(t, J = 5 Hz, 2 H), 2.90 (br t, J = 6 Hz, 2 H), 1.87–1.65 (m, 2 H), 1.20 (t, J = 6.5 Hz, 3 H). An analytical sample was obtained by vpc on column A (155°, 110 ml/mm).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.30; H, 8.31.

On a larger scale, both isomers were formed. The syn isomer nmr spectrum (60 MHz): 5.35 (br s, 1 H), 4.43 (d, J = 1 Hz, 2H), 3.92 (q, J = 6.5 Hz, 2 H), 3.52 (t, J = 5 Hz, 2 H), 2.32 (br t, J = 6 Hz, 2 H), 1.87–1.65 (m, 2 H), 1.20 (t, J = 6.5 Hz, 2 H).

3-Methyl-3-tetrahydropyranacetic Acid Ethyl Ester (23). A solution of methylmagnesium iodide was prepared from magnesium (243 mg, 10 mg-atoms) and methyl iodide (1.365 g, 9.58 mmol) in anhydrous ether (15 ml). After cooling to 0° a solution of tetrakisiodo(tri-*n*-butylphosphine)copper[61] (328 mg, 0.833 mmol) in ether (10 ml) was added. The bright yellow reaction mixture was stirred for 5 min before dropwise addition of a solution of **56** (1.432 g, 8.33 mmol) in ether (10 ml) at 0°.

Immediately after completion of the addition, the reaction mixture was poured with rapid stirring into a solution of saturated ammonium chloride containing 1 ml of ammonium hydroxide. After extraction with ether, drying, and removal of the ether, **23** was obtained by preparative vpc (41%) on column G: ir 2945 (m), 2845 (w), 1735 (s), 1460 (w), 1360 (w), 1085 (s), 1025 (m), 970 (w) cm^{-1}; nmr (220 MHz) δ 4.06 (q, J = 7 Hz, 2 H), 3.65–3.55 (m, 1 H), 3.47–3.41 (m, 1 H), 3.35 (d, J = 12 Hz, 1 H), 3.13 (d, J = 12 Hz, 1 H), 2.47 (d, J = 14 Hz, 1 H), 2.12 (d, J = 14 Hz, 1 H), 1.72–1.29 (br m, 4 H), 1.24 (t, J = 7 Hz, 3 H), 0.96 (s, 3 H).

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.70; H, 9.89.

3-Methyl-3-(3-phenylpropyl)cyclopentanone (29). A solution of 3-phenylpropylmagnesium bromide was prepared from magnesium (4.02 g, 0.165 g-atom) and 1-bromo-3-phenylpropane (29.3 g, 0.15 mol) in ether (130 ml). The reaction mixture was cooled to 0°, and tetrakisiodo(tri-*n*-butylphosphine)copper[61] (2.46 g, 0.00625 mol) was introduced with ether (60 ml), followed by dropwise addition of 3-methylcyclopent-2-enone (12.00 g, 0.125 mol) in ether (75 ml). Upon completion of the addition, the reaction mixture was poured into a solution of saturated ammonium chloride containing a few milliliters of ammonium hydroxide. Extraction with ether, drying, and removal of solvent yielded 29.46 g. The cyclopentanone was isolated from nonketonic material using Girard's reagent T, which afforded, after distillation, **29** (7.50 g, 28%): bp 114–115° (0.1 mm); ir 3040 (w), 2950 (m), 1750 (s), 1600 (w), 1495 (m), 1450 (m), 1400 (m), 1375 (w), 1250 (w), 690 (s) cm^{-1}; nmr (220 MHz) δ 7.24–7.05 (br m, 5 H), 2.57 (t, J = 7 Hz, 2 H), 2.20–2.09 (m, 2 H), 1.95 (d, J = 18 Hz, 1 H), 1.86 (d, J = 18 Hz, 1 H), 1.75–1.30 (br m, 6 H), 1.01 (s, 3 H). An analytical sample was obtained by preparative vpc on column F (240°, 200 ml/min).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.24. Found: C, 83.39; H, 9.24.

4-Methyl-4-(3-phenylpropyl)cyclopentenone (24). The procedure[49] of Garbisch was employed in this conversion of the cyclopentanone (1.895 g, 8.75 mmol). At the bromo ketal stage 3.05 g was obtained. Hydrolysis of the unsaturated ketal in ethanol–3% aqueous H_2SO_4, extraction, drying, and bulb-to-bulb distillation gave the enone (866 mg, 46%): ir 3040 (w), 2950 (m), 1720 (s), 1595 (w), 1490 (w), 1450 (w), 1405 (w), 685 (m) cm^{-1}; nmr (220 MHz) 7.26 (d, J = 6 Hz, 1 H), 7.24–7.07 (br m, 5 H), 5.93 (d, J = 6 Hz, 1 H), 2.61–2.54 (m, 2 H), 2.17 (d, J = 18 Hz, 1 H), 1.97 (d, J = 18 Hz, 1 H), 1.71–1.42 (br m, 4 H), 1.19 (s, 3 H). An analytical sample was obtained by preparative vpc on column E.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.94; H, 8.57.

Acknowledgments. It is a pleasure to acknowledge the partial support of this investigation by the donors of the Petroleum Research Fund administered by the American Chemical Society. Mr. S. T. Bella performed microanalyses; Mr. Peter Ziegler determined 220-MHz nmr spectra; Miss Luz Catan contributed valuable technical assistance. We are grateful to them all.

