Mechanistic Organic Photochemistry. XVI.[1] The Photochemistry of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one[2]

Howard E. Zimmerman, Reinhart Keese,[3a] Jacques Nasielski,[3b] and John S. Swenton[3c]

Contribution from the Department of Chemistry of the University of Wisconsin, Madison, Wisconsin 53706. Received May 23, 1966

Abstract: The photochemistry of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (2) was investigated. Evidence is reported for the structure of the photoacid previously described. This was shown to be 6,6-diphenyl-3,5-hexadienoic acid, the *cis* isomer of which was found to be initially formed. The phenolic product distribution was acid dependent with 2,3-diphenylphenol predominating under neutral and mildly acidic conditions but with a remarkable preference for 3,4-diphenylphenol resulting in more acidic medium. The reactions of the bicyclic ketone 2 were considerably less efficient than the rearrangement of 4,4-diphenylcyclohexadienone (1). Evidence was found in support of mesoionic zwitterion intermediates as precursors to the diphenylphenol products and suggesting that the phenolic products arose primarily from the triplet. The photoacid was found to come from both singlet and triplet processes. The excited states of bicyclic ketone 2 were shown not to revert to 4,4-diphenylcyclohexadienone. Additionally, the diphenylphenols obtained resulting from dienone 1 photolysis were shown to arise exclusively *via* the bicyclic ketone 2; no direct 4→3 phenyl migration in the dienone occurs.
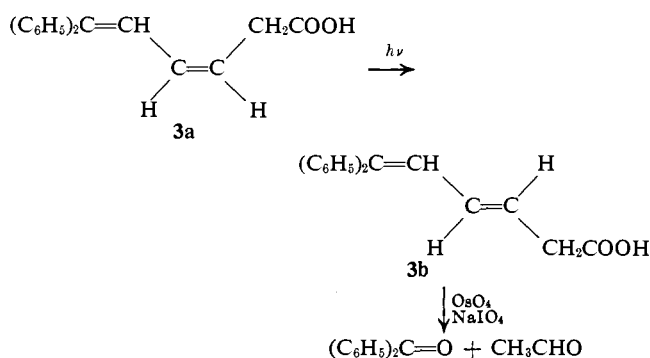
Previously the photolysis of 4,4-diphenylcyclohexadienone (1) was investigated qualitatively and shown to afford 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (2), which proved to be an intermediate leading onward to 2,3-diphenylphenol, and an acid analyzing for starting material plus one water molecule.[4a,b]

The purpose of the studies described in this and a subsequent paper was to explore further the details of the reaction and to investigate the mechanistic subtleties. The present paper confines its attention to bicyclic ketone (2) photochemistry.

Structural Questions

The first question requiring attention was the structure of photoacid 3. When the reaction was run with a filter transmitting at 330–380 mμ, an isomer (3a) melting at 92.5–94.0° was obtained. With shorter wavelength light and prolonged photolysis, the isomer 3b, mp 117.0–117.5°, described in our original paper,[4] was obtained.

Chart I

The structures of 3a and 3b were elucidated by chemical means as delineated in Chart I and confirmed by infrared, ultraviolet, and nmr. The spectral evidence, which additionally established 3a as the *cis* acid and 3b as the *trans* isomer, is discussed in the Experimental Section. In agreement with our initial studies, 2,3-diphenylphenol was found to be the major phenolic product. However, additionally, lesser quantities of 3,4-diphenylphenol could be obtained. Interestingly, irradiation of the bicyclic ketone afforded no 4,4-diphenylcyclohexadienone. The over-all reaction may now be written as shown in Chart II.

Chart II
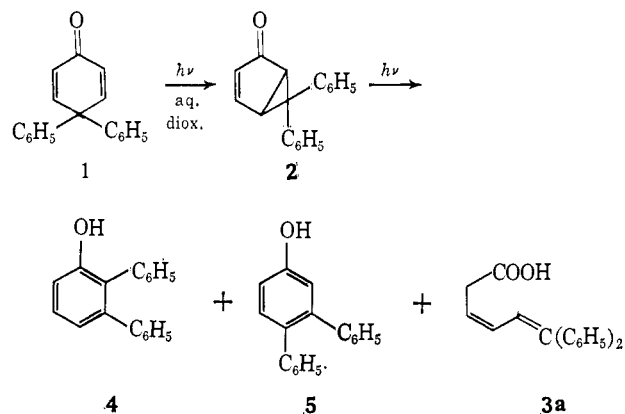
Mechanistic Studies. Dependence of Phenol Distribution on Acidity. One intriguing aspect of this study was encountered when the photolysis of 4,4-diphenylcyclohexadienone was run in 50% aqueous acetic acid. In contrast to the usual 4:1 preference for 2,3-diphenylphenol over the 3,4 isomer observed in aqueous dioxane, the photolysis in this acidic medium afforded an approximately 1:1 distribution. This suggested photolyses in buffered media; the results of these runs are summarized in Table I. A plot of the ratio of phenols *vs.* apparent pH is given in Figure 1.

Strikingly, the ratio of phenols actually inverts at the higher acidities, ultimately reaching a ratio of 1.8:1 at the highest acidity employed. That this change was

(1) For paper XV, see H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1965 (1966).

(2) Abstracted in part from the Ph.D. Thesis of J. S. Swenton, The University of Wisconsin, Jan 1966.

(3) (a) Research Associate, University of Wisconsin, 1961–1963; (b) Research Associate, University of Wisconsin, 1964–1965; on leave from the University of Brussels; (c) Wisconsin Alumni Research Foundation Fellow, 1962–1964; NSF Predoctoral Fellow, 1964–1965.

(4) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (b) *ibid.*, **84**, 4527 (1962).
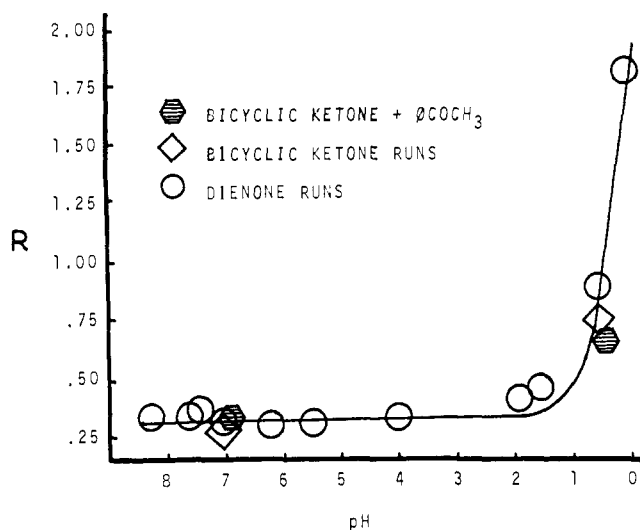
Figure 1. Ratio of 3,4- to 2,3-diphenylphenol vs. pH.

not due to a trivial dark, acid-catalyzed dienone–phenol rearrangement was demonstrated by control experiments showing no reaction without light.

Table I. Effect of Acidity on 2,3- to 3,4-Diphenylphenol Ratio and on Phenolic to Acid Product Distribution

Run	Starting material	pH[a]	Ratio phenols/ acid[b]	Ratio 3,4- to 2,3-phenol
1	Dienone	8.15	...	0.33
2	Dienone	7.50	...	0.34
3	Dienone	7.35	0.88	0.35
4	Dienone	7.00[c]	0.69	0.28
5	Photoketone	7.00[c]	0.69	0.28
6	Dienone[d]	7.00	0.74	0.26
7	Dienone	7.00	0.68	0.27
8	Photoketone[e]	7.00	...	0.25
9	Dienone	6.10	0.83	0.29
10	Dienone	5.35	0.58	0.30
11	Dienone	3.90	0.66	0.33
12	Dienone	1.80	0.70	0.39
13	Dienone	1.50	0.74	0.44
14	Dienone	0.50	0.74	0.88
15	Photoketone	0.45	0.63	0.72
16	Photoketone[e]	0.35	...	0.62
17	Dienone[f]	0.00	0.78	1.82

[a] Relative pH uncorrected for junction potential or standard emf. [b] Including 6,6-diphenylhex-5-en-1,4-olide formed in increasing amounts in acidic runs. [c] Unbuffered. [d] With 0.24 M LiCl. [e] Acetophenone sensitized. [f] 27% 1 M HCl–73% dioxane.

Three immediate questions posed themselves. The first was whether the increasing amounts of 3,4-diphenylphenol arose from the bicyclic ketone 2 as proposed in our earlier study for the formation of 2,3-diphenylphenol or instead by a direct route from 4,4-diphenylcyclohexadienone (1). The question was resolved quickly by comparison of runs made starting with the bicyclic ketone (2) and the dienone (1). It was noted that both bicyclic ketone and dienone points fall on the same acid dependence curve of Figure 1. This indicates that the same precursor is responsible in both dienone and bicyclic ketone photolyses.

The second question is whether the effect of acid is to change the multiplicity of the species leading to the diphenylphenols. Evidence was adduced that a change

in multiplicity is not responsible for the changing phenol ratios and will be considered later in connection with the singlet–triplet matter. The triplet is shown to rearrange to the diphenylphenols in both neutral and acidic media.

