Stereoselective Photochemical Electrocyclic Valence Isomerizations of α-Phellandrene Conformational Isomers[1]

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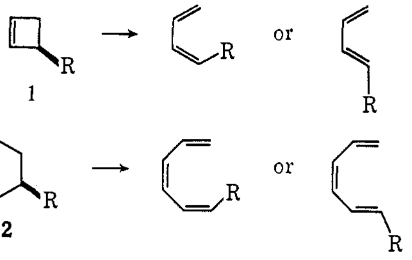
Abstract: The primary products from the unsensitized photolysis of α-phellandrene are the *cis,trans-* and *cis,cis-*3,7-dimethylocta-1,3,5-trienes; the *trans,trans* and *trans,cis* isomers are formed through photoisomerizations of the primary products. The temperature dependence of the ratio of the two primary products, when plotted as log (ratio) *vs.* T^{-1}, gives a linear correlation consistent with the postulate that the α-phellandrene conformer with a pseudoaxial isopropyl substituent is photoisomerized to the *cis,cis*-triene, while the conformer with a pseudoequatorial isopropyl group is converted only to the *cis,trans*-triene. The conversion of the pseudoaxial to the pseudoequatorial conformational isomer of α-phellandrene occurs with $\Delta H^\circ = -0.46$ kcal/mol. The data and interpretation correctly predict the sign reversal in the molecular rotation of α-phellandrene noted in independent ord and cd studies.

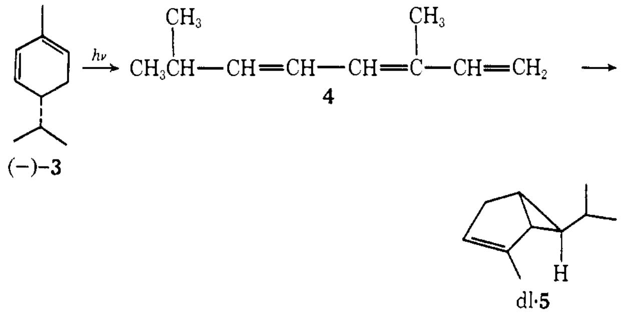
Molecules such as 3-substituted cyclobutenes (**1**) or 5-substituted cyclohexadienes (**2**) would be allowed, according to the theoretical principles codified in the Woodward–Hoffmann rules,[4] to give either *cis* or *trans* electrocyclic ring-opened valence isomers through concerted thermal or photochemical reactions.



Four cyclobutenes of type **1** have been pyrolyzed and found to give the *trans* product,[5-8] a result compatible with the simple notion that, of the two competitive activated complexes, the one minimizing steric interactions involving bulky substituents would be of lowest energy.

Analogous investigations of the stereochemistry of the thermal rearrangements of cyclohexadienes, and of the photorearrangements of cyclobutenes and cyclohexadienes, have been wanting.

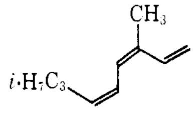
α-Phellandrene (**3**), the molecule selected for study in this work, was investigated earlier by de Kock, Minnaard, and Havinga,[9] and found to give a mixture of geometrical isomers of 3,7-dimethylocta-1,3,5-triene (**4**) which reacted further on prolonged irradiation. A later publication defined structure **5** for the bicyclic olefin reached by extended irradiation.[10]



$$\xrightarrow{h\nu} \mathrm{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH{=}CH{-}CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2} \longrightarrow$$

Results

Photoproducts. Irradiation at 253.7 nm of a 0.03 *M* solution of α-phellandrene in hexane until a 30% conversion of diene had been achieved gave a mixture of four isomeric 3,7-dimethylocta-1,3,5-trienes. These products were isolated by glpc and identified through spectroscopic data as, in order of increasing retention time on an analytical Carbowax 20M column, the *cis,-cis-* (**6**), *trans,cis-* (**7**), *cis,trans-* (**8**), and *trans,trans-* (**9**) isomers.



