may be either *exo* or *endo*. (3) The rate constants for ionization of *exo*- and *endo*-$OCD_3$ from the two possible isomers (III-$d_3$) are $k_{ex}$ and $k_{en}$, respectively. But only the fraction, $k_{en}/(k_{ex} + k_{en})$ or $k_{ex}/(k_{ex} + k_{en})$, respectively, of the resultant ions (IV) capture $D_3COD$ in such fashion as to effect conversion of one isomer into the other.

For solving the linear differential equations implied by these kinetics, a matrix method[17] is especially convenient, since it can readily be extended to correct for reversibility. Let **C** be a column matrix whose elements are the concentrations of the four chemical species, as a function of time, *t*, let $\dot{\mathbf{C}}$ be a column matrix whose elements are the time derivatives of these concentrations, and let $\mathbf{C}_0$ be **C** at time zero. The four differential equations may be abbreviated as a single matrix equation, $\dot{\mathbf{C}} = \mathbf{KC}$, where **K** is a 4 × 4 matrix of appropriate rate constants. The solution is given by $\mathbf{C} = \mathbf{X}\exp(\Lambda t)\mathbf{X}^{-1}\mathbf{C}_0$, where **X** is a 4 × 4 matrix whose columns are the eigenvectors of **K**, $\mathbf{X}^{-1}$ is its inverse, and $\exp(\Lambda t)$ is a diagonal matrix whose diagonal elements are the exponentials of *t* times the eigenvalues of **K**. Thus it is possible to solve for the total concentrations of *exo* and *endo* methoxyls as a function of time.

To take account of the incursion of reversibility, the rate constants for reactions replacing $OCH_3$ by $OCD_3$ must be multiplied by $f_D$, the fraction of $D_3COD$ in the solvent. Also, rate constants for the reverse reactions must be introduced, and these will involve instead $f_H$, the fraction of $H_3COD$ in the solvent. As a result, the rate constant matrix is no longer **K**, but $\mathbf{K} + f_H\mathbf{K}'$.

Since $f_H$ increases as the exchange reaction proceeds, a second-order component is introduced into the kinetics. These kinetics could not be solved analytically, but the effect of reversibility was considered as a small correction. Perturbation theory was used to determine the first-order correction to the eigenvector matrix, **X** (the first- and second-order corrections to the eigenvalues vanish), to obtain the form of a correction term to be applied to the experimental data, so that they could be related to the rate constants as shown in eq 1 and 2. Further details are available on request.

# The Mechanism of the Photochemical Valence Tautomerization of 2,3-Diphenylindenone Oxide. IV. Evidence for Vibrationally Excited Ground-State Intermediates[1a]

**Edwin F. Ullman**[1b] **and Wm. A. Henderson, Jr.**

*Contribution from the Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904.* *Received June 1, 1966*

**Abstract:** It has been shown that 2,3-diphenylindenone oxide (I) and its valence tautomer (II) are photochemically interconverted. Sensitization, quenching, and quantum yield measurements permit a quantitative analysis of the fate of each of the excited states of I. It is shown that the rate of crossing from the excited states to the ground state of I is much greater than in unreactive ketones. These data together with other evidence that tends to exclude interconversions of any of the electronically excited states of I with electronically excited states of II strongly suggest that both the forward and reverse reactions proceed through vibrationally excited ground states of the two tautomers. Vibrationally excited ground-state molecules are thought to arise during crossing from electronically excited states, and the data suggest that the vibrational energy is not randomly distributed immediately after crossing but is concentrated at the reaction site. In developing these arguments most of the side products of these reactions have been identified and data bearing on the mechanisms of their formation are described. A particularly interesting sequence of steps has been established for the formation of *cis*- and *trans*-3-ethoxy-2-hydroxy-2,3-diphenylindanones (VIII and IX) during irradiation of I in alcohol.

In recent years there has been considerable controversy concerning the mechanism of the photochemical rearrangements of unsaturated epoxy and cyclopropyl ketones.[2] While hypothetical dipolar intermediates derived by cleavage of the three-membered ring have been employed with substantial success in rationalizing the products of the reactions,[2,3] the question of the mechanism of formation of these intermediates and the nature of the electronic state (excited or ground) of the intermediates at the time of their formation remains a matter of conjecture.[4] The recent observations that 2,3-diphenylindenone oxide (I)[1a,5] and the related tri- and tetraphenyl-2,3-epoxycyclopent-4-en-1-ones (III, R = H and Ph, respectively)[6,7]

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[1] (a) A preliminary report of this work has appeared previously: E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **86**, 5050 (1964); (b) to whom inquiries should be addressed at Synvar Research Institute, Palo Alto, Calif.

[2] For reviews of these reactions see (a) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964); (b) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (c) O. L. Chapman, *ibid.*, **1**, 323 (1963).

[3] See *inter alia* (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) P. J. Kropp, *Tetrahedron*, **21**, 2183 (1965); (d) B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chem. Acta*, **48**, 1680 (1965); (e) O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, **85**, 3028 (1963).

[4] See discussions by G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963), and J. Saltiel, *Surv. Progr. Chem.*, **2**, 293 (1964).

[5] E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **84**, 1315 (1962); **86**, 3814 (1964).

[6] E. F. Ullman, *ibid.*, **85**, 3529 (1963).

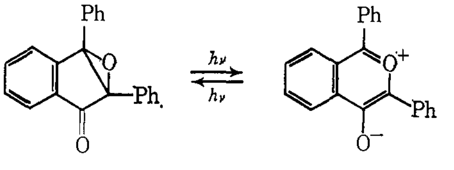
[7] J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964).

Table I. Product Ratios Obtained on Irradiation of Benzene Solutions of 2,3-Diphenylindenone Oxide

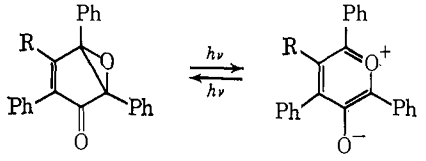
| | Reaction conditions | | | | | Products, % | | | |
|---|---|---|---|---|---|---|---|---|---|
| Run | Temp, °C | λ[a] | Time, hr | Wt of I, g | Vol., ml | I | V | VIa | VII |
| 1[b] | 25 | Ultraviolet | 52 | 1.58 | 50 | 55 | | 33 | |
| 2 | 25 | Ultraviolet | 24 | 0.10 | 10 | 38 | 29 | 26 | ~5 |
| 3 | 25 | 3650 A | 36 | 0.10 | 10 | 39 | 26 | 23 | ~5 |
| 4 | 145 | Visible | 102 | 0.10 | 60 | 100[c] | | | |
| 5 | 25 | Ultraviolet, visible | 24 | 0.20 | 70 | 39 | 53 | <1 | <1 |

[a] Runs marked ultraviolet or visible were irradiated with 3100–4000- (GE B-H6 lamp) or >4350-A (500-w projector) light, respectively. [b] The yields given in this run represent products isolated by crystallization only. [c] The reaction mixture consisted of pure I and no purification was carried out.

undergo reversible photoisomerization to analogous dipolar species, the deep red pyrylium oxides II and IV (R = H and Ph), lend support to this dipolar intermediate hypothesis.[8] Since these dipolar products are relatively stable and can be observed directly, the reactions of I and III permit a closer examination of the initial photoisomerization process than has been possible in the cyclopropyl ketone reactions where the existence of the dipolar species manifests itself only in the nature of its rearrangement products. We have therefore carried out an investigation of the mechanism of the photochemical interconversion of the epoxy ketone I with the benzopyrylium oxide II in the hope of defining the exact sequence of geometrical and energetic changes that occur after absorption of light energy.



I II

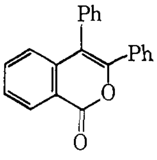


III IV

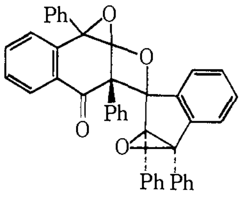
## Results

**Photochemical Products.** It has already been shown that the indenone oxide I undergoes a photochemically reversible isomerization to its red valence tautomer II, and that the parallel thermal interconversions between I and II also take place.[5] Thus, on irradiation of solutions of the colorless epoxide I, there are produced deeply colored solutions which eventually reach a nearly constant color intensity that is dependent on the relative rates of each of the thermal and photochemical isomerization processes. However, on continued irradiation, the color intensity slowly begins to drop off until eventually no color remains. The nature of the products formed during this process is dependent on a number of factors which have been examined in some detail.

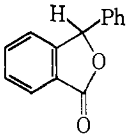
Irradiations of degassed benzene solutions of I with ultraviolet light (see runs 1–3, Table I) were continued until the photostationary color intensity was strongly reduced. The remaining pyrylium oxide II was then reconverted to I by irradiation with >4350-A light[5,9] and the products were isolated by chromatography. The photolysis mixtures yielded 3,4-diphenylisocoumarin[10] (V), the dimer VIa,[5] and 3-phenylphthalide[11] (VII) together with unchanged diphenylindenone oxide I, each of which was identified by direct comparison with an authentic sample. None of the reaction mixtures contained the dimer VIb, which was always formed along with its stereoisomer VIa on heating benzene solutions of I.[5]



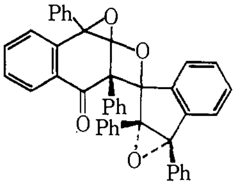
V



VIa



VII



VIb

The formation of each of these products might of course result from photoexcitation of either or both of the two valence tautomers I and II. In order to determine whether any of these photoproducts in addition to I were formed when only the red pyrylium oxide II absorbed light, it was necessary to devise an experiment in which only II would receive photo-

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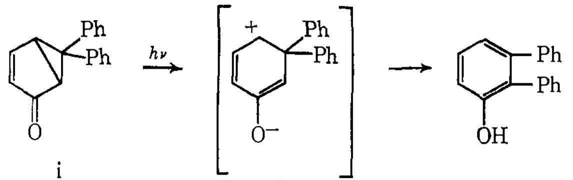
(8) Compare, for example, the closely related proposed intermediate ii in the photochemical rearrangement of i.[3b]



i ii

(9) Failure to reconvert II back to I before allowing air into the solution led to the formation of oxidation products of II: W. A. Henderson, Jr., unpublished results.

(10) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327, 2334 (1921).

(11) F. Ullmann, *Ann.*, **291**, 23 (1896).

**Table II.** Product Ratios Obtained on Irradiation of Ethanol Solutions of 2,3-Diphenylindenone Oxide

| | Reaction conditions | | | | | Percentage products | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Run[a] | Temp, °C | λ[b] | Time, hr | Wt of I, g | Vol., ml | I | V | VII | VIII | IX | XII |
| 6 | 25 | Ultraviolet | 36 | 2.0 | 150 | 8 | 8 | | 58 | 27 | |
| 7 | 25 | Ultraviolet | 11 | 0.075 | 20 | 5 | 7 | | 55 | 33 | |
| 8 | 25 | Ultraviolet, visible | 11 | 0.075 | 20 | 14 | 33 | Trace | 35 | 17 | |
| 9 | 125 | Visible | 22 | 0.5 | 60 | 48 | 40 | Trace | | 10 | Trace |
| 10 | 120 | Dark | 144 | 0.5 | 29 | | | | | 76 | 11 |
| 11 | 128 | Visible | 23 | 0.5 | 100 | 29 | 47 | Trace | | 23 | Trace |
| 12 | 128 | Dark | 23 | 0.5 | 100 | | 8 | | | | >64 |
| 13 | 125 | Visible | 32 | 0.5 | 100 | 15 | 57 | Trace | | 12 | 13 |
| 14 | 125 | Dark | 32 | 0.5 | 100 | | 6 | | | | 88 |

[a] Bracketed pairs of runs were conducted simultaneously under identical conditions except for the indicated differences in light sources.
[b] Runs marked ultraviolet or visible were irradiated with 3100–4000- (GE B-H6 lamp) or 4350-A (500-w projector) light, respectively.

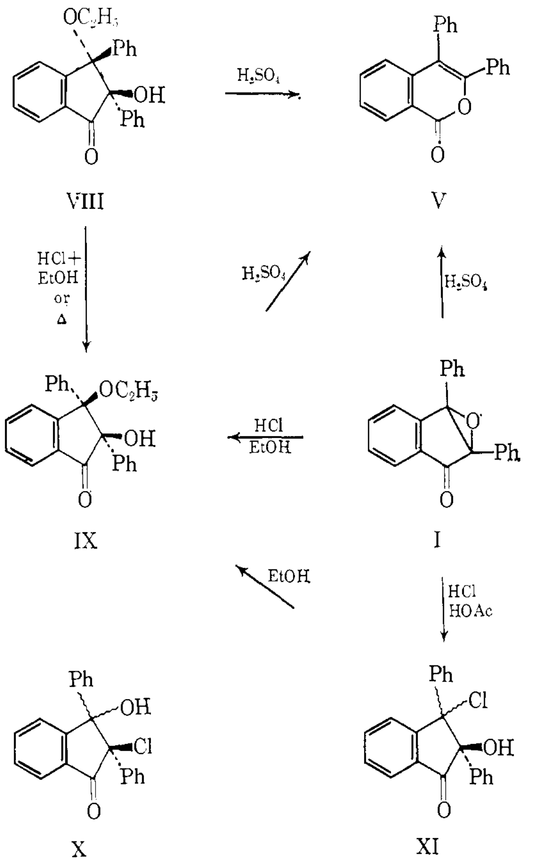
chemical excitation. For this purpose use was made of the fact that the thermal equilibrium concentration of II, while very low at room temperature, is increased at elevated temperatures.[5] The photochemistry of II alone could therefore be studied by irradiation of a hot (145°) degassed benzene solution of I with >4350 A light. Under these conditions only the red species II was photochemically excited, since the light was absorbed only by II, and energy transfer from excited II to I could be excluded by consideration of the excited energy levels of the two compounds (*vide infra*).

During the reactions, the solutions, which would normally be colored in the dark, were almost completely colorless due to the rapid reconversion of II to I by the intense light. From the rate of appearance of II on turning off the light it could then be shown that in one run (run 4, Table I) the indenone oxide I had recycled from I to II thermally and back to I photochemically about 36 times. Nevertheless, the residue that was obtained on evaporation of the solvent was indistinguishable from the starting material. Apparently, therefore, none of the reaction products observed on ultraviolet irradiation of I in benzene arise directly from photoexcitation of II. However, the formation of the dimer VIa appears to require the *presence* of II, for no dimer was formed even on absorption of light by I, if the concentration of II was kept low by the use of intense visible light (>4350 A) (run 5, Table I).[12]

As in benzene solution, when the indenone oxide I was irradiated in ethanol with 3100–4000-A light the red pyrylium oxide II was formed. The color did not become as intense in this solvent and continued irradiation led to a faster rate of destruction of the starting material. The reaction products consisted principally of two hydroxy ethers VIII and IX together with a smaller amount of the isocoumarin V (runs 6–7, Table II). The structures of the hydroxyethers VIII and IX were based on the following evidence.

Both compounds displayed ultraviolet absorption very similar to that of 1-indanone and infrared carbonyl absorption at 5.78 μ which was in accord with an aromatic five-membered ring ketone. The nmr spectra of both compounds showed signals for hydroxy and ethoxy groupings together with 14 aromatic hydrogens, and the ethoxy signals showed nonequivalence of the two methylene protons, as would be expected if the ethoxy groups were attached to asymmetric centers. The chemical transformations of these compounds, shown in Chart I, strongly suggest that the ethoxy grouping in IX is positioned *β* to the carbonyl. Thus, compound IX was readily prepared by alcoholysis of the previously known chlorohydrin XI.[13] The latter compound must have the indicated structure since it is very sensitive to solvolytic conditions whereas its structurally unambiguous position isomer X is quite inert.[14] The hydroxy ether VIII must likewise have its

**Chart I**



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(12) (a) These observations require that either the dimer is formed by reaction of an excited state of I with ground-state II, or, in the event that II cannot undergo intersystem crossing, that the dimer is formed by sensitization of II (by $^3$I) followed by reaction of $^3$II with ground-state I. (b) The thermal formation of the stereoisomeric dimers VIa and VIb also requires the presence of the red species II as is demonstrated by the suppression of this reaction with >4350-A light (run 4, Table I). It is noteworthy that this is an unusual example of a reaction which can proceed only in the absence of strong light.

