Experimental Section

General Procedure. ^1H NMR spectra at 270 MHz were taken for thermostated (within ±0.3 °C) $CDCl_3$ solutions of host **1**, **2**, or **3** (~5 × 10^{-3} M) on a JEOL-GX 270 spectrometer. The OH proton resonances were identified by deuteriation. IR spectra were obtained for dry $CHCl_3$ solutions of **1** (~5 × 10^{-3} M) at room temperature by using a JASCO IR-810 spectrophotometer. Electronic spectra were recorded for dry $CHCl_3$ solutions of **1** (~1 × 10^{-4} M) maintained at 25.0 ± 0.1 °C with a Hitachi 320 spectrophotometer. Fluorescence spectra were taken on a Hitachi F-4000 fluorescence spectrophotometer for degassed solutions of **1** or **4** (~1 × 10^{-5} M) in benzene (fluorescence grade) at 25.0 ± 0.1 or 11 ± 0.1 °C upon excitation at 544 nm; the fluorescence intensities at 633 nm (for **1**) or 634 nm (for **4**) were measured. Sample preparations were carried out in a dark room. The one-electron redox potential of tetramethoxybenzoquinone (**14**) in acetonitrile was determined by cyclic voltammetry using a Yanagimoto P-1100 polarographic analyzer.[15] Porphyrin derivatives **1**, **2**, and **4** were prepared as described.[33] Quinones and references **5–20** except for **14** were commercial products of the highest grades; tetramethoxybenzoquinone (**14**) was obtained in a practically quantitative yield by the reaction of chloranil (**6**) and methanol containing KF and purified by recrystallization from methanol.[34]

Binding Constants. The ^1H NMR spectra were taken for a series of solutions containing host **1** at a fixed concentration and varying concentrations of a guest, and the changes in the chemical shifts of the OH groups of **1** were followed. The guests were classified into three categories depending on their affinities to **1** and solubilities in $CDCl_3$: (1) high-affinity and high-solubility guests such as **5**, **10–12**, and **15**, (2) high-affinity and low-solubility guests such as **6–9** and **17**, and (3) low-affinity and high-solubility guests such as **13**, **14**, **16**, **18–20**. For category 1, saturation binding ($\Delta\delta_{comp}$) was readily attained at higher concentrations of guest[35] so that the concentrations of free **1**, free guest, and complex at lower guest concentrations were directly evaluated from $\Delta\delta_{obsd}$. The binding constants were determined from the equation K = [complex]/[**1**][guest]. For categories 3 and 2, the binding constants were obtained by the Benesi-Hildebrand analysis and the Lang's modification thereof, respectively, of the titration data. Similarly were obtained the binding constants for reference hosts **2** and **3** by either the Benesi-Hildebrand or the Lang's method. The concentrations of guests and the temperature ranges were chosen so as to allow a 20–80% range of complexation of host, taking solubilities of guests into account.

UV/visible titration of host **1** with selected quinones was also carried out. The absorbance change at λ_{max} of free **1** (510, 545, 576, or 628 nm) upon addition of a quinone was analyzed according to Benesi-Hildebrand. The binding constants obtained by analysis of the absorbance data at different λ_{max}'s were consistent with each other within 10%.

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(33) (a) Ogoshi, H.; Saita, K.; Sakurai, K.; Watanabe, T.; Toi, H.; Aoyama, Y.; Okamoto, Y. *Tetrahedron Lett.* **1986**, *27*, 6365. (b) Aoyama, Y.; Yamagishi, A.; Tanaka, Y.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1987**, *109*, 4735.

(34) Cf. ref 21a.

(35) The $\Delta\delta_{comp}$ value for 1,4-naphthoquinone (**15**) could not be determined experimentally because of overlap of the OH proton resonance of host **1** with the aromatic proton resonance of **15** in a large excess amount. The binding constant for **15** was therefore obtained by the Lang's method.

Photolytic and Solvolytic Reactions of β-[*o*-(Aryloxy)phenyl]vinyl Bromides. Intramolecular Arylation of Vinyl Cations into Dibenzoxepins

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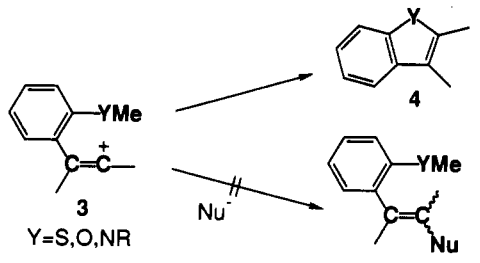
Abstract: Photolysis of β-[*o*-(aryloxy)phenyl]vinyl bromides, i.e., 2-[*o*-(aryloxy)phenyl]-1-bromo-1,2-diphenylethenes **5**, in dichloromethane gave dibenz[*b,f*]oxepins **6** quantitatively. Similar photolysis of vinyl bromides **5** in a mixed solvent of methanol and dichloromethane afforded methanol-incorporated products **7** together with the major dibenz[*b,f*]oxepins **6**. Solvolysis of β-[*o*-(*p*-tolyloxy)phenyl]vinyl bromide **5a** in 60% EtOH at 160 °C and acetolysis of β-[*o*-(aryloxy)phenyl]vinyl bromides **5a** and **5c** with silver acetate gave the same dibenz[*b,f*]oxepins **6a** and **6c**, respectively. The formation of dibenz[*b,f*]oxepins **6** via arylvinyl cations **9** is discussed.

Vinyl cations are recognized as intermediates in organic reactions,[1] especially in solvolytic reactions, where much interest has been paid to the mechanistic aspects. Some approaches to organic synthesis using vinyl cations are valuable, but must overcome several limitations for generating vinyl cations.[1] If these limitations are removed, the method using vinyl cations provides a direct vinylation of substrates. When the vinyl cations possess heteroatoms in the suitable position, this method is useful in the formation of heterocycles. Several studies on the reactivity of the vinyl cations containing heteroatoms have been conducted so far. Modena and co-workers[2] studied vinyl cations having heteroatoms in the β position and found formation of thiirenium ion **1**[2h-m] and

Scheme I



5-membered heterocycles **2** (benzothiophenes,[2a-c] benzofurans,[2f] and indoles[2g]).

† Yamaguchi University.