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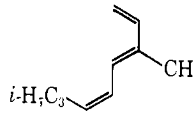

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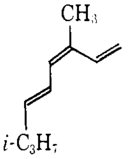

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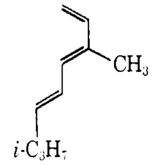

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The mass spectra of the trienes had molecular ion peaks at *m/e* 136, and abundant ions at 121 ($M^+ - CH_3$), 106 ($M^+ - 2CH_3$), and 93 ($M^+ - C_3H_7$); they

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[3] University Fellow (1966–1967) and Sun Oil Fellow (1967), University of Illinois; National Institute of General Medical Sciences Predoctoral Fellow (1968–1969).

[4] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and unpublished work.

[5] E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 257 (1964).

[6] H. M. Frey, *Trans. Faraday Soc.*, **60**, 83 (1964).

[7] H. M. Frey, D. C. Marshall, and R. F. Skinner, *ibid.*, **61**, 861 (1965).

[8] M. Pomerantz and P. H. Hartman, *Tetrahedron Lett.*, 991 (1968).

[9] R. J. de Kock, N. G. Minnaard, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **79**, 922 (1960).

[10] J. Meinwald, A. Eckell, and K. Erickson, *J. Amer. Chem. Soc.*, **87**, 3532 (1965).

were identical but for differences in relative ion abundances.

Isomers **8** and **9** had bands at 965 and 964 cm^{-1}, respectively, appropriate to a *trans*-disubstituted double bond.[11]

Isomers **6** and **8** had absorptions for C(2)–H at δ 6.88 and 6.87 ppm, respectively, while the corresponding C(3)–C(4)-*trans* isomers **7** and **9** showed this proton at much higher field (<6.5 in **7**, 6.28 ppm in **9**). The C(2) vinyl proton in the *cis,cis* and *cis,trans* isomers is deshielded by the proximate coplanar C(5)–C(6) double bond. Similarly, C(5)–H in **8** is deshielded relative to the same proton in **9**.

The vinyl methyl resonances at 1.90, 1.82, 1.87, and 1.80 ppm, respectively, for the four isomers seem contradictory in stereochemical implication at first glance, since the C(3)–CH_3 protons *cis* to the C(5)–C(6) double bond are at higher field. But both free rotation of these methyl groups and conformational factors favoring a C(2)–C(3) *s-trans* geometry in **6** and **8** more than in **7** and **9** reduce the relative deshielding effects on these protons; hence the net upfield shift relative to the vinyl methyl absorptions in **6** and **8**.

Primary Photoproducts. To establish which trienes were primary products derived directly from α-phellandrene, aliquots of a 0.03 *M* solution of purified α-phellandrene in hexane were degassed, sealed in Vycor tubes, and photolyzed in a "merry-go-round" apparatus for varying times. Analyses of products by glpc provided the data in Table I. No products other than the four trienes and traces of *p*-cymene were detected.

Table I. Photoproducts from α-Phellandrene

Irradiation time, min	Relative yields, %^{a} α-Phellandrene	c,c (6)	t,c (7)	c,t (8)	t,t (9)
0	99				
0.5	98	0.4		1.2	
1	96	0.8		2.2	
1.5	94	1.2	Trace	3.8	Trace
2	92	1.7	0.4	5.0	0.4
5	82	3	1.4	10	2
10	70	5	3	16	5
20	48	7	6	24	13
35	33	8	9	25	24
52	18	9	12	26	33

^{a} Based on total peak area.

In a parallel experiment, purified *cis,trans*-triene (**8**) was irradiated under identical conditions. The results summarized in Table II and the data in Table I make clear that trienes **6** and **8** are both genuine primary products, and that trienes **7** and **9** are secondary products reached through photoisomerization of the initially formed trienes. These findings are in agreement with the known photochemical isomerizations of 1,3-cyclohexadienes to trienes having a *cis*-C(3)–C(4) double bond.[12]

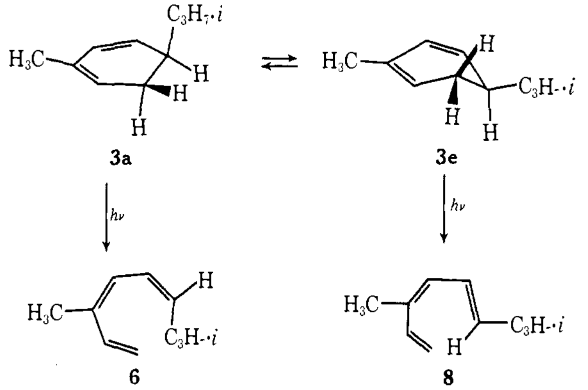
Table II. Photoisomerization of *cis,trans*-Triene (**8**)

Irradiation time, min	Trienes, %^{a} c,c (6)	t,c (7)	c,t (8)	t,t (9)
0			99	
5	1.5	0.7	86	11
15	3.8	1.8	69	25

^{a} No α-phellandrene was detected.

