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The Photochemistry of α -Keto Acids and α -Keto Esters. I. Photolysis of Pyruvic Acid and Benzoylformic Acid¹

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The dicarbonyl systems of pyruvic acid and benzoylformic acid have been found to be highly sensitive to ultraviolet irradiation. Aqueous solutions of pyruvic acid and benzoylformic acid upon irradiation rapidly evolve considerable quantities of carbon dioxide. The main organic products remaining in solution are acetoin and benzaldehyde, respectively. In various organic solvents pyruvic acid is readily photoreduced to give dimethyltartaric acid and, at least in methanol, a one-to-one solvent adduct. In the gas phase pyruvic acid undergoes decarboxylation to yield acetaldehyde.

In past years pyruvic acid and its analog benzoylformic acid have been decomposed by a number of methods to give a variety of products. In the early literature Lieben and co-workers² reported that an aqueous alkaline solution of pyruvic acid decomposed upon irradiation to give what they thought to be acetaldehyde and possibly acetic acid. They observed that this reaction was more rapid than the decomposition of lactic acid under the same conditions. There has been no other published account of the action of light on pyruvic acid. In purely thermal reactions it has been found that pyruvic acid, catalyzed by osmium, palladium, and ruthenium,³ decomposes to give carbon dioxide and acetaldehyde, while Urion⁴ reports acetaldehyde, biacetyl, and pyruvaldehyde from the thermal decomposition of pyruvic acid over copper.

The biochemical references to pyruvic acid are exceedingly numerous. Pertinent to our work, it is known that certain enzymes⁵ requiring thiamine pyrophosphate⁶ (cocarboxylase) are known to catalyze the decarboxylative condensation of pyruvic acid to acetoin.

Juday⁷ reports that the cathodic reduction of pyruvic acid in sulfuric acid gives lactic and small amounts of one isomer of dimethyltartaric acid. Juday also found that benzoylformic acid was electrolytically reduced in acid, buffered acid, and alkaline media. In alkaline solution mainly the *meso* isomer of diphenyltartaric acid was formed, while acidic solutions afforded primarily the racemic mixture.

Schönberg and co-workers have found that benzoylformic acid in the presence of isopropyl alcohol is photochemically reduced⁸ by sunlight to give diphenyltartaric acid.

The present work was undertaken to elucidate the general nature of photoreactions of α -keto acids in various media. In this paper we report our findings on the photochemistry of pyruvic and benzoylformic acids.

Experimental

Apparatus.—All runs in solution were carried out using a Hanovia 450-w. high pressure mercury arc with a quartz immersion reactor equipped with a eudiometer for collecting gases. The volume of solution was 150 ml. in each run. A 2800 Å. cut-off filter was used in all pyruvic acid runs and a 3100 Å. filter for the benzoylformic acid runs.

For the gas phase reactions a 4-l. Pyrex reaction vessel was used in conjunction with a Srinivasan-Griffin type reactor utilizing 12 Westinghouse 8-w. black-lamps giving mainly the 3660 Å. line.

A Cary recording spectrophotometer was used for all ultraviolet spectra.

(1) Part of this work has been previously reported in preliminary form: P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **28**, 1160 (1963).

(2) F. Lieben, L. Löwe, and B. Bauminger, *Biochem. Z.*, **271**, 209 (1934).

(3) E. Muller and F. Muller, *Z. Elektrochem.*, **31**, 41 (1925).

(4) M. Urion, *Ann. chim.*, [11] **1**, 5 (1934).

(5) H. Halm and W. Dircherl, *Chem. Ber.*, **83**, 415 (1950).

(6) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

(7) R. E. Juday, *J. Org. Chem.*, **23**, 1010 (1958).

(8) A. Schönberg, N. Latif, R. Moubasher, and A. Sima, *J. Chem. Soc.*, 1364 (1951).

Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer. The gas phase spectra were taken in a 10-cm. path-length cell. Solution spectra were taken in chloroform using a 0.1-mm. cell.

