# The Photochemistry of a Cyclohexadienone Structurally Incapable of Rearrangement. Exploratory and Mechanistic Organic Photochemistry. XLVII[1]

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Abstract: 7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (6) was synthesized as a cyclohexadienone specifically designed to be structurally incapable of undergoing the type A photochemical rearrangement while still able to undergo the initial β–β bonding, characteristic of the first stage of the reaction. Most intriguingly this dienone showed electronic behavior and reactivity more like benzophenone than like any known cyclohexadienone. When dienone 6 was photolyzed in benzene, no reaction occurred. However, in isopropyl alcohol hydrogen abstraction occurred with a rate in the range expected for an n–π^* excited ketone. The rate of triplet decay in solution proved to be closer to that of benzophenone than that of rearranging dienones. The hydrogen abstraction process was found to lead to 2-hydroxy-7-methoxy-4,5,9,10-tetrahydropyrene (7) with expulsion of methyl radical and formation of methane. For comparison purposes 4-methyl-4-phenylcyclohexadienone (8) was prepared and irradiated. This nonconstrained dienone rearranged as expected to give the type A product stereoisomers, 6-methyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one (9a,b); information on the rates of decay and rearrangement was obtained from quenching studies.

One of the most facile of photochemical reactions known is the type A rearrangement[2a] of cross-conjugated cyclohexadienones to give bicyclo[3.1.0]hex-3-en-2-one derivatives.
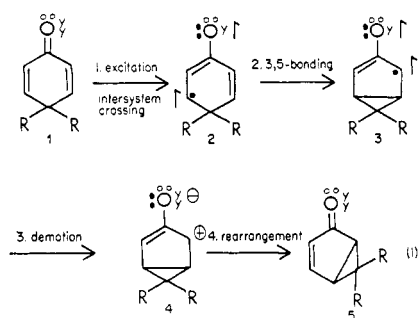
The quantum yields are near unity.[2b-d] The rates of triplet excited-state rearrangement are very rapid so that often even diffusion control does not lead to quenching.[2b] It has been established that 3,5 bonding is the initial n–π^* triplet process (*i.e.*, 2 → 3); however, the precise chronology and the extent to which the latter stages of the transformation (*i.e.*, 3 → 5) are merged are uncertain.[2b]

The intriguing possibility existed of so designing a molecule that the latter stages of the rearrangement would be structurally precluded. Not only would this allow study of the nature of the excited dienone species but it also promised to reveal the next most favored reactions available to dienone molecules. Finally, by having a molecule unable to rearrange it seemed possible to test for the actual existence of zwitterion 4 as a true ground-state intermediate. Such a study also needed a nonconstrained cyclohexadienone of otherwise closely related structure for comparison purposes.

Synthesis of Dienones. The constrained dienone selected was 7-methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (6). Also required was the comparison dienone, 4-methyl-4-phenylcyclohexadienone (8). The general approach was patterned after the synthesis of 15,16-dimethyldihydropyrene-2,7-quinone described by Boekelheide[3] with the exception that presently an unsymmetrical metacyclophane (*i.e.*, 12) was required. This compound was obtained from unsymmetrical coupling of 10 and 11. Also, in this case the penultimate intermediate produced in the final oxidation step was capable of tautomerizing to afford one aromatic ring. This synthesis is outlined in Chart I. One innovation which proved useful was the substitution of sodium–potassium alloy for sodium (note Experimental Section).

For the synthesis of 4-methyl-4-phenylcyclohexadienone (8), a Robinson type condensation of 2-phenylpropionaldehyde with methyl vinyl ketone to afford 4-methyl-4-phenylcyclohexenone proved a convenient first step. This synthesis is also outlined in Chart I.

Results

Exploratory Photochemistry. Initial efforts were directed toward determination of appropriate reaction conditions and product structures. Strikingly, irradiation of 7-methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (6) in either *t*-butyl alcohol or benzene proved this dienone to be totally inert, thus providing the only example of an unreactive and nonrearranging 2,5-cyclohexadienone.[4] Hence, dienone 6 had indeed provided a case where rearrangement is structurally precluded and where excited dienone electronics could be inspected.

(1) For the preliminary communication note: H. E. Zimmerman and G. Jones II, *J. Amer. Chem. Soc.*, **91**, 5678 (1969).

(2) (a) H. E. Zimmerman, Abstracts, 17th National Organic Symposium, Bloomington, Ind., June 1961, p 31; (b) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967); (c) D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968); (d) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137, 5145 (1968).

(3) V. Boekelheide and J. B. Phillips, *ibid.*, **89**, 1695 (1967).

(4) This statement is not meant to include examples (ref 5) where no rearrangement is observed for the trivial reason that a very facile expulsion of a substituent from C-4 dominates the photochemistry.

(5) (a) R. Warszawski, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **43**, 500 (1960) (loss of OAc); (b) T. Matsuura, *Bull. Chem. Soc. Jap.*, **37**, 564 (1964) (loss of OMe); (c) see ref 2d (loss of CCl$_3$); (d) D. I. Schuster and I. S. Krull, *Mol. Photochem.*, **1**, 107 (1969) (cleavage of spirocyclopropane ring).

Chart I. Synthesis of
7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (6)
and 4-Methyl-4-phenylcyclohexadienone (8)
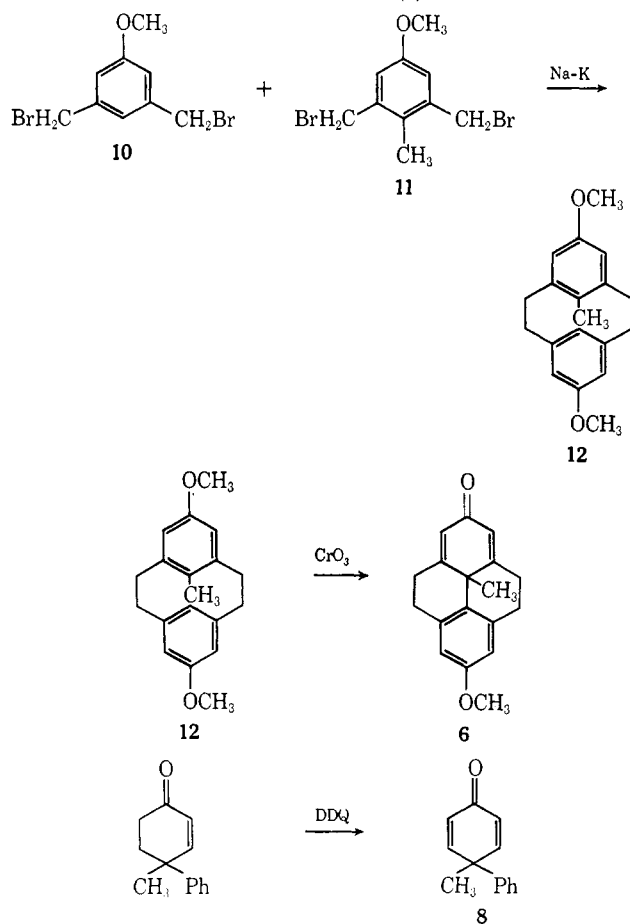
When the irradiation was run instead in hydrogen-donating solvents such as isopropyl alcohol, a reaction did take place; however, rather than the common type A process, the reaction gave 2-hydroxy-7-methoxy-4,5,9,10-tetrahydropyrene (7). The structure assignment of this product was supported by the nmr spectrum which revealed a methoxy methyl singlet (3 H) at τ 6.02, eight methylene hydrogens unsplit at τ 7.20, and two aryl singlet peaks at τ 3.40 (2 H) and 3.46 (2 H). The unsplit aryl peaks demonstrated the presence of only two types of aryl hydrogen atoms and that these were nonadjacent.

Further proof was provided in the conversion of dienone 6 to 2-hydroxy-7-methoxy-4,5,9,10-tetrahydropyrene (7) by ground-state means using activated zinc in pyridine. The aromatization product was identical with the photolytically derived phenol. This reaction has been reported[6] for a series of steroidal cross-conjugated dienones. Mass spectral analysis of the gas evolved photochemically showed the formation of methane, thus demonstrating the fate of the missing C-methyl group. The gross reaction may be formulated as shown in eq 2.

