170 mg (96%) of (±)-disulfoxide **1a**, mp 185–189°, undepressed with authentic **1a**.

Treatment of 0.65 mg of a 2:1 mixture of meso:(±)-disulfoxides (**1b** and **1a**, respectively) under the above reaction conditions gave no discernible change in the distribution of diastereomers.

B. Tri-n-butylphosphine. A solution of 0.20 g (0.60 mmol) of dichloro sulfoxide **3a** and 0.13 g (0.60 mmol) of tri-*n*-butylphosphine in 8 ml of methanol (under nitrogen) stood at room temperature for 30 min. Work-up (water–dichloromethane extraction) gave 0.125 (68%) of **2a**, mp 134–136°.

A solution of 0.20 g (0.67 mmol) of **2a** and 140 mg (0.67 mmol) of tri-*n*-butylphosphine in 5 ml of methanol (under nitrogen) stood at room temperature for 2 hr. The crystals that formed were filtered and washed with cold ether (3 ml) to give 115 mg of (±)-**1a**, mp 191–193°. The mother liquor yielded an addition 0.04 g of *1a*, total yield 0.165 g (90%).

Treatment of meso disulfoxide **1b** with dilute HCl in methanol in the presence or absence of tri-*n*-butylphosphine or tri-*n*-butylphosphine oxide gave no sign of epimerization to diastereomer **1a**.

Chlorination of Phenylsulfinylphenylsulfonylmethane (4). To a solution of 0.50 g (1.8 mmol) of **4**[11] and 0.50 g of sodium bicarbonate in 12 ml of dichloromethane was added dropwise 0.26 g (1.9 mmol) of sulfuryl chloride in 2 ml of dichloromethane. The reaction mixture was treated as in the analogous case of the chlorination of (±)-**1a**. An NMR spectrum of the crude reaction mixture showed a trace of unreacted **4** and two singlets (4:1 ratio) at δ 5.2 and 5.4, respectively. Crystallization from dichloromethane–hexane gave 310 mg (58%) of the major isomer (**5a**): mp 115–116°; ir ν_{SO_2} 1333 and 1142, $\nu_{S=O}$ 1095 cm^{-1}; ^1H NMR δ 5.25 (s, 1 H) and 7.3–8 (m, 10 H).

Anal. Calcd for $C_{13}H_{11}ClO_3S_2$: C, 49.59; H, 3.52. Found: C, 49.57; H, 3.47.

Further crystallization yielded 50 mg (9%) of the other diastereomer **5b**: mp 124–126°; ir ν_{SO_2} 1340 and 1135, $\nu_{S=O}$ 1092 cm^{-1}; ^1H NMR δ 5.43 (s, 1 H) and 7.3–8 (m, 10 H).

Anal. Calcd for $C_{13}H_{11}ClO_3S_2$: C, 49.59; H, 3.52. Found: C, 49.44; H, 3.60.

A similar result to the above was obtained when chlorination was run in the presence of pyridine instead of sodium bicarbonate.

Phenylsulfinylphenylsulfonyldichloromethane (6). To a solution of 0.300 g (1.07 mmol) of **4** in 12 ml of dichloromethane and 1 ml of pyridine was added 0.40 g of sulfuryl chloride in 2 ml of dichloromethane at room temperature. The solution stood for 1 hr and was worked up as usual. Crystallization from dichloromethane–hexane gave 0.315 g (90%) of **6**: mp 135–136° (from dichloromethane–ethanol); ir ν_{SO_2} 1152 and 1350, $\nu_{S=O}$ 1100 cm^{-1}; ^1H NMR δ 7.3–8.2 (m).

Anal. Calcd for $C_{13}H_{10}Cl_2O_3S_2$: C, 44.58; H, 2.88. Found: C, 44.49; H, 2.82.

Halogenation of Bis(Phenylsulfonyl)methane (7). To a solution of 0.90 g (3.0 mmol) of **7** in 10 ml of dichloromethane and 3 ml of pyridine was added 0.80 g of sulfuryl chloride in 2 ml of dichloromethane. After 1 hr, the mixture was diluted with 50 ml of dichloromethane, washed with 5% sodium bicarbonate (100 ml), and dried ($MgSO_4$) and the solvent was removed by rotary evaporation. Crystallization of the resulting oil gave 1.0 g (85%) of bis(phenylsulfonyl)dichloromethane (**8**), mp 157–159° (lit.[12] mp 159°).

In a similar manner, **7** treated with excess bromine gave an 80% yield of bis(phenylsulfonyl)dibromomethane (**9**), mp 156–158° (lit.[12] mp 159°). This dibromide was converted back to **7** quantitatively by sodium thiosulfate in aqueous acetone.

Registry No.—**1a**, 27995-61-5; **1b**, 27995-60-4; **2a**, 54384-32-6; **2b**, 54423-03-9; **2c**, 54423-04-0; **3a**, 54384-33-7; **4**, 54384-18-8; **5a**, 54384-34-8; **5b**, 54384-35-9; **6**, 54384-19-9; **7**, 3406-02-8; sulfuryl chloride, 7791-25-5; bis(phenylthio)methane, 3561-67-9.

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(8) Attempted iodination with molecular iodine failed under these conditions.
(9) Attempts to extend this reaction as a general method for halogenation of sulfones failed. For example, treatment of *p*-nitrobenzyl phenyl sulfone with sulfuryl chloride in dichloromethane in the presence of pyridine at 0° gave recovered unreacted sulfone. Sulfuryl chloride itself reacts slowly with pyridine to give an amorphous red polymer.
(10) The regioselectivity and stereochemistry of some halogenations of sulfoxides are affected by the presence of base; see (a) K. C. Tin and T. Durst, *Tetrahedron Lett.*, 4643 (1970); (b) G. Tsuchihashi, K. Ogura, S. Iriuchijima, and S. Tomisawa, *Synthesis*, 89 (1971); (c) G. Tsuchihashi and K. Ogura, *Bull. Chem. Soc. Jpn.*, **44**, 1726 (1971).
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Substituent Effects on the Efficiency of Hydrogen Migration vs. Electrocyclic Ring Closure in 1,2-Benzotropilidenes

