recrystallized from methanol to give 0.015 g (82%) of 1,4-dinitrobenzene, mp 172–174 °C [lit.[34] mp 172–173 °C].

1,2-Dinitrobenzene. *o*-Phenylenediamine (0.022 g, 0.20 mmol) was dissolved in 5 mL of acetone. To this solution was added 30 mL of 0.06 M 1 at room temperature with stirring. Stirring was continued for several hours while the reaction solution was sampled and GPC analysis used to follow production of the dinitro compound. After 6 h the yield had reached 85% and there was no further increase in yield with time.

***endo*-2-Nitronorbornane.** An acetone solution of 1 (145 mL, 0.036 M, 5.22 mmol) was placed into a 250-mL round-bottomed flask equipped with a magnetic stirrer. A solution of *endo*-2-aminonorbornane hydrochloride (0.051 g, 0.348 mmol) in 1 mL of water was added slowly to the dioxirane solution at 21 °C over a period of 3 min. The reaction mixture was stirred at room temperature for 7 h. The reaction mixture was diluted with 60 mL of water and then extracted with 4 × 50 mL of CH_2Cl_2. The combined organic solution was washed with 100 mL of water and dried over anhydrous Na_2SO_4 for 8 h. The solvent was evaporated in vacuo to give a yellow oil. Chromatography of the oil using a Chromatotron with a silica gel plate (2 mm) and eluting with CH_2Cl_2 (200 mL) gave, after concentration, a viscous oil, which solidified upon refrigeration to give 31 mg (58%) of *endo*-2-nitronorbornane as a white powder, mp 59–63 °C [lit.[35] mp 64–67 °C]. ^1H NMR ($CDCl_3$): δ 1–1.6 (m, 6 H), 1.7–2.0 (m, 1 H), 2.0–2.22 (m, 1 H), 2.3–2.5 (br s, 1 H, H_d), 2.8–3.0 (br s, 1 H, H_i), 4.7–4.9 (m, 1 H, H_a). ^{13}C NMR ($CDCl_3$): ppm 23.02 (C_6), 28.21 (C_5), 33.24 (C_7), 36.69 (C_4), 38.83 (C_3), 42.84 (C_1), 87.42 (C_2).

***exo*-2-Nitronorbornane.** An acetone solution of 1 (190 mL, 0.061 M, 11.59 mmol) was placed into a 250-mL round-bottomed flask equipped with a magnetic stirrer. A solution of *exo*-2-aminonorbornane (0.215 g, 1.93 mmol) in 25 mL of acetone was added slowly to the dioxirane solution over a period of 4 min. The reaction mixture was stirred at room temperatue for 30 min. The solvent was removed in vacuo. Fresh CH_2Cl_2 (150 mL) was added and the solution dried ($MgSO_4$, 30 min) and then filtered, and the solvent was removed in vacuo. The yellow oil obtained was diluted with 1 mL of CH_2Cl_2 and then subjected to TLC using hexane/ethyl acetate (4:1) as eluent. The band at R_f 0.68 was extracted 3 times with $CH_3COCH_3/CH_2Cl_2/CH_3OH$ (1:1:0.2) and the solvent evaporated to give a yellow oil. Bulb-to-bulb distillation of the oil gave 0.22 g (80.8%) of *exo*-2-nitronorbornane as a pale yellow liquid, bp 125–127 °C/2 mm. ^1H NMR ($CDCl_3$): δ 1.0–1.2 (m, 2 H, $H_h + H_f$), 1.4–1.55 (m, 2 H, $H_e + H_g$) (latter two assignments may be interchanged), 1.2–1.3 (m, 1 H, H_j), 1.5–1.7 (m, 1 H, H_k) (latter two assignments may be interchanged), 1.7–1.8 (m, 1 H, J = 13, 8, 2 Hz, H_b), 2.10–2.25 (m, 1 H, J = 13, 7, 5, 4 Hz, H_c), 2.25–2.48 (br s, 1 H, H_d), 2.7–2.82 (d, 1 H, J = 4.3 Hz, H_i), 4.25–4.4 (dd, 1 H, J = 6, 3 Hz, H_a). ^{13}C NMR ($CDCl_3$): ppm 26.20 (C_6), 27.91 (C_5), 35.65 (C_4), 35.69 (C_7), 36.85 (C_3), 43.50 (C_1), and 87.97 (C_2).

Acknowledgment. We are grateful to the National Institute of Environmental Health Sciences, the Office of Naval Research, and Geocenters, Inc., for support of this work. The Varian XL-300 NMR spectrometer was purchased with support from the National Science Foundation.

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Photochemistry of Some Extended π-Systems: Type A and Aryl Rearrangements of Systems with Extended Conjugation Related to Cyclohexadienones and Cyclohexenones. Mechanistic and Exploratory Organic Photochemistry[1]

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6,6-Diphenyl-2(6*H*)-naphthalenone and 5,6,6-triphenyl-2(6*H*)-naphthalenone were synthesized as extended relatives of 4,4-diphenylcyclohexadienone and their photochemistry was investigated. In the case of the diphenylnaphthalenone, irradiation resulted in a regioselective phenyl migration and formation of 5,6-diphenyl-2-naphthol whether the photolysis was in methanol or in benzene. Irradiation of the triphenylnaphthalenone in methanol or isopropyl alcohol afforded a product in which one molecule of solvent and one molecule of molecular oxygen were incorporated. Photolysis in acetonitrile led instead to a tricyclic photoproduct in a process reminiscent of the type A rearrangement of 2,5-cyclohexadienones. This tricyclic photoproduct itself was photochemically reactive and rearranged regioselectively to afford 5,7,8-triphenyl-2-naphthol. By trapping, a tricyclic zwitterion was shown to play a role in the rearrangement of the triphenylnaphthalenone. The photochemistry of both naphthalenones was shown by quenching to result from triplet excited states. Lack of reactivity on sensitization suggested the photochemistry derives from T_n. The quantum efficiencies were shown to be lower and the triplet reaction rate slower in a comparison with the monocyclic 4,4-diphenylcyclohexadienone. Finally, enone analogues were investigated. Both 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone and 6,6-diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone were synthesized. Only the former was reactive; phenyl migration resulted in formation of four stereoisomeric tricyclic ketones whose structures were established by X-ray analysis. For all of the various reactions, mechanisms are provided and discussed along with MNDO-CI computations.

Introduction

The photochemistry of 2,5-cyclohexadienones and 4-aryl-substituted cyclohexenones has been the object of a number of investigations at Wisconsin.[2,3] Thus, we found that the dienones undergo a "type A" rearrangement[2] while

(1) (a) This is paper 160 of our photochemical series and 220 of the regular sequence. (b) For paper 159, see: Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 2358–2361. (c) For paper 158, see: Zimmerman, H. E.; Zuraw, M. *J. Am. Chem. Soc.* **1989**, *111*, 7974–7989.

(2) For dienone photochemistry: (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527–4540. (b) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906–912. (c) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864–4875. (d) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876–4891. (e) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756.

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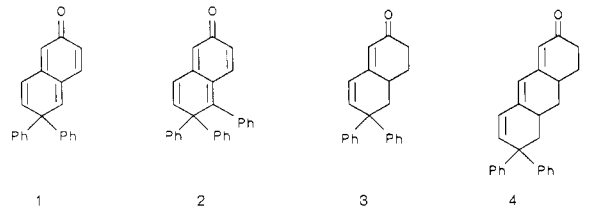
4-aryl-substituted cyclohexenones undergo a γ to β aryl migration leading to formation of bicyclo[3.1.0]hexanones.[3] These reactions have proved general and their chemistry has become extensive.[4]

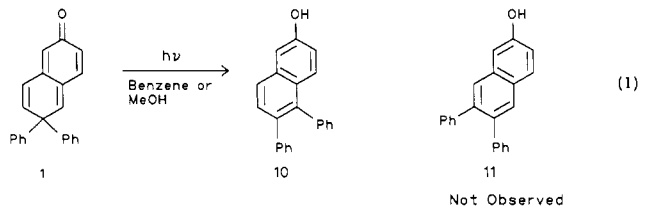
We wished to determine if related polycyclic compounds would exhibit similar photochemical reactivity. The phenyl-substituted ketones **1**, **2**, **3**, and **4** were of particular interest.



Results

Synthesis of Photochemical Reactants. The syntheses of reactants **1**, **2**, **3**, and **4** are outlined in Scheme I. The procedure of Woodward[5] permitted Robinson annulation to proceed smoothly by utilizing the formyl derivative **6**. This led to the linear dienone **3**, which was of photochemical interest itself. The further conversion of **3** to the desired naphthalenone **1** required the two steps indicated in Scheme I.

Exploratory Photolysis of Diphenylnaphthalenone 1. Direct irradiation of the diphenylnaphthalenone **1** in benzene or methanol led to a single photoproduct, mp 130–131 °C, which was isomeric with reactant. The NMR spectrum suggested the product to be a diphenylnaphthol (see Experimental Section). Interestingly, the same product was formed without light on treatment with dilute acetic acid. Two structures seemed a priori candidates, namely, diphenylnaphthols **10** and **11** (eq 1). However,



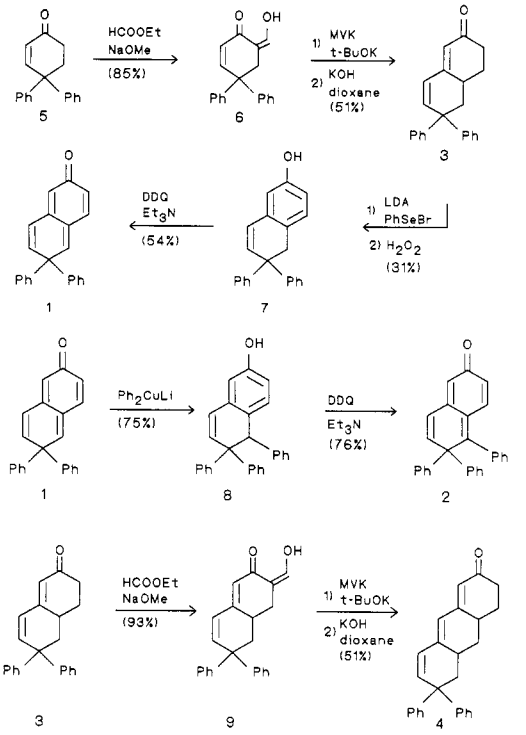
(1)

Not Observed

the formation of photoproduct from the acid treatment suggested, on mechanistic grounds (see the Discussion section), that **10** was the correct structure. Final assignment was made by X-ray analysis, which confirmed that the photoproduct had structure **10**.

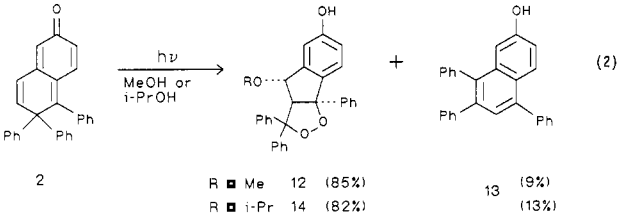
An unexpected result was obtained in sensitization experiments using Michler's ketone (E_T 62 kcal/mol[6]). Here no reactivity was observed.

Scheme I. Synthesis of Photochemical Reactants



Exploratory Photolysis of Triphenylnaphthalenone 2. Direct irradiation of **2** in methanol led to a photoproduct, mp 183–184 °C, whose NMR spectrum indicated incorporation of one molecule of solvent. Elemental analysis proved not to be routine and revealed incorporation of one molecule of molecular oxygen as well. The structure of the photoproduct was determined by X-ray analysis to be peroxide **12**.

In addition, a minor product (ca. 10%) was observed. X-ray analysis confirmed the structure as triphenylnaphthol **13**. Thus, the photochemistry of triphenylnaphthalenone **2** may be depicted as in eq 2.



(2)

Photolyses in isopropyl alcohol proved precisely parallel to those in methanol. As before, the photoproduct structure (**14**) was determined by X-ray analysis. This photochemistry is included in eq 2.

In view of the incorporation of hydroxylic solvents, photolyses in acetonitrile were carried out. In high conversion runs, 5,7,8-triphenyl-2-naphthol (**13**) was observed as the only photoproduct as indicated in eq 3.

As in the case of the diphenylnaphthalenone **1** photochemistry, sensitization with Michler's ketone (E_T 62 kcal/mol[6]) did not result in appreciable conversion despite a T_1 energy of 54 kcal/mol for **1** and a necessarily lower

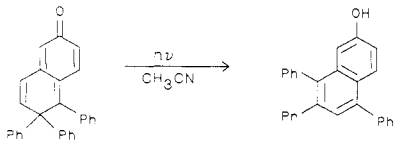
(3) For enone photochemistry: (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036–4042. (b) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047. (c) Zimmerman, H. E.; Sam, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 4905–4914. (d) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749–3760. (e) Zimmerman, H. E. Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954–966. (f) Zimmerman, H. E.; Lewin, N. *J. Am. Chem. Soc.* **1969**, *91*, 879–886. (g) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887–896. (h) Zimmerman, H. E.; King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724–7732. (i) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732–7744. (j) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276–6289. (k) Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 995–1007. (l) Zimmerman, H. E.; St. Clair, J. D. *J. Org. Chem.* **1989**, *54*, 2125–2137.

(4) For general reviews, see: (a) Schaffner, K.; Demuth, M. In *Rearrangements in the Ground and Excited States*, Vol. 3; DeMayo, P., Ed.; Academic Press; New York, 1980; pp 281–348. (b) Schuster, D. I. In *Rearrangements in the Ground and Excited States*, Vol. 3; DeMayo, P., Ed.; Academic Press: New York, 1980; pp 167–280.

(5) Woodward, R. B.; Sondheimer, F.; Taub, D.; Heulser, K.; McLamore, W. M.; *J. Am. Chem. Soc.* **1952**, *74*, 4223–4251.

(6) Murov, S. In *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 3.

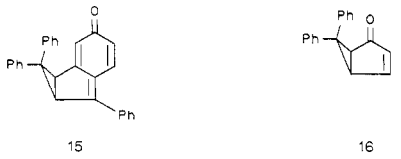
(7) (a) It has been noted[7b] that elemental analysis provides evidence of purity and composition of the entirety of a sample, as well as a safety factor, while mass spectral analysis alone would suggest a 99.9% sand sample contaminated with a desired material to be the desired compound. (b) Zimmerman, H. E.; Tolbert, l. M. *J. Am. Chem. Soc.* **1975**, *97*, 5497–5507.



(3)

triplet energy for 2 (see Experimental Section).

Evidence for a Quinone Methide Reaction Intermediate in the Photochemistry of Triphenylnaphthalenone 2. While in the preparative irradiations of triphenylnaphthalenone 2 in acetonitrile only triphenylnaphthol 13 resulted, in lower conversion (i.e. <10%) irradiations, a reaction intermediate was encountered. Thus NMR analysis of the photolysis mixture revealed an AB quartet characteristic of a pair of vicinal cyclopropyl methines (centered at δ 3.61, J = 5.3 Hz, δ_a 3.66, δ_b 3.57). Additionally, there was a methine peak at δ 6.18. Further peaks were not discernible due to overlap with reactant. The intermediate seemed most likely to be the tricyclic quinone methide 15. This tentative assignment was based on mechanistic reasoning and analogy to the intermediacy of bicyclo[3.1.0]hex-3-en-2-ones (e.g., 16) in the photochemistry of monocyclic 2,5-cyclohexadienones.



In view of the uncertainty of this assignment, it was advisable to synthesize authentic tricyclic quinone methide 15.

The synthesis, accomplished as outlined in Scheme II, proved to be nontrivial. Surprisingly, the demethylation of tricyclic 21 was unsuccessful with lithium iodide but proceeded nicely with lithium bromide. The generation of a tertiary monoacetate, such as 25, capable of loss of acetate with quinone methide formation proved elusive. For example, the diacetate 26 of diol 23 was accessible by reaction of 23 with butyllithium and acetic anhydride. However, aqueous bicarbonate led back to diol 23 rather than to the desired quinone methide 15, possibly due to the methide undergoing nucleophilic attack under the conditions. Success resulted, however, when the monosilated monoacetate 25, on treatment with tetrabutylammonium fluoride, was found to afford the required quinone methide 15.