The Nature of the Excited State. Irradiation at 350 nm of hexane solutions of α-phellandrene with acetophenone (E_T = 74 kcal/mol) as sensitizer, under conditions such that the acetophenone absorbed 90% of the incident light, consumed the substrate but failed to give any of the triene photoproducts discussed above. The sensitization results implicate the $\pi \rightarrow \pi^*$ singlet as the excited state giving the trienes. The low energy of the triplet state for conjugated dienes such as 1,3-cyclohexadiene (E_T = 53 kcal/mol[13]), and the fact that other products were produced in the sensitization experiment with α-phellandrene, indicate that triplet-energy transfer had occurred but trienes are not formed from the $\pi \rightarrow \pi^*$ triplet. Studies in the vitamin D series have previously identified the singlet-excited state as the one involved in cyclohexadiene to triene isomerizations.[14]

Temperature Dependence of Product Ratios. The electrocyclic photochemical valence isomerization of α-phellandrene gives both of the anticipated trienes corresponding to the two conrotatory options. We were intrigued by the possibility that these two modes of ring opening were related to the two principal conformational isomers of α-phellandrene.



Investigations of the ord and cd spectra of (−)-α-phellandrene as a function of temperature[15–18] have given some insight into the equilibrium between the pseudoaxial (**3a**) and pseudoequatorial (**3e**) conformers. If the photoisomerization of each conformer was highly stereoselective giving the product anticipated in a model emphasizing ground-state geometry as a stereochemical determinant,[19,20] then the triene product ratio [**8**]/[**6**] ought to be a quantitative measure of the equilib-

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(11) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 24.

(12) See, for example, E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); K. J. Crowley, *J. Org. Chem.*, **33**, 3679 (1968).

(13) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(14) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961).

(15) A. W. Burgstahler, H. Ziffer, and U. Weiss, *J. Amer. Chem. Soc.*, **83**, 4660 (1961).

(16) H. Ziffer, E. Charney, and U. Weiss, *ibid.*, **84**, 2961 (1962).

(17) G. Horsman and C. A. Emeis, *Tetrahedron*, **22**, 167 (1966).

(18) G. Snatzke, E. sz. Kováts, and G. Ohloff, *Tetrahedron Lett.*, 4551 (1966).

(19) W. G. Dauben, *Chem. Weekbl.*, **60**, 381 (1964).

(20) J. P. Malrieu, *Photochem. Photobiol.*, **5**, 291, 301 (1966).

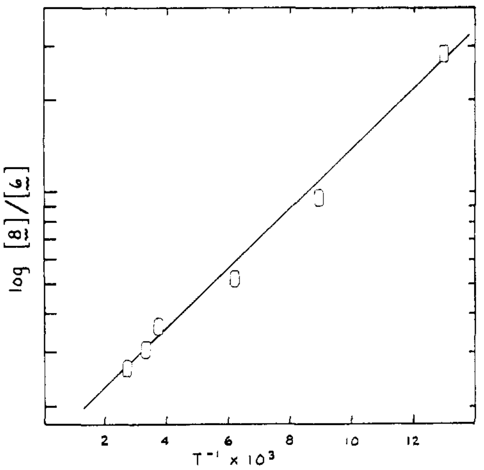

Figure 1. Plot of log [8]/[6] *vs.* T^{-1} for the trienes produced through photoisomerization of α-phellandrene.

rium constant K = [**3e**]/[**3a**]. This expectation assumes approximately equal molar extinction coefficients for the dienes **3a** and **3e**, and quantum yields for the isomerizations of each conformer. To test this hypothesis, product ratio data were obtained as a function of temperature (Table III).

Table III. Triene Product Ratios[a]

Temp, °C	Ratio, [8]/[6]
−196	29 ± 1
−160	9.7 ± 1.6
−110	5.2 ± 0.4
0	3.7 ± 0.2
30	3.0 ± 0.1
100	2.7 ± 0.1

[a] Determined in isopentane and hexane solutions, to less than 5% conversion of α-phellandrene.