Attention was next turned to the model compound containing the 4-methyl and 4-aryl groups. Thus, upon photolysis, 4-methyl-4-phenylcyclohexadienone (8) was found to rearrange smoothly in benzene and isopropyl alcohol, without any intervention of hydrogen abstraction or methyl expulsion products. There were

(6) K. Tsuda, E. Ohki, and S. Nozoe, *J. Org. Chem.*, **28**, 786 (1963).
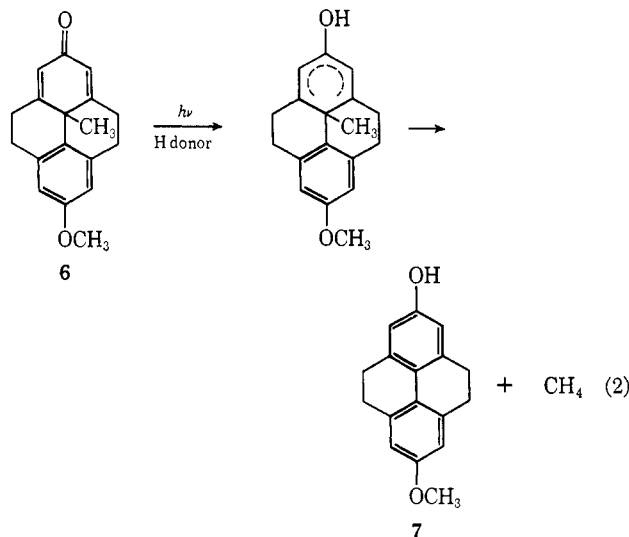
obtained the two stereoisomeric 6-methyl-6-phenyl-bicyclo[3.1.0]hex-3-en-2-ones (9a,b). The structures of these stereoisomers were established by spectral means (note Experimental Section). Thus, the nmr spectra of the isomers showed the presence of the unsaturated ketone vinyl hydrogens (note Table I) and vicinal

Table I. Vinyl Chemical Shifts of Bicyclic Ketones[a]

| Vinyl hydrogens | Dimethyl[b] | —"Lumiketones"— | | Diphenyl[c] |
		9a	9b	
α[d]	4.20	4.04	4.65	4.49
β	2.64[e]	2.53[e]	2.87[f]	2.86[f]

[a] Reported in τ parts per million relative to TMS. [b] 6,6-Di-methylbicyclo[3.1.0]hex-3-en-2-one; H. E. Zimmerman and J. M. McCall, unpublished results. [c] 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one; H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962). [d] Signals for α protons appear as slightly broadened doublets. [e] Well-defined doublet of doublets. [f] Buried under aryl peak.

cyclopropyl methines. In 9a the cyclopropyl protons appeared at τ 7.73 (1 H) and 7.21 (1 H) as a doublet and a doublet of doublets, respectively, the latter arising from coupling with the β vinyl hydrogen as shown by spin decoupling (see Experimental Section). The spectrum of 9b showed similar methine absorption at τ 7.78 and 7.33 and an analogous coupling pattern. Not only did comparison of the nmr with that of the known 4,4-dimethylcyclohexadienone and 4,4-diphenyl-cyclohexadienone photoproducts provide analogy supporting the structure assignments, but also the configurations of the isomers 9a and 9b could be assigned by the observation that an *endo*-phenyl group shifted the vinyl hydrogens upfield (note Table I).
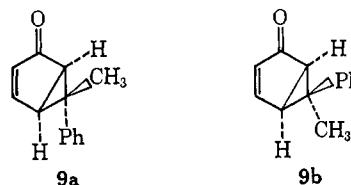
Mechanistic Aspects. Following the first goal of comparing the reactivity of the constrained dienone 6 with the unconstrained model 8, a quantitative study of the hydrogen abstraction–methyl expulsion reaction

was begun. Actinometric measurements in benzene confirmed the lack of reactivity. No rearrangement and no methyl expulsion could be found, with an upper limit of $\Phi \leq 0.005$. Hence, it appeared that hydrogen abstraction was requisite for methyl expulsion. This is in accord with the observations of Schuster[2d] on the expulsion of trichloromethyl radical from 4-methyl-trichloromethylcyclohexadienone.

Quenching studies were carried out in order to obtain excited-state reaction and decay constants. 2,5-Dimethyl-2,4-hexadiene was used as quencher[7] in isopropyl alcohol. It was observed that the hydrogen abstraction reaction of excited dienone 6 could be suppressed with even low concentrations of the diene. The results are summarized in Table II.

Table II. Quantum Yields in Quenched Irradiations of 7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (6)

Run[a]	Dienone concn, mM	Quencher concn,[b] mM	Light, mEin-steins	Quantum yields[c]
I-06	1.07	00.0	2.42	0.10
I-11	1.13	19.1	11.82	0.0076
I-12	1.13	12.6	12.31	0.011
I-13	1.05	6.26	4.87	0.020

[a] In isopropyl alcohol, filter transmission 320–385 nm. [b] The quencher absorbed less than 1% of the available light. [c] Appearance of 7, corrected for light absorption by product (corrections <10%); correction also for minor percentage of light transmitted.

With the Stern–Volmer relationship in mind (eq 3),[9] the reciprocal of the quantum yield was plotted against quencher concentration [Q]. This plot is given in Figure 1 and is seen to be perfectly linear over the quenching range studied. The slope of this plot gives k_q/k_r[HD], the bimolecular quenching rate divided by the rate of triplet reaction. It is assumed that f, the efficiency of intersystem crossing, is unity.[10a] Additionally, assuming that $k_q = 3 \times 10^9$ l. mol^{-1} sec^{-1}, the diffusion-controlled rate,[11] and taking the hydrogen donor concentration [HD] to be 13 M for isopropyl alcohol, k_r is calculated to be 3.6×10^4 l. mol^{-1} sec^{-1}. This value was used, together with the intercept, $(k_r$[HD] $+ k_d)/k_r$[HD], to solve for k_d, the rate of excited-state decay. Thus $k_d = 4.2 \times 10^6$ sec^{-1}.

$$\frac{1}{\Phi} = \frac{k_r[\text{HD}] + k_d}{fk_r[\text{HD}]} + \frac{k_q[\text{Q}]}{fk_r[\text{HD}]} \tag{3}$$

Of mechanistic interest also was the fact that the quantum yield for hydrogen abstraction–methyl expulsion is solvent dependent. Thus the hydrogen

(7) This quencher was selected since it proved to be one of the most efficient in previous studies[8] and competitive absorption was not a problem at the concentrations needed.
(8) H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).
(9) Equation 3 assumes that excited triplet reacts only by the process limited by rate k_r. In the present instance only one process was observed.
(10) (a) Since there is strong experimental evidence that dienones undergo intersystem crossing with unit efficiency[2d] and since this property should be closely related to molecular structure, this assumption seems valid; (b) D. I. Schuster and V. Y. Abraitys, *Chem. Commun.*, 419 (1969).
(11) This derives from the Debye equation.[12] Note J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 626.
(12) (a) P. Debye, *Trans. Electrochem. Soc.*, **82**, 205 (1942); (b) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).
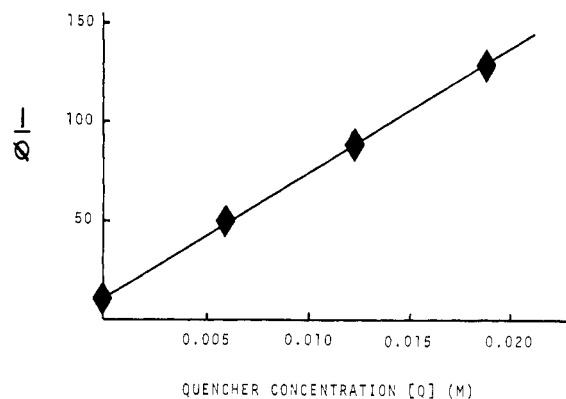

Figure 1. Stern-Volmer plot of 7-methoxy-10b-methyl-4,5,9,-10-tetrahydro-2(10bH)-pyrenone (6).

donating ability of the solvent system affected the reactivity of dienone 6 to the extent of at least a factor of twenty. These data are summarized in Table III.