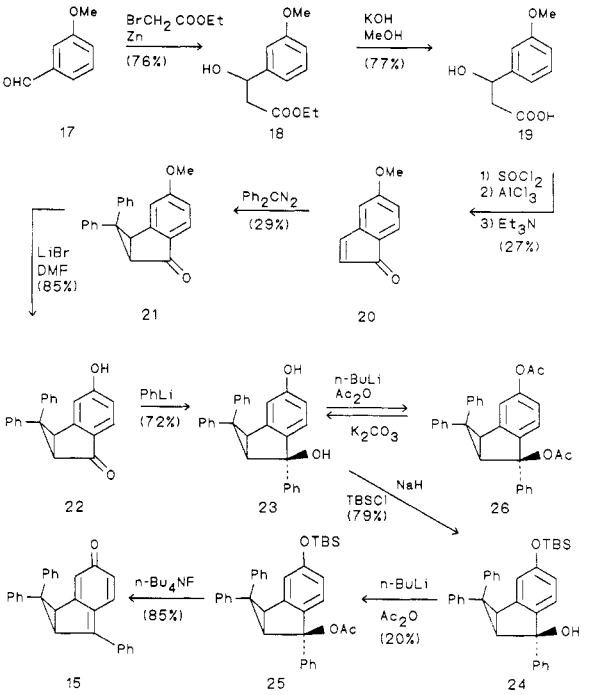
The NMR spectrum of the synthetic quinone methide 15 was observed to have the AB quartet as well as the methine peak found for the photolysis reaction intermediate, thus providing evidence for the identity of the intermediate.

Further evidence for this assignment was found in the photochemistry of the authentic quinone methide 15. In acetonitrile, irradiation led to the same triphenylnaphthol 13 that was observed in the photolysis of triphenylnaphthalenone 2.

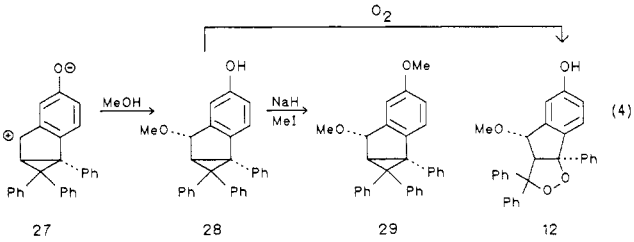
Evidence for a Zwitterionic Intermediate as an Initial Intermediate. As has been noted above (e.g., eq 2), on photolysis in methanol and isopropyl alcohol, solvent was incorporated in the reaction product. It seemed reasonable that this arose by nucleophilic attack on zwitterion 27, leading onward to the tricyclic triphenyl phenol 28.

This tricyclic triphenyl phenol 28 could be trapped as the corresponding methyl ether 29. Thus when the irradiation was followed by concentration in the absence of

Scheme II. Synthesis of Tricyclic Quinone Methide Photolysis Intermediate



oxygen followed by alkylation with methyl iodide and sodium hydride, the corresponding tricyclic triphenyl methyl ether 29 was isolated (eq 4). The structure of this product was established by X-ray analysis.

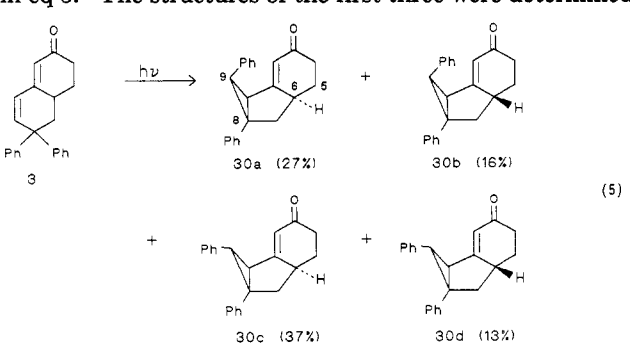


(4)

Furthermore, when the irradiation was run in a sealed NMR tube in methanol-d_4, NMR analysis of the photolysis mixture revealed a spectrum whose methine peaks were essentially identical with those of the tricyclic triphenyl ether 29. It was clear that the species present was the tricyclic triphenyl phenol 28.

When the sealed tube, containing the putative tricyclic triphenyl phenol 28, was opened after photolysis, the disappearance of 28 could be observed during 1 h along with the appearance of the NMR spectrum of peroxide 12.

Exploratory Photochemistry of Diphenyltetrahydronaphthalenone 3. Direct irradiation of the linear dienone 3 to high conversions resulted in the formation of four stereoisomeric photoproducts 30a–d as depicted in eq 5. The structures of the first three were determined



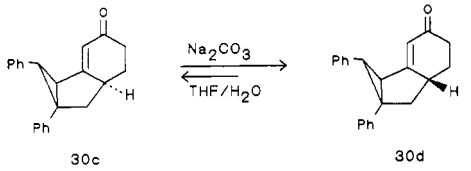
(5)

Table I. Quantum Yield Determinations

reactant	additive	λ	solvent	quantum[a] yield φ	product
diphenyl ketone 1	none	366	benzene	0.68[b]	naphthol 10
diphenyl ketone 1	none	313	benzene	0.67	naphthol 10
diphenyl ketone 1	Michler's ketone	366	benzene	<0.005	
triphenyl ketone 2	none	366	MeOH	0.30[b]	peroxide 12
triphenyl ketone 2	none	313	MeOH	0.33	peroxide 12
triphenyl ketone 2	Michler's ketone	366	MeOH	<0.008	
triphenyl ketone 2	none	366	CH_3CN	0.084[b]	ketone 15
diphenyl dienone 3	none	313	benzene	0.032[b]	exo-trans 30b
				0.066[b]	endo-trans 30a
diphenyl dienone 3	Michler's ketone	366	benzene	0.031[b]	exo-trans 30b
				0.66[b]	endo-trans 30a

[a] Error of ±10%. [b] Extrapolated value.

by X-ray analysis. The structure of the last photoproduct (i.e., **30d**) was established by base-catalyzed equilibration of **30c** to afford epimer **30d** as shown in eq 6. The formation of four stereoisomers proved to result from the high conversion of these runs, since only photoproducts **30a** and **30b** were observed in the low conversion quantum yield runs described below.



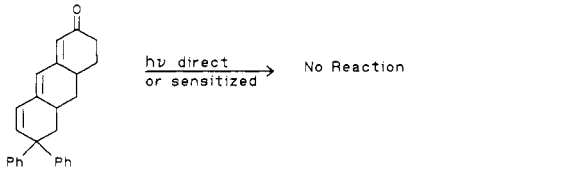
30c 30d (6)

Interestingly, sensitization with Michler's ketone (E_T 62 kcal/mol[6]) led only to the first two stereoisomers, **30a** and **30b**. In view of the relatively high conversions of the sensitized irradiations (ca. 70%), it seems likely that the formation of just stereoisomers **30a** and **30b** is a consequence of inefficient triplet energy transfer to photoproducts.

In the direct low conversion quantum yield runs on **3**, there was observed a large kinetic preference for formation of the *trans*-diphenyl isomers. In addition, the kinetically preferred stereochemistry not only has the phenyl groups trans to one another but also has the ring junction C-6 hydrogen anti to carbon-9 with the C-5 methylene becoming endo at C-6 on the five-membered ring. This results in a kinetic preference of stereoisomer **30a** over **30b**, with **30c** and **30d** being formed as secondary photoproducts. Experimentally it was observed that independent photolysis of **30a** afforded **30c**.

In the secondary photochemistry leading to the *cis*-diphenyl stereoisomers, again there is seen a preference for the C-5 methylene becoming endo. The mechanisms of the primary and secondary photochemistry are considered in the Discussion section.

Photochemistry of Diphenylanthracenone 4. As a third member of the enone series, it was of some interest to consider the photochemistry of the anthracenone **4**. Interestingly, this member of the series, despite its close structural similarity to the mono- and bicyclic ketones **5** and **3**, proved quite stable to direct irradiation (λ > 280 nm) and to sensitized photolysis with Michler's ketone. Note eq 7.



4 (7)

Quantum Yield Determinations. Quantum yields were determined for the reactions described. In the direct irradiation of tetrahydronaphthalenone **3**, an appreciable dependence of the measured efficiency on extent of conversion was noted. For each determination, a number of runs were made at varying conversions with the final value being obtained by extrapolation to 0% conversion. Where there was any question of dependence on extent of conversion in other cases, similar extrapolations were made, and these runs are so indicated in Table I. Runs were also checked for strongly absorbing contaminants. HPLC and NMR assays were used along with electronic actinometry[8] calibrated with potassium ferrioxalate.[9] The final quantum yields are listed in Table I.

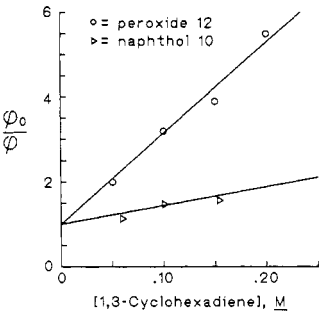


Figure 1. Stern–Volmer quenching plots of ϕ_0/ϕ for photoproducts **10** and **12**.

Table II. Excited State Lifetimes and Total Rates of Decay[a] for Naphthalenones 1 and 2

resulting product	slope,[b] L M^{-1}	τ, ns	$10^{-8}k_{dtot.}$, s^{-1}
naphthol **10**	4.4	0.73 (1.47)	13.6 (6.82)
peroxide **12**	21.4	3.57 (7.13)	2.8 (1.4)

[a] Lifetimes and rates were calculated by using 6×10^9 L M^{-1} s^{-1} (ref 10) and 3×10^9 L M^{-1} s^{-1} (in parentheses, ref 3k) for the rate of quenching by cyclohexadiene. [b] Slope of Stern–Volmer plot from Figure 1.

Excited Triplet Rearrangement Rates. We determined the reaction rates of the triplets of the diphenyl- and triphenylnaphthalenones **1** and **2** with Stern–Volmer methodology, the slopes of the ϕ_0/ϕ versus quencher plots giving $k_q\tau$. Cyclohexadiene (E_T 54 kcal/mol[6]) was used as the quencher. Two values of k_q were used in providing the total decay rates in Table II. One was the 6×10^9 L M^{-1} s^{-1} value[10] and the second was the 3×10^9 L M^{-1} s^{-1} value, which was obtained from viscosity studies in our recent investigations[3k] of cyclohexenone quenching. The

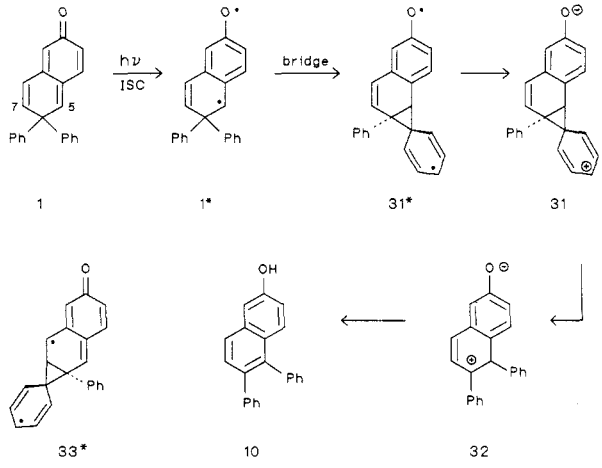
(8) (b) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. *J. Mol. Photochem.* **1977**, *8*, 379–385.
(9) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1965**, *235*, 518–536.
(10) (a) Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539–1542. (b) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777.

Table III. Summary of Reaction Efficiencies and Triplet Excited State Rates[a]

compounds	$\phi_{tot.}$	$10^{-8}k_r$, s^{-1}	$10^{-8}k_{dtot.}$, s^{-1}	ref
4,4-diphenylcyclohexadienone	0.85	124 (62.0)	146.0 (73.0)	14
4-methyl-4-trichloromethyl dienone	0.80	8.28 (4.15)	11.0 (5.50)	15
diphenylnaphthalenone 1	0.68	9.27 (4.64)	13.6 (6.82)	b
triphenylnaphthalenone 2	0.30	0.84 (0.42)	2.8 (1.40)	b
diphenyl enone 5	0.043	0.23 (0.11)	5.0 (2.5)	3d
tetrahydronaphthalenone 3	0.098	c	c	b

[a] Lifetimes and rates were calculated by using 6×10^9 L M^{-1} s^{-1} (ref 10) and 3×10^9 L M^{-1} s^{-1} (in parentheses, ref 3k) for the rate of quenching by cyclohexadiene. [b] This study. [c] Rates were not determined.

Scheme III. Rearrangement of Diphenylnaphthalenone 1



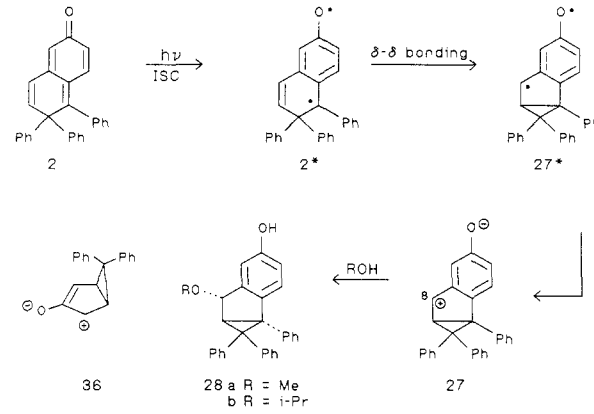
k_r's were derived from $k_r = \phi_r/\tau$ and are listed in Table III.

Discussion

Mechanistic Consideration in the Photochemistry of Diphenylnaphthalenone 1. The first point to be considered is the basic course of the rearrangement. A qualitative valence-bond representation is depicted in Scheme III. A point of particular interest is the marked regioselectivity favoring phenyl migration to C-5 rather than to C-7. This can be understood on the basis of comparison of the two possible half-migrated species **31*** and **33.*** Independent of which triplet (i.e., T_1, T_2, T_3) is the reactive species, the energy of **31*** can be seen to be lower than that of **33*** due to the presence of the extra aromatic ring. This is confirmed by SCF-CI calculations (vide infra). Interestingly, the same regiochemistry was noted for the acid-catalyzed rearrangement, which leads selectively to diphenylnaphthol **10**. The phenyl-bridged species involved here are the cationic counterparts **34** and **35**.

Mechanisms in the Photochemistry of Triphenylnaphthalenone 2 in Hydroxylic Solvents. The surprising behavior of diphenylnaphthalenone **1**, in which a phenyl migration occurred, suggested that the related triphenylnaphthalenone **2** might exhibit different reactivity as a consequence of steric blocking at C-5. Indeed this proved to be correct, since the phenyl migration reaction was not encountered in the triphenylnaphthalenone (i.e., **2**) rearrangements.

Scheme IV. Rearrangement of Triphenylnaphthalenone 2 in the Absence of Oxygen



It has been noted above that the tricyclic triphenyl phenols **28a** and **28b** appear as primary photochemical products in the irradiation of triphenylnaphthalenone **2** in methanol and isopropyl alcohol. This chemistry did demand (vide supra) the exclusion of oxygen following irradiation. The mechanism shown in Scheme IV is seen to be analogous to that which we proposed for the type A 2,5-cyclohexadienone rearrangment.[2] The initial δ–δ bridging step here is the counterpart of the β–β bonding seen in monocyclic dienones.[2] A difference is the facile trapping of the intermediate zwitterion **27** with solvent. In contrast, solvent incorporation has rarely been observed in the monocyclic zwitterions.[11] Solvent capture can be partly ascribed to intermediate zwitterion **27** having a higher positive charge concentrated at C-8 compared with zwitterion **36**.[2] In **36**, by symmetry the positive charge is equally distributed between two α-carbons. This charge concentration is anticipated in view of the phenolic nature of zwitterion **27** and is confirmed by MO calculations (vide infra). We note that solvent capture competes against the type A bicycle rearrangement[12] of the benzhydryl moiety. If benzhydryl bicycling were comparably enhanced by the increased positive charge at C-8, then one would not observe enhanced solvent trapping. However, it seems likely that this is not the case. Since the bicycle rearrangement is a "push-pull" process,[12] bicycling in the bicyclic zwitterion case would be anticipated to be inhibited by the lesser availability of the negative charge, which is more heavily localized on oxygen (note calculations below).

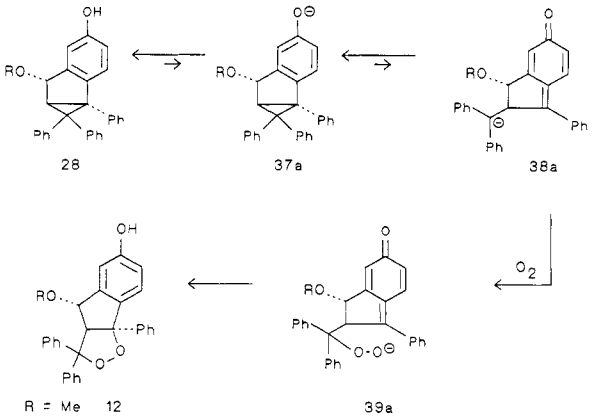
Finally, we have not yet discussed formation of the minor photoproduct, triphenylnaphthol **13**. This does derive from the bicycle rearrangement process. However, it is most relevant to a later section dealing with the photochemical reactivity of **2** in acetonitrile.

