lished. The reported $E_a$ for 1-methylaziridine[5b,c] of 19 kcal/mol is smaller than the 24 kcal/mol obtained here for 1 and may warrant further investigation for the same reasons that prompted this work. The much smaller $E_a$ of 11.4 kcal/mol obtained for 1-phenyl-sulfonylaziridine[9b] is expected on the basis of the electrical character of the sulfonyl groups.

The large positive $\Delta S^*$ values found for inversion of 1 seem consistent enough to warrant comment. That the transition state is less constrained than the ground state could be the result of inversion by way of homolytic breaking and re-forming the C–C bond across the, ring from the nitrogen, but this mechanism seems unlikely in view of the known C–C bond strengths in three-membered rings. More reasonably, there could be some measure of constraint associated with interactions between the N-methyl and gem-methyls which would be absent in the transition state or perhaps the aziridine molecules are substantially associated in the ground state and become unassociated in the transition state. In the latter connection, evidence has been presented recently for association of N-alkylaziridines in the pure liquid as well as in carbon tetrachloride solutions.[27]

The barrier to inversion of 1 seems very much less sensitive to solvent variations (except for the special case of chloroform) than the barrier for inversion of N-methoxy-N-methyl-N-benzylamine which decreases with increasing dielectric constant.[7a] A similar solvent insensitivity has been found for 1-phenylsulfonyl-aziridine.[9b] Chloroform seems to produce a remarkable effect on the activation parameters without, however, much changing the coalescence point of the methyl resonances (see Table III). Assuming that the data for chloroform solutions are correct (as mentioned earlier,

they seem reproducible), the effect of chloroform on the activation parameters is consistent with the known[27,28] substantial hydrogen bonding involving the imine nitrogen and the solvent, provided that the degree of hydrogen bonding is reduced in the transition state. Greater hydrogen bonding in the ground state than in the transition state would lead to both a larger $E_a$ and a more positive $\Delta S^*$.

## Experimental Section

1,2,2-Trimethylaziridine was synthesized from 2-amino-2-methyl-1-propanol by the following sequence:[29] formylation of the amino group by ethyl formate, reduction of the formylamino group by lithium aluminum hydride to 2-methylamino-2-methyl-1-propanol, formation of the sulfate with sulfuric acid, and ring closure to 1,2,2-trimethylaziridine by treatment with base.[30] The aziridine was purified after distillation (bp 66–68°) by preparative vpc through a 20-ft SE-30 column at 85°.

For determination of the nmr spectra, the samples of neat aziridine and solutions (about 25 wt %) in acetone-$d_6$ and deuteriochloroform each contained about 5% TMS. However, TMS was not used for the benzene solutions because it was found that TMS strongly reduced the chemical-shift difference between the methyl signals of 1.

The nmr spectra were taken on Varian A-56/60 and HA-100 spectrometers equipped with V-6040 variable-temperature accessories. The temperature readings of the probe were calibrated by measuring the hydroxyl-shift difference of ethylene glycol for temperatures above 40° and of methanol for temperatures below 40°. The temperatures are believed to be more accurate than ±2°. The samples were allowed to equilibrate for a minimum of 10 min with each change in temperature.

**Acknowledgment.** We are indebted to Dr. K. L. Servis and Mr. S. Surface of the University of Southern California for the variable-temperature spectra of 1 at 100 MHz.

(27) H. Saitô, K. Nukada, T. Kobayashi, and K. Morita, J. Am. Chem. Soc., 89, 6605 (1967).

(28) E. Lippert and H. Prigge, Ann., 659, 81 (1962).
(29) First carried through by Dr. J. F. Neumer (unpublished).
(30) K. N. Campbell, A. H. Sommers, and B. K. Campbell, Org. Syn., 27, 12 (1947).

# The Optical Rotatory Power of 2-Methylenebenznorbornene[1]

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Abstract: (+)-2-Methylenebenznorbornene, a simple prototype of a conformationally rigid, chiral homoconjugated styrene, was prepared from (+)-2-benznorbornenone by the Wittig reaction. The compound exhibits an intense Cotton effect centered near 224 m$\mu$ which is attributed to a transition arising from mixing of ethylenic and benzenoid electronic states. The ORD of 2-methylenebenznorbornene correlates satisfactorily with the position and intensity of the CD bands in the instrumentally accessible region.

