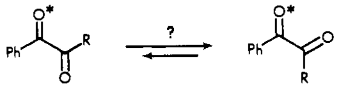
6

Since the rate of triplet δ-hydrogen abstraction in the phenyl ketone analogous to **6** is $\leqslant 4 \times 10^5$ s^{-1},[53] the expected rate of δ-hydrogen abstraction in triplet **6** would be $^1/_{500}$ of that or $\sim 10^3$ s^{-1}, too slow to compete measurably with enolization. On the other hand, γ-hydrogen abstraction by triplet β,β-dimethylbutyrophenone **14** is quite rapid, $k_\gamma = 6 \times 10^7$ s^{-1}.[53] The measured ($k_d + k_e$) value for **6** is 30% larger than the common value for **2**, **3**, **4**, and **5**. The difference could reflect experimental error, impurity quenching, or a slightly larger k_e value for **6**. The difference does indicate that any competing γ-hydrogen abstraction by the 2-keto group cannot be faster than 6×10^4 s^{-1}, 0.1% the monoketone value. Moreover, any such hydrogen abstraction would have to be totally revertible. There is no precedent for complete revertibility. Consequently, we feel that γ-hydrogen abstraction by the 2-keto group of **6** does not occur to any significant extent.

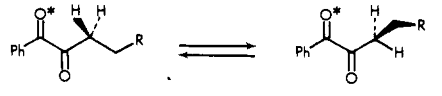
The puzzling preference of triplet α-diketones toward γ C–H bonds β to one carbonyl is well known and has been rationalized as reflecting a favorable entropy effect.[24] "Frozen" conformations apparently can enhance rates of intramolecular H abstraction by factors of 5-8.[49] The intra-/intermolecular rate ratio stressed above, however, indicates no particular rate enhancement for the preferred (observed) intramolecular hydrogen abstraction path in diketones. The proper conclusion may then be that the alternate mode of γ abstraction of a hydrogen δ to one carbonyl is for some reason retarded. The recent observation[54] of products derived from such a process in an aliphatic diketone, together with the lack of such products from **6**, does suggest that the electronic distribution in phenyl diketones tends to isolate reactivity on the 1-keto group. This conclusion is consistent with considerable evidence that the photocyclization of *o*-methylphenylpropanedione[27] proceeds via benzylic hydrogen abstraction by the 1-keto group.[55]



Conformational Requirements. Certain conformational aspects of triplet diketones deserve note. For γ-hydrogen abstraction to even occur, the triplet must exist in the transoid form. Because of our evidence for only one kinetically distinct triplet, we can conclude that the twisted ground state upon excitation rotates either exclusively to the transoid conformation or to a rapidly equilibrating mixture of cisoid and transoid forms.



Consideration of the conformation about carbons 2 and 3 is particularly intriguing. In the preferred conformation of simple carbonyl compounds, the largest α-substituent eclipses the carbonyl.[56] We have already pointed out how this conformational preference assists γ-hydrogen abstraction in monoketones.[53] In diketones, however, the same conformational preference would impede γ-hydrogen abstraction by the 1-keto group and favor γ-hydrogen abstraction by the 2-keto group, in opposite fashion to what actually happens. It would be easy to evade this problem by pleading that ignorance of excited-state structure makes knowledge of ground-state conformational preferences irrelevant. However, the greatly enhanced reactivity of diketone **8** does not seem to be understandable



u r

unless the other diketones exist preferentially in conformations such as u which do not allow γ-hydrogen abstraction. Only in **8**, with three methyl groups on C-3, must there be a γ-H near the 1-keto oxygen atom no matter what the conformational preference of the C-2–C-3 bond. The probable unfavored status of the conformation r would offset the positive entropy effect of the "frozen" 1,2 C–C bond, thus explaining the earlier noted fact that the intramolecular:intermolecular rate ratio for most of these diketones is not larger than for monoketones.

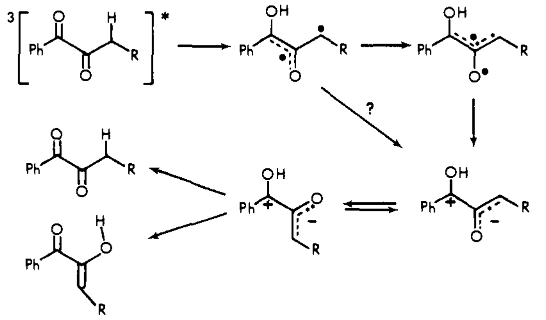
If these just-mentioned relative rate ratios and the enhanced reactivity of **8** together indicate that the diketone triplets exist primarily in conformation u, it becomes even more difficult to explain why the 2-keto group does not readily abstract hydrogen from C-5 without postulating localization of reactivity on the 1-keto group.