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1 2 Y = S, O, NR

We found that arylvinyl cations **3** having heteroatoms at the ortho position of the β-aryl group undergo exclusive intramolecular cyclization to afford 5-membered heterocycles[3] **4** (benzofurans,[3a,b] benzothiophenes,[3a] and indoles[3a]). This intramolecular cyclization proceeded successfully even in the presence of nucleophiles (thiolate ion, for example).[3b] Furthermore, we developed this cyclization reaction for other α-substituted vinylic systems by using a photochemical technique to generate vinyl cations.[4] Then, it became interesting to extend this type of intramolecular cyclization from a methoxy group to an aryloxy group for the following reason. There are two possible paths for intramolecular cyclization of β-[*o*-(aryloxy)phenyl]vinyl cations. One is the formation of 1-arylbenzofuranium ions by cyclization at the oxygen atom, which is the cyclization that has been observed in the β-(*o*-methoxyphenyl)vinyl cations. The other path is intramolecular arylation affording dibenz[*b,f*]oxepins. Thus, the present study was undertaken to determine the reaction path.

In a preliminary result,[5] however, the vinyl cation with an aryloxy group underwent intramolecular electrophilic aromatic substitution to give a new type of ring system, i.e., a dibenz[*b,f*]oxepin derivative. In this paper, we describe the details of the intramolecular cyclization by aryloxy groups to give dibenz[*b,f*]oxepin derivatives.

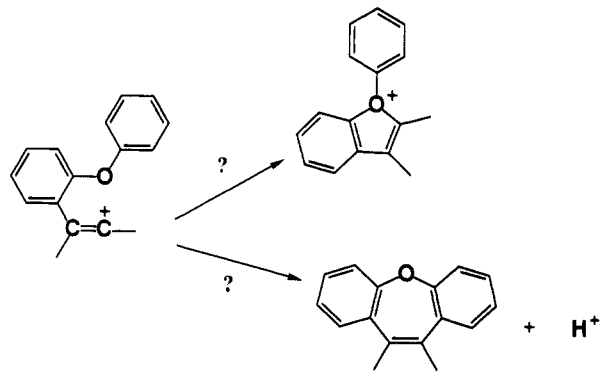
Results and Discussion

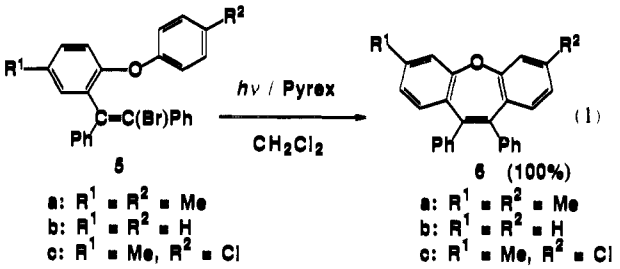
The methods employed in this work for generating vinyl cations are photolysis and mainly silver-assisted solvolysis in acetic acid.

Photolysis. It has been previously reported that photolysis of arylvinyl bromides gives products derived from the corresponding arylvinyl cations.[4,6] The advantage of the photolysis is that the reaction can be carried out at room temperature or below. Photolysis of β-[*o*-(aryloxy)phenyl]-substituted vinyl bromides **5a–d** was conducted in dichloromethane or a mixed solvent of methanol and dichloromethane by use of a Pyrex-filtered high-pressure Hg lamp. In the photolysis, a slight excess of pyridine was added to trap the hydrogen bromide (HBr) generated by cyclization of the aryl ring or by the reaction with methanol.

Photolysis of vinyl bromides **5a–c** in dichloromethane at 15 °C gave dibenz[*b,f*]oxepins **6a–c** quantitatively. No other products were detected. The expected 1-arylbenzofuranium ion and the products derived from it were not detected at all. Replacement of the methoxy group in the vinyl cation **3** (Y = O) by the aryloxy group led to selective cyclization by the aromatic ring. Further, photolysis was conducted in the case of β-(2-dibenzofuranyl)vinyl bromide **5d**, which could not permit interaction of the resulting vinyl cation with the aromatic ring and favored cyclization by the oxygen atom. However, photolysis of **5d** in dichloromethane resulted in recovery of the starting vinyl bromide **5d**.

Scheme II

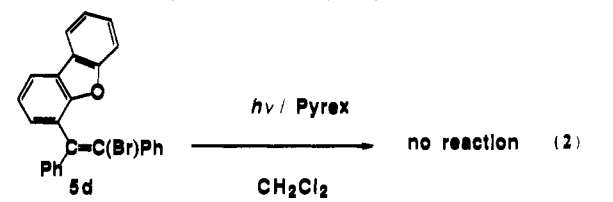




5
a: $R^1 = R^2 = Me$
b: $R^1 = R^2 = H$
c: $R^1 = Me$, $R^2 = Cl$

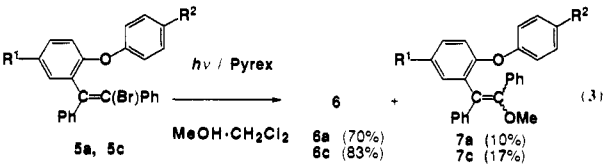
6 (100%)
a: $R^1 = R^2 = Me$
b: $R^1 = R^2 = H$
c: $R^1 = Me$, $R^2 = Cl$

(1)



5d (2)

Exclusive intramolecular cyclization was accomplished when the photolysis of vinyl bromides **5a–c** was carried out in *nonnucleophilic* dichloromethane. Then, to check the ease of the cyclization, the photolysis of vinyl bromides **5a**, **5c**, and **5d** was examined in a mixed solvent of methanol and dichloromethane. Although the photolysis of vinyl bromides **5a** and **5c** gave dibenz[*b,f*]oxepins **6a** and **6c** as the major products, the photolysis also provided the products **7a** and **7c** derived from the reaction of the resulting vinyl cations with methanol. The yields of the methanol-incorporated products **7a** and **7c** were 10% and 17%, respectively. The formation of enol ethers **7a** and **7c** in the photolysis of *o*-aryloxy-substituted vinyl bromides **5a** and **5c** is interesting because the corresponding *o*-methoxy-substituted vinyl bromides cyclize exclusively, even in nucleophilic solvents.[4]



5a, 5c **6** (6a (70%), 6c (83%)) + **7** (7a (10%), 7c (17%)) (3)

On the other hand, photolysis of dibenzofuranyl-substituted vinyl bromide **5d** gave the enol ether **7d** quantitatively. This means that the corresponding vinyl cation is generated by the photolysis of vinyl bromide **5d**, but the β-dibenzofuranylvinyl cation cannot undergo the intramolecular cyclization with the oxygen atom. Consequently, the β-dibenzofuranylvinyl cation is subject to attack by nucleophilic methanol during photolysis in the presence of

(1) (a) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, R. L. *Vinyl Cations*; Academic Press: New York, 1979. (b) Rappoport, Z. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3 and references cited therein.