The third question derived from the suggestion of Porter and Suppan[5] that a change in relative energy of electronic states may occur with change in solvent polarity. A case was reported by these workers where n–π* singlets and triplets were preferred in cyclohexane while charge-transfer π–π* singlet and triplet configurations became favored in isopropyl alcohol. Inspection of the ultraviolet absorption spectra of dienone (1) and the bicyclic ketone (2) showed no change with decreasing pH between 300 and 400 mμ, contrasting with the p-aminobenzophenone case of Porter. This suggests but does not prove that such a phenomenon is not operative in the present case.[6]

We prefer an interpretation based on the mesoionic zwitterion proposed by us much earlier[4] as accounting for much cyclohexadienone photochemistry. Thus, in the case of the rearrangement of the bicyclic ketone 2 we suggested[7] that the n–π* excited state affords mesoionic zwitterion 8 by 2,4-bond fission and electron demotion. The preferential migration of a phenyl group from C-3 to C-2 rather than C-4, although the positive charge of the zwitterion 8 is distributed at both C-2 and C-4, was discussed in our earlier publications.[4]

Chart III
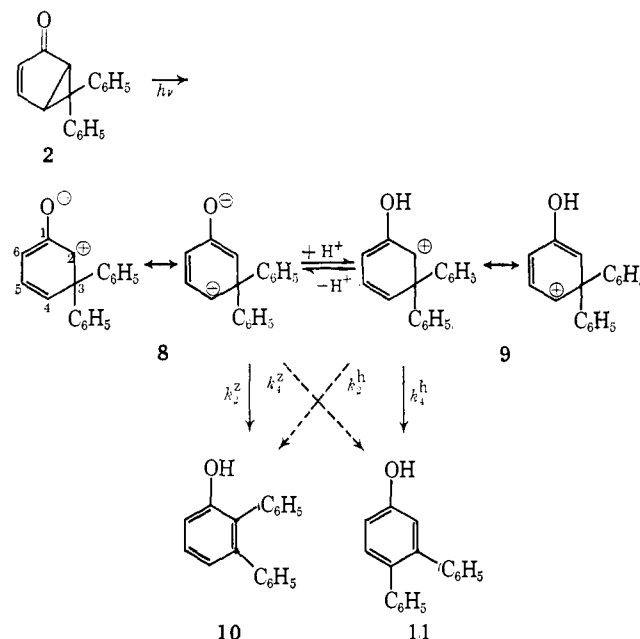
We now propose that the conjugate acid 9 of the zwitterion rearranges with predominant migration of the phenyl group to C-4, leading to 3,4-diphenylphenol as the major product in acidic medium. The observation (note Table I) that the ratio of total phenolic product to photoacid product was independent of

(5) (a) G. Porter and P. Suppan, Pure Appl. Chem., 9, 499 (1964); (b) Proc. Chem. Soc., 191 (1964).

(6) The absence of a configurational change in the singlet system of course does not prove the same lack in the triplet one. The reverse will generally be true; where the n–π* triplet is the lower energy configuration, the same order will generally obtain for the singlets.

(7) Note H. E. Zimmerman, Advan. Photochem., 1, 187 (1963), for a preliminary report of the acetic acid experiment.

acidity provided strong support for the view that the intervention of the proton affecting the 2,3- to 3,4-diphenylphenol distribution occurred subsequent to the initial stages of the reaction where the excited species partitions itself between pathways leading to phenolic and to acidic products.

The scheme in which zwitterion **8** leads mainly to 2,3 product and cation **9** affords primarily 3,4 material is outlined in Chart III. Based on this mechanism the kinetic expression $R_{34/23} = [k_4{}^h(H^+) + k_4{}^zK]/[k_2{}^h(H^+) + k_2{}^zK]$ may be written. Here $R_{34/23}$ is the ratio of 3,4- to 2,3-diphenylphenol, K is the ionization constant for **9**, and the k's are as defined in Chart III. The curve drawn in Figure 1 is the theoretical one based on this expression and using the asymptotic value of 0.30 for $k_4{}^z/k_2{}^z$ together with the empirical values of $k_4{}^h = 6.90Kk_4{}^z$ and $k_2{}^h = 0.90Kk_4{}^z$. The fit in Figure 1 is reasonably good.

Given the preferential migration to C-2 of the meso-ionic zwitterion **8** and the change to predominant migration to C-4 in the protonated species **9**, one desires a molecular rationale. Earlier we suggested[7] that migration to C-2 of the zwitterion was preferred because of more extensive electron delocalization in the enolate moiety of the phenonium intermediate leading to 2,3-diphenylphenol than in the corresponding species affording 3,4-diphenylphenol (note Chart IV). We further proposed that in the 50% acetic acid experiment, protonation of the oxygen afforded the protonated

Chart IV

12
3 enolate
contributors

13
2 enolate
contributors
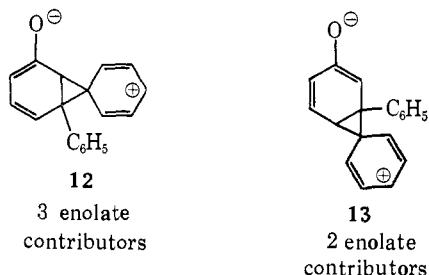
zwitterion in which electron delocalization from oxygen was much less important than for the zwitterion; this argument seemed to account for the observed 1:1 distribution of the 2,3- to 3,4-diphenylphenol. However, the present use of buffers clearly demonstrates that 3,4-diphenylphenol in excess of the 1:1 ratio is obtainable in strongly acidic media, an observation which requires further rationale.

Molecular orbital calculations were carried out on the phenonium zwitterion species **12** and **13** on the assumption that these represent transition states in the migration forming diphenylphenols from zwitterion. Similarly, the conjugate acids **14** and **15** were subjected to calculation. The results are in agreement with observation. Thus zwitterion **12**, leading to 2,3-diphenylphenol, is lower in energy by 0.4 kcal/mole than zwitterion **13**, which affords 3,4-diphenylphenol. Conversely, the protonated zwitterion **15** leading to 3,4-diphenylphenol is 0.8 kcal/mole lower in energy than protonated zwitterion **14**, which gives rise to 2,3-diphenylphenol. Although the predicted energy preferences are small, they are consistently in the correct direction independent of modest changes in parameters.

One point of relevance is the charge distribution in zwitterion **8**. MO calculations (cf. Figure 2) show
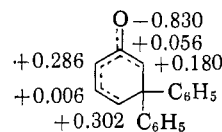
Figure 2. Calculated charge distribution in zwitterion **8**.

that C-4 is more electron deficient than C-2. Accordingly, the preference for migration to C-2 in the zwitterion cannot be attributed to preference for migration to the more electron-deficient center; maximization of enolate delocalization (vide supra) seems to be overriding. However, where the enolate moiety is no longer present (i.e., in the protonated zwitterion), migration to the more positive site becomes controlling. The MO calculations on the half-migrated species seem to bear this out.

12, OR = O⁻
14, OR = OH

13, OR = O⁻
15, OR = OH
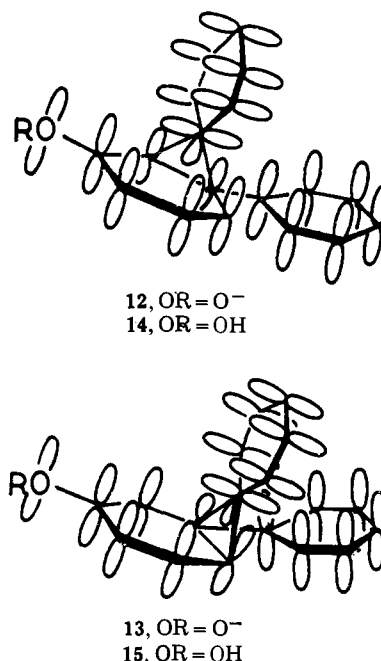
The Reaction Efficiency and Other Observations Bearing on the Reaction Multiplicity. It was found in the present study that in the photolysis of 4,4-diphenyl-cyclohexadienone (**1**), one could obtain yields of 30–40% of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (bicyclic ketone) (**2**) despite the known[4] susceptibility of this compound to further conversion and its possession of a high extinction coefficient (ϵ 500) relative to that of the dienone (ϵ 30). This suggested that the efficiency of conversion of the bicyclic ketone to phenolic and acidic products might be relatively low, a result which would be interesting to correlate with the bicyclic ketone structure. To answer this question and to provide information needed to compare with results of sensitization experiments, quantum yield determinations were run. The multiplicity of the reaction posed an especially intriguing question since, because several products were known to result, it was possible that excited states of differing multiplicity were involved.