(13) A. Banchetti, *Gazz. Chim. Ital.*, **81**, 419 (1951).

ethoxy group in the solvolytically reactive $\beta$ position since this compound could be converted to the isomeric IX in alcoholic acid. Moreover, a vicinal relationship of the hydroxy and carbonyl groupings in VIII could be demonstrated through the uptake by this compound of 1 equiv of periodic acid. On the other hand, IX surprisingly failed to react with periodic acid even though the above data leave little doubt that it too must have a vicinal relationship of the hydroxy and carbonyl groupings.

As regards the stereochemistry of these products, the infrared spectrum of isomer IX in dilute carbon tetrachloride solution displayed intra- and intermolecularly bonded O–H stretching absorption maxima at 2.821 and 2.894 $\mu$, respectively, whereas VIII showed corresponding maxima at 2.795 and 2.905 $\mu$. Hence, the hydroxy group in IX appears to be more strongly hydrogen bonded and *cis* to the adjacent ether oxygen, while the more weakly internally hydrogen-bonded VIII must then have the *trans* configuration.[15] The same conclusions are indicated by the nmr spectra of VIII and IX; stronger intramolecular hydrogen bonding in IX than in VIII is suggested by the lower field OH signal for IX at $\tau$ 5.88 than for VIII at $\tau$ 7.67 (extrapolated to infinite dilution in deuteriochloroform). Moreover, the abnormally high-field methyl signal of VIII ($\tau$ 9.19) as compared to the normal position of this signal in IX ($\tau$ 8.92)[16] is in accord with the expected effect of induced ring currents in the 2-phenyl group on the chemical shift of a *cis*-related 3-ethoxy group. These arguments thus lead to the unexpected conclusion that the more stable hydroxy ether IX has the more crowded *cis* configuration, a result which may possibly be due to stabilization of this isomer through internal hydrogen bonding.

An investigation of the origins of the products produced by irradiation of the indenone oxide I in alcohol gave quite different results from those obtained from experiments carried out with benzene as solvent. In a manner similar to the benzene runs, an ethanol solution of I was heated at 125° to generate the pyrylium oxide II, and the solution was simultaneously irradiated with >4350-A light which could be absorbed only by the red species II (run 9, Table II). On evaporation of the ethanol only a portion of the starting material could be recovered as compared to the quantitative recovery from the parallel benzene run (run 4, Table I). The remainder of the reaction mixture contained mostly the isocoumarin V together with small amounts of the *cis*-hydroxy ether IX, the phthalide VII, and 1-benzoyl-3-phenylisobenzofuran (XII).[17] None of the *trans*-hydroxy ether VIII could be detected. Apparently, therefore, VIII is not formed photochemically from the red species II, while the other products are either formed photochemically from II or else arise by thermal reactions.

In an attempt to sort out the thermal from the photochemical reactions, the above experiment was repeated with control runs (runs 11–12 and 13–14, Table II) that were carried out under identical conditions but in the dark. Product analyses showed that, as before, the major product of those runs that were carried out with irradiation (runs 11 and 13) was the isocoumarin V, while in the parallel dark reactions (runs 12 and 14) the isobenzofuran XII was the principal product. Since only low yields of the isocoumarin V were produced in the dark these observations seemed to suggest that V must be formed principally by a photochemical reaction of II. However, an alternative explanation required consideration; conceivably the isocoumarin V was formed during the photoreactions exclusively by a thermal reaction of I. The decrease in the yields of V obtained in the dark might then be caused by depletion of I through the failure of II to be thermally reconverted to I because of competitive thermal reactions of II leading to IX and XII. Since the starting material I was recovered from the photo but not from the dark reactions this interpretation seemed quite plausible.

In order to differentiate between these alternatives, the red species II was generated in two parallel runs by irradiation of an ethanolic solution of I with 3100–4000-A light rather than by heat. The effect of light on II alone was then determined by comparison of the products obtained in the two runs when one of the solutions had been simultaneously irradiated with strong visible light (>4350 A) that could be absorbed only by II. The product distributions (runs 7 and 8, Table II) demonstrate that the visible light again produced a marked increase in the percentage of the isocoumarin V formed. Thus the results support the conclusion that the isocoumarin V is produced photochemically from the pyrylium oxide II. However, they do not exclude the possibility that V might also be formed photochemically from the indenone oxide I.

As for the origin of the hydroxy ethers VIII and IX, the data in Table II suggest that the *cis*-hydroxy ether IX can be formed not only by irradiation but also by heating the indenone oxide I in ethanol. The thermal reaction is erratic (*cf.* run 10 with runs 12 and 14), and it could be demonstrated that the formation of both the *cis*-hydroxy ether IX and the isobenzofuran XII are controlled by adventitious catalysis by traces of acid or base. Acids were found to catalyze the formation of IX (Chart I) while the isobenzofuran XII could be formed in 73% yield by heating an ethanolic solution of I in a flask that had been pretreated with aqueous potassium hydroxide.[18] The photochemical reactions leading to formation of the hydroxy ethers were, on the other hand, readily reproducible. The *trans* compound VIII clearly is formed only with ultraviolet and not with visible light (*cf.* runs 6–8 with runs 9–14), and the same is probably also true of the *cis* compound IX (*cf.* runs 7 and 8) although the data is not compelling on this latter point. It therefore follows that VIII and probably IX are not formed photochemically from the pyrylium oxide II.

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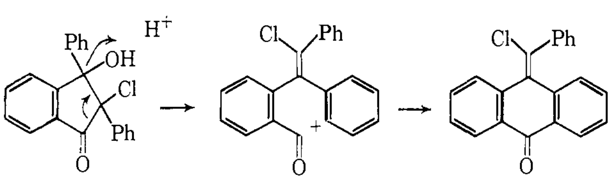
[14] Compelling evidence for structure X has been obtained by its sulfuric acid catalyzed conversion to iii.[13]



X

iii

[15] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

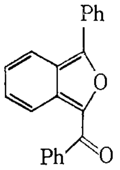
[16] *Cf.* the methyl signal of ethanol at $\tau$ 8.79: "High Resolution Nmr Spectra Catalogue," Varian Associates, Palo Alto, Calif.

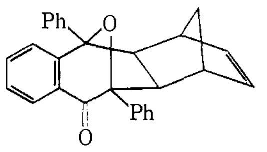
[17] C. F. H. Allen and J. W. Gates, Jr., *J. Am. Chem. Soc.*, **65**, 1230 (1943).

[18] Unpublished observation by Mr. R. Lopresti.

By elimination it would seem that the hydroxy ethers must be formed by a photochemical reaction of the indenone oxide I. Nevertheless it seemed necessary to demonstrate that this was the case. Accordingly, ethanol solutions of I containing 10% norbornadiene, a reagent that had been found to react almost instantaneously with II,[5] were irradiated with 3100–4000-A light, and the hydroxy ethers VIII and IX were looked for among the products. However, the only product detected was the norbornadiene adduct XIII[5] which was obtained in 98% yield. By using ethanol-1-C$^{14}$ as solvent it was found by the isotope dilution technique that the *trans*-hydroxy ether VIII had been formed in $\leqslant$0.21% yield. This was too low a value to account for the fact that VIII was the major product obtained when the norbornadiene was omitted (run 6), for the amount of light absorbed by I in run 6 would have produced <1% of the hydroxy ether VIII if VIII had been formed exclusively from I with 0.21% efficiency. Thus, these observations eliminate both I and II as immediate photochemical precursors of at least the *trans*-hydroxy ether VIII, and they cast doubt on the origin of the *cis* isomer IX as well!

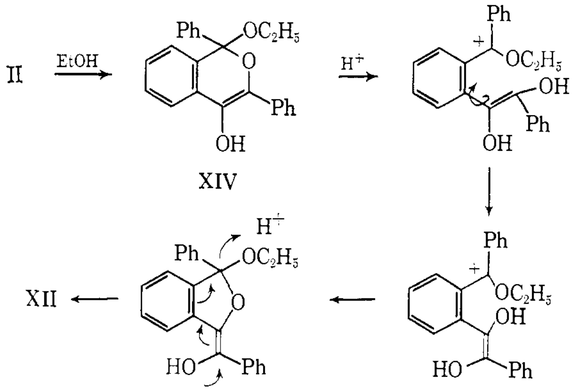
A clue to the true origin of the hydroxy ethers appeared in the observation that the red color faded nearly 1000 times more rapidly in alcohol ($k^{25} = 1 \times 10^{-3}$ sec$^{-1}$) than it did in benzene, even though polar solvents would be expected to stabilize the highly polar II relative to I. Moreover the spectral changes accompanying the disappearance of II in alcohol were not consistent with the reformation of the indenone oxide I.


XII


XIII

Thus even after complete disappearance of the long wavelength absorption of II there remained strong residual absorption near 327 mμ that was not associated with any isolable product. This new peak disappeared gradually over a period of several hours until the absorption in this region was only slightly different from that of a solution of pure indenone oxide I. This metastable species proved to be sensitive to a number of reagents. Bromine produced a nearly instantaneous disappearance of the 327-mμ peak, leaving residual absorption (after destruction of excess bromine with 2-octene) very similar to that obtained by allowing the peak to disappear spontaneously. On the other hand, dilute hydrochloric acid produced a slower (~5 min) disappearance of the peak with a concerted appearance of a new maximum at 425 mμ (isosbestic point at 368 mμ). The 425-mμ maximum proved to be identical in shape and position with the long wavelength maximum of the isobenzofuran XII. Finally, dilute sodium hydroxide solution caused an instantaneous shift of the 327-mμ peak to ~365 mμ which was followed by a rapid diminution in the 365-mμ peak intensity. However, if the solution was acidified a few seconds after adding the base, then the 365-mμ peak immediately shifted back to 327 mμ and then more slowly disappeared with concomitant formation of the 425-mμ peak attributable to the isobenzofuran XII.

These results are all readily explained if it is assumed that the transient 327-mμ absorbing species, which is formed thermally from the pyrylium oxide II, has the enol structure XIV. The thermal instability of this product might then be due either to its reconversion to I or to ketonization. The latter process should be accelerated by base with the formation of an intermediate anion as is indeed suggested by the base-induced reversible formation of the 365-mμ peak. Moreover, structure XIV could readily give rise to the isobenzofuran XII by the mechanism shown; the rapid reaction of XIV with bromine is consistent with its formulation as an enol; and the ultraviolet spectral maximum of XIV at 327 mμ ($\epsilon \approx 18{,}000$)[19] is consistent with a similar peak at 295 mμ ($\epsilon$ 12,000) in the spectrum of an ethanol solution of the model compound α,α′-dimethoxystilbene.[20]



From the conclusions that the pyrylium oxide II thermally gives the metastable enol XIV, and that neither I nor II is a direct photochemical precursor of the hydroxy ethers VIII and IX, it appears likely that the enol XIV is the photochemical precursor of the hydroxy ethers. In order to confirm this hypothesis, a degassed hexane solution of the indenone oxide I was irradiated with 2290–4200-A light from an Hanovia 100-w mercury lamp. The pyrylium oxide II was quite insoluble in this solvent and could be isolated by filtration. The crude solid was added to ethanol, and the resulting solution was allowed to stand until the color had nearly faded. Norbornadiene was then added to the reaction mixture to prevent the possible formation of II, and the mixture, which now contained the enol XIV, was irradiated with ultraviolet light (3100–4000-A). During the irradiation the 327-mμ peak of the enol rapidly diminished in intensity, which demonstrated that this intermediate was light sensitive. Chromatographic isolation of the products gave 50% *trans*-hydroxy ether VIII and 25% *cis*-hydroxy ether IX along with smaller amounts of the isocoumarin V and the norbornadiene adduct XIII. The appearance of the latter two compounds could be accounted for by the presence of V and I in the starting crude pyrylium oxide II. This experiment therefore confirms that the transient enol XIV is the true photochemical precursor of the hydroxy ethers.

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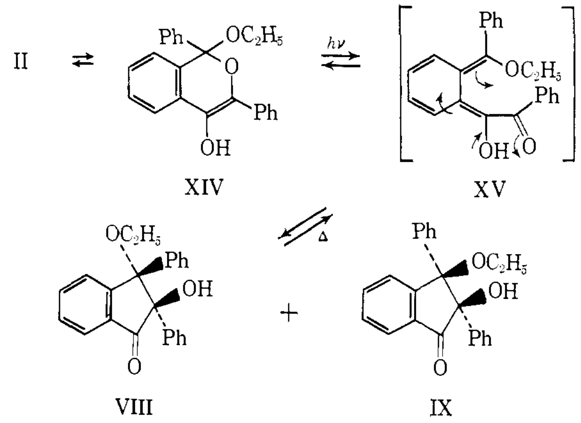
(19) The position of the ultraviolet absorption maximum of XIV was determined by subtracting the spectrum of a solution of XIV that had been treated first with excess bromine and then with 1-octene from the spectrum obtained before the bromine was added. The extinction coefficient of the maximum was estimated with the assumption that XIV was formed quantitatively on addition of ethanol to a known concentration of II in benzene.

(20) N. Kunimoto, *Nippon Kagaku Zasshi*, **83**, 1279 (1962).

The photochemical rearrangement of the enol XIV to give the hydroxy ethers probably is initiated by a photochemical ring-cleavage reaction analogous to the well-known ring openings of pyrans and 1,3-cyclohexadienes.[21] The resulting intermediate XV has the appropriate structural elements to undergo a rapid internal aldol condensation which would lead directly to the observed products VIII and IX. This reaction sequence seems quite plausible since the reverse series of reactions appears to occur thermally, as is suggested by the formation of the characteristic red color of the pyrylium oxide II on heating either hydroxy ether VIII or IX above 200°.



The discovery of the existence of the enolic intermediate XIV does not alter our conclusions concerning the photochemical origin of the isocoumarin V. The possibility that the enol XIV might be the immediate precursor of V can be readily excluded, for if it were a precursor, visible light would cause a decrease rather than the observed increase in the yield of V by suppressing the thermal formation of the enol XIV. The observed increase in the yield of V with visible light likewise eliminates the possibility that the hydroxy ethers VIII and IX might be precursors of the isocoumarin V since, like the enol, they do not absorb in the visible. Accordingly, the data still require that V must arise by direct photoexcitation of the pyrylium oxide II, although the possibility has yet to be eliminated that direct photoexcitation of the indenone oxide I might not also give V (however, see Quantum Yields).

**Absorption Spectra.** In order to study the kinetics and quantum yields of the thermal and photochemical reactions of the pyrylium oxide II it was necessary to determine its ultraviolet and visible spectra. However, the preparation of solutions of known concentrations of II presented difficulties. Although II could be isolated as blue-black crystals that precipitated during long 2537-A irradiation of concentrated hexane solutions of the indenone oxide I, dissolution of the solid in degassed solvents gave exceptionally unstable solutions. Unstable solutions were also obtained by adding triethylamine in benzene to the sulfuric acid salt of II, obtained as a precipitate on irradiation of an ether solution of I and sulfuric acid. Accordingly, it was found necessary to determine the concentration of solutions of II indirectly using tritium-recoil-labeled indenone oxide I. A solution of the labeled compound in a degassed solvent was irradiated with 3100–4000-A light, and the optical density and rate of disappearance of the long wavelength maximum of II was determined. Norbornadiene was then added and the amount of adduct XIII that was formed was determined by the isotope dilution technique. The amount of adduct formed was taken to equal the total amount of II in the solution, since II had been shown to react nearly instantaneously and quantitatively with norbornadiene. The extinction coefficient of the long wavelength maximum of II was then calculated from the optical density measurements extrapolated to the instant of norbornadiene quenching.

