J = 11.3, 14.8 Hz, $CH_2CH(SCH_3)_2$, 1 H), 3.70 (dd, J = 4.9, 11.3 Hz, $CH(SCH_3)_2$, 1 H), 4.28-4.49 (m, CH_2O, 2 H), 4.92-5.23 (m, CH_2=CH, 2 H), 5.58-6.07 (m, CH_2=CH, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.4 (q), 13.7 (q), 15.1 (q), 28.2 (t), 31.6 (d), 39.4 (t), 40.3 (t), 48.9 (s), 50.7 (d), 68.7 (t), 117.8 (t), 133.8 (d), 173.5 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{13}H_{22}O_2S_2$ 274.1062, found 274.1064.

***trans*-2-Benzyl-2-(2,2-bis(methylthio)ethyl)-3-methyl-5-pentanolide (3, R^1 = Me, R^2 = $CH_2CH(SMe)_2$, E = CH_2Ph) (entry 13)** was obtained in 50% yield as a pale yellow oil. The ratio was determined by GLC of the corresponding reduction product: ^{1}H NMR ($CDCl_3$) δ 1.18 (d, J = 7.1 Hz, CH_3, 3 H), 1.26-2.74 (m, 7 H), 1.96 and 2.12 (s, CH_3S, each 3 H), 2.88 (s, CH_2Ph, 2 H), 3.70 (dd, J = 4.9, 11.3 Hz, $CH(SCH_3)_2$, 1 H), 4.08-4.53 (m, CH_2O, 2 H), 7.20 (br s, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.5 (q), 13.6 (q), 15.1 (q), 27.5 (t), 31.6 (d), 39.8 (t), 41.7 (t), 50.5 (s), 50.7 (d), 68.9 (t), 126.5 (d), 127.8 (d), 130.1 (d), 136.8 (s), 173.4 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{17}H_{24}O_2S_2$ 324.1218, found 324.1231.

General Reduction Procedure of 3 (R^2 = $CH_2CH(SMe)_2$). A crude product **3** (0.10 g) (obtained in entries 4, 8, 9, 12, and 13) was heated under reflux over Raney nickel W4 in ethanol (4 mL) for 5 h. Filtration through Celite pad and concentration afforded a yellow oil. Purification through silica gel column chromatography (ethyl acetate-hexane = 1:4) afforded **3** (R^2 = Et) as a colorless oil.

***trans*-2-Ethyl-2,3-dimethyl-5-pentanolide (3, R^1, E = Me, R^2 = Et)** was obtained in 74% yield in two steps from **6** via **3** (entry 9) as a colorless oil. No isomer was detected by NMR (^{1}H, ^{13}C) and GLC (see reduction of **2** (R^2 = CH=CH_2)): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.4 Hz, CH_3, 3 H), 0.97 (d, J = 6.6 Hz, CH_3, 3 H), 1.16 (s, CH_3, 3 H), 1.20-2.31 (m, 5 H), 4.08-4.50 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.1 (q), 15.3 (q), 20.9 (q), 27.6 (t), 30.2 (t), 31.3 (d), 47.3 (s), 68.4 (t), 176.4 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_9H_{16}O_2$ 156.1148, found 156.1130.

***cis*-2-Ethyl-3-methyl-2-propyl-5-pentanolide (3, R^1 = Me, R^2 = Et, E = Pr)** was obtained in 79% yield as a colorless oil from **3** (entry 12). No isomer was detected by GLC (see reduction of **2** (R^2 = CH=CH_2)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, CH_3, 3 H), 0.90 (t, J = 7.3 Hz, CH_3, 3 H), 1.01 (d, J = 7.0 Hz, CH_3, 3 H), 1.24-1.37 (m, $CH_3CH_2CH_2$, 2 H), 1.37-1.47 (m, $CH_3CH_2CH_2$, 1 H), 1.45 (dq, J = 7.3, 14.6 Hz, CH_3CH_2, 1 H), 1.65 (ddd, J = 5.8, 11.0, 13.6 Hz, $CH_3CH_2CH_2$, 1 H), 1.75-1.95 (m, CH_2, 2 H), 1.96 (dq, J = 7.3, 14.6 Hz, CH_3CH_2, 1 H), 2.14-2.21 (m, CH_3CH_2, 1 H), 4.27 (ddd, J = 4.8, 10.3, 11.4 Hz, CH_2O, 1 H), 4.38 (ddd, J = 4.0, 5.5, 11.4 Hz, CH_2O, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.2 (q), 14.8 (q), 15.1 (q), 18.1 (t), 27.2 (t), 28.3 (t), 31.5 (d), 36.2 (t), 50.0 (s), 68.2 (t), 174.9 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{11}H_{20}O_2$ 184.1464, found 184.1520.

***cis*-2-Benzyl-2-ethyl-3-methyl-5-pentanolide (3, R^1 = Me, R^2 = Et, E = CH_2Ph)** was obtained in 78% yield as a colorless oil from **3** (entry 13). The ratio of 97:3 was determined by HPLC (see reduction of **2** (R^2 = CH=CH_2)): ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.4 Hz, CH_3, 3 H), 1.14 (d, J = 6.9 Hz, CH_3, 3 H), 1.30-2.46 (m, 5 H), 2.91 (s, CH_2Ph, 2 H), 4.07-4.49 (m, CH_2O, 2 H), 7.04-7.44 (m, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.0 (q), 14.9 (q), 27.1 (t), 28.1 (t), 31.2 (d), 40.4 (t), 51.8 (s), 68.7 (t), 126.3 (d), 127.7 (d), 130.0 (d), 137.2 (s), 174.0 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{15}H_{20}O_2$ 232.1464, found 232.1467.

Arylcyclopropane Photochemistry. Unusual Aromatic Substituent Effects on the Photochemical Rearrangement of (2-Arylcyclopropyl)methyl Acetates to 1-Arylhomoallyl Acetates

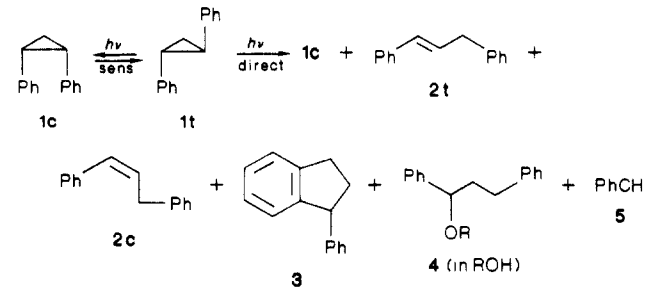
Stephen S. Hixson,* Lothar A. Franke, Jeffrey A. Gere, and Yi-de Xing

Contribution from the Chemistry Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received June 10, 1987*

Abstract: Irradiation of *trans*-(2-arylcyclopropyl)methyl acetates **6a** (Ar = Ph), **6b** (Ar = *p*-OMePh), **6c** (*m*-OMePh), **6d** (*p*-MePh), **6e** (*m*-MePh), **6f** (*p*-CNPh), **6g** (*m*-CNPh), and **6h** (*m*-CF_3Ph) affords in every case but **6c** a 4-butenyl-1-aryl acetate (**7a,b,d-h**) via an ionic mechanism from the singlet state. Similar rearrangements occurred with *exo*-(1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (**14a**) and the 4-cyano derivative (**14b**). Excited state reaction rate constants were determined from reactant fluorescence lifetimes and product quantum yields. A large rate increase relative to **6a** or **14a** was found for the cyano and trifluoromethyl derivatives **6f-h** and **14b**. It is concluded that the rate-determining step involves conversion of the initially formed aromatic excited state to a reactive cyclopropane excited state and that cyclopropane to aromatic ring charge transfer enhances this process.

Early studies of the photochemistry of arylcyclopropanes revealed a fascinating array of reactions.[1] Many of them are exemplified in the photochemistry of *trans*-1,2-diphenylcyclopropane (**1t**), easily the most studied of all arylcyclopropanes[1,2] (Scheme I). One of the most interesting aspects of the photochemistry of **1** is that reactions of apparently quite distinct electronic character occur from the same (singlet) manifold; that

Scheme I



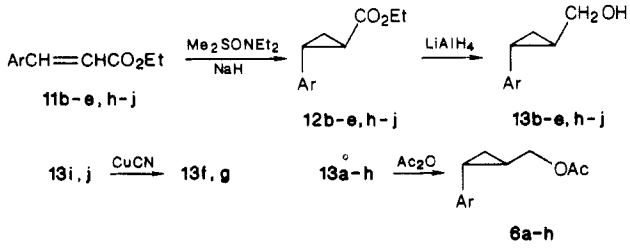
is, while all reactions involve fission of a cyclopropane bond, the pathways to **1c**, **2**, **3**, and **5** are most easily visualized as radical-like or concerted and not involving any highly polar intermediates, whereas the process leading to **4** is ionic.[2]

(1) Hixson, S. S. *Org. Photochem.* **1979**, *4*, 191.

(2) (a) Griffin, G. W.; Covell, J.; Petterson, R. C.; Dodson, R. M.; Close, G. *J. Am. Chem. Soc.* **1965**, *87*, 1410. (b) Irving, C. S.; Petterson, R. C.; Sarkar, I.; Kristinnson, H.; Aaron, C. S.; Griffin, G. W.; Boudreau, G. J. *J. Am. Chem. Soc.* **1965**, *88*, 5675. (c) Kristinnson, H.; Mehrotra, K. N.; Griffin, G. W.; Petterson, R. C. Irving, C. S. *Chem. Ind. (London)* **1966**, 1562. (d) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153. (e) Valyocsik, E. W.; Sigal, P. *J. Org. Chem.* **1971**, *36*, 66. (f) Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532.

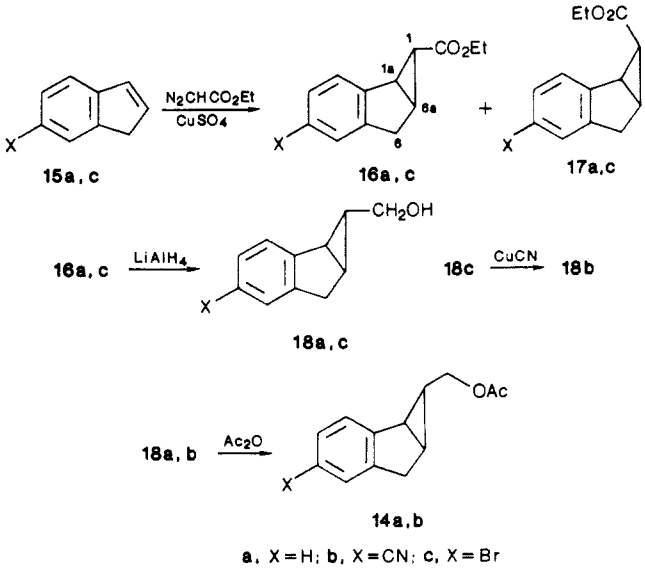
0002-7863/88/1510-3601$01.50/0

Scheme II



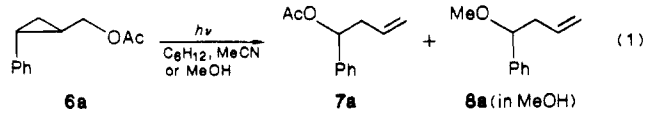
a, Ar = Ph; b, Ar = *p*-OMePh; c, Ar = *m*-OMePh; d, Ar = *p*-MePh; e, Ar = *m*-MePh; f, Ar = *p*-CNPh; g, Ar = *m*-CNPh; h, Ar = *m*-CF_3Ph; i, Ar = *p*-BrPh; j, Ar = *m*-BrPh

Scheme III



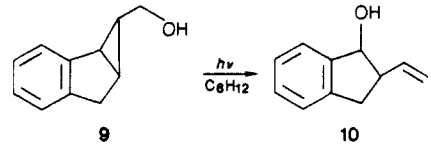
a, X = H; b, X = CN; c, X = Br

We later encountered a second ionic reaction of arylcyclopropanes, the rearrangement of (2-arylcyclopropyl)methyl acetates shown in eq 1.[3,4] The reaction occurs with a variety of (2-



(1)

arylcyclopropyl)methyl acetates in solvents of widely different polarity. A remarkable example of a similar reaction with hydroxide as the migrating group was encountered with **9**.[5]



Substituent-effect studies have proven useful for analyzing the electronic details of a variety of photochemical reactions, and given the ionic nature of the rearrangement of **6a** to **7a**, we thought that a study of the effects of substituents on this interesting process had the potential to be particularly revealing. Accordingly, a series of derivatives of **6a** substituted in the aromatic ring were prepared and studied as were some more rigid analogues.

Results

Synthesis of Reactants and Photoproducts. *trans*-(2-Phenylcyclopropyl)methyl acetate (**6a**) was prepared from *trans*-2-phenylcyclopropanecarboxylic acid. The procedures used for the preparation of the other derivatives of **6** are shown in Scheme II.