Enolization is the major competing triplet state reaction of diketones **7** and **2-5** and apparently the only chemical reaction of **6** and **9**. Compounds **2-6** all have the same structure about the chromophore, in particular a secondary hydrogen being involved in the enolization process. Kinetic analysis indicates very similar values of ($k_e + k_d + k_p$) $\sim 2 \times 10^5$ s^{-1} for all five. That ($k_d + k_p$) is negligible with respect to k_e for **2-6** is indicated by the long triplet lifetime of **1** and by the measured value of k_p for **1** $\leq 3 \times 10^2$ s^{-1}.

The deuterium isotope effects on the triplet lifetimes and quantum yields for disappearance of **2** and **3** indicate that the C-3-H bond is broken in the triplet state reaction which produces enol. The rate of this reaction is much more strongly dependent on the type of C-H bond than is γ-hydrogen abstraction. The selectivity for primary:secondary:tertiary hydrogens is at least 1:1000:300 000 per hydrogen. The relative reactivity of primary hydrogens may be even lower. We could detect no disappearance of **1** after prolonged irradiation. This fact, together with the slight deuterium isotope effect on the long triplet lifetime of **1**, indicates a maximum k_e value of 2 $\times$ 10^2 s^{-1}. The actual triplet lifetime of **1** in solution is comparable with that of the nonenolizable benzil,[14] so that k_d is the dominant decay term, whatever combination of solvent or impurity quenching and radiationless decay it represents.

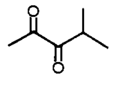
The mechanism of enolization is not altogether obvious. It is formally an allowed suprafacial [1,3] sigmatropic rearrangement,[59] but there are good reasons to doubt that such a description characterizes the actual mechanism. First, the reaction is initiated by n,π^* excitation, whereas the sigmatropic description is more apt for π,π^* excitation. Second, triplet reactions rarely proceed concertedly, especially when they are not exothermic enough to populate an excited state of the product. Moreover, the process which leads to enolization apparently involves some intermediate half of which can revert to ground-state diketone. This conclusion is prompted by the observation that in all of the diketones which do enolize, only about half of the triplets which do *not* abstract a γ-hydrogen yield enol (as measured by diketone disappearance).

An adiabatic 1,4-hydrogen transfer would yield the relatively stable oxyallyl system. Various calculations place the triplet and zwitterionic (singlet) states of simple oxyallyl rather close in energy.[58] The triplet oxyallyl could then presumably cross readily to the ground-state surface and undergo a proton shift to either end of its enolate moiety to yield product enol and ground-state diketone. Note that in this unsymmetrical oxyallyl most of the negative charge would be on the enolate moiety and most of the positive charge at the benzylic position, so that there would be little double bond character between the two originally carbonyl carbons and therefore rather free rotation about that bond.



Since any 1,4-hydrogen transfer is constrained to an almost planar cyclic transition state, Salem's state symmetry correlations[59] can be applied. With the C-3-H bond in the plane of the oxygen n orbitals, the ground state is $4\pi,6\sigma$ and any n,π^* state must be $5\pi,5\sigma$. If the first-formed triplet diradical maintains the electronic symmetry of the reactant, the singly occupied p orbital on carbon 3 would be in the molecular plane and perpendicular to the carbonyl π-system. Formation of the fully conjugated $6\pi,4\sigma$ oxyallyl system requires a rotation about the C-2-C-3 bond. This rotation could in itself promote the intersystem crossing required for formation of the zwitterionic oxyallyl.[60]

Since Agosta has recently reported several examples of competitive β- and γ-hydrogen abstraction in α-methylene ketones,[61] photoenolization of these diketones might provide just another example of such positional competition. We think that such an interpretation is unlikely for three reasons. First, β-hydrogen abstraction by α-methylene ketones seems to be solely an excited singlet reaction.[61b] Second, in the α-methylene ketone **15**, the β/γ rate ratio, as roughly estimated from product ratios, is only 1.5/1. Extrapolation of the results for **2** and **7** indicates that the β/γ ratio for the analogous diketone **16** would be 75/1. Moreover, whereas allylic hydrogens such as the β-hydrogen in **15** are activated toward hydrogen abstraction, C-H bonds next to a carbonyl are *deactivated.*[45] Consequently, the relative β/γ ratio for **16** vs. **15**, corrected for the inductive effects, would be on the order of 3000/1. In fact, enolization in triplet **7** is almost as fast as γ-hydrogen abstraction in triplet monoketones. If, in **15**, the combination of a tertiary allylic β-hydrogen and frozen rotations of two C-C bonds together mitigate the factors which normally make 1,4-hydrogen transfers extremely unfavorable, something much better must help in diketones.