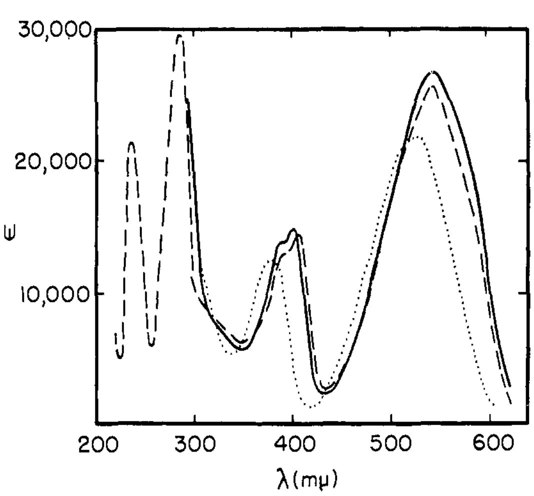


Figure 1. Ultraviolet and visible spectra of 1,3-diphenyl-2-benzopyrylium 4-oxide (II) in hexane - - - - - -, benzene ———, and ethanol · · · · .

The remainder of the spectrum of II was determined by irradiating a solution of the indenone oxide I, rapidly scanning the spectrum several times, and, after destroying the colored species by the addition of norbornadiene, scanning the spectrum again. With accurate timing of these steps the concentration of II and the optical density ($D_1$) at each wavelength at the instant of quenching could be calculated. The extinction coefficient of II at each wavelength ($\epsilon_{\mathrm{II}}$) could then be obtained from eq 1 where $D_0$ is the optical density determined after quenching and $\epsilon_{\mathrm{XIII}}$ is the extinction coefficient of the adduct XIII.[22] The resulting spectra and extinction coefficients are given in Table III and

$$\epsilon_{\mathrm{II}} = (D_1 - D_0)/[\mathrm{II}] + \epsilon_{\mathrm{XIII}} \qquad (1)$$

Figure 1, and the spectra of the indenone oxide I in the same solvents are shown in Figure 2.

**Emission Spectra.** Neither the indenone oxide I nor its valence tautomer II showed detectable phosphorescence emission of a lifetime greater than $10^{-3}$ sec at 77°K. However, shorter lived emission was observable in both 3-methylpentane and 3:1 ethanol–methanol glasses using 3130-A exciting light. The emission maxima of these glasses were at 630 and 608 m$\mu$, respectively. Since these maxima differ by only about 2500 cm$^{-1}$ from the absorption maxima of the pyrylium oxide II in the same media, and the emission and absorption bands display rough mirror image relationships (Figures 3 and 4), the emission is un-

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(21) See *inter alia* (a) W. G. Dauben, *Pure Appl. Chem.*, **9**, 543 (1964); (b) G. Buchi and N. C. Yang, *J. Am. Chem. Soc.*, **79**, 2318 (1957); (c) R. Dessauer and J. P. Paris, *Advan. Photochem.*, **1**, 288 (1963).

(22) Similar spectra could be obtained by using strong visible light to "quench" II and substituting $\epsilon_{\mathrm{I}}$ for $\epsilon_{\mathrm{XIII}}$ in eq 1.

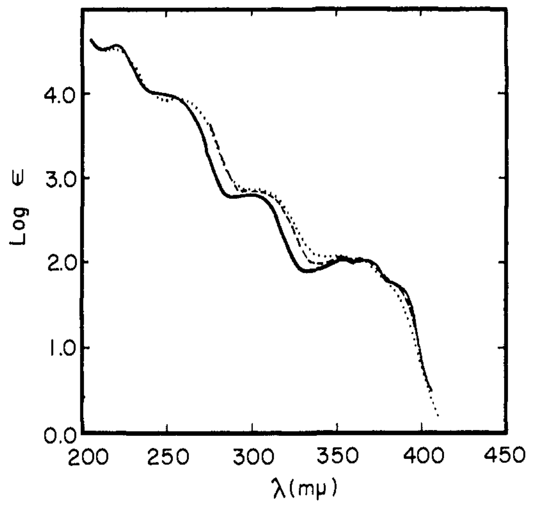

Figure 2. Ultraviolet spectra of 2,3-diphenylindenone oxide (I) in hexane ———, benzene - - - - - - -, and ethanol · · · · · · ·.

doubtedly due to the fluorescence of II. Moreover, II is identified as the emitting species since no emission was observed initially on irradiating a colorless glass (only I present), but measurable emission occurred within less than 1 sec and increased steadily in intensity as II was photochemically generated. On destroying II by irradiation with visible light the emission was eliminated. If the energy of the 0–0 band of II is taken as midway between the energies of the absorption and fluorescence maxima,[23] the 0–0 bands of II in 3-methylpentane and 3:1 ethanol–methanol glasses are 587 (49) and 556 mμ (51 kcal), respectively.

Table III. Absorption Maxima of 1,3-Diphenyl-2-pyrylium 4-Oxide (II)

| Hexane | | Benzene | | Ethanol[a] | |
|---|---|---|---|---|---|
| λ, mμ | ε | λ, mμ | ε | λ, mμ | ε |
| 236 | 21,100 | b | | | |
| 285 | 29,400 | b | | | |
| 392 | 12,900 | 390<br>(sh) | 13,800 | | |
| 406 | 14,200 | 403 | 14,700 | 378 | 12,300 |
| 544 | 25,300[c] | 544 | 26,750[c] | 525 | 21,250[c] |

[a] Studied at 310–610 mμ only. [b] Obscured by solvent absorption. [c] Average of two determinations made by isotope dilution method; average deviation $\leqslant$2.1%.

**Kinetics.** In order to determine the energy relationships between I and II, the equilibria and kinetics of interconversion of these valence tautomers were studied. The rates of disappearance of II were followed spectroscopically. Although the reproducibility of the measurements was poor, good first-order kinetics could be observed over several half-lives using hexane as solvent, and the average first-order rate constant was independent, within experimental error, of a 12-fold change in concentration of I. In 12 runs the average rate constant in hexane was $k^{30^\circ}{}_{\mathrm{II}\rightarrow\mathrm{I}} = (1.77 \pm 0.39) \times 10^{-5}$ sec$^{-1}$. Since even at the highest concentration of I ($3.6 \times 10^{-3}$ *M*), long standing of the hexane solution led to complete fading (optical density $\leqslant 0.002$, $[\mathrm{II}] \leqslant 7.8 \times 10^{-8}$ *M*), the constant for the equilibrium I $\rightleftarrows$ II must be $k^{30^\circ} = [\mathrm{II}]/[\mathrm{I}] \leqslant 2.2 \times 10^{-5}$ and $k^{30^\circ}{}_{\mathrm{I}\rightarrow\mathrm{II}} \leqslant 3.8 \times 10^{-10}$ sec$^{-1}$.

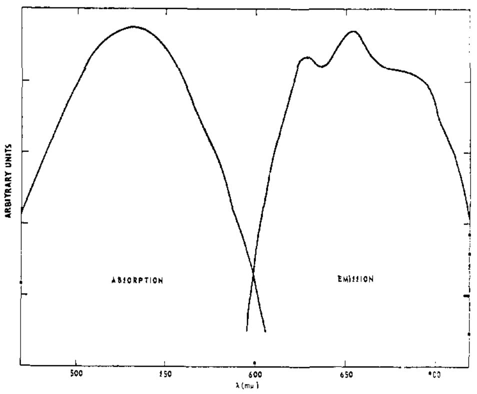

Figure 3. Visible emission and absorption spectra of 1,3-diphenyl-2-benzopyrylium 4-oxide (II) at 77°K in 3-methylpentane.

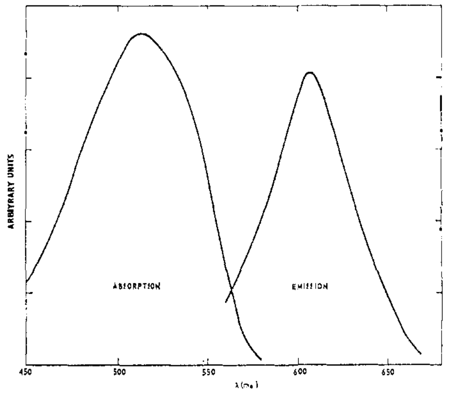

Figure 4. Visible emission and absorption spectra of 1,3-diphenyl-2-benzopyrylium 4-oxide (II) at 77°K in 1:1 ether–ethanol.

In benzene, the kinetics of reaction II → I displayed more serious deviations from first order, particularly toward the end of the runs. This effect was due in part to the reaction I → II, since initially colorless benzene solutions of I were found to become colored on standing in the dark at room temperature (~25°). The reverse reaction can be treated by using eq 2[24] where $D^{\mathrm{II}}$ is the optical density of II, $D_e^{\mathrm{II}}$ is the optical density at equilibrium, and $D_0^{\mathrm{II}}$ is the optical density calculated as though all of I were present as II. By using a value for $D_e^{\mathrm{II}}$ calculated from the equilibrium constant $K^{30^\circ} = 1.0 \times 10^{-4}$, satisfactory linear plots for the disappearance of II could be obtained at high concentrations

$$\ln\left(\frac{D_0^{\mathrm{II}} - D_e^{\mathrm{II}}}{D^{\mathrm{II}} - D_e^{\mathrm{II}}}\right) = (k_{\mathrm{I}\rightarrow\mathrm{II}} + k_{\mathrm{II}\rightarrow\mathrm{I}})t \tag{2}$$

of II, although deviations from linearity still occurred as the equilibrium position was approached. The linear portions of the curves yielded an average rate of fading in 10 runs ($4.5 \times 10^{-4}$ to $5.0 \times 10^{-3}$ *M* in I) of $k^{30^\circ}{}_{\mathrm{II}\rightarrow\mathrm{I}} \approx k^{30^\circ}{}_{\mathrm{I}\rightarrow\mathrm{II}} + k^{30^\circ}{}_{\mathrm{II}\rightarrow\mathrm{I}} = (1.8 \pm 0.8) \times 10^{-6}$ sec$^{-1}$.

For determination of $k_{\mathrm{I}\rightarrow\mathrm{II}}$ in benzene it appeared from the expected expression (3) that the appearance of II at very low concentrations of II should follow zero-order kinetics (eq 4). However, with $5 \times 10^{-2}$

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[23] A. Weller, *Z. Elektrochem.*, **56**, 662 (1952).

[24] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 173.

Table IV. Rate and Equilibrium Constants for the Interconversion of I and II

| Solvent | Temp, °C | $k_{I \rightarrow II}$, sec$^{-1}$ | $k_{II \rightarrow I}$, sec$^{-1}$ | $K$ | $\Delta F$, kcal |
|---|---|---|---|---|---|
| Hexane | 30.0[a] | $\leqslant 3.8 \times 10^{-10}$[b] | $1.8 \times 10^{-5}$ | $\leqslant 2.2 \times 10^{-5}$ | $\geqslant 6.5$ |
| Benzene | 30.0[a] | $4.4 \times 10^{-10}$ | $1.8 \times 10^{-6}$ | $1.0 \times 10^{-4}$[c] | $\sim 5.5$ |
| Benzene | 80.42 | $6.93 \times 10^{-7}$ | | | |
| Benzene | 99.69 | $5.77 \times 10^{-6}$ | | | |
| Benzene | 117.10 | $3.55 \times 10^{-5}$ | | | |

[a] The rate constants at 30° must be considered only approximate due to complications described in the text. [b] Calculated from $Kk_{II \rightarrow I}$. [c] Determined at 25°.

$$\mathrm{d}D^{II}/\mathrm{d}t = k_{I \rightarrow II}(D_0^{II} - D^{II}) - k_{II \rightarrow I}D^{II} \quad (3)$$

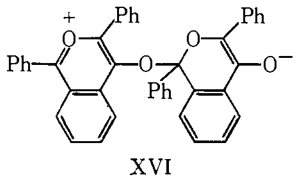
$$D^{II} = k_{I \rightarrow II}D_0^{II}t \quad (4)$$

$M$ solutions of I, the zero-order plots were curved, and the initial slopes gave a wide range of rate constants. The zero-order rates fell off rapidly with time, and apparent steady-state concentrations of II were reached within a few hours. These apparent equilibrium concentrations were generally much greater than had been measured by allowing similar solutions to stand for a period of months, and on longer standing the concentrations of II gradually dropped again toward the true equilibrium position. In general, solutions of I that had been standing for long periods in a highly colored condition and then were photobleached just prior to a kinetic run gave the highest rates of appearance and reached the highest concentrations of II.

The simplest explanation for this behavior is that high concentrations of II lead to the formation of an unstable species Y which is in a much more rapid thermal equilibrium with II than is I. The amount of Y present will then depend on the concentration of II and on the period of time that the solution has been allowed to stand prior to photobleaching. The rate of re-formation of II after photobleaching will depend in turn on the concentration of Y. If the equilibrium between II and Y is strongly in favor of II, then, after photobleaching, decomposition of Y will proceed virtually to completion and the concentration of II will temporarily surpass its equilibrium position. In support of this explanation, the kinetics fitted eq 5, where $[Y]_0$ is the concentration of Y at the instant of photobleaching and $D_{max}^{II}$ is the maximum optical

$$\ln\left(\frac{[Y]_0}{[Y]}\right) = \ln\left(\frac{D_{max}^{II}}{D_{max}^{II} - D^{II}}\right) = k_{Y \rightarrow II}t \quad (5)$$

density reached ($k^{30°}{}_{Y \rightarrow II} = 3.5 \times 10^{-4}$ sec$^{-1}$). While the structure of Y is unknown, it possibly may be a covalently bonded dimer or higher polymer of the pyrylium oxide II such as XVI.



XVI

Based on the conclusion that Y was responsible for the anomolous kinetics, $k_{I \rightarrow II}$ was measured using solutions that had been allowed to stand with relatively low concentrations of II. Initial zero-order plots (eq 4) were then obtained, $k^{30°}{}_{I \rightarrow II} = (4.4 \pm 0.8) \times 10^{-10}$ sec$^{-1}$, which were in reasonable agreement with the value $k^{30°}{}_{I \rightarrow II} = 6.3 \times 10^{-10}$ sec$^{-1}$ calculated by extrapolation of rate data obtained by heating previously unirradiated benzene solutions of I containing norbornadiene. These latter data were obtained by following the appearance of the carbonyl infrared absorption of the adduct XIII, and they provide the Arrhenius parameters, $A = 1.03 \times 10^{12}$ sec$^{-1}$ and $E = 29.4$ kcal/mole. The rate data are summarized in Table IV.

**Quantum Yields.** The rates of formation and disappearance of the pyrylium oxide II on irradiation of degassed solutions of the indenone oxide I were measured spectroscopically. The rate of the formation of II with 3650-A light provided a direct measure of the quantum yield of reaction I → II ($\phi_{I \rightarrow II}$). On the other hand, the rate of the bleaching process produced by 5460-A light was a measure of the sum of the quantum yields for formation of I ($\phi_{II \rightarrow I}$) and the isocoumarin V ($\phi_{II \rightarrow V}$). The results of these measurements are tabulated in the first two columns of Table V.