Table I. Photolysis of *trans*-(2-Arylcyclopropyl)methyl Acetates **6a–h**[a]

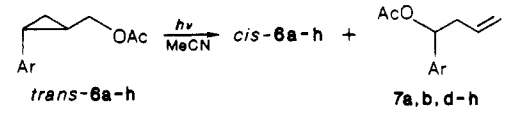
			yield,[b] %			
reactant (Ar)	mmol	time, h	**6t**	**6c**	**7**	other[c]
6a (Ph)	3.16	20	46	13	6 (15)	1
6a (Ph)[d]	1.58	36	77	10		
6b (*p*-OMePh)	2.41	16	27	24	10 (20)	~1
6c (*m*-OMePh)	0.454	16	13	5	≤0.2[e]	
6d (*p*-CH_3Ph)	1.13	8	46	25	18 (62)	
6e (*m*-CH_3Ph)	1.37	8	37	18	2 (4)	~1
6f (*p*-CNPh)	2.56	16	29	3	1.5 (5)	32
6g (*m*-CNPh)	0.349	1	50	~2	4 (8)	~2
6h (*m*-CF_3Ph)	0.775	3	56	21	13 (57)	7
6h (*m*-CF_3Ph)[d]	0.388	1	49			<1

[a] Irradiations were carried out on 100-mL solutions with a Hanovia 450-W medium-pressure mercury arc equipped with a Corex filter except where noted. [b] Determined by GC and based on total amount of **6** irradiated; yields of **7** in parentheses are based on total **6** (trans plus cis) consumed. [c] Approximate yields of other unidentified roducts; see text. [d] Containing 0.079 M *N,N*-dimethylaniline; Pyrex filter used. [e] None detected.

The cycloprop[*a*]indene reactants **14a,b** were prepared as illustrated in Scheme III.

The homoallyl acetate photoproducts derived from **1a–h** (except **1c**) were independently prepared by unexceptional methods. Details are provided in the Experimental Section.

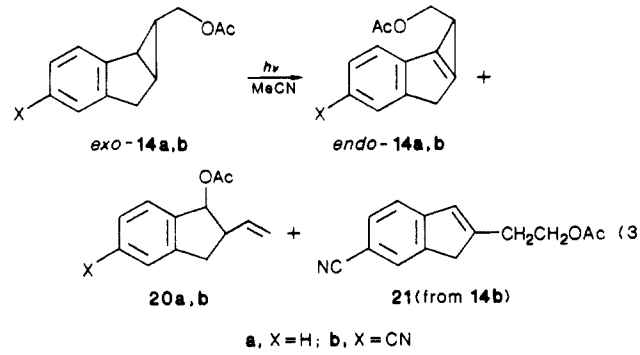
Photolysis of (2-Arylcyclopropyl)methyl Acetates 6a–h and 14a,b. Preparative-scale photolysis of the (2-arylcyclopropyl)-methyl acetates **6a–h** in acetonitrile solution resulted in relatively efficient trans–cis isomerization and slower rearrangement to the homoallyl acetates **7**[6] (eq 2). Product yields as determined by



(2)

GC analysis are given in Table I. The yields of **7** were generally low, in part because the photoproducts were themselves light sensitive. Only in the case of *m*-methoxy derivative **6c** was no homoallyl product formed, and control studies showed that our failure to observe rearrangement to **7c** was not due to the fact that the latter was being formed and then rapidly destroyed. In most cases the cis isomers of **6** and the homoallyl acetates **7** were the only major photoproducts. However, with **6f–h**, such was not the case; complex mixtures of photoproducts were formed in addition to **7f–h**. These were not identified (see below).

The photolyses of the geometrically constrained analogues of **6a** (**14a**) and **6f** (**14b**) proceeded in a fashion similar to that of the less rigid compounds. Thus, irradiation of **14a** to 64% conversion afforded 31% of **20a**; recovered **14a** was a mixture of exo and endo isomers in the ratio of approximately 3:1. Likewise, **14b** afforded **20b** in 13% yield at 86% conversion with **14b** recovered as a 5:3 exo–endo mixture. In this case the major isolated



(3)

a, X = H; b, X = CN

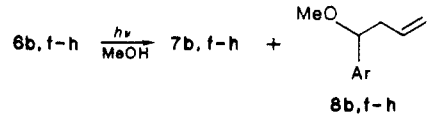
(3) Hixson, S. S. *J. Chem. Soc., Chem. Commun.* **1974**, 681.
(4) Hixson, S. S.; Factor, R. E. *Tetrahedron Lett.* **1975**, 3111.
(5) Hixson, S. S.; Borovsky, J. *J. Chem. Soc., Chem. Commun.* **1975**, 607.

(6) (a) The pivalate esters corresponding to acetates **1a–h** behave essentially the same as the acetates.[6b] (b) Gere, J. Ph.D. Thesis, University of Massachusetts, 1977.

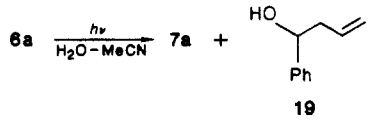
product proved to be olefin **21** (44%). Another product formed in significant quantities (GC) could not be isolated; it appeared to be converted to **21** on workup and chromatography. In general, there appeared to be a greater abundance of minor photoproducts from cyano derivative **14b** as opposed to unsubstituted **14a**, similar to what was found for **6f** (*p*-CN) vs **6a** (H).

The photorearrangement products **7a,b,d–h** were isolated chromatographically and compared with samples prepared independently. The structures of **20a,b** and **21** were deduced from the NMR spectra of the isolated materials. The identities of the cis cyclopropane isomers produced by photolysis of **6a**, *exo*-**14a**, and *exo*-**14b** were established by independent synthesis. The identification of the cis isomers obtained from **6b–h** was in each case done by a comparison of the GC retention time with that of the cis isomers produced in the sensitized photolyses (see below).

Photolysis of acetates **6b** (*p*-OMe), **6f** (*p*-CN), **6g** (*m*-CN), and **6h** (*m*-CF_3) in methanol afforded the methyl ethers **8b,f–h** in addition to **7b,f–h**, a finding similar to that observed earlier for **6a**.[3] Control experiments revealed that in every case the ethers



8 were not derived via secondary photolysis of the corresponding acetates **7**. Irradiation of **6b** (*p*-OMe) and **6g** (*m*-CN) in methanol with added sodium bicarbonate gave the acetates **7** and ethers **8** in the usual yield, demonstrating that the observed reactions are truly photochemical and not thermal acid-catalyzed processes. Irradiation of **6a** in 5% water–acetonitrile gave the expected alcohol **19** in addition to **7a**.



Reaction Multiplicity. Acetone solutions of cyclopropyl reactants **6a,b,d–f** and **14a,b** were irradiated under conditions where nearly all of the incident light was absorbed by the acetone. Under these circumstances acetone serves as both solvent and triplet sensitizer. In every case trans–cis isomerization was observed. There were traces of other products as well, but in no case was the formation of homoallyl products **7** (**20**) detected.

Reaction Quantum Yields and Rate Constants. Quantum yields for rearrangement of **6** to **7** and of **14** to **20** were measured at very low conversion so as to ensure that product absorbance was negligible and that only the rearrangement of the trans (exo) isomers was being studied (<5% isomerization to the cis or endo isomer). Fluorescence lifetimes were determined by the single photon counting technique. Excited singlet state reaction rate constants were then calculated by using the equation $k_r = \phi_r/\tau_s$ (Table II).

Discussion

All of the (2-arylcyclopropyl)methyl acetates studied except for the *m*-methoxy derivative **6c** were found to rearrange to the corresponding homoallyl acetate product **7** (**20a**). For **6a** (Ar = Ph), **6b** (*p*-OMePh), **6d** (*p*-CH_3Ph), **6e** (*m*-CH_3Ph), and **14a** (X = H), the reactions appeared to be relatively clean. In the case of **6f** (*p*-CNPh), **6g** (*m*-CNPh), **6h** (*m*-CF_3Ph) and **14b** (X = CN), the reaction mixtures were more complex; a variety of products were formed in addition to **7** (**20b**) and the cis (endo) isomer. Only in the case of **14b**, however, was there a sufficient quantity of any other product produced, i.e., olefin **21**, to allow for identification. The formation of olefins from arylcyclopropanes is a commonly observed photochemical process[1] (see, for example, **1** → **2** in Scheme I) so **21** is an unexceptional product. It seems likely that some if not all of the additional products observed for **6f–h** are olefins analogous to **21**.

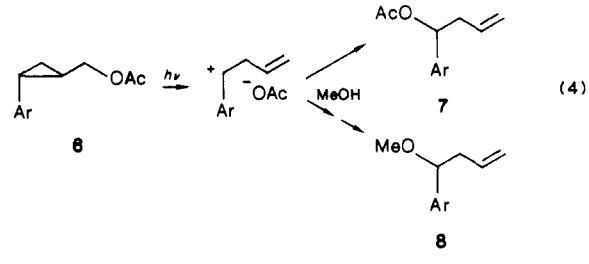
Multiplicity Studies. Triplet sensitization of **6a–h** and **14a,b** with acetone as both solvent and sensitizer resulted in trans–cis isomerization but no rearrangement to **7** (**20, 21**), strong evidence that the latter is a singlet process. These results are in accord with the general observation that, commonly, the only reaction of arylcyclopropane triplets is stereoisomerization about the three-membered ring (see, e.g., Scheme I).[1] On the other hand, the singlet states undergo a variety of reactions.

Table II. Reaction Quantum Yields, Singlet Lifetimes, and Reaction Rate Constants for Cyclopropanes **6a–h** and **14a,b**

reactant (Ar)	ϕ_7 (**20**)[a,b]	τ_s, ns[b]	$10^{-6}k_r$, s^{-1} [c]	k_r (rel)
6a (Ph)	0.039	18.4	2.1	1.0
6b (*p*-OMePh)	0.012	5.0	2.4	1.1
6c (*m*-OMePh)	≤0.002[d]	8.0	<0.25[d]	<0.12[d]
6d (*p*-CH_3Ph)	0.026	18.0	1.4	0.67
6e (*m*-CH_3Ph)	0.010	22.8	0.44	0.21
6f (*p*-CNPh)	0.033	<0.6[e]	>55	>26
6g (*m*-CNPh)	0.094	<0.6[e]	>157	>75
6h (*m*-CF_3Ph)	0.088	0.65	140	67
14a[f]	0.025	5.3	4.7	2.2 (1.0)[g]
14b	0.047	<0.6[e]	>78	>37(>17)[g]

[a] Quantum yield for formation of **7a–h** or **20a,b**; 254-nm light; ferrioxalate actinometry; error ± 20%. [b] Acetonitrile solvent; room temperature. [c] Rate constant for formation of **7a–h** (**20a,b**) calculated with $k_r = \phi_r/\tau_s$. [d] No **7e** detected. [e] Lifetime too short to measure. [f] $\phi_{exo-endo} = 0.023$. [g] Relative to **14a**.

Reaction Mechanism. The ionic nature of the rearrangement **6** → **7** and **14** → **20** is clear. The simultaneous formation of the methyl ethers **8** and acetates **7** when the irradiations are performed in methanol and the production of alcohol **19** on irradiation of **6a** in water–acetonitrile are indicative of competitive reactions of a carbocation intermediate with different nucleophiles (eq 4). Early studies on ^{18}O-labeled **6a** showed that the two ester oxygens become completely scrambled during the rearrangement to **7a**.[4]



Given an ionic mechanism, then, the substituent effects observed are quite striking, for they are not at all what one would expect of an ionic process. We find that electron-donating groups (methyl, methoxy) have little effect on the rate or actually retard reaction, whereas electron-withdrawing groups markedly accelerate it.

We considered the possibility that a bimolecular electron transfer mechanism might be operative. One could understand the rate enhancement by electron-withdrawing groups if reaction were initiated by single-electron transfer from some donor in solution to the aryl ring of the (2-arylcyclopropyl)methyl acetates. We do not believe this is occurring. For one thing, the reaction of **6a** proceeds quite well in a variety of media (cyclohexane, ether, methanol, acetonitrile), and we previously provided evidence that **6a** reacts only 50% faster in acetonitrile than cyclohexane.[3] It is difficult to conceive of some adventitious electron donor being present in effective quantities in all these solvents. Also, we saw no rearrangement of either **6a** (Ar = Ph) or **6h** (*m*-CF_3Ph) when irradiations were carried out in the presence of the deliberately added electron donor *N,N*-dimethylaniline. In the case of **6a**, only slow trans–cis isomerization and gradual loss of cyclopropane was noted, whereas with **6h** there was seen only a loss of starting material. Similar results were found for **6a** when the reaction with added dimethylaniline was carried out in methanol.

