

(12% 2,6-dimethylaniline and 19% *m*-xylene). With or without K metal, the mechanism of Scheme I is apparently followed, except that without K metal the identity of the initial electron donor is uncertain.²

The cleavage of diphenyl ether by sodium in ammonia forms benzene and sodium phenoxide.⁶ A similar cleavage occurs with potassium metal; a minor product of cleavage is aniline (17%); see Table I. Potassium amide is without effect on diphenyl ether, but the combination of KNH₂ and K metal affords aniline as a major product (53%). The mechanism of Scheme I, in which Ar is phenyl and X is phenoxy, provides interpretation. (The small amount of aniline formed in the absence of KNH₂ perhaps derives from reactions of the amino radical (H₂N·) formed in step 5 when RH is ammonia.)

Potassium anilide in ammonia does not react with iodobenzene, but with K metal also present reaction occurs to form diphenylamine (19%) and *o*- and *p*-amino-biphenyl (11% each). Again the SRN1 mechanism provides interpretation. It is noteworthy that the ambident anilide ion nucleophile is about as reactive with phenyl radical at ring carbons as it is at nitrogen.

The cyanomethyl anion (from acetonitrile) is unreactive with chlorobenzene,⁷ but in combination with K metal it affords phenylacetonitrile (36%), aniline (3%), benzene (26%), and toluene (18%). Toluene is evidently a product of degradation of the phenylacetonitrile radical anion; toluene is formed on treatment of phenylacetonitrile with K metal in ammonia.

To date, we have observed catalytic character in respect to K metal (*i.e.*, yields over 100%) only in the aforementioned reactions with *o*-haloanisoles and in reactions of bromo- and iodobenzene with *N*-methylanilide ion that are still under investigation. In order for steps 2, 3, and 4 to function as a propagation cycle, each of them must be rapid in comparison to the various side reactions which may occur with the reactive intermediates involved.

The scope of metal atom promoted aromatic "nucleophilic" substitution is not yet well defined. We expected, in view of evidence that propagation cycles analogous to steps 2, 3, and 4 are quite efficient in certain reactions of nitrobenzylic halides,⁸ that nucleophilic substitution at saturated carbon should also be promoted by solvated electrons, and have recently learned that such effects have been observed.⁹

(6) P. A. Sartoretto and F. J. Sowa, *J. Amer. Chem. Soc.*, **59**, 603 (1937); R. L. Burwell, Jr., *Chem. Rev.*, **54**, 672 (1954).

(7) F. W. Bergstrom and R. Agostinho, *J. Amer. Chem. Soc.*, **67**, 2152 (1945).

(8) N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5662 (1966); G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966); and subsequent publications.

(9) N. Kornblum and coworkers, personal communication.

* Address correspondence to this author.

Jhong Kook Kim, J. F. Bunnett*

University of California
Santa Cruz, California 95060

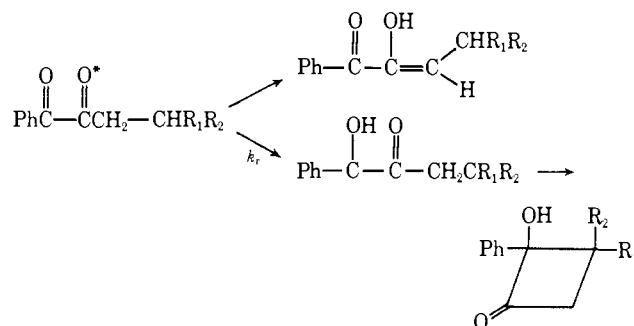
Received September 12, 1970

Competitive Photoenolization and Photocyclization of 1-Phenylalkane-1,2-diones

Sir:

Although the photoreduction of 1,2-diones has received a great deal of attention,¹ very few detailed

mechanistic studies have been reported. Urry and Trecker found that aliphatic α -diketones, like most carbonyl compounds containing γ C-H bonds, undergo photoinduced intramolecular hydrogen transfer, with exclusive formation of 2-hydroxycyclobutanones.² Some quantitative kinetic data on this photocyclization have been reported for aliphatic α -diketones.³ Because of the interesting behavior of 1-(*o*-alkylphenyl)-1,2-propanediones,⁴ we have investigated the excited-state kinetics of several phenyl alkyl α -diketones.⁵ We find that photoenolization of the 2-carbonyl is competitive with hydrogen abstraction from a γ -carbon by the 1-carbonyl.