Table V. Variation of Quantum Yield with Solvent

| Solvent | $\phi_{II \rightarrow I} + \phi_{II \rightarrow V}$ | $\phi_{I \rightarrow II}$ | $\phi_{II \rightarrow I}$[a] |
|---|---|---|---|
| Hexane | $0.043 \pm 0.006$ | $0.53 \pm 0.02$ | $0.043 \pm 0.006$ |
| Benzene | $0.056 \pm 0.001$ | $0.56 \pm 0.04$ | $0.056 \pm 0.001$ |
| Ethanol | $0.066 \pm 0.003$ | $0.61 \pm 0.03$ | $\leqslant 0.062$ |

[a] Calculated with the assumption that $\phi_{II \rightarrow V}$ in hexane and benzene is negligible; see run 4, Table I (results similar to those obtained in run 4 were obtained in an identical experiment using hexane as solvent) and that $\phi_{II \rightarrow V}$ in ethanol is $\geqslant 0.0045$ (see following discussion).

In order to determine the value for $\phi_{II \rightarrow I}$ alone and to establish quantitatively the origin(s) of the isocoumarin V, experiments were designed to measure directly the quantum yields of formation of V from the indenone oxide ($\phi_{I \rightarrow V}$) and from the pyrylium oxide ($\phi_{II \rightarrow V}$). The quantum yield for reaction I → V with 3650-A light was determined using an ethanol solution of tritium-labeled I containing 10% norbornadiene. The latter substance was added to remove II quantitatively during the reaction, and was found in a control experiment to have no effect on the quantum yield of formation of II. The irradiation was continued until I was completely destroyed, and the mixture was then analyzed for V by the isotope dilution technique. From the yield of V obtained in this manner (0.005 ± 0.025%) a quantum yield for the formation of V ($\phi_{I \rightarrow V}$) that was indistinguishable from zero [$(3 \pm 15) \times 10^{-5}$] was calculated using eq 6, where $\gamma_V$ and $\gamma_{II}$ are the yields of V and II, respectively, with $\gamma_{II}$ taken as unity (isolated yield of adduct XIII >98%).

$$\phi_{I \rightarrow V} = \phi_{I \rightarrow II}\gamma_V/\gamma_{II} \quad (6)$$

The quantum yield for the formation of the isocoumarin V from the pyrylium oxide II ($\phi_{\text{II}\rightarrow\text{V}}$) was determined by simultaneous irradiation of an ethanolic solution of tritium-labeled indenone oxide I with 3650-A light of known intensity together with an intense uncalibrated light of >4350 A (*cf.* run 8, Table II). Under these conditions the 3650-A light was absorbed nearly exclusively by the indenone oxide I, since the intense visible light produced a very low concentration of the pyrylium oxide II. Light absorption by the product V was avoided by carrying the reaction to no more than 1.5% of completion, and the yield of V was determined as before by the isotope dilution technique.

Since it had been shown by the qualitative experiments that no important photochemical products derived from II are formed under these conditions other than I and V, only the following reactions need be considered for estimation of the quantum yield $\phi_{\text{II}\rightarrow\text{V}}$.

$$\begin{tikzcd}
\text{I} \arrow[rr, shift left, "3650\ \text{A}"] \arrow[dr, "3650\ \text{A}"'] & & \text{II} \arrow[ll, shift left, ">4350\ \text{A}"] \arrow[dl, ">4350\ \text{A}"] \\
& \text{V} &
\end{tikzcd} \tag{7}$$

Hence, this quantum yield can be calculated by eq 8, where $\phi_{\text{obsd}}$ is the moles of V formed per einstein of 3650-A light absorbed by I. However, only poorly

$$\phi_{\text{II}\rightarrow\text{V}} = (\phi_{\text{II}\rightarrow\text{I}} + \phi_{\text{II}\rightarrow\text{V}})(\phi_{\text{obsd}} - \phi_{\text{I}\rightarrow\text{V}})/\phi_{\text{I}\rightarrow\text{II}} \tag{8}$$

reproducible values of $\phi_{\text{obsd}}$ could be obtained (Table VI). This result must be due to the failure of eq 8 to take into account the competing thermal reactions of II to give I and the enol XIV. These reactions compete with the photochemical process II → I + V, and their importance is inversely dependent on the visible light intensity which was not kept constant. Since the effect of these competing processes is to remove the pyrylium oxide II from the solution before it absorbs light energy, the experimental value for $\phi_{\text{obsd}}$ is lower than it would have been in the absence of the thermal process. The higher value for $\phi_{\text{obsd}}$ given in Table VI is therefore the more accurate and, from eq 8, $\phi_{\text{II}\rightarrow\text{V}} \geqslant 0.0045$.

**Table VI.** Observed Quantum Yields ($\phi_{\text{obsd}}$) of 3,4-Diphenylisocoumarin (V) on Irradiating 2,3-Diphenylindenone Oxide (I) with Calibrated 3650-A Light and Intense Visible Light

| Moles of V detected | | Einsteins of 3650-A light absorbed by I | |
|---|---|---|---|
| Run | Blank[a] | | $\phi_{\text{obsd}}$[b] |
| $9.36 \times 10^{-7}$ | $1.83 \times 10^{-7}$ | $1.79 \times 10^{-5}$ | 0.042 |
| $8.55 \times 10^{-7}$ | $1.78 \times 10^{-7}$ | $2.37 \times 10^{-5}$ | 0.029 |

[a] Identical with the runs but carried out in the dark. [b] Moles of V formed per einstein of 3650-A light absorbed by I.

While these data provide excellent evidence that the isocoumarin V is formed from the pyrylium oxide II, this point is of sufficient importance in the discussion to follow that an alternative method for determination of $\phi_{\text{II}\rightarrow\text{V}}$ was utilized. In this method the pyrylium oxide II was generated by heating an ethanol solution of I at 125°, and the photochemical conversion II → I + V was produced with intense visible light (>4350 A). The following reactions must be considered.

$$\begin{tikzcd}
\text{I} \arrow[rr, shift left, "125^\circ"] \arrow[dr, "125^\circ"'] & & \text{II} \arrow[ll, shift left, ">4350\ \text{A}"] \arrow[dl, ">4350\ \text{A}"] \\
& \text{V} &
\end{tikzcd}$$

The quantum yield $\phi_{\text{II}\rightarrow\text{V}}$ may then be calculated from eq 9 where $[\text{I}]_0$ is the initial concentration of I. For solution of 9, the rate constant $k^{125^\circ}{}_{\text{I}\rightarrow\text{II}} = 7.3 \times 10^{-5}$ sec$^{-1}$ was determined in the dark by following,

$$\phi_{\text{II}\rightarrow\text{V}} = (\phi_{\text{II}\rightarrow\text{I}} + \phi_{\text{II}\rightarrow\text{V}})\left[\frac{1}{tk_{\text{I}\rightarrow\text{II}}}\right] \times \left[\ln\left(\frac{[\text{I}]_0}{[\text{I}]_0 - [\text{V}]}\right) - \frac{k_{\text{I}\rightarrow\text{V}}}{k_{\text{I}\rightarrow\text{II}}}\right] \tag{9}$$

by means of infrared spectroscopy, the appearance of adduct XIII in an ethanol solution of I containing norbornadiene; and the rate constant $k^{125^\circ}{}_{\text{I}\rightarrow\text{V}} = 2.26 \times 10^{-7}$ sec$^{-1}$ was obtained in a similar experiment using tritium-labeled I and the isotope-dilution technique. For the actual quantum yield determination, carried to 2.3% completion without norbornadiene, V was again determined by isotope dilution, and a value of $\phi_{\text{II}\rightarrow\text{V}} \geqslant 0.0020$ was obtained. Thus this alternative method gave a somewhat lower quantum yield, though of a similar order of magnitude, as obtained by the previous method. This is consistent with the expected higher rate of the thermal reactions of II which become more competitive with the photoprocesses at the elevated temperature.

**Quenchers.** The effect of naphthalene on the quantum yield of the photochemical conversion of the indenone oxide I to the pyrylium oxide II in benzene was studied using 3650-A light. The quantum yield was found to drop off slightly with increasing concentrations of naphthalene but the Stern–Volmer equation was not obeyed. Rather, the quantum yields approached a limiting value of about 0.49 with increasing quencher concentration. Since the longest wavelength absorption of naphthalene is much shorter than the longest absorption maximum of the indenone oxide I at 385 mμ, singlet energy transfer from I is not possible, and naphthalene must act as a triplet quencher. The small reduction in quantum yield even at high quencher concentrations therefore requires that the reaction proceed to only a small extent (~13%) by way of the triplet of I, and the principal pathway must be a direct reaction of the singlet.

A Stern–Volmer plot of the quenching data is given in Figure 5. The curve shape was calculated by use of eq 10, where $\phi_{\text{I}\rightarrow\text{II}}$ is the quantum yield without quencher (Q), $\phi_{\text{q}}$ is the quantum yield with quencher, and $\phi_\infty$ is the limiting quantum yield at high quencher concentration and represents the probability of reaction

$$\frac{\phi_{\text{I}\rightarrow\text{II}}}{\phi_{\text{q}}} = \left(1 + \frac{k_{13}[\text{Q}]}{k_{11} + k_{12}}\right)\Bigg/\left(1 + \frac{k_{13}[\text{Q}]}{k_{11} + k_{12}}\frac{\phi_\infty}{\phi_{\text{I}\rightarrow\text{II}}}\right) \tag{10}$$

occurring without the intermediacy of the triplet of I. Good fits to the experimental points were obtained with rate constant ratios of $k_{13}/(k_{11} + k_{12}) = 10.4 \pm 4.$[25]

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[25] A straight line plot of $(\phi - \phi_\infty)/(\phi_{\text{q}} - \phi_\infty)$ *vs.* [Q] should be obtained by rearranging eq 10 to

$$(\phi - \phi_\infty)/(\phi_{\text{q}} - \phi_\infty) = 1 + k_{13}[\text{Q}]/(k_{11} + k_{12})$$

However, the magnification of errors caused by using differences between large numbers produces considerable scatter which is reflected in this range of rate constant ratios that fit the data.

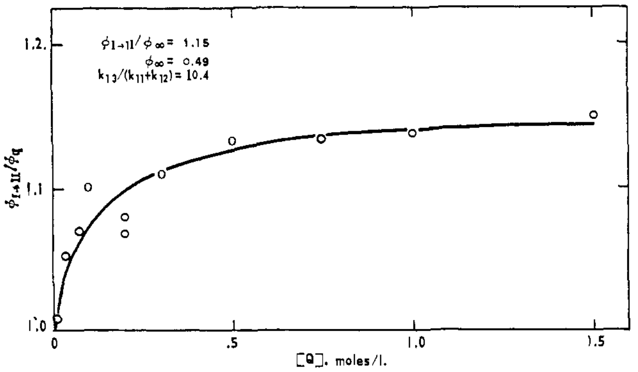

Figure 5. Effect of naphthalene concentration on the quantum yield for reaction I → II; [I] = $10^{-2}$ *M*.

Assuming that $k_{13}$ is diffusion controlled ($\sim 2 \times 10^9$ l. mole$^{-1}$ sec$^{-1}$),[26,27] the rate ratio gives a lifetime for $^3$I of $1/(k_{11} + k_{12}) = (5.2 \pm 2.0) \times 10^{-9}$ sec$^{-1}$.

$$^3\text{I} \longrightarrow \text{II} \tag{11}$$

$$^3\text{I} \longrightarrow \text{I} \tag{12}$$

$$\text{Q} + {}^3\text{I} \longrightarrow \text{I} + {}^3\text{Q} \tag{13}$$

When alcohol was used as solvent, addition of the naphthalene did not lead to reduction in the quantum yield of the pyrylium oxide II. Nevertheless, the triplet energy of naphthalene must lie below that of I in this solvent since energy transfer from naphthalene triplet to I is inefficient as shown by the tendency of naphthalene to reduce the quantum yield of benzophenone-sensitized reaction I → II in alcohol. Accordingly, the unsensitized reaction I → II in alcohol does not appear to proceed to an appreciable extent through the triplet of the indenone oxide I.

Attempts to quench the reverse reaction II → I in benzene with compounds having low triplet energies were unsuccessful. Since it seemed possible that quenching did not occur because the triplet energy of II was lower than that of the quenchers studied, the stable free radical di-*t*-butylnitroxide was tried. This compound is an efficient triplet quencher because of its paramagnetic properties.[28] However, even at a concentration of 1.0 *M*, it did not reduce the quantum yield for reaction II → I induced by 5460-A light. Therefore, this reaction, when unsensitized, probably also does not proceed through a triplet intermediate.

**Sensitizers.** The photochemical conversion of the indenone oxide I to the pyrylium oxide II could be sensitized. However, quantitative studies were complicated by the fact that I absorbed light in the same wavelength regions as most of the common sensitizers. Since the absorbance of I was relatively weak at 3650 A ($\epsilon$ 110, benzene), this wavelength of light was employed, and a ratio of sensitizer to I was used that permitted no more than 1% of the light to be absorbed by I. Only benzene was used in these studies because of the superior stability of II in this solvent.

Using the relatively weakly absorbing benzophenone as sensitizer, the quantum yield ($\phi_{I\to II}$) was studied as a function of the concentration of I. The results were found to obey eq 14, which takes the same form whether energy transfer occurs from the singlet or from the triplet of the sensitizer. In this expression $k_{15}$ and $k_{16}$ are, respectively, the rate constants for energy transfer

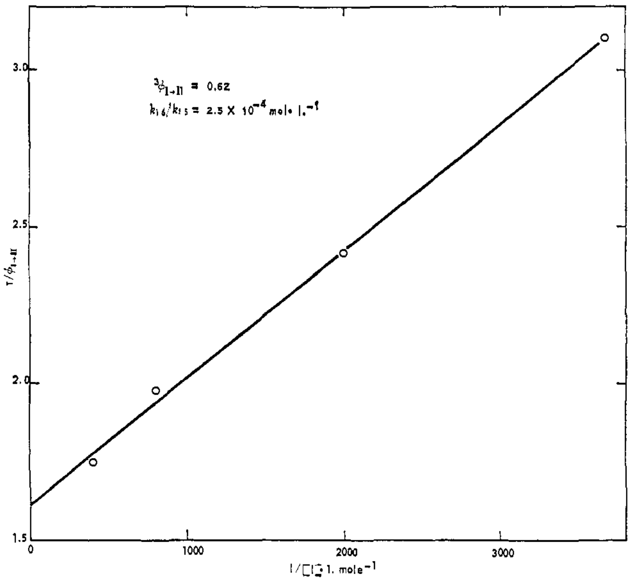

Figure 6. Quantum yields for reaction I → II sensitized with 0.025 *M* benzophenone, extrapolated to infinite concentration of I (eq 14).

$$\frac{1}{\phi_{I\to II}} = \frac{1}{^3\phi_{I\to II}\phi_S} + \frac{k_{16}}{k_{15}[\text{I}]\,^3\phi_{I\to II}\phi_S} \tag{14}$$

$$\text{I} + {}^3\text{S} \longrightarrow \text{S} + {}^3\text{I} \tag{15}$$

$$^3\text{S} \longrightarrow \text{S} \tag{16}$$

to I and for spontaneous decay of excited sensitizer (S), $\phi_S$ is the quantum yield for formation of excited sensitizer, and $^3\phi_{I\to II}$ is the quantum yield expected if I were present in sufficient concentration to quench all the excited sensitizer molecules. From the intercept of the plot in Figure 6 it is found that $^3\phi_{I\to II}\phi_S = 0.62$ and from the slope, the ratio $k_{16}/k_{15} = 2.5 \times 10^{-4}$ mole l.$^{-1}$ is obtained. If it is assumed that the energy-transfer process, eq 15, is diffusion controlled ($k_{15} \approx 2 \times 10^9$ l. mole$^{-1}$ sec$^{-1}$),[26,27] the lifetime of the excited sensitizer molecule must be $1/k_{16} = 2.0 \times 10^{-6}$ sec. This is in excellent agreement with the previously reported lifetime of $3.8 \times 10^{-6}$ sec for benzophenone triplet in benzene,[26,27] and thus excludes the short-lived ($\leqslant 2 \times 10^{-10}$ sec) singlet of benzophenone[29] as the sensitizing species. The reaction must therefore proceed by triplet sensitization, and the limiting quantum yield at high concentrations of I is defined as $^3\phi_{I\to II} = k_{11}/(k_{11} + k_{12})$. Since the intersystem crossing ratio for benzophenone is unity,[30] $^3\phi_{I\to II} = (^3\phi_{I\to II}\phi_S) = 0.62$.