The results of direct excitation quantum yield determinations in several solvents are given in Table II. We see that the suspicion of low efficiency is confirmed. The source of this inefficiency will be considered subsequently in the discussion of molecular details of the

mechanism. However, we should note the insensitivity of the quantum yield of bicyclic ketone disappearance, of photoacid formation, and of total phenolic product formation to solvent polarity. These quantum yields in different solvents are within experimental error of one another.[8] The small increase in per cent of 3,4-diphenylphenol with increasing solvent polarity seems most likely due to increased hydrogen bonding of the zwitterion.[8]

Table II. Quantum Yields in Direct Irradiations

Solvent	Quantum yields[a]			% 2,3-diphenyl-phenol[d]
	Bicyclic ketone[b]	Photo-acid[c]	Phenols[c]	
t-BuOH	0.155	...	0.057	86.4
73% aqueous dioxane	0.160	0.094	0.066	79.8
80% aqueous t-BuOH	0.150	0.087	0.063	82.0

[a] 330–380-mμ irradiation. [b] Disappearance. [c] Appearance. [d] Relative to 3,4-diphenylphenol.

In order to determine whether a triplet was involved in the reactions of bicyclic ketone **2** sensitization experiments were run using acetophenone as the sensitizer. These runs are summarized in Table III.

Table III. Acetophenone Sensitization Runs

Solvent	Quantum yields[a,b]		
	Bicyclic ketone[c]	Photo-acid[d]	Phenols[d]
73% aqueous dioxane[e]	...	(0.014)[e]	(0.037)[e]
80% t-BuOH	(0.087)	0.027	0.051
80% t-BuOH	(0.056)	0.034	0.051
80% t-BuOH	(0.13)	0.026	0.056

[a] 310–350-mμ filter; $C_6H_5COCH_3$ absorbing 97% of light except run 4 with 93% (correction applied). [b] Large uncertainty in bicyclic ketone due to contamination. [c] Disappearance. [d] Product appearance. [e] Quantum yields low due to competitive hydrogen abstraction from solvent by sensitizer.

In these runs bicyclic ketone concentration was maintained at ca. 2×10^{-3} M, a concentration sufficient to efficiently accept energy from acetophenone triplets prior to their decay while still low enough to ensure that acetophenone singlets would not survive long enough to collide and transfer energy prior to their destruction by intersystem crossing.[9]

With the same objective in mind, that of determining multiplicity, quenching of the reaction by naphthalene was attempted. These runs are summarized in Table

(8) Although the change in phenol distribution is of the same order as the variation in the total quantum yield, the latter are subject to an experimental error up to 10% while the phenol composition could be determined with greater precision. The trend in phenol composition thus seems real.

(9) The bimolecular rate of diffusion in t-BuOH has been estimated[1] as 2×10^9 l. mole^{-1} sec^{-1}. At 2×10^{-3} M bicyclic ketone, the pseudo-unimolecular rate of diffusion of acetophenone excited states to give collisions with bicyclic ketone becomes 4×10^6 sec^{-1}. However, the destruction of acetophenone singlet by unimolecular intersystem crossing to triplet has been found to be greater than 10^{10} sec^{-1},[10] and singlet destruction can be seen to be too fast for collision with bicyclic ketone. On the other hand, the unimolecular decay rate of triplet acetophenone has been measured (ref 11) as ca. 1×10^5 sec^{-1} in i-PrOH at room temperature, a rate low enough to allow most of the triplets to collide with bicyclic ketone prior to decay.

(10) F. Wilkinson and J. T. Dubois, J. Chem. Phys., **39**, 377 (1963).

(11) S. G. Cohen, D. A. Laufer, and W. Sherman, J. Am. Chem. Soc., **86**, 3060 (1964).

IV. In contrast to the sensitization experiments it can be seen that the presence of naphthalene had little effect on the quantum yields. The slight increase in 2,3-diphenylphenol per cent with increasing naphthalene is most likely a medium effect and follows the trend noted earlier.

Table IV. Quantum Yields with Naphthalene Present

Naph-thalene, M	Quantum yields[a,b]			% 2,3-diphenyl-phenol
	Bicyclic ketone[c]	Photoacid[d]	Phenols[d]	
0.063	0.145	0.091	0.070	82.5
0.099	0.145	0.091	...[e]	...[e]
0.156	...[e]	...[e]	...[e]	83.0
0.412	0.155	0.091	0.064	85.4
0.443	0.150	0.100	...[e]	...[e]

[a] 340–380-mμ filter; complete absorption by bicyclic ketone. [b] 73% aqueous dioxane. [c] Disappearance. [d] Appearance. [e] Not determined.

One other type of experiment was performed bearing on the reaction multiplicity. This was the determination of the ratio of phenols in sensitized photolyses as compared with unsensitized runs. These experiments were run in several solvents. For accuracy higher conversions were used than in the quantum yield runs. The results are compiled in Table V.

Table V. Distribution of Phenolic Products in Direct and Sensitized Irradiations

Solvent	% 2,3-diphenylphenol	
	Direct	Sensitized
t-BuOH	86.4	86.7
73% aqueous dioxane	79.8	79.9
80% aqueous t-BuOH	82.0	86.0

The Reaction Multiplicity. Discussion. The first indication that more than one multiplicity excited state was involved in the reactions of bicyclic ketone **2** was the marked change in the ratio of phenolic to acidic product when sensitization was employed. In the unsensitized runs the ratio averaged 0.7 while in acetophenone-sensitized runs the ratio was 1.9–2.6.

Several other experimental observations are relevant. First, the ratio of the isomeric phenols was essentially identical in sensitized and unsensitized runs in three different solvent systems (note Table V) and the effect of changing pH in sensitized runs was found close to that in unsensitized ones (note Figure 1). Second, despite difficulties in sensitization experiments which tended to give low quantum yields due to competitive hydrogen abstraction from solvent, the efficiency of phenolic product formation in the sensitized runs was close to that of the unsensitized experiments (note t-BuOH runs, Tables II and III).[12] Third, we find the

(12) It is to be noted that the quantum efficiency of acetophenone intersystem crossing is essentially unity,[8] signifying that the quantum yields of phenolic and acidic product in the sensitization experiments represent the true efficiency of formation of phenols starting with the triplet itself.

(13) (a) C. A. Parker and C. G. Hatchard, Analyst, **87**, 664 (1962), have reported a unity phosphorescence efficiency for acetophenone at low temperatures. (b) F. Wilkinson, J. Phys. Chem., **66**, 2569 (1962), has found acetophenone and benzophenone to photosensitize the reaction of 1-iodonaphthalene with equal efficiency, and the intersystem
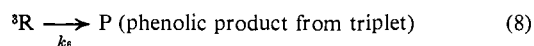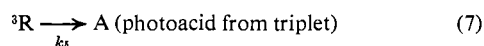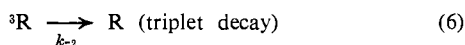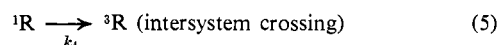
Table VI

k_4/L	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$^1\phi_A = k_2/L$	0.087	0.084	0.081	0.078	0.075	0.072	0.069	0.066	0.063	0.060	0.058
$^1\phi_P = k_3/L$	0.063	0.058	0.052	0.047	0.041	0.036	0.030	0.025	0.019	0.014	0.010
k_{-1}/L	0.850	0.758	0.667	0.575	0.483	0.391	0.299	0.207	0.115	0.023	...[a]

[a] Not a possible combination of rate constants.

average quantum yield for photoacid formation drops from 0.087 in direct irradiations to 0.029 in the sensitized runs. That the decrease in photoacid production on sensitization was real, and not due to the acetophenone triplet causing photoacid destruction, was demonstrated by control runs. Except for *cis–trans* isomerization, the photoacid was found to be stable.

At first glance one might be tempted to conclude that the identity of phenol isomer distribution with and without sensitization and the lack of major quantum yield change on sensitization demonstrate the phenol rearrangement to proceed exclusively by the triplet. Also, in the case of photoacid formation, one might attribute the 0.058 drop in quantum yield to absence of a singlet process constituting 0.058/0.087 (*i.e.*, *ca.* two-thirds) of the ordinary modes of formation of photoacid.