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(61) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, 9 (1963).

Generation of Photochemical Intermediates without Light. The Type B Zwitterion. Mechanistic Organic Photochemistry. LXXI[1]

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Abstract: 6-Bromo-5,5-diphenylcyclohex-2-en-1-one was synthesized as a precursor to the zwitterion previously postulated as an intermediate in the type B photochemical rearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones. For example, irradiation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one gives a mixture of 2,3-diphenylphenol and 3,4-diphenylphenol. The ratio of phenols now has been found to be a smooth function of solvent polarity with the amount of 3,4 isomer increasing with increasing polarity. Turning to the dark reaction of 6-bromo-5,5-diphenylcyclohex-2-en-1-one with potassium *tert*-butoxide, a reaction designed to generate the Favorski-like zwitterion postulated for the type B photochemical rearrangement, we find that both the 2,3- and the 3,4-diphenylphenols are formed. Even more strikingly, the 2,3-diphenylphenol predominates as in the photochemical process and the ratio of phenols is the same as photochemically. Beyond this, the change in the ratio as a function of solvent polarity is the same for both dark and photochemical runs. Thus, convincing proof is available that the zwitterion **B** is indeed a true photochemical intermediate.

In 1961 we suggested that the photochemical rearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones to give 2,3- and 3,4-disubstituted phenols and their tautomers (*e.g.*, note eq 1) proceeds *via* the mesoionic zwitterion **B**.[2–5] This hypothesis was designed to resolve an inconsistency. On one hand, the triplet n–π* excited state was known to be the species

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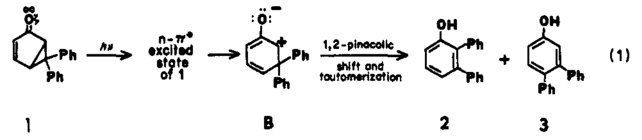
(1) For paper LXX of the series, note H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **94**, 6208 (1972).

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

(3) (a) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); (b) *ibid.*, **84**, 4527 (1962).

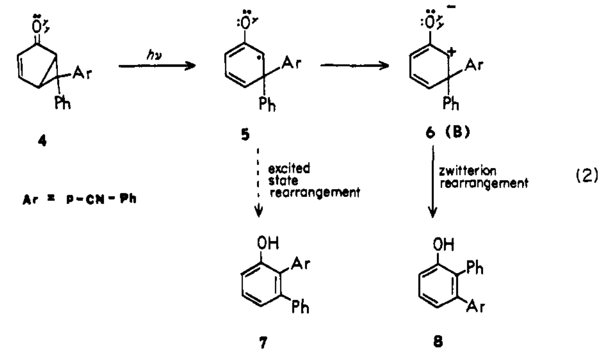
(4) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(5) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).



involved in the bicyclic enone-type B process, and the n–π* triplet has an electron-rich π system. On the other hand, the skeletal rearrangements suggested a cationic π system.

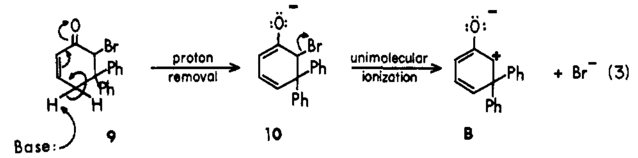
Later, in 1967, a critical test of whether it was (a) an n–π* species, with its added antibonding π electron, which was rearranging or (b) the mesoionic zwitterion B was devised,[6] involving the photorearrangement of 6-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one (**4**). While all evidence is that aryl migrations to π systems of n–π* excited species are facilitated by *p*-cyano substitution,[7,8] it was observed that in the type B rearrangement of bicyclic ketone **4** it was the phenyl group which migrated exclusively (note eq 2). Hence,



it was concluded[6] that migration was to a cationic center as in zwitterion B (*i.e.*, **6** in eq 2) rather than to the odd-electron center of the π system of excited state **5**.[9] Nevertheless, the evidence for intervention of zwitterions of type B was still inductive. Therefore, more direct evidence was desired.

The Approach. One very useful technique for showing one reactive species of excited state to be common to two reactions is the "fingerprint method" which we have previously proposed for photochemical use.[10] With this in mind, we considered alternative methods of generating zwitterion B for comparison with the photochemical reactivity (*cf.* eq 1) of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**).

Since the zwitterions of photochemistry are reminiscent of Favorskii intermediates, 6-bromo-5,5-diphenylcyclohex-2-en-1-one (**9**) seemed like an ideal nonphotochemical precursor to zwitterion B. Base treatment would most logically lead to proton removal from carbon 4 to afford enolate **10**, and unimolecular ionization of bromide from this 2-oxy-2,4-pentadienyl system should be exceedingly facile (eq 3).[11]

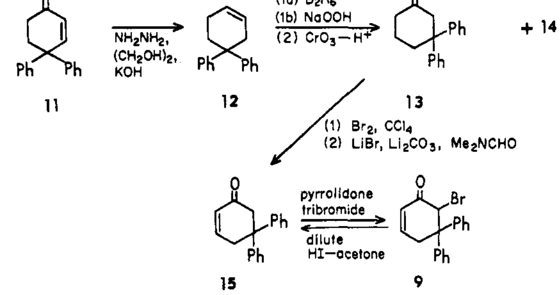


More than just generating zwitterion B without light and comparing its reactivity with the photochemical intermediates, the aim of the present study was to investigate the distribution of 2,3-diphenylphenol (**2**) relative to 3,4-diphenylphenol (**3**) if these were indeed formed in the dark process. Furthermore, it was the present intent to perturb this distribution with solvent changes and then determine if the photochemical and dark fingerprints were altered in duplicative fashion.