Mechanisms Accounting for Formation of the Triphenyl Peroxides 12 and 14. The observation of peroxidic photoproducts upon access to oxygen after photolysis is understood by reference to Scheme V, which depicts an ionic version of the mechanism. The phenolate **37a** reversibly three-ring opens to afford a small equilibrium concentration of carbanion **38a**. The latter then reacts with oxygen to afford hydroperoxy anion **39a**, which,

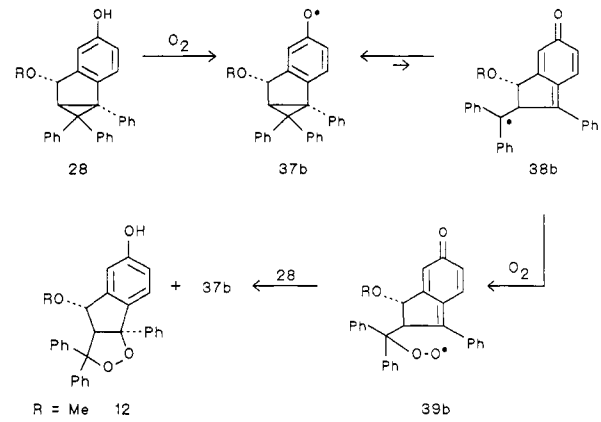
(11) (a) Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5137–5145. (b) Schuster, D. I.; Abraitys, V. Y. *J. Chem. Soc., Chem. Commun.* **1969**, 419–420.

(12) Zimmerman, H. E. *Chimia* **1982**, *36*, 423–428.

Scheme V. Mechanism A for Peroxide Formation



Scheme VI. Mechanism B for Peroxide Formation



on Michael addition, regenerates the aromatic ring and affords final product **12**.

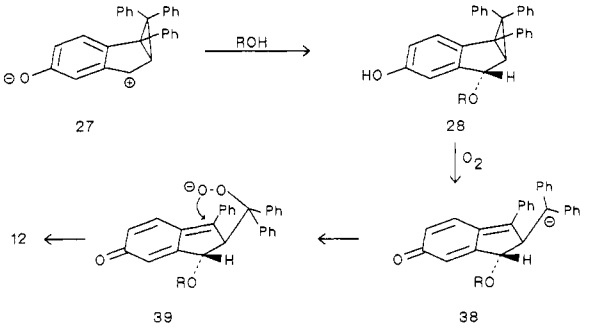
This mechanism requires that carbanion **38a** protonation occurs slowly prior to introduction of the oxygen at the end of the photolyses (vide supra) and reaction of this center with oxygen to be more rapid than protonation. The concentration of carbanion **38a** is expected to be low partially due to repression of ionization of the phenol **28**.

There is a free-radical counterpart of the mechanism that does not require slow protonation. In this, initial oxidation affords the phenoxy radical **37b**, which undergoes three-ring fission to afford the benzhydryl radical **38b**. Reaction of **38b** with oxygen leads to the peroxy radical **39b**, which can ring close. The phenoxy radical thus formed then abstracts a hydrogen from starting tricyclic triphenyl phenol **28** to give peroxide **12** and phenoxy radical **37b**, thereby continuing the chain process. This mechanism is presented in Scheme VI.

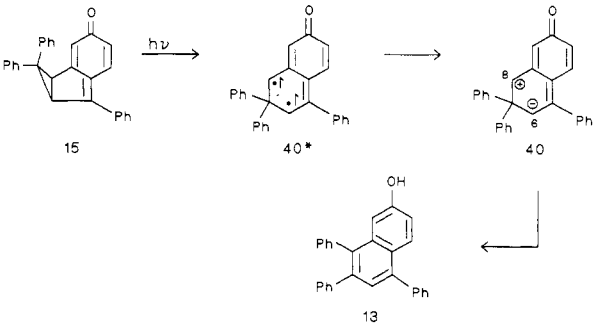
Interestingly, the two mechanisms are very closely related and differ only in whether heterolytic or homolytic processes are involved. The homolytic variation nicely rationalizes the role of oxygen in the three-ring opening of **28**. This is needed, since NMR monitoring (vide supra) revealed that the cyclopropane ring remains intact during irradiation and until oxygen is introduced.

A particularly interesting facet of the peroxide formation is the stereoselectivity of its formation. The entire stereochemistry is determined in the initial nucleophilic attack by solvent. Thus, it is seen in Scheme VII that the less hindered attack by methanol and isopropyl alcohol on zwitterion **27** is from the side opposite to the blocking *endo*-phenyl group of the three-ring. Ring opening to **38** followed by oxygenation and peroxide ring formation can be seen to lead specifically to the observed stereoisomer

Scheme VII. Stereochemical Aspects of Peroxide Formation

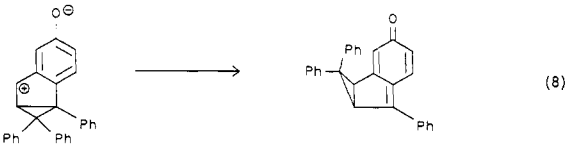


Scheme VIII. Photochemistry of Tricylic Quinone Methide 15



of peroxide **12**. Scheme VII has been written using the ionic version of the mechanism; however, the diradical counterpart exhibits precisely the same stereochemical outcome.

Mechanisms in the Photochemistry of Triphenylnaphthalenone 2 in Acetonitrile. In contrast to the photochemical behavior of triphenylnaphthalenone **2** in hydroxylic solvents, with no nucleophile present, zwitterion **27** clearly must find other ways to react. Equation 8 depicts the sigmatropic rearrangement of zwitterion **27** to give triphenyl quinone methide **15**. This process is precisely



(8)

analogous to the type A rearrangement so characteristic of monocyclic 2,5-cyclohexadienones.

The triphenyl quinone methide **15** is seen to undergo secondary photochemistry. As noted in the Results section, the same chemistry was observed by independent irradiation of the synthetic material (i.e., **15**) as well. The mechanism in Scheme VIII accounts for the formation of triphenylnaphthol **13**. We note that this process is the counterpart of the "type B" rearrangement that is common[13] in the photochemistry of bicyclo[3.1.0]hex-3-en-2-ones.

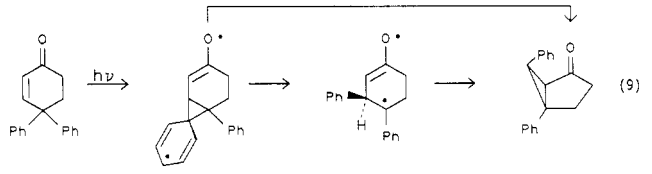
Diradicals provide a close energetic approach of T_1 and ground-state S_0 and thus triplet **40*** is shown as intersystem crossing to the ground-state zwitterionic counterpart **40**. An interesting point is the regioselectivity of phenyl migration in the the type B zwitterion **40**. A simplistic rationale for the observed direction of migration is

(13) Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895–4904.

based on a preference for migrations to electron-deficient centers rather than electron-rich ones. The resonance structure shown for zwitterion **40** is depicted for simplicity; however, a more heavily weighted structure would have the negative charge on the oxygen of an aromatic phenolate ring. In confirmation of this qualitative reasoning, MNDO calculations indicate a very large positive charge (+0.26) at C-8 along with a large negative charge (−0.45) on the oxygen. More sophisticated reasoning compares the two alternative bridged zwitterions **41** and **42**. Phenyl bridging to C-8 retains the aromatic phenolate resonance while bridging to C-6 does not.

41 42

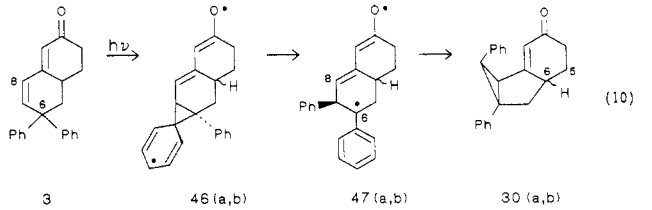
Consideration of the Photochemistry of Tetrahydronaphthalenone 3. The rearrangement of tetrahydronaphthalenone **3** proceeds in a manner similar to the well-studied[3] monocyclic 4,4-diphenylcyclohexenone. The primary reaction stereochemistry shows the same predilection for formation of the *trans*-diphenyl stereosiomers (note eq 5). Originally, this kinetic preference was ascribed, in the monocyclic enone photochemistry (e.g., note eq 9),



5 43 44 45 (9)

to a concerted process with inversion of configuration at the diphenyl-substituted carbon. An alternative rationale involved completion of migration with formation of the open diradical **44**, which closes preferentially to the *trans*-diphenyl stereoisomer. More recent studies[3j-l] have favored the latter mechanism. The preference for closure of the trans diradical is ascribed to the requirement that to form the cis product, the two phenyl groups must conformationally twist past one another at a stage where the C-4 phenyl is rotationally fixed by its delocalizing the odd electron at C-4. We use this version of the mechanism throughout the present discussion.

In the present instance (note eq 10) diradical **47** closes to the *trans*-diphenyl product by overlap of the p orbital lobes at carbons 6 and 8 behind the plane of the drawing.



3 46(a,b) 47(a,b) 30(a,b) (10)

The phenyl group at C-6 is fixed in the paper plane and the phenyl group at C-7 is above this plane in an incipient transoid conformation. Closing the three-membered ring to form cis product would require the C-7 phenyl to pass the flattened C-6 phenyl, and this proves to be just a minor process.

Also of interest is the stereoselectivity favoring migration of the phenyl group that is trans to the axial ring-junction

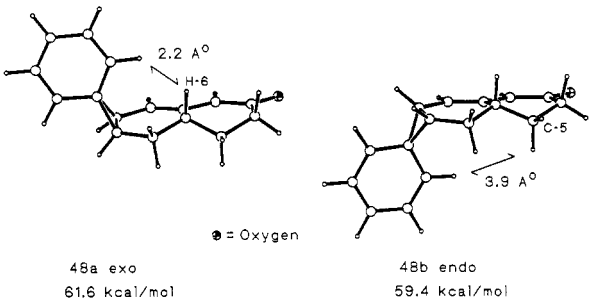
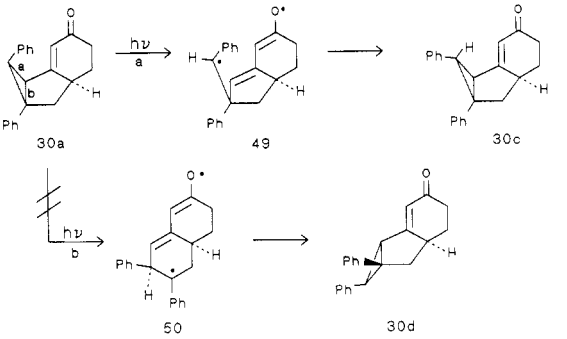


Figure 2. Stereochemistry and relative MNDO energies of two half-migrated species.

Scheme IX. Secondary Photochemistry of Tetrahydronaphthalene Photoproducts



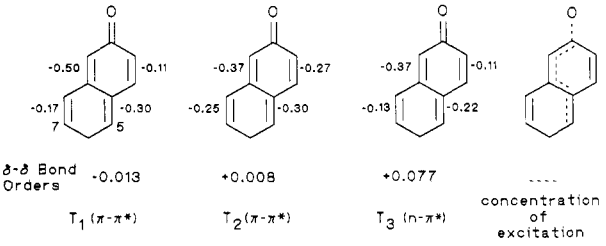
30a 49 30c 50 30d

hydrogen (i.e., C-6 of photoproduct **30**). Clearly, this stereochemistry, having C-5 (note structure **30**) endo on the five-membered ring is energetically less stable, although it is observed to be kinetically preferred. Base-catalyzed equilibration of the two epimers **30c** and **30d** (note eq 6) favored the C-5 exo methylene stereoisomer. The *trans*-diphenyl isomers should thermodynamically favor the exo stereochemistry even more. Nevertheless the C-5 endo methylene configuration is kinetically preferred. MNDO geometry-optimized computations were run on the half-migrated species **48a**, and **48b** lacking the nonmigrating phenyl group. Inspection of Figure 2 reveals the source of this selectivity. The migrating phenyl encounters severe steric hindrance from the axial hydrogen (H-6) at the bicyclic ring junction, but very little steric interaction with the C-5 endo methylene group. Ring fusion flattens out the ring, making hydrogen more sterically demanding than methylene. This stereochemical course has precedent in our earlier studies of monocyclic systems.

There is an interesting point resulting from higher conversion runs where two further stereoisomers, **30c** and **30d**, are observed. Both are *cis*-diphenyl stereoisomers of the trans isomers **30a** and **30b**. For the cis–trans isomerization reaction that leads to these photoproducts there are, a priori, two mechanisms. One involves fission of bond a and the other cleavage of bond b. Since reaction of **30a** was observed to afford only **30c**, the **30d** that is formed in the secondary photochemistry must arise from reaction of **30b**. This leads us to the conclusion that it is bond a rather than b which is broken in the isomerization process. The mechanism is depicted in Scheme IX. The distinction between these two mechanism, favoring out-of-plane bond scission, was established for the monocyclic counterparts with considerably greater difficulty many years ago.[16]

(14) Schuster, D. I. *Mol. Photochem.* **1969**, *1*, 415–432.
(15) Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5145–5152.

Scheme X. ΔP Values from MNDO-CI Calculations on the Naphthalenone System

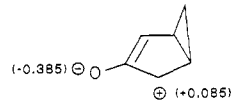


Significance of the Reaction Efficiencies and Triplet Rates. It is interesting to compare the efficiencies and rates of the presently studied triplet rearrangements along with the monocyclic counterparts. Note Table III.

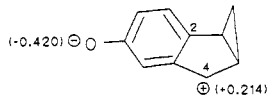
One of the most interesting aspects of the comparisons is the lower efficiency and slower rate exhibited in the type A rearrangement for the bicyclic "phenalogue" compared with the monocyclic 2,5-cyclohexadienones. This difference may arise from a steric effect resulting from two phenyl groups becoming cis on the three-membered ring in **27***.

The case of diphenylnaphthalenone **1**, which undergoes a phenyl migration rather than the type A process, results because of the high reactivity of this reaction. Thus, the quantum yield and rate for diphenylnaphthalenone **1** are approximately 2- and 10-fold greater, respectively, than the type A process of triphenylnaphthalenone counterpart **2**. Assuming that the type A rearrangment rate of diphenylnaphthalenone **1** is close to that of **2**, we can understand its inability to compete with phenyl migration.

Theoretical Aspects: Type A Zwitterion. One of the intriguing observations is the regioselectivity of nucleophilic attack of the solvent on the type A zwitterion **52**. This contrasts with the symmetry-determined lack of selectivity in the case of the monocyclic zwitterion **51**. As noted above, one might anticipate zwitterion **52** to have its positive charge more heavily concentrated at C-4 relative to C-2 on the basis of retaining aromaticity. Indeed, MNDO-CI calculations (note Experimental Section) show a greater positive charge at this center (note structures **51** and **52** below).



51



52

Furthermore, the positive charges in the phenylog **52** are seen to be larger than those for the monocyclic zwitterion **51** in accord with expectation based on aromaticity being retained by localization of the negative charge on oxygen and the phenolic ring.

Theoretical Aspects; Reactivity of Triphenylnaphthalenone 2. MNDO-CI computations suggest that T_1 and T_2 are $\pi-\pi^*$ triplets while T_3 is $n-\pi^*$. In analogy to our earlier efforts[17] on the monocyclic 2,5-cyclohexadienones, these computations reveal $\pi-\pi^*$ T_1 to be antibonding between carbons 5 and 7 contrasted with $n-\pi^*$ T_3, which is bonding. $\pi-\pi^*$ T_2 is very slightly bonding between these carbon atoms (see Scheme X).

A measure of bonding versus antibonding character and thus excitation distribution can be obtained from our ΔP indices.[18] If one has ground- and excited-state bond order matrices and subtracts these, the resulting ΔP matrix has elements that give the change in each bond order on going from ground to excited state. It has been noted[18] that negative ΔP elements correspond to sites of high energy while the few positive ΔP elements reveal the presence of low energy sites (see Experimental Section). Points of zero ΔP's are parts of the molecule not excited at all (e.g., the end of a long aliphatic chain of an alkyl aromatic). Scheme X summarizes this situation for the naphthalenone system and includes the $\delta-\delta$ excited-state bond orders. Thus, it is the $n-\pi^*$ triplet that seems responsible for the type A rearrangement in the phenylog **2** in analogy to the monocyclic situation.[2a]

Table IV. Ground State and Triplet Energies in the Bridging of Enones

compd	heats of formation, kcal/mol: S_0	vertical T_1	phenyl-bridged T_1	bridging[a] energy, kcal/mol
enone **5**	−0.3	64.3	55.1	−9.2 (9.5)
dienone **3**	7.8	54.9	59.4	4.5 (22.3)
trienone **4**	16.8	62.0	73.8	11.8 (31.4)

[a] Bridging energies were calculated from energy of phenyl-bridged − vertical triplet, in parentheses (phenyl-bridged − relaxed triplet).

Two further points are germane. The first is that the ΔP treatment reveals positive, albeit smaller, ΔP values for the π bonding connecting each pair of formal ground-state double bonds. The second is that for the naphthalenone system, from the ΔP treatment, we note that the excitation is largely concentrated along one linear dienone pathway in this cross-conjugated system as shown in Scheme X.