Earlier theoretical and experimental work[3] has established that, with respect to its optical activity,

(+)-(1R)-5-methylenebicyclo[2.2.1]hept-2-ene (1) may be conveniently treated as an extended chiral $\pi$ system. Similar considerations also serve to account for the high rotation observed for pimara-8(14),15-diene[4] (2). However, due to instrumental limitations, only plain curves were measured in the optical rotatory dispersion (ORD) of 1 and 2. The present paper describes the observation of complete Cotton effects in (+)-2-methyl-

(3) (a) L. S. Forster, A. Moscowitz, J. G. Berger, and K. Mislow, J. Amer. Chem. Soc., 84, 4353 (1962); (b) K. Mislow, Ann. N. Y. Acad. Sci., 93, 457 (1962); (c) A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenheck, Biopolymers Symp., 1, 75 (1964); A. Moscowitz, Proc. Roy. Soc., Ser. A, 297, 16, 40 (1967).
(4) C. R. Enzell and S. R. Wallis, Tetrahedron Lett., 243 (1966).

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**1**

**2**

**3**
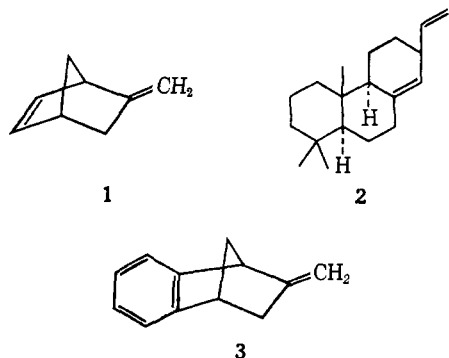
enebenznorbornene (**3**), a conformationally rigid *homoconjugated* styrene,[5,6] in which the geometrical situation allows for the coupling of the ethylenic and benzenoid chromophores.

## Results

### The olefin 3 was obtained in optically active form

(5) Cotton effects associated with homoconjugated styrene chromophores have been observed in several instances. It has been reported[6a] that (−)-1-*p*-anisylcamphene (i) exhibits an intense Cotton effect at 258 m$\mu$ ([$\theta$]$_{max}$ −35,200°) in methanol solution. A quantitative interpretation of the behavior of i is complicated, *inter alia*, by conformational heterogeneity which results from torsion about the carbon–aryl bond. The high-intensity (when compared to related systems[7a]) positive Cotton effects observed for the longest wavelength transition of haemanthamine (ii) and crinamine (iii) have been attributed to overlap of the double bond with the $\pi$ orbitals of the benzene ring.[7a] A reduction in the molecular ellipticity for both long-wavelength transitions of

**i**

**ii**

**iii**
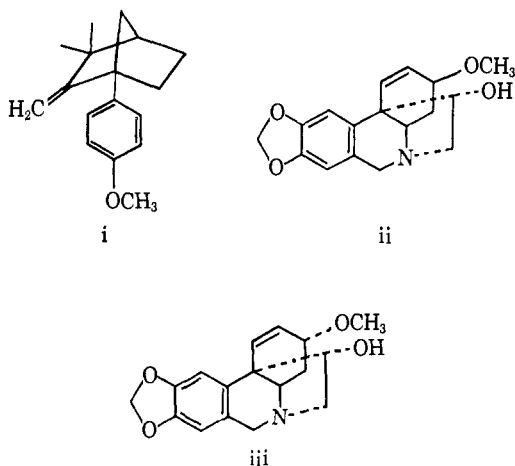
crinine (iv) and related alkaloids has been observed upon reduction to their dihydro derivatives,[7b] and an analogous observation has been made for tazettine[7] (v) and its dihydro derivative.[7a] Of the various alkaloids cited above, only v has a chromophoric geometry comparable

**iv**

**v**
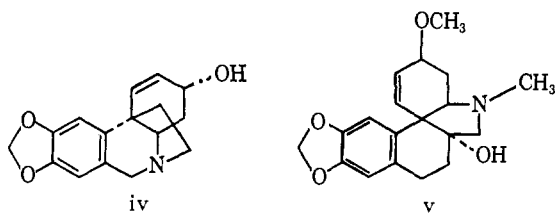
to **3**, as revealed by examination of molecular models, and none of the Cotton effects observed in compounds ii–v has a rotational strength which is comparable to that of **3** (see text) at 224 m$\mu$.