Table III. Quantum Yields for Irradiation of 7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (6) in Various Solvents and with Added Reagents

Run[a]	Solvent	Added reagent	Quantum yield[b]
I-01	Benzene		<0.005
I-02	t-Butyl alcohol		<0.005
I-03	Acetic acid		0.014
I-04	Methanol		0.021
I-05	n-Butylamine		0.11
I-06	Isopropyl alcohol		0.10
I-07	Benzene	DMAC[c]	<0.005
I-08	t-Butyl alcohol	H$_2$SO$_4$ (0.05 M)	0.079
I-09	Acetic acid	Lithium acetate (0.54 M)	0.027
I-10	Methanol	Lithium chloride (3.25 M)	0.034

[a] All runs at 25°, filter transmission 320–385 nm. [b] Quantum yield of formation of 7, corrected for light absorption by product. [c] Dimethyl acetylenedicarboxylate.

Another goal mentioned was the possible trapping of the potential zwitterionic species 4 proposed earlier as at least a transient species in the type A rearrangement process.[2a,b,d,18] Besides potentially nucleophilic solvents, added nucleophiles such as acetate anion and chloride anion were tried. In some runs proton donors were utilized as well. Finally, dimethyl acetylenedicarboxylate was employed with the idea of trapping the zwitterion by a 1,3-dipolarophile.[14] Strikingly, no adducts resulted, although certain of the systems acted as hydrogen donors. These experiments are included in Table III.

With the evidence in hand that the constrained dienone 6 was exhibiting very unusual behavior for a cyclohexadienone, the study of a structurally similar but nonconstrained dienone seemed all the more necessary. Hence, the reactivity of 4-methyl-4-phenyl-cyclohexadienone (8) was investigated. One experimental complication was the finding that the bicyclic ketone photoproducts, 9a and 9b, undergo the facile type B rearrangement[15] and absorb appreciably above

(13) H. E. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, **8**, 1 (1969).
(14) R. Huisgen, *ibid.*, **2**, 565 (1963).
(15) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

Table IV. Direct, Sensitized, and Quenched Quantum Yields of Conversion of 4-Methyl-4-phenylcyclohexadienone (8)[a]

Run[b]	Solvent	Additive	Disappearance quantum yield[c]	Appearance quantum yield[d]	Conversion, %
II-01	Isopropyl alcohol		0.44	0.30	12.3
II-02	Isopropyl alcohol		0.55	0.47	8.1
II-03	Isopropyl alcohol		0.65	0.58	3.6
II-04	Benzene and isopropyl alcohol	Piperylene[e] (1.0 M)	0.31[f]	0.19[f]	17.7
II-05	Benzene	Acetophenone[g] (0.12 M)	0.74	0.74	18.3

[a] The average of zero conversion extrapolated values for direct photolysis is $\Phi = 0.73$. [b] All runs at 25.0°, filter transmission 320–385 nm except II-05, 295–365 nm. [c] Disappearance of 8. [d] Appearance of 9a and 9b. [e] Did not absorb above 320 nm. [f] Values fall on line of extrapolated quantum yields. [g] Absorbed >95% of the incident light.

300 nm. Therefore, direct irradiations of **8** were carried to several conversions (note Table IV, runs II-01–II-03), and the quantum yields were extrapolated to 0% conversion. The extrapolated values for disappearance of dienone **8** and appearance of bicyclic ketones **9a,b** were 0.73 and 0.71, respectively. Further studies revealed that the type A reaction was sensitized with acetophenone, but could not be quenched with added piperylene. Piperylene was used because of its low absorption in the n–π* region allowing use of high concentrations. Quenching efficiency should be less but within a factor of four of cyclohexadiene.[8] These results are summarized in Table IV. Limits for the rate constants for re-arrangement and decay of the excited state of **8** could be estimated by assuming that a 20% decrease in the quantum yield would have been detected. Thus, the values $k_r \geq 1 \times 10^{10}$ and $k_d \geq 4 \times 10^9$ sec^{-1} were determined.

Interpretative Discussion of Results

The first observation to be considered, namely, the total lack of reactivity of constrained dienone **6** in solvent benzene, is especially dramatic when one considers that the type A dienone rearrangement is among[16] the most rapid of excited-state transformations known (*vide infra*). Indeed, reactivity of dienone **6** more closely parallels that of benzophenone than that of other cyclohexadienones. The contrastingly facile rearrangement of 4-methyl-4-phenylcyclohexadienone (**8**) ($k_r \geq 10^{10}$ sec^{-1}, $\Phi = 0.73$) shows that 4-aryl-4-alkyl substitution in dienone **6** does not inhibit rearrangement and that the lack of reactivity derives totally from the geometric constraint. The un-reactivity is consistent with the view[2a,17] that a contin-uous electron redistribution process must be available for excited-state transformations just as in ground-state chemistry. Thus, despite the availability of an initial 75–90 kcal/mol excitation energy, single bonds of dienone **6** remain intact. Consideration of the geom-etry of the constrained dienone **6** reveals no inhibition of the 3,5 bonding common to all type A dienone rearrangements (step 2, Chart II). However, migra-tion of carbon 4 from C-5 to C-2, either in the zwitterion or its precursor, can be seen to be sterically impossible and to lead to the hopelessly strained prod-uct, **13**, independent of the reaction stereochemistry.

(16) Probably the most rapid is the proton ionization of excited-state acids; see A. Weller, *Progr. Reaction Kinetics*, **1**, 199 (1961).
(17) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

Chart II. Blocking of the Type A Process in Dienone 6
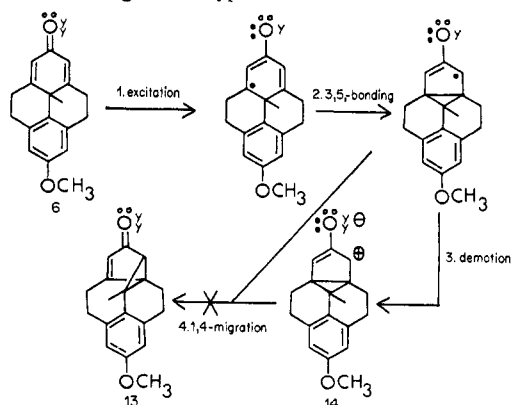
With the 3,5-bridging process sterically (step 2) allowed but the rearrangement (*i.e.*, step 4) precluded on geometric grounds and with the experimental observation of nonreactivity in benzene in hand, it appeared that there existed an ideal case for trapping a discrete zwitterion intermediate. The present zwit-terion **14**, in contrast to the zwitterion species **4**, is incapable of further rearrangement, and it has been noted earlier that a return to dienone from zwitterion is symmetry forbidden.[2a,18] However, as noted earlier, such zwitterions may be mere transient points along a potential energy surface and not energy minima; this corresponds to our earlier[19] comments that the steps, delineated separately by us for clarity, may actually be merged. Also, it is entirely reasonable that for different molecules, there might be a spectrum of situations ranging from (1) existence of a discrete intermediate zwitterion to (2) this species being merely a point on the downside slope of a concerted potential energy surface to (3) concertedness in the extreme where demotion is merged with C-4 migration without appreciable charge separation prior to this molecular change.

The experiments with varying nucleophiles gave no evidence of trapping. That these nucleophilic systems were intercepting the excited state by hydrogen donation does not provide the rationale for lack of nucleophilic attack, since the quantum yield for hydrogen abstraction

(18) Experimental evidence does support the view that return from bridged species is relatively inefficient. Thus, generation of zwitterion **4** by ground-state means has been shown to lead to rearrangement without competition by a process reverting to dienone.[19] Also, the close to unity dienone quantum yields show that intermediate species cannot revert heavily to dienone.
(19) (a) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **88**, 5352 (1966); (b) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); (c) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969); (d) T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).