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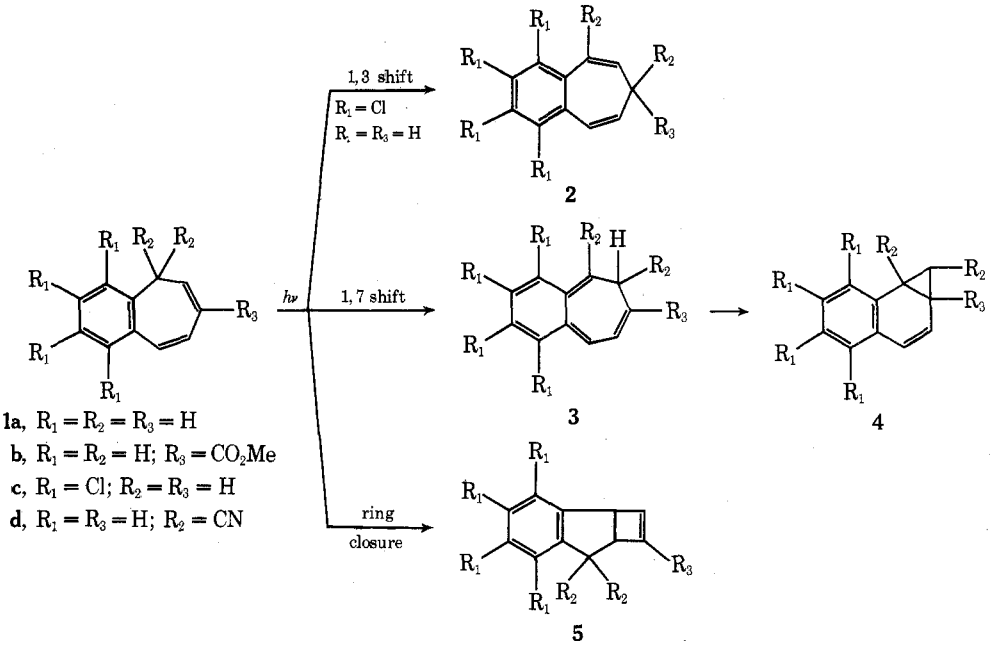
The photochemistry of 5-carbomethoxy- (**1b**), 5-cyano- (**1g**), 5-methyl- (**1e**), and 5-vinyl- (**1f**) 1,2-benzotropilidenes has been studied. Two major processes arise from the singlet excited state of these molecules: (1) production of benzonorcaradienes via a formal 1,7-hydrogen shift followed by tautomerization, and (2) electrocyclic ring closure to produce 6-substituted 2,3-benzobicyclo[3.2.0]hepta-2,6-dienes. While the overall quantum efficiency for the compounds is high (Φ = 0.53–0.85), the relative importance of the two processes is markedly substituent and modestly solvent dependent. The 5-cyano- and 5-carbomethoxy-1,2-benzotropilidenes give major amounts of electrocyclic ring closure while the remaining compounds give primarily hydrogen migration. The increased efficiency of the hydrogen shift process in going from cyclohexane to acetonitrile suggests a polar character in the transition state for this reaction.

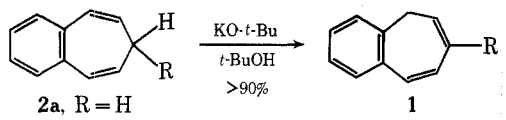
The photochemistry of cycloheptatrienes has been subject to extensive study over the past 10 years.[2] While electrocyclic ring closure of cycloheptatrienes to bicyclo[3.2.0]hepta-2,6-dienes was apparently noted first,[2a] later work established that photochemical 1,7-hydrogen shift occurs some 500 times faster than cyclobutene formation.[2e]



Since the characterization of this process, further examples of hydrogen shifts[2] as well as cases for alkyl[3,4] and phenyl migrations[6] have been reported. More recently the effect of substituents in directing the course of 1,7 shifts[7] and electrocyclic ring closure of substituted cycloheptatrienes has been reported.[8]

In contrast to the extensive investigations in cycloheptatriene photochemistry, only little work has been performed on the photochemistry of its 1,2-benzo derivatives, 1,2-benzotropilidenes. For this system three basic processes have been noted: (1) 1,3-hydrogen shift in **1c**,[9] (2) 1,7-hydrogen shift in **1a**[10] and **1b**,[11] and (3) electrocyclic ring closure in **1a**,[10] **1b**,[11] and **1d**.[12] Interestingly, the ratio of 1,7 shift to electrocyclic ring closure is markedly substituent dependent. For **1a** the 1,7 shift is virtually the exclusive process, while for **1b** the ring-closure reaction is highly favored. In our study of substituent effects on benzonorcaradiene photochemistry, it became important to know the basic photochemical reactions of substituted 1,2-benzotropilidenes. In this connection we have studied the photochemistry of several 5-substituted 1,2-benzotropilidenes. Since we have completed our work in this area and the photochemistry of the compounds is of interest in its own right, we report here details of the ancillary investigation.

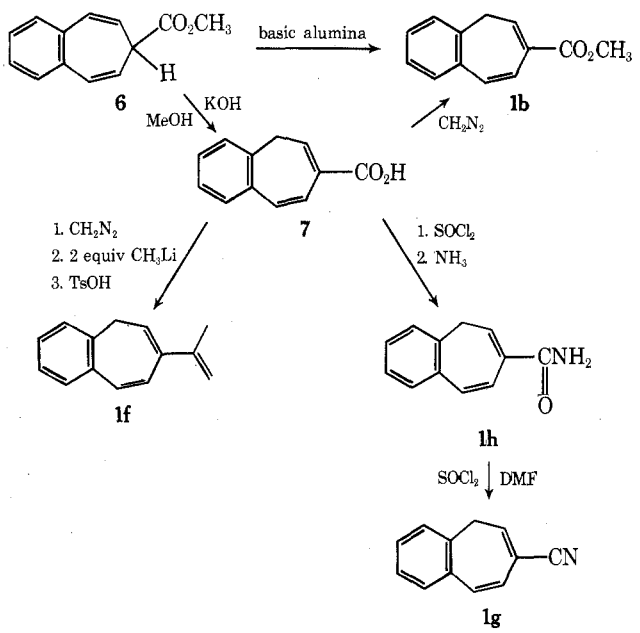
Synthesis of 5-Substituted 1,2-Benzotropilidenes. The synthesis of pure 1,2-benzotropilidenes was based on the higher thermodynamic stability of the 1,2 isomer vs.



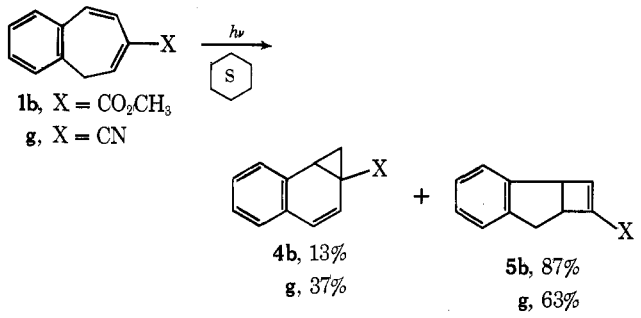
the readily available 3,4-benzotropilidenes.[13] For the unsubstituted and 5-methyl compounds, base-catalyzed isomerization of the 3,4 isomers afforded the corresponding 1,2 isomers in >90% yield. The more substituted systems were prepared from the 7-carbomethoxy-3,4-benzotropilidene as outlined in Scheme I.