A consideration of the kinetics of the reactions helps to discern the validity of these conclusions. The following processes are potentially available.

$$\text{(bicyclic ketone) R} \xrightarrow{h\nu} {}^1\text{R (excitation of reactant to singlet)} \quad (1)$$

$$^1\text{R} \xrightarrow{k_{-1}} \text{R (singlet decay)} \quad (2)$$

$$^1\text{R} \xrightarrow{k_2} \text{A (photoacid from singlet)} \quad (3)$$

$$^1\text{R} \xrightarrow{k_3} \text{P (phenolic product from singlet)} \quad (4)$$

$$^1\text{R} \xrightarrow{k_4} {}^3\text{R (intersystem crossing)} \quad (5)$$

$$^3\text{R} \xrightarrow{k_{-2}} \text{R (triplet decay)} \quad (6)$$

$$^3\text{R} \xrightarrow{k_5} \text{A (photoacid from triplet)} \quad (7)$$

$$^3\text{R} \xrightarrow{k_6} \text{P (phenolic product from triplet)} \quad (8)$$
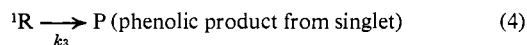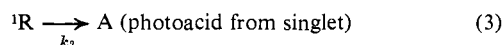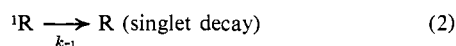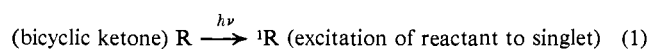
The steady-state assumption leads to expressions giving the partition of triplet

$$k_5/K = \phi_{AS} = 0.029 \quad (9)$$

$$k_6/K = \phi_{PS} = 0.053 \quad (10)$$

$$k_{-2}/K = (1 - \phi_{AS} - \phi_{PS}) = 0.918 \quad (11)$$

where $K = k_5 + k_6 + k_{-2}$. Also, for the singlets we find

$$^1\phi_A = k_2/L = \phi_A - (k_4/L)\phi_{AS} \quad (12)$$

$$^1\phi_P = k_3/L = \phi_P - (k_4/L)\phi_{PS} \quad (13)$$

where $L = k_{-1} + k_2 + k_3 + k_4$, $^1\phi_A$ is the contribution to the photoacid quantum yield derived from the singlet, $^1\phi_P$ is the portion of phenol quantum yield coming from the singlet, ϕ_{AS} is the observed sensitized quantum yield of the photoacid, ϕ_{PS} is the observed sensitized

quantum yield of phenols, and ϕ_A and ϕ_P are the unsensitized quantum yields.

We note from eq 12 that, since $k_4/L \leq 1$ by definition and $\phi_{AS} < \phi_A$ experimentally, $^1\phi_A$ is appreciable and must be equal to or greater than the difference in unsensitized and sensitized photoacid quantum yields (*i.e.*, $^1\phi_A \geq 0.058$).

However, in the case of the photophenols, the difference between ϕ_P and ϕ_{PS} is small and perhaps due in part to experimental difficulty or acetophenone quenching by photoacid. Thus, if k_4 approaches L, the singlet contribution $^1\phi_P$ to the quantum yield of phenols could be negligible. Although insufficient information is available to establish k_4, k_2, and k_3, these constants are interrelated by eq 12 and 13. Table VI gives the range of possibilities. The singlet contribution of photoacid production is seen to be $0.058 < {}^1\phi_A \leq 0.087$ and that for photophenols is $0.010 < {}^1\phi_P \leq 0.063$. Thus the kinetics does not establish the extent of singlet contribution although limits are set.

Since the argument above is not confined to the specific case in hand, it is worth stating as a general principle defining the extent of singlet contribution in a photochemical reaction. In general, the singlet participation in a photochemical process will be controlled by a relation of the type of eq 12. This states that the singlet contribution in an unsensitized reaction will lie between the upper limit of the unsensitized quantum yield and the lower limit of the unsensitized minus the sensitized quantum yield; if the latter quantity is negative, the lower limit is zero. The sensitization, however, must be of unit efficiency for this to be true.

Proceeding back to the identity of phenol isomer distribution with and without sensitization, we might conclude that this establishes a single multiplicity species as responsible for reaction and identified as the triplet. However, such evidence could merely mean that a common precursor to the phenols, and therefore controlling their ratio, is formed from both singlet and triplet. Such a precursor has been suggested above, namely the zwitterion, and, to the extent that some singlet contribution to phenolic product exists, the unchanging isomer ratio provides evidence for the zwitterion's existence rather than lack of multiplicity change. One argument favoring minimal singlet participation in phenol production is the lack of appreciable change in phenol quantum yield on sensitization. While this could be accounted for by any of the assortments of rate constants given in Table VI, this agreement would have to be fortuitous and resulting from a set of rate constants related in a unique way, and sensitization does show the availability of a triplet pathway. The simplest rationale is that all or almost all of the phenol is produced from the triplet. This is a reasonable but not rigorous conclusion.

Although, as can be seen in Table IV, there is no apparent quenching of either photoacid or phenolic

crossing of benzophenone is well accepted as of unite fficiency: *e.g.*, W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961). (c) S. G. Cohen, D. A. Laufer, and W. Sherman, *ibid.*, **86**, 3060 (1964). (d) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

product formation by naphthalene,[14] the data can be used to estimate a lower limit for the rates of rearrangement of triplet bicyclic ketone. If we signify the triplet concentration by (T), the quencher concentration by (Q), the rate at which triplet proceeds to product by k_r(T), the rate of unimolecular decay of triplet by k_d(T), and the quenching rate by k_q(Q)(T)—then we may write the quantum yield in presence of quencher as the rate of product formation divided by the sum of rates of all processes available to the triplet.

$$\Phi_q = k_r(T)/[k_r(T) + k_d(T) + k_q(T)(Q)] \qquad (14)$$

In absence of quencher this becomes

$$\Phi_0 = k_r(T)/[k_r(T) + k_d(T)] \qquad (15)$$

By dividing eq 14 by eq 15, we obtain the ratio of quantum yields for quenched and direct reactions as

$$\Phi_q/\Phi_0 = [k_r + k_d]/[k_r + k_d + k_q(Q)] \qquad (16)$$

Conservatively assuming that 20% quenching would have been observed if present in the run with 0.412 M naphthalene,[14] and assuming diffusion-controlled quenching with a rate of diffusion in t-butyl alcohol of 2×10^9 l. mole^{-1} sec^{-1},[1] we obtain a minimum value of 3.2×10^9 sec^{-1} for $(k_r + k_d)$. Taking the triplet quantum yield of phenol product as 0.063 and equating this to $k_r/[k_r + k_d]$, we obtain $k_d = 14k_r$ and a value of $k_r \gg 2 \times 10^8$ sec^{-1}. The rate of conversion of bicyclic ketone triplet to photoacid will have a comparable lower limit. Since this is a very conservative lower limit, k_a is probably tenfold or greater, $i.e.$, $k_r \geq 2 \times 10^9$ sec^{-1}.

General Mechanistic Discussion and Consideration of Molecular Details. Evidence has now been presented (A) that the conversion of bicyclic ketone **2** to 2,3-diphenylphenol and 3,4-diphenylphenol proceeds mainly via the triplet excited state, (B) that the formation of photoacid occurs from both singlet and triplet excited states of bicyclic ketone **2**, (C) that the triplet rearranges too rapidly to be quenched by naphthalene, (D) that the ratio of 2,3- to 3,4-diphenylphenol is dramatically changed by the medium acidity while the ratio of phenolic to acid product is not noticeably affected.

Several matters including these need further discussion. First, it has occasionally been suggested in the literature that the effect of solvent acidity on the reaction course derives from excited-state protonation. One might inquire whether it is operationally possible to distinguish between excited-state ($e.g.$, triplet) protonation and zwitterion protonation as originally proposed by us to account for the effect of acidity and medium on dienone product distribution,[4,15,16] and assumed above. In one case we proposed that a protonated zwitterion (**17**) led to isophotosantonic lactone (**19**)

while the mesoionic zwitterion (**16**) itself afforded lumisantonin (**18**)[17] (see Chart V). Actually the question is merely one of deciding at which stage the reacting species protonates, since our original suggestion and the later proposals of triplet-state protonation invoke our cationic species ($e.g.$, **17**) and the same reaction pathways of this intermediate. In fact,

Chart V
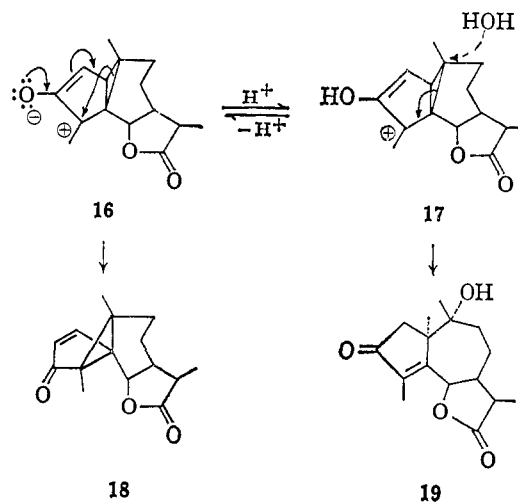
there will be all gradations of timing of protonation possible. The two extreme possibilities concur in using our species **16** and **17** in neutral and acidic media, respectively.
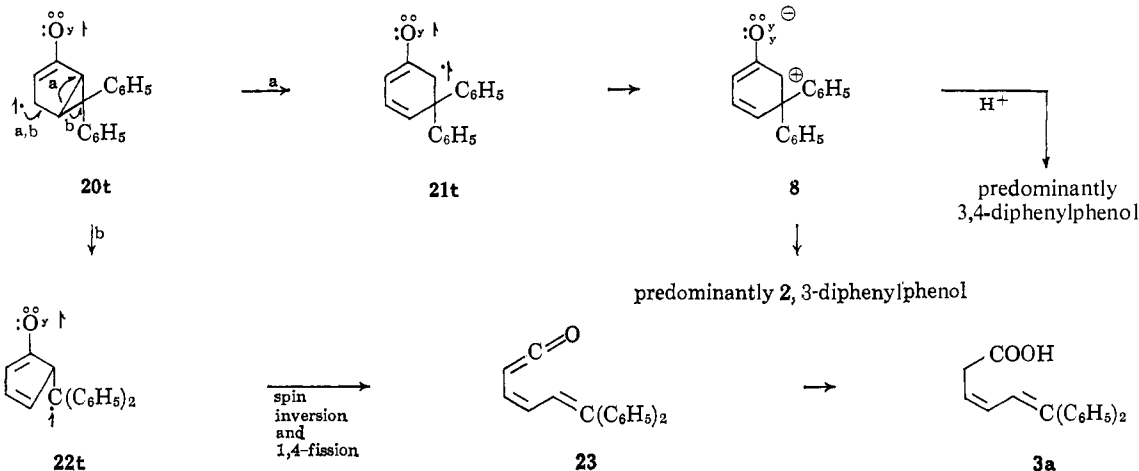
It proves possible to obtain evidence on protonation timing. First, we know that most of the phenolic product and $ca.$ one-third of the photoacid are derived from the triplet. Although the distribution of the isomeric phenols is pH dependent, the ratio of total phenolic product to photoacid is essentially independent of pH. It would be unreasonable to expect protonation of a single precursor to change the ratio of phenols to one another but not the ratio of their sum to the amount of photoacid. The results are, however, reasonably understood if the partition of triplet by the two acid-independent bond-fission processes labeled a and b in Chart VI determines the ratio of photophenols to photoacid while a subsequent, acid-dependent partition of mesoionic zwitterion **8** controls the distribution of the phenols.