Results

Synthesis of Reactant. The synthesis began with the readily available[3,13a] 4,4-diphenylcyclohexenone (**11**). This was converted to 4,4-diphenylcyclohexene (**12**) by Huang-Minlon Wolff–Kishner reduction.[13b] The alternative route involving successive catalytic reduction, lithium aluminum hydride reduction, and elimination proved less convenient. Hydroboration of **12** and oxidation gave 3,3-diphenylcyclohexanone (**13**) together with 4,4-diphenylcyclohexanone (**14**). Conversion of **13** to the desired 6-bromo-5,5-diphenylcyclohex-2-en-1-one (**9**) was accomplished by bromination, dehydrobromination, and pyrrolidone tribromide[14] bromination. That the product indeed was a simple α-bromo ketone formed without skeletal rearrangement was confirmed by mild debromination to give enone **15** with dilute hydriodic acid in acetone. The synthesis is outlined in Chart I and detailed in the Experimental Section.

Chart I. Synthesis of 6-Bromo-5,5-diphenylcyclohex-2-en-1-one



Nonphotochemical Generation of Zwitterion. For generation of zwitterion B, potassium *tert*-butoxide in *tert*-butyl alcohol was initially selected. In this experiment, treatment of bromoenone **9** with *tert*-butoxide in the dark for 6 hr was observed to afford both the 2,3-diphenylphenol (**2**) and 3,4-diphenylphenol (**3**). The reaction proved both facile and clean. Furthermore, there was a heavy predominance of 2,3-diphenylphenol (**2**) as is the case for the photochemical formation of these phenols from bicyclic ketone **1**. Note eq 4. Even more impressive was the quantitative distribution of phenols obtained compared with the photochemical runs. Thus 87.6% was 2,3-diphenylphenol (**2**) and

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(6) H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **89**, 5163 (1967).

(7) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).

(8) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

(9) In eq 2, the solid dots represent π-system electrons, the *y*'s signify p_y (or n) nonbonding electrons, and the empty dots depict sp hybrid electrons. Note ref 2–4.

(10) H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).

(11) Indeed, there is evidence in the case of 6-tosyloxyisophorone that methoxide treatment does afford a mesoionic species.[12]

(12) A. W. Fort, *J. Amer. Chem. Soc.*, **84**, 2625 (1962).

(13) (a) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966). (b) Note the frequent tendency for enones to give this tautomer of product; *cf.* H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 233, and following for a discussion and references.

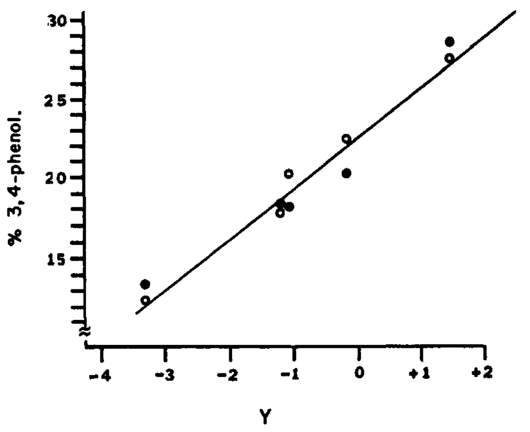
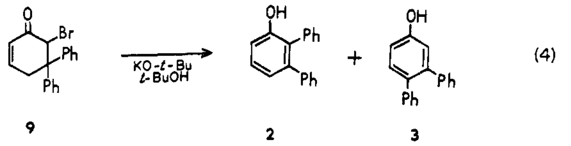


Figure 1. Plot of the per cent of 3,4-diphenylphenol obtained in dark (○) and photochemical (●) runs *vs.* *Y* values.



12.4% was 3,4-diphenylphenol (**3**) in the dark run compared with 86.4% 2,3 isomer and 13.6% 3,4-phenol product in the photochemical runs.[13]

Variation of Diphenylphenol Distribution with Solvent Polarity. With evidence in hand that the same species as obtained photochemically was being generated without light, attention was turned to the even more stringent test of solvent dependency as a fingerprint.

Previously it had been observed that the ratio of 2,3- and 3,4-phenols was pH dependent and some indication was available that there was an enhancement of 3,4-diphenylphenol relative to the 2,3 isomer as solvent polarity was increased.[13] Five solvent polarities were selected, ranging from *tert*-butyl alcohol as the least polar to 50% aqueous dioxane as the most polar. The solvents were selected strategically to give a useful spectrum of solvent *Y* values.[14,15] The results of base treatment of bromoenone **9** in these five solvents are included in Table I along with the results of the photochemical runs (*vide infra*).