Preparative Irradiation of 1,2-Benzotropilidene. The products and mechanism of 1,2-benzotropilidene irradiation were extensively studied by Pomerantz and Gruber,[10] who established by deuterium labeling that a formal 1,7 shift occurred, producing benzonorcaradiene as a primary product. Since the approximate quantum yield they reported seemed low relative to the values we had measured for similar systems (vide infra), we briefly investigated the products of the irradiation and redetermined the quantum efficiency for the process. Our reinvestigation was essentially in agreement with the results reported except that the quantum efficiency for benzonorcaradiene formation was found to be substantially higher ($\Phi = 0.79$) than the ca. 0.1 previously reported.

Scheme I
Synthesis of 5-Substituted 1,2-Benzotropilidenes

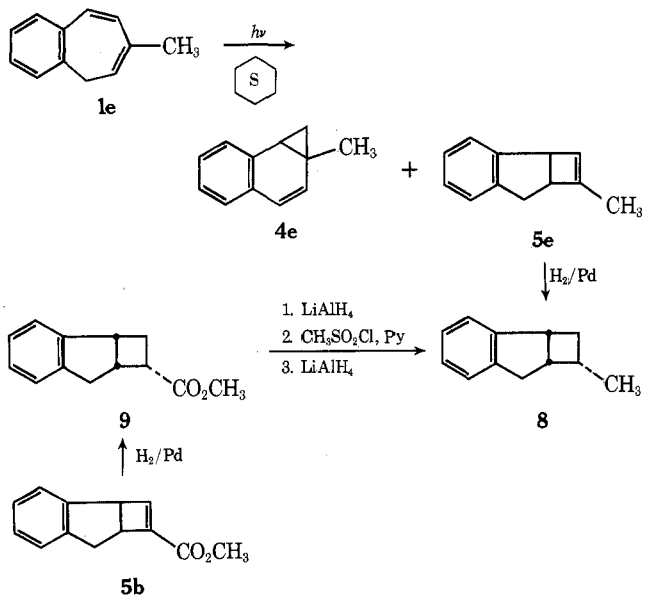


In contrast to the parent hydrocarbon, irradiation of the 5-carbomethoxy compound, **1b**, afforded only minor amounts of benzonorcaradiene, the major process being electrocyclic ring closure. The structures of the products were established by NMR and ir comparison with the known compounds.[13a] In view of the large alteration in product ratio between **1a** and **1b**, a modest number of systems were examined to establish the nature of substituent as it affected the product ratio. Irradiation of the 5-cyano compound, **1g**, produced a mixture of two products in yields of 37 and 63%, the structures **4g** and **5g** being as-



signed to these products on the basis of their spectroscopic properties. Thus, in the NMR **4g** showed the aromatic hydrogens as a multiplet at τ 2.94 and the vinyl hydrogens as a clean AB quartet [τ 3.80 (d, J = 10 Hz, 1 H), 4.03 (d, J = 10 Hz, 1 H)]. The benzylic cyclopropyl [τ 7.08 (J = 11, 7 Hz)], the exo cyclopropyl [τ 8.09 (J = 11, 4 Hz)], and the endo cyclopropyl [τ 9.79 (J = 7, 4 Hz)] appeared as clean doublets of doublets. The NMR spectrum of **5g** was equally informative, showing 1-vinyl hydrogen as a singlet at τ 3.21, one bridgehead as a multiplet at τ 5.75–5.85, a second bridgehead as a multiplet centered at τ 6.29, and the methylene group as a doublet at τ 7.03 (J = 6 Hz). The 5-cyano group then, while showing an altered ratio from the parent system, is less selective than the 5-carbomethoxy group.

While it was originally felt that alkyl substitution at the 5 position would have virtually no effect on product distribution, the availability of the 5-methyl compound dictated an examination of its photochemistry. Irradiation of **1e** at 350 nm led to a time-invariant mixture of two products in an 80:20 ratio. The major product was established as **4e** by spectroscopic comparison with the known compound.[13b] Spectroscopic data suggested **5e** as the structure of the minor product but did not rigorously exclude an alternate structure, 7-methyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene. However, the minor product was rigorously established as **5e** by relating it to the known compound, **5b**, as shown.

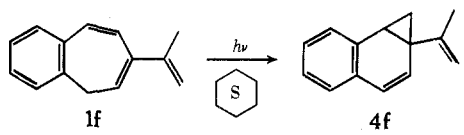


The increased amount of cyclobutene in the cases of **1b**, **1g**, and **1e** prompted us to examine a compound having a substituent which would stabilize the double bond in the cyclobutene product, yet one with much less electron-withdrawing character than a nitrile or carbomethoxy moiety. Irradiation of **1f** at 300 nm through Pyrex afforded up to 70% conversion of a single product. Preparative VPC of the reaction mixture afforded a 68% isolated yield of a compound assigned as **4f** on the basis of its spectroscopic properties. Thus, the NMR showed the aromatic protons as a broad multiplet at τ 3.0, the conjugated vinyl protons as a clean AB [τ 3.72 and 3.93 (J = 10 Hz)], the vinyl methylene as a multiplet at τ 5.2, the methyl group as a multiplet at τ 8.25, and the benzylic cyclopropyl, exo cyclopropyl, and endo cyclopropyl as doublets of doublets centered at τ 7.63 (J = 10, 5.5 Hz), 8.38 (J = 10, 3.5 Hz), and 10.02 (J = 5.5, 3.5 Hz).

Table I
Quantum Yields for Irradiation of Substituted 1,2-Benzotropilidenes in Cyclohexane

Compd	$\Phi_{disappearance}$	$\Phi_{cyclobutene}$	$\Phi_{norcaradiene}$
1a parent	0.85	*a*	0.79
1b 5-carbomethoxy	0.62	0.61	0.088
1e 5-methyl	0.65	0.11	0.42
1f 5-isopropenyl	0.53	*a*	0.54
1g 5-cyano	0.59	0.37	0.21

[a] Product not detected.



Quantum Yields of 1,2-Benzotropilidene Systems. To establish the effect of the substituent on the overall efficiency of the 1,2-benzotropilidene system, quantum yield determinations were made. As is evidenced by the data of Table I, the quantum yields for reaction in the substituted systems all fall in the range 0.53–0.65, with the parent system undergoing the most efficient reaction (Φ = 0.85). Thus, the substituents are not dramatically promoting some nonreactive decay process in the excited state, but simply altering the rates of the two photochemical processes.

Quantum Yields as a Function of Solvent. In the course of these studies a modest solvent effect on the ratio of the products formed from the 1,2-benzotropilidene irradiations was noted. Thus, the quantum efficiencies for the irradiation of **1b**, **1e**, and **1g** were examined in nonpolar media (cyclohexane) and polar media (acetonitrile). As evidenced by the data of Table II, the efficiency of the benzonorcaradiene formation increases by a factor of 1.6–2.0 while that of ring closure behaves less regularly. The overall effect is that the efficiency of the reaction increases in the polar acetonitrile relative to cyclohexane, and this increase is primarily due to a higher efficiency for the benzonorcaradiene formation.