Table V. Rate Constants for Triplet Excited-State Reaction and Decay of Unsaturated Ketones[a]

Reactant	k_a, l. mol⁻¹ sec⁻¹	k_r, sec⁻¹	k_d, sec⁻¹	Ref
Acetophenone	4×10^5		2×10^5	b
Benzophenone	6×10^5		1×10^5	b, c
7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2-(10bH)-pyrenone (6)	3.6×10^4		4.2×10^6	This work
Benzoylcyclobutane	1.3×10^5		6.6×10^5	d
4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone	3×10^3		3.9×10^7	e
4-Methyl-4-trichloromethylcyclohexadienone	3.9×10^8	6.9×10^8		f
α-Santonin		8.6×10^9	1.4×10^9	g
4,4-Diphenylcyclohexadienone		$\gg 4 \times 10^8$	$\gg 7 \times 10^7$	h
4-Methyl-4-phenylcyclohexadienone (8)		$>1 \times 10^{10}$	$>4 \times 10^9$	This work

[a] k_a refers to the bimolecular rate of hydrogen abstraction; k_r refers to the unimolecular rate of type A rearrangement; k_d refers to the unimolecular rate of triplet decay. [b] Reference 20. [c] Reference 22. [d] A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969). [e] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966). [f] Reference 2d. [g] Reference 2c. [h] Reference 2b.

was of the order of 0.1 while that for the type A rearrangement is, in general, almost an order of magnitude greater. A similar argument based on rates (*vide infra*) shows that hydrogen abstraction is a process taking place only in lieu of an efficient and rapid type A rearrangment and not excluding it. We conclude that in the present instance a zwitterion as a discrete intermediate is not present.

Hence, not only does the constrained dienone **6** contrast with most dienones in exhibiting hydrogen abstraction, but also remarkably, it gives no evidence for the zwitterionic species which seems to be involved in the type A rearrangement of the ordinary dienones. The parallelism with benzophenone actually is more than just qualitative, since the rate of hydrogen abstraction is $k_r = 3.6 \times 10^4$ l. mol⁻¹ sec⁻¹, compared with 6×10^5 l. mol⁻¹ sec⁻¹ for benzophenone.[20] Since hydrogen abstraction from isopropyl alcohol is characteristic of n–π* excited triplets, this evidence suggests that an n–π* excited state is present in the case of the constrained dienone **6**. The order of magnitude slower hydrogen abstraction compared to benzophenone may be mere variation with structure or could be evidence that the n–π* state lies slightly above a lowest π–π* state in this molecule and requires thermal population prior to hydrogen abstraction. This would fit the appearance of the phosphorescence spectrum which is complex (see Experimental Section) and more suggestive of π–π* emission than n–π*, in contrast with the 4,4-disubstituted dienones reported by us earlier.[21]

Thus far all of the experimental observations can be rationalized readily on the basis of the constrained nature of the dienone **6**. However, the excited-state decay rate (*vide supra*) of $k_d = 4.2 \times 10^6$ sec⁻¹ is seen to be much closer to that of benzophenone (1×10^5)[22] than to that of 4-methyl-4-phenylcyclohexadienone, with $k_d \gtrsim 4 \times 10^9$ sec⁻¹ (*vide supra*), and the decay rates of other dienones. Table V summarizes the triplet rate constants for decay, hydrogen abstraction, and

type A rearrangement, including both the present study and the literature.

In contrast to the dramatic hydrogen abstracting ability and lack of rearrangement of **6** which can be attributed to structure, the rate of decay of the constrained dienone (**6**) might have been expected to be similar to that of the rearranging dienones. This is because radiationless decay should in general be closely related to the array and nature of electronic states available and therefore related to molecular structure. The presence of a slightly lower lying and longer lived π–π* excited state, noted as a possibility above in connection with the tenfold slower rate of hydrogen abstraction relative to benzophenone, does not provide a rationale for the three orders of magnitude slower decay, since the hydrogen abstraction rate indicates that at most n–π* population might be inhibited by one order of magnitude. It does appear that for cyclohexadienone photochemistry, the decay process and the type A rearrangement are interrelated. A nonrearranging dienone seems unable to decay rapidly. One possibility is that demotion occurs only during stage 4 (Chart II) and that this molecular change facilitates intersystem crossing to ground-state product. Once such demotion has begun, reversion to reactant may compete. In unconstrained dienones the decay competition is minor despite a large k_d. In the case of the constrained dienone **6**, competition is necessarily major although a low k_d is observed.

According to this interpretation, the zwitterion would then be formed only as it is rearranging. Thus if this interpretation is correct, the dienone type A rearrangement may be depicted as being at least partially concerted (*vide supra*). One would nevertheless expect 3,5 bonding to predominate heavily in the early stages of the transformation with 4,6 bonding becoming increasingly important along the reaction coordinate. This is indicated in structure **15**, which utilizes heavy dotted lines for major overlap. This species, which
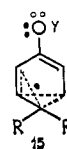
(20) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Amer. Chem. Soc.*, **86**, 3060 (1964).
(21) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).
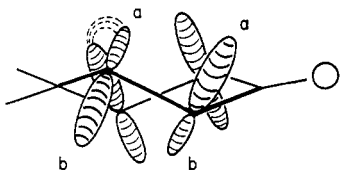(22) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

Figure 2. Twisted *cis–transoid*-dienone; 3,5-top–bottom overlap, --- ; a, originally above molecular plane (aa interorbital angle now > 90°); b, originally below molecular plane.

occurs prior to the rate-limiting stage of the rearrangement is then capable of reverting to ground-state reactant without necessarily affording zwitterion.[19c,28]

In this connection we note that Schuster[10b] has recently succeeded in trapping a 3,5-bridged species of a rearranging dienone in acidic solution. 4-Methyl-4-trichloromethylcyclohexadienone upon irradiation in acidified methanol gave the bicyclic methanol adduct (eq 4). This would have to be a case where at least protonated zwitterion is a true intermediate. This dienone is somewhat anomalous in that it rearranges to give lumiproduct at a relatively slow rate ($k_r = 6.9 \times 10^8$ sec^{-1})[2d] and in different media abstracts hydrogen at a very fast rate ($k_r = 3.9 \times 10^8$)[2d] compared to other ketones (*vide supra*).
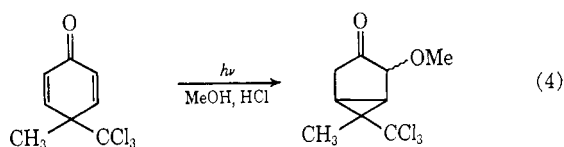
A second possibility is that twisting about at least one of the dienone double bonds is necessary, preliminary to 3,5 bonding.[26] This twisting is much more difficult for constrained dienone **6** than for dienones which rearrange. In the extreme, a *cis,trans*-cyclohexadienone would be formed and then bond to form zwitterion or decay to reactant. Formation of such a twisted species (note Figure 2) would provide for electronic energy dissipation.[28] This is because the ground- and first-excited electronic states of such a twisted species should be relatively close-lying, allowing efficient radiationless decay. Furthermore, top–bottom 3,5 overlap (note Figure 2) would be allowed.

(23) Recently the electrochemical reduction of diphenylcyclohexadienone to the corresponding pinacol has been reported,[24] and we ourselves have noted such behavior.[25] These authors have suggested that lack of isolation of a 3,5-bridged product bears on the question of briding in the n–π* excited state. However, even if bridging is endothermic (*e.g.*, unfavorable to the extent of $K_{eq} = 10^{-2}$), a rapid rearrangement (*i.e.*, $k_r > 10^{10}$ sec^{-1}) superimposed on reversible bridging would still allow a very rapid overall rate ($k_r \sim 10^9$ sec^{-1}) for the type A reaction. To the extent that the rearrangement is heavily concerted with bridging, the electrochemical observation becomes irrelevant.
(24) A. Mazzenga, D. Lomnitz, J. Villegas, and C. J. Polowczyk, *Tetrahedron Lett.*, 1665 (1969).
(25) H. E. Zimmerman and R. L. Morse, unpublished observations.
(26) A related but basically different alternative is that the very rapid decay of normal dienones comes from an A₂ vibration (not present in **6**) corresponding to conrotatory twisting about bonds 2,3 and 5,6. Such a vibration, superimposed on a low-lying A₁ π–π* triplet, would afford a triplet which is A₂ vibronically. Krishna[27] has given arguments for spin–orbital coupling being especially effective in admixing an A₂ triplet with an A₁ singlet, thus enhancing the singlet character of the triplet species. In this paper the argument was used to rationalize the polarization of emission. Presently however we see that A₁ singlet character would facilitate radiationless decay of the excited species to A₁ ground state as a result of identical symmetries. The magnitude of such an effect is difficult to assess.
(27) V. G. Krishna, *J. Mol. Spectrosc.*, **13**, 296 (1964).
(28) D. Phillips, J. Lemaire, C. S. Burton, and W. A. Noyes, Jr., *Advan. Photochem.*, **5**, 329 (1968).