Materials.—Pyruvic acid was Matheson Coleman and Bell 99% reagent grade. It was distilled prior to use, b.p. 39–42° at 1 mm. Organic solvents were reagent grade and were used without further purification. Benzhydrol (Eastman White Label) was recrystallized from petroleum ether; m.p. 69°. Benzoylformic acid was prepared by the method of Oakwood and Weisgerber,⁹ utilizing benzoyl chloride and cuprous cyanide with subsequent acid hydrolysis.

Quantum Yields.—Benzene solutions 0.5 *M* in benzophenone and 0.5 *M* in benzhydrol, degassed and sealed in small Pyrex ampoules, served as an actinometer. Water and methanol solutions 0.5 *M* in pyruvic acid were degassed and sealed in a similar manner. The actinometer and the pyruvic acid-containing ampoule were irradiated simultaneously for 30 min. The quantum yields were calculated relative to the benzophenone-benzhydrol system using $\phi = 0.90$ for that system.¹⁰ A Corning 7-39 filter was used to isolate primarily the 3660 Å. Hg line which was more than 95% absorbed by all solutions. The amount of decomposition in quantum yield runs as well as in all product runs was determined by ultraviolet analysis before and after irradiation.

Photolysis of Aqueous Pyruvic Acid.—In a typical run 150 ml. of 0.285 *M* aqueous pyruvic acid was irradiated for 75 min. (see Table I). The gas evolved was collected in a eudiometer and analyzed by infrared. The gas (295 ml.) was found to be exclusively carbon dioxide. At 25° an additional 113 ml. of carbon dioxide would be expected to be dissolved in solution (based on standard solubility tables) giving a total of 17.8 mmoles of carbon dioxide produced. The solvent was removed under vacuum and a viscous reddish brown liquid remained, which was dissolved in methanol and dried with anhydrous calcium sulfate. About half of the methanol was removed under vacuum and the remaining liquid was analyzed by v.p.c. (vapor phase chromatography) utilizing a 12-ft. Apiezon J column at 90°, and identified by comparison of infrared spectra with authentic samples. The main component in the liquid was found to be acetoin. Direct analysis of aqueous solution by v.p.c. (12-ft., Apiezon J, 60°) showed extremely minute quantities of acetaldehyde. No acetic acid was detected.

An identical aqueous solution of pyruvic acid was worked up by the above procedure omitting the irradiation. Analysis by v.p.c. showed no acetoin. A 0.285 *M* aqueous solution of sodium pyruvate (pH 6.08) was similarly irradiated. Decomposition was at least an order of magnitude slower, and no CO₂ was evolved. Products were not characterized.

Irradiation of Pyruvic Acid and Benzhydrol in Benzene.—A benzene solution 0.285 *M* in pyruvic acid and 0.285 *M* in benzhydrol was irradiated for 4 hr. In the course of the reaction crystals precipitated which were dissolved in methanol and evaporated to a yellow oil. The oil was dissolved in hot chloroform containing a small amount of methanol to effect solution. On cooling, white crystals precipitated, m.p. 140–163°,¹¹ neutralization equivalent 90.3. These crystals were identified as dimethyltartaric acid by infrared spectroscopy, n.m.r., and the neutralization equivalent; principal infrared absorption bands of the mixed isomers of dimethyltartaric acid in potassium bromide: 2.85, 3.30, 5.72, 7.95, 8.60, 9.10, 11.80 μ .

*Anal.*¹² Calcd. for C₈H₁₀O₆: C, 40.33; H, 5.62; O, 54.05. Found: C, 40.10; H, 5.80; O, 54.10.

(9) T. S. Oakwood and C. A. Weisgerber, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 112.

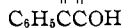
(10) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(11) Reported⁷ m.p. of one (unidentified) isomer of dimethyltartaric acid is 174–175°.

(12) The authors wish to thank Dr. J. A. Leermakers of the Eastman Kodak Co. for obtaining the elementary analyses.