Discussion

The data in Table III give a fair linear plot (Figure 1) when substituted into the equation appropriate for a thermal equilibrium, $\log K = -\Delta H°(2.303RT)^{-1}$. From the slope of the plot, and within the framework of assumptions stated above, $\Delta H°$ for the isomerization **3a** → **3e** is −0.46 kcal/mol.

Now the experimentally derived values of $K(T)$ may be juxtaposed with the temperature-dependent spectral data for quantitative scrutiny. Let the pseudoaxial and pseudoequatorial conformers of (−)-α-phellandrene have molecular rotations $[\Phi_a]$ and $[\Phi_e]$ which are invariant to changes in temperature; then

$$[\Phi] = \chi_a[\Phi_a] + \chi_e[\Phi_e]$$

where χ_a and χ_e are the mole fractions of the two conformers. Then one can derive the relationship[21]

$$[\Phi] = (K + 1)^{-1}([\Phi_a] - [\Phi_e]) + [\Phi_e]$$

where $K = \chi_e/\chi_e$.

A plot of $[\Phi]$ against $(K + 1)^{-1}$ should give a straight line. To test for this linear relationship, ord data from the literature[15-17,22] and $K(T)$ values calculated from the present work were used. The graphical outcome of this test is shown in Figure 2.

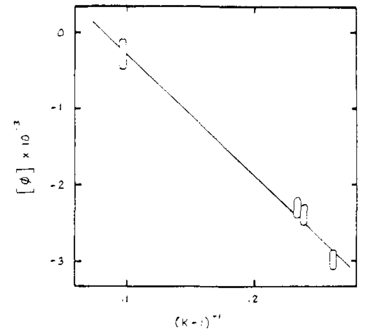

Figure 2. Plot of molecular rotation [Φ] at 320 nm for (−)-α-phellandrene against $(K + 1)^{-1}$.

From this plot may be estimated a slope of $-(17 \times 10^3)°$ and an intercept of $+(1.5 \times 10^3)°$, and thus $[\Phi_a] \cong -(16 \times 10^3)°$ and $[\Phi_e] \cong +(1.5 \times 10^3)°$. The predicted change from negative to positive rotation at 320 nm is at $T \cong -160°$. This estimation of the temperature of sign inversion falls between the temperatures at which Snatzke and coworkers[18] observed a positive cd curve for (−)-α-phellandrene (−186°) and Horsman and Emeis[17] observed a weakly negative Cotton effect in the ord spectrum of the diene (−150°). While the numerical values for $[\Phi_a]$, $[\Phi_e]$, and the temperature of sign inversion obtained from the graph of Figure 2 cannot be precise, the analysis leading to them is fully consistent with the postulated stereoselectivity in the photochemical conversions **3a** → **6** and **3e** → **8**, and with the anticipation[16] that, at room temperature, both conformers would be present in comparable proportions, the pseudoaxial conformer having a negative molecular rotation up to an order of magnitude larger than the positive rotation of the pseudoequatorial isomer.

Other investigators have argued that photoisomerizations to one or another type of structure might be controlled by differences in ground-state geometry of different substrates.[19,20] The present investigation demonstrates that the stereochemistry of a common type of valence isomerization is controlled by conformer populations in the reactant. A planar 1,3-cyclohexadiene has two degenerate conrotatory modes available for photoisomerization. But a nonplanar 1,3-cyclohexadiene—as all or nearly all must be—[23] has two distinct conrotatory modes available for photochemical electrocyclic reaction, one in which the sense of the conrotatory process and the chirality of the diene are accordant, and one where they are discordant.

Thus, the photochemical electrocyclic valence isomerization of α-phellandrene is highly stereoselective; the two conformational isomers of α-phellandrene each give a single isomer of 3,7-dimethylocta-1,3,5-triene (**3a** → **6**; **3e** → **8**). This specificity provides a new variety of inducement supporting the proposition that the ground-state geometry of a molecule subjected to photolytic activation may determine the structure and stereochemistry of the photoproduct[19,20,24-27] and

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[21] G. Claeson, *Acta Chem. Scand.*, 22, 2429 (1968).