There is growing evidence that *cis–trans* isomerization dominates the photochemistry of medium-ring cyclic dienones. Upon irradiation in protic solvents, 2,6-cycloheptadienone has been shown[29] to undergo addition to give Michael adducts and bicyclic ketones arising, at least formally, from zwitterions analogous to **4**. Adducts of both types have been reported[30,31] also for 2,7-cyclooctadienone (eq 5), and Crandall and Haseltine have shown that a ground-state intermediate,
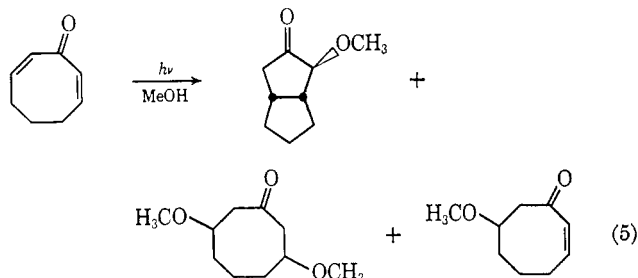
relatively stable at low temperatures in the absence of additives, is involved. Similar behavior has been found for 2-cyclooctenone[32,33] and 2-cycloheptenone[34a,b] in which there is excellent chemical[32–34] and spectral[34] evidence that *trans*-enones are the primary products of photolysis.

It is clear that in the six-ring case complete twisting is impossible. But starting with excited states of these cyclic dienones all gradations of mechanism should be possible ranging from partial to complete *cis–trans* isomerization. Hence, we may conclude that geometric constraint of the presently studied cyclohexadienone (**6**) has inhibited the electronic demotion processes normally present in dienones, and the type A rearrangement may be controlled by either or both of the suggested factors, demotion with final rearrangement and the requirement for π-bond twisting.

It is of interest that in certain organic photochemical reactions we have found that electronic demotion is a necessary consequence accompanying reaction and ensuring that excited states of products are not formed.[8] In the present instance, we have found that with rearrangement precluded, conversion to electronic ground state is slow. It seems likely that organic photochemical reactions will fall into two categories, (i) those where radiationless decay back to reactant and loss of excitation with rearrangement to product are molecularly related and (ii) those where the two processes are unrelated.[35] The latter case seems most probable where appreciable excited-state energy barriers exist.[36]

Experimental Section[37]

3,5-Bis(hydroxymethyl)anisole. A solution of 49.0 g (0.21 mol) of 3,5-dicarbomethoxyanisole[38] in 1000 ml of anhydrous ether was

(29) H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, 3635–8 (1968).
(30) R. Noyori and M. Kato, *ibid.*, 5075–7 (1968).
(31) J. K. Crandall and R. P. Haseltine, *J. Amer. Chem. Soc.*, **90**, 6251 (1968).
(32) P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).
(33) R. Noyori, A. Watanabe, and M. Kato, *Tetrahedron Lett.*, 5443 (1968).
(34) (a) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **87**, 2052 (1965); (b) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).
(35) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).
(36) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).
(37) All melting points were taken on a hot-stage apparatus checked with known compounds.

added dropwise with stirring to 25.0 g (0.66 mol) of lithium aluminum hydride in 300 ml of anhydrous ether under nitrogen. The mixture was refluxed for 5 hr and then stirred at room temperature for 18 hr. Excess lithium aluminum hydride was destroyed with ethyl acetate followed by aqueous sulfuric acid. The ether layer was washed with water, dried, and concentrated *in vacuo*. The resulting clear oil (37.0 g) crystallized on standing and was used in the next step without further purification. A sample crystallized twice from hexane–chloroform gave white crystals, mp 67–68°.

The spectral data were: ir (CHCl₃) 2.77, 2.96, 6.27, 6.86, 7.71, and 11.05 μ; nmr (CDCl₃) τ 3.13 (m, 3 H, arom), 5.35 (s, 4 H, CH₂), 6.18 (s, 3 H, OCH₃), and 8.14 (s, 2 H, OH).

Anal. Calcd for C₉H₁₂O₃: C, 64.29; H, 7.14. Found: C, 64.13; H, 7.14.

3,5-Bis(bromomethyl)anisole. A solution of 35 ml (0.40 mol) of phosphorus tribromide in 50 ml of benzene was added with stirring over 15 min to a solution of 37.0 g of crude 3,5-bis(hydroxymethyl)-anisole in 300 ml of benzene. The mixture was refluxed for 45 min, cooled, decanted from inorganic residue, and poured onto 400 g of ice. The organic layer was extracted, combined with benzene washings of the aqueous layer, dried, and concentrated *in vacuo*. The crude product was crystallized from hexane–benzene to give 29.5 g (48 % for two steps) of white crystals, mp 74–76°.

The spectra data were: ir (CHCl₃) 6.26, 6.85, 7.52, 7.70, 8.60, and 9.42 μ; nmr (CDCl₃) τ 3.02 (m, 1 H, arom), 3.16 (m, 2 H, arom), 5.60 (s, 4 H, CH₂), and 6.22 (s, 3 H, OCH₃).

Anal. Calcd for C₉H₁₀OBr₂: C, 36.74; H, 3.40. Found: C, 36.81; H, 3.37.

2,6-Bis(bromomethyl)-4-methoxytoluene. The seven-step sequence described by Boekelheide and Phillips[39] was carried out on 280.0 g of *p*-cresol to give 110 g of crystalline dibromide, mp 125–130° (overall yield 13 % from *p*-cresol).

Reductive Coupling of 2,6-Bis(bromomethyl)-4-methoxytoluene and 3,5-Bis(bromomethyl)anisole. Sodium–potassium alloy was prepared in a 3 l. three-necked flask by pressing together 3.0 g (0.13 g-atom) of sodium and 9.0 g (0.23 g-atom) of potassium in small pieces under nitrogen (benzophenone ketyl purified). To the resulting silvery paste was added 500 ml of freshly distilled (from LiAlH₄) tetrahydrofuran. Tetraphenylethylene (2.0 g) was dissolved in 500 ml of tetrahydrofuran and added to the alloy mixture to give immediately the deep purple color of the radical anion.

2,6-Bis(bromomethyl)-4-methoxytoluene (10.0 g, 0.032 mol) and 3,5-bis(bromomethyl)anisole (10.0 g, 0.034 mol), dissolved in 500 ml of tetrahydrofuran, were added dropwise to the vigorously stirred reaction mixture. The addition (6 hr) was timed so that the color of the radical anion remained dark and persistent. The formation of polymeric material and bromide salt was increasingly apparent as the reaction proceeded.

After the addition was complete, unreacted alloy was discharged by slow addition of methanol. Stirring was continued until all the metal had reacted, and finally a 100-ml portion of water was added to the reaction mixture. The solution was siphoned from insoluble material and concentrated *in vacuo* to give a yellow residue which was extracted with methylene chloride and 10 % hydrochloric acid. Concentration *in vacuo* of the dried organic layer gave a red oil, weighing 14.3 g. It was convenient to proceed in the work-up with the products from two reactions as described above. Thus the procedure was carried out a second time to give 14.0 g of crude product.

The red oil (28.3 g) obtained from two coupling reactions was eluted on a 4 × 27 cm column of Florisil (Fisher F-100, 60–100 mesh) with 5 % ether in hexane. The first 2000 ml gave 18.0 g of a partially solid light yellow material substantially separated from polymeric product. The crude product was rechromatographed on a 4 × 28 cm column of neutral alumina (Woelm, activity 1), slurry-packed in hexane. Elution in 500-ml fractions gave: fraction 1, 2 % ether in hexane, 3.885 g, tetraphenylethylene and tetraphenylethane; 2–7, 2 % ether in hexane, 4.587 g, containing the desired metacyclophanes; 8 and 9, 10 % ether in hexane, 2.139 g of a complex mixture.