TABLE I

Concn., <i>M</i>	Solvent	Time of irradiation	% keto acid decomposed	Major products isolated	% net yield
0.285 HOPy ^a	H ₂ O	75 min.	50	17.8 mmoles CO ₂ acetoin ^b	85
0.285 HOPy	MeOH	3.5 hr.	88	1.2 g. DMTA ^c 0.183 g. $\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{C}-\text{COOH} \\ \\ \text{CH}_2\text{OH} \end{array}$	37 4.1
0.285 HOPy	Benzene	4 hr.	75	2.3 mmoles CO ₂ 1.875 g. DMTA	5.5 65
0.285 benzhydrol				4.145 g. benzpinacol	71
0.285 HOPy	CHCl ₃	3 hr.	95	1.828 g. DMTA	50
0.134 OO	H ₂ O	1 hr.	51	9.7 mmoles CO ₂ 6.1 mmoles C ₆ H ₅ CHO	95 60



150 ml. of solution used in all runs.

^a HOPy = pyruvic acid. ^b The major isolable product, although not accurately determinable. ^c DMTA = dimethyltartaric acid.

The remaining benzene solution was slowly evaporated leaving crude benzpinacol. The benzpinacol was recrystallized from absolute ethanol, m.p. 185–187° (lit.¹⁰ 186°), and identified by comparison of its infrared spectrum with that of an authentic sample.

Irradiation of Pyruvic Acid in Ethyl Ether.—An anhydrous ether solution 0.285 *M* in pyruvic acid was irradiated for 3 hr. The solvent was removed by vacuum until a clear viscous residue remained. This product was dissolved in 1 ml. of methanol and 25 ml. of benzene and heated until an oil separated. The excess benzene was decanted and the oil crystallized in chloroform. The product, dimethyltartaric acid, was identified by comparison of the infrared spectrum with that obtained in earlier experiments.

Irradiation of Pyruvic Acid in Chloroform.—A solution 0.285 *M* in pyruvic acid in chloroform irradiated for 3 hr. produced considerable quantities of dimethyltartaric acid which crystallized out of solution. The dimethyltartaric acid was recrystallized from hot chloroform and identified by comparison of its infrared spectrum with that obtained in earlier experiments. Analysis by v.p.c. on a silica gel column at room temperature showed no CO₂ in the irradiated solution.

Irradiation of Pyruvic Acid in Methanol.—A methanol solution 0.285 *M* in pyruvic acid was irradiated and the solvent removed by vacuum. The remaining oil was dissolved in a small quantity of anhydrous ether and chromatographed on silica gel using ether as eluent. Two products were isolated. The first and larger fraction was identified as dimethyltartaric acid. The second, recrystallized from chloroform, was identified by infrared and n.m.r. as 2-methyl-2,3-dihydroxypropanoic acid, m.p. 102–103°, lit.¹³ 100°, neut. equiv. 124. The principal infrared bands of 2-methyl-2,3-dihydroxypropanoic acid in potassium bromide are at 2.90, 3.75, 5.80, 6.80, 9.50, 10.60, 11.20, and 13.10 μ . In an identical experiment the reaction mixture was directly analyzed by v.p.c. Small amounts of carbon dioxide and acetoin were found.

Anal. Calcd. for C₄H₆O₄: C, 40.0; H, 6.7; O, 53.3. Found: C, 40.0; H, 6.6; O, 53.4.

Photolysis of Aqueous Benzoylformic Acid.—An aqueous solution 0.137 *M* in benzoylformic acid was irradiated for 1 hr. The gas evolved was collected in a eudiometer and identified as carbon dioxide by its infrared spectrum. By comparison with a standard ether-benzaldehyde mixture the absolute amount of benzaldehyde was determined.

Gas Phase Photolysis of Pyruvic Acid.—Samples of pyruvic acid (usually 100 μ l.) were degassed in a 4-l. reaction vessel and photolyzed at 85° for 2 hr. using the 3660 Å. mercury line. The products were frozen out at 77°K. and identified by comparison of their infrared spectra with authentic samples. In the same vessel a sample of pyruvic acid was degassed and heated to 85° for 2 hr. in the dark. No reaction ensued; pyruvic acid was quantitatively recovered unchanged.

