Arylcyclopropane Photochemistry. The Role of Orbital Overlap Control in the Photochemical Cis–Trans Isomerization of Arylcyclopropanes

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Abstract: The preference for internal vs. external bond cleavage in the direct and triplet-sensitized (acetone) photochemical isomerizations of optically active *endo*- and *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indenes (**1N** and **1E**) has been examined. In the direct irradiations both **1N** and **1E** isomerize 19% of the time by internal bond fission and 81% of the time by external bond fission. In the sensitized irradiations both **1N** and **1E** show a much greater (~98%) preference for isomerization by external bond a fission. This indicates the cyclopropane singlets isomerize with a minimum of 19% internal bond b fission. Quantum yields for all the isomerization processes have been determined. It is concluded that reaction intermediate structure as well as initial orbital overlap is important in the rate-determining stage of reaction.

Excited-state orbital overlap has been put forth as significant in determining the preferred course of the photochemical reactions of cyclopropyl ketones.[1,2] Thus, it has been observed that in those photochemical processes of cyclopropyl ketones which involve cleavage of the three-membered ring the bond which overlaps best with the π system of the carbonyl group is the one broken preferentially, whether the reaction be the commonly observed cis–trans isomerization or some other structural rearrangement.[1,2] That overlap should be important is reasonable. One expects the excited-state interaction with the carbonyl π system to be greatest for the three-ring bond whose orbitals best overlap that π system. This bond should therefore acquire the most antibonding character and become the most weakened upon excitation. Further, if we focus on the fission process itself, it is apparent that cleavage of the bond which best overlaps with the carbonyl π system allows for maximum continuous electron delocalization throughout the cleavage process.[1,2]

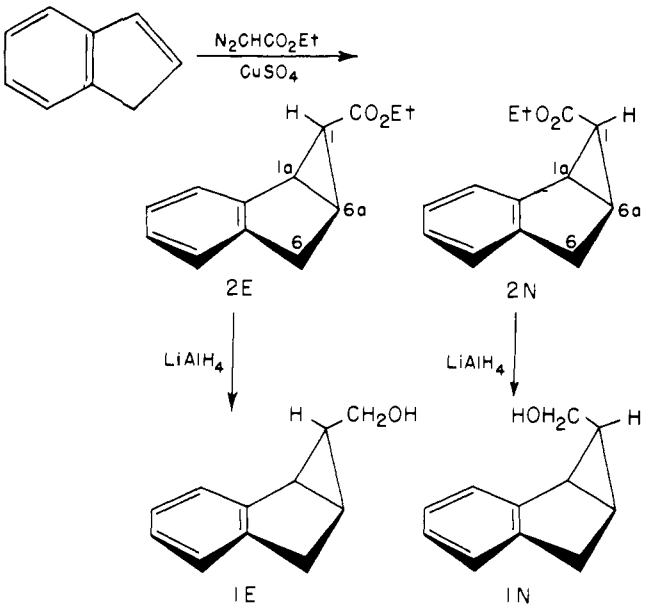
Arylcyclopropanes,[3] like cyclopropyl ketones,[2,4] undergo photochemical cis–trans isomerization as well as other structural rearrangements, and one might logically expect excited state orbital overlap to be of importance in controlling the course of these reactions. However, whereas with cyclopropyl ketones there is clear evidence from uv studies that the interaction between the ketone group and the three-membered ring is a sensitive function of the relative orientation of the carbonyl π bond and the σ bonds of the three-ring,[5] spectroscopic studies reveal no evidence for a preferred geometry for excited-state interaction between the adjacent aromatic and cyclopropane rings in arylcyclopropanes.[6-8] Similar conclusions have been obtained from an analysis of the uv spectra of vinylcyclopropanes.[9] This interesting spectral characteristic of arylcyclopropanes, as well as the report[10] that benzene does sensitize the cis–trans isomerization of 1,2-dimethylcyclopropane, led us to question and then investigate the role of orbital overlap in determining the course of the photochemical cis–trans isomerization of arylcyclopropanes.

Results

Synthesis. The isomeric cyclopropanes used in our study, **1E** and **1N**, were obtained by lithium aluminum hydride reductions of esters **2E** and **2N**, which were in turn prepared by copper-catalyzed addition of ethyl diazoacetate to indene (Scheme I).

While assignment of stereochemistry to the isomeric alcohols was not crucial for the purposes of this investigation, we felt it desirable to determine which of the isomers had the hydroxymethyl group endo and which exo. This determination

Scheme I. Synthesis of Cyclopropanes **1E** and **1N**

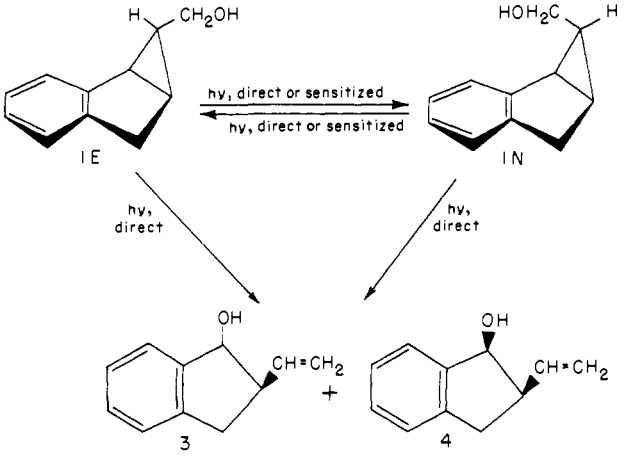


was carried out with the use of the NMR shift reagent $Eu(fod)_3$. Thus, addition of successive amounts of $Eu(fod)_3$ to a $CDCl_3$ solution of endo ester **2N** brought about progressive and substantial downfield shifts of the multiplet at ca. δ 1.97 and the quartet at δ 4.00 which we ascribe to the C-1 H and the CH_2 of the ethyl group, respectively; the asymmetric doublet for the C-6 hydrogens became more complex and was shifted partly to lower field. On the other hand, the multiplet at ca. δ 2.00–2.20 (C-6a H), the (pseudo) triplet at 2.87 (C-1a H), and the triplet at 0.90 ($-CH_2CH_3$) were shifted but little by the reagent. Addition of the shift reagent to the exo ester **2E** brought about substantial downfield shifts of the signals for all three cyclopropyl hydrogens—the C-1 H multiplet at ca. δ 1.18 (superimposed on the $-CH_3$ triplet), the C-6a H multiplet at 2.25–2.50, and the C-1a H multiplet centered at ca. δ 2.85—as well as the $-CH_2CH_3$ quartet at δ 4.20. On the other hand, the asymmetric doublet at δ 3.05 due to the C-6 H's and the $-CH_3$ triplet at δ 1.20 were but slightly affected by the $Eu(fod)_3$.

Photolysis of Racemic 1E and 1N. Direct photolysis of either **1E** or **1N** resulted in efficient isomerization to the other stereoisomer. Though **1E** and **1N** could not be efficiently separated preparatively, the presence of both isomers was readily detected by examination of the NMR and ir spectra of the

mixture of the two obtained by silica gel chromatography of the photolysis product obtained from either isomer as well as by a comparison of GC retention times. Less efficient conversion of the cyclopropanes to other products was also noted. Of these other products the only ones which were formed in quantities sufficient for isolation and identification were the homoallylic alcohols **3** and **4**. The formation of **3** and **4** has been discussed elsewhere.[11] Irradiation of acetone solutions of **1N** and **1E** using Pyrex-filtered light resulted in a triplet-sensitized interconversion of **1E** and **1N** as the only observed process. The fact that the minor products observed in the direct irradiation of **1E** and **1N** were not observed in the sensitized runs indicates that singlet energy transfer from acetone to the cyclopropanes was negligible. The interconversions noted are shown in Scheme II.