(2) (a) Capozzi, G.; Melloni, G.; Modena, G.; Piscitelli, M. *Tetrahedron Lett.* **1968**, 4039. (b) Capozzi, G.; Melloni, G.; Modena, G.; Tonellato, U. *J. Chem. Soc., Chem. Commun.* **1969**, 1520. (c) Modena, G.; Tonellato, U. *J. Chem. Soc. B* **1971**, 381. (d) Capozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc. C* **1971**, 3018. (e) Molloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 218. (f) Capozzi, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 216. (g) Capozzi, G.; Modena, G.; Ronzini, L. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1136. (h) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1975**, 248. (i) Capozzi, G.; Lucchini, V.; Modena, G.; Scrimin, P. *Tetrahedron Lett.* **1977**, 911. (j) Capozzi, G.; Lucchini, V.; Modena, G. *Rev. Chem. Intermed.* **1979**, *2*, 347. (k) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 900. (l) Capozzi, G.; Da Col, L.; Lucchini, V.; Modena, G.; Valle, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 68. (m) Lucchini, V.; Modena, G.; Valle, G.; Capozzi, G. *J. Org. chem.* **1981**, 446, 4720.

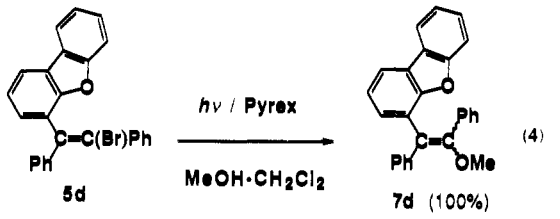
(3) (a) Sonoda, T.; Kawakami, M.; Ikeda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 612. (b) Sonoda, T.; Kobayashi, S.; Taniguchi, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2560.

(4) (a) Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 180. (b) Suzuki, T.; Kitamura, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 5324.

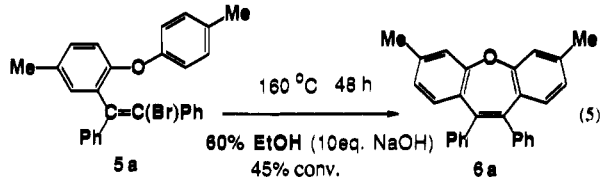
(5) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1984**, 547.

(6) (a) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Am. Chem. Soc.* **1986**, *108*, 2641. (b) Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Fiakpui, C. Y.; Lee, C. C.; Rappoport, Z. *J. Org. Chem.* **1984**, *49*, 3167. (c) Berbeck, J. M.; Cornelisse, J.; Lodder, G. *Tetrahedron*, **1986**, *42*, 5679.

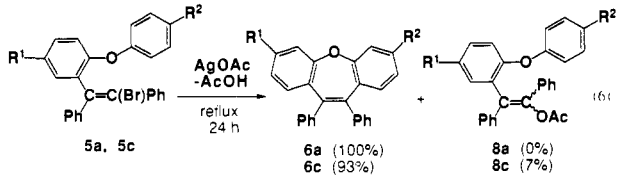
methanol, or attack by the liberated bromide ion to return to the starting bromide **5d** during photolysis in dichloromethane.

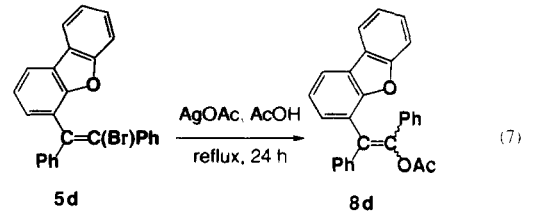


Solvolysis. 2,2-Bis(*p*-methoxyphenyl)-1-phenylvinyl bromide and 2,2-bis(*o*-methoxyphenyl)-1-phenylvinyl bromide are solvolyzed in 80% EtOH with $k = 2.26 \times 10^{-6}$ s^{-1} at 160.4 °C[7] and $k = 2.6 \times 10^{-6}$ s^{-1} at 160 °C,[3b] respectively. Although a buffered solvolysis of α-phenylvinyl bromides is a relatively slow process, it is significant that the solvolysis of β-[*o*-(aryloxy)phenyl]vinyl bromides be carried out to confirm that the intramolecular cyclization does proceed via vinyl cations. Solvolysis of vinyl bromide **5a** was conducted in 60% EtOH with NaOH as a buffer at 160 °C for 48 h. The sole product was dibenz[*b,f*]oxepin **6a** but the conversion was 45%.



It has been well known that solvolysis of vinyl bromides is accelerated by silver salts.[1] Thus, the vinyl bromides **5a**, **5c**, and **5d** were solvolyzed in acetic acid with silver acetate. The silver acetate assisted solvolysis of vinyl bromide **5a** in acetic acid at the refluxing temperature gave dibenz[*b,f*]oxepin **6a** quantitatively, but the reaction of vinyl bromide **5c** gave dibenz[*b,f*]oxepin **6c** and vinyl acetate **8c** in 93% and 7% yields, respectively. Furthermore, the solvolysis of vinyl bromide **5d** afforded vinyl acetate **8d** quantitatively.





On the Formation of Dibenz[*b,f*]oxepins 6. It is reasonable to consider that arylvinyl cations **9** are the key reactive intermediates in the formation of dibenz[*b,f*]oxepins **6**. Although the studies on the direct observation of vinyl cations have not been conducted yet for these β-[(aryloxy)phenyl]-substituted systems, formation of the analogous arylvinyl cations has been observed during the laser flash photolysis of the corresponding arylvinyl bromides.[8] Photolysis of β-[*o*-(aryloxy)phenyl]-substituted vinyl bromides **5** in a nucleophilic solvent gave solvent-incorporated products **7**, suggesting the intervention of the arylvinyl cations **9**.

Solvolysis of the vinyl bromides **5** produced the same dibenz[*b,f*]oxepins **6** as the photolysis did. The solvolytic conditions (in the presence of NaOH and at 160 °C) seem to be somewhat severe but they are typical conditions for solvolyzing α-phenylvinyl bromides.[1] Moreover, silver salts assist the solvolysis to provide mild conditions and are well known in the solvolysis of vinyl halides.[1] Therefore, both photolysis and solvolysis generate the same intermediate vinyl cation **9** to give the dibenz[*b,f*]oxepin **6**.