Nearly the same quantum yield, $\phi_{I\to II} = 0.60$, was obtained directly by the use of thioxanthone as sensitizer, which by virtue of its intense absorption at 3650 A permitted the use of a relatively high concentration of I ([I] = $5 \times 10^{-3}$ *M*, [S] = $1.4 \times 10^{-2}$ *M*). This confirms the above value for $^3\phi_{I\to II}$ and in addition shows that the intersystem crossing ratio $\phi_S$ for thioxanthone must also be near unity.

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

(27) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

(28) S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(29) G. S. Hammond and W. M. Moore, *ibid.*, **81**, 6334 (1959).

(30) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Table VII. Effect of Different Sensitizers on the Photostationary State

| Sensitizer | Sensitizer triplet energy $E_t$, kcal[a] | Sensitizer concn, mole/l. | Benzophenone concn, mole/l. | Initial indenone oxide concn, $[\mathrm{I}]_0$, mole/l. | % direct excitation of I[b] | Minimum photostationary ratio × 100, $100[\mathrm{II}]/([1]_0 - [\mathrm{II}])$ |
|---|---|---|---|---|---|---|
| Benzophenone | 68.5 | 1.00 | | $2.05 \times 10^{-4}$ | 0.03 | 36.3 |
| | | 1.06 | | $2.11 \times 10^{-4}$ | 0.03 | 36.3 |
| | | 0.0159 | | $3.73 \times 10^{-4}$ | 3.36 | 35.5 |
| Fluorene | 67.6 | 0.0200 | 0.195 | $9.8 \times 10^{-5}$ | 1.19 | 6.3[c] |
| | | 0.0206 | 0.226 | $9.8 \times 10^{-5}$ | 1.10 | 4.4[c] |
| | | 0.0414 | 0.056 | $3.36 \times 10^{-4}$ | 1.77 | 17.3[c] |
| Triphenylene | 66.6 | 0.0100 | 0.160 | $9.8 \times 10^{-5}$ | 1.06 | 57.5 |
| Biphenyl | 65.6[d] | 0.0200 | 0.215 | $9.8 \times 10^{-5}$ | 0.57 | 35.5 |
| Thioxanthone | 65.5 | 0.0100 | | $1.07 \times 10^{-4}$ | 0.03 | 45.8 |
| | | 0.0100 | | $2.15 \times 10^{-4}$ | 0.04 | 51.3 |
| | | 0.0140 | | $5.03 \times 10^{-3}$ | 0.66 | 34.4 |
| Anthraquinone | 62.4 | 0.0127 | | $2.45 \times 10^{-5}$ | 0.89 | <0.38 |
| | | 0.0190 | | $4.09 \times 10^{-4}$ | 0.98 | 0.20 |
| Phenanthrene | 62.2 | 0.0200 | 0.220 | $2.45 \times 10^{-5}$ | 0.14 | 0.81 |
| | | 0.0200 | 0.230 | $9.8 \times 10^{-5}$ | 0.55 | 1.55 |
| α-Naphthoflavone | 62.2 | 0.0103 | | $9.8 \times 10^{-5}$ | 0.13 | 0.36 |
| β-Naphthyl phenyl ketone | 59.6 | 0.0530 | | $9.8 \times 10^{-5}$ | 0.09 | 0.38 |
| β-Acetonaphthone | 59.3 | 0.0198 | 0.220 | $2.0 \times 10^{-5}$ | 0.11 | <0.38 |
| | | 2.00 | | $2.9 \times 10^{-4}$ | 0.06 | 0.65 |
| | | 2.00 | | $5.34 \times 10^{-4}$ | 0.11 | 0.63 |
| | | 2.00 | | $7.70 \times 10^{-4}$ | 0.16 | 0.55 |
| | | 2.00 | | $4.49 \times 10^{-3}$ | 0.93 | 0.25 |
| Fluoranthene | 52.8[e] | 0.0091 | | $4.18 \times 10^{-4}$ | 0.09 | 0.35 |
| | | 0.0091 | | $4.25 \times 10^{-4}$ | 0.09 | 0.58 |
| Benzylideneanthrone | 45.5[f] | 0.0050 | | $5.64 \times 10^{-4}$ | 0.12 | 0.40 |
| 9,10-Dichloroanthracene | 40[g] | 0.0207 | 0.230 | $2.00 \times 10^{-5}$ | 0.11 | <0.40 |

[a] Taken from ref 31 except as indicated. [b] Per cent of light absorbed directly by I, plus, where applicable, the per cent of benzophenone triplets involved in energy transfer directly to I rather than to the lower energy sensitizer; *i.e.*, $100[\mathrm{I}]_0/([\mathrm{S}] + [\mathrm{I}]_0)$ (assumes equal rates of energy transfer from benzophenone to I and sensitizer). [c] See ref 35. [d] Y. Kanda, R. Shimada, and Y. Sakai, *Spectrochim. Acta*, **17**, 1 (1961). [e] C. Dijkgraaf and G. J. Hoijtink, *Tetrahedron Suppl.*, **2**, 179 (1963). [f] Determined from the singlet–triplet absorption in $CHCl_3$ under high-oxygen pressure; this work. [g] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

In order to determine the effect of varying the triplet energy of sensitizers on the photoequilibrium I $\rightleftarrows$ II, benzene solutions of I containing a sensitizer were irradiated, and the appearance of II was followed spectroscopically until no further increase occurred. Further irradiation of solutions which had high photostationary concentrations of II generally caused a slow drop in the concentration of II, which suggested the existence of a side reaction. Since the concentration of I could be measured only by difference, a minimum value for the photostationary ratio [II]/[I] that would obtain in the absence of side reactions was estimated from the ratio $[\mathrm{II}]/([\mathrm{I}]_0 - [\mathrm{II}])$, where $[\mathrm{I}]_0$ was the initial concentration of I, and [II] was the maximum concentration of II attained. In these experiments a sensitizer concentration of no more than $2 \times 10^{-2}$ *M* was generally used in order to avoid significant quenching by energy transfer back to the sensitizer (see Quenchers). However, an exception was made for the weakly absorbing benzophenone ($\epsilon_{3650} \sim 70$), since the photostationary ratio was not sensitive to changes in its concentration. Since a number of the sensitizers with triplet energies less than that of benzophenone ($E_t$ = 68.5 kcal)[31] did not absorb at all at 3650 A, benzophenone was added along with these sensitizers to act as an energy-transfer agent for their excitation. Direct sensitization of I by benzophenone was minimized by employing at least 100 times more of the sensitizer than I, and direct photoexcitation of I was minimized by permitting no more than 1% of the light to be absorbed by I. The results of these measurements are given in Table VII.

The sharp reduction in the minimum photostationary ratio on changing the triplet energy of the sensitizer from 65 to 63 kcal strongly suggests that the indenone oxide triplet ($^3$I) lies about 64 kcal above the ground state.[32] This conclusion stems from the fact that energy transfer, which is normally diffusion controlled, becomes very inefficient as the donor energy drops below the triplet energy of the acceptor.[33] Thus sensitizers which do not transfer energy efficiently to I would be expected to have triplets with energies near or below that of I. On the other hand, the absence of further changes in the photostationary ratio at still lower triplet energies provides no hint of the triplet energy of II. If the rate of energy transfer to II fell off when sensitizers with sufficiently low triplet energies were used, it might be expected that the photostationary ratio would rise again. However, since it does not, either II has a triplet energy lower than that of the lowest energy sensitizer used, or II is removed from solution by a process that does not require energy transfer to II. Therefore the triplet energy for II can only be set as <49 kcal, the energy of the lowest singlet of II (see Emission Spectra).

Further insight into the effect of sensitizers on the pyrylium oxide II was gained through attempts to determine the quantum yield for its sensitized con-

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(31) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(32) Due to the use of fewer sensitizers together with an experimental error this value was previously reported erroneously.[1]

(33) (a) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964); (b) K. Sandros and H. L. J. Backström, *ibid.*, **16**, 958 (1962).

version to I that would obtain if all sensitizer triplets were quenched by II: namely ${}^3\phi_{II\to I} = k_{18}/(k_{18} + k_{19})$. For this purpose the rate of the sensitized disappearance of II as a function of the concentration of II was needed. This could be calculated from the

$$\text{II} + {}^3\text{S} \longrightarrow \text{S} + {}^3\text{II} \quad (17)$$

$$^3\text{II} \longrightarrow \text{I} \quad (18)$$

$$^3\text{II} \longrightarrow \text{II} \quad (19)$$

rate of appearance of II on irradiation of I in the presence of high concentrations (2 $M$) of the low energy sensitizer, $\beta$-acetonaphthone ($E_t$ = 59.3 kcal, $\phi_S$ = 0.84).[30] Under these conditions sensitized formation of II was precluded, since at this high concentration the sensitizer acted as an efficient quencher of $^3$I (see section on Quenchers). The pyrylium oxide II could therefore be formed only by direct absorption of light by I, and its theoretical rate of formation $R_{I\to II}$ could be calculated from the fraction of light of known intensity $E$ absorbed by I multiplied by the quantum yield of conversion of I to II in the presence of high quencher concentrations, $\phi_\infty$ = 0.49. In practice, the measured rate $R$ of appearance of II dropped off continuously as [II] increased. Based on eq 20, where $R_{II\to I}$ is the rate of unsensitized conversion of II to I (calculated from

$$\frac{\phi_S E}{R_{I\to II} - R_{II\to I} - R} = \frac{k_{16}}{k_{17}{}^3\phi_{II\to I}[\text{II}]} + \frac{1}{{}^3\phi_{II\to I}} \quad (20)$$

the fraction of light absorbed by II), plots of $\phi_S E/(R_{I\to II} - R_{II\to I} - R)$ *vs.* 1/[II] were constructed (Figure 7). Although the reproducibility was poor due to the low optical densities of II (0.005–0.050), nearly straight-line plots were obtained if points derived from the very lowest optical densities were omitted. The intercepts gave ${}^3\phi_{II\to I} = (6.0 \pm 1.8) \times 10^{-4}$. Because of the large systematic errors introduced by the use of so many measured parameters, this figure is perhaps correct only to an order of magnitude, but the quantum yield nevertheless must be very low. Moreover, even this low quantum yield is a measure of the sensitized conversion of II to other products as well as I (*vide infra*).

The very low quantum yield for sensitized disappearance of II raises questions about the significance of the photostationary ratio measurements. If it is assumed that the concentrations of II reached in these measurements were a function only of the sensitized interconversions of I and II, then the ratio of rates of energy transfer to I and to II would be given by eq 21.[30,34] On substituting the measured photostationary ratios [II]/([I]$_0$ − [II]) obtained with low energy sensitizers into eq 21, $k_{15}/k_{17}$ falls in the range $\lesssim 10^{-6}$ to $10^{-5}$. This range is not unreasonable, since reaction 15 should be endothermic and very slow compared to reaction 17 which should be exothermic and near diffusion controlled.[33] However, on substituting the

$$\frac{k_{15}}{k_{17}} = \frac{[\text{II}]}{[\text{I}]}\frac{{}^3\phi_{II\to I}}{{}^3\phi_{I\to II}} \quad (21)$$

photostationary ratio [II]/([I]$_0$ − [II]) produced by a high energy sensitizer such as benzophenone into eq 21, $k_{15}/k_{17} \lesssim 4.4 \times 10^{-4}$. This value is impossibly low; it should be near unity since energy transfer from triplet benzophenone to both I and II should be exothermic and near diffusion controlled.

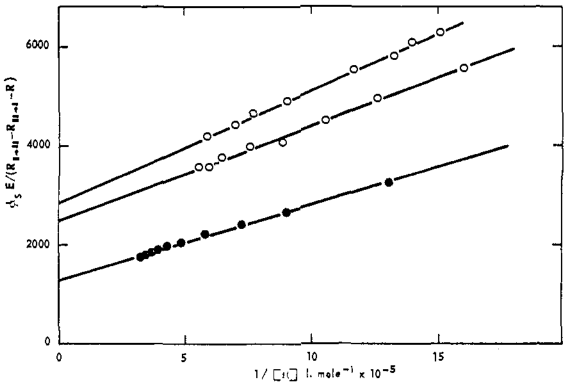

Figure 7. Quantum yields for disappearance of II sensitized by 2.0 $M$ $\beta$-acetonaphthone, extrapolated to infinite concentration of II (eq 20). [I] = 2.87 × 10$^{-4}$ $M$, open circles; [I] = 5.37 × 10$^{-4}$ $M$, closed circles.

This anomaly is in accord with the observation that the maximum concentration of II attained using high energy sensitizers always fell off with continued irradiation. This suggested the existence of a side reaction which depleted the total concentration of I plus II and caused our estimate [II]/([I]$_0$ − [II]) of the true photostationary ratio [II]/[I] to be too low. However, if this were the only source of error, over two-thirds of the original I would have to be converted to a side product to permit a reasonable fit with eq 21. No such accumulation of side product arose, for when a benzophenone-sensitized solution of I at the photostationary state was bleached by visible light and then reirradiated with ultraviolet light, the new photostationary concentration of II was only slightly lower.

The poor fit with eq 21 must therefore be due in part to the use of too low a value for the quantum yield for sensitized disappearance of II, ${}^3\phi_{II\to I} = 6 \times 10^{-4}$. This value was obtained by extrapolation from very low concentrations of II (10$^{-7}$–10$^{-6}$ $M$) to infinite concentration. The quantum yield for certain side reactions might not be reflected in this measurement if the side reactions were strongly concentration dependent, as might obtain in a self-condensation reaction. However, at the higher concentrations of II (10$^{-5}$–10$^{-4}$ $M$) produced with high energy sensitizers, such a side reaction could become very important and the over-all quantum yield for disappearance of II might be quite high. Direct evidence that self-condensation of II was important was found in the observation that visible light bleaching of some of the solutions used in the photostationary ratio measurements was followed by rapid reappearance of II (compare the kinetic behavior requiring a dimer or polymer Y that dissociates to II).

These considerations are sufficient to explain, at least qualitatively, most of the variations in the photostationary ratios given in Table VII.[35] As regards the

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(34) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963); G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Corwan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(35) Since the pyrylium oxide II is exceptionally sensitive to free-radical sources[5] and can be partially stabilized by radical inhibitors, some of the apparently random variations in the photostationary ratios given in Table VII may be due to the presence of traces of radical chain carriers, initiators, radical traps, etc. The very pronounced deviation from regular behavior that was observed when fluorene was used as sensitizer no doubt is due to the hydrogen donor properties of this compound.