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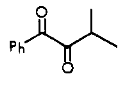


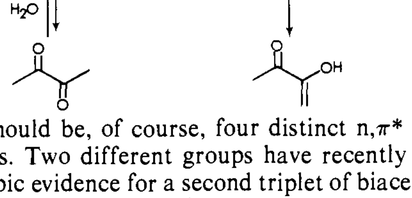
16

The third piece of evidence which suggests that enolization does not arise from a simple hydrogen atom transfer is the vastly increased primary:secondary:tertiary C-H selectivity for enolization compared with γ-hydrogen abstraction. The observed selectivity is even greater than that displayed by bromine atoms[62] and reflects carbonium ion stabilities more than radical stabilities.

Finally, the two ring substituents alter the k_e values more than they affect k_γ values. Although results for more substituents are needed, the two studied suggest that, in the transition state for the triplet reaction leading to enolization, the benzoyl carbonyl group gains electron density relative to the triplet itself. The value of k_e is the same in wet acetonitrile as in benzene, so the reaction probably does not create or destroy significant charge separation.

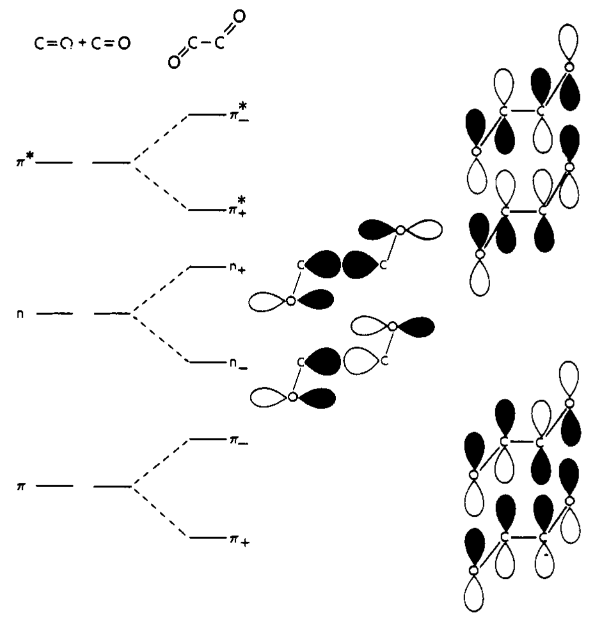
We conclude that enolization involves a process intrinsically different from the simple hydrogen atom abstraction responsible for cyclization. This conclusion prompts two related questions. First, do the two processes (β- and γ-hydrogen transfer) arise from the same triplet or from different triplets? Second, can the geometry or electronic distribution (or both) of α-diketone triplets differ enough from these of monoketone triplets to produce such dual reactivity?

Lemaire has suggested that biacetyl undergoes photoenolization only from an upper triplet (corresponding to the second UV band at ~300 nm) and photoreduction from the kinetically distinct lowest triplet.[20b] Such definitely is not the case with the phenyl diketones that we have studied. The quenching kinetics are wavelength independent and demand that all three competing triplet reactions originate from the lowest triplet or possibly from a pair of equilibrated, nearly isoenergetic triplets. In fact, Lemaire's observation may well involve photoinduced dehydration[63] of the hydrate of biacetyl rather than enolization of biacetyl itself, since many of his experiments were performed in water solutions.



There should be, of course, four distinct n,π^* triplets of α-diketones. Two different groups have recently presented spectroscopic evidence for a second triplet of biacetyl some 5 kcal above the lowest triplet.[64] It is therefore quite conceivable that two triplets of these phenyl diketones are close together

Scheme I



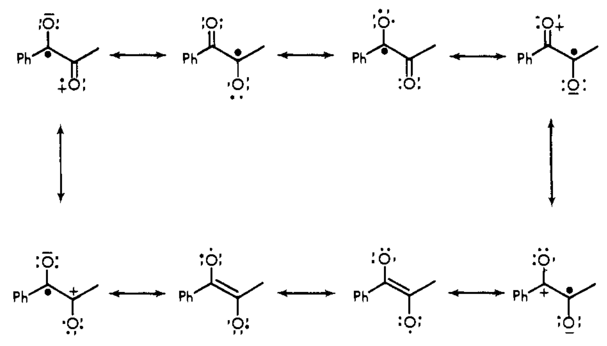
energetically but different enough geometrically and/or electronically that one might preferentially enolize, the other abstract γ-hydrogens. We conclude this paper with an analysis of α-diketone spectroscopy in order to probe this possibility.