As discussed for the intramolecular cyclization of vinyl cations containing heteroatoms at the ortho position of the β-aryl group,[4] the vacant p orbital of the vinyl cation can easily interact structurally with the lone pair of the heteroatom. However, the vinyl cations containing an aryloxy group at the ortho position of the β-aryl group produced neither the benzofuranium ions nor the benzofurans derived from the cleavage of the aryl–oxygen bond. The result that dibenz[*b,f*]oxepins **6** are formed from β-[*o*-(aryloxy)phenyl]vinyl cations **9** suggests that the nucleophilicity of the oxygen atom is weakened by the aryl group, but that the aryl group is activated by the oxygen atom in an inverse relationship. Activation of the aryl group by the oxygen atom and the proximity of the aryl group make easy the intramolecular arylation of the vinyl cations.

To explain further why the formation of a seven-membered ring is more favorable than the formation of a five-membered ring from β-[*o*-(aryloxy)phenyl]vinyl cation **9**, we optimized the geometries of the intermediate cations by use of semiempirical molecular-orbital calculations.[10] We used H atoms instead of phenyl groups at the α and β positions for the simplicity of the computation. As shown in Figure 1, the stability of the intermediate cations increases in the order: **11** < **10** < **12**. This result showed that cyclization at the oxygen atom forming a five-membered ring from vinyl cation is an endothermic process, but the process forming a seven-membered ring is exothermic. Therefore, vinyl cation **9** undergoes cyclization most favorably at the phenyl group, producing dibenz[*b,f*]oxepin **6**.

Intramolecular arylation of β-[*o*-(aryloxy)phenyl]vinyl cations **9** is not exclusive in comparison with the case of β-(*o*-methoxyphenyl)vinyl cations.[4] That is, nucleophilic methanol as the solvent can attack the resulting vinyl cation, and an electron-withdrawing chlorine atom on the aryloxy group slightly increases attack by methanol. This is probably because the aryloxy group is distanced from the olefinic double bond due to the repulsion at the ortho position.

It is expected that the fused 2-benzofuranylvinyl cation leads to more favorable interaction with the oxygen atom than the corresponding [(aryloxy)phenyl]vinyl cations. However, the formation of the 1:1 *E* and *Z* products from the acetolysis of **1d** denies the interaction because of the ring strain resulting from the tricyclic system. Accordingly, this vinyl cation is open and is allowed to accept the attack by AcOH from both sites of the vacant p orbital, leading to the mixture of *E* and *Z* isomers.

In summary, we have found that both photolysis and solvolysis of β-[*o*-(aryloxy)phenyl]vinyl bromides **5** produce the same products, dibenzo[*b,f*]oxepins **6**. It is considered that the cyclization to dibenz[*b,f*]oxepins **6** occurs by the arylvinyl cations **9** generated by photolysis or solvolysis. The aryl group activated by the oxygen atom plays an important role in the determination of the reaction path. In addition to the mechanistic interest, the high yields and simple procedure are indicative of the synthetic utility of the preparation of substituted dibenz[*b,f*]oxepins.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were taken on Hitachi R-24B and R-600 spectrometers. Mass spectra were obtained with a JEOL JMS-07 spectrometer. IR spectra were obtained with a Hitachi 270-30 infrared spectrometer. ^{13}C NMR spectra were taken on a JEOL GSX 400 spectrometer.

Preparation of *o*-(Aryloxy)benzophenones. To a mixture of diaryl ether (50 mmol) [bis(*p*-methylphenyl) ether[8] or *p*-chlorophenyl *p*-methylphenyl ether[9]], anhydrous aluminum chloride (10 g, 75 mmol), and carbon disulfide (50 mL) was added dropwise 8.7 mL (75 mmol) of benzoyl chloride at 0 °C. After the addition was complete, the mixture was stirred for 3 h at 0 °C, poured into ice, and extracted with ether. The

(7) Rappoport, Z.; Gal, A.; Holuminer, Y. *Tetrahedron Lett.* **1973**, 641.
(8) Reilly, J.; Drumm, P. J.; Barrett, H. S. B. *J. Chem. Soc.* **1927**, 67.
(9) Huang, R. L. *J. Chem. Soc.* **1954**, 3088.
(10) We used the AM1 method in MOPAC. Ver 5.0. Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10.

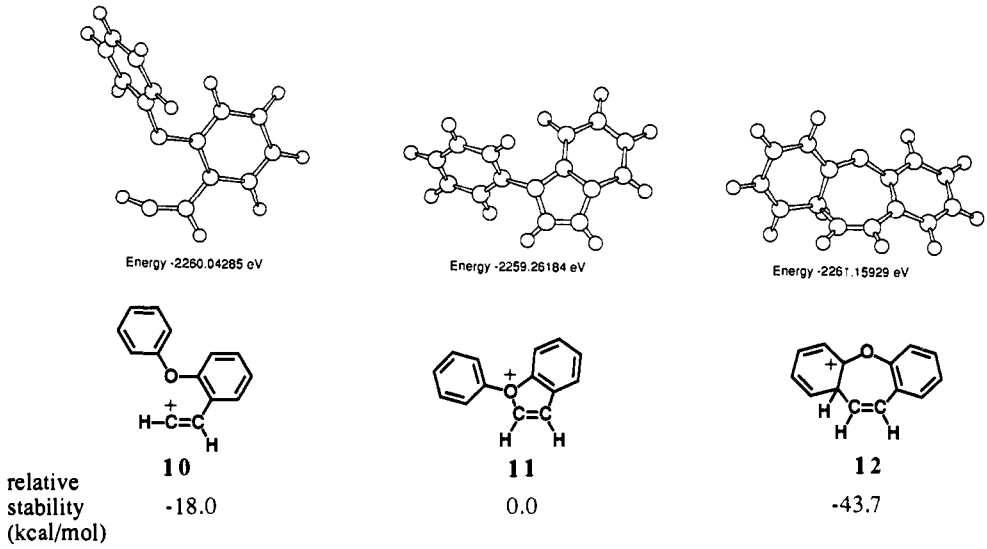
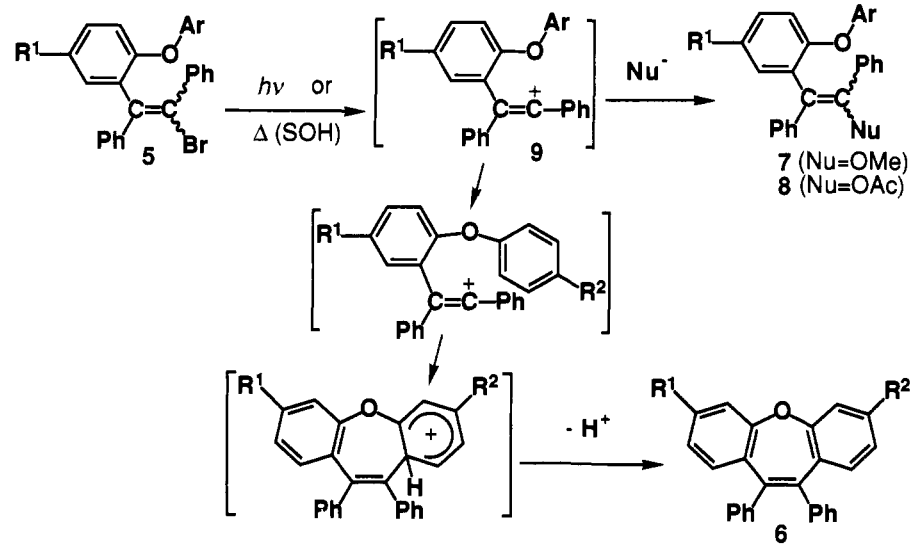