Multiplicity Studies. The change in product ratio as a function of substituent and solvent might be due to excited states of different multiplicity being responsible for the two different photochemical processes. The idea of a triplet state being responsible for cyclobutene formation did not appear unreasonable, since cis–trans isomerization of a 1,2-benzotropilidene would produce a highly strained isomer which might easily undergo thermal electrocyclic ring closure to afford the cyclobutene product. Sensitization studies were only performed on the 5-methyl- and 5-cyano-1,2-benzotropilidenes, since these systems showed appreciable amounts of both types of products; thus a change in product ratio upon sensitization could be readily discerned.

The triplet energies of the 5-substituted 1,2-benzotropilidenes are unknown to our knowledge. However, a reasonable upper limit for their triplet energy would be β-methylstyrene, 59.8 kcal mol^{-1}.[14a,b] One would expect the triplet energy for the 1,2-benzotropilidene system to be in fact

Table II
Quantum Yields for Irradiation of the 5-Carbomethoxy-, 5-Methyl-, and 5-Cyano-1,2-Benzotropilidene in Cyclohexane and Acetonitrile

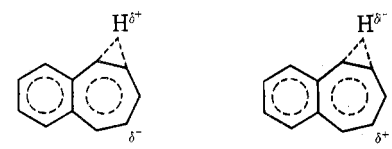
Compd	Solvent	$\Phi_{cyclobutene}$	$\Phi_{norcaradiene}$	$\Sigma\Phi$	$\Phi_{cyclobutene}/\Phi_{norcaradiene}$
1b 5-carbomethoxy	Cyclohexane	0.61	0.088	0.70	6.9
	Acetonitrile	0.64	0.17	0.81	3.7
1e 5-methyl	Cyclohexane	0.11	0.42	0.53	0.26
	Acetonitrile	0.006	0.81	0.82	0.007
1g 5-cyano	Cyclohexane	0.37	0.21	0.58	1.7
	Acetonitrile	0.28	0.44	0.72	0.64

much lower owing to the additional conjugation of a second double bond. Sensitization experiments in these systems encountered difficulties. Thus, we initially hoped to use benzophenone as a sensitizer, since energy transfer to the 1,2-benzotropilidene could be readily established by the quenching of its photoreduction to benzpinacol.[15] However, attempted sensitization of the reaction by benzophenone (E_T = 68.5 kcal mol^{-1}) led to disappearance of the starting compounds but no appearance of products. Since the products **1e** and **1g** were not stable under the sensitization conditions, thioxanten-9-one, Michler's ketone, and 2-acetonaphthone were tried as sensitizers. Only in the case of 2-acetonaphthone (E_T = 59 kcal mol^{-1}) were the products sufficiently stable under the sensitization conditions to make the reaction meaningful. For 2-acetonaphthone a direct irradiation of **1e** was made simultaneously with a sensitized run at 350 nm and the reaction progress followed by VPC. In the time that 60% coversion had been reached in the direct irradiation, less than 2% of products were formed in the sensitized reaction. A similar series of experiments were performed with **1g**, again affording no evidence for a triplet reactant being responsible for products in this system.

Discussion

The results presented here establish that the relative importance of the two major photochemical processes observed for 5-substituted 1,2-benzotropilidenes, namely electrocyclic ring closure or hydrogen shift to eventually produce a benzonorcaradiene, may be strongly altered by the nature of the 5 substituent. We have not detected the 1,3-hydrogen shift in our studies; thus, this process would appear to be of only minimal importance. The inability to sensitize the production of cyclobutene or benzonorcaradiene formation strongly suggests that these processes are originating from an excited singlet state and is in agreement with multiplicity studies on the parent 1,2-benzotropilidene.[10]

An explanation of the manner in which the substituents alter the product ratio in this system is of some interest. Of course, one might argue that the carbomethoxy and cyano groups so alter the electronic character of the 1,2-benzotropilidene excited state that a consistent interpretation for the entire group of substituents would not be expected. On the other hand, several generalizations can be noted. First, the electron-withdrawing conjugating carbomethoxy and nitrile groups favor the cyclobutene formation, while all the other substituents give major amounts of benzonorcaradienes. It is obvious that the increased amount of cyclobutene formation is not simply due to the substituent stabilizing the double bond in the product.[16] Had this been the case, then the methyl group should have been as effective as carbomethoxy, and the 5-vinyl system should certainly have given rise to appreciable amounts of electrocyclic ring closure. The increased efficiency of the benzonorcaradiene formation with increasing solvent polarity suggests that some stabilization for this transition state operates in the more polar medium. With these observations in mind, a possible rationale for the substituent effects should be noted. The increased efficiency of the benzonorcaradiene formation with increasing solvent polarity could be accommodated by either a proton-like migration in a "benzotropilium anion-like" π system, **10**, or a hydride-like migration in a "benzotropilium cation-like" π system, **11**.[17] A transi-



10 11

tion state of the latter type would readily accommodate the low efficiency of the 1,7-hydrogen migration in the 5-carbomethoxy and 5-cyano systems, since a positively charged π system would be destabilized by these moieties.[18] Thus, for this limited number of substituents, invoking a transition state such as **11** would rationalize both the substituent and solvent effect data. Obviously much additional work remains to be done before a clear interpretation of the substituent effect is at hand.

Experimental Section

Melting points were taken in a Thomas-Hoover Unimelt apparatus and are corrected. Infrared spectra were taken as neat films or KBr pellets with a Perkin-Elmer Model 137 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60A or a Jeolco MH-100 instrument in chloroform-*d* or carbon tetrachloride and are reported in τ units using tetramethylsilane as internal standard. Mass spectra were obtained with an AEI-MS-9 instrument with an ionizing potential of 70 eV. Preparative irradiations were performed with a Rayonet photochemical reactor equipped with 16 RPR-3000 Å lamps or 16 RPR-3500 Å lamps. Gas chromatographic analyses were performed on a Varian Aerograph Model 1200 or 1400 flame ionization instrument using the following columns: column A, 25 ft × 0.125 in., 5% SE-30 on DMCS-treated 60/80 Chromosorb G; column B, 12 ft × 0.125 in., 5% PDEAS on 60/80 Chromosorb W; column C, 10 ft × 0.25 in., 10% PDEAS on 60/—] Chromosorb W; column D, 5 ft × 0.125 in., 3% SE-30 on 100/120 Varaport 30; column E, 25 ft × 0.375 in., 5% SE-30 on DMCS-treated 60/80 Chromosorb G; column F, 10 ft × 0.25 in., 5% SE-30 on 60/80 Chromosorb; column G, 13 ft × 0.125 in., 5% SE-30 on DMCS-treated 60/80 Chromosorb G. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. NMR spectra were obtained at 60 MHz unless otherwise noted.