How, then, does one understand the substituent effects? The data indicate that the reaction, while involving ionic intermediates, does not proceed via rate-determining carbocation formation. We suggest instead a two-stage mechanism in which some step prior to ionization is rate-determining and is the one primarily being

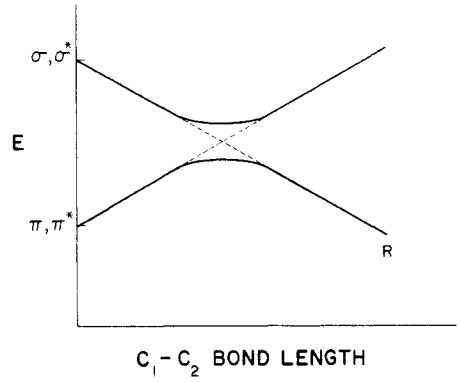


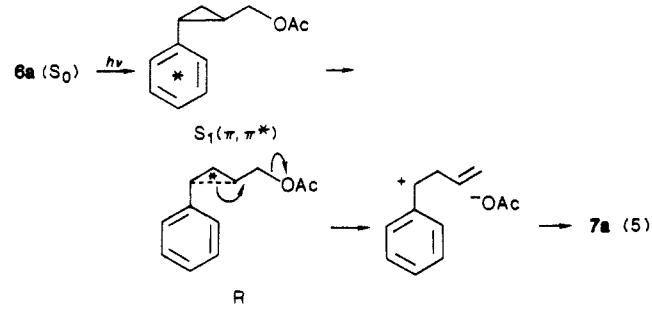
Figure 1. Correlation diagram for photochemical cyclopropane ring opening of arylcyclopropanes.

studied in the photochemical kinetics experiments. Such a mechanism is, in fact, readily accommodated within the present framework of thought about arylcyclopropane excited states.[1]

Spectroscopic studies of a variety of phenylcyclopropanes led Becker and Griffin to postulate the formation of "radical-like" singlet and triplet states on UV irradiation of phenylcyclopropanes.[7,8] They concluded from their results that the spectroscopic singlets and, they argue, triplets of phenylcyclopropanes are basically benzene-like. However, these benzene-like states may be converted more or less rapidly (depending on the substitution) to radical-like states, which have a greatly lengthened and weakened cyclopropane bond. It was suggested that these latter states might mediate the observed photochemistry. Put in slightly different terms, excitation energy, which is initially localized in the aromatic ring, is transferred to the cyclopropane ring concomitant with a bond lengthening to give a cyclopropane excited state, which, in turn, performs the chemistry.

That such a diradical cyclopropane excited state should exhibit both radical (covalent) and ionic behavior is understandable in terms of what we know about the electronic structure of diradical states,[9] for such a state is expected to have zwitterionic character, to be polarizable, and to possibly exhibit ionic reactivity. The rearrangemment of **6** and **14** is one example of this, and, in fact, **6a** was prepared and irradiated in the expectation that such a reaction might occur.

A valence-bond mechanism for the rearrangement of **6a** is shown in eq 5. It should be noted that we refer to the diradical state R as an intermediate for discussion and illustrative purposes. We have no evidence that it has a finite lifetime. Maximally it would be very short lived.



The counterpart of the valence-bond mechanism (the $S_0 \rightarrow R$ sequence) in terms of a qualitative state correlation diagram[10] provides important insight (Figure 1). In Figure 1, the π,π^* and σ,σ^* states are excited (singlet) states assumed to be localized in the aromatic and cyclopropane rings, respectively. R is the nonspectroscopic diradical state from which noticeable chemistry ensues. The π,π^* representation is a good approximation for S_1, since the excitation is heavily localized in the aromatic ring.[7] This state correlates with a high energy (π,π^*) state of the diradical species. On the other hand, the high-lying σ,σ^* state correlates with R.[11] The increase in energy of the π,π^* state and the decrease in energy of the σ,σ^* cyclopropane excited state lead to an avoided crossing at some unspecified C_1–C_2 bond length. For a molecule generated in S_1, the slow step in the reaction is traversing the energy barrier at this avoided crossing.

Conceivably, substituents could affect the reaction rate by affecting the energy of the spectroscopic π,π^* singlet (S_1). However, the absence of any correlation between the fluorescence (or UV absorption) λ_{max} for **6a–h** and reaction rate suggests such energy factors are minor [compound (λ_{max}(fl), λ_{max}(abs)]: **6a** (292, 267), **6b** (314, 280), **6c** (298, 273), **6d** (300, 270), **6e** (290, 270), **6f** (305, 245), **6g** (337, 283), **6h** (300, 271)]. Also, it is not clear that stabilizing effects on R are important; the rates do not correlate with odd-electron-stabilizing capabilities of the substituents, and the preferred polarization in R would appear to be the opposite of that suggested by the relative rate data. And, electron-withdrawing groups should certainly not enhance the tendency of R to fragment in the observed fashion. A different rationale is needed.

UV studies of conjugated arylcyclopropanes have amply demonstrated that the cyclopropane ring acts as an electron donor and that the conjugative interaction between the rings is enhanced as the aromatic ring becomes more electron-withdrawing.[12] We suggest this to be the important factor here; that is, the substituents in **6a–h** and **14a,b** affect the rate of S_1 (π,π^*) $\rightarrow$ R primarily by their ability to promote charge transfer from the cyclopropane ring. Clearly, such charge transfer will facilitate ring opening. In terms of the correlation diagram (Figure 1), this charge transfer is effected by the progressive mixing into S_1 (π,π^*) of σ,π^* character, lowering the barrier to R. The extent of the mixing of σ,π^* character into S_1 will be greatest with the trifluoromethyl- and cyano-substituted compounds, thus the marked rate enhancement by these groups. On the other hand, the substantial rate inhibition by the *m*-methoxy group most probably derives from the enhanced electron-donating ability of a methoxy group to the meta position of an excited aromatic ring.[13] This should decrease excited state electron donation from the cyclopropane ring.

One would expect from the above model that other photoreactions of arylcyclopropanes which involve cyclopropane bond fission would exhibit similar charge-transfer enhancement. Such is indeed the case with the two other reactions we have examined—the formation of olefins and indans from 1,1-diarylcyclopropanes[14] and the 1,3-hydrogen migration of (alkylphenyl)cyclopropanes.[15]

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR spectra were recorded on Perkin-Elmer R-12A, Varian XL-200, and Varian XL-300 spectrometers. Infrared spectra were obtained on a Perkin-Elmer 727 or 1310 spectrometer. Fluorescence spectra were recorded with a Perkin-Elmer MPF-44 instrument. Ultraviolet spectra

(7) Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G. *J. Am. Chem. Soc.* **1972**, *94*, 6584.

(8) Recently the triplet diradical product from either *cis*- or *trans*-1,2-bis(4-acetylphenyl)cyclopropane has been observed spectroscopically: Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797.

(9) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(10) (a) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. (b) Bigot, B.; Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6. (c) Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1. (d) Devaquet, A. *Pure Appl. Chem.* **1975**, *41*, 455.

(11) For calculations on the changes in energy of the excited states of cyclopropane with C–C–C bond angle, see: (a) Buenker, R. J.; Peyerimhoff, S. D. *J. Phys. Chem.* **1969**, *73*, 1299. (b) Siu, A. K. Q.; St. John, W. J., III; Hayes, E. F. *J. Am. Chem. Soc.* **1970**, *92*, 7249.

(12) (a) Hahn, R. C.; Howard, P. H.; Kong, S.-M.; Lorenzo, G. A.; Miller, N. L. *J. Am. Chem. Soc.* **1969**, *91*, 3558. (b) Kellog, R. M.; Buter, J. *J. Org. Chem.* **1971**, *36*, 2236. (c) Strait, L. A.; Ketcham, R.; Jambotkar, D.; Shah, U. P. *J. Am. Chem. Soc.* **1964**, *86*, 4628. (d) Goodman, A. L.; Eastman, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 908.

(13) (a) Zimmerman, H. E.; Sandel, V. P. *J. Am. Chem. Soc.* **1963**, *85*, 915. (b) Cornelisse, J. *Pure Appl. Chem.* **1975**, *41*, 433 and references therein.

(14) Hixson, S. S.; Franke, L. A. *J. Org. Chem.*, in press.

(15) Hixson, S. S.; Gallucci, C. R. *J. Org. Chem.*, in press.

were recorded with a Cary-14 spectrophotometer. Analytical gas chromatography was carried out on Varian 2400 or Perkin-Elmer 990 gas chromatographs, each of which was equipped with a flame-ionization detector. Mass spectral analyses were performed by the Cornell University Mass Spectral Services and the Massachusetts Institute of Technology Mass Spectral Facility. Microanalyses were carried out in the University of Massachusetts Microanalytical Laboratory, G. Dabkowski, Director.

***trans*-(2-Phenylcyclopropyl)methyl Acetate (6a).** To 0.35 g (9.2 mmol) of lithium aluminum hydride in ether under nitrogen was added dropwise with stirring a solution of 1.0 g (6.2 mmol) of *trans*-2-phenylcyclopropane-1-carboxylic acid in ether. Upon completion of the addition, the mixture was refluxed for 6 h. It was then cooled, and excess lithium aluminum hydride was destroyed with water. The product was extracted with ether, and the combined ether solution was dried ($MgSO_4$) and concentrated in vacuo to give 0.75 g (82%) of crude *trans*-2-phenylcyclopropanemethanol. This material was taken up in 4 mL of dry pyridine to which was added 2 mL of acetic anhydride. The solution was let stand at room temperature for 36 h. It was then poured into ether and washed sequentially with 20% HCl, 5% $NaHCO_3$, and water and dried ($MgSO_4$). The solvent was removed by rotary evaporation, and the crude product was chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (60–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, to give 0.54 g (54%) of (*trans*-2-phenylcyclopropyl)methyl acetate (**6a**): NMR ($CDCl_3$) δ 0.80–2.0 (m, 4 H, cyclopropyl), 2.04 (s, 3 H, CH_3), 4.06 (d, J = 5.5 Hz, 2 H, CH_2O), and 7.00–7.35 (m, 5 H, arom); IR (neat) 3040, 1740, 1230, 1020, 750, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.51; H, 7.52.

***trans*-[2-(*p*-Methoxyphenyl)cyclopropyl]methyl Acetate (6b). a. Ethyl *trans*-2-(*p*-Methoxyphenyl)cyclopropane-1-carboxylate (12b).**[16] Sodium hydride, 1.24 g (26 mmol, 50% oil dispersion), 6.39 g (27 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate[17] and 25 mL of freshly distilled (CaH_2) dimethyl sulfoxide were combined in a flask under nitrogen. A vigorous evolution of hydrogen was observed. The reaction mixture was stirred and maintained at room temperature with the aid of a cold-water bath until it became homogeneous. A solution of 5.09 g (24.7 mmol) of ethyl *p*-methoxycinnamate (**11b**)[18] in 25 mL of freshly distilled (CaH_2) dimethyl sulfoxide was then added dropwise with stirring. After the addition was complete, the mixture was stirred at room temperature for 72 h and then poured into 200 mL of ice water and extracted with ether. The combined ether extracts were washed with water and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL), 5% ether–hexane (500 mL), and 10% ether–hexane (1 L). The 10% ether–hexane fraction contained 2.85 g (52%) of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**): NMR ($CDCl_3$) δ 1.15–2.00 (m, 3 H, cyclopropyl), 1.27 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.32–2.60 (m, 1 H, cyclopropyl), 3.78 (s, 3 H, OCH_3), 4.22 (q, J = 5.5 Hz, 2 H, CH_2CH_3), and 6.76–7.15 (m, 4 H, arom).

b. *trans*-[2-(*p*-Methoxyphenyl)cyclopropyl]methyl Acetate (6b). To a stirred suspension of 182 mg (4.8 mmol) of lithium aluminum hydride in 25 mL of ether was added dropwise under nitrogen a solution of 0.80 g (3.2 mmol) of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**) in ether. After the addition was complete, the reaction mixture was refluxed for an additional 6 h. It was then cooled to room temperature, and excess lithium aluminum hydride was destroyed by water. Fifty milliliters of 10% H_2SO_4 and 25 mL of ether were added, the layers were separated, and the aqueous layer was extracted several times with ether. The combined ether extracts were washed with water and 5% $NaHCO_3$ and dried ($MgSO_4$). The solvent was removed by rotary evaporation. An IR spectrum of the crude *trans*-2-(*p*-methoxyphenyl)cyclopropanemethanol (**13b**) showed a broad band at 3200–3400 cm^{-1}. The crude alcohol was treated as above with acetic anhydride and pyridine, and the product thus obtained was chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL) followed by 10% ether–hexane. The 10% ether fraction contained 0.44 g of product, which was further purified by molecular distillation to give 0.35 g (50%) of *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**): NMR ($CDCl_3$) δ 0.80–2.00 (m, 4 H, cyclopropyl), 2.05 (s, 3 H, acetyl), 3.77 (s, 3 H, OCH_3), 4.06 (d, J = 5.25 Hz, 2 H, CH_2O), and 6.73–7.12 (m, 4 H, arom); IR (neat) 2950, 1735, 1510, 1240, 1030, 825 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.84; H, 7.53.