[22] The assumption that both groups reporting ord data for α-phellandrene utilized samples of comparable optical purity seems both reasonable and preferable to the alternative, limiting the temperature range considered and extrapolating further to reach the temperature where [Φ] = 0.

[23] H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

exemplifies an interesting composite of elements influencing a type of electrocyclic reaction. Orbital-symmetry rules limit the possible modes of reaction for concerted processes; ground-state geometrical characteristics dictate which of the allowed modes will obtain.

Experimental Section

The nmr spectra were determined as solutions in CCl_4 at 100 MHz using a Varian spectrometer; infrared spectra were obtained as films between salt plates with a Beckman-IR5 spectrophotometer; ultraviolet spectra were recorded with Cary 14 and 15 instruments; and mass spectra were run by Mrs. Mary Mitchell on a CEC 21-110 spectrometer. Perkin-Elmer Model F-11 and Varian Aerograph A90-P3 and 1520 gas chromatographs were employed.

Photolysis of α-Phellandrene. A 0.03 *M* solution of α-phellandrene in hexane (20 ml) was photolyzed through base-washed Vycor in a Rayonet photoreactor at 253.7 nm. The reaction mixture was concentrated from an ice–water bath at reduced pressure and products were separated by glpc on a 6-mm × 1.2-m 21% oxydipropionitrile on Chromosorb P column at 75°.

Triene **6** showed absorptions at δ 1.0 (d, J = 7 Hz, 6 H), 1.9 (s, 3 H), 2.8 (m, 1 H), 5.4–5.9 (3 H), 6.5–6.0 (2 H), and 6.88 ppm (q, 1 H). Double irradiation demonstrated that the proton absorbing at 6.88 was coupled to two others of chemical shift 1.7 ppm upfield. A sample of this isomer, further purified by glpc on a 6-mm × 4-m 20% silicone grease on Chromosorb W column at 110°, had infrared bands at 3003 (m), 2960 (s), 2860 (m), 1640 (w), 1600 (w), 1490 (w), 1470 (w), 1455 (m), 1440 (s), 1370 (s), 1075 (m), 1034 (m), 980 (w), 890 (w), 815 (m), and 752 (s) cm^{-1}. The ultraviolet spectrum had λ_{max}^{EtOH} 257 nm (sh; ϵ 14,000), 266 (14,700), 276 (sh; 13,000) with strong end absorption at 210 (6,900). The mass spectrum had M^+ at *m/e* 136, *m/e* 121 ($M^+ - CH_3$) as base peak, and *m/e* 93 ($M^+ - C_3H_7$) of 31% relative abundance.

Triene **7**, the isomer obtained in lowest yield, had nmr absorptions at δ 1.0 (d, 6 H), 1.8 (s, 3 H), 2.8 (m, 1 H), 5.4–4.9 (3 H), and 6.5–6.0 ppm (3 H), and infrared bands at 3050 (w), 3000 (s), 2925 (sh), 2860 (m), 1590 (w), 1575 (m), 1460 (m), 1440 (m), 1380 (m), 1290 (w), 1235 (w), 1100 (w), 985 (s), 965 (m), 890 (s), and 760 (s) cm^{-1}.

The *cis,trans*- and *trans,trans*-trienes **8** and **9** were collected together from the ODPN column, then separated by glpc on a 6-mm × 2-m 20% XF-1150 on Chromosorb W column at 100°.

Triene **8** had nmr absorptions at δ 1.03 (d, 6 H), 1.87 (s, 3 H), 2.34 (m, 1 H), 5.05 (d (J = 11) of t (J = 1.5); 1 H), 5.13 (d of d, J = 11,17; 1 H), 5.53 (d of d, J = 7,15; 1 H), 5.84 (d, J = 11, 1 H). 6.38 (d of d, J = 11,15; 1 H), and 6.87 ppm (d of d, J = 11,17; 1 H). Irradiation at 2.37 ppm gave a doublet at 5.53, J = 15 Hz; irradiation at 5.60 gave a doublet at 6.38, J = 11 Hz. This isomer had λ_{max}^{EtOH} 259 nm (ϵ 28,400), 268 (36,700), and 278 (28,200) and infrared absorptions at 3000 (s), 2920 (m), 1780 (w), 1620 (m), 1580 (m), 1465 (m), 1444 (m), 1418 (w), 1382 (w), 1360 (w), 1332 (w), 1175 (w), 1155 (w), 1036 (m), 985 (s), 965 (s), and 895 (s) cm^{-1}.