Results

Table I lists the yields of the major products obtained in the photoreactions of the keto acids in water and various organic solvents.

Pyruvic acid in water rapidly photodecomposes yielding a nearly quantitative¹⁴ amount of carbon dioxide. Benzoylformic acid in water also readily evolves carbon

(13) P. Meikoff, *Ann.*, **234**, 218 (1886).

(14) The yields are based on the amount of pyruvic acid decomposed.

dioxide upon irradiation. The other organic products are analogous in the two cases but formed in vastly different relative yields. The pyruvic acid system gives mainly acetoin¹⁵ (contrary to the report of Lieben, *et al.*²) with minute traces of acetaldehyde and what appears to be biacetyl.¹⁶ These latter products may come from the photolysis of the acetoin since Pitts¹⁷ has found that these products are formed from the decomposition of acetoin in the vapor phase. Benzoylformic acid in water exhibits different photochemical behavior, the main product left in solution being benzaldehyde (60%). Traces of benzoin (identified by its infrared spectrum) crystallize out of solution during photolysis.

In the presence of hydrogen-donating *organic* solvents, pyruvic acid is rapidly photoreduced without significant decarboxylation. Irradiation of equal molar quantities of pyruvic acid and benzhydrol in benzene yields dimethyltartaric acid and benzpinacol. Pyruvic acid is photochemically inert in pure benzene. The nuclear magnetic resonance spectrum¹⁸ of dimethyltartaric acid in deuterium oxide shows two unsplit methyl peaks at 3.2 and 2.6 p.p.m. upfield from H₂O (corresponding to τ -values of about 8.8 and 8.2, respectively). The peaks have an integrated ratio of about 8:5. The fact that there are *two* methyl peaks with different chemical shifts is not unexpected since both the *d,l*-pair and the *meso* form of dimethyltartaric acid would be expected to be formed in the reaction. Our wide melting point range (140–163°) despite the apparent purity of the compound (neutralization equivalent, elementary analysis) is consistent with a *rac-meso* mixture. No attempt was made to separate the two isomers.

In other organic solvents such as methanol, ethyl ether, *t*-butyl alcohol, dioxane, and chloroform, pyruvic acid is rapidly consumed upon irradiation. In methanol, ether, and chloroform (the solvents in which products were characterized), pyruvic acid is photoreduced yielding dimethyltartaric acid and, at least in the case of methanol, a 1:1 solvent adduct. Only dimethyltartaric acid was isolated from photoreaction of pyruvic acid in ether and in chloroform. In these two solvents no attempt was made to isolate solvent dimer, which is

(15) Water elutes simultaneously with acetoin on the v.p.c. so an absolute yield of acetoin could not be obtained. Acetoin cannot be quantitatively extracted into another solvent.

(16) Determined tentatively, but not absolutely, by comparison of v.p.c. retention times and a rather poorly resolved infrared spectrum.

(17) J. N. Pitts, private communication.

(18) The authors wish to thank Edmond J. O'Connell of Yale University for obtaining the n.m.r. spectra reported in this paper.

presumably present, and solvent adduct which also could be present. Pyruvic acid in methanol is very efficiently photoreduced to dimethyltartaric acid and a solvent adduct 2-methyl-2,3-dihydroxypropanoic acid. The n.m.r. spectrum of the latter compound in deuterium oxide shows an unsplit methyl peak at 3.3 p.p.m., and an AB pattern for the methylene protons centered at 1.0 p.p.m., both upfield from H₂O. The areas are in the expected ratio of 3:2. The hydroxylic protons are lost due to deuterium exchange. Ethylene glycol was not isolated, although it is presumably present. Gas chromatographic analysis indicated that about 5% of the photoreaction in methanol proceeds *via* the decarboxylation mechanism. Both carbon dioxide and acetoin were observed. The quantum yield for the disappearance of pyruvic acid in methanol is within experimental error of unity (Table III).