A noteworthy point is that, as the acidity is increased, a noticeable change in the ratio of phenols begins at $ca.$ 0.01 M hydrogen ion while even 0.4 M naphthalene produces no noticeable triplet quenching. Thus the proton is capable of reaching the unknown intermediate controlling phenol isomer distribution while naphthalene cannot reach the triplet. The proton has a fast rate of diffusion, one which is $ca.$ 20 times more rapid[18] than that of naphthalene, but the 40-fold greater naphthalene concentration balances this giving the naphthalene a net advantage of twofold. Thus to a rough approximation the pseudo-unimolecular rate of protonation of the unknown species partitioning the

(14) No emission could be observed from the bicyclic ketone and a direct estimate of its triplet energy is unavailable. However, the n–π* singlet system for this compound is of normal energy (74 kcal/mole) although of anomalously high extinction (note Experimental Section) and the vertical triplet excitation energy of monoenones ($e.g.$, ref 1) is well above the 61 kcal/mole triplet energy of naphthalene. Hence naphthalene is a potential quencher.

(15) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, Abstracts, p 31.

(16) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963).

(17) The formation of isophotosantonic lactone provides one of the more convincing direct pieces of evidence for a species such as **16** and **17**, for here a nucleophile is picked up indicating the substrate to be cationic.

(18) The rate of hydronium ion protonation of acetate anion has been reported by M. Eigen and J. Schoen, *Z. Elecktrochem.*, 59, 483 (1955), as 4.5×10^{10} l. mole^{-1} sec^{-1} in aqueous solution. One might expect protonation in dioxane solution to be slower.

Chart VI

:Ö: C₆H₅
     a,b ᵇC₆H₅
20t

— a →

:Ö: C₆H₅
          C₆H₅
21t

→

:Ö:⊖   ⊕C₆H₅
           C₆H₅
8

H⁺ →

predominantly
3,4-diphenylphenol

|b

:Ö:
  C(C₆H₅)₂
22t

spin inversion and 1,4-fission →

C=O
    C(C₆H₅)₂
23

→

COOH
    C(C₆H₅)₂
3a

predominantly 2,3-diphenylphenol
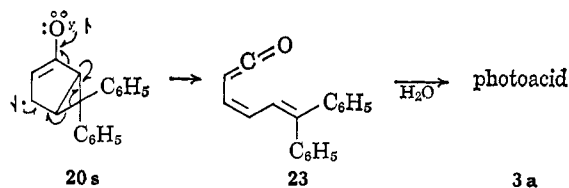
isomeric phenols should be one-half the corresponding rate of naphthalene quenching. Since the triplet is not quenched, it is concluded that the unknown species being protonated cannot be the triplet. Also, we note that the reactions of the triplet (steps a and b in Chart VI) are faster than naphthalene diffusion while phenyl migration in the unknown species is slower than protonation. A reasonable formulation for this longer lived species being protonated and rearranging to the 2,3- and 3,4-diphenylphenols is the mesoionic zwitterion **8**.[19]

A second matter requiring attention is the question why photoacid formation occurs heavily from the singlet in contrast to photophenol production. We note that the process originating from triplet to give photoacid, denoted b in Chart VI, is depicted as giving rise to a 1,4-biradical (**22t**) with unpaired electrons which then leads to ketene **23** by spin inversion and central bond fission. However, since the two odd electrons in the corresponding singlet excited-state **20s** are paired, there is the possibility of direct conjugation of the two electrons through the σ system so that bonds 1,2 and 3,4 can break concertedly, allowing singlet **20s** to collapse directly to cis-ketene **23** (see Chart VII). This fission process thus provides a

planar,[20] one might expect better overlap between the p orbital at the β-carbon with the external cyclopropane bond (a) compared with the internal bond (b); note Figure 3. In the case of the triplet this factor cannot be controlling, since more photophenols, deriving from internal bond fission, result than photoacid, which arises from peripheral bond scission.
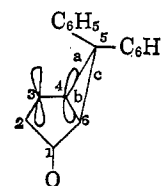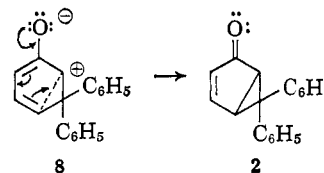
C₆H₅
        C₆H₅
Figure 3. Overlap in bicyclic ketone **2**.

A third aspect of the problem needing discussion is the reason for the low quantum yields for conversion of bicyclic ketone **2** to afford the diphenylphenols and photoacid. That at least the singlet process forming photoacid is rapid is evidenced by the partially successful competition of this process with intersystem singlet-triplet crossing which is generally very rapid in ketones.[9] It is therefore interesting that the corresponding triplet processes, where there is no rapid intersystem crossing to compete, do not prove to be efficient. One possibility is the intervention of a reversible reaction of the triplet. Potential candidates are: (i) reversal of bond a fission, (ii) reversal of bond b cleavage, (iii) reversal of bond breaking c, (iv) reversal of ketene formation.[21]

The reclosure of an internal bond-opened species might occur by 2,4 bonding of the zwitterion **8** to regenerate bicyclic ketone **2**. This would compete

Chart VII

:Ö: C₆H₅
          C₆H₅
20 s

→

C=O
    C₆H₅
    C₆H₅
23

H₂O → photoacid
3 a

direct single-step route from singlet excited state to product. We suggest that those singlet reactions in which the excited state can proceed directly to product in a one-step process will be particularly rapid. One other factor favoring the successful competition of singlet conversion to ketene over intersystem crossing in contrast to the unsuccessful conversion of singlet to photophenols is the geometry of the excited state. To the extent that the singlet excited enone moiety is

:Ö:⊖   ⊕C₆H₅
           C₆H₅
8

→

Ö:
    C₆H₅
    C₆H₅
2

(19) The weak points of this argument are the existence of a safety factor of only 2 and the uncertainty in the rate of hydrogen ion diffusion in the case of interest.

(20) The n–π* singlet and triplet of formaldehyde have been found to be pyramidal while the acrolein n–π* singlet seems to be planar or nearly so; note J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963), and references cited therein.

(21) Processes involving reclosure of an opened cyclopropane ring are reminiscent of the rationale suggested by J. N. Pitts and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954), to account for the low quantum yield of reaction of methyl cyclopropyl ketone.
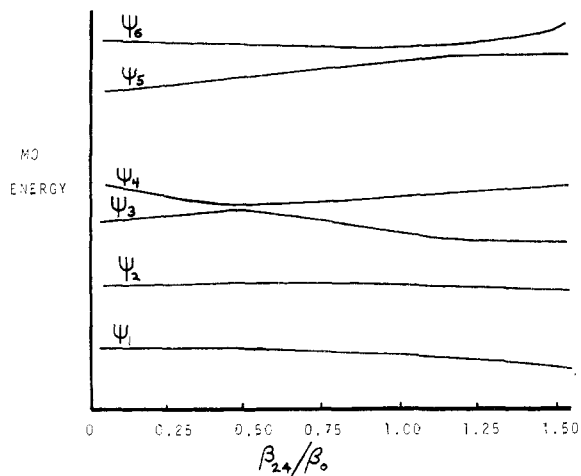
Figure 4. Correlation diagram for closure of zwitterion **8**.

with diphenylphenol formation. Simple one-electron, π-system calculations (Figure 4) show that as closure proceeds there is a tendency for the highest occupied MO, ψ_3, of the zwitterion to rise while the lowest vacant MO, ψ_4, lowers. The total energy of the species increases. If this situation were to persist with continued closure and increasing 2,4 overlap, MO's ψ_3 and ψ_4 would cross as in certain thermally difficult ("forbidden") processes.[22-24] Actually, it is found that crossing does not occur; MO's ψ_3 and ψ_4 "repel." The result, however, approaches that where a crossing actually occurs and one can predict the closing zwitterion **8** to have some barrier.[25,26] Closure cannot be dismissed as unreasonable. Similarly, the other reclosure processes may compete with reactions affording product.