(6) The strong Cotton effects associated with the skewed styrene chromophore have been discussed: (a) J. J. Santos, Ph.D. Thesis, University of New Hampshire, 1967; (b) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., B*, 215 (1967); (c) P. Crabbé and W. Klyne, *Tetrahedron*, **23**, 3449 (1967).

(7) (a) K. Kuriyama, T. Iwata, M. Moriyama, K. Kotera, Y. Hamada, R. Mitsui, and K. Takeda, *J. Chem. Soc., B*, 46 (1967); (b) G. G. DeAngelis, Ph.D. Thesis, Iowa State University of Science and Technology, 1966; *Tetrahedron*, **24**, 5469 (1968); (c) W. Döpke and P. W. Jeffs, *Tetrahedron Lett.*, 1307 (1968).
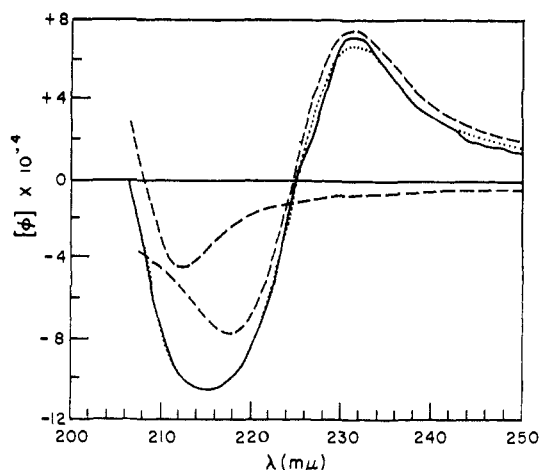


Figure 1. Experimental optical rotatory dispersion (solid line), computer-decomposed ORD curves (dashed lines), and summation curve (dotted line) of (+)-**3** in isooctane solution, corrected to optical purity.
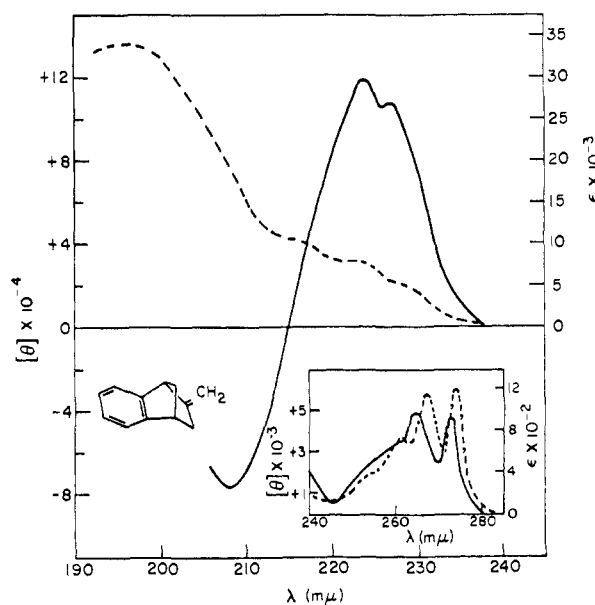


Figure 2. Circular dichroism (solid line) and absorption spectrum (dashed line) of (+)-**3** in isooctane solution. The molecular ellipticity is corrected to optical purity.

([$\alpha$]$^{23}$D +138° (isooctane)) from 46% optically pure (+)-2-benznorbornenone[8] (**4**), [$\alpha$]$^{24}$D +261° (isooctane), by Corey's modification of the Wittig reaction.[9] Since **4** has the 1$R$ configuration,[8] the configuration of **3** is 1$S$. The ORD and uv absorption spectrum of **3** in isooctane solution are displayed in Figures 1 and 2, respectively. Although it is clear from Figure 1 that **3** has an intense Cotton effect ($a$ +1800) centered at *ca.* 225 m$\mu$, the shape of the trough of this Cotton effect prompted further analysis. Decomposition of the ORD of **3** through use of a computer program described by Carver, Shechter, and Blout[10] yielded two Cotton

(8) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Amer. Chem. Soc.*, **90**, 4877 (1968).