Scheme II. Photolysis of Racemic Cyclopropanes **1E** and **1N**



Quantum yield measurements for the direct irradiations of **1E** and **1N** in nitrogen-purged cyclohexane solutions were carried out on a merry-go-round apparatus using 254-nm light and potassium ferrioxalate actinometry.[12] For the acetone-sensitized runs samples were degassed and 313-nm light was used; light output was measured with benzophenone-benzhydrol actinometry.[13] Conversions to product were <1% in the direct irradiations and between 1 and 5% (except for two runs at ca. 10% conversion) for the sensitized cases. The results of the determinations are summarized in Table I.

Optically Active 1E and 1N. In order to determine the pathways for the **1E** ⇄ **1N** interconversions, it was necessary to prepare both isomers in optically active form and to correlate their configurations. Thus, the esters **2N** and **2E** were each saponified to the corresponding acids **5N** and **5E** which were in turn resolved via their cinchonidine salts. The optically active acids were then reesterified to give optically active **2E** and **2N** (**2E**(−) and **2N**(−)); lithium aluminum hydride reduction then provided **1E** (**1E**(−)) and **1N** (**1N**(−)) in optically active form.

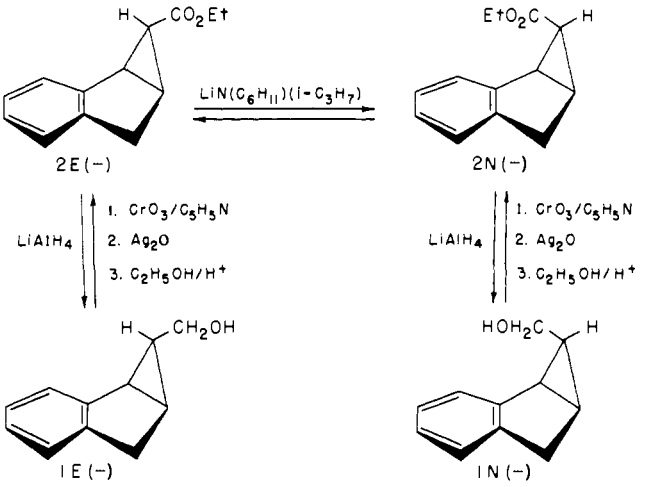
For relating configurations the transformations of both of the optically active esters **2E**(−) and **2N**(−) to their C-1 epimers were carried out with lithium *N*-isopropylcyclohexylamide. This interconversion results in inversion of configuration about C-1, the carbon bearing the carboethoxy group. We found that on isomerization **2E**(−) gave **2N**(−) and vice versa; the starting ester was in each case recovered unracemized. The data are shown in part in Table II and are presented more completely in the Experimental Section. These interconversions also showed that the optical purity of the **2E**(−) which we had prepared was 3.7 times that of the **2N**(−). Since we find (vide infra) that no racemization occurs on lithium aluminum hydride reduction of the esters to the alcohols, the same difference in optical purity holds for the **1E**(−) and **1N**(−) prepared from **2E**(−) and **2N**(−). The above experiments allow us to assign the relative configurations shown in Scheme III.

Table I. Quantum Yield Determinations for **1E** and **1N**

Reactant	Irradiation type	ϕ(1E)[f]	ϕ(1N)[f]	ϕ(3 + 4)[f]
1E	Direct[a]		0.10 ± 0.01	<0.003
1N	Direct[a]	0.13 ± 0.01		0.022 ± 0.002
1E	Sensitized[b,c]		0.13 ± 0.01	
1E	Sensitized[b,c]		0.12 ± 0.01	
1E	Sensitized[b,d]		0.13 ± 0.01	
1N	Sensitized[b,c]	0.38 ± 0.02		
1N	Sensitized[b,c]	0.39 ± 0.02		
1N	Sensitized[b,e]	0.43 ± 0.03		

[a] Cyclohexane solvent, 254-nm light, concn 1.7–2.6 × 10^{-2} M. [b] Acetone solvent, 313-nm light. [c] Cyclopropane concn 0.024–0.032 M. [d] Cyclopropane concn 0.13 M; [e] Cyclopropane concn 0.12 M. [f] Average of two runs.

Scheme III. Correlation of Relative Configurations of **1E**(−) and **1N**(−)



Neither alcohols **1E** or **1N** nor their corresponding acetates could be separated by column or thin-layer chromatography. Therefore, following photolysis (vide infra) of the optically active alcohols, the product mixture was converted to a mixture of the active esters **2E** and **2N** (plus other products derived from by-products obtained in the direct photolysis runs). The mode of conversion is shown in Scheme III. The esters were readily separated and their optical rotations taken.[14] Determination of the rotations of the esters provided a measure as to how much of the photochemical isomerizations of the alcohols involved inversion at C-1. Appropriate controls showed that the conversions of the alcohols to the esters gave no epimerization or racemization of the cyclopropanes.

Photolysis of Optically Active Cyclopropanes 1E(−) and 1N(−). The photolyses of **1E**(−) and **1N**(−) were carried out as with the inactive materials, and the photolysis mixtures were treated as discussed above (Scheme III). The results are summarized in Table II. (Note in Table II that the rotations shown for alcohols **1E** and **1N** are actually those of the esters **2E** and **2N** derived from the alcohols.) It may be seen that in all cases the preferred course of reaction involves inversion at C-1. In the triplet-sensitized isomerizations of both **1E**(−) and **1N**(−) only about 2% retention of stereochemistry at C-1 was observed; however, in both of the direct irradiations this figure rose to ca. 19%.

Discussion

Either direct or acetone-sensitized irradiation of cyclopropanes **1E** and **1N** leads to efficient formation of the corre-

Table II. Interconversion of **1E** and **1N**[a]

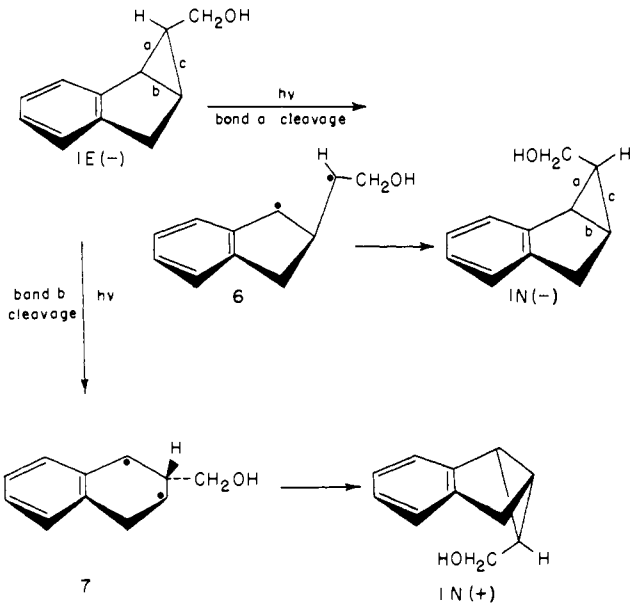
Reactant rotation[b,c]	Conditions	Recovered reactant rotation[b,c]	Isomerized product rotation[b,c] (% racemization)	% inversion at C-1[d]	% retention at C-1[d]
2E, −113.1 ± 1.2	Base	−113.1 ± 0.1	−106.5 ± 0.4		
1E,[c] −113.1 ± 1.2	Direct *hν*	−113.2 ± 0.1	− 64.6 ± 0.4 (39.3)	80.6 ± 1.2	19.4 ± 1.2
1E,[c] −113.1 ± 1.2	Sensitized *hν*	−113.0 ± 0.1	−103.3 ± 1.6 (3.0	98.0 ± 3.2	2.0 ± 3.2
2N, −389.0 ± 0.3	Base	−388.8 ± 0.7	−428.0 ± 1.5		
1N,[c] −389.0 ± 0.3	Direct *hν*	−388.9 ± 0.2	−262.0 ± 1.8 (28.8)	80.7 ± 0.6	19.3 ± 0.6
1N,[c] −389.0 ± 0.3	Sensitized *hν*	−388.7 ± 0.4	−412.4 ± 0.9 (3.7)	98.0 ± 0.6	2.0 ± 0.6