A fourth and final point is of considerable interest. It was found that the dark, acid-catalyzed reaction of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**) did not afford the photochemically observed products. Rather 4-diphenylmethylenecyclopent-2-en-1-one (**24**) was obtained as the major product (83%). The formation of this substance is readily understood as protonation of the carbonyl oxygen of the bicyclic ketone followed by a typical carbonium ion process. To the extent that this process defines the behavior of the electron-

conjugate acid
of 2

24
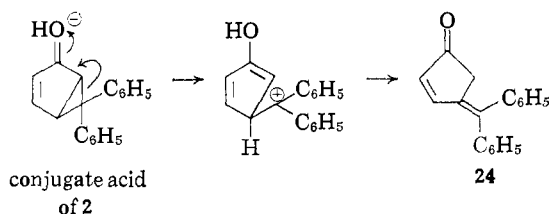
(22) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965), and related papers by R. B. Woodward and R. Hoffmann cited therein and in ref 20.

(23) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2046 (1965).

(24) H. E. Zimmerman, *ibid.*, **88**, 1564, 1566 (1966).

(25) Thus one notes that the absence of crossing of bonding and antibonding MO's does not ensure a facile reaction devoid of energy maxima. What is pertinent here is the "attempt to cross."

(26) One might have assessed the problem qualitatively by making the gross assumption that the negative charge is localized on the oxygen, in which case the remaining pentadienyl cation system needs to undergo a disrotatory[22] or Hückel[24] closure. Four-electron, five-carbon ring closures can be predicted to be preferred conrotatory[22] or Möbius,[24] which is sterically impossible in the present instance.

deficient carbon system of the bicyclic ketone, one may conclude that the excited-state reaction is not characteristic of such an electron-deficient system.

It is apparent that the evidence presented in the present paper has served to expand upon and refine the views we presented earlier to rationalize the reactions of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The related photochemistry of 4,4-diphenylcyclohexadienone will be described in a forthcoming paper in the present series.

Experimental Section[27]

Improved Synthesis of 4,4-Diphenylcyclohexenone. A mixture of 107 g (0.546 mole) of diphenylacetaldehyde and 38.3 g (0.547 mole) of methyl vinyl ketone in 800 ml of dry ether was stirred under nitrogen with cooling in ice. A solution of 9.95 g (0.178 mole) of potassium hydroxide in 60 ml of 95% ethanol was added dropwise during 30 min at the end of which time the solution was light orange; after stirring for an additional 30 min at 0° a light orange solid separated, and the mixture was poured onto ice. Enough benzene was added to dissolve the solid, and the mixture was neutralized to litmus with HCl affording two pale yellow layers. The aqueous layer was ether extracted and the combined extracts were dried and concentrated *in vacuo*. The gummy residue was dissolved in refluxing 95% ethanol (80 ml); crystallization resulted on cooling. Crystallization of the product yielded 85.8 g (0.346 mole, 63%) of colorless crystals, mp 91–94° (softening 88–91°) (lit.[4b] 88–91°).

4,4-Diphenylcyclohexadienone. This compound, mp 124.5–125.5° from hexane–methylene chloride, was prepared by a slight modification of the previously described[4] procedure.

Synthetic Photolysis of 4,4-Diphenylcyclohexadienone to Afford 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one. Filter combination B was used with the AH6 apparatus described below in connection with the quantum yield determinations. Separate runs of *ca.* 1 g were made in 700 ml of benzene and 50 ml of methanol at 25° under oxygen-free nitrogen using acetophenone as a sensitizer. The details were: run 1, 1.02 g (4.17 mmoles) of 4,4-diphenylcyclohexadienone, 20.3 g (0.169 mole) of acetophenone; run 2, 1.02 g (4.17 mmoles) of dienone, 20.4 g (0.170 mole) of acetophenone; run 3, 1.04 g (4.25 mmoles) of dienone, 20.6 g (0.172 mole) of acetophenone; run 4, 1.00 g (4.07 mmoles) of dienone, 21.0 g (0.175 mole) of acetophenone; runs 5 and 6, same as run 4. Runs 1–3 utilized 6.5 mEinsteins each and were processed together as were runs 4–6 which were irradiated with 8.3 mEinsteins. The photolysis mixtures were concentrated *in vacuo*, and the acetophenone was removed by short-path distillation at 39–42° bath temperature and 0.025 mm for 3–4 hr. The oily solid, mp 96–138°, from runs 1–3 was recrystallized from methanol and then from hexane–ethyl acetate to give 900 mg of colorless crystals of 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one, mp 137.8–139.9°. The filtrates were concentrated and subjected to liquid–liquid partition chromatography to give 1.16 g (4.72 mmoles) of recovered dienone, 700 mg of bicyclic ketone, 0.222 g (0.903 mmole) of mixed diphenylphenols, and 0.170 g of photoester; the last two fractions were not investigated. The light yellow bicyclic ketone was crystallized from hexane–ethyl acetate to give 0.550 g of colorless 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 138.5–142.0°, bringing the total yield to 1.45 g (47%, or 75% based on unrecovered dienone). Runs 4–6 afforded 1.17 g of bicyclic ketone, mp 140.0–140.2°, by crystallization and an additional 0.632 g from liquid–liquid partition chromatography.

Characterization of the *trans*-Photoacid. The major acidic product resulting from long irradiations was prepared and isolated as described by Zimmerman and Schuster.[4b] The solid was recrystallized from hexane–chloroform to give mp 116–117°. *Anal.* Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.69; H, 6.16. The infrared spectrum (CHCl$_3$) showed broad absorption from 2.8–4.5 μ characteristic of carboxylic acids and a carbonyl group at 5.85 μ. Other bands were at 6.70 (m), 6.92 (m), 7.08 (m), 7.78 (m), 8.21 (m), 9.30 (w), 9.70 (w), 10.26 (s), 10.68 (w) μ. The 10.26-μ band is characteristic of a *trans*-disubstituted double bond. The ultraviolet spectrum (95% EtOH) showed λ_{max} 227 mμ (14,250), 290 (24,600); nmr (CDCl$_3$): τ 2.76 singlet (10 H, aromatic),

(27) All melting points were taken on a hot-stage apparatus and are corrected.

3.2–4.3 multiplet (3 H, =CHCH=CH—), 6.85 doublet (2 H, $J =$ 6 cps, CH₂ adjacent to CH=).

Oxidative Degradation of *trans*-**6,6-Diphenyl-3,5-hexadienoic Acid.** The general method of Pappo, Allen, Lemieux, and Johnson[28] was employed. To a stirred solution of 0.264 g (1.0 mmole) of *trans*-photoacid in 30 ml of ether were added 30 ml of water and a solution of 0.466 g (1.8 mmoles) of osmium tetroxide in 3.0 ml of water. During 2 hr, 0.90 g (2.1 mmoles) of sodium metaperiodate was added to the dark solution, and the reaction mixture was refluxed for 0.5 hr. The dark ether phase was separated, the aqueous layer was ether extracted, and the combined extracts were dried and distilled. Sublimation of the residue using a hot water bath yielded 94 mg (51.5%) of colorless crystals, mp 44°, whose infrared spectrum was identical with that of authentic benzophenone, mp 47–48°.

The distilled solvent was stirred 4 hr with 2,4-dinitrophenylhydrazine reagent (3 g, 20 ml of 95% ethanol, 1 ml of sulfuric acid); the yellow ether phase was separated and the solvent removed *in vacuo*. The yellow residue was recrystallized from methanol to give 107 mg (47%) of yellow crystals, mp 164°, whose infrared spectrum was identical with that of acetaldehyde 2,4-dinitrophenylhydrazone, mp 167°. A mixture melting point with authentic material showed no depression.

Hydrogenation of *trans*-**6,6-Diphenyl-3,5-hexadienoic Acid.** The photoacid, mp 116–117°, was hydrogenated at 25° at atmospheric pressure; 142 mg of photoacid and 62 mg of platinum dioxide in 20 ml of ethanol were used. After 4 hr, 26.1 ml of hydrogen (746 mm), corresponding to 1.9 equiv, had been absorbed and the uptake diminished. Filtration and concentration *in vacuo* left 154 mg of residue, mp 83–88°, which was recrystallized from ether to afford colorless crystals, mp 92–93°. *Anal.* Calcd for C₁₈H₂₀O₂: C, 80.56; H, 7.71. Found: C, 80.02; H, 7.43. The infrared spectrum of this acid was identical with that of independently synthesized 6,6-diphenylhexanoic acid, mp 94–95°. A mixture melting point gave no depression.