(9) R. Greenwald, M. Chaykowsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(10) J. P Carver, E. Shechter, and E. R. Blout, *J. Amer. Chem. Soc.*, **88**, 2550 (1966). We are indebted to Mr. M. Goldstein and Dr. J. Jacobus for performing the computations.

effects, one centered at 224 m$\mu$ ($R = +5.1 \times 10^{-39}$ erg cm$^3$) and one at *ca.* 208 m$\mu$ ($R = 2.0 \times 10^{-39}$ erg cm$^3$). The decomposed ORD curves and their summation curve are also displayed in Figure 1, and comparison of the summation curve with the experimental ORD indicates a relatively satisfactory fitting of the data. Since there is no absorption maximum near 208 m$\mu$, the uv spectrum was decomposed by a nonlinear least-squares curve-fitting computer program.[11] The observed absorption data were best fit by a five-band combination,[12] as follows: $\lambda_{max}$, m$\mu$ (half-band width in m$\mu$, $\epsilon$) 229.9 (2.0, 670), 223.9 (7.7, 6560), 216.7 (3.7, 1340), 206.9 (2.6, 2150), 196.2 (14.8, 35200). It would thus appear that the observed spectrum is best fitted on the assumption that a relatively low intensity absorption band is situated near 207 m$\mu$.

The observed circular dichroism (CD) of 3 (Figure 2) confirmed the prediction of the ORD computer decomposition and provided further detail. The positive Cotton effect at 224 m$\mu$ has an observed rotational strength ($R = +4.35 \times 10^{-39}$ erg cm$^3$) in satisfactory agreement with that predicted from the ORD ($R = +5.1 \times 10^{-39}$ erg cm$^3$). Further, the CD reveals a negative Cotton effect centered at *ca.* 207.5 m$\mu$. Although the complete Cotton effect could not be recorded, it is clear that the rotational strength predicted from the ORD is of the right order of magnitude.

## Discussion

The Cotton effect at 224 m$\mu$ in 3 is attributable to a transition which arises from the mixing of the ethylenic states with the states of the primary benzenoid[13] transition. This suggestion is principally based on a comparison of the intensity of the 224-m$\mu$ effect with the normally low intensity of the Cotton effect in comparable nonhomoconjugated compounds. Thus, the CD of (+)-*exo*-2-benznorbornenol (5) shows only a weak Cotton effect ([$\theta$]$_{max}$ +4400°, corrected to optical purity) at 226 m$\mu$.[14] It is also noteworthy that the absorption of 3 in the region under discussion is intensified and shifted to somewhat longer wavelengths, when compared with 5 (see Experimental Section). Such behavior is reminiscent of similar behavior in the n → $\pi^*$ transition in $\beta,\gamma$-unsaturated ketones.[16]

The nature of the transition giving rise to the negative Cotton effect at *ca.* 207.5 m$\mu$ is unknown, and our remarks concerning it should be regarded as speculative. The possibility that this transition is largely olefinic in nature merits some consideration. The absorption spectrum of 1[3a,c] reveals a shoulder at 207 m$\mu$ ($\epsilon$ 10,300), and a number of exocyclic olefins show absorption in this wavelength region.[17] Cotton effects of modest intensity have been observed for this transition in simple olefins.[18]

Although the absorption of 3 for the B$_{2u}$ ← A$_{1g}$ transition at 250–280 m$\mu$ is intensified only slightly when compared to 5, the optical rotatory power (as measured by the molecular ellipticity) of 3 in this spectral region is considerably stronger than that of 5: whereas no Cotton effect was observable for the B$_{2u}$ ← A$_{1g}$ transition of 5, 3 exhibits a positive Cotton effect for this transition, with [$\theta$]$_{max}$ +5 × 10$^3$ at 265 m$\mu$.[19]

The compounds 3 and 4 are structurally similar and have corresponding absolute configurations, yet their optical rotatory properties provide some interesting contrasts. For example, while the Cotton effects associated with the long-wavelength benzenoid transitions[19] of 3 and 4[8] are of comparable intensity ([$\theta$]$_{max}$ +5000 and −7200°,[8] respectively), they have opposite signs and both are intense when compared to 5, yet the intensity of the absorption for this transition is comparable in 3 and 5, and both are stronger than 4. While 4[8] exhibits a relatively weak Cotton effect ([$\theta$]$_{max}$ +4000°) near 232 m$\mu$, only the beginnings of a strong negative Cotton effect centered below 210 m$\mu$ are observable, while 3 exhibits the intense Cotton effect ([$\theta$]$_{max}$ +12 × 10$^4$) at 224 m$\mu$. These contrasts are attributed to the manner in which the benzenoid states interact with the ethylenic and carbonyl states, respectively, with the details of these interactions unavailable at present.