1,2-Benzotropilidene (1a). A solution of 0.6 *M* potassium *tert*-butoxide in *tert*-butyl alcohol (20 ml) was added to 200 mg of **5a**[13a] in 5 ml of *tert*-butyl alcohol and refluxed for 3 hr on a steam bath. The cooled solution was diluted with water and extracted with ether. Removal of the ether yielded an orange oil which was chromatographed on neutral Woelm alumina (2 × 10 cm column, slurry packed with hexane). One fraction was collected, 150 ml, 180 mg (90%) of **1a** which was greater than 99% pure by VPC analysis (column A).[20]

5-Methyl-1,2-benzotropilidene (1e). To an ethereal solution containing 0.298 g of **2e**[13a] was added 25 ml of 0.6 *M* potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was refluxed in a steam bath for 1.5 hr under nitrogen; the cooled reaction mixture was diluted with water and extracted with ether. The organic layer was washed with water, then with saturated sodium chloride solution, dried over calcium sulfate, and concentrated, yielding 0.290 g of an orange oil. The oil was chromatographed on Alcoa alumina (0.25 × 10 in., 2% ether–hexane). One fraction was collected (50 ml), yielding 0.267 g (90%) of **1e** greater than 99% pure by VPC (column A): ir (neat) 3.27 (m), 3.36 (s), 6.75 (m), 6.90 (s), 7.05 (m), 11.88 (m), 12.71 (s), 13.34 (s), 13.64 (m), and 13.85 μ (m); NMR (CCl_4) τ 2.93 (s with shoulder at 2.99, 4 H), 3.13 (d, J = 11 Hz, 1 H), 3.78 (d, J = 11 Hz, 1 H), 4.60 (t, broad, J = 7 Hz, 1 H), and 7.12 (d, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.45; H, 7.73.

5-Carbomethoxy-1,2-benzotropilidene (1b). A solution of 0.473 g of **6**[13b] in 2 ml of 4% ether–hexane was passed through a column of Woelm activity III basic alumina (2 × 23 cm column, slurry packed with 4% ether–hexane). Elution proceeded as follows: 4% ether–hexane, 100 ml, nil; 4% ether–hexane, 150 ml, 0.424 g (89%) of **1b** as a colorless oil homogeneous by NMR and VPC (column B) analysis: ir (neat) 3.43 (w), 5.80 (s), 6.13 (m), 6.26 (m), 6.98 (s), 7.95 (s), 9.28 (s), 12.41 (s), 13.36 (s), and 13.93 μ (s); NMR (CCl_4) τ 2.61–3.28 (m, 7 H), 6.30 (s, 3 H), and 6.98 (d, J = 7 Hz, 2 H).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00. Found: C, 78.24; H, 6.16.

1,2-Benzotropilidene-5-carboxylic Acid (7). A potassium hydroxide–methanol solution (6.0 g of potassium hydroxide, 24 ml of methanol, and 40 ml of water) was added to a solution of 4.2 g (0.021 mol) of **6** in 20 ml of ether at room temperature. The solution immediately turned blood red and gradually faded to a pale yellow. The ether layer was distilled and the remaining mixture refluxed at 90° for 4 hr. The cooled hydrolysis solution was extracted with 30 ml of ether. The aqueous layer was decolorized with Norit, acidified to a pH of 2 with concentrated hydrochloric acid, and extracted with a hot benzene–methylene chloride solution. The organic layer was washed with saturated brine solution, dried over calcium sulfate, and concentrated in vacuo, yielding 3.77 g (96%) of **7**, mp 196–198.5°. Two recrystallizations from ethyl acetate–hexane yielded the analytical sample: mp 203.8–204.8°; NMR (Me_2SO-d_6) τ 2.75 (broad s, 4 H), 2.90–3.35 (five-line multiplet, 3 H), and 6.98 (d, J = 7 Hz, 2 H); ir (KBr) 3.2–3.5 (m), 3.7–3.9 (m), 5.9 (s), 7.0 (m), 7.55 (m), 7.85 (s), 11.1 (m), 12.42 (s), 12.87 (s), 13.13 (s), 13.40 (m), and 13.9 μ (s).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.41; H, 5.38. Found: C, 77.20; H, 5.40.

1,2-Benzotropilidene-5-carboxamide (1h). A three-molar excess of thionyl chloride was added to a refluxing mixture of 3.38 g (0.0182 mol) of **7** in 20 ml of dry benzene. When the acid completely dissolved, ir analysis showed that there was complete conversion to the acid chloride. The solvent and excess thionyl chloride were removed in vacuo, yielding a brown oil which was taken up in 100 ml of anhydrous ether. Dry ammonia was bubbled through the solution until the mixture showed pH 10. The mixture was diluted with water and extracted with methylene chloride; the organic layer was washed with saturated sodium chloride, dried over calcium sulfate, and concentrated in vacuo, yielding 2.53 g (77.5%) of the amide, mp 155–165°. Two recrystallizations from ethanol–water yielded the analytical sample: mp 161–162°; ir (KBr) 2.94 (m), 3.10 (m), 6.01 (s), 6.18 (s), 6.30 (m), 7.00 (m), 7.11 (m), 8.95 (m), 9.06 (m), 12.36 (m), and 13.35 μ (s).

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.84; H, 5.95; N, 7.57. Found: C, 77.37; H, 6.00; N, 7.57.

5-Cyano-1,2-benzotropilidene (1g). Thionyl chloride, 4.05 ml (0.0563 mol), dissolved in approximately 1 ml of *N,N*-dimethylformamide was added dropwise over 1 min to a stirred solution of 2.61 g (0.0141 mol) of the amide in 10 ml of *N,N*-dimethylformamide maintained at 0° in the dark under a nitrogen atmosphere. The solution was allowed to warm to room temperature and stirred for 48 hr. The solvent was distilled from the reaction mixture and the remaining oil was diluted with water and extracted with 50% ether–benzene. The organic layer was washed with water (2 × 30 ml) and saturated sodium chloride, dried over calcium sulfate, and concentrated, yielding 2.5 g of a brown oil. The oil was chromatographed on silica gel (2.3 × 60 cm column, slurry packed in 5% ether–hexane). Elution proceeded as follows: 5% ether–hexane, 250 ml, nil; 5% ether–hexane, 525 ml, 1.52 g (64.5%) of **1g**, mp 64–65°. Two recrystallizations from ether–hexane yielded the analytical sample: mp 65.9–66.8°; ir (KBr) 4.50 (m), 6.35 (m), 6.77 (m), 11.15 (m), 11.35 (m), 12.30 (w), 12.60 (s), 13.16 (s), 13.4 (m), and 13.84 μ (m); NMR (CCl_4) τ 2.81 (broad singlet with shoulder at 2.9, 5 H), 3.5–3.8 (three lines, broad, 2 H), and 6.90 (d, J = 7.5 Hz, 2 H).