Figure 1. Stereoviews and relative stabilities of the intermediate cations **10**, **11**, and **12**.

Scheme III



organic layer was washed with water and saturated NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was passed through a column of alumina. Elution with benzene–ether gave *o*-(aryloxy)benzophenone. Further purification was carried out by bulb-to-bulb distillation.

2-[(*p*-Methylphenyl)oxy]-5-methylbenzophenone was obtained in 90% yield: bp 150 °C (oven temperature) (3×10^{-4} Torr); ^{1}H NMR δ (CCl_4) 2.16 (s, Me), 2.27 (s, Me), 6.49–7.77 (m, ArH); IR (neat) 1665 cm^{-1} (C=O). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.36; H, 5.93.

2-[(*p*-Chlorophenyl)oxy]-5-methylbenzophenone was obtained in 99% yield: bp 155 °C (oven temperature) (3×10^{-4} Torr); ^{1}H NMR δ (CCl_4) 2.33 (s, Me), 6.67–7.73 (m, ArH); IR (neat) 1665 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{15}O_2Cl$: C, 74.42; H, 4.68. Found: C, 74.37; H, 4.72.

Preparation of 1,2,2-Triarylethanols. Method A. To a mixture of Mg (0.73 g, 30 mmol) and dry ether (50 mL) was added a small portion of benzyl chloride. After initiation of the reaction, a solution of benzyl chloride in dry ether (20 mL) was added dropwise (a total of 3.45 mL (30 mmol) of benzyl chloride was used), and then the mixture was stirred for 30 min at room temperature. To the resulting benzylmagnesium chloride solution was added dropwise a solution of an *o*-(aryloxy)-benzophenone derivative (20 mmol) in ether (30 mL), and then refluxed for 1 h. The mixture was then decomposed by the dropwise addition of 1 M HCl with cooling, and the aqueous layer was separated and extracted with ether. The combined organic layers were washed with water and saturated sodium chloride solution, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a crystalline 1,2,2-triarylethanol, which was recrystallized from hexane or hexane-benzene.

1-[5-Methyl-2-[(*p*-methylphenyl)oxy]phenyl]-1,2-diphenylethanol was obtained in 98% yield: mp 119–122 °C (hexane–benzene); ^{1}H NMR ($CDCl_3$) δ 2.22 (s, Me), 2.33 (s, Me), 3.48 (d, J = 13 Hz, CH), 3.85 (d, J = 13 Hz, CH), 3.92 (br s, OH, exchangeable with D_2O), 6.29–7.44 (m, ArH). Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64. Found: C, 85.10; H, 6.63.

1-[2-[(*p*-Chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethanol was obtained in 75% yield: mp 117–118 °C (hexane–benzene); ^{1}H NMR (CCl_4) δ 2.32 (s, Me), 3.48 (d, J = 13 Hz, CH), 3.58 (br, s, OH), 3.87 (d, J = 13 Hz, CH), 6.23–7.40 (m, ArH). Anal. Calcd for $C_{27}H_{23}O_2Cl$: C, 78.16; H, 5.59. Found: C, 77.94; H, 5.59.

Method B. To a solution of diphenyl ether or dibenzofuran (40 mmol) in THF (100 mL) was added *n*-BuLi in hexane (1.2 M, 65 mL, 78 mmol) dropwise at room temperature under nitrogen atmosphere, and the resulting solution was stirred at room temperature overnight. The mixture was cooled to 0 °C and a solution of benzyl phenyl ketone (7.85 g, 40 mmol) in THF (50 mL) was added. After the addition was complete, the mixture was warmed to room temperature and then refluxed for 1 h. The mixture was quenched with water and extracted with ether. The organic phase was washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crystalline triarylethanol, which was recrystallized from hexane or hexane–benzene.

1,2-Diphenyl-1-[2-(phenyloxy)phenyl]ethanol was obtained in 64% yield: mp 152–153 °C (hexane); ^{1}H NMR (CCl_4) δ 3.49 (d, J = 13 Hz, CH), 3.78 (br s, OH), 3.90 (d, J = 13 Hz, CH), 6.42–7.30 (m, ArH). Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.11; H, 6.05.

1-(4-Dibenzofuranyl)-1,2-diphenylethanol was obtained in 82% yield: mp 166–167 °C (hexane–benzene); ^{1}H NMR ($CDCl_3$) δ 3.00 (d, J = 13 Hz, CH), 4.16 (d, J = 13 Hz, CH), 6.30–6.92 (m, ArH). Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.33. Found: C, 85.48; H, 5.54.

Preparation of 1,2,2-Triarylethenes. A mixture of 1,2,2-triarylethanol

(20 mmol) and 85% phosphoric acid (20 mL) was refluxed for 2 h. The mixture was diluted with water and extracted with ether. The ether solution was washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crystalline 1,2,2-triarylethene, which was recrystallized from ethanol.