Quantitative data for several diketones are summarized in Table I. All reactions are completely quenchable by pyrene or anthracene and can be sensitized efficiently by benzophenone. These results indicate exclusive triplet-state reactions and high intersystem crossing yields. Product formation was measured at low conversions (<5%) by vpc; diketone disappearance by uv analysis at higher conversions (20-50%).

Although quantum yields for disappearance of phenyl ketones with γ -hydrogens increase to unity in polar solvents,⁶ quantum yields for the corresponding phenyl diketones are only slightly greater in acetonitrile than in benzene. The effect of polar solvents on photoelimination of phenyl ketones has been attributed to retardation of the disproportionation of 1,4-biradical intermediates.^{6,7} If we assume that with the diketones a small amount of biradical reversal occurs in benzene but is eliminated in acetonitrile, we can divide the calculated triplet state lifetimes into k_r and k_d values, as shown in Table I. Both values turn out to be solvent independent. Importantly, the uniform k_d values for all three reactive diketones attest to the validity of our kinetic assumptions. The previously reported behavior of aliphatic α -diketones³ unfortunately is not as simple, and the triplet-state rate constants could not be evaluated accurately.

The $2 \times 10^5 \text{ sec}^{-1}$ triplet decay rate common to all the phenyl diketones studied not only is faster than that indicated for aliphatic diketones,³ but apparently involves a chemical reaction. We originally noted that

(1) M. Rubin, *Fortschr. Chem. Forsch.*, **13**, 251 (1969).

(2) W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962); (b) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962).

(3) N. J. Turro and T. Lee, *J. Amer. Chem. Soc.*, **91**, 5651 (1969).

(4) (a) R. Bishop and N. K. Hamer, *Chem. Commun.*, 804 (1969); (b) J. L. Burkoth and E. F. Ullman, *Tetrahedron Lett.*, 145 (1970).

(5) All diketones were prepared by the method of N. Kornblum and H. W. Frazier, *J. Amer. Chem. Soc.*, **88**, 865 (1966).

(6) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(7) P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5383 (1969).

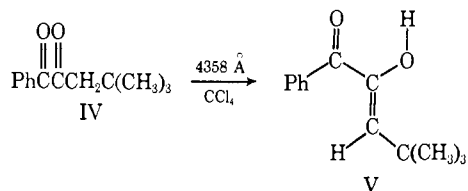
Table I. Photoreactivity of Some 1-Phenyl-1,2-alkanediones at 25° (PhCOCOCH₂R)^a

R	Solvent	Φ_{HCB}^b	$\Phi_{\text{-DK}}^c$	$k_q\tau^d$	$1/\tau,^e$ 10 ⁵ sec ⁻¹	$k_{13},^f$ 10 ⁵ sec ⁻¹	$k_d,^g$ 10 ⁵ sec ⁻¹
I CH ₃	Benzene	0.04	0.23	30,000 ^o	1.7	0.10	1.6
	wet CH ₃ CN	0.06	0.33	53,000 ^o	1.9	0.11	1.8
II CH ₂ CH ₃	Benzene	0.58 ^h	0.63	10,700 ^{h-i}	5.7	3.3	1.4
	wet CH ₃ CN	0.71	0.80	16,800 ⁱ	6.0	4.2	1.8
III CH(CH ₃) ₂	Benzene	0.81 ^{h,k}	0.88	3,400 ^{h-i}	14.7	13.0	1.7
	wet CH ₃ CN	0.88	0.93	6,800 ⁱ	14.7	13.0	1.7
IV C(CH ₃) ₃	Benzene	<0.001	0.62	22,000 ^o	2.3		2.3

^a Irradiated at 3660 Å in sealed degassed tubes. ^b Quantum yield for hydroxycyclobutanone formation, determined relative to benzophenone-piperylene actinometer. All values extrapolated to zero diketone concentration to correct for concentration dependence. ^c Quantum yield for disappearance of 0.05 M diketone. ^d Stern-Volmer quenching slopes with pyrene as quencher. ^e Calculated assuming that $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in benzene and $1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ in acetonitrile. ^f Calculated by multiplying Φ_{HCB} in acetonitrile by $1/\tau$. ^g From phosphorescence quenching, 0.005 M diketone. ^h Same values obtained with 4358-Å radiation. ⁱ From quenching of cyclobutanone formation, extrapolated to zero diketone. ^j Same values observed with anthracene as quencher. ^k 0.82 for benzophenone-sensitized reaction.

the major photoproduct from I is not the cyclobutanone. Although a peak corresponding to the major product does appear under low-temperature vpc conditions, at 200° injector temperature the new product peak is replaced by a peak corresponding to starting α -diketone. Likewise, after 100% disappearance of III, vpc analysis of photosylate regenerates 8% III.