Anal. Calcd for $C_{12}H_9N$: C, 86.22; H, 5.39; N, 8.38. Found: C, 85.90; H, 5.46; N, 8.38.

5-Isopropenyl-1,2-benzocycloheptatriene (1f). An ethereal diazomethane solution was added dropwise to a partial solution of 0.4 g (0.215 mol) of **7** in 2 ml of dry ether. When the acid had dissolved the solution was concentrated, dissolved in 25 ml of dry tetrahydrofuran, and cooled to −78° by an acetone–Dry Ice bath. To this solution was added 2.35 ml (0.514 mmol) of a 2.2 *M* methyllithium solution over a 10-min period and the reaction mixture was stirred for 1 hr. The reaction mixture was then quenched with 75 ml of water and extracted with ether. The organic layer was washed with water (2 × 20 ml) and saturated sodium chloride, dried over calcium sulfate, and concentrated. The ir of the oil indicated incomplete conversion; so the reaction was executed a second time with the same amount of reagents. After another hour of reaction time, the reaction was worked up as before. The crude alcohol, a clear oil, was dissolved in 50 ml of dry benzene to which was added 15 mg of *p*-toluenesulfonic acid and the mixture was heated at 50° for 2 hr. The reaction mixture was concentrated to an oil which was dissolved in ether and washed with water (2 × 20 ml) and saturated sodium chloride, dried over calcium sulfate, and concentrated, yielding 385 mg of a dark oil. The oil was chromatographed on Alcoa alumina (1 × 30 cm column, hexane). One fraction of 500 ml was taken, yielding 250 mg (64%) of **1f**, mp 65–70°. Two recrystallizations from ethanol–hexane yielded the analytical sample: mp 77.5–78.5°; ir (KBr) 6.22 (m), a series of three medium bands between 6.71 and 7.3 with a fourth strong band at 6.9, 11.25 (s), 11.40 (m), 11.6 (m), 12.5 (s), 13.3 (s), 13.6 (m), and 14.4 μ (m); NMR (CCl_4) τ 2.91 (m, 5 H), 3.35 (d, J = 12 Hz, 1H), 4.2 (broad t, J = 7.5 Hz, 1 H), 5.09 (broad d, J = 6 Hz, 2 H), 7.0 (d, J = 7.5 Hz, 2 H), and 8.12 (d, J = 1 Hz, 3 H).

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.93; H, 7.56.

Irradiation of 5-Carbomethoxy-1,2-benzotropilidene (1b). A solution of 252 mg of **1b** in 70 ml of cyclohexane was degassed for 15 min with purified nitrogen, then irradiated in a stoppered quartz test tube for 57 min with a bank of 16 RPR-3500 Å lamps in a merry-go-round apparatus. By VPC two products were produced, one major and one minor. The irradiation mixture was separated by preparative VPC (column C at 130°). The major product had ir and NMR spectra identical with those of 6-carbomethoxy-2,3-benzobicyclo[3.2.0]hepta-2,6-diene. The minor product had ir and NMR spectra identical with those of 6-carbomethoxy-2,3-benzonorcaradiene.

In a similar experiment, a solution of 168.0 mg of 5-carbomethoxy-1,2-benzotropilidene and 24.5 mg of eicosane in 45 ml of cyclohexane was prepared. The solution was degassed for 30 min with purified nitrogen, and 20 ml of it was irradiated in a Pyrex test tube with a bank of 16 RPR-3500 Å lamps in a merry-go-round apparatus for 65 min. By VPC analysis the total product yield was quantitative: 6-carbomethoxy-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 85.7%; 6-carbomethoxy-2,3-benzonorcaradiene, 14.3%.

Irradiation of 5-Cyano-1,2-benzotropilidene (1g). A solution containing 0.7 g of **1g** in 150 ml of purified cyclohexane was irradiated in the Rayonet with 350-nm light. Periodic analysis of the reaction by VPC (column D at 150°) showed that two products were formed at a constant ratio of 60:40. After 148 min of irradiation, VPC analysis indicated complete consumption of starting material. The reaction mixture was concentrated to afford a light yellow solid which was chromatographed on silica gel (1.7 × 88 cm column, slurry packed, 3% ether–hexane). Elution proceeded as follows: 3% ether–hexane, 250 ml, nil; 5% ether–hexane, 190 ml, nil; 5% ether–hexane, 330 ml, 0.309 g (44%) of **5g**, mp 69–71°.

Recrystallization of this material from ether–hexane yielded the analytical sample: mp 71.5–72.5°; NMR (CCl_4) τ 2.95 (s, 4 H), 3.21 (s, 1 H), 5.75–5.85 (broad s, 1 H), 6.29 (five-line multiplet, 1 H), and 7.03 (d, J = 6.0 Hz, 2 H); ir (KBr) 3.39 (m), 4.5 (s), 6.35 (m), 6.8 (s), 7.02 (m), 8.15 (s), 10.2 (m), 10.45 (m), 11.1 (m), 11.4 (m), 11.65 (m), 12.15 (m), 12.69(m), and 13.35 μ (s).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.65; H, 5.42; N, 8.23.

Continued elution with 325 ml of 7% ether–hexane yielded 0.183

g (26%) of **4g**. Recrystallization of this material from 10% ether–hexane yielded the analytical sample: mp 59–60°, NMR (CCl_4) τ 2.94 (m, 4 H), 3.8 (d, J = 10 Hz, 1 H), 4.03 (d, J = 10 Hz, 1 H), 7.08 (d of d, J = 11, 7 Hz, 1 H), 8.09 (d of d, J = 11, 4 Hz, 1 H), and 9.79 (d of d, J = 7, 4 Hz, 1 H); ir (KBr) 4.5 (s), 6.79 (m), 6.93 (m), 9.51 (s), 12.31 (s), 12.71 (s), 13.0 (s), 13.50 (m), and 13.95 μ (m).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.49; H, 5.34; N, 8.12.

Preparative Irradiation of 5-Methyl-1,2-benzotropilidene (1e). A solution of 0.179 g of **1e** in 20 ml of purified cyclohexane was degassed for 10 min with nitrogen and irradiated for 2 hr in a Pyrex test tube with a 400-W Hanovia lamp. The solvent was removed in vacuo and the resulting oil was purified by preparative vpc (column E at 160°). Peak 1, **5e** (28%): ir (neat) 6.12 (m), 6.75 (s), 6.95 (s), 8.0 (s), 10.25 (m), 12.5 (s), and 13.40 μ (s); NMR (CCl_4) τ 3.00 (s, 4 H), 4.07 (m, 1 H), 6.0 (m, 1 H), 6.60 (m, 1 H), 7.15 (broad d, J = 6.0 Hz, 2 H), and 8.31 (m, 3 H).