[a] Results given are the average of two different runs in each case. [b] Rotation values (in degrees) given are at 435.83 nm. [c] Rotations given for the alcohols **1E** and **1N** are actually the rotations of the derived esters **2E** and **2N**. [d] These are averages of results obtained at six different wavelengths.

sponding C-1 epimer. The conversion of **1E** to **1N** could conceivably proceed by initial cleavage of either bond a or bond b (Scheme IV) to give a ring-opened species which undergoes bond rotation and ring closure to product. We consider fission of bond c to be very unlikely since it is not conjugated with the aromatic portion of the molecule where the initial excitation energy is heavily localized, and since cleavage of this bond would yield a ring-opened (diradical) species considerably less stable than that obtained by bond a or bond b fission.[3a] (Such a process would be stereochemically equivalent to bond a cleavage.) The σ orbitals of bond a have very good overlap with the π system of the aromatic ring, while those of bond b have significantly poorer overlap. Should such overlap with the aromatic π system be important in determining the extent to which a bond becomes weakened in the excited state and then cleaves, then one would expect isomerization via bond a cleavage to be favored.

The isomerization processes occurring via bond a and by bond b cleavage are indistinguishable with racemic **1E**. However, with optically active **1E** they may be differentiated. As shown in Scheme IV isomerization of **1E**(−) via external

Scheme IV. Possible Isomerization Pathways for **1E**(−)



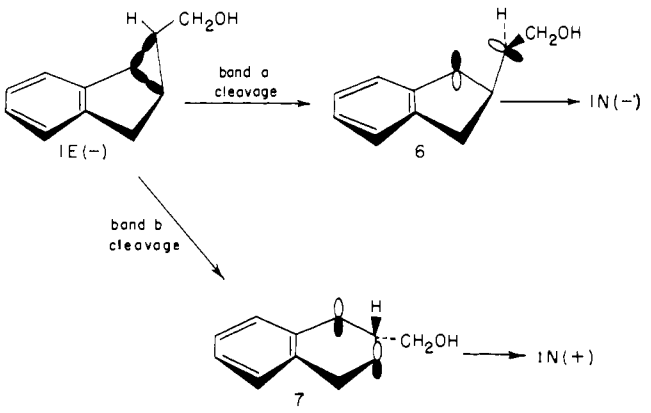
bond a fission gives **1N**(−) in which the configuration of C-1 has been inverted. On the other hand, isomerization via internal bond b cleavage gives product **1N**(+) with retained configuration at C-1. Similar conclusions hold for the isomerization of optically active **1N**(−) to **1E**.

The isomerizations of **1E**(−) and of **1N**(−) under conditions of both direct and acetone-sensitized irradiation were carried out; the results obtained are shown in Table II. When we interpret the results in terms of bond-cleavage mechanisms, we see that the triplet-sensitized isomerizations of both **1E**(−) and **1N**(−) proceed almost entirely (98%) via bond a fission. On the other hand, the isomerizations observed on direct irradiation, while still proceeding mostly via bond a fission, involve significant amounts (19%) of bond b fission. We emphasize that our results in Table II refer solely to the percentage of bond cleavages which lead to isomerization. Reversible fission processes in which recyclization leads to regeneration of starting material cannot be detected except by virtue of the fact that they lower the observed quantum yield of reaction.

Our data provide no precise indication as to the extent of the contribution of the triplet states of **1E** and **1N** to the isomerizations observed on direct irradiation. We do know, however, that the triplets isomerize 98% of the time by bond a cleavage and that therefore the singlet state isomerizations proceed at least 19% of the time by fission of internal bond b. This minimum would be the actual percent singlet-state bond b isomerization in the case where no intersystem crossing occurred. Should intersystem crossing in fact be a significant process, and we see no reason why it should not be, then the actual percentage of singlet state isomerization proceeding via bond b fission would be higher than this minimum. That bond a does undergo singlet-state cleavage is shown by the formation of rearranged alcohols **3** and **4** upon direct photolysis of **1E** and **1N**. As **3** and **4** are not formed upon triplet-sensitized photolysis of the cyclopropanes, they must arise from the singlet states; however, the efficiency of formation of **3** and **4** is much lower than that of the exo $\rightleftarrows$ endo isomerizations. We conclude that singlet-state bond b fission is minimally a significant isomerization reaction process.

The difference in bond cleavage selectivity found between the singlet- and triplet-state reactions, particularly the sizable proportion of the singlet-state isomerizations proceeding by bond b cleavage, indicates initial orbital overlap is not the only important factor governing the isomerization pathways. This conclusion is in line with what one might expect on the basis of the uv studies of arylcyclopropanes, which indicate that the excited-state conjugative interaction between the adjacent cyclopropane and aromatic rings is rather small and is not orientationally biased.[6,8] A significant difference in (Franck-Condon) excited state weakening of bonds a and b is not anticipated. Additionally, considering the bond fission process itself, we point out that whereas in **1E** and **1N** it is true that the C-1a orbital comprising bond a initially overlaps much better with the π system than does the C-1a orbital in bond b, the stretching motion which is involved in the cleavage of bond b is accompanied by a twisting which considerably increases the overlap of the bond b C-1a orbital with the adjacent π system (Scheme V). Indeed, if we visualize the two different isomerization reaction paths as proceeding via diradical intermediates **6** and **7**, we see that both **6** and **7** have odd-electron centers equally well aligned for benzylic stabilization and, based on this, ought to be of comparable stability.

Scheme V



However, closer inspection of **6** and **7** reveals an important difference between them and the two reaction paths in which they are involved, a difference analogous to that noted by Zimmerman and Epling in their discussion of the photochemistry of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene.[3f] Structure **6** at the midpoint of the bond a isomerization pathway is of the [0,90] form; the C-1 and C-1a orbitals originally comprising bond a are orthogonal to each other. On the other hand, diradical **7**, occurring halfway through the bond b isomerization pathway, is of the [0,0] configuration; a species with orthogonal orbitals is never encountered during reaction, and, in fact, in **7** the newly formed p orbitals may be seen to form part of a cyclic orbital array analogous to cyclobutadiene (benzocyclobutadiene). Such an orbital array provides energetically favorable excited-state electron delocalization. Additionally, as a result of the considerable ionic character of the ^1S states of diradicals such as **6** and **7**,[15] the formation of **7** would be particularly favorable for a singlet process, for the two nonbonding orbitals containing the valence electrons are close together in space.[16] One would also expect facile excited-state–ground-state internal conversion to occur in **7** since the two potential energy surfaces are close.[3f] Therefore to the extent that intermediate, i.e., diradical, structure and stability rather than just initial overlap considerations enter into determining the reaction pathway, one would expect the bond b isomerization process to become more competitive with bond a process for the singlets.

It is known, on the other hand, that triplets prefer to react to produce molecular configurations in which the unpaired electrons are maximally separated;[3f,16,17] electron–electron repulsion is thereby minimized. Clearly maximal electron separation is achieved in the orthogonal orbital orientation of intermediate **6** rather than with **7**. Thus in the triplet-state isomerizations both reaction intermediate considerations as well as orbital overlap factors favor isomerization by bond a cleavage. From our results we conclude that diradical structure plays a significant role in the rate-limiting stage of the cyclopropane isomerizations. In the singlet-state reactions this factor opposes preferences based on initial overlap, and we see minimally significant isomerization via bond b fission. With the triplets the factors reinforce and the isomerization is highly selective.