***trans*-[2-(*m*-Methoxyphenyl)cyclopropyl]methyl Acetate (6c). a. Ethyl *trans*-2-(*m*-Methoxyphenyl)cyclopropane-1-carboxylate (12c).** Ethyl *trans*-2-(*m*-methoxyphenyl)cyclopropane-1-carboxylate (**12c**) was prepared as described previously for ethyl *trans*-2-(*p*-methoxyphenyl)-cyclopropane-1-carboxylate (**12b**). Ethyl *m*-methoxycinnamate[18] (**11c**), 2.8 g (13.6 mmol), was reacted with 0.72 g (15.0 mmol) of NaH and 3.75 g (15.8 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate to give 2.45 g of crude product. This material was chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 4% ether–hexane (500 mL) and 10% ether–hexane (1000 mL). The 10% ether–hexane fraction contained 1.45 g (49%) of ethyl *trans*-2-(*m*-methoxyphenyl)cyclopropane-1-carboxylate: NMR ($CDCl_3$) δ 1.15–2.05 (m, 3 H, C-2 and C-3 H's), 1.25 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.33–2.66 (m, 1 H, C-1 H), 3.76 (s, 3 H, OCH_3), 4.17 (q, J = 5.5 Hz, 2 H, CH_2CH_3), and 6.60–7.35 (m, 4 H, arom); IR (neat) 2980, 1700, 1640, 1170, 1040, 770 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.09; H, 7.21.

b. *trans*-[2-(*m*-Methoxyphenyl)cyclopropyl]methyl Acetate (6c). Ethyl *trans*-2-(*m*-methoxyphenyl)cyclopropane-1-carboxylate (**12c**) was reduced with lithium aluminum hydride as described previously for *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**). From 2.20 g (10.1 mmol) of the ester and 0.574 g (15.2 mmol) of lithium aluminum hydride, 1.44 g of crude *trans*-2-(*m*-methoxyphenyl)cyclopropanemethanol (**13c**) was obtained, IR (neat) 3300 cm^{-1} (br). A portion of this material (0.9 g) was acetylated as described previously for *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**). Workup and chromatography on a column of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (250 mL), 5% ether–hexane (750 mL), 8% ether–hexane (500 mL), and 10% ether–hexane (250 mL), gave 0.57 g (41%) of *trans*-[2-(*m*-methoxyphenyl)cyclopropyl]methyl acetate (**6c**). The product eluted in the 10% ether–hexane fraction: NMR ($CDCl_3$) δ 0.74–1.86 (m, 4 H, cyclopropyl), 1.96 (s, 3 H, acetyl), 3.86 (s, 3 H, OCH_3), 3.97 (d, J = 5.25 Hz, 2 H, CH_2O), and 6.56–7.36 (m, 4 H, arom); IR (neat) 2850, 1740, 1240, 1040, 780, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.12; H, 7.56.

***trans*-[2-(*p*-Methylphenyl)cyclopropyl]methyl Acetate (6d). a. Ethyl *trans*-2-(*p*-Methylphenyl)cyclopropane-1-carboxylate (12d).**[16] Ethyl *trans*-2-(*p*-methylphenyl)cyclopropane-1-carboxylate (**12d**) was prepared from ethyl *p*-methylcinnamate[18] (**11d**) as described previously for the preparation of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**). From 1.9 g (10 mmol) of ethyl *p*-methylcinnamate, 0.528 g (11 mmol, 50% dispersion) of sodium hydride, and 3.3 g (14 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate, a crude yield of 1.92 g was realized. Chromatography on a column of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, yielded 1.1 g (54%) of ethyl *trans*-2-(*p*-methylphenyl)cyclopropane-1-carboxylate (**12d**): NMR ($CDCl_3$) δ 0.75–2.0 (m, 3 H, C-2 and C-3 H's), 1.25 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.29–2.65 (m, 1 H, C-1 H), 2.29 (s, 3 H, CH_3), 4.15 (q, J = 5.5 Hz, 2 H, OCH_2CH_3), and 7.05 (s, 4 H, arom).

b. *trans*-[2-(*p*-Methylphenyl)cyclopropyl]methyl Acetate (6d). Ethyl *trans*-2-(*p*-methylphenyl)cyclopropane-1-carboxylate (**12d**), 1.16 g (5.0 mmol), was reduced with lithium aluminum hydride as described previously for the preparation of *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]-methyl acetate (**6b**) to yield 0.69 g of crude *trans*-2-(*p*-methylphenyl)-cyclopropanemethanol (**13d**) [IR (neat) 3300 cm^{-1} (br)]. This material was acetylated as described previously. Workup and chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane, yielded 0.5 g (49%) of *trans*-[2-(*p*-methylphenyl)cyclopropyl]methyl acetate (**6d**): NMR ($CDCl_3$) δ 0.80–2.00 (m, 4 H, cyclopropyl), 2.05 (s, 3 H, acetyl), 2.30 (s, 3 H, CH_3), 4.06 (d, J = 5.5 Hz, 2 H, CH_2O), and 7.05 (s, 4 H, arom); IR (neat) 2770, 1740, 1280, 1150, 1040, 970, 810 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.32; H, 8.03.

***trans*-[2-(*m*-Methylphenyl)cyclopropyl]methyl Acetate (6e). a. Ethyl *m*-Methylcinnamate (11e).** To a stirred suspension of 6.43 g (94.8 mmol) of sodium ethoxide in 100 mL of dry dimethylformamide under nitrogen was added over 0.5 h a solution of 19.9 g (88 mmol) of triethyl phosphonoacetate[19] in 50 mL of dimethylformamide. The resulting mixture was cooled to 0 °C and stirred 1 h, after which time a solution of 5.0 g (42 mmol) of *m*-tolualdehyde in 50 mL of dimethylformamide was added dropwise. The mixture was allowed to warm to room temperature, stirred for 24 h, and then poured into 400 mL of ice water. The resulting

(16) Kaiser, C.; Lester, B. M.; Zirkle, C. L.; Burger, A.; Davis, C. S.; Delia, T. J.; Zirngibl, L. *J. Med. Pharm. Chem.* **1962**, *5*, 1243.
(17) Johnson, C. R.; Rogers, P. E. *J. Org. Chem.* **1973**, *38*, 1793.
(18) Phillips, W. M.; Currie, D. J. *Can. J. Chem.* **1969**, *47*, 3137.
(19) Speziale, A. J.; Freeman, R. C. *J. Org. Chem.* **1958**, *23*, 1883.

mixture was extracted with ether. The ether was washed with 3 N HCl and water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 8.63 g of crude product. Chromatography on a column (2 × 40 cm) of Florisil, which was packed in hexane and eluted with 5% ether–hexane, yielded 5.37 g (68%) of ethyl *m*-methylcinnamate (**11e**): NMR ($CDCl_3$) δ 1.32 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.35 (s, 3 H, CH_3), 4.26 (q, J = 5.5 Hz, 2 H, CH_2CH_3), 6.41 (d, J = 13 Hz, 1 H, =CHC), 7.07–7.38 (m, 4 H, arom), and 7.69 (d, J = 13 Hz, 1 H, Ar CH=); IR (neat) 2990, 1710, 1310, 1150, 1030, 775, 660 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.72; H, 7.65.

b. Ethyl *trans*-2-(*m*-Methylphenyl)cyclopropane-1-carboxylate (12e). Ethyl *trans*-2-(*m*-methylphenyl)cyclopropane-1-carboxylate (**12e**) was prepared from ethyl *m*-methylcinnamate (**11e**) as described previously for the preparation of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**). From 2.1 g (11 mmol) of ethyl *m*-methylcinnamate, 0.49 g (10 mmol) of sodium hydride, and 2.37 g (10.3 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate, a crude yield of 1.13 g was realized. This material was further purified by silica gel preparative TLC (Kieselgel, 20 × 20 cm plates, chloroform eluent) to yield 0.79 g (36%) of ethyl *trans*-2-(*m*-methylphenyl)cyclopropane-1-carboxylate: NMR ($CDCl_3$) δ 1.25 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 1.1–2.0 (m, 3 H, C-2 and C-3 H's), 2.30 (s, 3 H, CH_3), 2.25–2.60 (m, 1 H, C-1 H), 4.18 (q, J = 5.5 Hz, 2 H, CH_2CH_3), and 6.83–7.35 (m, 4 H, arom); IR (neat) 2950, 1720, 1610, 1180, 1040, 770, 690 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.54; H, 7.92.

c. *trans*-[2-(*m*-Methylphenyl)cyclopropyl]methyl Acetate (6e). Ethyl *trans*-2-(*m*-methylphenyl)cyclopropane-1-carboxylate, 1.68 g (8.23 mmol), was reduced with lithium aluminum hydride (0.47 g, 12.5 mmol) as described previously for the preparation of ethyl *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**) to yield 1.13 g of crude *trans*-2-(*m*-methylphenyl)cyclopropanemethanol (**13e**) [IR (neat) 3300 cm^{-1} (br)]. This material was acetylated as described previously. The product was worked up and chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL) followed by 10% ether–hexane (500 mL). The 10% ether fraction contained 0.90 g (54%) of *trans*-[2-(*m*-methylphenyl)cyclopropyl]methyl acetate (**6e**): NMR ($CDCl_3$) δ 1.0–2.0 (m, 4 H, cyclopropyl), 2.05 (s, 3 H, acetyl), 2.31 (s, 3 H, CH_3), 4.06 (d, J = 5.25 Hz, 2 H, CH_2O), and 6.95–7.23 (m, 4 H, arom); IR (neat) 2920, 2850, 1735, 1230, 1030, 770 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.48; H, 8.07.

***trans*-[2-(*p*-Cyanophenyl)cyclopropyl]methyl Acetate (6f). a. Ethyl *trans*-2-(*p*-Bromophenyl)cyclopropane-1-carboxylate (12i).**[20] Ethyl *trans*-2-(*p*-bromophenyl)cyclopropane-1-carboxylate (**12i**) was prepared from ethyl *p*-bromocinnamate (**11i**)[21] as described previously for the preparation of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**). From 1.61 g (6.33 mmol) of ethyl *p*-bromocinnamate, 0.34 g (7.0 mmol, 50% dispersion) of sodium hydride, and 1.65 g (7.0 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate, a crude yield of 2.16 g was realized. Chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, yielded 0.53 g (31%) of ethyl *trans*-2-(*p*-bromophenyl)cyclopropane-1-carboxylate (**12i**): NMR ($CDCl_3$) δ 0.90–1.95 (m, 3 H, C-2 and C-3 H's), 1.27 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.30–2.74 (m, 1 H, C-1 H), 4.19 (q, J = 5.5 Hz, 2 H, CH_2CH_3), and 6.92–7.50 (m, 4 H, arom).

b. *trans*-[2-(*p*-Cyanophenyl)cyclopropyl]methyl Acetate (6f). Ethyl *trans*-2-(*p*-bromophenyl)cyclopropane-1-carboxylate, 7.95 g (29.6 mmol), was reduced with lithium aluminum hydride as described previously for the preparation of ethyl *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**) to yield 5.4 g of crude *trans*-2-(*p*-bromophenyl)cyclopropanemethanol (**13i**) [IR (neat) 3300 cm^{-1} (br)]. This material was taken up in 50 mL of freshly distilled 1-methyl-2-pyrrolidinone, and 3.1 g (37.5 mmol) of cuprous cyanide was added in one portion. The solution was stirred vigorously and heated at 160 °C under nitrogen for 10 h. The solution was cooled and poured into 200 mL of 4% aqueous NaCN. This mixture was extracted with benzene, and then the aqueous layer was poured into 200 mL of 20% aqueous NaCN. This new mixture was extracted with benzene, and the combined benzene extracts were washed sequentially with 20% NaCN and water and dried ($MgSO_4$). The solvent was removed by rotary evaporation to yield 4.9 g of crude *trans*-2-(*p*-cyanophenyl)cyclopropanemethanol (**13f**) [IR 3300 (br) and 2220 cm^{-1} (sh)], which was acetylated as described previously. The 4.55 g of crude acetate was purified by chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane (500 mL), 10% ether–hexane (500 mL), 20% ether–hexane (250 mL), and 40% ether–hexane (500 mL). The 40% fraction contained 3.62 g (57%) of *trans*-[2-(*p*-cyanophenyl)cyclopropyl]methyl acetate (**6f**): NMR ($CDCl_3$) δ 0.90–2.00 (m, 4 H, cyclopropyl), 2.05 (s, 3 H, acetyl), 4.07 (d, J = 5.2 Hz, 2 H, CH_2O), and 7.07–7.63 (m, 4 H, arom); IR (neat) 2980, 2240, 1740, 1610, 1240, 1030, 840 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.08; N, 6.50. Found: C, 72.80; H, 6.31; N, 6.56.