Anal. Calcd for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.00; H, 7.97.

The second peak, isolated in 53% yield, was identified as **4e** by ir and NMR comparison with the known compound.[13b]

6-*endo*-Carbomethoxy-2,3-benzobicyclo[3.2.0]hept-2-ene (9). A solution of 5-carbomethoxy-1,2-benzotropilidene (**1b**) in 200 ml of purified cyclohexane in a Pyrex vessel was inrradiated for 3 hr with a bank of 16 RPR-3500 Å lamps. After removal of the cyclohexane in vacuo the residue was dissolved in 100 ml of ethyl acetate, 20 mg of 5% Pd/C was added, and the mixture was hydrogenated for 2 hr on a Parr hydrogenation apparatus. The residue from the hydrogenation was chromatographed on 120 g of silica gel (2.3 × 36 cm column slurry packed in 2% ether–hexane). Elution proceeded as follows: 0.2 l., 2% ether–hexane, nil; 0.1 l., 5% ether–hexane, nil; 0.5 l., 5% ether–hexane, 0.48 g (48%) of **9** as a clear oil: ir (neat) 3.40 (m), 5.76 (s), 6.76 (m), 6.86 (m), 6.97 (m), 7.40 (m), 8.33 (br), 8.49 (br), and 13.30 μ (s); NMR (CCl_4) τ 2.72 (s, 4 H), 6.0–6.75 (m, 3 H), 6.38 (s, 3 H), 6.75–7.00 (m, 2 H), and 7.2–7.7 (m, 2 H). The material was hydrolyzed to its carboxylic acid: mp 101.5–104°; ir (KBr) 2.7–4.3 (br, s), 5.83 (s), 7.03 (m), 7.43 (m), 8.08 (s), 8.13 (s), 10.60 (m), 13.22 (s), and 13.50 μ (m).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.43; H, 6.30.

6-*endo*-Hydroxymethyl-2,3-benzobicyclo[3.2.0]hept-2-ene. A solution of **9** (0.566 g, 2.78 mmol) in 15 ml of anhydrous ether was added dropwise over 0.5 hr to a slurry of 0.200 g (5.27 mmol) of lithium aluminum hydride in 15 ml of anhydrous ether. Following addition, the mixture was refluxed for 10 hr. Subsequently the excess hydride and reduction complex were decomposed by cautious addition of water (2.4 ml). The organic portion was decanted and the alumina salt was dissolved in 5% HCl (20 ml). The aqueous acid solution was extracted with ether (2 × 20 ml), and the combined organic layers were washed with saturated sodium chloride solution (30 ml) and dried over anhydrous calcium sulfate. After removal of the ether by distillation, the remaining light yellow oil was chromatographed on deactivated silica gel (2.0 × 28 cm column slurry packed with 30% ether–hexane). Elution with 30% ether–hexane proceeded as follows: 50 ml, 0.0110 g of mixture of an unidentified oil and a small amount of unreacted ester; 100 ml, 0.432 g (89%) of 6-*endo*-hydroxymethyl-2,3-benzobicyclo[3.2.0]-hept-2-ene: ir (neat) 2.93 (s), 3.38 (s), 3.46 (m), 6.80 (m), 9.47 (m), 9.66 (m), 9.83 (m), 10.03 (m), and 13.39 μ (s); NMR ($CDCl_3$) τ 2.88 (s, 4 H), 6.0–7.1 (series of overlapping m, 6 H), 7.1–7.7 (m, 1 H), and 8.2–8.7 (m, 2 H).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 8.20.

6-*endo*-Methyl-2,3-benzobicyclo[3.2.0]hept-2-ene (8). To an ice-cooled solution of 0.306 g (1.76 mmol) of 6-*endo*-hydroxymethyl-2,3-benzobicyclo[3.2.0]hept-2-ene in 10 ml of dry, freshly distilled pyridine, 0.5 ml of freshly distilled methanesulfonyl chloride was added dropwise over 0.25 hr. After stirring for 5 hr, the reaction mixture was poured onto 30 g of ice in 30 ml of water and extracted with ether (2 × 50 ml). The organic layer was washed with 5% hydrochloric acid (3 × 30 ml) and saturated sodium chloride solution (30 ml), and dried over anhydrous calcium sulfate. The ether was removed in vacuo to give ca. 450 mg (100%) of the mesylate. Infrared spectroscopic analysis showed that no alcohol remained. The mesylate was then dissolved in anhydrous ether (10 ml) and added slowly to an ice-cooled slurry of 0.200 g of lithium aluminum hydride in 10 ml of ether. Following addition, the ice bath was removed and the mixture was refluxed for 14 hr. After cooling to room temperature, the excess hydride was decomposed by cautious addition of water. The organic portion was removed by filtration and the alumina salt was dissolved in 5% hydrochloric acid (20 ml). The aqueous acid solution was extracted with ether (2 × 20 ml) and the combined organic layers were washed with saturated sodium chloride solution (30 ml) and dried over anhydrous calcium sulfate. After removal of ether by distillation, there remained 247 mg of liquid. Vapor phase chromatography (column F at 110°) gave pure 6-*endo*-methyl-2,3-benzobicyclo[3 2.0]hept-2-ene: ir (CS_2) 3.26 (m), 3.38 (s), 7.34 (m), 7.63 (m), 8.10 (m), 8.36 (m), 8.70 (m), 9.36 (m), 9.82 (m), 10.26 (m), 10.35 (m), 13.55 (s), and 14.16 μ (m); NMR (CCl_4) τ 2.98 (s, 4 H), 6.0–7.5 (aliphatic absorption with broadened s at τ 6.98, 6 H), 8.52 (m, 1 H), and 9.04 (d, J = 6.5 Hz, 3 H); mass spectrum m/e (rel intensity) 158 (M, 6), 115 (20), 116 (B, 100), 117 (10), 128 (8), and 129 (9).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.67; H, 8.83.

Hydrogenation of 6-Methyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (5e). An 8-mg sample of **5e** was dissolved in 10 ml of ethyl acetate containing 2 mg of 5% Pd/C and the mixture was hydrogenated for 8 hr at atmospheric pressure. After filtration through Celite, the ethyl acetate was removed by distillation and the hydrogenation product was isolated by preparative VPC (column F at 130°). The purified material showed a VPC retention time and ir spectra (CCl_4 and CS_2) identical with those of the synthesized authentic sample.