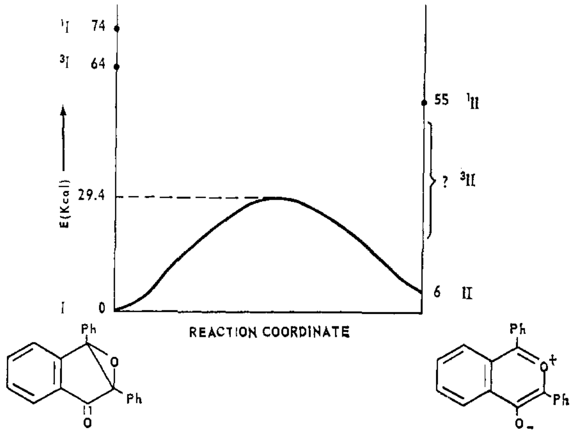

Figure 8. Relative energies of the ground, transition, and lowest excited states of 2,3-diphenylindenone oxide (I) and 1,3-diphenyl-2-benzopyrylium 4-oxide (II) in benzene (energy of $^1$II determined at 77 °K in 3-methylpentane).

discussion to follow, the important conclusions from these observations are as follows: first, the observed photostationary ratios $[\mathrm{II}]/([\mathrm{I}]_0 - [\mathrm{II}])$ with high energy sensitizers must be much *lower* than they would be if the self-condensation reaction of II did not intervene and only the sensitized interconversion of I and II took place. Second, the photostationary ratios observed with low energy sensitizers are less seriously affected by this side reaction because of the low concentrations of II involved, and in fact, the ratios are higher than they would be if only sensitized interconversion of I and II took place. This follows from the observation that the photostationary ratios were not greater with low concentrations of a low energy sensitizer, β-acetonaphthone, than with high concentrations where quenching of $^3$I becomes very important. The principal process contributing to the formation of II therefore must be the unsensitized reaction of I, and if this process could be completely avoided, the photostationary concentration of II with low energy sensitizers would be greatly reduced.

## Discussion

The previous sections provide a picture of both the qualitative and quantitative aspects of the photochemical interconversion of the indenone oxide I and its valence tautomer II. We wish now to consider the significance of these data as regards the sequence of events immediately following absorption of a photon by I or II. For this purpose, the energy diagram given in Figure 8 has been constructed from the spectroscopic, kinetic, and equilibrium data obtained in benzene as solvent. All the possible interconversions between I and II in their ground and lowest singlet and triplet states that might be involved in the photoisomerization reactions are given by eq 22–29. The diagram demonstrates that the reverse processes in four of these equations, 22–25, are strongly endothermic and are therefore unlikely to occur within the short lifetime of an excited state, and the reverse of 23 and 24 must in any event play an unimportant role since $^3\phi_{\mathrm{II}\to\mathrm{I}}$ is only $6 \times 10^{-4}$. The remaining forward processes are all energetically allowed, and the possibility of the participation of each one in the phototautomerization reaction will be considered separately.

$$^1\mathrm{I} \rightleftarrows {}^1\mathrm{II} \tag{22}$$

$$^3\mathrm{I} \rightleftarrows {}^3\mathrm{II} \tag{23}$$

$$^1\mathrm{I} \rightleftarrows {}^3\mathrm{II} \tag{24}$$

$$^3\mathrm{I} \rightleftarrows {}^1\mathrm{II} \tag{25}$$

$$^1\mathrm{I} \longrightarrow \mathrm{II} \tag{26}$$

$$^3\mathrm{I} \longrightarrow \mathrm{II} \tag{27}$$

$$^1\mathrm{II} \longrightarrow \mathrm{I} \tag{28}$$

$$^3\mathrm{II} \longrightarrow \mathrm{I} \tag{29}$$

**Equation 22.** We believe the rearrangement of the indenone oxide singlet $^1$I to the pyrylium oxide singlet $^1$II is unambiguously excluded by the above data. When ethanol was used as solvent, it was shown that the isocoumarin V was not formed to a detectable extent through direct light absorption by I, whereas V was formed through direct light absorption by II in a quantum yield of $\phi_{\mathrm{II}\to\mathrm{V}} \geqslant 0.0045$. The wavelengths of light used in these determinations must have led to initial population of the lowest singlets of I and II, so if II had formed through an interconversion of the singlets (reaction 22) followed by crossing of $^1$II to the ground state, then $\phi_{\mathrm{I}\to\mathrm{V}}$ should have been equal to $\phi_{\mathrm{I}\to\mathrm{II}}\phi_{\mathrm{II}\to\mathrm{V}} \geqslant 0.0027$. Since the experimental value for $\phi_{\mathrm{I}\to\mathrm{V}}$ was $(3 \pm 15) \times 10^{-5}$, an absolute maximum of only 6.7% of II could have been formed by the reaction pathway 22.

The same conclusion is also demanded by the studies of the emission spectra. If the forward eq 22 were an important process, then absorption of light by the indenone oxide I (to $^1$I) should have led to population of $^1$II which would result in fluorescence emission characteristic of the pyrylium oxide II. However, the initial intensity of fluorescence emission of II could be conservatively estimated as less than 2% of the intensity attained after II had been formed during several minutes' irradiation.[36] This was true in both the alcohol and hydrocarbon glasses. Accordingly the process given by eq 22 does not play a significant role in the photochemical conversion of the indenone oxide I to the pyrylium oxide II in either hydrocarbon or hydroxylic media.

**Equation 23.** The rearrangement of the indenone oxide triplet $^3$I to the pyrylium oxide triplet $^3$II cannot be excluded rigorously by the present data. However, the reaction does not compare favorably with reactions that do proceed by this type of process. Since the photointerconversion of *cis*- and *trans*-stilbenes has been demonstrated to proceed through the triplet states and has been thoroughly studied,[34] it is instructive to compare this reaction with the reaction of I.

*cis*-Stilbene has a higher energy triplet than the *trans* isomer and appears to react by rearrangement of its triplet to a geometrically distinct, lower energy triplet. The most compelling evidence for this conclusion is that sensitizers with progressively lower energy triplets transfer energy to *cis*-stilbene by a process that does not decrease in efficiency as rapidly as would be expected of classical energy transfer. The data suggest that energy transfer from low-energy sensitizer triplets to *cis*-

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(36) Since $\phi_{\mathrm{I}\to\mathrm{II}}$ did not change greatly between 25 and 77 °K, the initial fluorescence intensity produced by absorption of light by I would have been expected to be near 60% of the intensity obtained by direct irradiation of II if the reaction actually proceeded by eq 22.

stilbene must proceed with concerted rearrangement of the newly forming stilbene triplet. This process has been called nonvertical energy transfer.[37] Additional examples of apparent endothermic energy transfer have been observed which suggest that this behavior may be quite common.[38] It appears likely that nonvertical energy transfer may occur whenever the spectroscopic triplet of an acceptor can undergo a predissociative process; that is, when vibrational relaxation of the spectroscopic triplet leads directly to a lower energy triplet species with a grossly different geometry. We therefore propose that the ability or inability of a molecule to accept energy by a nonvertical process may serve as a diagnostic test for the capability of that molecule to undergo rapid exothermic reactions within the triplet manifold. Since eq 23 represents such a reaction, it is instructive to compare those data that implicate nonvertical energy transfer to *cis*-stilbene with the analogous data for the indenone oxide I.

Nonvertical energy transfer to *cis*-stilbene manifests itself in a relatively gradual change in the photostationary [*cis*]/[*trans*] ratio as the sensitizer triplet energies drop below that of *cis*-stilbene ($E_t \sim 57$ kcal). Sensitizers with triplet energies near 57 kcal produce a photostationary ratio near 2.8 while sensitizers having ~4 kcal lower energy triplets lead to photostationary ratios that are only a factor of 3–4 greater.[34] If we attempt to analyze these data without taking into account nonvertical energy transfer then eq 32 applies, where ${}^3\phi_{c\rightarrow t}$ and ${}^3\phi_{t\rightarrow c}$ refer to the theoretical quantum yields of the sensitized reactions when all the sensitizer triplets are quenched by *cis*- (c) and *trans*- (t) stilbene, respectively.

$$ {}^3S + c \longrightarrow {}^3c + S \tag{30} $$

$$ {}^3S + t \longrightarrow {}^3t + S \tag{31} $$

$$ \frac{k_{31}}{k_{30}} = \frac{[c]}{[t]}\frac{{}^3\phi_{c\rightarrow t}}{{}^3\phi_{t\rightarrow c}} \tag{32} $$

From this equation, $k_{30}$ may be evaluated if the photostationary ratio [c]/[t] and $k_{31}$ are known. Although $k_{31}$ is not known, it must be nearly constant for sensitizers having triplet energies of 53–57 kcal because reaction 31 should be exothermic (*trans*-stilbene $E_t$ = 49.5 kcal)[44] and thus nearly diffusion controlled.[33] Even assuming that $k_{31}$ might be reduced by as much as a factor of three with this change in sensitizer triplet energy,[45] substitution of the above photostationary ratios into eq 32 indicates that $k_{30}$ drops by no more than 12-fold. This is not in accord with the precipitous drop in this rate expected if classical energy transfer by eq 30 were to become endothermic by 4 kcal,[33] and hence nonvertical energy transfer must be postulated.

In marked contrast to this behavior, the photostationary ratio [I]/[II] increased by a factor of about 100 on lowering the triplet energy of the sensitizer from 65 to 62 kcal. This shows (eq 21) that there must be at least a 100-fold drop in the rate constant ($k_{15}$) for energy transfer to I, since the rate of energy transfer to II ($k_{17}$) must be diffusion controlled and thus nearly invariant. Moreover, this change in $k_{15}$ must actually be even greater because of the above described errors inherent in these photostationary ratio measurements. Thus, if only sensitized interconversion of I and II took place during these measurements, the photostationary ratios [I]/[II] would be even lower with high energy sensitizers and higher with low energy sensitizers. From these facts, we can make a conservative estimate that $k_{15}$ is actually diminished by at least a factor of 1000 with the 3-kcal reduction in the sensitizer triplet energy. This sharp change in the rate of energy transfer to I as the process becomes exothermic stands in contrast to the relatively gradual change in the rate of energy transfer to *cis*-stilbene. Therefore, unlike *cis*-stilbene, I behaves as though it can accept energy only through classical energy transfer, and nonvertical energy transfer to I does not take place. Accordingly, if it is accepted, as proposed above, that the capability of a molecule to undergo nonvertical energy transfer is directly related to its tendency to undergo a rapid exothermic rearrangement within the triplet manifold, then rearrangement of ${}^3$I to ${}^3$II (eq 23) probably is not an important process.

**Equation 24.** The available data provide no information about the forward reaction, although the process appears *a priori* to be improbable since it involves a concerted change of multiplicity and geometry. As will become clear, its inclusion in the mechanism requires *ad hoc* explanations that are avoided by the interpretation of the reaction given below.

**Equation 25.** This process is rigorously excluded at least in a hydrocarbon medium by the fluorescence data. It has been demonstrated (see section on Quenchers) that the formation of II in benzene proceeds by way of ${}^3$I in the unsensitized reaction to the extent of about 13%. If ${}^3$I gave ${}^1$II, absorption of light by I would be expected to produce the fluorescence emission of II. Since no emission was observed when only I absorbed the light, this process does not occur (*cf.* discussion of eq 22). In alcohol, the unsensitized reaction proceeds nearly exclusively by way of ${}^1$I and hence process 25 is unimportant in this solvent at least in the unsensitized reaction.

**"Phantom" Intermediates in Eq 22 and 23.** The probable existence of nonplanar ("phantom")[34,37] triplet intermediates in the *cis–trans* photoisomerization of olefins suggests the possibility that energy surfaces connecting the corresponding singlet or triplet levels of I and II may have minima having geometries intermediate between the two tautomers. However, in contrast to the olefins, it is difficult to envision a geometry that is intermediate between I and II that could represent an energy minimum. Moreover, the existence of energy minima in processes 22 and 23 would

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(37) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

(38) Recent examples of apparent uphill energy transfer include the sensitization of the *cis–trans* isomerization of olefins,[34,39] the ring fragmentation of cyclobutanes to olefins, and probably the reverse reaction as well,[40] the *cis–trans* isomerization of cyclopropanes,[40,41] the rearrangement of cyclohexadienones,[42] the homolytic cleavage of dibenzoyl peroxide,[43] and energy transfer to diphenylacetylene with probable formation of a nonlinear triplet (unpublished observation of E. F. Ullman).

(39) (a) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (b) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

(40) (a) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964); (b) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4674 (1961); (c) A. A. Lamola, *ibid.*, **88**, 813 (1966).

(41) G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965).

(42) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964).

(43) C. Walling and M. J. Gibian, *ibid.*, **87**, 3413 (1965).

(44) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(45) The rates for energy transfer to biacetyl from sensitizer triplets that were 0.04 to 8 kcal more energetic than the biacetyl triplet were found to vary by no more than a factor of 3.[33]

not affect the arguments used to exclude these processes, since such minima should not inhibit temporary formation of the low energy planar species $^1$II and $^3$II from the corresponding high energy species $^1$I and $^3$I.

**Vibrationally Excited Ground-State Intermediates (Eq 26–29).** From the preceding arguments, the only mechanisms for the photochemical conversion of II to I that have not been eliminated are those equations, 28 and 29, which do not involve electronically excited states of the product. In the photochemical conversion of I to II, eq 23 has been shown to be improbable, eq 24 appears *a priori* to be unlikely though it cannot be excluded, and eq 22 and 25 are positively excluded. This leaves for serious consideration those equations (26 and 27) which again do not involve electronically excited states of the product. Each of the processes 26–29 might be considered to take place by crossing from an electronically excited state of the starting material to a vibrationally excited ground-state molecule which, at the instant of its formation, has a geometry and energy identical with that of its electronically excited precursor. Provided this energy is greater than the activation energy required for the thermal reaction, rearrangement might then take place followed by loss of vibrational energy through collision with solvent molecules.

An argument that has been advanced against proposals for the intermediacy of vibrationally excited states in photochemical reactions in solution[46] is based on the Rice–Ramsperger–Kassel (RRK) theory of unimolecular reactions,[47] given by eq 33, where $*k$ is the rate of reaction of a vibrationally excited molecule with vibrational energy $E$, $A$ is the frequency factor and $E_0$ the activation energy of the normal thermal reaction, and $n$ is the number of vibrational degrees of freedom

$$*k = A\left(\frac{E - E_0}{E}\right)^{n-1} \tag{33}$$

that act along the reaction coordinate. It was concluded that when realistic values for these parameters were employed for a moderate size (35 atoms) molecule, the rate of reaction $*k$ of a photochemically produced, vibrationally excited intermediate in solution could not compete with collisional deactivation by the solvent.

The present evidence requires that this argument be reexamined for the indenone oxide reaction. If we make the rather liberal assumption that the pseudo-first-order rate constant for collisional deactivation by benzene might be as low as $10^{10}$ sec$^{-1}$ (the previous authors[46b] estimated $10^{11}$ sec$^{-1}$ by assuming that deactivation occurs with every collision), then the quantum yield data require that $*k_{\text{I}\rightarrow\text{II}} = \phi_{\text{I}\rightarrow\text{II}} \times 10^{10} = 5.6 \times 10^9$ sec$^{-1}$ and $*k_{\text{II}\rightarrow\text{I}} = \phi_{\text{II}\rightarrow\text{I}} \times 10^{10} = 5.6 \times 10^8$ sec$^{-1}$. In the forward reaction I → II, if we let $E$ equal the triplet energy of I (64 kcal) and use the measured Arrhenius parameters $A = 10^{12}$ and $E_0 = 29.4$ kcal, eq 33 gives $n = 9.2$. A similar value was obtained for the reverse reaction when the same frequency factor was used and $E$ was taken as the singlet energy of II (the reaction proceeds almost exclusively from the singlet). By comparison the total number of vibrational degrees of freedom in I and II is $3N-6 = 105$. In gas-phase reactions of vibrationally excited molecules a value for $n$ of about one-half the total vibrational degrees of freedom is frequently assumed. However, it has recently been pointed out that any value of $n$ may actually arise depending on the vibrational frequency patterns, the activation energy $E_0$, and the temperature.[47a] Nevertheless, considering the liberal assumption we have made concerning the rate of collisional deactivation, $n = 9.2$ is exceptionally low for this large a molecule, and, as will be shown, some modification of the simple vibrationally excited ground-state hypothesis is required.