For comparison with the dark runs, there were available three photochemical runs from our earlier study.[13] Additionally, two new runs were carried out. Since our previous studies showed that the ratio of phenols was independent of whether 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was irradiated or instead was generated *in situ* from 4,4-diphenylcyclohexadienone, the present runs were made using the dienone for convenience. The earlier photochemical studies utilized an infrared technique with accuracy of ±2.5%. In the present research quantitative column chromatography, the quantitative infrared method,[13] and vpc analysis were used.

Table I. Distribution[a] of Phenols from Zwitterion

Solvent	Photochemical 3,4-diphenylphenol, %	Dark reaction 3,4-diphenylphenol, %	*Y*
tert-Butyl alcohol[b]	13.6[e]	12.4[d]	−3.3[f]
95% ethanol–water[c]	18.4[d]	17.6[d]	−1.3[f]
80% *tert*-butyl alcohol–water[c]	18.0[e]	20.4[e]	−1.1[g]
73% dioxane–water[c]	20.2[e]	22.6[e]	−0.2[g]
50% dioxane–water[c]	28.5[d]	27.5[d]	+1.4[f]

[a] Tabulating the percentage of 3,4-diphenylphenol in the mixture of 2,3-diphenylphenol and 3,4-diphenylphenol. [b] Potassium *tert*-butoxide used as a base. [c] Potassium hydroxide used as a base. [d] Vpc analysis. [e] Quantitative infrared analysis; vpc analysis not performed. [f] Values of Winstein.[14] [g] Values not reported in the literature; obtained using the observation of W. H. Cropper, F. Spieth, and A. R. Olson [*J. Amer. Chem. Soc.*, **76**, 6248 (1954)] that the plot of *Y* *vs.* per cent water is linear in the region of low percentages of water.

The results of these runs are also included in Table I for comparison with the dark reactions.

It is seen that the ratio of 3,4-diphenylphenol to 2,3-diphenylphenol is enhanced with an increase in solvent polarity both in the photochemical and the dark runs. Over the range of polarity available the percentage of 3,4-diphenylphenol proved to be a smooth, and essentially linear function of *Y* value. This is seen in Figure 1.

However, the most dramatic aspect is that the *same dependence* of per cent 3,4-diphenylphenol (**3**) on *Y* value is obtained in the dark runs as in the photochemical reactions. While the spread of product distributions is only 15%, the disparity between dark and photochemical points averages only 1.6% and the agreement is too remarkable to be fortuitous.

Finally, a point of interest is the lack of formation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**), this being an *a priori* product of the dark reaction. Vpc analysis, which proved capable of detecting very minor amounts of this compound, showed it not to be present significantly (*i.e.*, <1%).

Interpretative Discussion

Zwitterion B as a Reality. The first and most important conclusion possible derives from the identity of the "fingerprints"[10] of the photochemical and nonphotochemical experiments. Thus, not only are the same phenolic products formed in the dark and photochemical runs but also these are formed in the same characteristic ratio. Even more impressive, in the five solvent systems used, the ratios of phenol isomers (2,3- *vs.* 3,4-) varied identically in the photochemical and nonphotochemical runs. We can therefore conclude that there is an intermediate common to the photochemical and dark runs. Since electronically excited species are not expected[19] in the dark runs and since the photochemical source of the intermediate

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(14) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **63**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(15) Although *Y* values are sometimes thought[16] to be linear with E_T[17] and Z[18] values, our present experience is that the linearity is less than perfect and that there is a leveling of E_T as solvent polarity is increased from 70% aqueous dioxane to 50%.

(16) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(17) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).

(18) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3523 (1958).

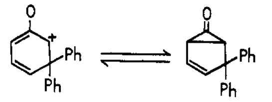
(19) Excited species would have to be formed in nearly unit quantum efficiency to account for the high yield of phenolic product per amount of bromoenone consumed. This point is important since excited states can be generated without light, but the efficiencies are quite low.[20]

(20) E. H. White, J. Wiecko, and C. C. Wei, *J. Amer. Chem. Soc.*, **92**, 2167 (1970).

lacks any molecular bromine, we can reason that the common intermediate is electronically unexcited and does not contain bromine. With the pinacolic-like rearrangement observed, zwitterion B becomes the most reasonable candidate.

An alternative structure for the intermediate is cyclopropanone **16**. Indeed, the work of Fort[12] describing methoxide treatment of 6-tosyloxyisophorone gave products which could be interpreted as arising from both a zwitterionic intermediate and also a cyclopropanone species. Methyl migration, paralleling the present phenyl migration, was not observed, despite evidence for a species similar to zwitterion B. Whether this is due to absence of such products or nonisolation is uncertain. From the work of Swenton and Srinivasan[21] one would expect methyl migration.

However, a cyclopropanone intermediate in the rearrangement of 6-bromo-5,5-diphenylcyclohex-2-en-1-one (**9**) does not rationalize the observed rearrangement which is characteristic of a cationic species[6] and an intermediate which is valence deficient, unlike the cyclopropanone. Yet, the Fort evidence does suggest that cyclopropanone **16** may be in dynamic equilibrium with zwitterion B (eq 5). We note that this interconversion is electronically allowed.[22] Recently, Chapman has reported evidence that a cyclopropanone such as **16** is detectible at low temperature.[23] In any case, the reversible formation of cyclopropanone **16** as a side process seems quite reasonable. Thus the evidence supports zwitterion B as the reactive intermediate, and the mechanisms of eq 1 (photochemical) and 3 (dark) are confirmed.