Aside from bond-cleavage selectivity another interesting question regarding cyclopropane triplet states is whether they are effectively dissociative. More particularly, in the case of isomeric cyclopropanes, does every triplet once formed undergo bond cleavage and form a common biradical much in the same way that many olefins form twisted triplets with unit efficiency? The work of DeBoer[18] suggests the answer is an affirmative one for 1,2-diphenylcyclopropane, perhaps a special case because it is so highly conjugated. That such might also be true with monoarylcyclopropanes was suggested by the observation of Becker and Griffin[19] that phenylcyclopropane does not phosphoresce; conversion to a very short-lived "radical-like" triplet—one with a very long, weakened three-ring bond—is felt to be much faster. In the present case of arylcyclopropanes **1E** and **1N**, strong evidence for unit triplet cleavage efficiency to give a common biradical would be provided by a finding that $\phi_{1E\rightarrow 1N} + \phi_{1N\rightarrow 1E} = 1$ in the sensitized irradiations. Such, however, is not the case; the sum of quantum yields for isomerization is only 0.51–0.56.

There is a difficulty in coming to any firm conclusion about the nature of the triplet states, however, and this lies in the fact that energy transfer from acetone ($E_t \sim 80$ kcal/mol[20]) to the cyclopropanes may not be totally efficient due to the high triplet energy of the latter (E_t for phenylcyclopropane = 81 kcal/mol[21]). Therefore, the best we can say at present is that the triplets do cleave with at least moderate efficiency.

With respect to the singlet-state cyclopropane isomerizations, we point out that as with olefins it is generally very difficult to determine whether cyclopropane cis–trans isomerizations observed on direct irradiation proceed via the singlet or the triplet state. However, because of the multiplicity dependence of the isomerization mechanism, with **1E** and **1N** we do know that at least ca. 17% of the direct photolysis isomerizations proceed via the singlet states. Since these minimum values assume all singlet state isomerizations go via internal bond b cleavage, it is almost certain that the singlets contribute more than 17% to the observed direct photolysis isomerizations. Salisbury has recently obtained evidence suggesting the ^1S state of methylphenylcyclopropane likewise undergoes (vapor phase) cis–trans isomerization;[3g] it seems likely that this reaction will prove to be a general one for arylcyclopropane singlets.

Experimental Section

General. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. NMR spectra were obtained with either a Varian A-60 or a Perkin-Elmer R12 A instrument using tetramethylsilane as an internal standard. All optical rotations were taken with a Perkin-Elmer Model 141 polarimeter in a constant-temperature cell of 10-cm path length. CD spectra were recorded on a Cary-60 spectrophotometer. Gas chromatography was carried out with either a Perkin-Elmer Model 900 gas chromatograph or a Varian Model 2400 gas chromatograph, both equipped with flame ionization detectors. Microanalyses were performed by the University of Massachusetts Microanalytical Laboratory.

Ethyl *exo*- and *endo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylates. To a three-necked flask equipped with a dropping funnel, mechanical stirrer, and nitrogen atmosphere were added 24.6 g (0.213 mol) of indene and 3.0 g of anhydrous $CuSO_4$. The mixture was heated to 70–80 °C and stirred rapidly while a solution of 20 g (0.18 mol) of ethyl diazoacetate in 24.6 g (0.213 mol) of indene was added dropwise. The reaction was then stirred overnight at 80°. Benzene (100 ml) was added to the cooled reaction and the cupric sulfate collected on a filter. After removal of the benzene under vacuum, the product mixture was distilled to give 25.2 g (29.1%) of a 1:2 mixture of ethyl *endo*- and *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, bp 110–115 °C (1.5–2.0 mm). The mixture of isomers was chromatographed on a 5 × 93 cm deactivated (8% H_2O) silica gel column slurry-packed in hexane and eluted with 1 l. of hexane followed by 2 l. of 1% ether–hexane to give 6.2 g of pure exo ester and 10.0 g of a mixture of the endo and exo esters. Elution with 2% ether–hexane then gave 9.0 g of pure endo ester. The endo and exo configurations were assigned by inspection of the effect of the shift reagent $Eu(fod)_3$ on the NMR spectra of the isomeric esters.

For ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate the spectral data are: ir (neat) 2980, 1730, 1480, 1385, 1333, and 752 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (t, 3, CH_3), ca. 1.97 (m, 1, C-1 H), ca. 2.00–2.20 (m, 1, C-6a H), 2.87 (t, 1, C-1a H), 3.22–3.28 (m, 2, C-6 H's), 3.80 (q, 2, $-CH_2CH_3$), 7.00–7.20 (m, 4, arom).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.97. Found: C, 77.29; H, 6.91.

For ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate the spectral data are: ir (neat) 2980, 1730, 1480, 1385, 1333, and 752 cm^{-1}; NMR ($CDCl_3$) δ ca. 1.18 (m, 1, C-1 H), 1.20 (t, 3, CH_3), 2.25–2.50 (m, 1, C-6a H), ca. 2.85 (m, 1, C-1a H), 3.00–3.10 (m, 2, C-6 H's), 4.20 (q, 2, $-CH_2CH_3$), 7.00–7.20 (m, 4, arom).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.97. Found: C, 77.43; H, 7.02.

***endo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylic Acid.** A solution of 42.1 g (0.208 mol) ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate in 400 ml of potassium hydroxide in ethanol was heated under reflux for 2 h and stirred overnight. The solution was then treated with 200 ml of 6 N HCl and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated under vacuum to yield 34.1 g (0.196 mol) of solid *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid. Three recrystallizations from hot methanol gave 29.4 g (81.2%) of pure acid, mp 162.0–162.5 °C. The spectral data are: ir ($CHCl_3$) 3020, 1700, 1440, 1210, and 710 cm^{-1}; NMR ($CDCl_3$) δ 1.90 (t, 1, C-1 H), 1.95–2.47 (m, 1, C-6a H), 2.87–3.10 (m, 1, C-1a H), 3.18–3.26 (m, 2, C-6 H's), 7.12–7.35 (m, 4, arom).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78. Found: C, 75.65; H, 5.61.

***exo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylic Acid.** Ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, 50.4 g (0.249 mol), was converted to 42.6 g (0.245 mol) of crude exo acid as was done for the endo isomer. Three recrystallizations from hot methanol provided 35.8 g (82.6%) of *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid, mp 148.5–149.0°C. The spectral data are: ir ($CHCl_3$) 3020, 1700, 1440, 1210, and 710 cm^{-1}; NMR ($CDCl_3$) δ 1.18 (t, 1, C-1 H), 2.38–2.48 (m, 1, C-6a H), 2.93–3.30 (m. 3, C-1a H and C-6 H's), 7.10–7.45 (m, 4, arom).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78. Found: C, 75.56; H, 5.65.

Resolution of *exo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylic Acid. A solution of 5.91 g (0.0340 mol) of *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid in 50 ml of hot ethyl acetate was added to a solution of 10.0 g (0.0340 mol) of (−)-cinchonidine in 100 ml of hot ethyl acetate. The mixture was concentrated to 100 ml, filtered, and let stand for 1 day at room temperature. After this time 4.94 g of the cinchonidine salt was isolated. A portion of the salt was hydrolyzed with 10% HCl solution to give optically active exo acid, mp 147.5–149.0 °C, $[\alpha]^{25}_{435.8}$ −87 ± 3° (*c* 0.00157, $CHCl_3$). The salt was recrystallized five times from hot ethyl acetate to give 3.50 g of resolved salt. A portion of the resolved salt thus obtained was hydrolyzed with 10% HCl to give optically active exo acid, $[\alpha]^{25}_{435.8}$ −103.0 ± 2.0° (*c* 0.00109, $CHCl_3$), mp 148.0–149.0 °C.