The nature of excited states in diketones remains ill-defined despite many years of spectroscopic and theoretical study. It is now widely accepted that strong through-bond coupling splits the otherwise degenerate n orbitals of α-dicarbonyl compounds.[12] Scheme I presents an orbital diagram for a planar diketone. Noting the 1.9-eV splitting of the two lowest energy PE transitions and the 1.7-eV splitting of the two lowest energy UV transitions of biacetyl, Drent and Kommandeur have pointed out that, if the n orbitals are widely split and if the two UV transitions are symmetry allowed, the two π* orbitals cannot be significantly split.[13] Such would certainly be the case when the two carbonyl groups are twisted, as in the ground states of these phenyl diketones.[41] The ability of α-diketones to undergo photocleavage between the two carbonyls[17] combines with vibrational analyses of biacetyl absorption spectra[10,65] to suggest that the central C–C bond does *not* take on additional bonding character in the lowest excited states. It has not been pointed out previously that loss of an electron from the n_+ orbital would necessarily weaken the C–C bond because of the substantial amount of C–C σ character mixed into that orbital by through-bond coupling.[12,66] However, if the populated π* orbital were strongly π bonding between C-2 and C-3, the overall bond strength might not be expected to be diminished enough to allow ready cleavage.

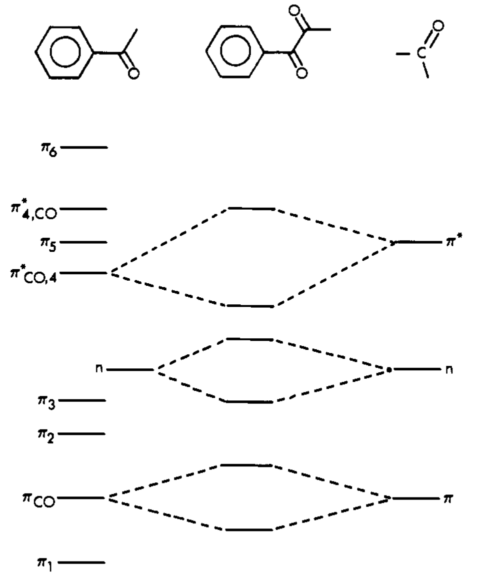
These simple considerations suggest that there could be two nearly isoenergetic triplets corresponding to $n_+ \rightarrow \pi_+{}^*$ and $n_+ \rightarrow \pi_-{}^*$ in these diketones. Such assignments could also explain the two proximate triplets detected spectroscopically in biacetyl,[64] unless one is due to an impurity.[65] However, the CD spectra provide no evidence for two nearby, oppositely polarized n,π* singlets.

McGlynn has expressed strong reservations about the accuracy of the MO picture based upon the one-electron approximation.[41] Certainly the dependence of λ_{max} on the dihedral angle between the carbonyl groups of α-diketones[2-6] is most conveniently explained by strong and variable conjugation of the π system. CNDO/CI calculations suggest strong splitting of the π* levels in planar glyoxal[41] and a lowest (planar) singlet that is mostly $n_+,\pi_+{}^*$, with some $n_-,\pi_-{}^*$ character. The CD spectra of **5** and **13** certainly suggest a relatively "pure" lowest n → π* transition. The second (planar) singlet would be considerably higher in energy and would be strongly mixed ($n_-,\pi_+{}^*$ and $n_+,\pi_-{}^*$).[41] The CNDO calculations do not place the triplet levels. It is conceivable that the $S_1{}^*$–$S_2{}^*$ separation is not maintained in the triplet manifold, although the $S_1{}^*$–$T_1{}^*$ splitting is normal for n,π* states.[5] However, minimum basis set ab initio calculations on glyoxal[67] verify the CNDO conclusions and indicate similar behavior for the n,π* triplets. However, these same calculations suggest a π,π* lowest triplet for glyoxal! All studies of diketone phosphorescence suggest an n,π* lowest triplet.

Scheme II. Some VB Forms for $n,\pi_+{}^*$ Triplets



Scheme III

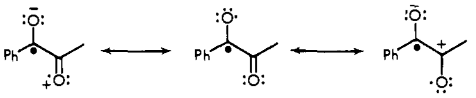


Since we find only one kinetically distinct triplet even for the diketones with triplet lifetimes shorter than 10^{-6} s, if two rapidly equilibrating triplets were involved they could differ in energy by no more than 3 kcal/mol. Current theoretical and spectroscopic results do not allow one to rule out such a possibility. In the absence of more definitive information, it is worthwhile to inquire whether the facility of enolization might best be ascribed simply to the electronic nature of the lowest n,π* triplet.