1-[5-Methyl-2-[(*p*-methylphenyl)oxy]phenyl]-1,2-diphenylethene was obtained in 79% yield: mp 145–148 °C (ethanol); ^{1}H NMR (CCl_4) δ 2.16 (s, 2Me), 2.21 (s, Me), 2.26 (s, Me), 6.30–7.40 (m, ArH). Anal. Calcd for $C_{28}H_{24}O$: C, 89.33; H, 6.43. Found: C, 89.14; H, 6.42.

1,2-Diphenyl-1-[2-(phenyloxy)phenyl]ethene was obtained in 89% yield: mp 101–105 °C (ethanol); ^{1}H NMR (CCl_4) δ 6.45–7.30 (m, ArH). Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.50; H, 5.75.

1-[2-[(*p*-Chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethene was obtained in 91% yield: mp 147–151 °C (ethanol); ^{1}H NMR (CCl_4) δ 2.29 (s, Me), 2.35 (s, Me) 6.32–7.30 (m, ArH). Anal. Calcd for $C_{27}H_{21}OCl$: C, 81.70; H, 5.33. Found: C, 81.68; H, 5.26.

1-(4-Dibenzofuranyl)-1,2-diphenylethene was obtained in 100% yield: mp 109–115 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 6.91–7.82 (m, ArH). Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.12; H, 5.25.

Preparation of 1,2,2-Triarylvinyl Bromides 5a–d. To a solution of 1,2,2-triarylethene (5 mmol) in dichloromethane (20 mL) was added dropwise a solution of bromine (0.26 mL, 5 mmol) in dichloromethane (5 mL) with stirring at 0 °C. After completion of the addition, the mixture was stirred at 0 °C for 30 min. The mixture was concentrated and passed through a column of alumina (50 g) with dichloromethane. Evaporation of the solvent gave a crystalline vinyl bromide, which was recrystallized from ethanol.

1-Bromo-2-[5-methyl-2-[(*p*-methylphenyl)oxy]phenyl]-1,2-diphenylethene (5a) was obtained in 64% yield: mp 124–125 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 2.29 (s, Me), 2.36 (s, Me), 6.71–7.25 (m, ArH); MS (*m/z*, rel intensity) 456 (M^+ + 2, 26), 454 (M^+, 26), 375 (M^+ – Br, 100). Anal. Calcd for $C_{28}H_{23}OBr$: C, 73.85; H, 5.09. Found: C, 73.69; H, 5.21.

1-Bromo-2-[2-(phenyloxy)phenyl]-1,2-diphenylethene (5b) was obtained in 65% yield: mp 103–105 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 6.60–7.35 (m, ArH); MS (*m/z*, rel intensity) 428 (M^+ + 2, 32), 426 (M^+, 32) 347 (M^+ – Br, 100). Anal. Calcd for $C_{26}H_{19}OBr$: C, 73.08; H, 4.48. Found: C, 72.67; H, 4.62.

1-Bromo-2-[2-[(*p*-chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethene (5c) was obtained in 76% yield: mp 103–107 °C (ethanol); ^{1}H NMR (CCl_4) δ 2.38 (s, Me), 6.62–7.26 (m, ArH): MS (*m/z*, rel intensity) 478 (M^+ + 4, 17), 476 (M^+ + 2, 56), 474 (M^+, 41), 397 (M^+ + 2 – Br, 40), 395 (M^+ – Br, 100), 360 (M^+ – Br – Cl, 70). Anal. Calcd for $C_{27}H_{20}OBrCl$: C, 68.16; H, 4.24. Found: C, 68.20; H, 4.27.

1-Bromo-2-(4-dibenzofuranyl)-1,2-diphenylethene (5d) was obtained in 69% yield: mp 113–114 °C (EtOH–benzene); ^{1}H NMR ($CDCl_3$) δ 7.07 (s, ArH), 7.14–8.04 (m, ArH); MS (*m/z*, rel intensity) 426 (M^+ + 2, 36), 424 (M^+, 36), 345 (M^+ – Br, 100). Anal. Calcd for $C_{26}H_{17}OBr$: C, 73.42; H, 4.03. Found: C, 73.68; H, 4.00.

Photolysis of 1,2,2-Triarylvinyl Bromides 5a–d in Dichloromethane. A solution of a vinyl bromide **5** (0.3 mmol) in dichloromethane (7 mL) containing pyridine (0.05 mL) was placed in a Pyrex tube, degassed, and irradiated by a high-pressure Hg lamp (400 W) at 15 °C for 2 h (for **5a** and **5d**) or 3 h (for **5b** and **5c**). Evaporation of the solvent gave a crystalline dibenz[*b,f*]oxepin **6** quantitatively, which was filtered and washed with ethanol. Recrystallization was carried out with ethanol–benzene. Physical and spectral data of the dibenz[*b,f*]oxepin **6a–c** are given as follows. However, in the case of vinyl bromide **5d**, after removal of the solvent no products were obtained, but the starting vinyl bromide **5d** was recovered.

2,7-Dimethyl-10,11-diphenyldibenz[*b,f*]oxepin (6a): mp 184–185 °C (EtOH–benzene); ^{1}H NMR ($CDCl_3$) δ 2.13 (s, Me), 6.80–7.25 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 20.81, 120.14, 126.23, 127.40, 130.03, 130.52, 130.81, 132.42, 133.78, 139.49, 141.68, 156.79; MS (*m/z*, rel intensity) 375 (M^+ + 1, 31), 374 (M^+, 100), 297 (M^+ – Ph, 32). Anal. Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.45; H, 6.02.

10,11-Diphenyldibenz[*b,f*]oxepin (6b): mp 208–209 °C (EtOH–benzene); ^{1}H NMR ($CDCl_3$) δ 6.94–7.31 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 120.72, 124.62, 126.47, 127.59, 129.49, 130.66, 130.76, 133.00, 139.68, 141.73, 158.74; MS (*m/z*, rel intensity) 347 (M^+ + 1, 14), 346 (M^+, 50), 269 (M^+ – Ph, 100), 258 (61). Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.85; H, 5.31.

