

of 0.05 M benzene solutions of 1-H ($\tau_f = 10.0$ nsec) and 1-D ($\tau_f = 11.7$ nsec).

An independent check of some of our spectroscopic data at 25° was possible since Stern-Volmer quenching of 1-H and 1-D by $(\text{CH}_3)_2\text{CHOH}$ was observed.

$$\Phi_p^0/\Phi_p = 1 + k_q\tau_p[Q]$$

These results are reported in Table III and are consistent with a deuterium enhancement of lifetime and also with literature data^{14a,18} for quenching of triplet 1-H.

Table III. Stern-Volmer Quenching by Isopropyl Alcohol

Biacetyl concn, M	$k_q\tau_p$, M ⁻¹	k_q , 10 ³ l. mole ⁻¹ sec ⁻¹ ^a
0.05 ^b	1.50	3.3
0.05 ^c	1.55	3.2
0.05 ^d	1.63	3.5
0.05 ^e	2.22	3.6
0.01 ^b	1.50	3.3
0.01 ^c	1.66	2.7
0.01 ^d	1.57	3.0
0.01 ^e	2.28	3.0
0.005 ^b	1.57	3.1
0.005 ^c	1.92	2.7

^a k_q calculated from τ_p values in Table II. ^b 1-H in benzene. ^c 1-D in benzene. ^d 1-H in benzene-*d*₆. ^e 1-D in benzene-*d*₆.

In conclusion, the response of the radiationless rate processes of biacetyl toward intra- and intermolecular deuterium substitutions appears to be unique among studies reported to date. This uniqueness derives in part from the dearth of published data concerning deuterium effects on molecules other than aromatic hydrocarbons, but implies that a theoretical study of a possible special role of the n,π^* state in determining radiationless rates should be considered.¹⁹

(18) H. L. J. Backstrom and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955).

(19) Although chemical mechanisms generally have not been considered to provide an important mechanism for radiationless deactivation of biacetyl in benzene, we are attempting to determine whether the reversible photochemical processes are significant.^{20,21}

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

(21) J. Baltrop and J. A. Smith, *J. Chem. Soc., B*, 227 (1968).

(22) Alfred P. Sloan Fellow, 1966-1968.

(23) National Institutes of Health Predoctoral Fellow, 1965-present.

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Received March 29, 1968

A Criterion for Zwitterionic Intermediates in the Photochemistry of 2,5-Cyclohexadienones

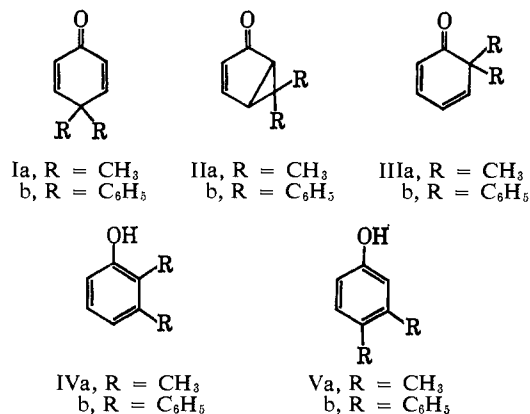
Sir:

The wealth of information on the photochemistry of 2,5-cyclohexadienones which has appeared in the literature in the past 12 years has been interpreted, almost without exception, in terms of zwitterionic species as intermediates.^{1,2} This belief in ionic pathways seems to be based on the parallelism between the chemistry of the phototransformations and polar rearrangements of nonphotochemical origin in related compounds.

(1) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); O. L. Chapman, *ibid.*, **1**, 330 (1963).