The metacyclophane mixture was used directly in the next step. It showed unique absorption ascribed to internal 8- and 16-hydrogens at τ 6.00 and 6.47 and internal methyls at τ 9.32 and 9.42.

7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone. A 5.0-ml (13.3 mmol) quantity of chromic acid reagent, prepared from

2.67 g (26.7 mmol) of chromium trioxide, 2.13 g of concentrated sulfuric acid, and water to bring the volume to 10.0 ml, was added dropwise with stirring to a solution of 4.59 g of the metacyclophane mixture (fractions 2–7 from above) in 100 ml of acetone. Precipitation of a brown complex was complete in 5 min, and stirring was continued another 10 min before decomposing the complex by addition of 100 ml of water. Methylene chloride extraction and concentration under vacuum of the dried organic extract yielded 4.43 g of an oil which was chromatographed on a 4 × 35 cm column of silica gel (Grace 950, 60–200 mesh), slurry packed in benzene. Elution in 1000-ml fractions gave: fractions 1, benzene, and 2 and 3, 5 % ethyl acetate in benzene, 2.74 g, tetraphenylethylene and unreacted metacyclophanes; fractions 4 and 5, 20 % ethyl acetate in benzene, 1.39 g of the desired dienone; fraction 6, ethyl acetate, 0.216 g, bisdienone.

The dienone as obtained from the column, 1.39 g (8.0 % overall yield from the dibromides), was substantially uncontaminated and crystallized on standing. Crystallization from a small amount of methanol gave 820 mg of yellow crystals, mp 125–129°. A second crystallization gave pale yellow crystals, mp 132–133°. The spectral data were: λ_{max}^{MeOH} 244 nm (ϵ 14,400); ir (CHCl₃) strong 6.02, 6.20, 8.70; medium 7.38, 7.20, 9.55, 11.12, and 11.30 μ; nmr (CCl₄) τ 3.57 (s, 2 H, arom), 4.02 (s, 2 H, =CH–), 6.30 (s, 3 H, OCH₃), 6.80–7.50 (m, 8 H, CH₂), and 8.50 (s, 3 H, CH₃).

Anal. Calcd for C₁₈H₁₈O₂: C, 81.20; H, 6.77. Found: C, 80.96; H, 6.98.

4-Methyl-4-phenylcyclohexenone. Potassium hydroxide (5.60 g, 0.10 mol) in 30 ml of 95 % ethanol was added dropwise with stirring under nitrogen at 0° over 45 min to 18.0 g (0.25 mol) of methyl vinyl ketone and 33.5 g (0.25 mol) of 2-phenylpropionaldehyde in 400 ml of anhydrous ether.

The mixture became cloudy, then clear again, and finally developed a light yellow color. Stirring was continued for 2 hr and for 2 hr at room temperature. The mixture was washed with dilute hydrochloric acid and then water, dried, and concentrated *in vacuo*, giving a yellow oil, weighing 49.0 g.

Distillation of the crude product at 0.25 mm gave a colorless liquid, bp 93–94°, which crystallized, mp 30–35°, on standing (32.2 g, 74 %). Recrystallization from methanol gave colorless crystals, mp 41–42°; ir (CCl₄) 3.36, 5.95, 7.20, and 14.32 μ; nmr (CCl₄) τ 2.77 (m, 5 H, arom), 3.67 (q, 2 H, J_{ab} = 10 cps, =CH–), 7.82 (m, 4 H, CH₂), 8.44 (s, 3 H, CH₃).

Anal. Calcd for C₁₃H₁₄O: C, 83.87; H, 7.53. Found: C, 83.94; H, 7.55.

4-Methyl-4-phenylcyclohexadienone. 4-Methyl-4-phenylcyclo-hexenone (5.00 g, 26.9 mmol) and 8.00 g (35.2 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were refluxed in 60 ml of dioxane for 22 hr. Filtration of 7.0 g of precipitated hydroquinone, dilution with ether, washing with 10 % aqueous sodium hydroxide, and then water, drying, and concentration *in vacuo* gave a yellowish solid.

The crude product was sublimed, 1.0 mm at 100°, to give 3.80 g (76 %) of white crystals, mp 46–51°. Recrystallization from methanol gave white needles, mp 53–55°; $\lambda_{max}^{C_6H_{12}}$ 222 nm (ϵ 16,000), 348 nm (ϵ 30); ir (CCl₄) 6.00, 6.13, 11.52, 11.76, and 14.38 μ; nmr (CCl₄) τ 2.65 (s, 5 H, arom), 3.38 (q, 4 H, J_{ab} = 10 cps, =CH–), 8.30 (s, 3 H, CH₃).

Anal. Calcd for C₁₃H₁₂O: C, 84.78; H, 6.52. Found: C, 84.59; H, 6.49.

Photolysis Apparatus and Equipment. The light source was a GE AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector 13.7 cm long and 14.0 cm in diameter. The light was filtered by a cell of three water-cooled compartments, separated by gasketed quartz disks, 2.4 cm thick and 12 cm in diameter.

The photolysis cell contained two identical compartments each 12 cm in diameter with a 5-cm optical path and aliphatic epoxy (uv transparent and nonfluorescent) cemented quartz faces. The cells were equipped with a thermistor probe inlet, Trubore stirrer, heat exchanger coil, and nitrogen inlet. The light output was monitored with an RCA 935 phototube mounted between the filter and irradiation cells to check for filter decomposition and lamp decay. All irradiations were carried out at 25.0 ± 0.1°. Before irradiation, vanadous-purified nitrogen[40] was bubbled through the solution for 0.5 hr, and during the irradiation a positive pressure of nitrogen was maintained over the solution.

Actinometry. Each determination required three runs: (1) irradiation with both cells containing actinometer, (2) irradiation

(38) J. C. Calandra and J. J. Svarz, *J. Amer. Chem. Soc.*, **72**, 1027 (1950).

(39) V. Boekelheide and J. B. Phillips, *ibid.*, **89**, 1695 (1967).

(40) L. Meites, *Anal. Chem.*, **20**, 984 (1948).

with the first cell containing photolysis solution and the second cell containing actinometer, (3) irradiation with both cells containing actinometer. Potassium ferrioxalate actinometry[41] was employed, and a quantum yield of 1.23[41] was assumed.

Filter Solutions. For preparation of filter solutions, nickel sulfate hexahydrate and cobalt sulfate heptahydrate were used in 10% sulfuric acid. Stannous chloride dihydrate, bismuth trichloride, and copper sulfate pentahydrate were used in 10% hydrochloric acid, 40% hydrochloric acid, and water, respectively.

Filter A: cell I, 36.0 g of nickel salt/l.; cell II, 280.0 g of cobalt salt/l.; cell III, 74.0 g of tin salt/l.; transmission (320–385 nm, maximum at 343 nm) 220–320 nm, 0%; 330 nm, 13.0%; 340 nm, 27.5%; 350 nm, 26.2%; 360 nm, 6.0%; 385–400 nm, 0%.

Filter B: cell I, 127 g of nickel salt/l.; cell II, 137 g of cobalt salt/l.; cell III, 29.0 g of copper salt/l.; transmission (295–365 nm, maximum at 326 nm) 220–290 nm, 0%; 300 nm, 3.5%; 310 nm, 20.0%; 320 nm, 36.5%; 330 nm, 37.7%; 340 nm, 28.5%; 350 nm, 15.8%; 360 nm, 3.5%; 365–400 nm, 0%.

Filter C: cell I, 262 g of nickel salt/l.; cell II, 560 g of cobalt salt/l.; cell III, 31.6 mg of bismuth salt/l.; transmission (250–315 nm, maximum at 297 nm) 220–250 nm, 0%; 260 nm, 2.6%; 270 nm, 6.0%; 280 nm, 13.2%; 290 nm, 27.0%; 300 nm, 9.0%; 315–400 nm, 0%.

Solvents, Quenchers, and Sensitizer. Benzene was purified by stirring for 12 hr with sulfuric acid, washing in water, drying with sodium sulfate, and distilling from phosphorus pentoxide. t-Butyl alcohol was distilled from calcium hydride.