A total of 42.4 g (0.243 mol) of exo acid and 71.5 g (0.243 mol) of (−)-cinchonidine was carried through this procedure to give a total of 38.3 g of resolved salt. This salt was hydrolyzed with 10% HCl to give 12.54 g (29.9%) of optically active *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid, mp 148.5–149.0 °C, $[\alpha]^{25}_{435.8}$ −99.0 ± 1.0° (*c* 0.00213, $CHCl_3$). The ir ($CHCl_3$) and NMR ($CDCl_3$) spectra of the active acid were identical with those of the racemic acid.

Resolution of *endo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylic Acid. A solution of 6.50 g (0.0374 mol) of *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid in 50 ml of hot ethyl acetate was added to a solution of 11.0 g (0.0374 mol) of (−)-cinchonidine in 100 ml of hot ethyl acetate. The mixture was concentrated to 75 ml and filtered, and the filtrate was allowed to stand overnight at room temperature to yield 5.73 g of cinchonidine salt. A portion of the salt was hydrolyzed with 10% HCl to give optically active endo acid, $[\alpha]^{25}_{435.8}$ −303.5 ± 1.5° (*c* 0.00136, $CHCl_3$), mp 160.0–162.0 °C. The salt was further recrystallized four times to give 2.56 g of resolved salt. A small portion of this resolved salt thus obtained was hydrolyzed with 10% HCl to give optically active acid, $[\alpha]^{25}_{435.8}$ −346.8 ± 1.8° (*c* 0.00178, $CHCl_3$), mp 161.5–162.0 °C. Further recrystallization of the salt did not improve the rotation of the recovered acid.

A total of 50.7 g (0.291 mol) of endo acid and 85.5 g (0.291 mol) of cinchonidine was carried through this procedure to give a total of 41.6 g of resolved salt which was hydrolyzed with 10% HCl to yield 15.4 g (30.2%) of optically active *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid, $[\alpha]^{25}_{435.8}$ −345.2 ± 1.7° (*c* 0.00211, $CHCl_3$), mp 161.6–162.0 °C.

Optically Active Ethyl *exo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylate. A solution of 12.5 g (0.0719 mol) of optically active exo acid, $[\alpha]^{25}_{435.8}$ −103.6 ± 2.0°, in 500 ml of 3% sulfuric acid in absolute ethanol was refluxed for 1 h and then stirred overnight. Then 200 ml of 10% sodium bicarbonate solution was added slowly and the ethanol was removed under vacuum. The exo ethyl ester was extracted from the aqueous solution with ether, and the ether extract was washed with water, dried ($MgSO_4$), and concentrated to yield 13.25 g of crude exo ester. The crude product was chromatographed on a 5 × 93 cm deactivated (8% H_2O) silica gel column slurry-packed in hexane and eluted first with 1 l. of hexane followed by 3 l. of 1% ether–hexane to give 12.84 g (88.5%) of ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, $[\alpha]^{25}_{366.3}$ −347.1 ± 1.0°, $[\alpha]^{25}_{404.7}$ −147.7 ± 1.4°, $[\alpha]^{25}_{434.7}$ −114.0 ± 1.0°, $[\alpha]^{25}_{435.8}$ −113.1 ± 1.2°, $[\alpha]^{25}_{577.0}$ −45.1 ± 0.6°, $[\alpha]^{25}_{579.1}$ −44.8 ± 0.5°, (*c* 0.00808, $CHCl_3$). The NMR and ir spectra were identical with those of the racemic ethyl exo ester. The CD spectrum (CH_3OH) showed a maximum at 227.2 ± 0.3 nm.

Optically Active Ethyl *endo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylate. Optically active *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid was converted to the ethyl endo ester exactly as was the exo acid. From 15.40 g (0.0885 mol) of acid, $[\alpha]^{25}_{435.8}$ −345.2 ± 1.7°, was obtained 16.96 g of crude endo ester. This crude product was chromatographed on a 5 × 93 cm deactivated (8% H_2O) silica gel column slurry-packed in hexane and eluted with 1 l. of hexane, 2 l. of 1% ether–hexane, and then 1 l. of 2% ether–hexane to give 15.52 g (86.5%) of pure ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, $[\alpha]^{25}_{366.3}$ −756.2 ± 0.3°, $[\alpha]^{25}_{404.7}$ −505.3 ± 0.3°, $[\alpha]^{25}_{434.7}$ −392.3 ± 0.4, $[\alpha]^{25}_{435.8}$ −389.0 ± 0.3°, $[\alpha]^{25}_{577.0}$ −168.6 ± 0.1°, $[\alpha]^{25}_{579.1}$ −166.9 ± 0.2°, (*c* 0.00891, $CHCl_3$). The NMR and ir spectra were identical with those of the racemic ester. The CD spectrum (CH_3OH) showed a maximum at 229.8 ± 0.3 nm.

***exo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene.** To a stirred mixture of 3.00 g (0.0882 mol) of lithium aluminum hydride in 200 ml of anhydrous ether was added dropwise under nitrogen 2.412 g (0.0120 mol) of ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate in 75 ml of anhydrous ether. The mixture was refluxed for 1 h and stirred overnight, after which was carefully added 10 ml of water followed by 20 ml of 5% sulfuric acid. The ether layer was separated from the white precipitate and the precipitate was washed with an additional 100 ml of ether. The combined ether extracts were washed with 10% sodium bicarbonate solution and with water, dried ($MgSO_4$), and concentrated to yield 1.880 g of crude exo alcohol. The product was chromatographed on a 2 × 20 cm deactivated (10% H_2O) silica gel column slurry-packed with hexane and eluted with 1 l. of 2% ether–hexane followed by 10% ether–hexane. This provided 1.794 g (93.4%) of *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. The spectral data were: ir (neat) 3350, 2980, 2950, 1600, 1410, 1255, 1100, 1050, and 780 cm^{-1}; NMR ($CDCl_3$) δ 0.55–0.90 (m, 1, C-1 H), 1.55–1.90 (m, 1, C-6a H), 2.15–2.40 (m, 1, C-1a H), 2.55 (s, 1, OH), 2.95–3.15 (m, 2, C-6 H's), 3.50 (d, 2, CH_2OH), 7.00–7.40 (m, 4, arom).

Anal. Calcd for $C_{11}H_{10}O$: C, 82.46; H, 7.54. Found: C, 82.13; H, 7.45.

***endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene.** Ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, 2.890 g (0.0143 mol), was converted to 2.162 g (94.5%) of *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene via a procedure identical with that used for the exo isomer. The spectral data were: ir (neat) 3350, 2980, 2950, 1600, 1410, 1255, 1100, 1050, and 780 cm^{-1}; NMR ($CDCl_3$) δ 1.09–1.60 (m, 1, C-1 H), 1.73–2.10 (m, 1, C-6a H), 2.00–2.40 (br, 1, OH), 2.58 (t, 1, C-1a H), 2.88–3.53 (m, 2, C-6 H's), 3.10 (d, 2, CH_2OH), 7.00–7.35 (m, 4, arom).

Anal. Calcd for $C_{11}H_{10}O$: C, 82.46; H, 7.54. Found: C, 82.14; H, 7.31.

Optically Active *exo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. In a manner identical with that used for the preparation of the racemic exo alcohol, 3.554 g (0.0176 mol) of optically active ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, $[\alpha]^{25}_{435.8}$ −113.1 ± 1.2°, was converted to 2.682 g (94.9%) of optically active *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −109.3 ± 2.0° (*c* 0.00174, $CHCl_3$). The ir and NMR spectra of the optically active alcohol were identical with those of the racemic material.