Pyruvic acid in the vapor phase under low pressures undergoes photodecomposition yielding acetaldehyde and carbon dioxide. No other product was observed. The two gases were formed in approximately equivalent amounts.

Discussion

Pyruvic and benzoylformic acids both show two near-ultraviolet absorption maxima; an $n-\pi^*$ band (Table II) in the 3000–3500 Å. region with low (and solvent-dependent) extinction showing the expected blue shift in polar solvents, and a $\pi-\pi^*$ band. For pyruvic acid the $\pi-\pi^*$ transition occurs at 2000 Å. (in water), ϵ 2100; for benzoylformic acid the $\pi-\pi^*$ transition is (in water) at 2625 Å., ϵ 9530.

TABLE II

Solvent	$n-\pi^*$ λ_{\max} , Å	ϵ
Pyruvic acid		
H ₂ O	3212	11.3
MeOH	3250	4.55
CHCl ₃	3375	11.5
Et ₂ O	3425	14.7
C ₆ H ₆	3585	18.9
Benzoylformic acid		
H ₂ O	3375	48
C ₆ H ₆	3760	77

The emission spectrum¹⁹ of pyruvic acid in an ethanol glass at 77°K. shows two well defined phosphorescence bands, the 0–0 band at 4230 Å., and the 0–1 band at 4550 Å., the former corresponding to a triplet state energy of 68 kcal. The emission spectrum of benzoylformic acid taken under the same conditions show the 0–0 band at 4705 Å. and the 0–1 band at 5100 Å., the 4705 Å. band corresponding to a triplet energy of 60.8 kcal. The phosphorescence from both of these compounds seems to be even more intense than that from benzophenone²⁰ which has a phosphorescence quantum yield of greater than 0.80.²¹ These results, coupled with our observation of efficient photoreduction of pyruvic acid (even with relatively low concentration of hydrogen donor, as in the benzhydrol–benzene run), indicate exceedingly facile intersystem crossing, the efficiency quite possibly equal to unity.

The photochemistry of the keto acids in nonaqueous solvents appears reasonably straightforward. In benzene, with no abstractable hydrogen atoms, pyruvic acid is photochemically inert. Addition of benzhydrol, a good hydrogen donor,¹⁰ causes pyruvic acid to be

(19) The authors express their appreciation to Angelo A. Lamola of the California Institute of Technology for obtaining the emission spectra of the keto acids.

(20) A. A. Lamola, private communication.

(21) E. Gilmore, G. Gibson, and D. McClure, *J. Chem. Phys.*, **23**, 399 (1955).

readily reduced by light of 3130 and 3600 Å. to dimethyltartaric acid (the pinacol derived from pyruvic acid) while the benzhydryl radicals (formed by hydrogen abstraction from benzhydrol) dimerize to benzpinacol. The net yields of both products are relatively high (Table I).

Photoreduction in methanol proceeds by a similar path. Triplet pyruvic acid abstracts a hydrogen atom from methanol onto the ketone carbonyl leaving the radicals $\cdot\text{CH}_2\text{OH}$ and $\text{CH}_3\dot{\text{C}}(\text{OH})\text{COOH}$ which can dimerize or cross couple. Both dimethyltartaric acid and the cross-coupled product 2-methyl-2,3-dihydroxypropanoic acid are observed. Presumably a similar mechanism applies in the other organic solvents studied, although cross-coupled products were not isolated. Decarboxylation was not an important side reaction in the photoreaction of pyruvic acid in organic solvents. It was virtually nonexistent in reaction in chloroform and amounted to only 5.5% net yield in methanol.²²

Photoreduction of benzoylformic acid was not carried out in the present investigation, but the work of Schönberg and co-workers⁸ who obtained diphenyltartaric acid upon irradiation of benzoylformic acid in isopropyl alcohol indicates that the two keto acids behave similarly in the presence of hydrogen-donating solvents.