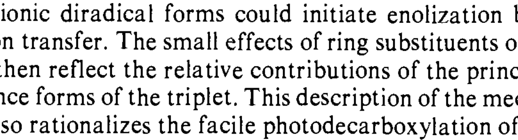
It is now well accepted that the radical-like reactivity of monoketone n,π* triplets results because they really are 1,2-diradicals electronically.[68] It is not possible to draw a predominant valence bond structure for diketones, since each n and π orbital involves both carbonyls. Scheme II shows the most reasonable structures for $n,\pi_+{}^*$ states. Electrons above or below the oxygen are π electrons; those to the left or right are n electrons. Each of the four lefthand structures results from promotion of an n electron from the 2-keto group into the π system; the four on the right from a similar promotion of an n electron on the 1-keto group. The right and left halves would be equivalent in symmetric diketones. In all structures the negative charge in the π system is on oxygen; it is cancelled by a positive charge on the same atom in the middle structures. The two middle structures in the second row accentuate the nodal properties of the π_+* orbital; in a n,π_-* state these structures presumably would not contribute.

The unsymmetrical nature of these phenyl alkyl diketones may well cause one subset of structures to be favored (Scheme III). Since the 1-keto group is part of a benzoyl group, its π* orbital is stabilized by mixing with the benzene π* orbitals[69] and therefore contributes more to the lowest diketone π* orbital. This unsymmetrical mixing accounts for the 3 kcal/mol lower triplet energies of these phenyl diketones relative to aliphatic diketones.

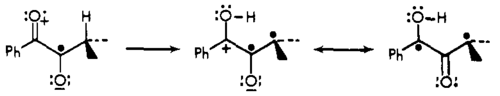
These considerations prompt us to suggest the following VB structures as the most important contributors to the n$_+$,π_+* triplet.



(The 1,4-diradical forms are probably of minor importance since most of the spin density of enolate radicals resides on the α carbon.[70]) These simple structures in themselves may explain the chemical reactivity of triplet diketones. The diradical form is analogous to the radical-like n,π* triplet of monoketones and initiates γ-hydrogen abstraction. The zwitterionic diradical forms could initiate enolization by a β-proton transfer. The small effects of ring substituents on k_e might then reflect the relative contributions of the principal resonance forms of the triplet. This description of the mechanism also rationalizes the facile photodecarboxylation of pyruvic acid.[71] The driving force for the reaction may well be neutralization of charge: the positively charged 2-keto group enhances the acidity of the C-3-H bond; the resulting electron pair at C-3 is in an orbital in the molecular plane, like the carbonyl n orbitals.



This mechanism does not readily explain the large dependence of k_e on alkyl substitution at C-3. It is possible that T-S conversion (with rotation about the C-2–C-3 bond) occurs during hydrogen transfer, so that a zwitterionic oxyallyl is formed immediately. There is no obvious way in which even a partial positive charge can get onto C-3 during hydrogen transfer from the alternate zwitterionic resonance form of the n,π* state.



It is worth note that enolization has also been observed in the more electronically symmetric aliphatic α-diketones.[21] Even in cases where no enolic products were actually isolated,[26] the excited-state kinetics revealed that, competitive with cyclization, there is a decay process with a rate about half that of k_e for these phenyl diketones. Further experiments must be directed toward better understanding the mechanism of enolization.

Experimental Section

Diketone Preparation. Conversion of phenyl ketones to the corresponding α-diketones was accomplished by Kornblum's technique.[72] All diketones were purified by fractional vacuum distillation. Diketones **1**, **2**, **5**, **6**, and **7** were also purified by preparative VPC. Structure assignments were confirmed by IR, NMR, UV, and mass spectra, which in all cases were routine. A representative procedure is described for **3**. Liquid bromine (40 g, 0.25 mol) was added dropwise over 30 min to a vigorously stirred solution of 40.5 g (0.25 mol) of valerophenone in 100 ml of glacial acetic acid. The solution was kept from rising above room temperature by occasional cooling in an ice–water bath. After addition of all the Br_2, the mixture was allowed to stir for 10 min and was then poured into 500 ml of ice–water. The mixture was stirred for a few minutes, and then the organic and aqueous layers were separated. The aqueous layer was saturated with NaCl and then extracted with ether. This ether extract was added to the crude bromoketone, and the solution was dried over $MgSO_4$. Solvent was removed on a rotary evaporator; residual acetic acid was removed by stirring the crude bromoketone under high vacuum (0.1 Torr).