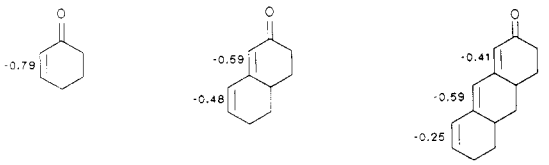
In order to ascertain the reliability of the MNDO calculations, simple ab initio computations were carried out on the naphthalenone. Again, the $n-\pi^*$ triplet was above T_1. However, here it was the second triplet. While differing in energies and exact placement of the $\pi-\pi^*$ versus $n-\pi^*$ triplets, the methods agreed in T_1 being $\pi-\pi^*$. Additionally, the molecular orbitals of corresponding eigenvalues were qualitatively similar. We can conclude that neither method is precise but may be used qualitatively. More details of the two methods are given in the Experimental Section.

Theoretical Aspects: Lack of Triplet Reactivity on Sensitization of Triphenylnaphthalenone 2. We have noted that the reactive excited state in naphthalenone **2** is an upper triplet. This contrasts with the simple 2,5-cyclohexadienones where the lowest energy and reacting triplet is $n-\pi^*$.[2a,17] On direct irradiation, S_1 has sufficient energy (72 kcal/mol) to afford an upper triplet. We note that even monocyclic $n-\pi^*$ triplets have a T_1 energy of 69 kcal/mol.[17] Furthermore, the absorption spectrum has the intensity and long wavelength anticipated for a $\pi-\pi^*$ configuration. Intersystem crossing is expected kinetically to favor formation of the $n-\pi^*$ triplet.[19] In contrast, sensitization seems likely to afford the lower energy $\pi-\pi^*$ excited state whose bond order is inappropriate for initiation of the type A rearrangement.

Theoretical Aspects: Molecular Orbital Considerations in Phenyl Migration Reactions of Linear Enones. It was of some interest to inspect the phenyl migration reaction of linear enones **3**, **4**, and **5**. To this end,

(16) Zimmerman, H. E.; Hancock, K. G.; Licke, G. *J. Am. Chem. Soc.* **1968**, *90*, 4892–4911.
(17) Zimmerman, H. E.; Binkley, R. W.; McCullough, J. J.; Zimmerman, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 6589–6595.
(18) (a) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *43*, 1775–1803. (b) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T. *J. Chem. Soc., Chem. Commun.* **1978**, 228–230.
(19) El-Sayed, M. A. *J. Chem. Phys.* **1964**, *41*, 2462.

Scheme XI. ΔP Values from MNDO-CI Calculations on Polycyclic Ketones



geometry-optimized MNDO-CI computations were run on the S_0 states of each of the reactant enones and on the T_1 states for the phenyl-bridged diradicals **43**, **46**, and **53**. As before, the nonmigrating phenyl groups were omitted. This provided vertical triplet excited-state energies for the reactants and also the energies of the phenyl-bridged species relative to both an optimized S_0 and a vertical T_1 reactant. From this information, one can obtain an energy of the phenyl-bridging step (i.e., T_1 of bridged diradical – vertical T_1 of reactant). These values are given in Table IV.

Since relaxation of the triplets can be a factor, we performed similar calculations on the parent systems without the phenyl groups to determine the energies of the relaxed (i.e., geometry optimized) triplets. Interestingly, the relaxation energies are relatively constant throughout the series. Table IV includes bridging energies starting with the relaxed T_1's.

As can be seen in Table IV, the energies required for phenyl bridging to the terminus of the enone system increases in proceeding from monoenone **5** to bicyclic linear dienone **3**, to tricyclic linear trienone **4**. Since the quantum yield for linear dienone **3** is higher (ϕ = 0.098) than that for monoenone **5** (ϕ = 0.043[4d]), there must be a higher rate of radiationless decay for monoenone **5**. With a more compressed π system and the promoted electron thus closer to the oxygen, one would anticipate enhanced spin-orbit coupling and intersystem crossing to ground state to be more rapid for enone **5**. The total lack of triplet reactivity of tricyclic linear trienone **4** would derive from an excessive energy of bridging, as in Table IV, which is not sufficiently compensated by the anticipated greater triplet lifetime. Thus, in this series, two factors appear to compete—namely, the rate of phenyl migration versus the rate of radiationless decay.

In summary, the calculations suggest an increasing difficulty of disturbing the phenyl aromaticity as the triplet enone chromophore is extended and becomes progressively lower in energy. This is reasonable, if the phenyl group is largely unexcited in the triplet of reactant.

One further factor in considering relative reactivity is the distribution of excitation energy in the vertical triplet of the polyenones. Scheme XI gives the ΔP values for the three enone systems. We note that the ΔP value at the enone terminus remote from the carbonyl becomes progressively less negative as the enone chromophore is extended, and one would anticipate diminished reactivity.

Conclusion. This research has revealed that the type A rearrangement of monocyclic 2,5-cyclohexadienones and the type B process of bicyclo[3.1.0]hexenones have counterparts in polycyclic systems. Similarly, polycyclic enone rearrangements have been found to follow a phenyl migration mechanism formally similar to that of monocyclic enones. In this research evidence has been adduced for two types of polycyclic zwitterions, one a type A and the other a type B. In the case of the type A zwitterions, these rearrange slowly enough to permit facile nucleophilic trapping with hydroxylic solvents. This new photochemistry has been found to correlate nicely with theoretical considerations.

Experimental Section[20]

4,4-Diphenyl-2-(hydroxymethylene)cyclohex-5-en-1-one (6). A modification of the method of Woodward[23] was employed. To 2.21 g (55.0 mmol) of freshly prepared sodium methoxide in 150 mL of dry benzene was added 9.53 mL (122 mmol) of ethyl formate. The solution was then cooled to 0 °C and stirred for 15 min. A solution of 5.0 g (20.2 mmol) of 4,4-diphenylcyclohex-2-en-1-one[25] in 25 mL of dry benzene was added over 30 min. The solution was then stirred at room temperature for 24 h. The resulting yellow gelatinous mixture was acidified with 10% hydrochloric acid. The aqueous layer was ether extracted and the combined organic layers were shaken with ice-cold 2% potassium hydroxide. The basic layer was washed with ether, then cooled to 0 °C, and carefully acidified with concentrated hydrochloric acid. Concentration in vacuo yielded 4.90 g of a light tan solid, mp 113–115 °C, which was recrystallized from methylene chloride in hexane to yield 4.72 g (84.6%) of 4,4-diphenyl-2-(hydroxymethylene)cyclohex-5-en-1-one as a light tan solid, mp 118–118.5 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.60 (br, 1 H, OH), 7.2–7.0 (m, 12 H, Ar, vinyl), 6.26 (d, J = 10.0 Hz, 1 H, α-vinyl), 3.14 (s, 2 H, CH_2); IR ($CHCl_3$) 3500, 3080, 3050, 3000, 2980, 1625, 1610, 1560, 1490, 1442, 1420, 1250, 1190, 1100 cm^{-1}; MS m/e 276.1130 (calcd for $C_{19}H_{16}O_2$ m/e 276.1150).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.84. Found: C, 82.09; H, 6.13.

6,6-Diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (3). A mixture of 10.5 g (38.2 mmol) of 4,4-diphenyl-2-(hydroxymethylene)cyclohex-5-en-1-one and 4.5 mL (48.5 mmol) of freshly

(20) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratores, Inc., Knoxville, TN. All reactions were performed under an atmosphere of dry nitrogen. Anhydrous magnesium sulfate was used as the drying agent. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns permitting monitoring by a hand-held UV lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector an LDC 6000-psi minipump, using a 0.46 × 25 cm polished stainless steel column packed with 3–7-μm porous silica beads.[21] Preparative HPLC employed a 0.95 × 50 cm polished stainless steel column packed with 8–12-μm porous silica gel beads.[21] Neutral workup refers to quenching the reaction with water, ether extraction, washing the organic layer with water and brine, drying, filtering, and concentration in vacuo. Acidic workup included a 2 M aqueous hydrochloric acid wash after ether extraction. Basic workup included a saturated aqueous sodium bicarbonate wash after ether extraction. Basic acidic workup used sequential base and acid washings after ether extraction. Exploratory photolyses were carried out with a Hanovia 450-medium-pressure mercury lamp equipped with a Pyrex filter and cooled with a recirculating filter solution. Filter solution A employed was 0.01 M sodium metavanadate in 0.10 M sodium hydroxide (λ > 340 nm). Filter solution B employed was 0.10 M sodium metavanadate in 0.10 M sodium hydroxide (λ > 370 nm). All photolysis solutions were thoroughly purged with purified nitrogen[22] both prior to and during photolysis. Acetonitrile and benzene were distilled from calcium hydride. Dichloromethane was purified by distillation from phosphorous pentoxide. Tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by storage over potassium hydroxide, followed by successive distillation, under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium–benzophenone ketyl. Hexane used for HPLC was washed with nitric acid and sulfuric acid (1:1), water, aqueous saturated sodium bicarbonate, and brine, dried over calcium chloride, passed through alumina, and distilled from calcium hydride. Photograde benzene was purified by washing with saturated aqueous potassium permanganate and concentrated sulfuric acid, water, sulfuric acid until no discoloration, saturated aqueous sodium bicarbonate, and brine, followed by drying over anhydrous calcium chloride, then reflux, and distillation from calcium hydride.

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distilled methyl vinyl ketone in 350 mL of *tert*-butyl alcohol was cooled on an ice bath. A solution of 471 mg (4.19 mmol) of potassium *tert*-butoxide in 30 mL of *tert*-butyl alcohol was added over 5 min. Stirring was then continued at room temperature for 18 h. Acidic workup[20] yielded 13.4 g of a yellow oil. This Michael addition product was cyclized without further purification as follows. The above oil was taken up in 350 mL of dioxane and cooled on an ice bath. A solution of 10.0 g (178 mmol) of potassium hydroxide in 100 mL of water was added over 10 min. The solution was then stirred at room temperature for 5 h. Acidic and basic workup[20] yielded 10.1 g of a yellow oil, which was chromatographed on a 4.0 × 30 cm silica gel column: fraction 1, 0.75 L of 2% ether in hexane, nil; 2, 0.75 L of 5% ether in hexane, nil; 3, 3.5 L of 10% ether in hexane, 6.21 g of a white solid, mp 107–110 °C. Recrystallization from methylene chloride in hexane gave 5.89 g (51.4%) of 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (**3**) as a white solid, mp 112–113 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20–7.30 (m, 10 H, Ar), 6.63 (d, J = 9.7 Hz, 1 H, δ-vinyl), 6.44 (d, J = 9.7 Hz, 1 H, γ-vinyl), 5.87 (s, 1 H, α-vinyl), 2.0–2.6 (m, 7 H, aliph CH); IR ($CHCl_3$) 3010, 3000, 2925, 2860, 1645, 1615, 1590, 1500, 1450, 1330, 1310, 710, 690 cm^{-1}; UV (95% EtOH) λ_{max} 288 (ε 25,400); MS m/e 300.1514 (calcd for $C_{22}H_{20}O$ m/e 300.1514).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.97; H, 6.71. Found: C, 87.78; H, 6.93.

6,6-Diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2-(3*H*)-naphthalenone. The method of Reich[24] was employed. To a solution of 0.55 mL (3.96 mmol) of diisopropylamine in 20 mL of dry tetrahydrofuran at −78 °C was added dropwise 2.64 mL (3.96 mmol) of a 1.6 M *n*-butyllithium solution in hexane. After being stirred for 30 min, a solution of 1.00 g (3.30 mmol) of 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone in 10 mL of tetrahydrofuran was added dropwise over 10 min, and the resulting solution was stirred at −78 °C for 30 min. To a solution of 0.62 g (1.98 mmol) of diphenyl diselenide in 5.0 mL of tetrahydrofuran was added 0.10 mL (1.98 mmol) of bromine. After being stirred for 2 min, this solution was added rapidly to the enolate with complete decoloration. After 2 min at −78 °C, the solution was poured into ether/10% hydrochloric acid (70 mL/50 mL). Acidic and basic workup[20] gave 1.52 g of a yellow oil, which was chromatographed on a 2.5 × 40 cm silica gel column: fraction 1, 1 L of 2% ether in hexane, diphenyl diselenide; 2, 1.5 L of 8% ether in hexane, nil; 3, 1 L of 8% ether in hexane, 205 mg (13.6%) of a diastereomer mixture of selenide; 4, 1 L of 8% ether in hexane, 940 mg (62.4%) of a yellow oil. Recrystallization from methylene chloride in hexane gave 866 mg (57.5%) of 6,6-diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone as a white solid, mp 120–121 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.30 (m, 15 H, Ar), 6.64 (d, J = 9.6 Hz, 1 H, δ-vinyl), 6.44 (d, J = 9.7 Hz, 1 H, γ-vinyl), 5.85 (s, 1 H, α-vinyl), 4.04 (br, 1 H, C*H*SePh), 2.9 (m, 1 H, CH), 2.0–2.5 (m, 5 H, aliph CH); IR ($CHCl_3$) 3020, 3000, 2910, 1650, 1620, 1500, 1490, 1450, 1390, 1360, 1320, 1260, 1035, 920, 890, 700 cm^{-1}; MS m/e 456.0984 (calcd for $C_{28}H_{24}SeO$ m/e 456.0971).

Anal. Calcd for $C_{28}H_{24}SeO$: C, 73.84; H, 5.31. Found: C, 73.51; H, 5.29.

1,2-(4′-Hydroxybenzo)-5,5-diphenylcyclohex-3-ene (7). To a 0 °C solution of 890 mg (1.96 mmol) of 6,6-diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone and 3.32 mL (3.92 mmol) of pyridine in 15 mL of methylene chloride was added a solution of 598 mg (5.20 mmol) of hydrogen peroxide in 1.0 mL of water over a period of 3 min. The solution was then stirred at room temperature for 2 h. Acidic workup[20] gave 524 mg of a yellow foam, which was chromatographed on a 2.5 × 40 cm silica gel column: fraction 1, 0.5 L of 5% ether in hexane, nil; 2, 2 L of 6% ether in hexane, nil; 3, 1 L of 6% ether in hexane, 401 mg (68.6%) of phenol **7** as a pale yellow oil. This was rechromatographed on a 2.5 × 20 cm silica gel column with the top 5 cm consisting of (1:1) silica gel/Norite. Elution with 1.5 L of 20% ether in hexane gave 320 mg (54.7%) of 1,2-(4′-hydroxybenzo)-5,5-diphenylcyclohex-3-ene as a white powder, mp 127–128 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20–7.30 (m, 10 H, Ar), 7.02 (d, J = 7.9 Hz, 1 H, meta H), 6.62 (dd, J = 7.9, 2.6 Hz, 1 H, ortho H), 6.52 (m, 3 H, ortho H, vinyl), 4.59 (s, br, 1 H, OH), 3.38 (s, 2 H, CH_2); IR ($CHCl_3$) 3580, 3300, 3030, 3010, 3000, 2940, 2920, 2865, 1605, 1575, 1490, 1445, 1385, 1270, 1140, 1030, 950, 870, 690 cm^{-1}; MS m/e 298.1357 (calcd for $C_{22}H_{18}O$ m/e 298.1358).

The spectral data for 1,2-(4′-acetoxybenzo)-5,5-diphenylcyclohex-3-ene were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20–7.00 (m, 11 H, Ar), 6.80 (dd, J = 8.0, 2.4 Hz, 1 H, ortho H), 6.70 (d, J = 2.4 Hz, 1 H, ortho H), 6.47 (m, 2 H, vinyl), 3.37 (s, 2 H, CH_2), 2.19 (s, 3 H, CH_3); IR ($CHCl_3$) 3058, 3029, 2976, 2957, 2931, 2897, 2859, 1760, 1749, 1491, 1445, 1370, 1218, 1193, 1144, 1013, 919, 912, 690 cm^{-1}; MS m/e 340.1463 (calcd for $C_{24}H_{20}O_2$ m/e 340.1458); mp 145–146 °C.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.72; H, 5.98.

6,6-Diphenyl-2(6*H*)-naphthalenone (1). To a mixture of 100 mg (0.34 mmol) of 1,2-(4′-hydroxybenzo)-5,5-diphenylcyclohex-3-ene and 0.18 mL (2.44 mmol) of triethylamine in 5.0 mL of ether was added 100 mg (0.45 mmol) of 3,4-dichloro-5,6-dicyano-1,4-benzoquinone in 40 mL of ether. After being stirred for 24 h at room temperature, the green solution was filtered through a plug of glass wool to remove the hydroquinone and then through a pad of Celite/Norite (10:1). Removal of solvent in vacuo gave 96.7 mg (97.1%) of a yellow oil, which was crystallized from ether at −20 °C to give 53.9 mg (54.2%) of 6,6-diphenyl-2-(6*H*)-naphthalenone (**1**) as golden yellow crystals, mp 108–109 °C.