***trans*-[2-(*m*-Cyanophenyl)cyclopropyl]methyl Acetate (6g). a. Ethyl *trans*-2-(*m*-Bromophenyl)cyclopropane-1-carboxylate (12j).**[20] Ethyl *trans*-2-(*m*-bromophenyl)cyclopropane-1-carboxylate (**12j**) was prepared from ethyl *m*-bromocinnamate[21] (**11j**) as described previously for the preparation of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**). From 5.0 g (19.7 mmol) of ethyl *m*-bromocinnamate, 1.04 g (21.7 mmol, 50% dispersion) of sodium hydride, and 5.1 g (21.7 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate, a crude yield of 4.4 g was realized. Chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, yielded 2.3 g (43%) of ethyl *trans*-2-(*m*-bromophenyl)cyclopropane-1-carboxylate (**12j**): NMR ($CDCl_3$) δ 1.07–2.04 (m, 3 H, C-2 and C-3 H's), 1.25 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.29–2.63 (m, 1 H, C-1 H), 4.16 (q, J = 5.5 Hz, 2 H, CH_2CH_3), and 7.02–7.45 (m, 4 H, arom).

b. *trans*-[2-(*m*-Cyanophenyl)cyclopropyl]methyl Acetate (6g). Ethyl *trans*-2-(*m*-bromophenyl)cyclopropane-1-carboxylate (**12j**), 6.55 g (24.4 mmol), was reduced with lithium aluminum hydride as described previously for the preparation of ethyl *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**) to yield 5.05 g of crude *trans*-2-(*m*-bromophenyl)cyclopropanemethanol (**13j**) [IR (neat) 3300 cm^{-1} (br)]. This material was converted to *trans*-2-(*m*-cyanophenyl)cyclopropanemethanol (**13g**) as described previously in the preparation of *trans*-[2-(*p*-cyanophenyl)cyclopropyl]methyl acetate (**6f**). The total yield of *trans*-2-(*m*-cyanophenyl)cyclopropanemethanol was 3.75 g [IR (neat) 3300 (br) and 2220 cm^{-1} (sh)]. A 1.9-g portion of this material was acetylated as described previously. The crude product, which weighed 1.4 g, was chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane (250 mL), 10% ether–hexane (250 mL), 20% ether–hexane (250 mL), and 40% ether–hexane (500 mL). The 40% ether fraction contained 0.88 g (33%) of *trans*-[2-(*m*-cyanophenyl)cyclopropyl]methyl acetate (**6g**): NMR ($CDCl_3$) δ 0.9–2.0 (m, 4 H, cyclopropyl), 2.07 (s, 3 H, acetyl), 4.00–4.14 (dd, 2 H, CH_2O), and 7.25–7.55 (m, 4 H, arom); IR (neat) 2950, 2240, 1740, 1370, 1230, 1020, 780, 670 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.08; N, 6.50. Found: C, 72.25; H, 6.33; N, 6.20.

***trans*-[2-[*m*-(Trifluoromethyl)phenyl]cyclopropyl]methyl Acetate (6h). a. Ethyl *trans*-2-[*m*-(Trifluoromethyl)phenyl]cyclopropane-1-carboxylate (12h).**[16] Ethyl *trans*-2-[*m*-(trifluoromethyl)phenyl]cyclopropane-1-carboxylate (**12h**) was prepared from ethyl [*m*-(trifluoromethyl)-phenyl]cinnamate (**11h**)[18] as described earlier for the preparation of ethyl *trans*-2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (**12b**). From 2.47 g (10.1 mmol) of ethyl *m*-(trifluoromethyl)cinnamate (**11h**), 0.57 g (12 mmol, 50% dispersion) of sodium hydride, and 2.83 g (12 mmol) of dimethyl(diethylamino)oxosulfonium fluoborate, a yield of 1.9 g was realized. Chromatography on a column (1.5 × 50 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, yielded 0.75 g (29%) of ethyl *trans*-2-[*m*-(trifluoromethyl)phenyl]cyclopropane-1-carboxylate (**12h**): NMR ($CDCl_3$) δ 0.80–2.10 (m, 3 H, C-2 and C-3 H's), 1.25 (t, J = 5.5 Hz, 3 H, CH_2CH_3), 2.40–2.74 (m, 1 H, C-1 H), 4.17 (q, J = 5.5 Hz, 2 H, CH_2CH_3), and 7.25–7.65 (m, 4 H, arom).

b. *trans*-[2-[*m*-(Trifluoromethyl)phenyl]cyclopropyl]methyl Acetate (6h). Ethyl *trans*-2-[*m*-(trifluoromethyl)phenyl]cyclopropane-1-carboxylate (**12h**), 0.75 g (2.9 mmol), was reduced with lithium aluminum hydride as described previously in the preparation of *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]methyl acetate (**6b**) to yield 0.58 g of crude *trans*-2-[*m*-(trifluoromethyl)phenyl]cyclopropanemethanol (**13h**) [IR (neat) 3300 cm^{-1} (br)]. This material was acetylated as described previously. The crude product, which weighed 1.1 g, was chromatographed on a column (1.5 × 50 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL), 5% ether–hexane (500 mL), and 10% ether–hexane (500 mL). The 10% ether fraction contained 0.5 g (66%) of *trans*-[2-[*m*-(trifluoromethyl)phenyl]cyclopropyl]methyl acetate (**6h**): NMR ($CDCl_3$) δ 0.85–2.0 (m, 4 H, cyclopropyl), 2.05 (s, 3 H, CH_3), 4.07 (d, J = 5.25 Hz, 2 H, CH_2O), and 7.20–7.50 (m, 4 H, arom); IR (neat) 3000, 2940, 1740, 1330, 1230, 1120, 690 cm^{-1}. Anal. Calcd for $C_{13}H_{13}F_3O_2$: C, 60.46; H, 5.07. Found: C, 60.76; H, 5.02.

Ethyl *exo*- and *endo*-4-Bromo-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate (16c and 17c). To a rapidly stirred mixture of 1.95 g (0.01 mol) of 5-bromoindene[22] (**15c**) and 0.32 g (0.002 mol) of an-

(20) Fuchs, R.; Bloomfield, J. J. *J. Org. Chem.* **1963**, *28*, 910.
(21) Silver, R. F.; Kerr, K. A.; Frandsen, P. D.; Kelley, S. J.; Holmes, H. L. *Can. J. Chem.* **1967**, *45*, 1001.

hydrous $CuSO_4$, heated at 70–80 °C, was added dropwise 2.28 g (0.02 mol) of ethyl diazoacetate under nitrogen. After the addition was complete, the reaction mixture was stirred overnight at 70–80 °C. The cooled reaction mixture was diluted with ether, and the cupric sulfate was removed by filtration. After removal of the ether in vacuo, the crude product mixture was chromatographed on a 3.5 × 93 cm deactivated (8% H_2O) silica gel (60–200 mesh) column slurry packed in hexane and eluted with 2% ether–hexane (2 L) and 4% ether–hexane (5 L) to give 0.039 g of 5-bromoindene followed by 1.41 g (66%) of ethyl *exo*-4-bromo-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate (**16c**) and finally 0.96 g of the endo isomer (**17c**). A small amount (0.16 g) of an overlap fraction of **16c** and **17c** was also obtained. For the exo isomer (**16c**) were found the following: NMR ($CDCl_3$) δ 0.90–1.02 (m, 1 H, C-1 H), 1.25 (t, J = 6.8 Hz, 3 H, CH_3), 2.40–2.50 (m, 1 H, C-6a H), 2.80 (dd, J = 6.8, 13.2 Hz, 1 H, C-1a H), 3.00–3.20 (m, 2 H, C-6 H's), 4.15 (q, J = 6.8 Hz, 2 H, OCH_2), 7.10–7.25 (m, 3 H, arom). Anal. Calcd for $C_{13}H_{13}O_2Br$: C, 55.51; H, 4.62. Found: C, 55.30; H, 4.48. For the endo isomer (**17c**) were found the following: NMR ($CDCl_3$) δ 1.03 (t, J = 6.9 Hz, 3 H, CH_3), 1.98–2.08 (m, 1 H, C-1 H), 2.31 (q, J = 6.1 Hz, 1 H, C-6a H), 2.91 (t, J = 6.9 Hz, 1 H, C-1a H), 3.08–3.40 (m, 2 H, C-6 H's), 3.85 (q, J = 6.9 Hz, 2 H, OCH_2), 7.00–7.20 (m, 3 H, arom). Anal. Calcd for $C_{13}H_{13}O_2Br$: C, 55.51; H, 4.62. Found: C, 55.77; H, 4.71.

***exo*-(4-Cyano-1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl Acetate (14b).** Ethyl *exo*-4-bromo-1,1a,6,6a-tetrahydrocycloprop[*a*]-indene-1-carboxylate (**16c**), 1.34 g (0.0048 mol), was reduced with lithium aluminum hydride to give 1.06 g (92%) of *exo*-4-bromo-1-(hydroxymethyl)-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**18a**): NMR δ 0.55–0.87 (m, 1 H, C-1 H), 1.65–1.85 (m, 1 H, C-6a H), 2.15–2.27 (m, 1 H, C-1a H), 2.94–3.03 (m, 2 H, C-6 H's), 3.48 (d, J = 7.4 Hz, 2 H, OCH_2), 3.82 (s, 1 H, OH), 7.13–7.30 (m, 3 H, arom).

A solution of 5.0 g (0.021 mol) of the bromo alcohol **18c** obtained as above, and 3.4 g (0.038 mol) of cuprous cyanide in 37 mL of *N*-methylpyrrolidinone (vacuum distilled prior to use) was stirred and heated at 180 °C under nitrogen for 15 h. Ether (50 mL) and 5% ammonium hydroxide (50 mL) were added to the cooled reaction mixture. A solid precipitate was filtered. The ether portion of the filtrate was washed with 5% ammonium hydroxide until the aqueous layer was colorless and then sequentially with water and saturated aqueous sodium chloride. All the aqueous solutions were combined and extracted with ether three times. The combined ether layers were dried with $MgSO_4$ and evaporated to give 2.3 g (59%) of *exo*-4-cyano-1-(hydroxymethyl)-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**18b**) as an oil. NMR: ($CDCl_3$) δ 0.60–0.90 (m, 1 H, C-1 H), 1.70–2.10 (m, 1 H, C-6a H), 2.30 (s, 1 H, OH), 2.15–2.55 (m, 1 H, C-1a H), 3.08–3.19 (m, 2 H, C-6 H's), 3.60 (d, J = 6.6 Hz, 2 H, OCH_2), 7.25–7.58 (m, 3 H, arom); IR (KBr) 2210 cm^{-1} (CN).

The cyano alcohol **18b** (2.2 g, 0.012 mol) was acetylated as described previously. The crude product was chromatographed on a deactivated silica gel column (60–200 mesh, 8% H_2O) packed with hexane and eluted with 5% (300 mL), 10% (1200 mL), and 25% ether–hexane (3000 mL) to afford 1.1 g (45%) of *exo*-(4-cyano-1,1a,6,6a-tetrahydrocycloprop-[*a*]inden-1-yl)methyl acetate (**14b**): mp 36–37 °C; NMR ($CDCl_3$) δ 0.78–0.85 (m, 1 H, C-1 H), 1.90–2.00 (m, 1 H, C-6a H), 2.08 (s, 3 H, CH_3), 2.45 (br s, 1 H, C-1a H), 3.05 (d, J = 12.8 Hz, 1 H, C-6 H), 3.20 (dd, J = 6.2, 12.8 Hz, 1 H, C-6 H), 3.96–4.10 (m, 2 H, CH_2O), 7.34–7.44 (m, 3 H, arom). Anal. Calcd for $C_{14}H_{13}O_2N$: C, 74.01; H, 5.72; N, 6.17. Found: C, 73.90; H, 5.80; N, 6.22.

***endo*-(4-Cyano-1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl Acetate.** Ethyl *endo*-4-bromo-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate (**17c**), 77 mg (0.27 mmol), was reduced with lithium aluminum hydride and reacted with cuprous cyanide to give 37 mg (74%) of *endo*-4-cyano-1-(hydroxymethyl)-1,1a,6,6a-tetrahydrocycloprop[*a*]-indene: NMR ($CDCl_3$) δ 1.25–1.43 (m, 2 H, C-1 and C-6a H's), 2.00–2.20 (m, 1 H, C-1a H), 2.60–3.20 (m, 2 H, C-6 H's), 2.95 (s, 1 H, OH), 3.13-3.60 (m, 2 H, CH_2O), 7.26–7.41 (m, 3 H, arom).

Acetylation of the cyano alcohol, 51 mg (0.20 mmol), afforded 33 mg (73%) of *endo*-(4-cyano-1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)-methyl acetate (*endo*-**14b**): NMR ($CDCl_3$) δ 1.58–1.68 (m, 1 H, C-1 H), 1.99 (s, 3 H, CH_3), 2.10–2.20 (m, 1 H, C-6a H), 2.70 (d, J = 5.7 Hz, 1 H, C-1a H), 2.90–3.1 (m, 2 H, C-6 H's), 3.60 (d, J = 4.8 Hz, 2 H, CH_2O), 7.20–7.50 (m, 3 H, arom). Anal. Calcd for $C_{14}H_{13}O_2N$: C, 74.01; H, 5.72; N, 6.17. Found: C, 73.44; H, 6.17; N, 5.90.

***exo*-(1,1a,6,6a-Tetrahydrocycloprop[*a*]inden-1-yl)methyl Acetate (14a).** *Exo*-1-(hydroxymethyl)-1,1a,6,6a-tetrahydrocycloprop[*a*]-indene,[23] 1.79 g (0.011 mol), was acetylated as above to give a yellow oil, which upon distillation gave 1.9 g (86%) of *exo*-(1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (**14a**) as a colorless oil: bp 122–123 °C (1 mm); NMR ($CDCl_3$) δ 0.76 (m, 1 H, C-1 H), 1.79 (m, 1 H, C-6a H), 2.05 (s, 3 H, CH_3), 2.35 (d, J = 7.5 Hz, 1 H, C-1a H), 2.99 (d, J = 17 Hz, 1 H, C-6 H), 3.16 (dd, J = 7.5, 17 Hz, C-6 H), 4.00 (m, 2 H, OCH_2), 7.08–7.28 (m, 4 H, arom.). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.22; H, 6.93. Found: C, 77.30; H, 6.96.