The crude α-bromovalerophenone (54.5 g, 0.23 mol) was dissolved in 100 ml of reagent grade acetonitrile. A solution of 51 g (0.3 mol) of silver nitrate in 150 ml of acetonitrile was then added, and the flask was kept in the dark for 2 days. The reaction mixture was then filtered. After being washed with 100 ml of ether, 38.5 g of AgBr (0.2 mol) was collected. The ether washings were combined with the acetonitrile solution, and all solvent was removed on a rotary evaporator. The residue was redissolved in 200 ml of ether, and the solution was washed with 100 ml of water. The ether solution was then dried over $MgSO_4$. After the ether was evaporated, the residue was flash distilled; everything which came over under 100 °C at 0.25 Torr was collected, yielding 34 g (0.15 mol) of α-nitratovalerophenone.

All of the nitratoketone was dissolved in 500 ml of dried dimethyl sulfoxide, to which was then added a slurry of 12.5 g (0.15 mol) of anhydrous sodium acetate in 75 ml of Me_2SO. The gold reaction mixture was stirred at room temperature for 90 min and was then poured into 2000 ml of ice-cold saturated aqueous sodium chloride. The crude product was taken up into ether, washed with 10% sodium bicarbonate, and dried over $MgSO_4$. The solvent was evaporated, and the diketone was distilled under vacuum. 1-Phenyl-1,2-pentanedione (**3**) (20.5 g, 0.14 mol), bp 67–68 °C (0.15 Torr), was collected: IR (CCl_4) 3010, 2920, 1720, 1680, 1600, 886, 690 cm^{-1}; NMR (CCl_4) δ 7.95 (m, 2 H) and 7.48 (m, 3 H, benzoyl), 2.80 (t, J = 7 Hz, 2 H, α-CH_2), 1.72 (m, 2 H, β-CH_2), 1.00 (t, J = 7 Hz, 3 H, CH_3); UV λ_{max} (CH_3CN) 250 (ϵ 8200), 388 nm (ϵ 36); MS (75 eV) *m/e* 176, 105 (base), 77, 71, 51.

The UV and IR spectra of all the diketones were similar; the *m/e* 105 base peak in the mass spectrum is also common to all the phenyl diketones.

Starting monoketones were available either commercially or from previous studies[45,51,53] for **1–6** and **9**. Attempted preparation of **8** from β,β-dimethylbutyrophenone was unsuccessful, but the synthesis starting with benzyl *tert*-butyl ketone proceeded smoothly. The β-ethylvalerophenone for **7** was prepared by adding the Grignard of 2-ethyl-1-bromobutane to benzonitrile in the standard fashion.[45] The bromide was obtained by treating 2-ethyl-1-butanol (Aldrich) with PBr_3.

The deuterated diketones **1-D** and **2-D** were prepared by refluxing ~1.5 g of the diketone dissolved in 6 ml of CCl_4 with 15 ml of a 5.7 M DCl/D_2O solution[73] for several days, until NMR and mass spectral analysis revealed equilibration. Under these conditions **1-D** was 75% d_2, 25% d_1; **2-D** was 67% d_2, 33% d_1.

Optically active diketone **13** was prepared as usual from (*S*)-β-methylvalerophenone, which was prepared by adding the Grignard of (*S*)-2-methyl-1-bromobutane to benzonitrile. The bromide was prepared by treating Aldrich (*S*)-2-methyl-1-butanol with PBr_3. The diketone preparation apparently resulted in extensive racemization, since no optical activity was measurable at 578 nm.

Solvents and Quenchers. Commercial thiophene-free benzene was purified by chlorination, distillation, washing with aqueous hydroxide solution and water, and redistillation from phosphorous pentoxide. Acetonitrile was purified by distillation from permanganate.[74] Pyrene (J. T. Baker Co.) was chromatographed on alumina and recrystallized from alcohol. Reagent grade anthracene and acridine were used without further purification. Chemical Samples Co. *cis*-piperylene (99.9%) was used as received.