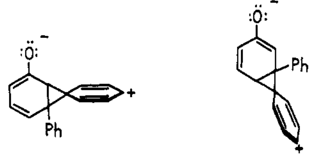


(5)

B **16**

The reaction of bromoenone **9** with base to afford the photochemical intermediate zwitterion B can be considered another example of "photochemistry without light."[24] This term has been used more recently by White[20] to describe the generation of electronically excited states without light. In the present instance the potential energy surface utilized by the photochemical process is accessed by the nonphotochemical approach only subsequent to transformation of the excited state and after loss of electronic excitation energy.[25] This then adds another example of a photochemical reaction which loses electronic excitation prior to reaching product geometry and in which the excited state of product is not produced.[26] With a few exceptions this seems to be characteristic of photochemistry.[28]

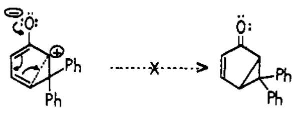
Effect of Solvent Polarity. Another point of interest is the effect on rearrangement product distribution of solvent polarity. The preference for migration of phenyl to carbon-2 of zwitterion B rather than to carbon-4 has been rationalized[13a] in terms of the greater enolate stabilization (*i.e.*, three enolate resonance contributors) for the phenonium, half-migrated species **17** contrasted with the cross-conjugated intermediate **18** (having two enolate structures).



17 **18**

To the extent that solvent polarity is increased (increasing Y values) negative charge on oxygen can be stabilized and enolate delocalization should be diminished and its importance decreased; this leads to less 2,3-diphenylphenol as observed. With less polar solvents (lower Y values) electron density spreading should be enhanced and the greater delocalization of species **17** becomes a more important factor with increased 2,3-diphenylphenol formation.

Forbiddeness of Reversion to Bicyclic Ketone. The preferential rearrangement of zwitterion B to the diphenylphenols **2** and **3** to the exclusion of formation of any 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**) is both curious and interesting. The usual electron pushing, as in eq 6, makes the formation of **1** look quite reasonable,



(6)

B **1**

and the process is superficially parallel to the allowed cyclopropanone formation discussed above. Furthermore, the nonclosure to bicyclic ketone **1** is important since it bears critically on the photochemistry previously reported. In this earlier study[13a] it was not possible to determine if the relatively inefficient (*i.e.*, $\phi = 0.067$) quantum yield of phenol formation derived from reversion of zwitterion B to reactant 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**), thus providing a mode of "pseudo-decay" (*i.e.*, decay along the reaction coordinate but not of the excited state and indistinguishable kinetically from ordinary radiationless decay). However, the present study shows that such pseudodecay does not occur in the photochemistry.

We are left with the question of why the process in eq 6 does not occur. It was noted earlier[13a] that the reaction is expected to have a barrier due to an "attempt" of the highest occupied MO of both reactant and product to cross the corresponding lowest anti-

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(21) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *J. Amer. Chem. Soc.*, **90**, 2990 (1968).

(22) The closure is necessarily disrotatory. This corresponds to a Hückel closure of an allyl cation to cyclopropyl cation to the extent that oxygen and the second π bond are neglected.

(23) (a) O. L. Chapman, 3rd International IUPAC Symposium on Photochemistry, St. Moritz, July 1971; (b) L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, **91**, 3664 (1969). (c) Whether the cyclopropanones or the zwitterions are the primary photochemical product is difficult to determine operationally. The preferences for zwitterion found in ref 2–4 and for cyclopropanone in ref 23 must still be considered esthetics rather than certainty at this point. In view of the likely facile equilibration, the problem is difficult.

(24) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968).

(25) This presumes that molecular processes just following the primary photochemical process are considered as part of the "photochemistry" of the reaction.

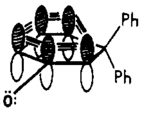
(26) For previous discussions note ref 10 and 27.

(27) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, in press.

(28) Exceptions seem to occur when only a very small molecular change occurs, as in ionization of a proton from electronically excited naphthols[29] or proton abstrction by excited aromatic bases.[29]

(29) (a) A. Weller, *Z. Phys. Chem.* (*Frankfurt am Main*), **3**, 328 (1955); (b) A. Weller, *Progr. React. Kinet.*, **1**, 189 (1961).

bonding MO's. To the extent that one approximates the system with the oxygen unshared pair being localized, the reaction is the cyclization of the pentadienyl cation in a disrotatory (top–top overlap) fashion. This is a "Hückel system"[30] since there is no necessary plus–minus overlap between any of the five pair of p orbitals constituting the cyclic array. But with four delocalized electrons in the cyclic transition state, a Hückel system is forbidden to close.[30] Note structure **19**. The effect of inclusion of oxygen in the electronics of the reacting system is to break the symmetry with the result of only a near crossing as demonstrated earlier.[13a]



19

five orbital cyclic array with zero sign inversions between sets of orbitals and thence Hückel rather than Möbius; four delocalized electrons excluding oxygen

Conclusion

Thus, another example has been added in which the potential energy surface accessed by an excited state reaction is also proven attainable by nonphotochemical means. It does seem that much about excited state pathways can be discerned by independent generation of potential unstable reaction intermediates.