***endo*-(1,1a,6,6a-Tetrahydrocycloprop[*a*]inden-1-yl)methyl Acetate.** *endo*-1-(Hydroxymethyl)-1,1a,6,6a-tetrahydrocycloprop[*a*]indene,[23] 37 mg (0.18 mmol), was acetylated as before to give 33 mg of crude acetate. Purification by preparative TLC (Kieselgel, 20 × 20 cm plates, developing solvent 40% ether–hexane) afforded 10 mg (22%) of *endo*-(1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (*endo*-**14a**): NMR ($CDCl_3$) δ 1.45–1.55 (m, 1 H, C-1 H), 1.98 (s, 3 H, CH_3), 1.95–2.10 (m, 1 H, C-6a H), 2.66 (t, J = 4.7 Hz, 1 H, C-1a H), 2.85 (d, J = 14.3 Hz, 1 H, C-6 H), 3.10–3.20 (dd, J = 7.0, 14.3 Hz, 1 H, C-6 H), 3.55–3.75 (m, 2 H, OCH_2), 7.08–7.38 (m, 4 H, arom.). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93. Found: C, 76.99; H, 7.08.

4-Acetoxy-4-(*p*-methoxyphenyl)-1-butene (7b). A solution of 3-propenylmagnesium bromide in ether was prepared from 1.33 g (11.0 mmol) of 3-bromopropene, 0.27 g (11.0 mmol) of magnesium turnings, and 45 mL of ether. To this was added dropwise with stirring under nitrogen a solution of 1.5 g (11.0 mmol) of *p*-anisaldehyde in 50 mL of ether. After the addition was complete, the mixture was refluxed for an additional 20 min, cooled, treated with saturated NH_4Cl, washed with water, and then dried ($MgSO_4$). The solvent was removed to yield 0.75 g (39%) of crude 1-(*p*-methoxyphenyl)-3-buten-1-ol, IR (neat) 3300 cm^{-1} (br). A portion of this material, 0.3 g (1.67 mmol), was then reacted with acetic anhydride in pyridine as described previously to give a crude product, which was chromatographed on a column (1.5 × 70 cm) of deactivated silica gel (100–200 mesh, 6% H_2O) that was packed in hexane and eluted with 1% ether–hexane (1 L) followed by 2% ether–hexane (1 L). The 2% ether fraction contained 0.21 g (61%) of 4-acetoxy-4-(*p*-methoxyphenyl)-1-butene (**7b**): NMR ($CDCl_3$) δ 2.02 (s, 3 H, acetyl), 2.58 (t, J = 5.5 Hz, 2 H, C-3 H's), 3.76 (s, 3 H, OCH_3), 4.85–5.93 (m, 4 H, C-1, C-2, C-4 H's), and 6.78–7.35 (m, 4 H, arom); IR (neat) 2975, 1740, 1630, 1260, 1050, 850 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.66; H, 7.45.

4-Acetoxy-4-(*m*-methoxyphenyl)-1-butene (7c). *m*-Anisaldehyde was converted to 1-(*m*-methoxyphenyl)-3-buten-1-ol as described previously for the preparation of 4-acetoxy-4-(*p*-methoxyphenyl)-1-butene (**7b**). From 2.26 g (16.6 mmol) of *m*-anisaldehyde, a crude yield of 2.1 g of alcohol was realized; IR (neat) 3300 cm^{-1} (br). This material was acetylated as described previously. Workup and chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL), 3% ether–hexane (500 mL), and 5% ether–hexane (500 mL), yielded in the 5% ether–hexane fraction 0.40 g (11%) of 4-acetoxy-4-(*m*-methoxyphenyl)-1-butene (**7c**): NMR ($CDCl_3$) δ 2.05 (s, 3 H, acetyl), 2.60 (t, J = 5.5 Hz, 2 H, C-3 H's), 3.80 (s, 3 H, OCH_3), 4.80–6.0 (m, 4 H, C-1, C-2, C-4 H's), and 6.83–7.05 (m, 4 H, arom); IR (neat) 2950, 1740, 1600, 1240, 1050, 920, 780, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.08; H, 7.43.

4-Acetoxy-4-(*p*-methylphenyl)-1-butene (7d). *p*-Tolualdehyde was converted to 1-(*p*-methylphenyl)-3-buten-1-ol as described previously for the preparation of 4-acetoxy-4-(*p*-methoxyphenyl)-1-butene (**7b**). From 6.6 g (55 mmol) of *p*-tolualdehyde, a crude yield of 6.0 g of alcohol was realized, IR (neat) 3300 cm^{-1} (br). This material was acetylated as described previously. Workup and chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 1% ether–hexane (500 mL) followed by 2% ether–hexane, yielded 1.46 g (13%) of 4-acetoxy-4-(*p*-methylphenyl)-1-butene (**7d**). The product was eluted in the 2% ether–hexane fraction: NMR ($CDCl_3$) δ 2.02 (s, 3 H, acetyl), 2.31 (s, 3 H, CH_3), 2.57 (t, 2 H, J = 5.5 Hz, C-3 H's), 4.87–5.96 (m, 4 H, C-1, C-2, C-4 H's), and 7.20 (s, 4 H, arom); IR (neat) 2920, 1740, 1380, 1250, 1040, 830 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.32; H, 8.08.

4-Acetoxy-4-(*m*-methylphenyl)-1-butene (7e). *m*-Tolualdehyde was converted to 1-(*m*-methylphenyl)-3-buten-1-ol as described previously for the preparation of 4-acetoxy-4-(*p*-methoxyphenyl)-1-butene (**7b**). From 2.0 g (16.6 mmol) of *m*-tolualdehyde, a crude yield of 1.75 g of 1-(*m*-methylphenyl)-3-buten-1-ol [IR (neat) 3300 cm^{-1} (br)] was realized. This material was acetylated as described previously. Workup and chromatography on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, yielded 0.4 g (12%) of 4-acetoxy-4-(*m*-methylphenyl)-1-butene (**7e**): NMR ($CDCl_3$) δ 2.02 (s, 3 H, acetyl), 2.34 (s,

(22) Marechal, E.; Cailland, P. *C. R. Seances Acad. Sci., Ser. C* **1968**, *C266* (7), 447.

(23) Hixson, S. S.; Borovsky, J. *J. Am. Chem. Soc.* **1976**, *98*, 2840.

3 H, CH_3), 2.59 (t, J = 5.5 Hz, 2 H, C-3 H's), 4.85–6.06 (m, 4 H, C-1, C-2, C-4 H's), and 7.15 (s, 4 H, arom); IR (neat) 2920, 1740, 1380, 1350, 1150, 800, and 720 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.20; H, 8.15.

4-Acetoxy-4-(*p*-cyanophenyl)-1-butene (7f). A solution of allylmagnesium bromide, prepared[24] from 4.6 g (38 mmol) of 3-bromopropene, 2.23 g (92 mmol) of magnesium turnings, and 50 mL of ether was decanted from the magnesium and then added dropwise under N_2 over a period of 4 h to a solution of 4.0 g (21.6 mmol) of *p*-bromobenzaldehyde in 40 mL of ether. Following completion of addition, the solution was stirred at room temperature for an additional 24 h and then washed with saturated NH_4Cl and water and dried ($MgSO_4$). The solvent was removed by rotary evaporation to yield 4.6 g (94%) of crude 1-(*p*-bromophenyl)-3-buten-1-ol, IR (neat) 3300 cm^{-1} (br).

This alcohol was then converted to 1-(*p*-cyanophenyl)-3-buten-1-ol as described previously in the preparation of *trans*-[2-(*p*-cyanophenyl)-cyclopropyl]methyl acetate (**6f**). From 4.6 g (20 mmol) of crude 1-(*p*-bromophenyl)-3-buten-1-ol and 3.0 g (33.7 mmol) of cuprous cyanide, a crude yield of 2.1 g of 1-(*p*-cyanophenyl)-3-buten-1-ol was realized: IR (neat) 3300 (br) and 2240 cm^{-1}. A portion of this material (0.5 g) was acetylated as described previously. The crude acetate, which weighed 0.45 g, was purified by silica gel preparative TLC (Kieselgel, 20 × 20 cm plates, 10% ether–hexane eluent) to yield 79.0 mg (7% based on *p*-bromobenzaldehyde) of 4-acetoxy-4-(*p*-cyanophenyl)-1-butene (**7f**): NMR ($CDCl_3$) δ 2.09 (s, 3 H, acetyl), 2.60 (t, J = 5.5 Hz, 2 H, C-3 H's), 4.87–6.0 (m, 4 H, C-1, C-2, C-4 H's), and 7.40–7.79 (m, 4 H, arom); IR (neat) 2950, 2240, 1740, 1370, 1240, 1050, 920, 850 cm^{-1}; MS, *m/e* (relative intensity) (EI) 174 (44.5), 154 (8.2), 132 (8.5), 130 (8.6), 102 (10.6), 43 (100.0); MS, *m/e* (CH_4, CI) 256 (4.0), 244 (10.7), 217 (13.7), 216 (100.0), 174 (6.0), 157 (7.0), 156 (57.2). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.08; N, 6.50. Found: C, 72.61; H, 6.30; N, 6.21.

4-Acetoxy-4-(*m*-cyanophenyl)-1-butene (7g). 1-(*m*-Bromophenyl)-3-buten-1-ol was prepared as described previously in the preparation of 4-acetoxy-4-(*p*-cyanophenyl)-1-butene (**7f**). From 4.0 g (22 mmol) of *m*-bromobenzaldehyde and 4.6 g (38 mmol) of 3-bromopropene, a crude yield of 4.7 g (96%) of 1-(*m*-bromophenyl)-3-buten-1-ol was realized: IR (neat) 3300 cm^{-1} (br). This material was converted to 1-(*m*-cyanophenyl)-3-buten-1-ol as described previously in the preparation of *trans*-[2-(*p*-cyanophenyl)cyclopropyl]methyl acetate (**6f**). From 4.7 g of alcohol, a yield of 2.2 g of crude 1-(*m*-cyanophenyl)-3-buten-1-ol was realized: IR (neat) 3300 (br) and 2240 cm^{-1}. A portion of this material (0.5 g) was acetylated as described previously. The crude product (0.42 g) was purified by silica gel preparative TLC (Kieselgel, 20 × 20 cm plates, 10% ether–hexane eluent) to yield 69 mg (6% based on *m*-bromobenzaldehyde) of 4-acetoxy-4-(*m*-cyanophenyl)-1-butene: NMR ($CDCl_3$) δ 2.09 (s, 3 H, CH_3), 2.59 (t, J = 5.5 Hz, 2 H, C-3 H's), 4.87–6.0 (m, 4 H, C-1, C-2, C-4 H's), and 7.55–7.73 (m, 4 H, arom); IR (neat) 2960, 2240, 1740, 1380, 1240, 1030, 690 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.08; N, 6.50. Found: C, 72.28; H, 6.23; H, 6.11.

4-Acetoxy-4-[*m*-(trifluoromethyl)phenyl]-1-butene (7h). 1-[*m*-(Trifluoromethyl)phenyl]-3-buten-1-ol was prepared as described previously in the synthesis of 4-acetoxy-4-(*p*-cyanophenyl)-1-butene (**7f**). From 5.0 g (28.7 mmol) of *m*-(trifluoromethyl)benzaldehyde a crude yield of 6.3 g of alcohol was realized, IR (neat) 3300 cm^{-1} (br). A 1-g portion of this material was acetylated as described previously. The crude product (1.32 g) was chromatographed on a column (1.5 × 70 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, to yield 0.62 g (52%) of 4-acetoxy-4-[*m*-(trifluoromethyl)phenyl]-1-butene (**7h**): NMR ($CDCl_3$) δ 2.09 (s, 3 H, CH_3), 2.60 (t, J = 5.5 Hz, 2 H, C-3 H's), 4.82–6.0 (m, 4 H, C-1, C-2, C-4 H's), and 7.42–7.66 (m, 4 H arom); IR (neat) 2950, 1740, 1340, 1250, 1170, 1140, 800 cm^{-1}. Anal. Calcd for $C_{13}H_{13}F_3O_2$: C, 60.46; H, 5.07. Found: C, 60.61; H, 5.23.