3-Chloro-7-methyl-10,11-diphenyldibenz[*b,f*]oxepin (6c): mp 197–198 °C (EtOH–benzene); ^{1}H NMR ($CDCl_3$) δ 2.13 (s, Me), 6.82–7.23 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 20.85, 120.15, 121.82, 126.52, 126.66, 127.52, 127.71, 129.17, 129.77, 130.19, 130.38, 130.43, 130.96, 132.15, 134.27, 134.49, 138.39, 140.80, 140.95, 141.29, 156.49, 157.26; MS (*m/z*, rel intensity) 397 (M^+ + 3, 10), 396 (M^+ + 2, 37), 395 (M^+ + 1, 31), 394 (M^+, 100), 317 (M^+ – Ph, 42). Anal. Calcd for $C_{27}H_{19}OCl$: C, 82.12; H, 4.85. Found: C, 81.88; H, 4.93.

Photolysis of 1,2,2-Triarylvinyl Bromides 5a, 5c, and 5d in Methanol–Dichloromethane. A solution of a vinyl bromide **5** (0.3 mmol) in methanol–dichloromethane (4 mL and 3 mL, respectively) containing pyridine (0.05 mL) was irradiated similarly by use of a high-pressure Hg lamp (400 W) at 15 °C for 3 h. In the case of vinyl bromides **5a** and **5c**, evaporation of the solvent gave crystalline dibenz[*b,f*]oxepins **6a** and **6c**, respectively, which were filtered and washed with ethanol. The filtrate was concentrated and submitted to column chromatography on alumina. Elution with hexane–benzene gave methanol-incorporated products **7a** and **7c**. Since these products could not be purified completely, the yields of the products were determined by ^{1}H NMR.

1-Methoxy-2-[5-methyl-2-[(*p*-methylphenyl)oxy]phenyl]-1,2-diphenylethene (7a): a 56:44 mixture of *E* and *Z* isomers; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, Me), 2.23 (s, Me), 2.27 (s, 2 Me), 3.38 (s, OMe), 3.44 (s, OMe), 6.33–7.30 (m, ArH); MS (*m/z*, rel intensity) 406 (M^+, 100).

2-[2-[(*p*-Chlorophenyl)oxy]-5-methylphenyl]-1-methoxy-1,2-diphenylethene (7c): a 1:1 mixture of *E* and *Z* isomers; ^{1}H NMR ($CDCl_3$) δ 2.16 (s, Me), 2.33 (s, Me), 3.31 (s, OMe), 3.45 (s, OMe), 6.33–7.24 (m, ArH); MS (*m/z*, rel intensity) 428 (M^+ + 2, 37), 426 (M^+, 100).

In the case of vinyl bromide **5d**, after evaporation of the solvent, the resulting pyridinium hydrogen bromide was removed by passage through a column of alumina with dichloromethane; the eluent was concentrated. The residue was checked by spectral means and found to be a 57:43 mixture of *E*- and *Z*-vinyl ethers **7d** (100%).

2-(4-Dibenzofuranyl)-1-methoxy-1,2-diphenylethene (7d): a 57:43 mixture of *E* and *Z* isomers; ^{1}H NMR ($CDCl_3$) δ 3.47 (s, OMe), 3.54 (s, OMe), 6.93–7.98 (m, ArH); MS (*m/z*, rel intensity) 376 (M^+, 100), 361 (M^+ – Me, 26), 333 (M^+ – Me – CO, 53). Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.12; H, 5.36. Found: C, 86.17; H, 5.10.

Solvolytic Reaction of Vinyl Bromide 5a in 60% Ethanol. In a Pyrex ampule was placed 142 mg (0.31 mmol) of vinyl bromide **5a** together with 60% aqueous ethanol (v/v) (15 mL) containing sodium hydroxide (120 mg, 3 mmol); the mixture was degassed and sealed. The ampule was heated at 160 °C for 48 h. The product was extracted with ether–benzene, the organic layer was washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The filtrate was concentrated and the residue was separated by column chromatography on alumina. Elution with 50% benzene–hexane gave the vinyl bromide **5a** (100 mg). Elution with 20% ether–benzene gave a crystalline dibenz[*b,f*]oxepin **6a** (30 mg).

Solvolytic Reaction of Vinyl Bromides 5a, 5c, and 5d in Silver Acetate–Acetic Acid. A mixture of vinyl bromide **5** (0.5 mmol) and silver acetate (100 mg, 0.6 mmol) in acetic acid (10 mL) was refluxed for 24 h. Then, the reaction mixture was poured into water and extracted with ether–benzene. The organic layer was washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Concentration of the filtrate gave crystalline products. Vinyl bromide **5a** gave dibenz[*b,f*]oxepin **6a** quantitatively. In the case of vinyl bromide **5c**, a crystalline dibenz[*b,f*]oxepin **6c** was obtained in 93% yield, but a 7% yield of vinyl acetate **8c** was obtained from the filtrate.

1-Acetoxy-[2-[(*p*-chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethene (8c): a 1:1 mixture of *E* and *Z* isomers; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 2 Me), 2.19 (s, Me), 2.33 (s, Me), 6.28–7.21 (m, ArH); MS (*m/z*, rel intensity) 456 (M^+ + 2, 1), 454 (M^+, 6), 413 (M^+ + 2 – Ac, 37), 411 (M^+ – Ac, 100).

In the case of vinyl bromide **5d**, after the workup described above, crystals were obtained, which were recrystallized from ethanol. The ^{1}H NMR and other spectral data showed a 1:1 mixture of (*E*)- and (*Z*)-vinyl acetates **8d**.

1-Acetoxy-2-(4-dibenzofuranyl)-1,2-diphenylethene (8d): mp 130–151 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 1.76 (s, Me), 2.05 (s, Me), 7.08–8.00 (m, ArH); IR (Nujol) 1745 cm^{-1} (C=O); MS (*m/z*, rel intensity) 404 (M^+, 6), 361 (M^+ – Ac, 100). Anal. Calcd for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found: C, 82.68; H, 4.95.