2,5-Dimethyl-2,4-hexadiene (Aldrich) was fractionated, bp 134°, using a spinning-band column. Piperylene (Aldrich) was distilled under nitrogen. Both of these quenchers were removed after photolysis along with solvent under reduced pressure. Acetophenone (Matheson Coleman and Bell) was distilled, bp 91° (36 mm), and was removed after photolysis by chromatography on a 5 × 65 cm column of Florisil with 10% ether in hexane eluent.

Preparative Photolysis of 7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone. A solution of 205.4 mg (0.771 mmol) of dienone in 275 ml of isopropyl alcohol was irradiated through filter A. In 1 hr 2.42 mEinsteins of light was absorbed. Evaporation of the solvent *in vacuo* gave a clear oil, weighing 242.0 mg.

The product was chromatographed on a 3 × 30 cm column of Florisil, slurry packed in benzene. Elution in 1000-ml fractions gave: fraction 1, benzene, nil; fraction 2, 5% ethyl acetate, 53.3 mg, photophenol, 29%; fractions 3 and 4, 20% ethyl acetate, 129.2 mg, recovered dienone. The crystalline product was recrystallized from hexane–chloroform to give white needles, mp 164–165°.

The spectral data were: λ_{max}^{MeOH} 288 nm (ϵ 32,000); ir (CHCl$_3$) 2.78, 6.23, 6.84, 7.82, and 8.72 μ; nmr (CDCl$_3$) τ 3.40 (s, 2 H, arom), 3.46 (s, 2 H, arom), 6.20 (s, 3 H, –OCH$_3$), 7.20 (s, 8 H, –CH$_2$–).

Anal. Calcd for C$_{17}$H$_{16}$O$_2$: C, 80.95; H, 6.37. Found: C, 80.77; H, 6.22.

Synthesis of 2-Hydroxy-7-methoxy-4,5,9,10-tetrahydropyrene.[42] A mixture of 98 mg (0.37 mmol) of 7-methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone, 20 ml of pyridine, 0.2 ml of water, and 10.0 g of freshly activated zinc dust (washed with 5% HCl, water, methanol, and ether) was refluxed with stirring for 1 hr. Excess zinc was filtered and washed with ethyl acetate. The clear filtrate was extracted with 5% HCl. Evaporation of the dried organic portion *in vacuo* gave 95 mg (100%) of a crystalline solid, mp 150–158°. Crystallization from hexane–chloroform gave white crystals, mp 164–165°, whose ir and nmr spectra were identical with photolytically derived phenol **7**. The mixture melting point was undepressed.

Quantum Yields in the Photolysis of 7-Methoxy-10b-methyl-4,5,-9,10-tetrahydro-2(10bH)-pyrenone. The pyrenone was irradiated in dilute solution (10^{-3} M) through filter A to low conversion. The solvent was removed *in vacuo* below 40°, and extraction with chloroform and water was carried out in photolyses with added inorganic reagent. The product was chromatographed on a 3 × 30 cm column of Florisil, slurry packed in benzene. Elution in 1000 ml fractions gave: fraction 1, benzene, nil; fraction 2, 5% ethyl acetate in benzene, product phenol; fractions 3 and 4, 20% ethyl acetate in benzene, recovered dienone; fraction 5, 50% ethyl acetate in benzene, nil.

Quantum yields were based on amounts of isolated phenol and starting material. Light capture of phenol relative to dienone, calculated from absorption spectra of equimolar solutions in the

region of filter transmission, was 0.79. Corrections made for light absorption by product were <10%. All runs were made in 725 ml of solvent. Data for individual quantum yield runs are listed as follows: weight, solvent, any added reagent, amount of light, weight of recovered materials, and quantum yields.

Run I-01. Starting dienone (200.4 mg, 0.753 mmol), benzene, 1.14 mEinsteins; recovered dienone (196.3 mg, 0.737 mmol), photophenol (0 mg); $\Phi \leq 0.005$.

Run I-02. Starting dienone (205.1 mg, 0.770 mmol), t-butyl alcohol, 4.43 mEinsteins; recovered dienone (200.3 mg, 0.752 mmol), photophenol (4.0 mg, 0.016 mmol); $\Phi < 0.005$.

Run I-03. Starting dienone (95.0 mg, 0.357 mmol), glacial acetic acid, 5.67 mEinsteins; recovered dienone (77.1 mg, 0.289 mmol), photophenol (19.1 mg, 0.075 mmol); $\Phi = 0.014$.

Run I-04. Starting dienone (183.1 mg, 0.688 mmol), methanol, 4.35 mEinsteins; recovered dienone (159.2 mg, 0.598 mmol), photophenol (22.0 mg, 0.083 mmol); $\Phi = 0.021$.

Run I-05. Starting dienone (122.0 mg, 0.458 mmol), n-butylamine, 2.69 mEinsteins; recovered dienone (34.0 mg, 0.128 mmol), photophenol (64.4 mg, 0.254 mmol); $\Phi = 0.11$.

Run I-06. Starting dienone (205.4 mg, 0.771 mmol), isopropyl alcohol, 2.42 mEinsteins; recovered dienone (129.2 mg, 0.512 mmol), photophenol (53.3 mg, 0.210 mmol); $\Phi = 0.10$.

Run I-07. Starting dienone (247.2 mg, 0.928 mmol), benzene, dimethyl acetylenedicarboxylate (1.39 g, 0.011 M), 6.37 mEinsteins; recovered dienone (240.4 mg, 0.903 mmol), photophenol (0 mg); $\Phi \leq 0.005$.

Run I-08. Starting dienone (213.2 mg, 0.802 mmol), t-butyl alcohol, sulfuric acid (3.66 g, 0.05 M), 4.54 mEinsteins; recovered dienone (133.0 mg, 0.500 mmol), photophenol (80.4 mg, 0.317 mmol); $\Phi = 0.079$.

Run I-09. Starting dienone (195.3 mg, 0.733 mmol), glacial acetic acid, lithium acetate dihydrate (40.0 g, 0.54 M), 4.67 mEinsteins; recovered dienone (159.3 mg, 0.597 mmol), photophenol (30.1 mg, 0.119 mmol); $\Phi = 0.027$.

Run I-10. Starting dienone (228.3 mg, 0.857 mmol), methanol, lithium chloride (100 g, 3.25 M), 5.78 mEinsteins; recovered dienone (169.2 mg, 0.635 mmol), photophenol (45.2 mg, 0.179 mmol); $\Phi = 0.034$.

Run I-11. Starting dienone (217.1 mg, 0.816 mmol), isopropyl alcohol, 2,5-dimethyl-2,4-hexadiene (1.52 g, 0.0191 M), 11.82 mEinsteins; recovered dienone (181.4 mg, 0.680 mmol), photophenol (22.0 mg, 0.087 mmol); $\Phi = 0.0076$.

Run I-12. Starting dienone (217.2 mg, 0.816 mmol), isopropyl alcohol, 2,5-dimethyl-2,4-hexadiene (1.01 g, 0.0126 M), 12.31 mEinsteins; recovered dienone (180.2 mg, 0.678 mmol), photophenol (37.1 mg, 0.147 mmol); $\Phi = 0.011$.

Run I-13. Starting dienone (203.0 mg, 0.763 mmol), isopropyl alcohol, 2,5-dimethyl-2,4-hexadiene (0.499 g, 0.00626 M), 4.87 mEinsteins; recovered dienone (167.2 mg, 0.628 mmol), photophenol (25.0 mg, 0.099 mmol); $\Phi = 0.020$.

Photolysis of 7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (Gas Analysis). A solution of 100 mg (0.378 mmol) of dienone in 25 ml of isopropyl alcohol was placed in a small Pyrex tube connected to a 25-ml gas buret and to a 14/20 jointed, evacuated 50-ml round-bottomed flask fitted with a high-vacuum stopcock. The Pyrex tube was strapped to the cooling jacket of a 450-W Hanovia immersion apparatus and irradiated for 15 min.

The gas above the sample was collected by opening the stopcock and the 50-ml collection flask was removed for mass spectral analysis. Spectra at 25 and 70 V showed significant peaks of almost equal intensity at m/e 15 and 16 (separated from ^{18}O), demonstrating the formation of methane.