Experimental Section[31]

4,4-Diphenylcyclohex-2-en-1-one was prepared in 72% yield by the condensation of diphenylacetaldehyde and methyl vinyl ketone according to the method of Zimmerman, Keese, Nasielski, and Swenton.[13]

4,4-Diphenylcyclohexene. A solution of 28.00 g (0.113 mol) of 4,4-diphenylcyclohex-2-en-1-one, 11.3 ml (0.233 mol) of hydrazine hydrate, 18.5 g (0.330 mol) of potassium hydroxide, and 150 ml of ethylene glycol was refluxed for 1.5 hr; 20 ml of water–ethylene glycol was distilled until the head temperature was constant. After refluxing for 4 hr, the cooled solution was extracted with ether; the ether phase (washed with water and dilute hydrochloric acid) was dried over anhydrous magnesium sulfate. Concentration gave 22.6 g of a yellow oil.

The oil was chromatographed on a 3.5 × 100 cm column of silica gel with 5% chloroform–hexane as an eluent. Elution in 250-ml fractions gave the following results: fractions 2–6, 0.472 g, unidentified yellow solid; 7–9, nil; 10–11, 0.919 g, 3,3-diphenylcyclohexene; 12–14, 2.315 g, overlap; 15–45, 14.730 g (57%), 4,4-diphenylcyclohexene.

The olefin was recrystallized from pentane to a constant melting point of 65.0–66.5°. The infrared spectrum showed bands at (KBr) 3.32, 3.48, 6.40, 6.73, 6.98, 9.78, 13.05, 13.39, 14.40, and 15.20 μ; nmr (CCl_4) τ 2.97 (s, 10 H), 4.34 (mult, 2 H), 7.32–7.90 (mult, 4 H), and 8.05–8.50 (mult, 2 H).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.34; H, 7.57.

3,3-Diphenylcyclohexanone. A solution of 33.0 g (0.14 mol) of 4,4-diphenylcyclohexene in 100 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was treated under nitrogen with 140 ml (0.14 mol) of 1 *M* borane in tetrahydrofuran (Alfa Inorganics). The mixture was stirred at ice bath temperature for 1.5 hr, followed by stirring at room temperature for an additional 1.5 hr. The resulting solution was cooled and cautiously treated with 140 ml of 10% water in tetrahydrofuran. Following addition of 230 ml of 3 *M* (0.69 mol) sodium hydroxide solution and 155 ml (1.90 mol) of 30% hydrogen peroxide the mixture was stirred for 2 hr and poured into 600 ml of water. Acidification with dilute hydrochloric acid, extraction with ether, washing ether phase with water, drying over anhydrous magnesium sulfate, and concentration *in vacuo* gave 33.0 g (0.13 mol) of a mixture of 3,3- and 4,4-diphenylcyclohexanols as a white solid.

A solution of 104 g (0.413 mol) of the mixture of alcohols in 605 ml of acetone was added dropwise to a solution of 247 ml of water, 1000 ml of acetone, 23.6 ml of concentrated sulfuric acid, 27.3 g (0.273 mol) of chromium trioxide, and 77.3 g (0.454 mol) of manganous sulfate monohydrate, with cooling in an ice–acetone bath. After addition was complete the mixture was stirred for 4 hr, 88 ml of isopropyl alcohol was added, and the mixture added to 1200 ml of water. The suspension was extracted with ether, dried, and concentrated *in vacuo* to give 93 g of white crystals. Chromatography on a 8 × 95 cm silica gel column and elution with 3 l. of 8% ether–hexane, 4 l. of 10% ether–hexane, 4.5 l. of 15% ether–hexane, 4.5 l. of 20% ether–hexane, 4 l. of 25% ether–hexane, 4 l. of 30% ether–hexane, 6.5 l. of 35% ether–hexane, 3 l. of 50% ether–hexane, and 2 l. of 50% methylene chloride–hexane in 500-ml fractions gave the following results: fractions 34–43, 33.6 g (34%) of 3,3-diphenylcyclohexanone; 44–46, 11.6 g (12%) of overlap; and 47–62, 40.8 g (41%) of 4,4-diphenylcyclohexanone.

The 3,3-diphenylcyclohexanone was recrystallized from methylene chloride–hexane to a constant melting point at 114–115°. The spectral characteristics were ir (KBr) 3.31, 3.49, 5.90, 6.26, 6.68, 6.91, 7.07, 7.40, 7.60, 7.81, 8.15, 8.37, 9.58, 9.70, 10.62, 11.13, 12.45, 13.27, 14.30, and 15.30 μ; nmr ($CDCl_3$) τ 2.90 (s, 10 H), 7.12 (s, 2 H), and 7.30–8.95 (mult, 6 H).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.40; H, 7.35.

5,5-Diphenylcyclohex-2-en-1-one. A solution of 6.0 g (0.024 mol) of 3,3-diphenylcyclohexanone in 50 ml of carbon tetrachloride was treated with 4.00 g (0.252 mol) of bromine in 6.15 ml of carbon tetrachloride. Solvent removal *in vacuo* gave 8.2 g of bromo ketone as an amber, viscous oil.