(2) P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 1,

A possible test for the nature of the intermediates in these systems is a study of the behavior of isolated molecules of the reactant, *i.e.*, in the vapor phase at low pressure. At the photon energies used in the excitation of the dienones (<4 eV), in isolated molecules, it is unlikely that polar structures in which unit charges are separated by the distance of one C-C bond are attainable.³ On the other hand, in polar solvents the large dielectric constant of the medium, as well as solvation, can lower the energy (with respect to the ground state) of these structures to a point where they may be accessible to the electronically excited dienone molecules. Hence a comparison of the photochemistry of a given compound in the gas phase at low pressure and in solution in a polar solvent can be used as a significant test for the intermediacy of ionic species along a given pathway. By the use of this reasoning, we shall demonstrate that in a typical 4,4-disubstituted 2,5-cyclohexadienone (I) the photoisomerization to a 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-one (II) and in turn to the 6,6-disubstituted cyclohexa-2,4-dienone (III) need not involve zwitterionic species while the photorearrangements of II to the phenols IV and V are, in all probability, polar reactions.



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Irradiation of 4,4-dimethylcyclohexa-2,5-dienone (Ia) at 3000-3700 Å in solution in cyclohexane to conversions of 40% gave two isomeric ketones. One of these was identified as 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (IIa) on the basis of its infrared (conjugated C=O at 5.85 μ; medium absorptions at 7.49, 8.48, 11.72, and 11.90 μ), nmr (quartet at τ 2.73 (1 H), doublet at 4.18 (1 H), quartet at 7.73 (1 H), doublet 8.20 (1 H), and singlets at 8.77 (3 H) and 8.85 (3 H)), mass (parent peak at 122), and ultraviolet spectra (structureless absorption similar to IIb).⁴ The second compound was identified as 6,6-dimethylcyclohexa-2,4-dienone (IIIa)⁵ by comparing its spectra with those of an authentic sample.⁶ Irradiation of Ia at the same wavelength in aqueous dioxane gave, in addition to IIa, two compounds which were separated by extraction with sodium hydroxide. By comparison with authentic samples on a thin layer chromatogram these compounds were identified as the phenols IVa and Va, the latter being in ex-

(3) A quantitative calculation of the energy separation between a given polar intermediate and the ground state of the reactant is difficult to carry out since the exact charge separation and its magnitude are not known.

(4) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(5) E. N. Marvell and E. Morgan, *ibid.*, **77**, 2542 (1955).

(6) K. Alder, F. H. Flock, and H. Lessenich, *Chem. Ber.*, **90**, 1709 (1957).

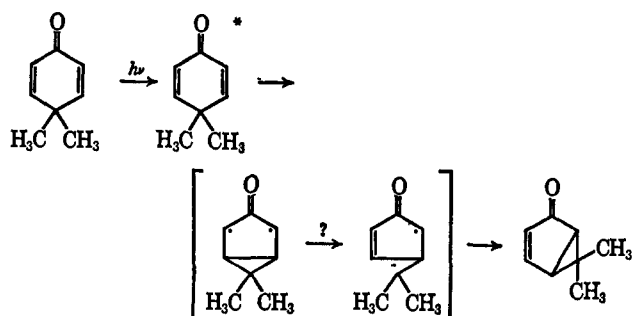
cess.⁷ Irradiation of IIa in cyclohexane solution gave IIIa in 70% yield. These products are, without exception, those that could have been predicted from the well-documented studies of Zimmerman and his co-workers on Ib.^{4,8}

Irradiation of Ia in the gas phase was carried out at 3660 Å at a temperature of 85° and a pressure of 6 torr.^{9,10} *Exactly as with Ib, the initial product of the photoisomerization of Ia was IIa only.* As soon as about 6% of IIa had built up in the system, IIIa began to appear. The mass balance was excellent up to about 15% conversion of Ia. There is no doubt that Ia leads to IIa which in turn gives IIIa. After prolonged irradiation there were small amounts of other carbonyl compounds besides IIa and IIIa, but there was no detectable amount of the phenolic products IVa or Va. In relation to the yields of IVa and Va in aqueous dioxane, their yields in the gas-phase reaction can be estimated to be less than 0.01. Addition of methanol vapor was seen to decrease the yield of IIIa but not of IIa.

The quantum yield for the formation of IIa from Ia in the vapor phase was 0.40 ± 0.03 at 3660 Å. This may be compared to the quantum yield for the formation of IIb from Ib of 0.85 in this wavelength region.¹¹

The scheme in terms of which the photoisomerization of Ib to IIb has been explained¹¹ involves a mesoionic intermediate¹² which is not likely to be involved in the gas-phase reaction. It follows that Ia can be transformed to IIa *via* nonionic intermediates in at least this instance.