Preparative Photolysis of 4-Methyl-4-phenylcyclohexadienone. Filter combination C was used with the AH6 apparatus as described above for the quantum yield determinations. 4-Methyl-4-phenylcyclohexadienone (2.123 g, 11.44 mmol) was photolyzed in four batches of about 500 mg each in 725 ml of reagent acetone (sensitizer). The four runs utilized 6.0 mEinsteins each and were processed together. The solvent was removed *in vacuo* to give a clear oil weighing 2.281 g.

The crude product was chromatographed and individual fractions were assayed by nmr. A 4 × 70 cm column of silica gel (Grace 950, 60–200 mesh), slurry packed in 5% ether in hexane, was employed. Elution in 500-ml fractions gave: fractions 1–4, 25% ether in hexane, 429 mg, photophenol; fractions 5–8, 30% ether in hexane, 109 mg, 90% photoketone A; fractions 9 and 10, 30% ether in hexane, 206 mg, 50% photoketone A and 50% starting dienone; fraction 11, 30% ether in hexane, 255 mg, starting dienone; fractions 12–14, 30% ether in hexane, 614 mg, 50% starting dienone

(41) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **235**, 518 (1956).

(42) Following the procedure described in ref 6.

and 50% photoketone B; fractions 15–17, 40% ether in hexane, 235 mg, 20% starting dienone and 80% photoketone B. Yields determined from the assays of the chromatographic fractions were: photophenol, 530 mg, 25.1%; photoketone A, 235 mg, 11.1%; photoketone B, 520 mg, 24.5%; recovered dienone, 640 mg, 30.2%; material balance, 90.9%.

Rechromatography on silica gel of fractions from several chromatograms enriched in photoketone A gave a clear oil which resisted crystallization. The spectral data were: λ_{max}^{MeOH} 205 (ϵ 12,100), 332 nm (369); ir (CCl$_4$) 5.90, 7.45, 8.53, 9.26, 11.60, 14.36 μ; nmr[43] (CCl$_4$) τ 2.53 (d of d, J_{34} = 2.5 cps, J_{45} = 1.5 cps, 1 H, β =CH–), 2.77 (s, 5 H, arom), 4.04 (d, J_{34} = 2.5 cps, 1 H, α =CH–), 7.21 (d of d, J_{45} = 1.5 cps, J_{15} = 2 cps, 1 H, allyl cyclopropyl), 7.73 (d, J_{15} = 2 cps, 1 H, α cyclopropyl), 8.59 (s, 3 H, –CH$_3$).

Anal. Calcd for C$_{13}$H$_{12}$O: C, 84.78; H, 6.52. Found: C, 84.88; H, 6.60. Photoketone A was assigned structure 9a.

Rechromatography on silica gel of fractions enriched in photoketone B from several chromatograms gave a clear oil which partially crystallized on standing. This material was sublimed at 100° (1.0 mm) to give white crystals which were crystallized from hexane, mp 84–85°. The spectral data were: λ_{max}^{MeOH} 205 (ϵ 12,500), 328 mμ (207); ir (CCl$_4$) 5.90, 7.42, 8.21, 8.46, 11.78, and 14.30 μ; nmr[43] (CCl$_4$) τ 2.87 (m, 6 H, arom and β =CH–), 4.65 (d, J_{34} = 2.5 cps, 1 H, α =CH–), 7.33 (d of d, J_{45} = 1 cps, J_{15} = 2 cps, allyl cyclopropyl), 7.78 (d, J_{15} = 2 cps, 1 H, α cyclopropyl), 8.54 (s, 3 H, CH$_3$).

Anal. Calcd for C$_{13}$H$_{12}$O: C, 84.78; H, 6.52. Found: C, 84.50; H, 6.78. Photoketone B was assigned structure 9b.

The photophenol was obtained from chromatography as a clear oil which crystallized on standing. Two crystallizations from hexane gave white crystals, mp 56–57°. The spectral data were: ir (CCl$_4$) 2.78, 6.30, 6.82, 6.93, 7.79, 7.93, 8.47, 8.60, and 14.23 μ; nmr (CCl$_4$) τ 2.60–3.50 (m, 8 H, arom), 5.49 (broad s, 1 H, OH), 8.02 (s, 3 H, CH$_3$).

Anal. Calcd for C$_{13}$H$_{12}$O: C, 84.78; H, 6.52. Found: C, 84.76; H, 6.41.

Quantum Yields in the Photolysis of 4-Methyl-4-phenylcyclohexadienone. Dilute solutions of 4-methyl-4-phenylcyclohexadienone in 725 ml of isopropyl alcohol were irradiated through filter combination A to low conversion. The quenched run contained piperylene, which did not absorb light above 320 nm, 300 ml of benzene, and 425 ml of isopropyl alcohol as solvent. The sensitized run utilized filter combination B, benzene solvent, and acetophenone, which absorbed >95% of the incident light. The solvent was removed *in vacuo* below 40° and quencher and sensitizer were removed as described above.

(43) The coupling constants were obtained from the spin-decoupled 100-Mc spectra.

From the crude product starting dienone was crystallized from methanol in runs in which conversion was very low. Good material balance was achieved, and relative amounts of the starting material and products (only photoketones 9a,b and the photophenol detected) were determined by integration of the nmr spectra of the mother liquors. Specific data for individual determinations are listed as follows: weight, added quencher or sensitizer, amount of light, per cent conversion, nmr assays, and quantum yields for appearance of photoketones and disappearance of starting material.

Extrapolation of the quantum yield data for runs II-01-03 to 0% conversion gave Φ_{app} = 0.71 and Φ_{dis} = 0.73 for direct irradiation. For runs 2 and 3, 9b:9a ratios were calculated to be 1.6 and 1.7, respectively.

Run II-01. Starting dienone (0.978 g, 5.32 mmol), 1.49 mEinsteins, 12.3% conversion; photophenol (38.1 mg, 0.206 mmol), photoketones 9a,b (82.0 mg, 0.446 mmol), recovered dienone (0.858 g, 0.467 mmol); Φ_{app} = 0.30, Φ_{dis} = 0.44.

Run II-02. Starting dienone (3.133 g, 17.02 mmol), 2.51 mEinsteins, 8.1% conversion; photophenol (38.2 mg, 0.207 mmol), photoketones 9a,b (218.2 mg, 0.118 mmol), recovered dienone (2.877 g, 15.67 mmol); Φ_{app} = 0.47, Φ_{dis} = 0.55.

Run II-03. Starting dienone (3.185 g, 17.32 mmol), 0.960 mEinsteins, 3.6% conversion; photophenol (15.0 mg, 0.081 mmol), photoketones 9a,b (101.3 mg, 0.548 mmol), recovered dienone (3.069 g, 16.68 mmol); Φ_{app} = 0.58, Φ_{dis} = 0.65.

Run II-04. Starting dienone (3.034 g, 16.45 mmol), piperylene (49.3 g, 1.0 *M*), 9.20 mEinsteins, 17.7% conversion; photophenol (209.4 mg, 1.14 mmol), photoketones 9a,b (328.0 mg, 1.78 mmol), recovered dienone (2.497 g, 13.57 mmol); Φ_{app} = 0.19, Φ_{dis} = 0.31.

Run II-05. Starting dienone (1.008 g, 5.47 mmol), acetophenone (10.54 g, 0.121 *M*), 1.36 mEinsteins, 18.3% conversion; photophenol (0 mg), photoketones 9a,b (185.1 mg, 1.01 mmol), recovered dienone (0.823 g, 4.47 mmol); Φ_{app} = Φ_{dis} = 0.74.

Emission Measurements. Phosphorescence measurements were made on an Amino-Kiers spectrophosphorimeter modified with internal baffles to eliminate scatter. 7-Methoxy-10b-methyl-4,5,-9,10-tetrahydro-2(10bH)-pyrenone in a methylcyclohexane–isopentane glass (3.5 × 10^{-3} *M*) exhibited broad, structureless phosphorescence emission (λ_{max} 468 nm). The emission was calibrated by use of a low-pressure mercury lamp in each run.