## Experimental Section[20]

(+)-2-Methylenebenznorbornene (3). The mineral oil was removed from sodium hydride mineral oil dispersion (0.193 g, 3.75 mmol as sodium hydride) by washing with several portions of *n*-pentane.[9] Dimethyl sulfoxide (DMSO) (4 ml) was introduced, and the mixture was heated with stirring under nitrogen at 75–80° until hydrogen evolution ceased (*ca.* 30 min). The solution was cooled to 0°, and methyltriphenylphosphonium bromide (1.250 g, 3.5 mmol), in DMSO (4 ml) was introduced. The yellow mixture was allowed to warm to room temperature, where it became homogeneous. The ketone (+)-4,[8] [$\alpha$]$^{24}$D +261° (isooctane) (0.471 g, 2.98 mmol), and DMSO (2 ml) were added, and the solution was heated at 55–60° for 9 hr. The solution was cooled and poured into water, and the aqueous portion was washed five times with 15-

(11) H. Stone, *J. Opt. Soc. Amer.*, **52**, 998 (1962). We are indebted to Mr. M. Goldstein and Dr. J. Jacobus for performing the initial computations. The component bands are taken to be pure Gaussian.
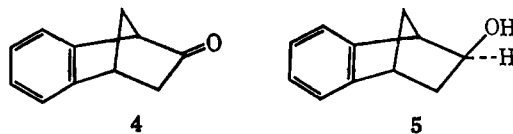
(12) In a four-band combination in which a band near 208 m$\mu$ is omitted from the analysis, the summation of the decomposed curves shows considerable deviation from the observed spectrum in the wavelength region near 210 m$\mu$.

(13) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, New York, N. Y., 1962, Chapter 12. This nomenclature is used for this transition because of the existing uncertainties in its assignment; *e.g.*, see the discussion in G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966, p 555 ff.

(14) This Cotton effect in 5, undoubtedly of benzenoid origin, is unexceptional in its intensity. For example, $\beta$-tetralol has a molecular rotation of only 3800° at 227 m$\mu$, with only a slight inflection in the region of 270 m$\mu$.[6c] Also, a Cotton effect associated with the primary benzenoid transition has been observed in *trans*-1-methyl-2-phenylcyclopropane at 222 m$\mu$ ([$\theta$]$_{max}$ *ca.* +14 × 10$^3$).[15]

(15) L. Verbit and Y. Inouye, *J. Amer. Chem. Soc.*, **89**, 5717 (1967).

(16) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

(17) O. H. Wheeler and J. L. Mateos, *J. Org. Chem.*, **21**, 1110 (1956).

(18) (a) A. Yogev, D. Amar, and Y. Mazur, *Chem. Commun.*, 339 (1967); (b) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, **44**, 1803 (1966); (c) M. Legrand and R. Viennet, *C. R. Acad. Sci., Paris, Ser. C*, **262**, 1290 (1966).

(19) Since this Cotton effect in 3 is somewhat more intense than is usually observed for the lowest benzenoid transition,[6c] a characterization of it as B$_{2u}$ ← A$_{1g}$ is probably an oversimplification.

(20) Elemental analysis by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y. The nmr spectrum was measured on a Varian A-60A spectrometer in *ca.* 10% carbon tetrachloride solution using tetramethylsilane as internal standard. Ultraviolet absorption spectra were measured on a Cary 14 recording spectrophotometer. Optical rotatory dispersion and circular dichroism were measured on a Cary 60 recording spectropolarimeter and a Cary Model 6001 circular dichroism accessory, respectively.