2-Acetonaphthone Sensitized Irradiation of 5-Methyl-1,2-benzotropilidene (1e). Stock solutions of 0.2 M 2-acetonaphthone in benzene and 0.02 M **1e** in benzene were prepared. For a typical run 1.5 ml of 0.2 M 2-acetonaphthone and 0.2 ml of 0.0016 M **1e** were placed in a Pyrex test tube and diluted to 2 ml with benzene. In a matching test tube was placed 0.2 ml of 0.02 M **1e**

Table III
Quantum Yield Data for 1,2-Benzotropilidenes

Compd	Light absorbed, mE	Concn, $M \times 10^3$	% conversion	$\Phi_{disappearance}$	$\Phi_{cyclobutene}$	$\Phi_{norcaradiene}$
1a[c]	0.139	10.2	15	0.80	*a*	0.73
1a[c]	0.126	10.2	16	0.90	*a*	0.85
1b[c]	0.214	18.4	12	*b*	0.62	0.09
1b[c]	0.287	18.4	15	0.60	0.57	0.08
1b[c]	0.266	18.4	17	0.61	0.68	0.09
1b[c]	0.263	18.4	17	0.65	0.64	0.08
1g	0.0873	15.7	25	0.57	0.36	0.21
1g	0.0434	15.7	13.5	0.61	0.37	0.22
1e	0.0117	16.5	13.5	0.64	0.12	0.45
1e	0.0041	16.5	4.3	0.59	0.10	0.38
1f	0.0298	16.5	10.0	0.58	*a*	0.59
1f	0.0368	16.5	10.0	0.47	*a*	0.49

[a] Product was not detected. [b] Value was not determined. [c] This value was measured in a 65-ml actinometer cell. All other numbers determined in a 12-ml cell.

and the volume was made up to 2 ml with benzene. At these concentrations the uv absorptions of the sensitizer and substrate are such that the tropilidene can capture <0.5% of the incident light. Both solutions were degassed for 10 min with a stream of nitrogen and then irradiated simultaneously in the Rayonet with 350-nm light. The reaction was followed by VPC (column G at 125°) with the following results. In the time that the unsensitized reaction had reached 60% conversion to products the sensitized run showed ~2% products and ca. 50% loss of **1e**.[21] To the direct run was added 0.051 g of 2-acetonaphthone to bring the solution to 0.15 *M* sensitizer and the solution was irradiated again. VPC analysis showed that the products were essentially stable to the sensitizer.

2-Acetonaphthone Sensitized Irradiation of 5-Cyano-1,2-benzotropilidene (1g). The same procedure and concentrations were used as described for **1e**. This irradiation was monitored with column D at 145°, giving the following results. At a time in which the direct irradiation had gone to 94% conversion, the sensitized reaction gave <2% products. Sensitizer (0.051 g) of 2-acetonaphthone was then added to the direct reaction and irradiated again. VPC analysis showed that both photoproducts were stable to the sensitizer.

Benzophenone Sensitization of 5-Methyl-1,2-benzotropilidene (1e). Into three matched test tubes were placed the following solutions: (1) 0.15 *M* benzophenone and 0.15 *M* benzhydrol in 2 ml of benzene; (2) 0.15 *M* benzophenone, 0.15 *M* benzhydrol, and 1.7×10^{-3} *M* of **1e** in 2 ml of benzene; and (3) 1.73×10^{-3} *M* **1e** in benzene. The concentrations in tube 2 ensured that benzophenone was capturing greater than 99% of the light. Irradiation for 30 min at 3500 Å followed by VPC analysis showed that in tube 3 there was 70% conversion to products while in tube 2 no product was formed yet starting material had essentially disappeared. Uv analysis for remaining benzophenone in tube 2 using tube 1 as a standard indicated that the disappearance of benzophenone in tube 2 had been quenched by ~70%. Thus, energy transfer had occurred from benzophenone to **1e**. Unfortunately, when a reaction mixture consisting of 70% **4e** and 30% **1e** was irradiated in the presence of 0.15 *M* benzophenone and 0.15 *M* benzhydrol, VPC analysis indicated that both **4e** and **1e** disappeared with no production of volatile products.

Preparative Irradiation of 5-Isopropenyl-1,2-benzocycloheptatriene (1f). A degassed solution of 0.200 g of **1f** in 100 ml of spectral grade cyclohexane was irradiated for 4 hr in the Rayonet with 300-nm light. Periodic analysis of the reaction by VPC (column D at 150°) showed formation of one major product. When the reaction reached 60% completion the solution was concentrated and the resultant oil was purified by preparative VPC (column F at 145°). The recovered starting material was identical with the authentic material by NMR, while the photoproduct (68% yield in an extended irradiation) had the following spectral data: NMR (CCl_4) τ 3.0 (broad m, 4 H), 3.72 (d, J = 10 Hz), 3.93 (d, J = 10 Hz, 2 H), 5.2 (m, 2 H), 7.63 (d of d, J = 10, 5.5 Hz, 1 H), 8.25 (m, 3 H), 8.38 (d, J = 3.5 Hz, 1 H, the other portion of the doublet lies under the methyl absorption), 10.02 (d of d, J = 6, 3.5 Hz, 1 H); ir (neat) 6.1 (m), 6.71 (m), 6.90 (m), 11.0 (m), 12.8 (s), 13.1 (m), and 13.5 μ (s). Exact mass analysis: calcd *m/e* 182.10954440; found *m/e* 182.10978794; difference, 0.00024.

Quantum Yield Determinations. These were made as previously described[13b] using either a 12-ml or 65-ml actinometer cell. The pertinent data from these determinations are presented in Table III.

Registry No.—**1a**, 264-08-4; **1b**, 35393-09-0; **1e**, 54276-79-8; **1f**, 54276-80-1; **1g**, 54276-81-2; **1h**, 54276-82-3; **4f**, 54276-83-4; **4g**, 54276-84-5; **5a**, 18511-42-7; **5e**, 54276-85-6; **5g**, 54276-86-7; **6**, 31399-17-4; **7**, 54276-87-8; **8**, 54276-88-9; **9**, 54276-89-0; **9** free acid, 54276-90-3; **9** OH analog, 54276-91-4.

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(16) J. Hine and N. W. Flachskam, *J. Am. Chem. Soc.*, **95**, 1179 (1973).

(17) This type of rationalization is not entirely new, since a charged transition state employing a hydride shift has been suggested to explain the increased rate of thermal isomerization of some 7-substituted tropilidenes.[2g]

(18) A referee has noted that the quantum yields for the 1,7-shift product decrease in going from the parent to the 5-methyl to the 5-vinyl system and asks if this is consistent with transition state **11**. We wish to note here that this trend is not inconsistent with our consideration of **11**, since a methyl has been considered as an electron-withdrawing group inductively[19] and vinyl is certainly electron-withdrawing inductively. However, we do not feel strongly about this point.

(19) V. W. Laurie and J. S. Muenter, *J. Am. Chem. Soc.*, **88**, 2883 (1966).

(20) The properties of this material were in agreement with those published by G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958).

(21) At these concentrations of substrate, energy transfer would not be completely efficient. However, the disappearance of starting material indicates that energy transfer is occurring.