4-(*p*-Bromophenyl)-4-methoxy-1-butene. Sodium hydride, 0.63 (13 mmol, 50% mineral oil dispersion), was washed repeatedly under nitrogen with hexane to remove the mineral oil. The hexane was decanted, and dimethyl sulfoxide (10 mL) was introduced into the flask. The suspension was stirred and heated at 70 °C until the evolution of hydrogen had ceased. The mixture was then cooled, and a solution containing 2.0 g (8.8 mmol) of 1-(*p*-bromophenyl)-3-buten-1-ol (vide supra) in 20 mL of dimethyl sulfoxide was added dropwise with stirring. This solution was then cooled in an ice bath, and 2.0 mL (4.7 g, 33 mmol) of methyl iodide was added dropwise. Following completion of the addition, the mixture was poured into ether, extracted with water, and dried ($MgSO_4$). The solvent was removed by rotary evaporation to yield 2.15 g of crude product, which was chromatographed on a column (1.5 × 30 cm) of deactivated 6% H_2O) silica gel (100–200 mesh) that was packed in hexane and eluted with 5% ether–hexane, to yield 1.5 g (71%) of 4-(*p*-bromophenyl)-4-methoxy-1-butene: NMR ($CDCl_3$) δ 2.28–2.68 (m, 2 H, C-3 H's), 3.19 (s, 3 H, OCH_3), 4.13 (t, J = 5.5 Hz, 1 H, C-4 H), 4.80–6.0 (m, 3 H, C-1, C-2 H's), and 7.10–7.58 (m, 4 H, arom); IR (neat) 2940, 1650, 1600, 1490, 1410, 1100, 1010, 920, 830 cm^{-1}. Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.68; H, 5.70.

4-(*p*-Cyanophenyl)-4-methoxy-1-butene (8f). 4-(*p*-Cyanophenyl)-4-methoxy-1-butene (**8f**) was prepared from 4-(*p*-bromophenyl)-4-methoxy-1-butene as described previously in the preparation of *trans*-[2-(4-cyanophenyl)cyclopropyl]methyl acetate (**6f**). From 1.25 g (5.2 mmol) of 4-(*p*-bromophenyl)-4-methoxy-1-butene and 0.69 g (7.8 mmol) of cuprous cyanide, a crude yield of 1.15 g of product was realized. This material was purified by chromatography on a column (1.5 × 30 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL), 5% ether–hexane (250 mL), and 10% ether–hexane (500 mL). Fractions 12–18 (20 mL each) contained 0.26 g of 4-(4-bromophenyl)-4-methoxy-1-butene, and fractions 46–53 contained 0.20 g (26%) of 4-(*p*-cyanophenyl)-4-methoxy-1-butene (**8f**): NMR ($CDCl_3$) δ 2.30–2.65 (m, 2 H, C-3 H's), 3.25 (s, 3 H, OCH_3), 4.25 (t, J = 5.5 Hz, 1 H, C-4 H), 4.80–6.00 (m, 3 H, C-1, C-2 H's), and 7.35–7.77 (m, 4 H, arom); IR (neat) 2950, 2240, 1610, 1410, 1090, 920, and 840 cm^{-1}; MS, *m/e* (relative intensity) (EI) 147 (9.5) 146 (100.0), 130 (5.1), 116 (15.9), 102 (9.5), 91 (7.5), (CH_4, CI) 216 (9.0), 189 (12.5), 188 (100.0), 156 (9.4), 146 (24.3). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 6.99; N, 7.48. Found: C, 77.03; H, 7.10; N, 7.37.

4-(*m*-Bromophenyl)-4-methoxy-1-butene. 4-(*m*-Bromophenyl)-4-methoxy-1-butene was prepared as described previously in the preparation of 4-(*p*-bromophenyl)-4-methoxy-1-butene. From 2.0 g (8.8 mmol) of 4-(*p*-bromophenyl)-1-buten-4-ol, a crude yield of 1.85 g of product was realized. This material was chromatographed on a column (1.5 × 30 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, to yield 1.40 g (66%) of 4-(*m*-bromophenyl)-4-methoxy-1-butene: NMR ($CDCl_3$) δ 2.30–2.72 (m, 2 H, C-3 H's), 3.20 (s, 3 H, OCH_3), 4.13 (t, J = 5.5 Hz, 1 H, C-4 H), 4.80–6.0 (m, 3 H, C-1, C-2 H's), and 7.15–7.59 (m, 4 H, arom); IR (neat) 2920, 1570, 1430, 1350, 1190, 1090, 1000, 920, 780, 690 cm^{-1}. Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.94; H, 5.48.

4-(*m*-Cyanophenyl)-4-methoxy-1-butene (8g). 4-(*m*-Cyanophenyl)-4-methoxy-1-butene (**8g**) was prepared from 4-(*m*-bromophenyl)-4-methoxy-1-butene as described previously in the preparation of *trans*-[2-(*p*-cyanophenyl)cyclopropyl]methyl acetate (**6f**). From 1.25 g (5.2 mmol) of 4-(*m*-bromophenyl)-4-methoxy-1-butene, a crude yield of 1.20 g of product was realized. This material was purified by chromatography on a column (1.5 × 30 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 2% ether–hexane (500 mL), 5% ether–hexane (250 mL), and 10% ether–hexane (500 mL). Fractions 14–19 (20 mL each) contained 0.29 g of unreacted 4-(*m*-bromophenyl)-4-methoxy-1-butene (**8f**), and fractions 37–46 contained 0.24 g (32%) of 4-(*m*-cyanophenyl)-4-methoxy-1-butene (**8g**): NMR ($CDCl_3$) δ 2.30–2.65 (m, 2 H, C-3 H's), 3.25 (s, 3 H, OCH_3), 4.25 (t, J = 5.5 Hz, 1 H, C-4 H), 4.80–6.00 (m, 3 H, C-1, C-2 H's), and 7.52–7.70 (m, 4 H, arom); IR (neat) 2950, 2240, 1650, 1440, 1100, 920, 800, 690 cm^{-1}; MS, *m/e* (relative intensity) (EI) 147 (10.8), 146 (100.0), 130 (4.2), 116 (13.2), 102 (7.3), 91 (6.2), (CH_4, CI) 216 (10.7), 189 (13.6), 188 (100.0), 156 (9.3), 146 (18.7). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 6.99; N, 7.48. Found: C, 77.03; H, 7.16; N, 7.34.

4-[*m*-(Trifluoromethyl)phenyl]-4-methoxy-1-butene (8h). 1-[*m*-(Trifluoromethyl)phenyl]-3-buten-1-ol (vide supra) was methylated as described previously in the preparation of 4-(*p*-cyanophenyl)-4-methoxy-1-butene (**8f**). From 1.5 g (7 mmol) of alcohol, a crude yield of 1.62 g was realized. This material was chromatographed on a column (1.5 × 50 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, to yield 1.15 g (72%) of 4-[*m*-(trifluoromethyl)phenyl]-4-methoxy-1-butene: NMR ($CDCl_3$) δ 2.34–2.67 (m, 2 H, C-3 H's), 3.23 (s, 3 H, OCH_3), 4.24 (t, J = 5.5 Hz, 1 H, C-4 H), 4.83–6.00 (m, 3 H, C-1, C-2 H's), and 7.52 (s, 4 H, arom); IR (neat) 2940, 1470, 1350, 1140, 930, 810, 710 cm^{-1}; MS, *m/e* (relative intensity) (EI) 190 (9.8), 189 (100.0), 173 (4.1), 159 (8.3), 145 (9.9), 141 (27.9), 91 (4.5); (CH_4, CI) 212 (12.9), 211 (100.0), 199 (71.3), 189 (74.0), 183 (13.7), 175 (12.3), 85 (56.0), 62 (18.0). Anal. Calcd for $C_{12}H_{13}F_3O$: C, 62.60; H, 5.69. Found: C, 62.41; H, 5.57.

***cis*-(2-Phenylcyclopropyl)methyl Acetate (*cis*-6a).** A mixture of *cis*- and *trans*-2-phenylcyclopropane-1-carboxylic acids[25] (ca. 66% cis) was

(24) Murray, J. I. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 744.

(25) Burger, A.; Yost, W. C. *J. Am. Chem. Soc.* **1948**, *70*, 2198.

reduced with lithium aluminum hydride as described previously in the preparation of *trans*-(2-phenylcyclopropyl)methyl acetate (**6a**). From 0.40 g (2.4 mmol) of the mixture of cis and trans acids, a total of 0.35 g of a mixture of the cis and trans alcohols was obtained, IR (neat) 3300 cm^{-1} (br). This mixture of alcohols was acetylated as described previously. The crude product, which weighed 0.4 g, was chromatographed on a column (1.5 × 50 cm) of deactivated (6% H_2O) silica gel (100–200 mesh), which was packed in hexane and eluted with 5% ether–hexane, to yield 0.26 g (57%) of a mixture of *cis*- and *trans*-(2-phenylcyclopropyl)methyl acetates: NMR ($CDCl_3$) δ 0.80–2.0 (m, cyclopropyl H's), 1.95 (s, *cis*-CH_3), 2.05 (s, *trans*-CH_3), 3.76 (d, J = 5.5 Hz, *cis*-carbinyl H's), 4.07 (d, J = 5.5 Hz, *trans*-carbinyl H's), and 7.15–7.4 (m, arom). The mixture contained approximately 66% of the cis isomer as determined by NMR.

Preparative-Scale Photolyses. Solutions of the *trans*-(2-arylcyclopropyl)methyl acetates **6a–h**, **14a,b** in 100–200 mL of dry acetonitrile (cyclohexane was used in the case of **14a**, in the preparative photolysis only) were irradiated in a water-cooled immersion well apparatus with Corex-filtered light from a Hanovia 450-W medium-pressure mercury arc. Progress of the reaction was monitored by gas chromatography with the following columns: a 7 ft × $^1/_8$ in. stainless-steel column packed with 10% C6-DEGS on 90–100 mesh Anakrom SD (**6a**, 140 °C; **14b**, 190 °C), a 5 ft × $^1/_8$ in. stainless steel column packed with 3% XE-60 on 100–120 mesh Varaport 30 (**6b**, 150 °C; **6c**, 150 °C; **6d**, 140 °C; **6e**, 170 °C; **6f**, 170 °C; **6g**, 170 °C; **6h**, 130 °C), a 5 ft × $^1/_8$ in. stainless steel column packed with 3% QF-1 on 90–100 mesh Anakrom ABS (**14a**, 150 °C). In every case a product of slightly shorter GC retention than the trans reactant was formed along with (except for **6c**) another product of much shorter retention time. The latter products were in every case isolated by either silica gel (100–200 mesh, 6% H_2O deactivated) column chromatography with ether–hexane elution (for **6b,d,g,h**, **14a,b**), or preparative TLC (Kieselgel, 20 × 20 cm plates, developed with ether–hexane for **6a,e,f**). The identities of these compounds were established with **7a,b,d–h** (from **6a,b,d–h**) by comparison of NMR and IR spectra with the spectra of samples prepared independently. In the case of **20a,b** (from **14a,b**), the identities were deduced from the NMR spectra (see below). The product having a retention time slightly shorter than the reactant was established as the cis (endo) isomer in the case of **6a**, **6e**, **14a**, and **14b** and assumed by analogy in the others. For **6a** and **6e** the NMR spectra of the mixture of *cis*- and *trans*-**6a** (**6e**) isomers recovered from photolysis were compared with similar mixtures prepared independently, either chemically (**6a**, see above) or by triplet sensitization (**6e**, see below). In the case of *endo*-**14a,b**, the identities were established by comparison of the NMR spectra with the spectra of samples prepared independently. The detailed procedures given next for **14a** and **14b** are typical.

Photolysis of *exo*-(1,1a,6,6a-Tetrahydrocycloprop[*a*]inden-1-yl)methyl Acetate (14a). A solution of 0.500 g (2.40 mmol) of *exo*-(1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (**14a**) in 200 mL of cyclohexane was irradiated with Corex-filtered light from a Hanovia 450-W medium-pressure mercury arc. Nitrogen was bubbled through the solution for 0.5 h prior to photolysis and throughout the irradiation period. Progress of the reaction was monitored by GC. Only two new compounds were formed in significant quantity. After 26 h of total irradiation, the reaction solution was concentrated under reduced pressure and chromatographed on a 2 × 22 cm silica gel (60–200 mesh, 8% H_2O) column packed with hexane and eluted with 1% ether–hexane to give 0.100 g (31%) 2-vinyl-1-indanyl acetate (**20a**) and 0.180 g of a 3:1 mixture of *exo*- and *endo*-**14a**. The NMR spectrum ($CDCl_3$) of **20a** showed δ 2.02 (s, 3 H, CH_3), 3.04 (d, J = 5.7 Hz, 2 H, C-3 H's), 3.18–3.30 (m, 1 H, C-2 H), 5.05–5.21 (m, 2 H, =CH_2), 5.75–5.85 (m, 1 H, CH=), 6.17 (d, J = 4.8 Hz, 1 H, C-1 H), 7.20–7.45 (m, 4 H, arom). There was observed a small doublet at δ 6.10 (J = 4.8 Hz) with an area about 20% of the doublet at δ 6.17, indicating the **20a** is a ca. 4:1 mixture of stereoisomers: MS, *m/e* 202.0980 (calcd for $C_{13}H_{14}O_2$, 202.0994).