The way out of the dilemma imposed by the low value for $n$ resides in the assumption implicit in the RRK theory that the vibrationally excited species is formed with a random distribution of vibrational energy. The rate of reaction of this vibrationally excited molecule is a function of the probability of finding this energy concentrated at the reaction site, and this probability is expected to fall off rapidly as the number of atoms in the molecule increases. However, a vibrationally excited ground-state molecule derived by adiabatic crossing from an electronically excited state would not be expected to have a random distribution of vibrational energy at the instant of its formation. Instead, its distribution of vibrational energy would be controlled by the restrictions implicit in the Franck–Condon principle, namely conservation of momentum of the atomic nuclei and quantum mechanical overlap between vibrational levels of the ground and electronically excited states. *In a vibrationally excited ground state produced by crossing from an electronically excited state, much of the energy required for reaction might therefore already be concentrated at the reaction site.*

If this interpretation is correct, one might expect that the probability for reaction of the vibrationally excited molecule would depend on the ratio of the rate of its reaction to the rate of its deactivation both by collision and by randomization of the vibrational energy distribution within the molecule. The energy parameters given by eq 33 would then still have an influence on the rate of reaction of the vibrationally excited molecule, but the rate would also be a function of the specific distribution of vibrational energy associated with crossing from a given electronically excited state.

These concepts may be tested by considering the relative probabilities for different modes of decay of the lowest excited states of I and II given in the following diagrams.

$$\begin{tikzcd}
 & \text{I} & \\
{}^1\text{I} \arrow[ur, "0.40"] \arrow[rr, "\phi_i = 0.11"] \arrow[dr, "\phi_\infty = 0.49"'] & & {}^3\text{I} \arrow[ul, "0.38"'] \arrow[dl, "{}^3\phi_{\text{I}\rightarrow\text{II}} = 0.62"] \\
 & \text{II} &
\end{tikzcd}
\qquad
\begin{tikzcd}
 & \text{II} & \\
{}^1\text{II} \arrow[ur, "?"] \arrow[rr, "\phi_i = ?"] \arrow[dr, "\phi_\infty = 0.056"'] & & {}^3\text{II} \arrow[ul, ">0.99"'] \arrow[dl, "{}^3\phi_{\text{II}\rightarrow\text{I}} \leqslant 6 \times 10^{-4}"] \\
 & \text{I} &
\end{tikzcd}$$

These probabilities are taken from the experimental values for the quantum yields in benzene solution, where $\phi_\infty$ is the quantum yield for the direct light-induced reaction at very high quencher concentrations, and $^3\phi$ is the quantum yield for the sensitized reaction extrapolated to infinite concentration of the reactant.

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[46] (a) G. Zimmerman, L. Chow, and U. Paik, *J. Am. Chem. Soc.*, 80, 3528 (1958); (b) H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).

[47] For leading references see (a) D. W. Placzek, B. S. Rabinovitch, and G. Z. Whitten, *J. Chem. Phys.*, 43, 4071 (1965); (b) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, 3, 1 (1964).

The probability of intersystem crossing, $\phi_i$, calculated from eq 34 ($\phi$ taken from Table V), is given for the indenone oxide I but is indeterminate for the pyrylium oxide II.

$$\phi_i = \frac{\phi - \phi_\infty}{{}^3\phi} \qquad (34)$$

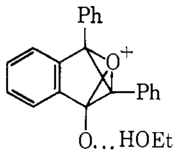
These data are quite revealing. First, we note that if $^1$I and $^3$I are assumed to undergo crossing to vibrationally excited ground states of I prior to formation of II, *the probabilities are remarkably similar for formation of II from the vibrationally excited ground-state molecules derived from either precursor*, *viz.*, $\phi_\infty/(1 - \phi_i) = 0.55$ and ${}^3\phi_{\mathrm{I}\rightarrow\mathrm{II}} = 0.62$, respectively. This certainly suggests that very similar intermediate states arise during formation of II from the two electronically excited states of I. Nevertheless, the probability is lower for formation of II from the vibrationally excited species derived from $^1$I than from the vibrationally excited species derived from $^3$I, whereas eq 33 would predict the opposite order. We therefore suggest, as postulated above, that the two vibrationally excited species may be formed with slightly different energy distributions. Second, the probability for reaction of a vibrationally excited ground state derived from $^1$II is far greater than that derived from $^3$II, *viz.*, $\phi_\infty/(1 - \phi_i) \geqslant 0.056$ and ${}^3\phi_{\mathrm{II}\rightarrow\mathrm{I}} \leqslant 6 \times 10^{-4}$. This is not an unreasonable result since the triplet level of II may well be near to the activation energy barrier for the thermal reaction (*cf.* Figure 8). The reaction probabilities for the vibrationally excited ground states of II are therefore likely to be more heavily influenced by the energy considerations in eq 33 than by differences in energy distribution associated with crossing from different electronically excited states. Third, the above data show that the indenone oxide singlet $^1$I undergoes internal conversion to the ground state nearly four times more efficiently than it undergoes intersystem crossing, whereas related unreactive ketones such as acetophenone undergo nearly quantitative intersystem crossing.[30] This suggests that the rate of internal conversion of I is considerably greater than in normal aromatic ketones. A similar increase in the rate of intersystem crossing from $^3$I is evident from the short lifetime of $^3$I of $\sim 5 \times 10^{-9}$ sec (see Quenchers) compared to the benzophenone triplet lifetime of $3.8 \times 10^{-6}$ sec.[26] *The ability of compound I to undergo a photochemical reaction therefore seems to be associated in some way with increased rates of crossing from its electronically excited states.* The reasons for these increased rates are not understood. They are clearly not merely due to fast reactions of the electronically excited states of I to give II since 40% or more of the molecules that undergo crossing from either excited state end up unchanged. Possibly quantum mechanical coupling between the vibrational modes of the excited and ground states is enhanced in some manner by the ability of the vibrationally excited ground state to undergo large geometrical changes. In any event, *it seems clear that the photochemical reaction is closely associated with crossing to the ground state, and that the alternative processes, 23 and 24, that were considered above, are most unlikely.*

A qualitative test of this vibrationally excited state hypothesis is possible from the predictions based on the RRK theory. Equation 33 shows that the rate of reaction of a vibrationally excited ground-state molecule should increase as the difference between the energy of the vibrationally excited molecule and the activation energy of the normal thermal reaction increases. In the photochemical reaction I → II, we note that an increase in the polarity of the solvent increases the energy of the lowest singlet (probably an $n,\pi^*$ state, see Figure 2). Provided the corresponding triplet has the same electronic configuration, its energy would also be expected to increase with solvent polarity. At the same time, the activation energy of the thermal reaction would be expected to be reduced because of the increase in polarity on proceeding from the starting indenone oxide I to the highly polar product II. Increases in solvent polarity therefore increase the energy difference between the electronically excited states and the transition state. The rearrangement of vibrationally excited species derived by crossing from these electronically excited states should then compete more efficiently with collisional deactivation and intramolecular redistribution of vibrational energy. That is, the quantum yield of the reaction should increase with solvent polarity, and, as shown in Table V, this proves to be the case.

As regards the reverse process II → I, no prediction of the effect of solvent polarity on the quantum yield is possible since an increase in solvent polarity produces changes in the transition state and electronically excited state energies that are in the same direction. The quantum yield data for the reverse reaction given in Table V can therefore be readily rationallized but it provides no information concerning the vibrationally excited state hypothesis.[48]

**Related Compounds.** It remains to be considered whether the vibrationally excited ground-state mechanism for the photochemical interconversion of the indenone oxide I and its valence tautomer II might explain the little that is known of the photochemistry of related compounds. As for other indenone oxides, it has been noted that 3-ethyl-2-phenylindenone oxide (XVII, $R_1 = C_2H_5$, $R_2 = H$)[50] develops color on irradiation in benzene more slowly than does I or its methyl derivative XVII ($R_1 = Ph$, $R_2 = CH_3$). Assuming that the extinction coefficients of II and the pyrylium oxide tautomers of XVII are not tremendously different, the quantum yield of the valence tautomerization of XVII ($R_1 = C_2H_5$, $R_2 = H$) must be considerably lower than that for I and XVII ($R_1 = Ph$, $R_2 = CH_3$).

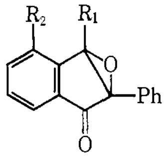
[48] In arguing that I and II are interconverted through intermediate vibrationally excited ground states, we do not wish to imply that all the photochemical reactions of these compounds necessarily proceed in this way. In particular, the isocoumarin V, which is formed from I in benzene and from II in ethanol, may well be produced in these reactions by unrelated processes involving high energy intermediates or electronically excited states of the product. A reasonable mechanistic proposal for a rearrangement of a derivative of I to an isocoumarin in benzene has previously been offered.[49] A possible path for the reaction II ⟶ V in ethanol might involve a benzvalene-like intermediate stabilized by bonding to the solvent.



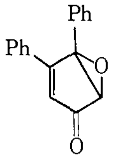
[49] H. E. Zimmerman and R. D. Simkin, *Tetrahedron Letters*, 1847 (1964).

[50] We are indebted to Mr. W. F. Cordes III for preparing this compound.

Among the cyclopentadienone oxides III and XVIII that have been studied,[6,7,51] the efficiency of the photochemical reaction is of the order III (R = Ph) $\approx$ III (R = H) $\gg$ XVIII. Thus both groups of compounds show a tendency for the quantum yields to drop off as less massive substituents are attached to the oxirane ring. One possible explanation for this tendency might be that the presence of heavy substituents on the oxirane ring directs the distribution of vibrational energy into the oxirane C–C bond at the time of crossing from an electronically excited state. This would be consistent with a simple mechanical model in which the initial distribution of energy in the vibrationally excited molecule would permit synchronous vibration of both ring substituents perpendicular to the plane of the molecule. The resulting torque on the C–C bond, and hence the quantum yield, would then depend on the mass of the vibrating substituents. While this is obviously an oversimplified picture, it may provide a working hypothesis for new experiments designed to gain an understanding of these substituent effects.



XVII



XVIII

## Experimental Section

**Materials.** Lehigh Valley Chemical Co. reagent grade benzene and U. S. Industrial Chemical Co. absolute ethanol were used without further purification. Phillips Petroleum Co. hexane was purified by stirring successively with four portions of potassium permanganate–sulfuric acid solution, four portions of concentrated sulfuric acid, water, aqueous sodium bicarbonate, and again water. The hexane was dried over magnesium sulfate, chromatographed on basic alumina, and distilled, bp 67°.

With the exception of di-*t*-butyl nitroxide all the sensitizers and quenchers were obtained commercially and were recrystallized to constant melting point. Benzophenone was, in addition, sublimed *in vacuo*, and phenanthrene was freed of anthracene impurity and further purified by the method of Kooyman and Farenhorst.[52] We are indebted to Dr. A. K. Hoffmann for the di-*t*-butyl nitroxide sample which had been purified by distillation.

The 2,3-diphenylindenone oxide (I) was prepared according to the literature procedure[10] and recrystallized from ethanol–water to a constant melting point of 142–143°. The tritium-labeled indenone oxide (I) was prepared by permitting the solid to stand in a tritium atmosphere for 10 days followed by recrystallization of the solid, dilution with inactive I, and further recrystallization.

**Light Sources.** For near-ultraviolet light, designated 3100–4000 A in the text, a G.E. B-H6 1000-w high-pressure mercury lamp was used with Hanovia No. 16223A and 6541 filters. For shorter wavelength ultraviolet light, designated 2290–4200 A in the text, a U-shaped, 100-w Hanovia No. 30620 medium-pressure mercury lamp was used with a Corning No. 9863 filter. An Argus 540 500-w projector together with a Corning No. 3387 cutoff filter was used as a source of visible light, designated >4350 A. Each filter combination transmitted <1% of the light outside the designated range.

For actinometry with 3650-A light, the Hanovia lamp was used with Corning No. 5860 and 7380 filters. For actinometry with 5460-A light, the G.E. B-H6 lamp was used with Corning No. 3484, 5031, and 5120 filters. This filter combination transmitted 12% of the light at 5460 A and <0.1% outside the range of 530–574 m$\mu$.

**Spectra.** Conventional spectroscopic methods were used except for the determination of the spectra of the pyrylium oxide II. For the determination of the extinction coefficient of the long wavelength band of II, solutions of 1–2 mg of tritium-labeled indenone oxide I (60,000 cpm/mg) in 3 ml of the desired solvent were bubbled with nitrogen in a 1-cm, ultraviolet cell and then irradiated with ultraviolet light. The visible spectra of the solutions were then recorded and 0.10 ml of norbornadiene was immediately added. After addition of 100–150 mg of the inactive norbornadiene adduct XIII to the solutions, the solvent was removed and the adduct recrystallized five times from benzene–ethanol. The activity of the adduct was measured by scintillation counting and the extinction coefficients were calculated from the amount of radioactive adduct XIII that had formed. Blanks that were carried out in an identical manner but without initial irradiation were, in each case, found to be inactive. The determination of the ultraviolet portion of the spectra of II has been described in the Results section.

A singlet–triplet absorption spectrum of benzylidineanthrone was determined using a 0.2 *M* chloroform solution in a 5.6-cm, high-pressure cell by the oxygen perturbation method of Evans.[53] Weak new peaks were observed under 120 atm of oxygen at 578 and 629 m$\mu$. In a similar experiment using a 0.2 *M* chloroform solution of the indenone oxide I, oxygen produced no change in the absorption spectrum.

**Kinetics.** Solutions of I were degassed by repeated freezing and thawing *in vacuo* in Pyrex glass ultraviolet cells which were then sealed under vacuum. After allowing the solutions to age by brief ultraviolet irradiation followed by standing in the dark, the solutions were bleached with >4350-A light or colored with 3100–4000-A light depending on the measurement to be made, and the kinetics were followed spectroscopically. The kinetics of the reaction I → II at elevated temperatures in benzene were determined using 0.013 *M* I in degassed benzene solutions containing 10% norbornadiene. The amount of adduct XIII formed was determined by infrared analysis of the residues obtained after evaporation of the solvent *in vacuo*.

**Quantum Yields and Stationary States.** For quantum yield studies using 3650-A light, the ferrioxalate actinometric method of Hatchard and Parker[54] was used. For measurements at 5460 A the method of Wegner and Adamson,[55] using Reinecke's salt, was employed. The quantum-yield determinations for the interconversion of I and II with or without sensitizers or quenchers and also the stationary-state measurements were made spectroscopically at room temperature (25°). The solutions were contained in Thunberg cells and were degassed by repeated freezing and thawing *in vacuo*. Because of the high absorptivity of II at 3650 A, measurements of $\phi_{I\rightarrow II}$ were carried to less than 0.05% of completion and corrections were made when necessary for the fraction of light (<3%) absorbed by II. For measurements of $\phi_{II\rightarrow I}$ solutions of II having absorptivities of 1–2 at 5460 A were prepared by ultraviolet irradiation of solutions of I. During the photochemical reconversion of II to I with 5460-A light the absorptivity at this wavelength was not allowed to fall below 1, and corrections were made for light not absorbed by the solution.