The mechanism of the photoreaction of the keto acids in water is far from clear. Indeed, water is a poor hydrogen atom donor; thus photoreduction would not be anticipated and, in fact, does not occur. Instead a highly efficient photodecarboxylation takes place, the quantum yield for the decarboxylation of pyruvic acid in water being only slightly smaller than that for photoreduction in methanol (Table III). The fact that the two processes are almost noncompetitive in methanol (the process being very predominantly reduction) indicates that a molecule or molecules of water must be intimately involved in the mechanism of aqueous photodecarboxylation.

TABLE III^a
QUANTUM YIELD DATA

System	ϕ	No. of runs
Pyruvic acid in water	0.79 ± 0.05	6
Sodium pyruvate in water	<0.04	3
Pyruvic acid in methanol	0.96 ± 0.08	4

^a Quantum yields of pyruvic acid in other solvents and of benzoylformic acid were not measured since the products precipitated out of solution and prevented the same amount of light from entering the sample solution and the actinometer.

The fact that it is the acidic and not the anionic species that is undergoing the decarboxylation is clear from the fact that the quantum yield for the decomposition of pure acid in water is more than twenty times that for the neutralized acid.

It would be attractive to postulate the same mechanism for the aqueous photodecompositions of both keto acids, and indeed this probably must be done since water seems to be an important key for the decarboxylation of either acid to occur. However, the principal organic products from the photodecarboxylations of the two acids differ. In benzoylformic acid the principal product is benzaldehyde, while from pyruvic acid the main isolable product is acetoin (with only the smallest traces of acetaldehyde). The formation of benzaldehyde in the former reaction could be rationalized on the basis of homolytic loss of carbon dioxide

(22) It should be pointed out that the authors were led to believe that carbon dioxide was quite insoluble in alcohol solvents due to an error in "The Handbook of Chemistry and Physics," 39th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958, p. 508. However, our assertion of the minor role of decarboxylation in organic solvents based on gas evolution was confirmed by gas chromatographic analysis on the reaction mixtures.

with subsequent recombination of the benzoyl radical and a hydrogen atom. However, such a cage mechanism will not account for the formation of acetoin in the latter reaction. One must rule out acetaldehyde as an intermediate in this reaction since in one run acetaldehyde was added to an aqueous solution of pyruvic acid (molar ratio acetaldehyde to pyruvic acid 3:4) and its concentration was found not to decrease even after 50% conversion of pyruvic acid. One can account for the formation of acetoin from the intermediacy of a triplet hydroxymethyl carbene formed by cyclic concerted loss of CO_2^1 but no concrete evidence for this has yet been found.

One probably cannot account for the difference in products from the aqueous decompositions of the two acids as being due to different photochemically active excited states (*i.e.*, an $n-\pi^*$ triplet for pyruvic acid, a $\pi-\pi^*$ triplet for benzoylformic acid) since both the vibrational structure of the phosphorescence and the S_1-T_1 energy gaps indicate that in both cases the lowest (and hence chemically active) triplet is of the $n-\pi^*$ type.

An approach that we previously suggested¹ to explain the discrepancy in the result of irradiation of pyruvic acid in water and in organic solvents, that is, the species existing as aggregates in the organic solvents, may not

be entirely valid. While in benzene (where no photochemical reaction occurs) pyruvic acid is definitely dimeric¹ and even trimeric at higher concentrations,²³ it is monomeric in chloroform, a solvent in which photoreduction readily occurs without any significant amount of accompanying decarboxylation. Further investigation into the mechanism of aqueous photodecarboxylation of the ketoacids is in progress.

A most interesting and promising area of study is the gas phase photochemistry of pyruvic acid. Preliminary experiments reveal that pyruvic acid at low pressures photodecarboxylates (obviously not requiring the presence of water) quite cleanly to yield principally *acetaldehyde* rather than acetoin. The effect of added gases on the reaction, and the relevance of the mechanism of this reaction to those in solution, is currently being investigated.