The spectral data were the following: ^{1}H NMR (C_6D_6, 270 MHz) δ 7.20 (m, 12 H, Ar, vinyl), 6.62 (m, 2 H, vinyl), 6.43 (dd, J = 9.7, 1.4 Hz, 1 H, vinyl), 6.29 (s, 1 H, vinyl); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 187.7, 149.9, 142.4, 140.8, 139.0, 138.8, 129.9, 129.8, 128.9, 127.9, 124.4, 124.3, 55.7; IR ($CHCl_3$) 3020, 1625, 1560, 1490, 1445, 690 cm^{-1}; UV (95% EtOH) λ_{max} 214 (ε 22 500), 232 (25 270), 326 (19 860), tails to 400 nm; UV (cyclohexane) λ_{max} 216 (18 950), 236 (23 240), 316 (27 800), tails to >380; MS m/e 296.1201 (calcd for $C_{22}H_{16}O$ m/e 296.1206).

Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.25; H, 5.29.

1,2-(4′-Hydroxybenzo)-5,5,6-triphenylcyclohex-3-ene (8). To a mixture of 190 mg (0.51 mmol) of 1,2-(4′-hydroxybenzo)-5,5-diphenylcyclohex-3-ene and 0.34 mL (4.64 mmol) of triethylamine in 5.0 mL of ether was added 200 mg (0.88 mmol) of 3,4-dichloro-5,6-dicyano-1,4-benzoquinone in 80 mL of ether. After being stirred for 24 h at room temperature, the yellow solution was filtered through a plug of glass wool to remove the hydroquinone. Removal of solvent in vacuo yielded 210 mg of a yellow oil, which was used without further purification. To a 0 °C solution of 0.82 mL (7.89 mmol) of bromobenzene in 2.0 mL of ether was added 5.3 mL of 1.5 M *n*-butyllithium. After stirring for 1 h, 496 mg (2.66 mmol) of cuprous iodide was added followed by stirring for 30 min. A solution of 210 mg of the above ketone in 10 mL of tetrahydrofuran was then added. The solution was then stirred at room temperature for 20 h. Acidic and basic workup[20] gave 320 mg of a brown oil, which was chromatographed on a 4 × 30 cm silica gel column: fraction 1, 1 L of 5% ether in hexane, bromobenzene; 2, 1 L of 15% ether in hexane, nil; 3, 1.5 L of 20% ether in hexane, 195 mg of phenol **8** as a pale yellow oil, which was crystallized from methylene chloride in hexane to give 180 mg (75.4%) of 1,2-(4′-hydroxybenzo)-5,5,6-triphenylcyclohex-3-ene as a clear solid, mp 230–232 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.30–6.50 (m, 20 H, Ar, vinyl), 4.73 (s, 1 H, C*H*Ph), 4.56 (s, 1 H, OH); IR ($CHCl_3$) 3595, 3320 (br), 3070, 3050, 1616, 1603, 1574, 1493, 1444, 1301, 1277, 1177, 1148, 1118, 1078, 1033, 953, 942, 869 cm^{-1}; MS m/e 374.1671 (calcd for $C_{28}H_{22}O$ m/e 374.1670).

Anal. Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.71; H, 6.04.

5,6,6-Triphenyl-2(6*H*)-naphthalenone (2). To a mixture of 180 mg (0.48 mmol) of 1,2-(4′-hydroxybenzo)-5,5,6-triphenylcyclohex-3-ene and 0.32 mL (4.39 mmol) of triethylamine in 5.0 mL of ether was added 180 mg (0.79 mmol) of 3,4-dichloro-5,6-dicyano-1,4-benzoquinone in 70 mL of ether. After being stirred for 24 h at room temperature, the yellow solution was filtered through a plug of glass wool to remove the hydroquinone. Removal of solvent in vacuo yielded 191 mg of a yellow oil, which was chromatographed on a 4.0 × 20 cm neutral alumina column: fraction 1, 1 L of 50% ether in hexane, nil; 2, 2 L of 60% ether

in hexane, 159 mg of a yellow oil. Crystallization from methylene chloride in hexane at −20 °C gave 135 mg (75.5%) of 5,6,6-triphenyl-2(6*H*)-naphthalenone as golden yellow crystals, mp 171–172 °C.

The spectra data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.30 (m, 11 H, Ar, vinyl), 7.06 (t, J = 7.3 Hz, 2 H, Ar), 6.89 (d, J = 9.8 Hz, 1 H, Ar), 6.62 (d, J = 7.3 Hz, 2 H, Ar), 6.55 (d, J = 9.7 Hz, 1 H, vinyl), 6.46 (d, J = 9.7 Hz, 1 H, vinyl), 6.32 (m, 2 H, vinyl); IR ($CHCl_3$) 3000, 1625, 1595, 1540, 1480, 1440, 1230, 1200, 790, 720, 690 cm^{-1}; UV (95% EtOH) λ_{max} 214 (ε 24 050), 240 (25 140), 340 (19 476), tails to >430 nm; UV (cyclohexane) λ_{max} 218 (ε 22 190), 240 (26 870), 326 (25 790), tails to >390 nm; MS m/e 372.1514 (calcd for $C_{28}H_{20}O$ m/e 372.1517).

Anal. Calcd for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.15; H, 5.48.

Ethyl β-(3-Methoxyphenyl)-β-hydroxypropionate (18). A modification of the method of Floyd and Allen[26] was employed. To a slurry of 2.97 g (45.5 mmol) of powdered zinc in 2.0 mL of dry benzene was added 3.0 mL of a solution of 4.10 mL (36.7 mmol) of ethyl bromoacetate and 4.46 mL (36.7 mmol) of *m*-anisaldehyde in 20 mL of dry benzene. After the ensuing mixture was brought to a gentle reflux, the remainder of the solution was added over a period of 40 min. The gentle reflux was continued for 3 h, followed by stirring at room temperature for 5 h. The slurry was poured into 50 mL of 1 N sulfuric acid and stirred for 10 min. Basic workup[20] yielded 6.6 g of a light yellow oil, which was chromatographed on a 4 × 20 cm silica gel column: fraction 1, 0.75 L of 5% ether in hexane, 210 mg of *m*-anisaldehyde; 2, 1 L of 10% ether in hexane, nil; 3, 1 L of 15% ether in hexane, 6.23 g (75.7%) of ethyl β-(3-methoxyphenyl)-β-hydroxypropionate as a clear oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.26 (t, J = 6.1 Hz, 1 H, meta H), 6.96 (m, 2 H, Ar), 6.80 (m, 1 H, Ar), 5.11 (m, 1 H, C*H*OH), 4.18 (q, J = 7.1 Hz, 2 H, CH_2CH_3), 3.81 (s, 3 H, OCH_3), 3.30 (d, J = 3.5 Hz, 1 H, CH_2), 2.73 (d, J = 3.5 Hz, 1 H, CH_2), 2.70 (s, 1 H, OH), 1.27 (t, J = 7.1 Hz, 3 H, CH_2CH_3); IR ($CHCl_3$) 3599, 3518, 3018, 2985, 2963, 2940, 2908, 2837, 1721, 1601, 1588, 1489, 1465, 1456, 1436, 1402, 1373, 1350, 1320, 1295, 1113, 1095, 997, 881, 871, 856 cm^{-1}; MS m/e 224.1049 (calcd for $C_{12}H_{16}O_4$ m/e 224.1042).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.28; H, 7.19. Found: C, 63.85; H, 7.21.

β-(3-Methoxyphenyl)-β-hydroxypropionic Acid (19). To a solution of 4.10 g (19.7 mmol) of ethyl β-(3-methoxyphenyl)-β-hydroxypropionate in 70 mL of methanol was added 3.28 g (58.6 mmol) of potassium hydroxide in 15 mL of water. The solution was allowed to stand with occasional shaking for 16 h. The majority of the solvent was removed in vacuo and the resulting oil was carefully acidified with concentrated hydrochloric acid. Acidic workup[20] yielded 3.28 g of an oil, which crystallized from ether in hexane at −20 °C to give 2.98 g (77.2%) of β-(3-methoxyphenyl)-β-hydroxypropionic acid as a white solid, mp 61–62 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.24 (t, J = 8.1 Hz, 1 H, meta H), 7.00–6.80 (m, 3 H, Ar), 5.93 (s, br, 2 H, OH, CO_2H), 5.10 (dd, J = 7.3, 8.5 Hz, 1 H, C*H*OH), 3.78 (s, 3 H, OCH_3), 2.8–2.7 (m, 2 H, CH_2); IR ($CHCl_3$) 3495 (br), 3009, 1710, 1601, 1489, 1465, 1435, 1407, 1312, 1291, 1265, 1231, 1219, 1191, 1042, 735, 700 cm^{-1}; MS m/e 196.0742 (calcd for $C_{10}H_{12}O_4$ m/e 196.0736).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.23; H, 6.51.

5-Methoxyindenone (20). To a solution of 6.63 mL (92.2 mmol) of thionyl chloride and 0.14 mL (1.06 mmol) of dimethylformamide in 20 mL of methylene chloride was added 7.50 g (38.2 mmol) of β-(3-methoxyphenyl)-β-hydroxypropionic acid in 15 mL of methylene chloride over 30 min. After being stirred for 2 h at room temperature, the solution was refluxed for 1 h and cooled and the solvent was removed in vacuo to yield β-(3-methoxyphenyl)-β-chloropropionic acid chloride as a yellow-orange oil. The resulting oil was taken up in 150 mL of methylene chloride and stirred at room temperature. To this was added 10.38 g (43.2 mmol) of aluminum chloride in small portions with bubbling. After the addition was complete, the solution was stirred for 10 min and then poured into 100 mL of ice. Neutral workup[20] yielded a green oil of the β-chloro-3-methoxyindanone. The oil was taken up in 100 mL of chloroform, to which was added 36 mL (48.6 mmol) of triethylamine. After being stirred for 2.5 h, the solution was cooled in an ice bath and neutralized with 5 N hydrochloric acid. Neutral workup[20] yielded 2.5 g of a yellow oil, which was chromatographed on a 4 × 15 cm neutral alumina column: fraction 1, 1 L of 35% ether in hexane, nil; 2, 1.5 L of 35% ether in hexane, 1.63 g (26.7%) of 5-methoxyindenone, which solidified at −20 °C to give a yellow solid, mp 24–25 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.44 (d, J = 5.9 Hz, 1 H, β-vinyl), 7.39 (d, J = 7.3 Hz, 1 H, meta H), 6.64 (s, 1 H, ortho H), 6.60 (d, J = 7.2 Hz, 1 H, ortho H), 5.90 (d, J = 5.9 Hz, 1 H, α-vinyl), 3.86 (s, 3 H, OCH_3); IR ($CHCl_3$) 3025, 3011, 2967, 1707, 1614, 1597, 1547, 1467, 1361, 1348, 1314, 1285, 1251, 1231, 1193, 1188, 1143, 1105, 1095, 1065, 1058, 1021, 908, 875, 800, 700 cm^{-1}; MS m/e 160.0524 (calcd for $C_{10}H_8O_2$ m/e 160.0537).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.36; H, 4.92.

1,2-(4′-Methoxybenzo)-6,6-diphenylbicyclo[3.1.0]hexan-3-one (21). To a solution of 1.63 g (10.19 mmol) of 5-methoxyindenone in 20 mL of benzene and 20 mL of chloroform was added over 2 h via syringe pump a solution of 2.22 g (11.5 mmol) of diphenyldiazomethane in 15 mL of benzene. A gentle reflux was maintained during the addition. After the addition was complete, the solution was refluxed for 3 h and then stirred at room temperature for 18 h. Neutral workup[20] yielded 3.20 g of a purple oil, which was chromatographed on a 4 × 35 cm silica gel column; fraction 1, 1 L of 2% ether in hexane, diphenyldiazomethane; 2, 0.5 L of 5% ether in hexane, nil; 3, 1 L of 10% ether in hexane, nil; 2.5 L of 10% ether in hexane, 1.21 g of a clear oil, which was recrystallized from methylene chloride in hexane to give 0.968 g (29.1%) of 1,2-(4′-methoxybenzo)-6,6-diphenylbicyclo[3.1.0]-hexan-3-one as clear crystals, mp 162–163 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.00–7.30 (m, 12 H, Ar), 6.58 (dd, J = 8.4, 2.1 Hz, 1 H, ortho H), 3.55 (s, 3 H, OCH_3), 3.55 (d, J = 5.1 Hz, 1 H, cyclopropyl), 3.13 (d, J = 5.1 Hz, 1 H, cyclopropyl); IR ($CHCl_3$) 3010, 1692, 1611, 1601, 1493, 1447, 1338, 1290, 1245, 1219, 1213, 1147, 1120, 1107, 1072, 1029 cm^{-1}; MS m/e 326.1315 (calcd for $C_{23}H_{18}O_2$ m/e 326.1307).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.96; H, 5.92.

1,2-(4′-Hydroxybenzo)-6,6-diphenyl[3.1.0]hexan-5-one (22). a mixture of 500 mg (1.54 mmol) of 1,2-(4′-methoxybenzo)-6,6-diphenylbicyclo[3.1.0]hexan-3-one and 2.0 g (20.8 mmol) of lithium bromide in 6.0 mL of dimethylformamide was refluxed for 36 h. The warm brown solution was poured into water and neutral workup[20] yielded 510 mg of a light brown oil, which was chromatographed on a 2.5 × 40 cm silica gel column; fraction 1, 1.5 L of 15% ether in hexane, nil; 2, 1.5 L of 20% ether in hexane, 450 mg of a white solid, mp 210–215 °C, which was recrystallized from methylene chloride in hexane to yield 407 mg (84.7%) of 1,2-(4′-hydroxybenzo)-6,6-diphenylbicyclo[3.1.0]hexan-3-one as a white powder, mp 218–219 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.30–6.95 (m, 12 H, Ar), 6.49 (dd, J = 8.2, 2.2 Hz, 1 H, ortho H), 5.55 (s, br, 1 H, OH), 3.55 (d, J = 5.1 Hz, 1 H, cyclopropyl), 3.13 (d, J = 5.1 Hz, 1 H, cyclopropyl); IR ($CHCl_3$) 3590, 3270 (br), 3022, 1694, 1602, 1495, 1465, 1450, 1300, 1205, 1120 cm^{-1}; MS m/e 312.1150 (calcd for $C_{22}H_{16}O_2$ m/e 312.1147).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.60; H, 5.16. Found: C, 84.57; H, 5.43.

***endo*-1,2-(4′-Hydroxybenzo)-5,6,6-triphenylbicyclo-[3.1.0]hexan-5-ol (23).** To a 0 °C solution of 0.21 mL (1.6 mmol) of bromobenzene in 3.0 mL of ether was added 1.06 mL (1.6 mmol) of 1.6 M *n*-butyllithium. After being stirred for 1.5 h, a solution of 125 mg (0.40 mmol) of 1,2-(4′-hydroxybenzo)-6,6-diphenylbicyclo[3.1.0]hexan-5-one in 3.0 mL of tetrahydrofuran was added, followed by stirring at room temperature for 24 h. Two runs on this scale were combined and neutral workup[20] yielded 325 mg of a brown oil, which was crystallized from methylene chloride in hexane to yield 181 mg (57.9%) of a white solid. The mother

(26) Floyd, M. B.; Allen, G. R. *J. Org. Chem.* **1970**, *35*, 2647–2653.

liquor was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting twice with 40% ether in hexane. Band 2 contained 45 mg of a white solid. The combined yield of *endo*-1,2-(4′-hydroxybenzo)-5,6,6-triphenylbicyclo[3.1.0]hexan-5-ol was 226 mg (72.1%) as a white solid, mp 212–213 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.00–7.40 (m, 15 H, Ar), 7.01 (d, J = 2.0 Hz, 1 H, ortho H), 6.66 (d, J = 8.3 Hz, 1 H, meta H), 6.49 (dd, J = 8.1, 2.3 Hz, 1 H, ortho H), 4.68 (s, 1 H, OH), 3.10 (d, J = 6.4 Hz, 1 H, cyclopropyl), 2.86 (d, J = 6.4 Hz, 1 H, cyclopropyl); IR ($CHCl_3$) 3592, 3290 (br), 3060, 1609, 1492, 1446, 1219, 1140 cm^{-1}; MS m/e 390.1620 (calcd for $C_{28}H_{20}O_2$ m/e 390.1628).

Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.58; H, 5.19. Found: C, 86.60; H, 5.73.