The quantum yield for reaction I → V in ethanol was calculated from the chemical yield of isocoumarin V on irradiating I with 3650-A light. Solutions of 20–25 mg of tritium-labeled I (60,000 cpm/mg) in 10 ml of ethanol containing 1 ml of norbornadiene were irradiated until all the indenone oxide I had been destroyed. The reaction mixture was then diluted with 250 mg of isocoumarin V and chromatographed on alumina. The isolated V was recrystallized twice from acetic acid–water and converted by alkaline hydrolysis to *o*-desylbenzoic acid. After separating this acid from neutral and basic contaminants, it was recrystallized two times each from benzene–heptane and from methanol–water. The acitivity of the product, mp 139–141° (lit.[56] 138–142°), was determined by liquid scintillation counting. Despite these precautions, the samples were not radiochemically pure, since two additional sets of three recrystallizations each lowered the activity by 6.5% and 2.5%, respectively. Blank runs carried out in exactly the same way but without irradiation gave *o*-desylbenzoic acid samples that displayed quantitatively identical behavior. Since the activities at each stage of the purification were reproducible in both runs and blanks, further purification was not attempted, and it was deemed

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(51) A. Padwa, *Tetrahedron Letters*, 813 (1964).

(52) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1943).

(53) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(54) (a) C. A. Parker, *Proc. Roy. Soc.*, **A220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956).

(55) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966). We are greatly indebted to these authors for making this method available to us prior to publication.

(56) C. F. Koelsch and C. D. LeClaire, *ibid.*, **65**, 754 (1943).

Table VIII. Per Cent Yields of 3,4-Diphenylisocoumarin (V) on Irradiation of I in Ethanol with 10% Norbornadiene

| Run | Blank |
|---|---|
| 0.28 | 0.29 |
| 0.32 | 0.30 |
| 0.30 ± 0.02 | 0.295 ± 0.005 |

permissible to subtract the activities of the blanks from the runs (see Table VIII).

A similar technique was used for the determination of $\phi_{II \rightarrow V}$ (see Quantum Yields in Results section).

The quantum yield for the formation of the hydroxy ether VIII from I was determined by irradiation with 3100–4000-A light of a 1.07 *M* solution of I in 50 ml of ethanol-1-$^{14}$C (16080 cpm/mg) containing 5 ml of norbornadiene. After all the I had been destroyed, 150 mg of the inactive hydroxy ether VIII was added. The resulting mixture was chromatographed, and the recovered VIII was recrystallized from methanol–water and then from benzene–heptane. The product was not purified to constant activity, but the observed activity showed that no more than 0.21% of I had been converted to VIII. Thus,$\phi_{I \rightarrow VIII} \leqslant 0.0021 \phi_{I \rightarrow II} = 1.2 \times 10^{-3}$

**Photochemical Reactions of I and II in Benzene and Ethanol.** In the runs described in Tables I and II the solutions were deoxygenated prior to irradiation by bubbling with nitrogen. The irradiations were carried out with stirring, and at elevated temperatures sealed Pyrex glass bulbs were used to prevent boiling of the solvent. Before admitting air to the irradiated solutions, the excess pyrylium oxide II was destroyed by irradiation with >4350-A light. The products were isolated by a combination of fractional crystallization and chromatography on alumina. The products were eluted in the following order: (indenone oxide I and dimer VIa), isocoumarin V, isobenzofuran XII, phthalide VII, and (hydroxy ethers VIII and IX). The pairs of compounds in parentheses did not separate by chromatography, and their relative proportions were determined by quantitative infrared analysis. With the exception of VIII and IX all the products had previously been reported and were compared with authentic samples prepared by methods described in the literature.

***cis*-2,3-Diphenyl-3-ethoxy-2-hydroxyindan-1-one (IX).** To a solution of 2.0 g (0.0067 mole) of the indenone oxide I in 100 ml of absolute ethanol was added 40 ml of ethanol saturated with dry hydrogen chloride. The resulting mixture was warmed on a steam bath for 5 min and then poured into 400 ml of water. The aqueous solution was extracted with chloroform, and the combined chloroform extracts were dried over magnesium sulfate and evaporated. On recrystallization of the residue from methanol, there was obtained 1.10 g (48%) of IX, mp 154–156° (red at 200°).

The same product was obtained by heating at reflux for 10 min a solution of 1.0 g (0.003 mole) of the chlorohydrin XI[13] in 10 ml of ethanol. The precipitate that formed on addition of water and cooling of this solution was recrystallized from benzene–heptane to give 0.88 g (87%) of IX, mp 154–156 (red at 200°).

*Anal.* Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.91; H, 5.63.

The compound displayed absorption maxima at $\lambda_{max}^{C_6H_{14}}$ 240 m$\mu$ (log $\epsilon$ 4.05), 265 sh (3.14), 282 (3.15), 290 (3.12), and 350 (1.93); $\lambda_{max}^{CCl_4}$ 2.821, 2.894, and 5.78 $\mu$; nmr signals ($CCl_4$) at $\tau$ 8.91 ($CH_3$, triplet, $J$ = 7 cps), 7.0 and 6.53 ($CH_2$, 9 lines, $J$ = ~7 cps), 5.87 (OH, broad, extrapolated to infinite dilution), and 1.8–3.3 (14 aromatic hydrogens). The compound did not react with periodic acid in ethanol, and its solutions were not photosensitive. Heating an ethanol solution for 45 hr at 125° was also without effect.

A solution of about 5 mg of IX in 0.5 ml of glacial acetic acid containing 1 drop of sulfuric acid was heated for 5 min on a steam bath. The reaction mixture was diluted with water and extracted with chloroform. The extracts were dried and the solvent evaporated to give the isocoumarin V, mp and mmp 166–168°.

***trans*-2,3-Diphenyl-3-ethoxy-2-hydroxyindan-1-one (VIII).** A stirred solution of 0.50 g (0.0017 mole) of the indenone oxide I in 50 ml of ethanol was bubbled with nitrogen and then irradiated with 3100–4000-A light for 20 hr. Evaporation of the solvent and recrystallization from benzene–heptane followed by two recrystallizations from methanol–water gave 0.27 g (48%) of VIII, mp 153–154° (red at 170°).

*Anal.* Calcd for $C_{23}H_{20}O_6$: C, 80.21; H, 5.85. Found: C, 80.13; H, 5.64.

The compound displayed absorption maxima at $\lambda_{max}^{C_6H_{14}}$ 240 (sh) m$\mu$ (log $\epsilon$ 4.11), 268 (3.12), 285 (3.19), 293 (3.17), and 335 (2.04); $\lambda_{max}^{CCl_4}$ 2.795, 2.905, and 5.78 $\mu$; nmr signals ($CCl_4$) at $\tau$ 9.20 ($CH_3$, triplet $J$ = 7 cps), 7.65 (OH, extrapolated to infinite dilution), 6.90 ($CH_2$, quintet, $J$ = ~7 cps), and 1.9–3.0 (14 aromatic hydrogens).

This compound was converted to the isocoumarin V with acetic and sulfuric acids in a manner similar to that used for conversion of IX to V. The compound consumed 0.93 equiv of periodic acid when allowed to stand for 4 days at room temperature in a dilute aqueous ethanolic solution of this reagent. The *trans*-hydroxy ether VIII was inert to ultraviolet light, but on heating a solution of VIII in hydrogen chloride saturated ethanol for 1 hr and chromatographing the products, there was obtained 73% of a 1:3 mixture of IX and VIII (infrared analysis). The remainder of the reaction mixture was the isocoumarin V. On heating a neutral ethanol solution of VIII at 125° for 45 hr a 2:1 mixture of IX and VIII was obtained.

**1,3-Diphenyl-2-benzopyrylium 4-Oxide (II).** A sitrred degassed solution of 200 mg of the indenone oxide I in 150 ml of hexane contained in a quartz flask was irradiated with 2290–4200-A light for 24 hr. During this period a green-black precipitate formed. The solvent was decanted and the precipitate washed with hexane in the dark to give 100 mg of crystalline II, mp 94–97°. The compound could not be redissolved without extensive decomposition, and on standing in the dark under nitrogen for a month, it gradually became oily. The infrared spectrum (mineral oil mull) showed only weak absorption in the region 5.2–6.4 $\mu$ but it had a strong C–O stretching peak at 6.58 $\mu$. On irradiation of the mull with >4350-A light for 30 sec the color was destroyed and the spectrum of the indenone oxide I was obtained.

**1,3-Diphenyl-4-hydroxy-2-benzopyrylium Bisulfate.** On irradiation with 3100–4000-A light of a solution of 600 mg of the indenone oxide I and 0.20 ml of sulfuric acid in 20 ml of dry ether, an orange precipitate was formed. The solvent was decanted, and the precipitate washed with ether to give 110 mg (18%) of bright orange crystals, mp 184–190° dec. Recrystallization from acetic acid–ether increased the melting point to 196–198° dec.

*Anal.* Calcd for $C_{21}H_{16}SO_6$: C, 63.62; H, 4.07; S, 8.09. Found: C, 63.88; H, 4.56; S, 8.05.

The infrared spectrum (mineral oil mull) showed distinctive peaks at 3.85 (OH, broad), 6.19, and 6.49 $\mu$. The solid was insoluble in acetone, ether, and benzene but dissolved in these solvents on addition of triethylamine to give deep red solutions which displayed the characteristic absorption of the pyrylium oxide II.

**2,3-Diphenyl-4-methylindenone Oxide.** A mixture of 74 g (0.46 mole) of 3-methylphthalic anhydride,[57] 78 g (0.57 mole) of phenylacetic acid, and 1 g of sodium acetate was heated to 240°, and maintained at that temperature for 4 hr. The reaction mixture was recrystallized three times from ethanol to give 50 g (47%) of 7-methyl-3-benzylidenephthalide, mp 153–54°.

*Anal.* Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.44; H, 4.98.

To 0.64 mole of phenylmagnesium bromide in 500 ml of ether was added 50 g (0.21 mole) of 7-methyl-3-benzylidenephthalide in 800 ml of benzene. The reaction mixture was heated at reflux for 1 hr and hydrolyzed, and the organic layer evaporated to dryness. The residue was steam distilled to leave an orange gum, which was recrystallized two times from isopropyl alcohol to give 44 g (71%) of 2,3-diphenyl-4-methylindenone as orange platelets, mp 144–146°.

*Anal.* Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.01; H, 5.37.

The location of the methyl group at the four position in this compound was shown by oxidation of the indenone with aqueous alkaline potassium permanganate. After boiling the mixture for 5 days a 72% yield of 2-benzoylisophthalic acid, mp 249–250° (lit.[58] 248–249°), was obtained.

To a mixture of 15.1 g (0.051 mole) of 2,3-diphenyl-4-methylindenone and 4.0 g (0.10 mole) of sodium hydroxide in 500 ml of 95% ethanol at 0° was added 0.13 mole of 30% hydrogen peroxide. The solution was boiled for 2 hr, cooled, and filtered. The resulting tan precipitate was recrystallized two times from ethanol (activated charcoal) to give 6.0 g (37%) of almost colorless 2,3-diphenyl-4-methylindenone oxide, mp 153–155°.

*Anal.* Calcd for $C_{22}H_{16}O_2$: C, 84.58; H, 5.16. Found: C, 84.66; H, 4.95.

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**Acknowledgment.** The authors are especially indebted to Dr. T. Ziegler for the radioactivity measurements. We also wish to thank Mr. J. Koren and Mrs. N. Searle for measurements of low-temperature absorption and emission spectra, Mr. N. Colthrup for aid in the interpretation of infrared spectra, and Dr. J. Lancaster and Mrs. M. Neglia for the nmr measurements.

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# Mechanism of the Thermal Isomerization of Some Diels–Alder Adducts of 1,4-Benzoquinone 2,3-Epoxides

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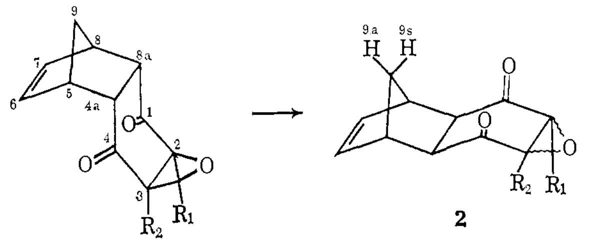
*Received June 28, 1966*

**Abstract:** The thermal isomerization of some *endo*-cyclopentadiene-1,4-benzoquinone 2,3-epoxide adducts gave the *exo* isomers. The configuration of the epoxide ring in the *exo* adduct is unknown. When the reaction of *endo*-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-epoxide was conducted in the presence of tetracyanoethylene, the products were 2,2,3,3-tetracyanonorborn-5-ene and 1,4-benzoquinone 2,3-epoxide. A dissociation–recombination mechanism is indicated. Evidence was obtained that isomerization does not accompany enolization.

Several studies of the isomerization of adducts of cyclopentadiene have been reported.[1-8] The conversion of *endo*-5-norbornene-2,3-dicarboxylic anhydride to the *exo* isomer has been carefully studied.[2,3,7,8] In decalin at 190° under heterogeneous conditions it has been reported to isomerize both by retrogression and by an internal mechanism.[2,3,7] The possibility of epimerization by an enolic species was discounted[2,3] because base catalysis was not observed in the molten state.[1] In *t*-pentylbenzene at 190° under homogeneous conditions no evidence for an internal mechanism was found.[8]

We wish to report the thermal isomerization of the *endo*-cyclopentadiene-1,4-benzoquinone 2,3-epoxide adduct (**1A**) to its corresponding *exo* isomer (**2A**). The *endo*-cyclopentadiene-1,4-benzoquinone 2,3-epoxide adduct (**1A**),[9] mp 120–121°, may be prepared in high yield by alkaline epoxidation of the *endo*-cyclopentadiene-1,4-benzoquinone adduct,[10] or by reaction of cyclopentadiene with 1,4-benzoquinone 2,3-epoxide in benzene at room temperature. In both precedures the epoxide was homogeneous; no *exo* isomer was produced. Neat **1A** was heated at 220° in a flask under a partial vacuum for 10 min. The product was judged to be approximately 50% **1A** and 50% **2A** from a comparison of its infrared spectrum with the spectra of known mixtures of **1A** and **2A**. Similar results were obtained with **1B**, **1C**, and **1D**. Pure **2** isomers were obtained by fractional recrystallization of each product mixture from ethanol. When pure **2A** was heated at 220° for 10 min, a 63% yield of a mixture of **1A** and **2A** (about 1:1) was obtained. The isomerization of **1A** could not be effected at 125 or 175°, and the rearrangement of **2A** was unsuccessful at 125°.



**1** **2**

| | $R_1$ | $R_2$ |
|---|---|---|
| **A**, | H | H |
| **B**, | $CH_3$ | H |
| **C**, | $C_6H_5$ | H |
| **D**, | $CH_3$ | $CH_3$ |

Treatment of **2B** with 1-phenyl-5-mercaptotetrazole in refluxing ethanol containing a catalytic amount of triethylamine gave the thioetherenedione (**4B**), which was identified by its nmr and infrared spectra. This thioetherenedione was different from that formed from **1B**.[11] Both thioetherenediones may be converted to the same hydroquinone (**5B**).[11]

The nmr spectrum of each *endo* isomer (**1A–D**) displays the 4a, 8a protons at $\tau$ *ca.* 6.5, whereas these protons appear at *ca.* 7.3 in the spectra of **2A–D** (Table I). Several authors have observed that *exo* protons are deshielded relative to *endo* protons in various substituted bicyclo[2.2.1]heptanes and bicyclo-[2.2.1]heptenes.[12-14] The spectra of the *exo* epoxides (**2**) are distinguished by the appearance of the 9 protons.

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