Acknowledgment.—This work has been supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

(23) Molecular weights of pyruvic acid in benzene, methylene chloride, chloroform, and acetone indicate, respectively, trimer, dimer, monomer, and monomer. Apparatus utilizing vapor pressure measurements was employed, similar to that described by Neumayer.²⁴ We are indebted to Drs. B. H. Klandermand and O. E. Schupp of the Eastman Kodak Co. for performing these measurements.

(24) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. III. An Example of Steric Control

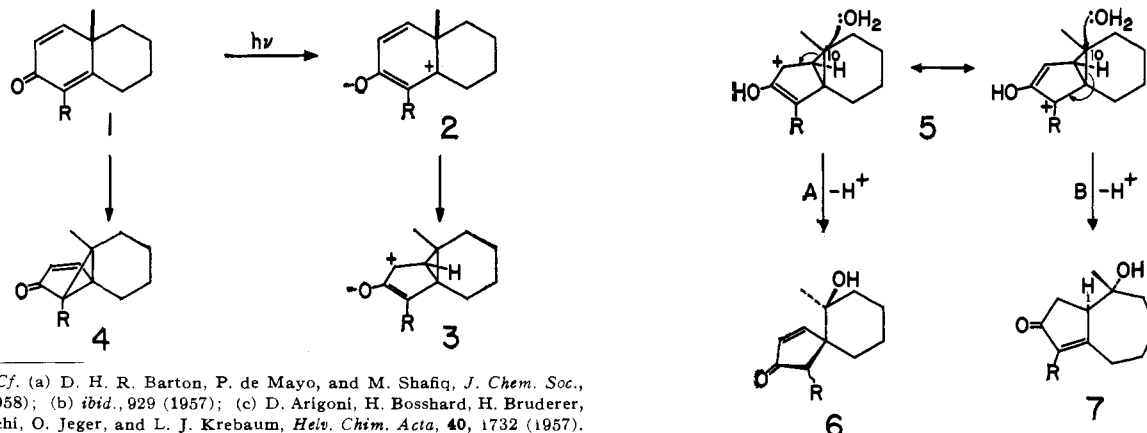
BY PAUL J. KROPP

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The photochemical behavior of the dienone **9** was examined in order to study the role of steric effects in photochemical rearrangements and to determine whether the marked influence of a 4-methyl substituent on the photochemical properties of 1,4-dien-3-ones can be attributed to steric factors. Irradiation of **9** in aqueous acidic media gave principally the *o*-cresol-type product **11a** and the 5/7-fused ketone **12**, accompanied by small amounts of the spiro ketone **10**. 1,4-Dien-3-ones of this type, unsubstituted at C-4, normally give *m*-cresol-type products and approximately equal amounts of spiro- (**6**) and 5/7-fused (**7**) hydroxy ketones in acidic media. Thus the properties of the dienone **9** are markedly influenced by steric factors. However, the behavior of **9** is not the same as that of 4-methyl-1,4-dien-3-ones; this suggests that the 4-methyl effect is not principally steric in origin.

Among the earliest photochemical rearrangements discovered were the light-induced transformations of the sesquiterpene santonin (**21**).¹ In recent years it has been found that almost all cross-conjugated cyclohexadienones undergo fascinating rearrangements under the influence of ultraviolet light. Moreover, all 1,4-dien-3-ones of the type **1** ($R = \text{CH}_3$), which bear a methyl substituent at C-4,² that have been studied to

date have been found to exhibit similar photochemical behavior.³ In neutral media they undergo facile isomerization to a cyclopropyl ketone **4** ($R = \text{CH}_3$), commonly known as a "lumiproduct." Lumiproduct formation occurs in aqueous acidic media as well, but under these conditions it is accompanied by a second reaction pathway leading to a hydroxy ketone **7** ($R = \text{CH}_3$) having a hydroazulene structure.



(1) Cf. (a) D. H. R. Barton, P. de Mayo, and M. Shafiq, *J. Chem. Soc.*, 140 (1958); (b) *ibid.*, 929 (1957); (c) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

(2) The steroid numbering system is used throughout the Discussion section.

(3) Cf. P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, 393 (1961).