Diketone IV has no hydrogens γ to the 1-carbonyl. Quenching of its phosphorescence indicates that its triplet decay rate is very similar to the k_d values of I-III. Vpc analysis reveals no photoproducts arising either from γ -hydrogen abstraction by the 2-carbonyl or from δ -hydrogen abstraction by the 1-carbonyl. A degassed CCl₄ solution 0.2 M in IV does photobleach very efficiently, however. After complete disappearance of the 405-nm band characteristic of the α -diketone, the solution had the following spectral properties: uv λ_{max} 282 nm ($\epsilon \sim 7000$); ir new absorbances at 3410 (concentration independent), 1670, 1630 cm⁻¹ (no absorbance in 1700-1800-cm⁻¹ region); nmr δ 1.18 (s, 9 H), 5.35 (s, 1 H), 6.55 (s, 1 H) washed out by shaking solution with D₂O, 7.4 (multiplet center, 5 H). In acetonitrile, the photolysate displays two λ_{max} 's, one at 252 nm (ϵ 7000) and one at 279 nm (ϵ 7500). Solutions of the photolysate are stable for days at room temperature, but aqueous acid or base or a 200° vpc injector rapidly regenerate diketone IV. All the observed properties fit the enol structure V as the photoproduct from IV.



Lemaire suggested such a photoenolization of biacetyl 3 years ago⁸ and Bishop and Hamer⁹ have just reported that an aliphatic diketone similar to IV yields a photoproduct with spectral characteristics very similar to those we find. What we consider remarkable is that the process is fast enough to compete with intramolecular hydrogen abstraction in compounds I-III. It is a reasonable assumption that the $k_d \sim 2 \times 10^5 \text{ sec}^{-1}$ represents the same process(es) in all four diketones studied, since they all have the same structure around the chromophore.

(8) J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967).

(9) R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970).

V may well undergo more chemistry than just reversion to IV. When the solvent is removed from the photolysate of IV, the ir absorbances ascribed to V slowly disappear (half-life 15 hr) and are replaced both by those characteristic of IV and by new absorbances, in particular a strong one at 1700 cm⁻¹ and a weaker one at 1740 cm⁻¹. We are studying this problem further.

Finally, we note that the thermal stability of dilute V is not too surprising in light of the known preference for cyclic α -diketones to exist in their enolic form.¹⁰ Probably more important, the uncatalyzed thermal reketonization would require a symmetry-forbidden suprafacial [1,3] sigmatropic shift. Whether the photoenolization can be viewed simply as an allowed [1,3] sigmatropic shift is another question.

Acknowledgment. This work is being supported by grants from the National Science Foundation. It is a pleasure to thank Professor Nicholas Turro for sharing information and ideas about his similar, independent studies.

(10) R. Bakule and F. A. Long, *J. Amer. Chem. Soc.*, **85**, 2309 (1963).

(11) Alfred P. Sloan Fellow, 1968-1970.

* Address correspondence to this author.

Richard G. Zepp, Peter J. Wagner*¹¹

Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

Received August 20, 1970

Photochemistry of Some α -Ketopropiophenones. Evidence for an Unusual Cyclic Transition State for Hydrogen Abstraction¹

Sir:

Photoinduced intramolecular hydrogen abstraction reactions of ketones possessing an alkyl side chain are believed to generally proceed *via* six-membered cyclic transition states which lead to biradical intermediates.² Evidence has been produced which leads

(1) Molecular Photochemistry. XXXVI. Paper XXXV: N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970). The authors wish to thank the Air Force Office of Scientific Research (Grants AFOSR-68-1381 and AFOSR-70-1848) for its generous support of this work.

(2) (a) Exceptions to this rule generally involve seven-membered (or larger) cyclic transition states: see, for example, P. Yates and J. M. Pal, *Chem. Commun.*, 553 (1970); R. Breslow and S. Baldwin, *J. Amer. Chem. Soc.*, **92**, 732 (1970); J. Meinwald and J. W. Kobzina, *ibid.*, **91**, 5177 (1969); N. C. Yang, *React. Photoexcited Org. Mol., Proc. Conf.*