***endo*-1,2-(4′-(*tert*-Butyldimethylsilyl)benzo)-5,6,6-triphenylbicyclo[3.1.0]hexan-5-ol (24).** To a 0 °C suspension of 232 mg (4.64 mmol) of sodium hydride (washed twice with tetrahydrofuran) in 2.0 mL of tetrahydrofuran was added 181 mg (0.46 mmol) of *endo*-1,2-(4′-hydroxybenzo)-5,6,6-triphenylbicyclo[3.1.0]hexan-5-ol in 2.0 mL of tetrahydrofuran followed by stirring for 30 min. A solution of 148 mg (0.93 mmol) of *tert*-butyldimethylsilyl chloride in 2.0 mL of tetrahydrofuran was added, followed by stirring at room temperature for 18 h. Neutral workup[20] gave 230 mg of a clear oil, which was crystallized from methylene chloride in hexane to give 185 mg (79.1%) of *endo*-1,2-(4′-(*tert*-butyldimethylsilyl)benzo)-5,6,6-triphenylbicyclo-[3.1.0]hexan-5-ol (**24**) as a clear solid, mp 149–150 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.00–7.40 (m, 16 H, Ar), 6.64 (d, J = 8.2 Hz, 1 H,meta H), 6.52 (dd, J = 8.2, 2.2 Hz, 1 H, ortho H), 3.08 (d, J = 6.4 Hz, 1 H, cyclopropyl), 2.84 (d, J = 6.4 Hz, 1 H, cyclopropyl), 1.02 (s, 9 H, $C(CH_3)_3$), 0.25 (s, 3 H, CH_3), 0.23 (s, 3 H, CH_3); IR ($CHCl_3$) 3566 [B3009, 2956, 2930, 2859, 1606, 1492, 1472, 1446, 1302, 1290, 1275, 1253, 1217, 1210, 1166, 1147, 1109, 976, 963, 876, 860, 840 cm^{-1}; MS m/e 504.2484 (calcd for $C_{34}H_{36}SiO_2$ m/e 504.2489).

Anal. Calcd for $C_{34}H_{36}SiO_2$: C, 80.91; H, 7.19. Found: C, 80.78; H, 7.37.

***endo*-1,2-(4′-(*tert*-Butyldimethylsilyl)benzo)-5,6,6-triphenylbicyclo[3.1.0]hex-5-yl Acetate (25).** To a solution of 20 mg (0.04 mmol) of *endo*-1,2-(4′-(*tert*-butyldimethylsilyl)-benzo)-5,6,6-triphenylbicyclo[3.1.0]-hexan-5-ol in 3.0 mL of tetrahydrofuran at 0 °C was added 1.5 mL of 1.0 M *sec*-butyllithium, and the solution was stirred for 1 h. Upon addition of 1.5 mL (13.5 mmol) of acetic anhydride, the blood red solution became colorless. After stirring at room temperature for 18 h, the reaction was quenched with ethyl acetate. Neutral workup[20] gave a yellow oil. Three runs on this scale were combined and chromatographed on a 20 × 20 cm preparative thick layer plate, eluting with 40% ether in hexane. The fastest moving band contained 31 mg of starting material **24**. Band 2 contained 21 mg of a 9:1 mixture of **23** and desired product **25**. This band was rechromatographed under the same conditions to give 17 mg (26%) of *endo*-1,2-(4′-(*tert*-butyldimethylsilyl)benzo)-5,6,6-triphenylbicyclo[3.1.0]-hex-5-yl acetate (**25**).

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.5–7.0 (m, 16 H, Ar), 6.74 (d, J = 8.3 Hz, 1 H, ortho H), 6.47 (dd, J = 8.4, 2.2 Hz, 1 H, ortho H), 3.70 (d, J = 6.1 Hz, 1 H, cyclopropyl), 3.25 (d, J = 6.1 Hz, 1 H, cyclopropyl), 2.07 (s, 3 H, CH_3), 1.01 (s, 9 H, $C(CH_3)_3$), 0.24 (s, 3 H, CH_3), 0.21 (s, 3 H, CH_3); IR ($CHCl_3$) 3090, 3000, 2960, 2870, 1735, 1607, 1595, 1590, 1570, 1550, 1470, 1310, 1255, 1170, 1140, 1030, 950 cm^{-1}; MS m/e – CH_3COOH 486.2371 (calcd for $C_{34}H_{34}SiO$ m/e – CH_3COOH 486.2379).

7,9,9-Triphenyltricyclo[4.4.0.0^{8,10}]deca-1,4,6-trien-3-one (15). To a solution of 15.0 mg (0.027 mmol) of *endo*-1,2-(4-*tert*-(butyldimethylsilyl)benzo)-5,6,6-triphenylbicyclo[3.1.0]hex-5-yl acetate in 3.0 mL of tetrahydrofuran was added 0.027 mL (0.027 mmol) of a solution of 1 M tetrabutylammonium fluoride. The solution immediately turned deep yellow and was stirred for 20 min. Two runs on this scale were combined and neutral quench and workup[20] gave 17.1 mg (88%) of an orange oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.60–7.10 (m, 16 H, Ar), 6.60 (d, J = 1.6 Hz, 1 H, ortho H), 6.18 (dd, J = 9.8, 1.6 Hz, 1 H, ortho H), 3.66 (d, J = 5.3 Hz, 1 H, cyclopropyl), 3.56 (d, J = 4.9 Hz, 1 H, cyclopropyl); IR ($CHCl_3$) 3070, 3020, 2950, 2920, 2870, 1655 (sh), 1630, 1600, 1580, 1535, 1495, 1450, 1275, 1170, 910 cm^{-1}; MS m/e 372.1519 (calcd for $C_{28}H_{20}O$ m/e 372.1517).

6,6-Diphenyl-4-(hydroxymethylene)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (9). To 1.2 g (29.9 mmol) of freshly prepared sodium methoxide in 35 mL of dry benzene was added 2.3 mL (29.4 mmol) of ethyl formate. The solution was then stirred for 30 min. A solution of 1.0 g (3.36 mmol) of 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone in 10 mL of dry benzene was added over 10 min followed by stirring for 18 h. Two runs on the above scale were combined and the green solution was acidified with 10% hydrochloric acid. The aqueous layer was ether extracted and the combined organic layers were shaken with ice-cold 2% potassium hydroxide. The basic layer was extracted with ether, then cooled to 0 °C, and carefully acidified with concentrated hydrochloric acid. Concentration in vacuo gave 2.05 g (93.1%) of a light tan oil, which refused to crystallize.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.52 (s, 1 H, OH), 7.2–7.0 (m, 11 H, Ar, vinyl), 6.58 (d, J = 10.0 Hz, 1 H, vinyl), 6.41 (d, J = 10.0 Hz, 1 H, vinyl), 5.90 (s, 1 H, α-vinyl), 3.6–3.2 (m, 5 H, CH); IR ($CHCl_3$) 3060, 3031, 2934, 2930, 2886, 1721, 1639, 1616, 1600, 1558, 1491, 1446, 1414, 1341, 1251, 1207, 1190, 1150, 906, 901, 876, 742, 737, 727, 717, 701 cm^{-1}; MS m/e 328.1463 (calcd for $C_{23}H_{20}O_2$ m/e 328.1427).

6,6-Diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone (4). A mixture of 1.55 g (4.73 mmol) of 6,6-diphenyl-4-(hydroxymethylene)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone and 0.53 mL (5.71 mmol) of freshly distilled methyl vinyl ketone in 100 mL of *tert*-butyl alcohol was cooled on an ice bath. A solution of 55 mg (0.49 mmol) of potassium *tert*-butoxide in 3.0 mL of *tert*-butyl alcohol was added over 3 min. The solution was then stirred at room temperature for 18 h. Acidic workup[20] gave 1.89 g of a yellow foam. This Michael addition product was cyclized without further purification as follows. The above oil was taken up in 80 mL of dry dioxane and cooled on an ice bath. A solution of 1.23 g (20.76 mmol) of potassium hydroxide in 50 mL of water was added over 5 min. The solution was then stirred at room temperature for 3 h. Acidic and basic workup[20] gave 1.65 g of a yellow foam, which was chromatographed on a 4.0 × 60 cm silica gel column: fraction 1, 1.5 L of 3% ether in hexane, nil; 2, 1 L of 5% ether in hexane, nil; 3, 2.5 L of 7% ether in hexane, nil; 1.5 L of 10% ether in hexane, nil; 2.5 L of 15% ether in hexane, 1.17 g of a yellow foam, which was recrystallized from methylene chloride in hexane to give 859 mg (51.6%) of 6,6-diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone as a light yellow solid, mp 162–163 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20–7.30 (m, 10 H, Ar), 6.42 (m, 2 H, vinyl), 6.11 (s, 1 H, γ-vinyl), 5.82 (s, 1 H, α-vinyl), 2.6–1.6 (m, 10 H, aliphatic); IR ($CHCl_3$) 3000, 2920, 1640, 1590, 1490, 1450, 1380, 1330, 1250, 1200, 910, 690 cm^{-1}; UV (95% EtOH) λ_{max} 335 (ε 43 300), tails to >400 nm; MS m/e 352.1827 (calcd for $C_{26}H_{24}O$ m/e 352.1827).

Anal. Calcd for $C_{26}H_{24}O$: C, 88.60; H, 6.86. Found: C, 88.68; H, 7.03.

Exploratory Direct Photolysis of 5,6,6-Triphenyl-2-(6*H*)-naphthalenone (2) in Methanol. A solution of 33 mg (0.089 mmol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone (**2**) in 150 mL of methanol was photolyzed through filter solution B[20] for 35 min. Concentration in vacuo gave 42.1 mg of a slightly yellow oil, which was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting twice with 40% ether in hexane. The most rapidly moving band contained 3.1 mg (9.3%) of naphthol **13**, which was recrystallized from hexane at −20 °C to give 2.0 mg (6.0%) of 5,7,8-triphenyl-2-naphthol (**13**) as a yellow solid, mp 147–148 °C. Band 2 contained 35 mg (85.6%) of peroxide **12**. Recrystallization from chloroform in hexane gave 30.1 mg (73.6%) of *cis*-2,3-(5′-hydroxybenzo)-1,6,6-triphenyl-4-methoxy-7,8-dioxabicyclo[3.3.0]hexane (**12**) as a clear solid, mp 183–184 °C.

The spectral data for *cis*-2,3-(5′-hydroxybenzo)-1,6,6-triphenyl-4-methoxy-7,8-dioxabicyclo[3.3.0]hexane were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.58 (dd, J = 8.2, 1.6 Hz, 2 H, Ar), 7.4–7.0 (m, 13 H, Ar), 6.92 (dd, J = 7.9, 1.4 Hz, 2 H, Ar), 6.74 (d, J = 2.3 Hz, 1 H, ortho H), 4.95 (s, 1 H, OH), 4.42 (d, J = 1.5 Hz, 1 H, $CHOCH_3$), 4.30 (d, J = 1.4 Hz, 1 H, CH), 3.23 (s, 3 H, OCH_3); IR ($CHCl_3$) 3594, 3320(br), 3060, 3031, 3011, 2956, 2927, 2871, 2854, 1602, 1493, 1447, 1278, 1259, 1234, 1205, 1188, 1079, 1033, 763, 745, 734, 700 cm^{-1}; UV (95% EtOH) λ_{max}

280 (ε 3717); MS *m/e* - CH_3OH 404.1415 (calcd for $C_{28}H_{20}O_3$ *m/e* - CH_3OH 404.1412).

Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 80.15; H, 5.49.

The spectral data for 5,7,8-triphenyl-2-naphthol were the following: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.90 (d, *J* = 8.8 Hz, 1 H, Ar), 7.6–7.0 (m, 18 H, Ar), 4.98 (s, br, 1 H, OH); IR ($CHCl_3$) 3588, 3300 (br), 3080, 3060, 3030, 3009, 1619, 1515, 1493, 1446, 1418, 1376, 1229, 1174, 982, 830, 702 cm^{-1}; MS *m/e* 372.1514 (calcd for $C_{28}H_{20}O$ *m/e* 372.1508).

The spectral data for 5,7,8-triphenylnaphth-2-yl acetate were the following: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.99 (d, *J* = 9.1 Hz, 1 H, Ar), 7.6–7.2 (m, 18 H, Ar), 2.27 (s, 3 H, CH_3); IR ($CHCl_3$) 3009, 2955, 2927, 1758, 1620, 1491, 1457, 1446, 1370, 1228, 1202, 1173, 1117, 1073, 1013, 983 cm^{-1}; MS *m/e* 414.1616 (calcd for $C_{30}H_{22}O_2$, *m/e* 414.1620); mp 186–187 °C.

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.78; H, 5.45.

Exploratory Direct Photolysis of 5,6,6-Triphenyl-2-(6*H*)-naphthalenone (2) in Isopropyl Alcohol. A solution of 38 mg (0.105 mmol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone in 150 mL of isopropyl alcohol was photolyzed through a Pyrex filter for 50 min. Concentration in vacuo gave 51.1 mg of a slightly yellow oil, which was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting twice with 30% ether in hexane. The most rapidly moving band contained 5.1 mg (13.1%) of 5,7,8-triphenyl-2-naphthol, which was recrystallized from hexane at −20 °C to give 3.5 mg (9.0%) of naphthol **13** as a light yellow solid, mp 146–148 °C. Band 2 contained 42 mg (81.6%) of peroxide **14**. Recrystallization from methylene chloride in hexane gave 36.5 mg (70.7%) of *cis*-2,3-(5′-hydroxybenzo)-1,6,6-triphenyl-4-isopropoxy-7,8-dioxabicyclo[3.3.0]hexane (**14**) as a solid, mp 116–117 °C.

The spectral data were the following: ^1H NMR ($CDCl_3$, 270 MHz) δ 7.54 (m, 1 H, Ar), 7.4–6.95 (m, 15 H, Ar), 6.84 (dd, *J* = 8.3, 2.5 Hz, 1 H, ortho H), 6.67 (d, *J* = 2.3 Hz, 1 H, ortho H), 5.0 (s, br, 1 H, OH), 4.56 (s, 1 H, C*H*OC_3H_7), 4.22 (s, 1 H, CH), 3.50 (m, 1 H, CH), 1.04 (d, *J* = 6.0 Hz, 3 H, CH_3), 0.92 (d, *J* = 5.8 Hz, 3 H, CH_3); IR ($CHCl_3$) 3600, 3300, 3050, 2980, 1610, 1500, 1450, 1385, 1370, 1320, 1290, 1245, 1050, 900 cm^{-1}; MS *m/e* - $(CH_3)_2$CHOH 404.1413 (calcd for $C_{28}H_{20}O_3$ *m/e* - $(CH_3)_2$CHOH 404.1412).

Anal. Calcd for $C_{31}H_{28}O_4$: C, 80.15; H, 6.08. Found: C, 80.35; H, 5.78.

Exploratory Direct Photolysis of 5,6,6-Triphenyl-2-(6*H*)-naphthalenone (2) in Acetonitrile. A solution of 20 mg (0.05 mmol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone in 150 mL of acetonitrile was photolyzed through a Pyrex filter for 20 min. Concentration in vacuo gave 22 mg of an orange oil. NMR analysis showed complete conversion. The oil was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting twice with 20% ether in hexane. The most rapidly moving band contained 6.4 mg of 5,7,8-triphenyl-2-naphthol (**13**) whose spectral data were identical with those reported above. The remainder of the mass was at or just above the origin. Mass balance was reasonable only at lower conversions (30–40%).

Exploratory Low Conversion Direct Photolysis of 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2) in Acetonitrile. A solution of 6.4 mg (0.017 mmol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone (**2**) in 40 mL of acetonitrile was photolyzed on the microoptical bench[27] until 0.0183 mEinsteins were absorbed. NMR analysis showed the presence of 5,7,8-triphenyl-2-naphthol (**13**) and 7,9,9-triphenyltricyclo[4.4.0.0^{8,10}]deca-1,4,6-trien-3-one (**15**).

Exploratory Direct Photolysis of 5,6,6-Triphenyl-2-(6*H*)-naphthalenone (2) in Benzene. A solution of 12.3 mg (0.033 mol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone (**2**) in 150 mL of benzene was photolyzed through filter solution B[20] for 12 min. Concentration in vacuo gave 14.2 mg of a dark yellow oil, which was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting twice with 20% ether in hexane. The fastest moving band gave 1.2 mg of an unidentified material. The remainder of the mass was unidentified polymeric material at the origin. Even in lower conversion runs, none of the previously observed photoproducts were detected.

Exploratory Direct Photolysis of 5,6,6-Triphenyl-2-(6*H*)-naphthalenone (2) in a Sealed NMR Tube. To 6.0 mg (0.016 mmol) of 5,6,6-triphenyl-(2(6*H*)-naphthalenone was added 0.10 mL of benzene and 1.0 mL of methanol-d_4 in an NMR tube, which was deoxygenated with 5 freeze–pump–thaw cycles, then sealed under vacuum, and photolyzed through filter solution B[20] for 35 min. NMR analysis (270 MHz) showed the following peaks, δ 7.40–6.85 (m, 16 H, Ar), 6.67 (dd, *J* = 8.3, 2.4 Hz, 1 H, ortho H), 6.48 (d, *J* = 2.4 Hz, 1 H, ortho H), 4.54 (s, 1 H, C*H*OCD_3), 3.43 (s, 1 H, cyclopropyl), attributable to *cis*-2,3-(5′-deuteroxybenzo)-1,6,6-triphenyl-4-(methoxy-d_3)bicyclo[3.1.0]hexane (**25-d**). In the absence of oxygen **28-d** was indefinitely stable (5 months), but upon exposure to the atmosphere, peaks corresponding to **28-d** decreased in intensity and peaks due to methoxy peroxide **12** grew in.