Photolysis of *exo*-(1-Cyano-1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl Acetate (14b). A solution of 0.370 g (1.60 mmol) of *exo*-(4-cyano-1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (**14b**) in 200 mL of dry acetonitrile was irradiated as above for 4 h. Progress of the reaction was monitored by GC. Four major photoproducts (two having a retention time longer than that of **14b**) and several minor ones were noted. The solvent was removed, and the products were isolated by chromatography on a 2 × 22 cm silica gel (60–200 mesh, 8% H_2O) column packed with hexane and eluted with 10% (1.6 L), 15% (2 L), 20% (1.5 L), and 25% (1 L) ether–hexane. There was obtained 40 mg (13%) of 6-cyano-2-vinyl-1-indenyl acetate (**20b**), 140 mg (44%) of 2-(5-cyano-2-indenyl)ethyl acetate (**21**), and 50 mg of a 5:3 mixture of *exo*- and *endo*-(4-cyano-1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (*exo*- and *endo*-**14b**). Product **21** was the only product having a GC retention time longer than that of **14b** that was isolated. Comparisons of the GC trace of the photolysis and the isolated yield of **21** suggests the other long-retention-time photoproduct was converted **21** upon workup. **20b**: NMR ($CDCl_3$) δ 1.96 (s, 3 H, CH_3), 2.75–3.25 (m, 3 H, C-2 and C-3 H's), 5.10–5.15 (m, 2 H, =CH_2), 5.70–5.85 (m, 1 H, CH=), 6.04 (d, J = 3.1 Hz, 1 H, C-1 H), 7.25–7.50 (m, 3 H, arom); MS, *m/e* 227.0935 (calcd for $C_{14}H_{13}NO_2$, 227.0946). **21**: NMR ($CDCl_3$) δ 2.06 (s, 3 H, CH_3), 2.87 (t, J = 2.5 Hz, 2 H, CH_2), 3.43 (s, 2 H, ring CH_2), 4.34 (t, J = 2.5 Hz, 2 H, OCH_2), 6.68 (s, 1 H, vinyl), 7.36–7.64 (m, 3 H, arom). **21**: Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74.01; H, 5.73; N, 6.17. Found: C, 74.15; H, 5.65; N, 6.14.

Multiplicity Studies. Solutions of cyclopropylmethyl acetates **6a,b,d–h** and **14a,b** in N_2-purged, spectral-grade acetone were irradiated under nitrogen through a Pyrex filter for 3–20 h. Progress of each reaction was monitored by GC. In every case except **14b** the only observed reaction was trans–cis (exo–endo) isomerization. With **14b** a minor amount of another product was observed as well. In no case was any rearrangement to **7a–h** (**20a,b**) detected. For **6a,b,d–h**, recovery of material (trans plus cis) was essentially quantitative; with **14a,b** losses of 8% and 18%, respectively, of volatile material were noted. After photolysis the solutions were concentrated in vacuo. The NMR spectra showed in each case signals attributable to the reactant trans (exo) isomers plus those derived from the cis (endo) isomers. Most characteristics of the latter were the signals due to the carbinyl (CH_2O) hydrogens which appeared as doublets or a pair of doublets ($J \sim 5.5$ Hz) upfield by 0.2–0.4 ppm from the corresponding signals for the trans (exo) isomers. Following are listed the δ values for the carbinyl H's of the cis isomers (**6a**, **14a,b** already given): **6b**, 3.76; **6d**, 3.75; **6e**, 3.77; **6f**, 3.72, 3.87; **6g**, 3.55; **6h**, 3.62, 3.84.

Photolyses in Methanol. The following procedure is typical. A solution of 0.300 g (1.40 mmol) of *trans*-[2-(*m*-cyanophenyl)cyclopropyl]-methyl acetate (**6g**) in 110 mL of methanol was irradiated as above (Corex filter) for 0.75 h. The solution was concentrated in vacuo, and the residue was chromatographed on a 1.5 × 70 cm deactivated (6% H_2O) silica gel (60–200 mesh) column packed in hexane and eluted with 2% (250 mL), 5% (1.5 L), 10% (0.5 L), 15% (0.5 L), 25% (0.5 L), and 40% (0.5 L) ether–hexane; 20-mL fractions were collected. Fractions 52–68 were combined and concentrated to give 15 mg (6%) of 4-(*m*-cyanophenyl)-4-methoxy-1-butene (**8g**). Fractions 110–116 contained 30 mg (10%) of 4-acetoxy-4-(*m*-cyanophenyl)-1-butene (**7g**), and fractions 130–143 afforded 45 mg of a mixture of *trans*- and *cis*-**6g**. Other products were formed (GC) but, as in the irradiation in acetonitrile, in insufficient quantity for isolation and identification.

Similarly irradiated were *trans*-[2-(*p*-methoxyphenyl)cyclopropyl]-methyl acetate (**6b**), *trans*-[2-(*p*-cyanophenyl)methyl acetate (**6f**), *trans*-[2-[*m*-(trifluoromethyl)phenyl]cyclopropyl]methyl acetate (**6h**). There was obtained from **6b** 24% of 4-methoxy-4-(*p*-methoxyphenyl)-1-butene (**8b**) and (7% of 4-acetoxy-4-(*p*-methoxyphenyl)-1-butene (**7b**); from **6f**, 1% of 4-(*p*-cyanophenyl)-4-methoxy-1-butene (**8f**) and 3% of 4-acetoxy-4-(*p*-cyanophenyl)-1-butene (**7f**); from **6h**, 2% of 1-methoxy-1-[*m*-(trifluoromethyl)phenyl]-1-butene (**8h**) and 11% of 1-acetoxy-1-[*m*-(trifluoromethyl)phenyl]-1-butene (**7h**).

All products were independently prepared except for **8b**. **8b**: NMR ($CDCl_3$) δ 2.30–2.65 (m, 2 H, CH_2), 3.18 (s, 3 H, CH_3O Ar), 3.77 s, 3 H, CH_3OCH), 4.85–6.00 (m, 3 H, vinyl), 6.10 (t, J = 5.5 Hz, 1 H, MeOC*H*), 6.80–7.31 (m, 4 H, arom); IR (neat) 2950, 1620, 1520, 1250, 1090, 920, 840 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$: C, 84.96; H, 8.38. Found: C, 74.90; H, 8.54.

Several microscale irradiations were also carried out. In one series, solutions (0.5 mL) of **6b,f–h** in methanol were irradiated in a quartz microtube under nitrogen with 254-nm light from a low-pressure mercury arc. The reactions were analyzed by GC at intervals of 1, 2, 5, 10, 15, 30, 60, and 90 min. In all four cases formation of both **7b,f–h** and **8b,f–h** was noted after 1 min of irradiation, and the formation of the products was observed to be ca. linear with time.

In separate experiments, solutions (0.5 mL) of acetates **7b,f–h** in methanol were irradiated with 254-nm light for 60 min. No methyl ethers (**8b,f–h**) were detected by GC.

Additionally, duplicate samples of **6b** and **6g** in methanol solution (1 mL) were prepared (four samples total). To one solution of each compound was added 100 mg of sodium bicarbonate. The solutions were irradiated 1 h at 254 nm. GC analysis showed that, for both **6b** and **6g**, formation of ether **8** and acetate **7** was equally efficient in the solutions with and without bicarbonate.

Quantum Yield Measurements. Duplicate 6.5-mL solutions of cyclopropanes **6a–h** and **14a,b** in spectral-grade acetonitrile (distilled from calcium hydride) were irradiated in serum-capped quartz vessels in a

(26) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, A* **1956**, *235*, 518.

merry-go-round apparatus with 254-nm light from a low-pressure mercury arc. Samples were purged with nitrogen for 20 min prior to irradiation. Actinometry was carried out by simultaneous irradiation of potassium ferrioxalate solutions.[24] Product yields were determined by GC with conditions appropriate for each sample. In every case except **6f** (*p*-CN), GC response factors for product **7** were determined with acetonitrile solutions of authentic samples of the appropriate derivative of **7**. With **6f** it was assumed that the response factors for **6f** and **7f** were the same as had been shown for the other derivatives of **6**.

Singlet lifetime measurements were carried out in the laboratory of Professor Arthur Halpern of Northeastern University. Samples (in acetonitrile) were excited with 250-270-nm light. Emission was filtered with either a 290-nm interference filter or two CS 0-54 cutoff filters. The flash lamp was a thyratron-driven (12.20 kHz), low-pressure (0.5 Torr) deuterium discharge constructed from platinum electrodes and run at ca. 7 kV. The decay of the lamp was about 0.8 ns. Single exponential decay curves were found for all samples except for the cyano derivatives **6f,g** and **14b**, which had lifetimes too short to allow deconvolution of the curves.

Acknowledgment. We thank Professor Arthur Halpern for his generous help in carrying out the singlet lifetime measurements. This work was supported by grants from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Photophysics of a Cofacial Porphyrin–Quinone Cage Molecule and Related Compounds: Fluorescence Properties, Flash Transients, and Electron-Transfer Reactions

Jonathan S. Lindsey,*[†] John K. Delaney,[‡] David C. Mauzerall,*[‡] and Henry Linschitz[§]

Contribution from the Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, The Rockefeller University, New York, New York 10021, and Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254.
Received July 28, 1987

Abstract: Fluorescence yields, fluorescence lifetimes, and flash photolysis transients have been measured for a tetrabridged cofacial porphyrin–quinone cage molecule and related derivatives. When the quinone is present and in the oxidized form, two fluorescence lifetimes are observed for the zinc complex, both shorter than the single lifetimes of control compounds. These are assigned to two conformers, with porphyrin to quinone interplanar separation of about 8.5 and 6.5 Å, respectively. The fluorescence lifetime data lead to electron-transfer times for the two conformers of between 0.5 and 15 ns. The fast electron-transfer time is only weakly dependent on solvent and is independent of temperature between 290 and 124 K. Following flash photolysis of the zinc–porphyrin–quinone in polar solvents, a transient band at 415 nm grows in more slowly (150 ns) and decays much more rapidly (1.4 μs) than the triplet seen in control compounds and is assigned to a charge-separated ZnP^+Q^- state. The reaction leading to this state exhibits an activation energy of only 6 kJ/mol. In contrast to the zinc chelate, the free base porphyrin–quinone shows no electron-transfer interactions. These results support a distance-sensitive nonadiabatic electron-tunneling mechanism for the transfer. Effects of solvent and protonation are interpreted in terms of conformational changes that modify the porphyrin–quinone distance. Attempts to study effects of orbital symmetry in a pair of chlorin–quinones were inconclusive. A larger fraction of energy is stored in forming the charge-separated state (1.4 eV, ΔG) from the triplet state (1.6 eV, ΔE) of the zinc–porphyrin–quinone than is stored in the bacterial reaction center (0.5 eV) from the singlet state (1.2 eV).

Electron-transfer reactions make possible the complex flow of energy in biological systems and are receiving increasing attention as the initial step in many chemical reactions. One of the most dramatic examples of energy flow via electron transfer occurs in the reaction centers of photosynthetic systems. These assemblies function with quantum yields greater than 95%, a maximum photon energy conversion efficiency of 30–50%, and are sufficiently robust and channeled to maintain function after $>10^7$ cycles. Understanding the determinants of such fast, efficient, and stable electron-transfer reactions remains a central challenge in chemistry.

A variety of studies involving temperature and transfer distance have shown that the primary reactions in photosynthesis involve electron–nuclear tunneling.[1] For example, the initial electron-transfer events in intact reaction centers occur at 4 K,[2] and the reverse electron transfer, from quinone to bacteriochlorophyll, has the remarkably low activation energy of $<1.7 \times 10^{-3}$ kJ/mol between 80 and 1.4 K.[3] Recent X-ray crystallographic structure determination has shown the minimum edge-to-edge distance of the reacting pigments to be >5 Å.[4] Thus, the electron-transfer reactions occur at distances greater than the sum of the van der Waals contact radii. This latter feature in particular is characteristic of electron tunneling and sharply distinguishes these reactions from the slow adiabatic electron-transfer reactions characteristic of more common redox processes.

Electron tunneling, a basic quantum mechanical phenomenon, is not restricted to the highly ordered photosynthetic structures but is observed in systems of widely varying complexity.[5] Photoinduced electron-transfer reactions of porphyrins in solution occur at an "encounter radius" of 20 ± 2 Å, much greater than the sum of the radii of the porphyrin macrocycles.[6] Photoexcited

[†] Carnegie Mellon University.
[‡] The Rockefeller University.
[§] Brandeis University.

(1) DeVault, D. *Quantum-Mechanical Tunnelling in Biological Systems*; Cambridge University: Cambridge, U.K., 1984.
(2) Arnold, W.; Clayton, R. K. *Proc. Natl. Acad. Sci. U.S.A.* **1960**, *46*, 769–776.
(3) McElroy, J. D.; Mauzerall, D. C.; Feher, G. *Biochim. Biophys. Acta* **1974**, *333*, 261–277.
(4) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature (London)* **1985**, *318*, 618–624.
(5) Khairutdinov, R. F.; Brickenstein, E. Kh. *Photochem. Photobiol.* **1986**, *43*, 339–356.
(6) Ballard, S. G.; Mauzerall, D. In *Tunneling in Biological Systems*; Chance, B., DeVault, D., Eds.; Academic: New York, 1979, pp 581–587. Carapellucci, P. A.; Mauzerall, D. *Ann. N.Y. Acad. Sci.* **1975**, *244*, 214–238.

0002-7863/88/1510-3610$01.50/0