Procedures. The 366- and 436-nm emission lines from a Hanovia 450-W medium-pressure mercury arc were isolated by the following filters: 366 nm, Corning glass filters 0-52 and 7-37; 436 nm, a uranium glass or Nonex filter sleeve and a 1-cm thickness of the following solution: 20 g of $CuSO_4$, 25 g of $NaNO_2$, 34 ml of concentrated ammonium hydroxide diluted to 500 ml. Preparative runs were performed by taping samples in degassed, sealed Pyrex culture tubes to the outside of the filter solution holder. Quenching studies and quantum yields were determined by parallel irradiation of similar degassed (<0.005 Torr) samples in sealed 13 × 100 Pyrex culture tubes in a rotating apparatus similar to the one described by Moses, Liu, and Monroe.[75] Quantum yields at 366 nm were determined at Michigan State University relative to a benzophenone-*cis*-1,3-pentadiene actinometer;[76] those at 435 nm were determined at Columbia relative to a ferrioxalate actinometer.[77]

The cis-trans isomerization of pentadiene was monitored on a 25 ft × ⅛ in. column packed with 25% 1,2,3-tris(β-cyanoethoxy)propane on Chromosorb P. Analyses for product formation (conversions <5%) were performed by VPC on a Varian Aerograph Model 1200 Hy-Fi III with a 6 ft × ⅛ in. column packed with 4% QF-1 and 1.2% Carbowax 20 M on 60/80 Chromosorb G. Ketone disappearance (conversion ~20%) was monitored by UV analysis at the long wavelength λ_{max} of the diketones. Emission studies were performed on an Aminco-Bowman spectrophotofluorometer. For quenching studies, the phosphorescence intensity was determined at the phosphorescence maximum by subtracting the emission of an aerated sample (fluorescence) from that of a carefully degassed sample. Actual phosphorescence and fluorescence intensities were compared with those of biacetyl and benzil and were roughly corrected by application of the manufacturer's response curve for the IP-21 photomultiplier tube. Ultraviolet spectra were recorded on Cary 14 spectrophotometers. ORD spectra of **5** and its photoproduct were recorded on a Cary 60 Spectrometer at Columbia. CD spectra of **5** and **13** were recorded on a Japan Spectroscopic Co. Model ORD/UV-5 with a Sproul Scientific SS-20 CD modification, courtesy of the Michigan State University Department of Biochemistry.

Identification of Photoproducts. Moderately dilute, degassed solutions of the diketones were irradiated through uranium glass (>330 nm) until the yellow color had faded completely. The cyclic products appear as one peak on most VPC columns and were collected on a 5 ft × ¼ in. 5% QF-1 column at Michigan State University and on a 3 ft × ¼ in. 3% FFAP column at Columbia. The IR, mass, and NMR spectra indicated that the products were 2-hydroxycyclobutanones isomeric with the starting material. For example, 2-hydroxy-2-phenyl-3,3-dimethylcyclobutanone from diketone **4** has the following spectra: IR (CCl$_4$) 3550, 3400, 3010, 2920, 1790, 1465, 1450 cm^{-1}; UV (CH$_3$CN) λ_{max} 215 (ϵ 1810), 280 nm (ϵ 500); NMR (CCl$_4$) δ 7.11 (s, 5 H, phenyl), 4.13 (broad s, 1 H, hydroxy), 2.63 (s, 2 H, CH$_2$), 1.23 (s, 3 H, CH$_3$), 0.81 (s, 3 H, CH$_3$); MS (9 eV) *m/e* 190 (10), 162 (38), 148 (100). The IR and UV spectra of the other hydroxycyclobutanones are very similar. Mass spectra in all cases show cleavage of the four-membered ring in both possible ways.

Benzene solvent was removed from a photobleached solution of **2**. All the residue was taken up in CCl$_4$. NMR analysis showed a doublet at δ 1.83 (J = 7 Hz) and a quartet at δ 5.53 (J = 7 Hz) in addition to the absorptions characteristic of the independently isolated 2-hydroxy-2-phenylcyclobutanone. The IR of the reaction products had a strong absorption at 1630 cm^{-1} in addition to those characteristic of the hydroxycyclobutanone. These additional IR and NMR peaks are ascribed to the enol **12**.

A 0.02 M benzene solution of **9** was irradiated overnight at 435 nm. After removal of solvent, the residual material was analyzed. Its NMR spectrum showed a singlet at δ 6.24 in addition to phenyl group absorption, whereas the starting material had a signal at δ 4.02. Its IR spectrum showed strong absorption at 1630 cm^{-1}, assigned to an enolic carbonyl stretch.

Irradiation of degassed solutions of diketone **6** resulted in complete bleaching of its yellow color. The gas chromatogram of the photosylate, with the injector at 200 °C, showed only a single peak which was collected and identified as diketone **6**. The spectral properties of a completely irradiated solution in carbon tetrachloride were as follows: IR 3410 (concentration independent), 1660, 1630 cm^{-1} (no carbonyl bands at 1700–1800 cm^{-1}); UV λ_{max} 282 nm (ϵ 7000); NMR δ 1.8 (s, 9 H, methyls), 5.35 (s, 1 H, vinyl), 6.55 (s, 1 H, exchangeable with D$_2$O, hydroxyl), 7.4 (m, 5 H, phenyl). Irradiation to completion in acetonitrile yielded a solution with two broad UV bands, λ_{max} 279 nm (ϵ 7500) and 252 nm (ϵ 7000). These data confirm the structure of **10**. Treatment of the photosylate of **6** with 10% aqueous sodium hydroxide or 10% sulfuric acid rapidly regenerated the diketone. Dilute solutions of the photoenol were stable for days. Eventually, it was oxidized by air to give benzoic acid and other unidentified products.