Trapping of the δ–δ Bonded Phenol. A solution of 25 mg (0.067 mmol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone in 15 mL of methanol in a round-bottom flask was purged with nitrogen[22] for 2 h prior to and during irradiation. Photolysis was carried out through filter solution B[20] for 40 min. The methanol was evaporated overnight with the purified nitrogen, the resulting solid was dissolved in 3.0 mL of tetrahydrofuran, and this was added to a suspension of 600 mg (360 mmol) of 60% sodium hydride (washed twice with tetrahydrofuran) in 2.0 mL of tetrahydrofuran. After stirring for 15 min at 0 °C, 1.5 mL (24.1 mmol) of methyl iodide was added, and the solution was stirred at room temperature for 18 h. Neutral quench and workup[20] yielded 32 mg of a light yellow oil, which was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting once with 40% ether in hexane. The fastest moving band yielded 2.8 mg (11.2%) of 5,7,8-triphenyl-2-naphthol (**13**). Band 2 contained 23 mg (82.5%) of the δ–δ bridged methyl ether **29**. Recrystallization from methylene chloride in hexane yielded 18.5 mg (66.3%) of *cis*-2,3-(5′-methoxybenzo)-1,6,6-triphenyl-4-methoxybicyclo[3.1.0]-hexane (**29**) as a white solid, mp 179–180 °C.

The spectral data were the following: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.40–6.90 (m, 16 H, Ar), 6.72 (dd, *J* = 8.3, 2.4 Hz, 1 H, ortho H), 6.55 (d, *J* = 2.5 Hz, 1 H, ortho H), 4.58 (s, 1 H, C*H*OCH_3), 3.65 (s, 3 H, OCH_3), 3.54 (s, 3 H, OCH_3), 3.43 (s, 1 H, cyclopropyl); IR ($CHCl_3$) 3007, 2957, 2929, 1610, 1601, 1489, 1465, 1456, 1446, 1435, 1249, 1221, 1215, 1190, 1148, 1081, 1032, 909, 772, 765, 753, 745, 739, 730, 703 cm^{-1}; MS *m/e* 418.1933 (calcd for $C_{30}H_{26}O_2$ *m/e* 418.1931).

Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.10; H, 6.26. Found: C, 86.42; H, 6.58.

Exploratory Direct Photolysis of 7,9,9-Triphenyltricyclo[4.4.0.0^{8,10}]deca-1,4,6-trien-3-one (15). A solution of 10.1 mg (0.027 mmol) of 7,9,9-triphenyltricyclo[4.4.0.0^{8,10}]deca-1,4,6-trien-3-one in 40 mL of acetonitrile was photolyzed on the microoptical bench[27] at 366 nm for 1 h. ^1H NMR analysis showed complete conversion of starting material. Concentration in vacuo gave 11.5 mg of a yellow oil, which was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting with 40% ether in hexane. The most rapidly moving band contained 7.2 mg of 5,7,8-triphenyl-2-naphthol (**13**), whose spectral data were identical with those reported above. The remainder of the mass was at the origin.

Exploratory Direct Photolysis of 6,6-Diphenyl-2(6*H*)-naphthalenone (1). A solution of 25 mg (0.085 mmol) of 6,6-diphenyl-2(6*H*)-naphthalenone in 25 mL of benzene was photolyzed through a Pyrex filter for 15 min. Concentration in vacuo gave 26 mg of a light yellow. NMR analysis showed complete conversion of starting material. The oil was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting once with 15% ether in hexane. A single rapidly moving band that contained 23 mg (92.0%) of 5,6-diphenyl-2-naphthol (**10**) resulted. This was recrystallized from hexane to give 19 mg (76%) of a light yellow solid, mp 130–131 °C.

The spectral data for 5,6-diphenyl-2-naphthol were the following: ^1H NMR ($CDCl_3$, 270 MHz) δ 7.72 (d, *J* = 8.5 Hz, 1 H, Ar), 7.56 (d, *J* = 9.2 Hz, 1 H, Ar), 7.50 (d, *J* = 8.5 Hz, 1 H, Ar), 7.20–7.10 (m, 11 H, Ar), 6.98 (dd, *J* = 9.2, 2.6 Hz, 1 H, Ar), 5.0 (s, br, 1 H, OH); IR ($CHCl_3$) 3570, 3290 (br), 3020, 3000, 2985, 2910, 2840, 1620, 1595, 1490, 1440, 1380, 1250, 1210, 1165, 1150,

(27) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.

1115, 930, 900, 865, 820 cm^{-1}; MS m/e 296.1200 (calcd for $C_{22}H_{16}O$ m/e 296.1201).

The spectral data for 5,6-diphenylnaphth-2-yl acetate were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.87 (d, J = 9.1 Hz, 1 H, Ar), 7.70–7.50 (m, 3 H, Ar), 7.20–7.00 (m, 11 H, Ar), 2.36 (s, 3 H, CH_3); IR ($CHCl_3$) 3082, 3061, 3056, 3009, 1757, 1371, 1228, 1198, 1148, 1013, 974 cm^{-1}; MS m/e 338.1310 (calcd for $C_{24}H_{18}O_2$ m/e 338.1307); mp 156–157 °C.

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.09; H, 5.63.

Exploratory Direct Photolysis of 6,6-Diphenyl-2(6*H*)-naphthalenone (1) in Methanol. A solution of 10 mg (0.034 mmol) of 6,6-diphenyl-2(6*H*)-naphthalenone in 150 mL of methanol was photolyzed through a Pyrex filter for 5 min. Concentration in vacuo gave 11.1 mg of a light yellow oil. NMR analysis (270 MHz) showed 80% conversion to 5,6-diphenyl-2-naphthol (**10**). The crude photolysate was chromatographed on a 20 × 20 cm preparative thick layer plate, eluting once with 20% ether in hexane to give 9.1 mg (91%) of 5,6-diphenyl-2-naphthol. Spectral data were identical with those reported above.

Acid-Catalyzed Rearrangement of 6,6-Diphenyl-2(6*H*)-naphthalenone (1). To a solution of 5.0 mg (0.017 mmol) of 6,6-diphenyl-2(6*H*)-naphthalenone in 3.0 mL of tetrahydrofuran was added 0.10 mL of glacial acetic acid. After 10 min of stirring at room temperature, ether was added and basic workup[20] gave 4.8 mg of a light oil. NMR analysis (270 MHz) showed complete conversion to 5,6-diphenyl-2-naphthol (**10**).

Control Experiment: Stability of 6,6-Diphenyl-2(6*H*)-naphthalenone (1). A solution of 11.1 mg (0.038 mmol) of 6,6-diphenyl-2(6*H*)-naphthalenone and 7.4 mg (0.025 mmol) of 5,6-diphenyl-2-naphthol in 30 mL of benzene was purged with purified nitrogen[22] for 24 h. ^{1}H NMR analysis after this time showed the same relative amounts of compounds as were observed prior to degassing.

Exploratory Direct Photolysis of 6,6-Diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (3). A solution of 150 mg (0.50 mmol) of 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-napthalenone was photolyzed through a Pyrex filter for 2.5 h. Concentration in vacuo gave 152 mg of an oil, which was chromatographed on a 4.0 × 100 cm silica gel column, collecting 40-mL aliquots: 1–237 of 4% ether in hexane, nil; 238–344 of 6% ether in hexane, nil; 345–385 of 6% ether in hexane, 23.5 mg (15.6%) of exo-trans bicyclic **30b**; 380–439 of 6% ether in hexane, nil; 440–500 of 6% ether in hexane, 41.2 mg (27.3%) of endo-trans bicyclic **30a**; 501–520 of 6% ether in hexane, nil; 521–530 of 10% ether in hexane, nil; 531–560 of 10% ether in hexane, 7.3 mg of unidentified material; 561–667 of 10% ether in hexane, 55.7 mg (37.1%) of endo-cis bicyclic **30c**; 668–700 of 10% ether in hexane, nil; 701–750 of 10% ether in hexane, 20.1 mg (13.3%) of exo-cis bicyclic **30d**. The exo-trans bicyclic was recrystallized from methylene chloride in hexane to give 17.8 mg (11.9%) of *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one as a white solid, mp 129–131 °C. The endo-trans bicyclic was recrystallized from ether in hexane to give 35.1 mg (23.3%) of *trans*-8,9-diphenyl-*endo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one as a white powder, mp 92–93 °C. The endo-cis bicyclo was recrystallized from ether in hexane to give 46.0 mg (30.9%) of *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]-dec-1-en-3-one as clear crystals, mp 156–158 °C. The exo-cis bicyclic was recrystallized from ether in hexane to give 14.1 mg (9.4%) of *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one as a white solid, mp 102–103 °C.

The spectral data for *trans*-8,9-diphenyl-*exo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.30 (m, 10 H, Ar), 6.16 (d, J = 2.0 Hz, 1 H, α-vinyl), 3.08 (d, J = 9.0 Hz, 1 H, cyclopropyl), 2.85 (d, J = 8.9 Hz, 1 H, cyclopropyl), 2.50 (dd, J = 13.0, 7.8 Hz, 1 H), 2.35–2.25 (m, 1 H, aliph), 2.0 (m, 3 H, aliph), 1.7–1.4 (m, 2 H, aliph); IR ($CHCl_3$) 3000, 2950, 1650, 1630 (sh), 1600, 1500, 1380, 1290, 1250, 1180, 750, 690 cm^{-1}; UV (95% EtOH) λ_{max} 250 (ε 5687); MS m/e 300.1514 (calcd for $C_{22}H_{20}O$ m/e 300.1514).

Anal. Calcd for $C_{20}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.70; H, 6.94.

The spectral data for *trans*-8,9-diphenyl-*endo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.40–7.10 (m, 10 H, Ar), 6.17 (d, J = 2.7 Hz, 1 H, α-vinyl), 3.3–3.2 (m, 1 H, CH), 3.03 (s, 1 H, CH), 2.95–1.5 (m, 7 H, CH); IR ($CHCl_3$) 3009, 2928, 2864, 2855, 1652, 1602, 1496, 1456, 1445, 1353, 1319, 1197, 700 cm^{-1}; MS m/e 300.1514 (calcd for $C_{22}H_{20}O$ m/e 300.1518).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.61; H, 6.93.

The spectra data for *cis*-8,9-diphenyl-*endo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.15 (m, 8 H, Ar), 6.75 (m, 2 H, Ar), 6.12 (d, J = 2.8 Hz, 1 H, α-vinyl), 3.50 (m, 1 H, CH), 3.30 (m, 1 H, CH), 2.96 (d, J = 3.0 Hz, 1 H, CH), 2.66 (dd, J = 11.2, 13.0 Hz, 1 H, CH), 2.38 (dd, J = 14.0, 4.9 Hz, 1 H, CH), 2.29 (d, J = 4.1 Hz, 1 H, CH), 2.15 (m, 1 H, CH), 1.98 (dd, J = 13.0, 9.2 Hz, 1 H, CH), 1.7 (m, 1 H, CH); IR ($CHCl_3$) 3000, 1655, 1490, 1430, 1280, 1250, 690 cm^{-1}; UV (95% EtOH) λ_{max} 250 (ε 5900); MS m/e 300.1514 (calcd for $C_{22}H_{20}O$ m/e 300.1518).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.58; H, 6.86.

The spectral data for *cis*-8,9-diphenyl-*exo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20–7.00 (m, 8 H, Ar), 6.8–6.7 (m, 2 H, Ar), 6.13 (s, 1 H, α-vinyl), 2.8–1.75 (m, 9 H, CH); IR ($CHCl_3$) 3009, 2939, 2927, 2866, 1653, 1617, 1603, 1498, 1456, 1446, 1354, 1323, 1247, 1196, 939, 887, 775, 766, 760, 753, 736, 699 cm^{-1}; MS m/e 300.1514 (calcd for $C_{22}H_{20}O$ m/e 300.1522).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.79; H, 7.13.

Exploratory Sensitized Photolysis of 6,6-Diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (3). A solution of 100 mg (0.33 mmol) of 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone and 44 mg (0.17 mmol) of Michler's ketone were irradiated through filter solution B[20] for 10 min. Concentration in vacuo gave 150 mg of an oil, which was chromatographed on a 2.5 × 40 cm silica gel column, eluting with 10% ether in hexane to give 105 mg of a clear oil. ^{1}H NMR analysis of the photolysate showed 65% conversion to the *trans*-diphenyl isomers **30b** and **30a**. The photolysate was then chromatographed on 4.0 × 100 cm silica gel column, collecting 40-mL aliquots: 1–240 of 4% ether in hexane, nil; 241–290 of 6% ether in hexane, nil; 291–340 of 6% ether in hexane, 30 mg (30.0%) of starting dienone **3**; 341–345 of 6% ether in hexane, nil; 346–370 of 6% ether in hexane, 19.2 mg (19.2%) of exo-trans bicyclic **30b**; 371–420 421–462 of 6% ether in hexane, 42.1 mg (42%) of endo-trans bicyclic **30a**. The spectral data were identical with that reported above.

Epimerization of *cis*-8,9-Diphenyl-*endo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one (30c). A solution of 10.0 mg (0.03 mmol) of the endo-cis bicyclic ketone **30c** and 15 mg (0.14 mmol) of sodium carbonate in 2.0 mL of tetrahydrofuran and 2.0 mL of water was refluxed for 2 h. Neutral workup[20] gave 9.7 mg of a clear oil. ^{1}H NMR analysis showed this to be a (3:1) mixture of exo-cis bicyclic **30d** and endo-cis bicyclic **30c**.

Exploratory Direct Photolysis of *trans*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (30a). A solution of 13.2 mg (0.044 mmol) of *trans*-8,9-diphenyl-*endo*-tricyclo-[4.4.0.0^{8,10}]dec-1-en-3-one in 150 mL of photograde benzene was irradiated through a Pyrex filter for 40 min. ^{1}H NMR analysis of the photolysis mixture showed the presence of only the cis-endo isomer **30c**.

Exploratory Direct Photolysis of 6,6-Diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone (4). A solution of 15.9 mg (0.045 mmol) of 6,6-diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone in 40 mL of benzene was irradiated on the microoptical bench[27] until 0.227 mEinstein of light had been absorbed. NMR analysis yielded 0.0009 as an upper limit for the quantum yield of disappearance of trienone **4**.

Photolysis Equipment for Quantum Yield Determinations. All direct and sensitized quantum yields were determined on a microoptical bench[27] equipped with an Osram 200-W high-pressure mercury lamp and a Bausch & Lomb Model 33-86-79 monochromator. The monochromator entrance and exit slits were set to 5.4 and 3.0 mm, respectively, to give a 22-nm band pass (width at half height). Light output was measured with a digital actinometer[28] calibrated by ferrioxalate actinometry.[29] The

(28) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

Table V. Summary of Crystal Data Collection Parameters for 5,6-Diphenyl-2-naphthol (10), 5,7,8-Triphenyl-2-naphthol (13), *cis*-2,3-(5′-Hydroxybenzo)-1,6,6-triphenyl-4-methoxy-7,8-dioxabicyclo[3.3.0]hexane (12), and *cis*-2,3-(5′-Hydroxybenzo)-1,6,6-triphenyl-4-isopropoxy-7,8-dioxabicyclo[3.3.0]hexane (14)

parameter	diphenylnaphthol 10	triphenylnaphthol 13	methoxy peroxide 12	isopropoxy peroxide 14
axis, Å				
a	8.187 (1)	10.058 (3)	9.490 (1)	10.115 (2)
b	18.241 (3)	13.324 (3)	19.431 (3)	9.360 (2)
c	10.696 (1)	18.156 (3)	12.105 (1)	29.652 (4)
angle, deg				
α	90.00	80.82 (1)	90.00	90.00
β	90.23 (1)	82.19 (1)	91.83 (1)	95.56 (2)
γ	90.00	85.66 (1)	90.00	90.00
molecules/cell (*Z*)	4	4	4	4
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
μ, cm^{-1}	0.6	5.4	6.0	6.1
radiatn type	Mo Kα	Cu Kα	Cu Kα	Cu Kα
scan mode	ω	θ–2θ	ω	ω
2θ limits, deg	4.0–45.7	4.0–115.0	4.5–115.0	4.0–115.0
scan range, deg	0.8/0.8	0.9/0.9	0.6/0.6	0.6/0.6
measd reflctns	2540	6697	2555	4362
unique reflctns	2186	6368	2249	3809
obsd reflctns	1780	4291	1760	2564
least-squares param	272	683	394	428
goodness of fit	1.73	2.88	1.73	2.57
$R_1(F)$	0.046	0.114	0.049	0.100
$R_W(F)$	0.054	0.124	0.054	0.091

solutions were purged with deoxygenated nitrogen[22] for 1 h prior to and during photolysis. Quantum yield runs on compounds 1 and 2 were analyzed by 270-MHz ^{1}H NMR, using triphenylmethane as the internal standard. For quenched quantum yield runs, samples were purged for 1 h prior to addition of quencher and were not purged during photolysis due to the volatility of 1,3-cyclohexadiene.