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Registry No. 5a, 90964-42-4; **5b**, 90964-43-5; **5c**, 134333-40-7; **5d**, 134333-41-8; **6a**, 134312-26-8; **6b**, 90964-45-7; **6c**, 134312-27-9; (*E*)-**7a**, 134312-28-0; (*Z*)-**7a**, 134312-29-1; (*E*)-**7c**, 134312-30-4; (*Z*)-**7c**, 134312-31-5; (*E*)-**7d**, 134312-32-6; (*Z*)-**7d**, 134333-42-9; (*E*)-**8c**, 134312-33-7; (*Z*)-**8c**, 134312-34-8; (*E*)-**8d**, 134312-35-9; (*Z*)-**8d**, 134312-36-0; $(p\text{-}MeC_6H_4)_2O$, 1579-40-4; $p\text{-}MeC_6H_4OC_6H_4Cl\text{-}p$, 6377-63-5; PhCOCl, 98-88-4; $PhCH_2Cl$, 100-44-7; Ph_2O, 101-84-8; $PhCH_2COPh$, 451-40-1; 2-[(*p*-methylphenyl)oxy]-5-methylbenzophenone, 134312-16-6; 2-[(*p*-chlorophenyl)oxy]-5-methylbenzophenone, 134312-17-7; 1-[5-methyl-2-[(*p*-methylphenyl)oxy]phenyl]-1,2-di-

phenylethanol, 134312-18-8; 1-[2-[(p-chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethanol, 134312-19-9; dibenzofuran, 132-64-9; 1,2-diphenyl-1-[2-(phenyloxy)phenyl]ethanol, 134312-20-2; 1-(4-dibenzofuranyl)-1,2-diphenylethanol, 134312-21-3; 1-[5-methyl-2-[(p-methylphenyl)oxy]phenyl]-1,2-diphenylethene, 134312-22-4; 1,2-diphenyl-1-[2-(phenyloxy)phenyl]ethene, 134312-23-5; 1-[2-[(p-chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethene, 134312-24-6; 1-(4-dibenzofuranyl)-1,2-diphenylethene, 134312-25-7.

Enone Photochemistry. Dynamic Properties of Triplet Excited States of Cyclic Conjugated Enones as Revealed by Transient Absorption Spectroscopy

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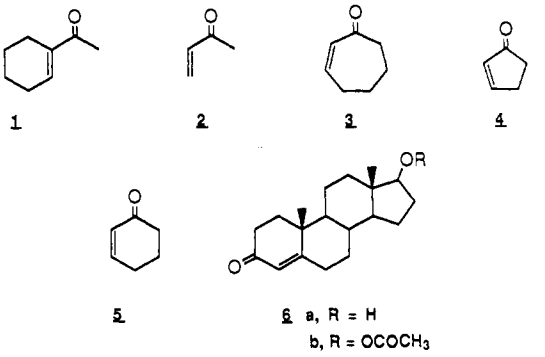
Abstract: Triplet π,π^* excited states of a large number of cyclic α,β-unsaturated ketones (enones) have been generated by pulsed laser excitation and detected by their characteristic ultraviolet absorption, λ_{max} 280–310 nm. The large variation in the lifetimes of these enone triplets as a function of molecular structure and the changes in rate constants for triplet energy transfer from enone triplets to naphthalene and methylnaphthalene for rigid vs nonrigid triplets are consistent with triplet relaxation by twisting around the olefinic bond. This has been confirmed by studies using time-resolved photoacoustic calorimetry (PAC), which afford both lifetimes and energies of the relaxed enone triplet states. The PAC lifetimes are in excellent agreement with those measured by transient absorption spectroscopy (TAS). The effect of substitution on the C=C bond on both lifetimes and energies of enone triplets is compatible with pyramidalization at the β-carbon atom of the triplet prior to intersystem crossing to the ground state. Rates of quenching by conjugated dienes are much lower than anticipated on consideration of the triplet energies of the enone as donor and the diene as acceptor. In systems in which enone–diene adducts are known to be formed, Stern–Volmer plots showed pronounced curvature. Self-quenching of enone triplets is particularly pronounced in the cases of cyclopentenone and some longer lived triplets but is not observed for simple cyclohexenones. In the latter case, the rate constant for self-quenching is too small to cause an unambiguous change in the short triplet lifetimes. The origin of the residual UV absorption observed for many enones following decay of the triplet has not been unambiguously established. Prominent candidates are dimeric triplet 1,4-biradicals en route to enone photodimers and deconjugated isomers of the starting enone.

Introduction

The photochemistry of cyclic enones has received much attention over the past 30 years, from mechanistic as well as synthetic perspectives.[1] The richness and complexity of this subject has been described in a recent review.[2] On the basis of classic sensitization and quenching studies, it was concluded that triplet states are exclusively responsible for the wide variety of photoreactions shown by these compounds, which include [2 + 2] cyclodimerization, reduction to saturated ketones and pinacols, molecular rearrangements, and [2 + 2] cycloaddition to alkenes.[1,2] Mechanistic investigations have frequently given ambiguous results. Some years ago we embarked on a program aimed at gaining a better understanding of the photoreactivity of cyclic enones as a function of variations in enone structure, by directly studying the dynamics of the various processes associated with radiationless decay of enone triplets using nanosecond flash photolysis.

The application of transient absorption spectroscopic (TAS) techniques to enone photochemistry was pioneered by Bonneau. His initial report[3] concerned 1-acetylcyclohexene (1-AC, **1**), which upon pulse excitation at either 265 or 353 nm produced two different transient absorptions. A species with maximum UV absorption at 280 nm appeared in less than 5 ns and decayed in about 20 ns, leading to a second species (lifetime 15 μs in acetonitrile or cyclohexane, 0.35 μs in methanol) with an absorption maximum at 345 nm. The short-lived transient absorption was assigned to a relaxed low-energy twisted triplet excited state of **1**, while the long-lived transient was suggested to be the ground-state trans isomer of **1**. The short lifetime of the triplet was attributed to facile intersystem crossing from the minimum on the triplet π,π^* (T_1) potential energy surface to the maximum on the ground state (S_0) surface, leading directly to the metastable *trans*-enone in competition with triplet decay to the *cis*-enone (**1**).[3]



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(1) (a) Chapman, O. L.; Weiss, D. S. *Org. Photochem.* **1973**, *3*, 197. (b) Schuster, D. I. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167–279. (c) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123. (d) Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; pp 61–144. (e) Carless, H. A. J. In *Photochemistry in Organic Synthesis*; Coyle, J. D., Ed.; Royal Soc Chem: London, 1986; pp 95–117. (f) Wender, P. A. In *Photochemistry in Organic Synthesis*; Coyle, J. D., Ed.; Royal Soc Chem: London, 1986; pp 163–188.

(2) Schuster, D. I. In *The Chemistry of Enones*; Patai, S.; Rappoport, Z., Eds.; John Wiley and Sons, Ltd.: Chichester, England, 1989; pp 623–756.

(3) Bonneau, R.; Fornier de Violet, P. *C. R. Acad. Sci., Ser. 3* **1977**, *284*, 631.

0002-7863/91/1513-6245$02.50/0