Optically Active *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocy-

cloprop[*a*]indene. In a manner identical with that used for the racemic alcohol, 4.203 g (0.0208 mol) of optically active ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, $[\alpha]^{25}_{435.8}$ −389.0 ± 0.3°, was converted to 3.168 g (95.2%) of optically active *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −327.0 ± 2.0° (*c* 0.00201, $CHCl_3$). The NMR and ir spectra of the optically active endo alcohol were identical with those of the racemic material.

Conversion of *exo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene to Ethyl *exo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylate. To 6 g of the pyridine–CrO_3 complex in 120 ml of dry methylene chloride was added 0.576 g (3.62×10^{-3} mol) of *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. The mixture was shaken for 15 min and filtered, and the methylene chloride was removed under vacuum. To the residue remaining was added 200 ml of ether and the mixture was filtered again. The filtrate was washed with 50 ml of 10% HCl followed by 50 ml of H_2O and dried ($MgSO_4$). The ether was removed under vacuum to yield 0.543 g (94.8%) of *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxaldehyde: ir (neat) 2980, 2940, 2880, 2820, 1705, 1600, and 1265 cm^{-1}.

The crude exo aldehyde was immediately oxidized to the exo acid. Thus 1.80 g (1.06×10^{-2} mol) of silver nitrate in 6 ml of water was added to a solution of 0.90 g (2.12×10^{-2} mol) of sodium hydroxide in 6 ml of H_2O. The mixture was shaken continuously during the addition and then cooled to 0° in an ice bath. To this cooled mixture was added the crude aldehyde, and the resulting mixture was shaken for 2 min. The black silver precipitate was removed by filtration and washed with several portions of hot water. The combined filtrate and washings were acidified with 50 ml of 6 N HCl and extracted with ether. The ether extract was dried ($MgSO_4$) and then concentrated under vacuum to yield 0.474 g (79.4%) of *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid.

The crude exo acid was not purified but was esterified in the usual manner to give 0.472 g (85.6%) of ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate. GC analysis (6 ft × ⅛ in. column of 4.1% QF-1 on gas-pack F at 150°) showed no trace of the endo ester. The overall yield of ester from the exo alcohol was 64.3%.

Conversion of *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene to Ethyl *endo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylate. In a manner identical with that used for the exo alcohol, 0.501 g (3.13×10^{-3} mol) of *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene was oxidized to give 0.470 g (94.8%) of crude *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxaldehyde: ir (neat) 2980, 2940, 2880, 2820, 1705, 1600, and 1265 cm^{-1}.

The crude aldehyde was immediately oxidized to the endo acid (0.400 g, 77.4%) in a manner indentical with that used for the exo aldehyde. The acid was esterified in the usual manner to give 0.317 g (79.3%) of ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate. The overall yield of ester from the alcohol was 58.6%. GC analysis indicated the absence of any trace of exo ester.

Base Isomerization of Optically Active Ethyl *exo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylate. To a three-necked flask equipped with a nitrogen atmosphere and a rubber septum was added 4.6 ml (0.025 mol) of *N*-isopropylcyclohexylamine (freshly dried and distilled from CaH_2) and 50 ml of dry tetrahydrofuran. The solution was cooled to −65° (dry ice–acetone) and 11.9 ml (0.025 mol) of 2.1 M *n*-butyllithium in hexane was added dropwise. The solution was stirred for an additional 15 min at −65° after which a solution of 0.444 g (2.19×10^{-3} mol) of optically active ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, $[\alpha]^{25}_{435.8}$ −113.1 ± 1.2°, in 50 ml of dry tetrahydrofuran was added dropwise. The temperature was kept at −65° during the addition. The mixture was then stirred for 45 min at −65° and then rapidly quenched by adding 50 ml of 20% HCl. The reaction mixture was allowed to warm to room temperature and then extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated. GC analysis (6 ft × ⅛ in. column of 4.1% QF-1 on gas-pack F at 150°) indicated the presence of a 1.5:1 mixture of exo and endo esters together with smaller amounts of other by-products. The crude mixture was chromatographed on a 2 × 89 cm deactivated (8% H_2O) silica gel column slurry-packed with hexane and eluted with 1 l. of hexane followed by 2 l. of 1% ether–hexane to provide 0.138 g of the starting exo ester. Elution with 2% ether–hexane provided 0.0873 g of slightly impure endo ester. Rechromatography on a similar silica gel column afforded 0.0247 g of pure ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate. The recovered exo ester showed specific rotations of (wavelength in parentheses) −347.3° (366.3 nm), −147.8° (404.7 nm), −114.1° (434.7 nm), −113.2° (435.8 nm), −45.3° (577.0 nm), and −44.9° (579.1 nm) (*c* 0.01375, $CHCl_3$). The endo ester showed specific rotations of −320.7° (366.3 nm), −136.5° (404.7 nm), −106.8° (434.8 nm), −106.1° (435.8 nm), −39.9° (577.0 nm), and −38.8° (579.1 nm) (*c* 0.00247, $CHCl_3$). The CD spectra of the recovered esters were identical in shape with those of the pure esters prepared above.

A second run utilized 0.3840 g of the same optically active exo ester and afforded 0.1036 g of the recovered exo ester and 0.0128 g of the endo ester. The recovered exo ester showed specific rotations of −347.0° (366.3 nm), −147.4° (404.7 nm), −114.2° (434.7 nm), −113.0° (435.8 nm), −45.2° (577.0 nm), and −44.8° (579.1 nm) (*c* 0.01036, $CHCl_3$). The endo ester showed specific rotations of −324.2° (366.3 nm), −139.8° (404.7 nm), −109.4° (434.7 nm), −107.0° (435.8 nm), −41.4° (577.0 nm), and −39.1° (579.1 nm) (*c* 0.00128, $CHCl_3$). The CD spectra of the recovered esters were identical in shape with those of the pure esters prepared above.

Base Isomerization of Optically Active Ethyl *endo*-1,1a,6,6a-Tetrahydrocycloprop[*a*]indene-1-carboxylate. The base isomerization of the endo ethyl ester was carried out in a manner identical with that used with the exo ester. Starting with 0.3850 g (1.90×10^{-3} mol) of optically active ethyl *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate, $[\alpha]^{25}_{435.8}$ −389.0 ± 0.3°, there was obtained 0.1372 g of recovered endo ester and 0.0551 g of ethyl *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylate. The recovered endo ester showed specific rotations of (wavelength in parentheses) −756.8° (366.3 nm), −505.7° (404.7 nm), −392.8° (434.7 nm), −389.5° (435.8 nm), −168.9° (577.0 nm), and −167.5° (579.1 nm) (*c* 0.01372, $CHCl_3$). The exo ester showed specific rotations of −811.4° (366.3 nm), −549.0° (404.7 nm), −430.6° (434.7 nm), −426.9° (435.8 nm), −188.2° (577.0 nm), and −187.6° (579.1 nm) (*c* 0.00551, $CHCl_3$). The CD spectra of the recovered esters were identical in shape with those of the pure esters prepared above.

A second run utilized 0.4242 g of the same optically active endo ester and afforded 0.1569 g of the recovered endo ester and 0.0631 g of the exo ester. The recovered endo ester showed specific rotations of −756.0° (366.3 nm), −505.0° (404.7 nm), −392.0° (434.7 nm), −388.1° (435.8 nm), −168.1° (577.0 nm), and −166.5° (579.1 nm) (*c* 0.1569, $CHCl_3$). The exo ester showed specific rotations of −823.9° (366.3 nm), −552.0° (404.7 nm), −432.5° (434.7 nm), −429.0° (435.8 nm), −189.8° (577.0 nm), and −189.0° (579.1 nm) (*c* 0.00631, $CHCl_3$). The CD spectra of the recovered esters were identical in shape with those of the pure esters prepared above.