Summary of Direct Quantum Yield Results for 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2) in Methanol. All runs were at 366 nm, except for one run at 313 nm, which yielded the same results. Extrapolation of the quantum yields for formation of *cis*-2,3-(5′-hydroxybenzo[-1,6,6-triphenyl-4-methoxy-7,8-dioxabicyclo[3.3.0]hexane (12) and 5,7,8-triphenyl-2-naphthol (13) to 0% conversion gave values of 0.30 and 0.00, respectively.

Summary of Quenched Quantum Yields for 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2). All runs were done in methanol at 366 nm with varying amounts of 1,3-cyclohexadiene (0.05–0.20 M). Stern–Volmer analysis gave a slope of 21.4 M^{-1} for peroxide 12 formation.

Summary of Sensitized Quantum Yield Results for 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2). A solution of 6.0 mg (0.016 mmol) of 5,6,6-triphenyl-2(6*H*)-naphthalenone and 45.8 mg (0.17 mmol) of Michler's ketone in 40 mL of methanol was irradiated at 366 nm on the microoptical bench[27] until 0.093 mEinstein of light had been absorbed. The Michler's ketone was separated by preparative HPLC[20] prior to NMR analysis, which showed no detectable conversion, indicating that ϕ was less than 0.008.

Summary of Direct Quantum Yield Results for 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2) in Acetonitrile. All runs were at 366 nm. Extrapolation of the quantum yields for formation of 7,9,9-triphenyltricyclo[4.4.0.0^{8,10}]deca-1,4,6-trien-3-one (15) to 0% conversion gave a value of 0.084.

Summary of Direct Quantum Yield Results for 6,6-Diphenyl-2(6*H*)-naphthalenone (1). All runs were at 366 nm, except for one run at 313 nm, which gave the same results. Extrapolation of the quantum yield of formation of 5,6-diphenyl-2-naphthol (10) to 0% conversion gave a value of 0.68.

Summary of Quenched Quantum Yields for 6,6-Diphenyl-2(6*H*)-naphthalenone (1). All runs were done in benzene at 366 nm with varying amounts of 1,3-cyclohexadiene (0.05–0.15 M). Stern–Volmer analysis gave a slope of 4.4 M^{-1} for naphthol 10 formation.

Summary of Sensitized Quantum Yield Results for 6,6-Diphenyl-2(6*H*)-naphthalenone (1). A solution of 15.0 mg (0.05 mmol) of 6,6-diphenyl-2(6*H*)-naphthalenone and 125 mg (0.47 mmol) of Michler's ketone in 40 mL of benzene was irradiated at 366 nm on the microoptical bench[27] until 0.096 mEinstein of light had been absorbed. The photolysate solution was then added to a previously prepared solution of 1.5 mmol of lithium diphenylcuprate followed by stirring for 4 h. Neutral workup[20] gave 170 mg of a brown oil, which was chromatographed on a preparative thick layer plate, eluting with 30% ether in hexane to give 14.0 mg (73%) of 1,2-(4′-hydroxybenzo)-5,5,6-triphenylcyclohex-3-ene. There was not observed any of the 5,6-diphenyl-2-naphthol, indicating that ϕ was less than 0.005.

Table VI. Summary of Crystal Data Collection Parameters for *cis*-2,3-(5′-Methoxybenzo)-1,6,6-triphenyl-4-methoxy-7,8-dioxabicyclo[3.1.0]hexane (29), 6,6-Diphenyl-2(6*H*)-naphthalenone (1), and 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2)

parameter	tricyclic anisole 29	diphenylnaphthalenone 1	triphenylnaphthalenone 2
axis, Å			
a	8.439 (1)	8.439 (1)	8.065 (1)
b	27.699 (3)	36.514 (3)	18.043 (3)
c	10.112 (1)	10.379 (1)	13.587 (1)
angle, deg			
α	90.00	90.00	90.00
β	102.61 (1)	90.00	94.67 (1)
γ	90.00	90.00	90.00
molecules/cell (*Z*)	4	8	4
space group	$P2_1/c$	*Pbca*	$P2_1/c$
μ, cm^{-1}	6.0	0.6	5.4
radiatn type	Cu Kα	Mo Kα	Cu Kα
scan mode	ω	ω	ω
2θ limits, deg	4.0–115.0	4.0–45.7	4.5–115.0
scan range, deg	0.7/0.7	0.9/0.9	0.9/0.9
measd reflctns	3473	2488	2974
unique reflctns	3137	2120	2700
obsd reflctns	2691	1213	2508
least-squares param	393	272	369
goodness of fit	2.54	1.58	2.88
$R_1(F)$	0.062	0.075	0.057
$R_W(F)$	0.071	0.068	0.075

Summary of Quantum Yield Results for 6,6-Diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (3). All runs were done in benzene at 313 nm for direct photolyses and at 366 nm for sensitized photolyses employing Michlers ketone. Analysis was done by using analytical HPLC,[20] eluting with 2% ethyl acetate in hexane (50% saturated with water) and with dimethoxybenzophenone as the internal standard. Extrapolation of the quantum yields for formation of *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (**30b**), *trans*-8,9-diphenyl-*endo*-tri-

(29) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1965**, *235*, 518–536.

Table VII. Summary of Crystal Data Collection Parameters for *trans*-8,9-Diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (30b), *trans*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (30a), *cis*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (30c), and 6,6-Diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone (4)

parameter	exo-trans bicyclic **30b**	endo-trans bicyclic **30a**	endo-cis bicyclic **30c**	diphenylanthracenone **4**
axis, Å				
a	8.339 (2)	10.387 (3)	8.081 (1)	8.615 (1)
b	10.917 (3)	27.719 (9)	20.684 (3)	8.987 (1)
c	9.866 (2)	11.382 (3)	10.466 (1)	14.228 (2)
angle, deg				
α	90.00	90.00	90.00	75.25 (1)
β	113.92 (2)	90.00	105.17 (1)	85.52 (1)
γ	90.00	90.00	90.00	63.65 (1)
molecules/cell (*Z*)	2	8	4	2
space group	$P2_1$	*Pbca*	$P2_1/n$	$P\bar{1}$
μ, cm^{-1}	0.6	0.6	0.6	5.4
radiatn type	Mo Kα	Mo Kα	Mo Kα	Cu Kα
scan mode	ω	ω	ω	ω
2θ limits, deg	4.0–52.8	4.0–45.0	4.5–45.0	4.0–115.0
scan range, deg	0.8/0.8	0.8/0.8	0.9/0.9	0.8/0.8
measd reflctns	1911	2607	2687	2715
unique reflctns	1783	2252	2320	2590
obsd reflctns	1588	1309	1878	2264
least-squares param	270	270	270	340
goodness of fit	1.47	2.02	1.87	2.40
$R_1(F)$	0.041	0.104	0.075	0.048
$R_W(F)$	0.047	0.104	0.068	0.056

cyclo[4.4.0.0^{8,10}]dec-1-en-3-one (**30a**), *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (**30c**), and *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-en-3-one (**30d**) to 0% conversion gave values of 0.032, 0.066, 0.0, and 0.0, respectively, for the direct photolysis and values of 0.031, 0.066, 0.0, and 0.0, respectively, for the sensitized photolysis.

Phosphorescence and Fluorescence Emission Measurements. All emission spectra were recorded on an Aminco-Keirs spectrophosphorimeter equipped with a Hanovia 901-C 150-W Xenon arc lamp, with internal baffles to eliminate scatter, and interfaced to a PDP 11/55 microcomputer. Samples were prepared in methylcyclohexane/isopentane (4:1), with concentrations of ca. 10^{-4} M being employed to achieve optical densities in the range of 0.5–0.8. Samples were thoroughly deoxygenated by 5 freeze–pump-thaw cycles prior to recording the spectra.

Fluorescence spectra were recorded for diphenylnaphthalenone **1**, triphenylnaphthalenone **2**, diphenyltetrahydronaphthalenone **3**, and diphenylanthracenone **4** at 295 K. All showed structureless emission with estimated 0–0 bands at 394 nm (72 kcal), 397 nm (72 kcal), 360 nm (79 kcal), and 390 nm (73 kcal), respectively. Phosphorescence spectra were recorded at 77 K; however emission was observed only for diphenylnaphthalenone **1**. The 0–0 band was estimated at 530 nm (54 kcal).

Attempted Fluorescence Quenching of 5,6,6-Triphenyl-2(6*H*)-naphthalenone (2). With use of the Aminco-Keirs instrument described above, the integrated fluorescence intensity of degassed samples of the ketone containing 0.20 M 1,3-cyclohexadiene was measured at 295 K. The excitation wavelength was 335 nm and the emission was detected at 395 nm. There was observed a ca. 10% decrease in fluorescence at quencher concentrations where photoproduct formation is quenched by 82%.

General Procedure for Single-Crystal X-ray Structure Determination.[30] X-ray data were collected on either a Nicolet (Syntex) $P\bar{1}$ or P3/F diffractometer. Unit cell parameters were determined from least-squares refinement of 25 high angle reflections. Data were collected, 3 check reflections being monitored every 97, and data with $F > 3\sigma(F)$ were considered observed. Lorentz and polarization corrections were applied, and each structure was solved under the appropriate space group symmetry by direct methods using SHELX-86[31] or MULTAN-80.[32] Hydrogen atoms were located from difference Fourier synthesis. Least-squares refinement[30] was carried out with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Blocked matrix least-squares refinement[33] was employed for naphthol **13** due to the large number of parameters. For peroxide **14** and naphthol **13**, difference Fourier syntheses revealed disordered solvent hexane molecules. These were modeled as rigid groups with a common group isotropic thermal parameter ($U = 0.10$). For naphthol **13**, the two molecules in the assymetric unit differed by rotation about one of the phenyl groups.

X-ray quality crystals were prepared as follows: diphenylnaphthol **10** by slow crystallization from hexane; triphenylnaphthol **13** by vapor diffusion of hexane into chloroform; methoxy peroxide **12** by slow crystallization from ether in hexane; isopropyl peroxide **14** by vapor diffusion of hexane into toluene; bicyclo[3.1.0]hexane **29** by slow crystallization from ether in hexane; diphenylnaphthalenone **1** by slow crystallization from ether; triphenylnaphthalenone **2** by slow crystallization from ether in hexane; exo-trans bicyclic **30b** by vapor diffusion of hexane into toluene; endo-trans bicyclic **30a** by vapor diffusion of hexane into toluene; endo-cis bicyclic **30c** by slow crystallization from ether in hexane; anthracenone **4** by vapor diffusion of hexane into chloroform. The results of the structure determination are summarized in Tables V–VII. ORTEP drawings, atomic coordinates, bond angles and distances, and anisotropic and isotropic thermal parameters are given in Tables 1a–e to 11a–e and Figures 1–11 in the supplementary material.

Molecular Mechanics Calculations. Molecular mechanics calculations were performed with the MMP2[34] program. For the structures in which a phenyl group is half migrated, the odd-electron centers were modeled as sp^2 carbons and the spiro ring as a cyclopropane.

Quantum Mechanics Calculations. Quantum mechanics calculations were performed with the "MOPAC" package,[35a] employing the MNDO approximation.[35b] For half-migrated species **31***, and **33***, **43**, **46**, and **53**, however lacking the nonreactive phenyl, and zwitterions **50** and **51** an internal coordinate was defined to include the cyclopropane ring atoms and was fixed at 60°. The geometry optimization was carried out on the state of interest. A single point configuration calculation using four

(30) Programs employed include CARESS (R. W. Broach, Argonne National Laboratory, ORFLS (ORNL-TM-30-5), ORFFE (ORNL-TM-306) and ORTEP (ORNL-TM-3794).

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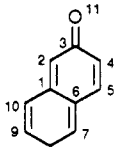
Table VIII. ΔP Values from MNDO-CI Calculations on the Naphthalenone System



bond	ΔP values T_1	T_2	T_3
1-2	-0.50	-0.37	-0.37
4-5	-0.11	-0.27	-0.11
6-7	-0.30	-0.30	-0.24
9-10	-0.17	-0.25	-0.13
3-11	-0.14	-0.14	-0.16
2-3	+0.12	+0.15	+0.15
3-4	+0.06	+0.05	+0.07
5-6	+0.14	+0.18	+0.11
1-6	+0.25	+0.12	+0.21
1-10	+0.13	+0.17	+0.07

electrons was done on the geometry-optimized species of interest to obtain the energies of upper excited states. The bond orders reported are those obtained from the appropriate linear combination of Slater determinants for each CI eigenstate. Single-point ab initio calculations were also performed on the MNDO-optimized geometry of the naphthalenone system using the GAMESS package.[36] Table VIII gives the ΔP values for the naphthalenone system. State energies for species **31***, **33***, and the MNDO and ab initio energies of the triplet excited states for the naphthalenone system are given in Tables 16 and 17 of the supplementary material.

(36) Ab initio calculations were performed with the GAMESS package written by Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC, Berkeley, CA.

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Registry No. **1**, 123208-69-5; **2**, 123208-70-8; **3**, 123208-71-9; **4**, 123208-72-0; **5**, 4528-64-7; **6**, 123208-73-1; **7**, 123208-74-2; **8**, 123208-75-3; **9**, 123208-76-4; **10**, 123208-77-5; **10** (acetate), 123208-78-6; **12**, 123208-79-7; **13**, 123208-80-0; **13** (acetate), 123208-83-3; **14**, 123208-81-1; **15**, 123208-82-2; **17**, 591-31-1; **18**, 123208-84-4; **19**, 123208-85-5; **20**, 72913-59-8; **21**, 123208-86-6; **22**, 123208-87-7; **23**, 123208-88-8; **24**, 123208-89-9; **25**, 123208-90-2; **26**, 123208-91-3; **28**, 123208-92-4; **29**, 123208-93-5; **30a**, 123208-94-6; **30b**, 123285-87-0; **30c**, 123285-88-1; **30d**, 123285-89-2; **48a**, 123208-99-1; **48b**, 123285-90-5; MVK, 78-94-4; HCOOEt, 109-94-4; $BrCH_2COOEt$, 105-36-2; 2-cyclohexen-1-one, 930-68-7; 4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone, 123208-96-8; 4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone, 123208-97-9; 6,6-diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (isomer 1), 123208-95-7; 6,6-diphenyl-3-(phenylseleno)-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (isomer 2), 123208-98-0.

Supplementary Material Available: ORTEP drawings and tables of positional parameters, interatomic distances, bond angles, and temperature factors for compounds **1**, **2**, **4**, **10**, **12**, **13**, **14**, **29**, **30a**, **30b**, and **30c**, primary quantum yield data, and additional state energies (59 pages). Ordering information is given on any current masthead page.

Photochemistry of (±)-4,4a,5,6-Tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone, a Rigid Linear Dienone[1]

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The rigid linear dienone, (±)-4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**), was synthesized, and its photochemistry was studied. Irradiation in *tert*-butyl alcohol through Pyrex resulted in a normal photoenone rearrangement involving the γ,δ double bond and one of the C-6 geminal phenyls to give products **8** and **9**, incorporating the trans and cis diphenyl [3.1.0] bicyclic subunits, respectively. The reaction was observed to parallel that of the parent 4,4-diphenyl-2-cyclohexen-1-one with comparable stereoselectivity for trans-oriented phenyls in the final product. Finally, the angular methyl exerts a strong steric effect on the reaction such that the three-ring in the final product is anti to this group. Observations suggest that the *trans*- and *cis*-diphenyl photoproducts derive from both primary and secondary processes leading to a photostationary mixture which favors the trans isomer. Finally, it was observed that the trans photoproduct is quantitatively converted back to starting dienone with catalytic acid; the cis product was observed to be stable under these same acidic conditions.

Introduction

One branch of our work has focused on extending studies of the photochemical 4,4-diaryl-2-cyclohexen-1-one rearrangement. The parent reaction, depicted in eq 1, was first described[3] in 1964 and has been thoroughly studied.[4] Low-conversion photolysis of **1** at 300-340 nm ($n \rightarrow \pi^*$), leads to the formation of the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**2t** and **2c**, respectively) in a ratio of ca. 140:1 as well as a small amount of 3,4-diphenyl-2-cyclohexen-1-one (**3**). Throughout our efforts in this area, this pioneering study has served as a benchmark for comparison of product structures, reaction ste-

(1) (a) This work was presented at the 197th National ACS Meeting in Dallas, TX, April 1989; ORGN 212. (b) As this work was in progress, we learned that a similar molecule had been studied by H. E. Zimmerman and P. H. Lamers, see accompanying paper. We acknowledge and appreciate several useful suggestions made by the above authors.

(2) (a) Author to whom correspondence regarding the photochemistry should be addressed. (b) Author to whom correspondence regarding the crystallographic determinations should be addressed.

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