6,6-Diphenylhexanoic Acid. To a solution of 33 mg (4.8 g-atoms) of lithium in 50 ml of liquid ammonia a solution of 530 mg (2.0 mmoles) of 6,6-diphenyl-5-hexenoic acid,[28] mp 112°, in 40 ml of ether was added with stirring. At the end of the addition, the color changed from blue to red. The reaction mixture was stirred for 3 hr with a Dry Ice condenser and sodium hydroxide drying tube and then 214 mg (4 mmoles) of ammonium chloride was added whereupon the solution became colorless. The ammonia was evaporated, 10 ml of 2 *N* hydrochloric acid was added, and the solution was ether extracted. The ether extract was dried and concentrated *in vacuo*. Recrystallization of the remaining solid from ether–hexane gave 339 mg (64%) of colorless crystals of 6,6-diphenylhexanoic acid, mp 94–95° (lit.[29] 94–95°). *Anal.* Calcd for C₁₈H₂₀O₂: C, 80.55; H, 7.51. Found: C, 80.11; H, 7.38.

Characterization of the *cis*-**Photoacid.** From quantum yield irradiations and short preparative runs made to low conversion an acid different from *trans*-6,6-diphenyl-3,5-hexadienoic acid was obtained. The new acid crystallized from hexane–ether to give colorless crystals, mp 92.5–94.0°. The infrared spectrum (CCl₄) showed 2.80–4.5 (broad), 5.84 (s, C=O), 6.70 (m), 6.93 (m), 7.08 (m), 7.16 (m), 8.27 (m), 9.03 (w), 9.32 (w), and 9.71 (w) μ. There was no absorption in the 10.1–10.4-μ region characteristic of a *trans*-disubstituted double bond. The ultraviolet spectrum (cyclohexane) showed λ_max 231 mμ (ε 15,390), 236 (ε 15,390), and 294 (22,800); nmr (CDCl₃): τ 2.64 (10 H, aromatic), 3.14 doublet (1 H, $J =$ 11 cps, Ar₂C=CH–), 3.73 triplet (1 H, $J =$ 11 cps, =CHCH=CH—), 4.2–4.6 multiplet (1 H, =CHCH₂), 6.71 doublet ($J =$ 7.5 cps, –CH₂–). *Anal.* Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.43; H, 6.12.

Irradiation of the *cis* acid with a Pyrex filter in 73% aqueous dioxane led to formation of the *trans* acid. Both the infrared and nmr spectra of the acidic fraction obtained from quantum yield determinations were identical with those of the pure *cis* acid while the spectra of the acidic fractions of prolonged irradiations approached that of the *trans* acid.

3,4-Diphenylphenol. The procedure of Zimmerman and Schuster,[4] as modified slightly, was employed. The product has mp 103.5–105.0° and an infrared spectrum identical with that of authentic material.[4]

2,3-Diphenylphenol. The previously described procedure[4] was used with slight modification. The product has mp 102.2–103.2° and an infrared spectrum identical with that of authentic material.[4]

Acid-Catalyzed Rearrangement of 6,6-Diphenylbicyclo[3.1.0]-hex-3-en-2-one. A solution of 104 mg of 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one in 10 ml of 1 *M* hydrochloric acid in 70% aqueous dioxane was refluxed for 2 hr. The yellow solution was then diluted with water, concentrated *in vacuo*, and ether extracted; the extracts were washed with 3% potassium hydroxide and dried over magnesium sulfate. Concentration *in vacuo* left 80 mg of an oil which was subjected to liquid–liquid partition chromatography on a 40 mm × 1 m column; 40-ml fractions were taken. Fractions 28–32 afforded 66 mg (83%) of a yellow solid. Fractions 33–45 gave 22 mg of impure starting material. Recrystallization of the yellow solid from 50% aqueous acetone gave yellow needles of 4-diphenylmethylenecyclopent-2-en-1-one, mp 109–110°. The infrared spectrum (KBr) showed 6.00, 6.73, 6.92, 7.23, 7.40, 9.30, and 12.90 μ; ultraviolet (95% EtOH): λ_max 243.5 mμ (ε 11,500) and 328 mμ (ε 19,800); nmr (CCl₄): τ 2.80 singlet (10 H, aryl), 2.22 doublet (1 H, $J =$ 6 cps, β =CH—), 3.82 doublet (1 H, $J =$ 6 cps, α =CH—), 6.95 singlet (2 H, CH₂). *Anal.* Calcd for C₁₈H₁₄O: C, 87.77; H, 5.73. Found: C, 87.39; H, 5.85.

6,6-Diphenyl-5-hexen-1,4-olide. From photolyses at pH values less than 3.9, increasing amounts of an additional component were obtained from the liquid–liquid partition chromatogram. This material was recrystallized from hexane–methylene chloride to give colorless crystals, mp 130.8–131.5°. The infrared spectrum of this compound in CCl₄ showed strong absorption at 5.70 μ characteristic of γ-lactones; other peaks were at 6.70, 6.91, 7.55, 8.55, 9.90, and 10.25 μ; ultraviolet (95% EtOH): λ_max 230 (ε 15,750) and 254 mμ (ε 16,500); nmr (CDCl₃): τ 2.75 multiplet (10 H, aryl), 3.96 doublet (1 H, $J =$ cps, =CH–), 5.0 multiplet (1 H, –CH–O–), and 7.55 multiplet (4 H, CH₂–CH₂). *Anal.* Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.44; H, 5.95.

Buffer Solutions. For the pH range 3.9–8.2, a buffer described by Robinson[30] was used. To 100 ml of solution 0.04 *M* in both phosphoric and acetic acids was added varying volumes of 0.2 *M* sodium hydroxide: 2.5 ml for pH 2.25, 17.5 ml for 3.25, 22.8 ml for 3.90, 31 ml for 4.75, 40 ml for 5.5, and 52 ml for 6.8. These pH's were observed using glass and calomel electrodes after dilution of 80 ml of the buffer with 200 ml of dioxane. For the range 1.0–2.2 a buffer[31] of 25 ml of 0.2 *M* potassium chloride with varying amounts of 0.2 *N* hydrochloric acid was employed followed by the same dilution with dioxane: 67.0 ml of HCl for pH 1.5, 42.5 ml for pH 1.8. For pH values less than 1.5, a buffer containing 25 ml of 0.2 *M* potassium bisulfate and variable amounts of 2 *N* sulfuric acid was used. For pH 0.4, 67 ml of acid was employed followed by the usual dioxane dilution. A pH of 0 was approached with 1 *N* hydrochloric acid in 70% dioxane–water. The measured pH of these buffer solutions was found not to change appreciably following irradiation.

Infrared Analysis. The method of Zimmerman and Cutshall[32] was employed; carbon disulfide was used. The optical density was taken as zero at 2 μ. Table VII summarizes the calibration data and analyses of known mixtures. Here D' refers to the optical density at 800 cm⁻¹ and D'' to the value at 820 cm⁻¹. The average value of $F = 1.02$ used. As usual[31] $R = QF$ where $Q = (D_m'D_{34}'')$

Table VII. Analysis of Known Mixtures of 2,3- and 3,4-Diphenylphenol

Actual % 2,3 isomer	D'	D''	Q	Actual R	Calcd F	Calcd R	Calcd % 2,3 isomer
0.0	0.5129	0.0409	...	...	...	...	...
24.4	0.1739	0.2684	0.309	0.323	1.04	0.315	24.0
51.8	0.2949	0.1945	1.06	1.07	1.01	1.08	51.9
73.5	0.4202	0.1203	2.78	2.78	1.00	2.83	73.9
100	0.0506	0.3098	...	...	...	...	...

(28) R. Pappo, D. S. Allen, R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

(29) G. Cauquil, J. Rouzard, R. E. Lyle, H. L. Fielding, and G. G. Lyle, *Bull. Soc. Chim. France*, (4) **43**, 861 (1955).

(30) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," 2nd ed, Academic Press Inc., New York, N. Y., 1959.

(31) H. T. S. Britton, "Hydrogen Ions," Vol. 1, D. van Nostrand Co., Inc., New York, N. Y., 1956, p 365.

(32) H. E. Zimmerman and T. W. Cutshall, *J. Am. Chem. Soc.*, **80**, 2893 (1958).

$- D_m''D_{34}')/(D_m''D_{23}' - D_m'D_{23}'')$, and the subscripts refer to the pure isomers or the mixture.

Irradiation Apparatus. Source I. For preparative irradiations a medium-pressure, 450-w Hanovia immersion lamp equipped with a Pyrex filter sleeve was used. Vanadous ion purified nitrogen and magnetic stirring were employed. The temperature was maintained at 10–20°. **Source II.** This was used for quantum yields and some preparative irradiations. The apparatus employed a GE AH6 high-pressure mercury arc centered at the focus of a parabolic reflector 13.7 cm long and 14 cm in diameter. The light was filtered by three water-cooled compartments, each with an optical path 12 cm in diameter and a 2.4-cm light path, placed in series and separated by gasketed quartz disks. In irradiations where light shorter than 300 mμ was not desired a 2-mm Corex D (Corning No. 9700) glass filter cutting off below 250 mμ (25% T at 276 mμ) was used preceding the filter cell to minimize filter solution decomposition. The photolysis cell contained two identical compartments 12 cm in diameter with a 5-cm optical path. Quartz plates were attached with epoxy cement to each end and between the cells; prior to use the cells were leached with methanol to remove potentially troublesome material. The cells were equipped with a thermistor probe, Trubore stirrer, heat-exchanger coil, nitrogen inlet, and capillary outlet. Light output was monitored by phototube as a check on filter and lamp decay.