Bromination of Enol 10. A CCl$_4$ solution of **6** was photobleached and then treated with a stoichiometric amount of bromine in CCl$_4$. HBr was generated spontaneously and all of the red color disappeared. The resulting yellow solution was chromatographed on silica gel with benzene eluent, and the major product was isolated in 90% yield. Its UV spectrum was similar to that of phenyl diketones; IR, no hydroxyl stretch, two carbonyl bands, 1720 cm^{-1} and 1675 cm^{-1}; NMR δ 1.28 (s, 9 H), 5.10 (s, 1 H) 7.5–7.9 (m, 5 H); mass spectrum parent ion *m/e* 284. These data fit the assigned structure **11**, the product expected from addition of bromine to enol **10**. Bromine does not react rapidly with diketone **6** under the above conditions.

Enol Acetate of 2. The solvent was removed from a photolysate of a degassed solution of 190 mg of **2** in 25 ml of benzene. The material left was dissolved in 3 ml of ether and cooled by dry ice-acetone mixture. A 1.75 M methyllithium solution in ether (0.8 ml) was then added with strong stirring. About 10 min later, 0.3 ml of acetyl chloride was added, and the mixture was kept on stirring for 20 min. The solvent was then stripped off on a rotary evaporator. The residual material was subjected to column chromatography on silica gel and eluted with benzene. The main fraction isolated had the following spectral characteristics which identify it as an enol acetate: ir (CCl$_4$) 3010, 1770, 1675, 1270, 1200, 1160 cm^{-1}; NMR (CCl$_4$) δ 7.66 (m, 2 H) and 7.40 (m, 3 H, benzoyl), 6.06 (q, J = 7 Hz, 1 H, olefinic proton), 2.17 (s, 3 H, acetyl), 1.78 (d, J = 7 Hz, 3 H, methyl); UV λ_{max} (CH$_3$CN) 222 (11 000), 295 nm (162).

A mixture of 993 mg (6.1 mmol) of **2** and 5 ml of acetic anhydride in the presence of 270 mg of tosylsulfonic acid was refluxed for 3 days. The mixture was then poured into cold water and worked up as usual. The removal of the solvent and distillation at 125 °C (0.3 mm) gave 577 mg (2.9 mmol, yield 47%) of the enol acetate, which exhibits spectral properties identical with those of that prepared from the photolysate.

Photoracemization of (*S*)-(+)-5. A solution of 602 mg of (*S*)-(+)-**5** dissolved in 15 ml benzene was degassed and irradiated at 435 nm for 22 min. UV analysis of the sample indicated that 35% of the diketone had reacted. The solvent was stripped off, and the residual material was subjected to column chromatography on silica gel. The α-diketone, which was easily recognized by its yellow color, came through the column first when it was eluted with benzene. Diketone (401 mg) was recovered. The column was then eluted with 10/1 (by volume) benzene/ether solvent mixture, and 166 mg of the cyclobutanone product was collected. The optical rotations of the recovered α-diketone were measured and found to be same as those of the starting α-diketone. The ORD of the cyclobutanone product appeared as a negative plain curve.

An acetonitrile solution 0.062 M in (+)-**5** was irradiated for 14 h at 366 nm on the merry-go-round. Initial rotation at 578 nm in a 1 cm cell = +0.269°; final rotation = 0.156°, a 42% decrease. Both UV analysis at 385 nm and VPC analysis indicated a 41% decrease in diketone concentration. A similar experiment on 0.03 M (+)-**5** in benzene resulted in an 88% drop in optical rotation at 578 nm, only an 83% decrease in diketone concentration: 30% racemization of unreacted diketone.

A degassed benzene solution 0.33 M in (+)-**5** was irradiated at 435 nm to 74% conversion (by UV analysis). VPC analysis indicated 5% enol formation. Diketone (84% unreacted, 16% converted enol) was recovered by chromatography of the photosylate through silica gel with benzene eluent. Specific rotations at 578 nm (in benzene at 25 °C) were 18.8° before irradiation, 17.0° after irradiation.

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