Direct Photolysis of Racemic *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (1N). A solution of 1.802 g (11.26 mmol) of *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene in 160 ml of anhydrous ether was irradiated for 14 h with Vycor-filtered light from a Hanovia 450-W medium-pressure mercury arc. Nitrogen was bubbled through the photolysis solution for 20 min prior to irradiation and throughout the photolysis. Progress of the reaction was monitored by GC using a 5 ft × ⅛ in. 3% XE-60 column (140°). After photolysis the solvent was removed under vacuum, and the product was chromatographed on a 2 × 50 cm deactivated (10% H_2O) silica gel column slurry-packed with 2% ether–hexane and eluted with 1 l. each of 5, 10, and 15% ether–hexane. The 10% ether–hexane fractions provided 0.021 g of a 2:1 mixture of *trans*- and *cis*-2-vinylindan-1-ol;[11] the 15% ether–hexane fractions afforded 1.407 g of a 4:3 mixture of *exo*- and *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. The identity of the materials isolated was confirmed by comparison of the NMR and ir spectra of the isolated mixtures with the spectra of the known compounds.

Acetone-Sensitized Photolysis of Racemic *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (1N). A solution of 0.873 g (5.46 mmol) of *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene in 160 ml of acetone was irradiated (5 h) as done in the direct photolysis of this compound, except that Pyrex-filtered light was used. Chromatography of the product mixture as before provided 0.731 g of a 1:1 mixture of *endo*- and *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. The products were identified by comparison of the NMR and ir spectra and GC retention times of the product mixture with those of the known compounds.

Direct Photolysis of Racemic *exo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (1E). A solution of 1.720 g (10.75 mmol)

of *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene in 160 ml of anhydrous ether was irradiated (22 h) in a manner identical with that used in the direct photolysis of the endo alcohol. Chromatography as before provided 0.008 g of a 2:1 mixture of *trans*- and *cis*-2-vinylindan-1-ol[11] and 1.094 g of a 2:3 mixture of *endo*- and *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. The products were identified by comparison of the NMR and ir spectra and GC retention times of the isolated mixtures with those of the known compounds. (For identification purposes the indan-1-ols from several photolyses were combined.)

Acetone-Sensitized Photolysis of Racemic *exo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (1E). A solution of 0.539 g (3.37 mmol) of *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene in 110 ml of acetone was irradiated (9 h, Pyrex filter) in the usual manner. Chromatography (see direct photolysis of endo alcohol) provided 0.397 g of a 4:3 mixture of *exo*- and *endo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, identified by comparison of the NMR and ir spectra and GC retention times of the isolated mixture with those of the known compounds.

Photolysis of the Optically Active *endo*- and *exo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indenes. All photolyses were carried out in a manner similar to that used for the racemic alcohols. Sensitized photolyses were carried out with Pyrex-filtered light; direct irradiations were done with Vycor-filtered light. All photolyses were monitored by GC using a 5 ft × ⅛ in. 3% XE-60 column at 150° and were terminated when conversion of starting material to its isomer had reached 10%. The mixtures of alcohols resulting from the photolyses were converted to mixtures of the ethyl *endo*- and *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylates as was done with the racemic alcohols. The esters were separated by chromatography on a 2 × 90 cm deactivated (8% H_2O) silica gel column slurry-packed with hexane and eluted with 1 l. of hexane, 1 l. of 1% ether–hexane, and 1 l. of 2% ether–hexane. The exo ester eluted with the 1% ether–hexane; the endo ester, with 2% ether–hexane. Column fractions containing the pure esters were combined and concentrated. Optical rotations ($CHCl_3$ solution) were then determined for each ester at six different wavelengths. In addition CD spectra (methanol solution) were obtained for each sample to check for optical impurities. In no case were any such impurities noted.

Run 1. Optically active *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −327.0 ± 2.0°, 0.4725 g (2.95 mmol), in 110 ml of acetone was irradiated for 23 min. The crude product was converted to 0.3477 g of a mixture of the endo and exo esters. The endo ester showed specific rotations of −756.1° (366.3 nm), −504.9° (404.7 nm), −392.0° (434.7 nm), −388.3° (435.8 nm), −168.2° (577.0 nm), and −166.8° (579.1 nm) (*c* 0.02714, $CHCl_3$). The exo ester showed specific rotations of −765.7° (366.3 nm), −527.8° (404.7 nm), −415.7° (434.7 nm), −411.4° (435.8 nm), −181.6° (577.0 nm), and −179.2° (579.1 nm) (*c* 0.00578, $CHCl_3$).

Run 2. Optically active *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −327.0 ± 2.0°, 1.1040 g (6.89 mmol), in 110 ml of acetone was irradiated for 50 min. The crude product was converted to 0.9147 g of a mixture of the endo and exo esters. The endo ester showed specific rotations of −756.4° (366.3 nm), −505.6° (404.7 nm), −392.5° (434.7 nm), −389.1° (435.8 nm), −168.6° (577.0 nm), and −167.1° (579.1 nm) (*c* 0.02901, $CHCl_3$). The exo ester showed specific rotations of −777.3° (366.3 nm), −531.7° (404.7 nm), −416.6° (434.7 nm), −413.3° (435.8 nm), −182.9° (577.0 nm), and −181.0° (579.1 nm) (*c* 0.00896, $CHCl_3$).

Run 3. Optically active *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −327.0 ± 2.0°, 0.9378 g (5.86 mmol), in 160 ml of ether was irradiated for 60 min. The crude product was converted to 0.8109 g of mixture of the endo and exo esters. The endo ester showed specific rotations of −756.0° (366.3 nm), −505.0° (404.7 nm), −392.1° (434.7 nm), −388.7° (435.8 nm), −168.3° (577.0 nm), and −166.9° (579.1 nm) (*c* 0.02763, $CHCl_3$). The exo ester showed specific rotations of −515.2° (366.3 nm), −340.0° (404.7 nm), −266.5° (434.7 nm), −264.3° (435.8 nm), −116.5° (577.0 nm), and −116.8° (579.1 nm) (*c* 0.00704, $CHCl_3$).

Run 4. Optically active *endo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −327.0 ± 2.0°, 0.4138 g (2.58 mmol), in 160 ml of ether was irradiated for 35 min. The crude product was converted to 0.2902 g of mixture of the endo and exo esters. The endo ester showed specific rotations of −756.9° (366.3 nm), −506.1° (404.7 nm), −392.7° (434.7 nm), −389.1° (435.8 nm), −168.8° (577.0 nm), and −167.3° (579.1 nm) (*c* 0.02375, $CHCl_3$).

Table III. Direct Photolysis Quantum Yields

Reactant (mg, mmol)	Light absorbed, mEinstein	Product (mg, μmol)	Φ (product)
1N)26.9, 0.168)	9.14×10^{-3}	**1E** (0.20, 1.25)	0.14 ± 0.01
		3 + **4** (0.03, 0.20)	0.022 ± 0.002
1N (25.8, 0.161)	9.14×10^{-3}	**1E** (0.19, 1.18)	0.13 ± 0.01
1E (17.9, 0.112)	9.14×10^{-3}	**1N** (0.16, 0.97)	0.11 ± 0.01
		3 + **4** (<0.004, <0.03)	<0.003
1E (20.3, 0.127)	9.14×10^{-3}	**1N** (0.14, 0.86)	0.094 ± 0.01

The exo ester showed specific rotations of −505.3° (366.3 nm), −336.7° (404.7 nm), −261.9° (434.7 nm), −259.7° (435.8 nm), −115.2° (577.0 nm), and −114.6° (579.1 nm) (*c* 0.00232, $CHCl_3$).