Liquid–Liquid Partition Chromatography. This was employed since many of the compounds were not stable on common adsorbents. A two-phase system was obtained from 1000 ml of distilled cyclohexane, 400 ml of reagent dimethylformamide, 250 ml of reagent ethyl acetate, and 30 ml of distilled water, all equilibrated at 25°. The 42 mm × 1.5 m thermostated column was packed with Celite treated with 40% by weight of the lower phase and elution was with the upper phase. Monitoring was with ultraviolet at 250 or 280 mμ using a 0.006-in. quartz flow cell.

Phenol Isomer Ratio Photolyses. Irradiation apparatus I was used for these runs which were made to high conversion. Approximately 0.25 g of 4,4-diphenylcyclohexadienone was dissolved in 200 ml of 70% dioxane–buffer mixture and irradiated through Pyrex for up to 6 hr. The solution was concentrated *in vacuo* and extracted with ether. The extracts were washed with 3% potassium hydroxide solution, dried, and concentrated, and the residue was subjected to liquid–liquid partition chromatography. The phenolic fractions were analyzed by quantitative infrared to determine the ratio of 2,3- to 3,4-diphenylphenol.

In order to check the infrared analysis, in two cases the phenolic fraction from photolysis was separated by chromatography on a 100 × 3 cm silica gel column slurry packed in 1% ether-hexane. The 2,3-diphenylphenol was eluted with 5% ether–hexane while the 3,4-diphenylphenol was not eluted until 20% ether–hexane. The percentages of 2,3 isomer were: infrared, 81.9, isolation 78.6; infrared 77.4, isolation 80.5.

Stability of the Diphenylphenols under Irradiation. A 0.1658-g (0.674 mole) sample of phenolic mixture, 82.0% 2,3-diphenylphenol, was irradiated in 70% aqueous dioxane through a Pyrex filter with source I for 4 hr. The usual work-up gave 0.1580 g (95%) of crystalline solid analyzing as 80.8% 2,3-diphenylphenol.

Resistance of the Diphenylphenols to Base Extraction. A mixture of 313 mg of 2,3-diphenylphenol and 157 mg of 3,4-diphenylphenol was dissolved in 250 ml of ether, and the solution was base extracted in the usual manner. The ether phase was washed and dried as usual and concentrated *in vacuo* to leave 482 mg (100.2%) of an oily solid whose infrared analysis showed 66.6% 2,3 isomer. The starting percentage was 66.6.

Stability of Photoacid to Acetophenone-Sensitized Photolysis. A 89.0-mg, 1:1, mixture of *cis*- and *trans*-6,6-diphenyl-3,5-hexadienoic acids was irradiated under quantum yield conditions (2.35 mEinsteins of light) in 80% aqueous *t*-butyl alcohol. The usual work-up gave 93.5 mg (105%) of yellow oil with an infrared spectrum very similar to that of the *trans* acid; nmr showed the presence of both *cis* and *trans* acids plus small extraneous absorption at τ 6.58. Integration gave a *cis*:*trans* ratio of 1:1.7.

Stability of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one under Acidic Photolysis Conditions but without Light. A solution of 90.0 mg of bicyclic ketone in 200 ml of the 0.5 pH buffer (*vide supra*)-dioxane mixture was allowed to stand at room temperature for 6 hr in the dark and worked up as usual. Liquid–liquid partition chromatography afforded one peak, this consisting of 76 mg (85%) of solid bicyclic ketone.

Similar treatment of 116 mg of bicyclic ketone in 150 ml of 1 N hydrochloric acid in 70% aqueous dioxane afforded 105 mg (91%) of bicyclic ketone.

Quantum Yield Determinations. All quantum yield determinations were carried out at either 25.0 ± 0.1° or at 27.0 ± 0.1° in the described apparatus with appropriate filter. Each determination required three runs: (1) with both cells containing actinometer solution, (2) irradiation with the first cell containing reactants and the second cell filled with actinometer, (3) both cells with actinometer. In practice, less than 3% of the light reached the second cell. Before irradiation, vanadous-purified nitrogen was bubbled through the stirred solution for 1 hr, and during the irradiation a positive pressure of nitrogen was maintained. Both uranyl oxalate[33] and potassium ferrioxalate[34] actinometry were employed. A quantum yield of 0.55 was assumed for the former and 1.23 for the latter.

Quantum yield determinations of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one were run with filter C. Runs in the presence of naphthalene of this compound were done with filter E. Acetophenone-sensitized runs were carried out using filter D.

Filter Solutions. Transmission curves for the filter solutions were measured using a three-compartment cell with quartz end and separating plates; each compartment was 2.4 cm long. A 7.2-cm water reference cell was used. Transmission curves were determined just prior to and following each run. Owing to variations in commercial metal salts, it was necessary to adjust concentrations to fit the standard transmission curve desired. Nickel sulfate hexahydrate, cobalt sulfate heptahydrate, and copper sulfate pentahydrate were used in 10% sulfuric acid while stannous chloride dihydrate was used in 10% hydrochloric acid. Filter A: cell I, 26.3 g of nickel salt/l.; cell II, 225.0 g of cobalt salt/l.; cell III, 45.0 g of tin salt/l. (transmission: 325–385 mμ, maximum at 351 mμ; 210–320 mμ, 0%; 340 mμ, 39%; 350 mμ, 53%; 360 mμ, 44%; 370 mμ, 21%; 380 mμ, 7%; 390–430 mμ, 1%; 440–570 mμ, 0%. Filter B: cell I, 26.3 g of nickel salt/l.; cell II, 250.0 g of cobalt salt/l.; cell III, 4.75 g of tin salt/l. (transmission: 310–365 mμ, maximum at 330 mμ; 210–305 mμ, 0%; 310 mμ, 4%; 320 mμ, 41%; 330 mμ, 50%; 340 mμ, 35%; 350 mμ, 20%; 360 mμ, 5%; 370–570 mμ, 0%). Filter C: cell I, 36.0 g of nickel salt/l.; cell II, 281.0 g of cobalt salt/l.; cell III, 75.0 g of tin salt/l. (transmission: 330–380 mμ, maximum at 351 mμ; 210–320 mμ, 0%; 330 mμ, 0.5%; 340 mμ, 20%; 350 mμ, 40%; 360 mμ, 30%; 370 mμ, 11%; 380 mμ, 2%; 390–410 mμ, 1%; 420–570 mμ, 0%). Filter D: cell I, 450.0 g of nickel salt/l.; cell II, 281.0 g of cobalt salt/l.; cell III, 3.50 g of tin salt/l. (transmission: 310–350 mμ, maximum at 323 mμ; 210–300 mμ, 0%; 310 mμ, 10%; 320 mμ, 28%; 330 mμ, 28%; 340 mμ, 10%; 350 mμ, 1%; 360–570 mμ, 0%). Filter E: cell I, 50.0 g of nickel salt/l.; cell II, 281 g of cobalt salt/l.; cell III, 150.0 g of tin salt/l. (transmission 340–380 mμ, maximum at 355 mμ; 210–330 mμ, 0%; 340 mμ, 3%; 350 mμ, 22%; 360 mμ, 22.5%; 370 mμ, 7%; 380 mμ, 1%; 390–460 mμ, 0%). The above filters afforded 3–13 mEinsteins/hr with the AH6 apparatus.

Products and starting material were assayed by isolation using liquid–liquid partition chromatography. Additionally, the ultraviolet spectrum in the 310–400-mμ region proved useful as a second means of assaying disappearance of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. 6,6-Diphenyl-3,5-hexadienoic acid was isolated by extraction with 5% sodium hydroxide solution. In acetophenone-sensitized runs, the concentrate was subjected to treatment at 35–40° (0.08 mm) with a Dry Ice receiver to remove acetophenone. In runs with naphthalene quencher, naphthalene was removed either by crystallization from methanol followed by partition chromatography or initial vacuum sublimation; the naphthalene removed was shown to be free of other materials. Products were identified by infrared and nmr spectra.

Calculations. LCAO MO calculations were carried out on species **12, 13, 14,** and **15** using the general procedure of Zimmerman and Zweig[34] for phenonium species. The same parameters were used except that the incremental value of the Coulomb integral for the phenonium hybrid orbital was taken as 2β, the increment for the zwitterionic oxygen as 0β, and that for the protonated oxygen as 2β. For the zwitterion itself (Figure 2, species **8**) the oxygen increment was 1β; however, the relative charges at C-2 and C-4 proved very insensitive to this choice.

(33) C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry," Vol. II, 2nd ed, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 257.
(34) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).