The mass spectrum gave a molecular ion peak at *m/e* 136, base peak at 93 ($M^+ - C_3H_7$), and relatively abundant ions at 121 and 106.

Triene **9** was obtained in >95% purity. The nmr spectrum showed absorptions at δ 1.02 (d, J = 7 Hz, 6 H), 1.80 (s, 3 H), 2.35 (m, 1 H), 4.90 (d, J = 11, 1 H), 5.06 (d, J = 17, 1 H), 5.60 (unsym q, J = 17,15, 1 H), 5.90 (broad d, J = 11, 1 H), 6.25 (unsym q, J = 11,15, 1 H), and 6.28 ppm (unsym q, J = 11,17, 1 H). Upon saturation at 2.37 ppm, the quartet at 5.60 ppm collapsed to a doublet with J = 15 Hz. Saturation at 5.54 ppm caused the absorption at 6.25 ppm to appear as a doublet with J = 11 Hz. The ultraviolet spectrum in 95% ethanol showed λ_{max} 259 nm (ϵ 33,500), 268 (45,300), and 279 (35,800). The infrared spectrum showed absorptions at 3000 (s), 2900 (m), 1620 (m), 1580 (m), 1470 (m), 1450 (w), 1425 (w), 1385 (m), 1358 (m), 1330 (m), 1295 (w), 1250 (w), 1173 (w), 1062 (m), 986 (s), 964 (s), 947 (m), and 886 (s) cm^{-1}.

Sensitization of α-Phellandrene. Acetophenone was distilled at reduced pressure through a Vigreux column prior to use. Hexane solutions (0.20 ml) of purified α-phellandrene (0.03 *M*) and acetophenone (0.3 *M*) were degassed at 1μ pressure, sealed in 6-mm Pyrex tubes, and photolyzed in a "merry-go-round" apparatus in a Rayonet photoreactor with 350-nm lamps for varying times.

Analyses of the photolysis mixtures after addition of 1,3-cyclooctadiene as an internal standard by glpc on a 3 mm × 3 m column of 5% Carbowax 20M on Anakrom ABS at 70° failed to detect triene photoproducts. The photolyses ranged from 14 to 85% conversion of α-phellandrene.

Primary Photoproducts from α-Phellandrene. Commercial (−)-α-phellandrene (Aldrich) was purified by preparative glpc on a 1 cm × 6 m 20% Carbowax 20M on Chromosorb P column at 150°. Reagent grade solvent hexane was washed with sulfuric acid and water, dried and distilled, and stored over sodium.

Aliquots of a 0.03 *M* solution of α-phellandrene in hexane were placed in 6-mm O.D. Vycor tubes, degassed at 1μ, and photolyzed at 253.7 nm in a "merry-go-round" apparatus. The photolysis products were analyzed on a 3 mm × 3 m 5% Carbowax 20M on Anakrom ABS column at 70°; the peaks were integrated with a polar planimeter and the data obtained are summarized in Table I. No products were detected at longer retention times.

Photochemical Isomerization of *cis,trans*-Triene 8. The triene **8** was isolated and purified by glpc on ODPN and XF-1150 columns. Aliquots of a 0.03 *M* solution of the triene in hexane in Vycor tubes were degassed, sealed, photolyzed, and analyzed as described immediately above for photolyses of α-phellandrene. The results are given in Table II.

Variable Temperature Photolysis of α-Phellandrene. Solutions of α-phellandrene (0.03 *M*) in isopentane or hexane in Vycor tubes were prepared as described. The solutions were placed in a quartz dewar in an appropriate constant temperature slush and photolyzed utilizing 253.7-nm lamps. The reaction mixtures were analyzed on a Carbowax 20M column as described, giving the results summarized in Table III.

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(24) J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, **90**, 6118 (1968).

(25) M. R. Morris and A. J. Waring, *Chem. Commun.*, 526 (1969).

(26) J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 2396 (1969).

(27) S. M. Krueger, J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., B*, 796 (1969).