The conversion of Ia to IIa is formally a specific example of the divinylmethane to vinylcyclopropane rearrangement which is known to be a general photochemical process.¹³ A mechanism based on this idea would be as follows.



The transformation of IIa to IIIa should also involve a nonionic pathway at least when it takes place in the

(7) In contrast, neither phenolic product was detectable in the photolysate in cyclohexane solution.

(8) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966).

(9) Qualitatively, the same results were obtained when the irradiation was carried out at 25° at ~0.5 torr. Under both conditions the vapor pressure of ketone Ia was well below its saturation vapor pressure so that any possibility that the material may have been irradiated as a liquid film can be discounted.

(10) The identities of the products from the vapor-phase reaction were established from both their infrared spectra and their retention times.

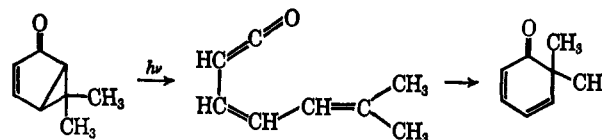
(11) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967).

(12) Since irradiation of Ib gives IIb but scarcely any of its photo-products, it has been argued that the excited state of the product IIb is not involved in this pathway. The same reasoning can be applied to Ia as well since the initial product in this case is only IIa.

(13) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Am. Chem. Soc.*, **89**, 3932 (1967).

vapor phase, whereas the formation of the phenols IVa and Va from IIa probably involves zwitterionic intermediates since it is observed only in a polar medium. The latter route is likely to be the same as the one that has been proposed for the conversion of IIb to IVb and Vb in a polar solvent.¹⁴

The formation of IIIa is reduced by the presence of methanol which supports the intermediacy of a ketene in this reaction. This ketene, in turn, can cyclize to give IIIa.¹⁵



It is hardly surprising that in the vapor phase the formation of the phenols IVa and Va from IIa is not to be observed since these transformations require the intramolecular migration of a methyl group by a non-free-radical process. In fact, there appears to be no well-documented instance of any gas-phase interaction in which a methyl group undergoes such a shift. Among the reactions of 2,5-cyclohexadienones that have been discussed here, this seems to be the only process that *demand*s the intermediacy of polar intermediates.

Acknowledgment. Support from the Research Corporation to John S. Swenton and from the National Science Foundation Undergraduate Research Program to Edward Saurborn are acknowledged. It is a pleasure to thank Mrs. Jane M. Picone for her able technical assistance.

(14) This would be in line with the results obtained by H. E. Zimmerman and J. O. Grunewald [*ibid.*, **89**, 3354 (1967)] on the migratory aptitudes of substituted phenyl groups in IIb.

(15) For analogs of this process see ref 4 and 8 and also B. Miller and H. Margulies, *Chem. Commun.*, 314 (1965).

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Received February 26, 1968

The Enzymatic Oxidation of a Quinol Phosphate. Position of Bond Cleavage

Sir:

Their possible involvement in biological energy-transfer reactions has stimulated interest in the oxidative cleavage of monoesters of quinols (I, X = CH₃CO,¹ HSO₃,² or H₂PO₃.³). The most important of these are the phosphate esters, partly because of the central role of phosphates in biological processes and partly because of evidence directly implicating quinones in oxidative phosphorylation.⁴ Involvement of quinol phosphates in the latter process requires that their

(1) J. W. Thanassi and L. A. Cohen, *J. Am. Chem. Soc.*, **89**, 5733 (1967); (b) C. A. Bunton and J. Hellyer, *ibid.*, **89**, 6252 (1967).

(2) S. W. Weidman, D. F. Mayers, O. R. Zaborsky, and E. T. Kaiser, *ibid.*, **89**, 4555 (1967).

(3) V. M. Clark, D. W. Hutchinson, G. W. Kirby, and A. R. Todd, *J. Chem. Soc.*, 715 (1961).

(4) R. A. Morton, Ed., "Biochemistry of Quinones," Academic Press Inc., New York, N. Y., 1965.