The bromo ketone was added to a solution of 1.146 g (0.0269 mol) of lithium chloride and 1.988 g (0.0988 mol) of lithium carbonate in 80 ml of dimethylformamide and refluxed under nitrogen for 23 hr. The cooled orange suspension was diluted with 200 ml of ether, washed with water and dilute hydrochloric acid, and again washed with water. Drying over anhydrous magnesium sulfate and concentration *in vacuo* gave 6.12 g of an orange solid. Chromatography on a 3 × 90 cm column of deactivated silica gel (30% water w/w) and elution with 5 l. of 5% ether–hexane, 3 l. of 8% ether–hexane, and 1 l. of 50% ether–hexane in 500-ml fractions gave the following results: fractions 1–12, 3.278 g of unidentified yellow material; 13–16, 2.06 g (34%) of 5,5-diphenylcyclohex-2-en-1-one, mp 95–101°.

The 5,5-diphenylcyclohex-2-en-1-one was recrystallized from methylene chloride–hexane to give an analytical sample, mp 110.5–112.0°. The spectral characteristics were ir (KBr) 3.32, 6.00, 6.25, 6.69, 6.92, 7.21, 7.96, 10.97, 13.22, 13.58, and 14.32 μ; nmr ($CDCl_3$) τ 2.75 (s, 10 H), 3.10 (mult, 1 H), 3.97 (d, 1 H), and 6.80–6.96 (mult, 4 H).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.12; H, 6.50.

6-Bromo-5,5-diphenylcyclohex-2-en-1-one. To a solution of 0.924 g (3.72 mmol) of 5,5-diphenylcyclohex-2-en-1-one in 500 ml of tetrahydrofuran was added dropwise over 3 hr 2.032 g (4.11 mmol) of pyrrolidone hydrotribromide[32] in 500 ml of tetrahydrofuran. The solution was stirred in the dark for 17 hr. The solution was concentrated *in vacuo* to a volume of *ca.* 100 ml and filtered. Concentration of the filtrate gave the crude bromination mixture as an orange oil.

The oil was subjected to liquid–liquid partition chromatography on a 5 × 150 cm column of Celite bearing 40% by weight of the lower phase of a system of cyclohexane (1000 ml)–dimethylformamide (400 ml)–ethyl acetate (250 ml)–water (30 ml). The upper phase was used as an eluent. Eluted 40-ml fractions were washed with water, dried, and concentrated *in vacuo* to give the following results: fractions 44–50, 309 mg of recovered 5,5-diphenylcyclohex-2-en-1-one; 51–57, 452 mg of a mixture containing 6-bromo-5,5-diphenylcyclohex-2-en-1-one and 2-bromo-5,5-diphenylcyclohex-2-en-1-one; 58–62, 195 mg of 6-bromo-5,5-diphenylcyclohex-2-en-1-one; and 63–72, 141 mg of 6-bromo-5,5-diphenylcyclohex-2-en-1-one and a small amount of an uncharacterized compound. Fractional crystallization from chloroform–carbon tetrachloride of the fractions containing 6-bromo-5,5-diphenylcyclohex-2-en-1-one gave 395 mg (49%) of white needles, mp 162–166°.

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(30) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); (b) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966).

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

(32) D. V. C. Awang and S. Wolfe, *Can. J. Chem.*, **47**, 706 (1969).

Recrystallization from chloroform–carbon tetrachloride gave an analytical sample, mp 165–166°. The spectral characteristics were ir (KBr) 3.34, 6.00, 6.20, 6.29, 6.36, 6.72, 6.95, 7.22, 7.48, 7.94, 8.29, 8.40, 8.56, 8.93, 9.36, 9.70, 10.45, 11.31, 12.19, 12.74, 13.20, 13.35, 14.32, and 14.75 μ; nmr ($CDCl_3$) τ 2.65 (partially resolved singlets, 10 H), 3.00 (mult, 1 H), 4.00 (broadened d, 1 H, J = 11 cps), 4.80 (s, 1 H), and 5.5–5.7 (mult, 2 H). The mass spectrum showed peaks for a molecular ion at 326 and 328.

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.19; H, 4.65; Br, 24.20.

Reduction of 6-Bromo-5,5-diphenylcyclohex-2-en-1-one. A solution of 89 mg (0.27 mmol) of 6-bromo-5,5-diphenylcyclohex-2-en-1-one in 15 ml of acetone was treated under nitrogen with 0.25 ml of 48% hydriodic acid. The solution immediately turned orange. After stirring for 1.5 hr, the mixture was added to a solution of 0.5 g of sodium thiosulfate in 50 ml of water. Extraction with ether, drying, and solvent removal *in vacuo* gave 76.8 mg of a crystallizing oil.

The oil was dissolved in chloroform–carbon tetrachloride and crystallized 19.6 mg of recovered 6-bromo-5,5-diphenylcyclohex-2-en-1-one. The mother liquor was concentrated and chromatographed on a 1 × 35 cm silicic acid column to give 31.0 mg (59%) of crystalline 5,5-diphenylcyclohex-2-en-1-one.

4,4-Diphenylcyclohexadienone was prepared from 4,4-diphenylcyclohex-2-en-1-one by enol acetate formation, bromination, and dehydrobromination using the procedure of Zimmerman, Hackett, Juers, McCall, and Schröder.[33]

2,3- and 3,4-diphenylphenols were prepared as described by Zimmerman and Schuster[3] by the dehydrogenation of 5,6-diphenylcyclohex-2-en-1-one and the acid-catalyzed rearrangement of 4,4-diphenylcyclohexadienone, respectively.