Run 5. Optically active *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −109.3 ± 2.0°, 0.5219 g (3.39 mmol), in 110 ml of acetone was irradiated for 50 min. The crude product was converted to 0.4062 g of a mixture of the exo and endo esters. The exo ester showed specific rotations of −347.5° (366.3 nm), −147.7° (404.7 nm), −113.9° (434.7 nm), −113.0° (435.8 nm), −45.0° (577.0 nm), and −44.7° (579.1 nm) (*c* 0.02803, $CHCl_3$). The endo ester showed specific rotations of −313.9° (366.3 nm), −136.5° (404.7 nm), −104.9° (434.7 nm), −104.5° (435.8 nm), −40.0 (577.0 nm), and −39.3 (579.1 nm) (*c* 0.00285, $CHCl_3$).

Run 6. Optically active *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −109.3 ± 2.0°, 0.4745 g (2.96 mmol), in 110 ml of acetone was irradiated for 45 min. The crude product was converted to 0.3633 g of a mixture of the exo and endo esters. The exo ester showed specific rotations of −347.3° (366.3 nm), −147.4° (404.7 nm), −113.8° (434.7 nm), −113.0° (435.8 nm), −45.0 (577.0 nm), and −44.7° (579.1 nm) (*c* 0.01954, $CHCl_3$). The endo ester showed specific rotations of −306.8° (366.3 nm), −129.8° (404.7 nm), −99.6 (434.7 nm), −102.2° (435.8 nm), −37.4° (577.0 nm), and −36.6° (579.1 nm) (*c* 0.00265, $CHCl_3$).

Run 7. Optically active *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −109.3 ± 2.0°, 0.5634 g (3.52 mmol), in 110 ml of ether was irradiated for 15 min. The crude product was converted to 0.4691 g of a mixture of the exo and endo esters. The exo ester showed specific rotations of −347.1° (366.3 nm), −147.2° (404.7 nm), −113.8° (434.7 nm), −113.1° (435.8 nm), −45.0° (577.0 nm), and −44.7° (579.1 nm) (*c* 0.02755, $CHCl_3$). The endo ester showed specific rotations of −196.7° (366.3 nm), −85.0° (404.7 nm), −66.3° (434.7 nm), −65.1° (435.8 nm), −25.2° (577.0 nm), and −24.4° (579.1 nm) (*c* 0.00401, $CHCl_3$).

Run 8. Optically active *exo*-1-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, $[\alpha]^{25}_{435.8}$ −109.3 ± 2.0°, 0.6800 g (4.25 mmol), in 110 ml of ether was irradiated for 25 min. The crude product was converted to 0.5650 g of a mixture of the exo and endo esters. The exo ester showed specific rotations of −347.4° (366.3 nm), −147.5° (404.7 nm), −114.3° (434.7 nm), −113.3° (435.8 nm), −45.0° (577.0 nm), and −44.9° (579.1 nm) (*c* 0.02311, $CHCl_3$). The endo ester showed specific rotations of −193.7° (366.3 nm), −85.0° (404.7 nm), −65.6° (434.7 nm), −23.9° (577.0 nm), and −23.6° (579.1 nm) (*c* 0.00271, $CHCl_3$).

Quantum Yields for Direct Photolyses of *exo*- and *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. Quartz irradiation vessels containing 6.5-ml portions of cyclohexane solutions of the exo and endo alcohols were stoppered with serum caps. Nitrogen was bubbled through each sample via very thin syringe needles. The samples were then irradiated on a merry-go-round apparatus at ambient temperature using the 2537-Å light from a low-pressure mercury lamp. Light intensity was determined by simultaneous irradiation of tubes containing potassium ferrioxalate solution.[12] The reaction solutions were then analyzed by gas chromatography using a 6 ft × ⅛ in. column packed with 3% Silar 5CP on Gas-Chrom Q, 80/100, at 130°.

Product concentrations were determined by comparison of the GC response of the photolysis solutions with that of samples containing known amounts of the pure product; GC peak areas were measured

Table IV. Sensitized Photolysis Quantum Yields

Reactant (mg, mmol)	Light absorbed, mEinstein	Product (mg, mmol)	Φ (product)
1N (27.0, 0.168)	0.0449	**1E** (2.80, 0.018)	0.39 ± 0.02
1N (28.4, 0.180)	0.0449	**1E** (2.72, 0.017)	0.38 ± 0.02
1N (33.3, 0.208)	0.0160	**1E** (0.97, 0.00606)	0.38 ± 0.02
1N (26.7, 0.167)	0.0160	**1E** (1.01, 0.00632)	0.40 ± 0.03
1N (131.7, 0.823)	0.0773	**1E** (5.44, 0.0340)	0.44 ± 0.03
1N (135.5, 0.847)	0.0773	**1E** (5.28, 0.0330)	0.43 ± 0.03
1E (27.6, 0.172)	0.0449	**1N** (0.99, 0.0062)	0.14 ± 0.01
1E (26.6, 0.166)	0.0449	**1N** (0.94, 0.0059)	0.13 ± 0.01
1E (26.4, 0.165)	0.0160	**1N** (0.31, 0.00195)	0.12 ± 0.01
1E (25.3, 0.158)	0.0160	**1N** (0.30, 0.00187)	0.12 ± 0.01
1E (124.5, 0.778)	0.0773	**1N** (1.60, 0.0100)	0.13 ± 0.01
1E (127.9, 0.799)	0.0773	**1N** (1.63, 0.0102)	0.13 ± 0.01

by the cut and weigh method. The results are compiled in Table III.

Quantum Yields for Sensitized Photolyses of *exo*- and *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. Pyrex vessels containing 6.5-ml portions of acetone solutions were degassed using the freeze–pump–thaw method at <1 μm pressure. The vessels were then sealed and irradiated on a merry-go-round apparatus at room temperature using the light from a Hanovia 450-W medium-pressure mercury arc. The light was passed through a potassium chromate filter solution (0.2994 g/250 ml of 5% aqueous potassium carbonate, 0.9 cm path length) to isolate the 313 nm band (305–322 nm). Benzophenone-benzhydrol actinometry was used to determine light output.[13] Product analyses were carried out as in the direct photolyses. The results are compiled in Table IV.

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The Gear Effect.[1-3] V. A Model for Conformational Transmission

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Abstract: Polyhedral substituents like alkyl groups can be involved in a "geared" [2] system when they are in close contact. In 3-isopropyl-4-alkyl-Δ^4-thiazoline-2-thiones and the 3-cyclohexyl analogues, the conformational state of the 3-isopropyl (3-cyclohexyl) group is strongly dependent on the substituents in positions 4 and 5, and when the 4 substituent is an isopropyl group, the conformational equilibria cannot be explained by the "classical" steric effect. In this "geared" system, substitution at one side of the structural block of two interacting groups affects the reactivity at the other end of the block. The barriers to rotamer interchange have been studied by dynamic ^{1}H NMR, and the rotations of the 3- and 4-isopropyl groups in the 3,4-diisopropyl-5-methyl derivative have been shown to be nonsynchronous. Rotamer conformations and routes of interchange are discussed in relation to calculated nonbonded energies.

A conformational transmission process may be evidenced in a molecular system in which the groups involved occupy a suitable spatial disposition to carry conformational information through the framework. Such suitable dispositions have previously been exemplified in the steroid field.[5] More recently it has been reported that the locking of a side chain in a conformation which is favorable for the reaction gives rise to spectacular rate enhancement.[6] The time honored "geminal dialkyl effect"[7,8] rests on a similar mechanism. In the biochemical field the allosteric mechanism[9] and the induced fit theory[10,11] are important applications of the induced conformational effects.

The purpose of the present communication is to show with a simple model that polyhedral substituents like alkyl