Reaction of 6-Bromo-5,5-diphenylcyclohex-2-en-1-one with Base. A solution of 107.8 mg (0.329 mmol) of 6-bromo-5,5-diphenylcyclohex-2-en-1-one in 15 ml of 50% dioxane–water was added to 365 mg (6.50 mmol) in 50 ml of 50% dioxane–water. The solution was stirred under nitrogen in the dark for 6 hr, concentrated *in vacuo* to *ca.* 10 ml, diluted with 75 ml of water, neutralized, and extracted with ether. Drying the ether extracts and solvent removal *in vacuo* gave 77.0 mg (86%) of a mixture of 2,3- and 3,4-diphenylphenols. Analysis of the mixture, *vide infra*, gave the composition as 72.5% 2,3-diphenylphenol and 27.5% 3,4-diphenylphenol. The reaction of the 6-bromo ketone with base in other solvents was performed similarly, and the results are shown in Table I.

Quantitative Analysis of the Phenol Mixture. The relative amounts of 2,3- and 3,4-diphenylphenols were determined by three methods: (1) vapor phase chromatography, (2) quantitative infrared spectroscopic analysis, and (3) isolation. The three methods gave consistently good agreement (differing at most by 3.6%) but the greatest accuracy in analysis of mixtures of known composition was obtained using vpc.

The vpc analysis was performed on a $^1/_8$ in. × 5 ft column of 5% SE-30 on Varaport 30 (100–120 mesh). Analysis of the phenol mixture at 170° gave a retention time of 9.2 min for 2,3-diphenylphenol and 18.5 min for 3,4-diphenylphenol. The quantitative infrared analysis was performed using the relative absorption at 800 and 820 cm^{-1} as described by Zimmerman.[13] The phenols were isolated by silica gel chromatography, eluting with ether–hexane.

Photolysis of 4,4-Diphenylcyclohexadienone. Dilute solutions of *ca.* 0.001 *M* were photolyzed using a 450-W Hanovia mercury lamp until no dienone or bicyclic ketone remained. The phenol mixture was isolated as described earlier[13] and analyzed by the same procedure as described above for the nonphotochemical runs. The results of these runs are shown in Table I.

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[33] H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3653 (1971).

Photochemistry of Metalloporphyrin Complexes. Ligand Photoisomerization *via* Intramolecular Energy Transfer[1,2]

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Abstract: An investigation of the photochemistry of complexes in which metalloporphyrins (zinc, magnesium, and cobalt etioporphyrin and mesoporphyrin complexes) are bound to reactive extraplanar ligands, isomerizable azastilbenes, is reported. Light absorbed by the long-wavelength transitions of zinc and magnesium porphyrins promotes efficient cis–trans isomerization of azastilbene ligands such as 4-stilbazole, 1-(1-naphthyl)-2-(4-pyridyl)-ethylene (NPE), and 1-(1-naphthyl)-2-(4-pyridyl)propene (NPP). The extremely high quantum yields for cis to trans isomerization of several azastilbenes ($\Phi_{c\rightarrow t}$ = 7 for NPE) are explained by a mechanism involving reversible intramolecular transfer of triplet excitation from porphyrin to azastilbene ligand. An intramolecular "azulene effect" involving energy transfer from a transoid azastilbene triplet to the porphyrin coupled with rapid ligand exchange during the relatively long excited state lifetime allows the operation of a photocatalytic or quantum chain process. Triplet energy transfer from porphyrin to complexed *cis*-NPE involves a surprisingly low activation energy, indicating that the excited state populated lies *at least* 8 kcal/mol below the spectroscopic or cisoid excited state. Triplet energy transfer from porphyrin to *trans*-NPE requires approximately the energy expected for vertical excitation to a transoid triplet. The high negative entropy of activation observed for triplet energy transfer from porphyrin to *cis*-NPE is consistent with several previously developed mechanisms of "nonvertical" triplet energy transfer to produce an excited state having different geometry than the *cis*-NPE ground state.

Light-induced reactions of metalloporphyrins and related compounds have been the subject of considerable attention, especially due to the importance of these compounds in photobiological and electron-transport phenomena. Due to interest in the role of chlorophyll in photosynthesis,[4] emphasis has been

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[1] Preliminary accounts of portions of this work have appeared: (a) D. G. Whitten, P. D. Wildes, and I. G. Lopp, *J. Amer. Chem. Soc.*, **91**, 3393 (1969); (b) P. D. Wildes and D. G. Whitten, *ibid.*, **92**, 7609 (1970).

[2] Abstracted in part from the Ph.D. Thesis of P. D. Wildes.

[3] (a) Alfred P. Sloan Foundation Fellow; (b) National Defense Act Predoctoral Fellow, 1969–1970.

[4] For some reviews, see N. K, Boardman, *Advan. Enzymol.*, **30**, 1 (1968); "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N. Y., 1966; L. P. Vernon and M. Avron, *Annu. Rev. Biochem.*, **34**, 269 (1965); J. H. Wang, *Proc. Nat. Acad. Sci. U. S.*, **62**, 653 (1969); G. N. Cheniae, *Annu. Rev. Plant Physiol.*, **21**, 2019 (1970).