ml portions of pentane. The combined pentane extracts were washed with aqueous DMSO (50:50 v/v) and half-saturated sodium chloride solution, and dried over magnesium sulfate. Evaporation of the pentane gave an oil which was shown to contain a trace amount of 4 by glpc analysis. Accordingly, the crude product was chromatographed on alumina (80–200 mesh), and 3 was eluted with pentane. The product was distilled (Kugelrohr, 30–45°, 0.05 mm) to give 0.252 g of 3 (54% yield) as a colorless liquid, $n^{20}D$ 1.5654, $[\alpha]^{23}D$ +138° (c 0.91, isooctane). The neat ir spectrum of 3 features olefinic absorption at ca. 1665 and ca. 885 cm$^{-1}$. The nmr spectrum featured the following resonances: aromatic multiplet at $\tau$ 2.80–3.15 (4 H), olefinic protons at 4.87–5.08 and 5.28–5.48 (2 H) as broadened signals, 6.30–6.50 and 6.55–6.80 (2 H) bridgehead protons as broadened signals, methylene multiplet at 7.30–8.45 (4 H). The ultraviolet absorption spectrum in isooctane solution exhibited the following features $[\lambda_{max}(\epsilon)]$: 273.8 (1220), 267 (1170), 261 (760), 254 sh (410), 228 sh (5400), 224 sh (7800), 216 sh (9200), 196 (34,000). The ORD characteristics in isooctane (c 0.0790 g/100 ml at $\lambda$ >225 m$\mu$, c 0.00316 g/100 ml at $\lambda$ <225 m$\mu$), corrected to optical purity,

were: $[\phi]_{276}$ +10,600°, $[\phi]_{274}$ +11,200°, $[\phi]_{271}$ +8200°, $[\phi]_{269}$ +9500°, $[\phi]_{268}$ +10,300°, $[\phi]_{264}$ +8000°, $[\phi]_{262}$ +9200°, $[\phi]_{231}$ +74,000°, $[\phi]_{225}$ 0, $[\phi]_{213}$ −105,000°, $[\phi]_{206}$ 0. The CD in isooctane, corrected to optical purity (c 0.0644 g/100 ml at $\lambda$ >235 m$\mu$, c 0.00644 g/100 ml at 220–235 m$\mu$, c 0.002576 g/100 ml at $\lambda$ <220 m$\mu$), was as follows $[\lambda_{max}, m\mu ([\theta] \times 10^{-4})]$: 280 (0), 272 (+0.46), 265 (+0.50), 260 sh (+0.3), 253 sh (+0.2), 227 (+11), 224 (+12), 215 (0), 207 (−8).

*Anal.* Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.13; H, 7.95.

**Circular Dichroism of (+)-exo-2-Benznorbornenol (5).**[8] The sample of 5 used had $[\alpha]^{25}D$ +12.6° (c 4.7, chloroform) and was 46% optically pure.[8] The ultraviolet absorption spectrum in isooctane solution exhibited the following features $[\lambda_{max}(\epsilon)]$: 272.5 (1050), 265.5 (930), 259 (580), 252 sh (300), 226.5 (1400), 220.5 sh (3500), 216 sh (4800), 211 (5600). The CD in isooctane, corrected to optical purity (c 0.00882 g/100 ml), was as follows: $[\theta]_{226}$ +4400. No Cotton effect was observed in the long-wavelength region, and $[\theta]_{max}$ (observed) < 360 (c 0.00882 g/100 ml, l 1.0 cm).

# Photosensitized Isomerizations of 10-Methyl-1(9)-octalins

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*Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received August 7, 1968*
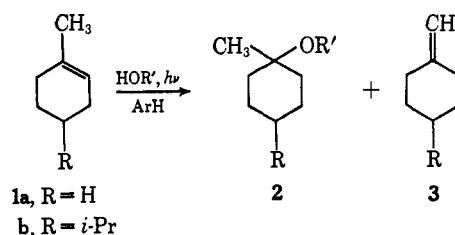
**Abstract:** 8,8,10-Trimethyl-, trans-8,10-dimethyl-, and cis-8,10-dimethyl-1(9)-octalin (7, 11, and 13) were prepared and subjected to ultraviolet irradiation in isopropyl alcohol containing xylene as the photosensitizer. The first two octalins required an added proton source (acetic acid) for isomerization to occur. The first afforded mainly 1-methylene-cis-9,10-dimethyldecalin (18) and the second gave chiefly 1-methylene-cis-10-methyldecalin (30) under these conditions. The cis-dimethyloctalin 13 isomerized smoothly without added acetic acid and gave 1-methylene-trans-10-methyldecalin (35) as the sole product. These findings suggest a pathway for isomerization involving conversion of the 1(9)-octalin to an incipient C-9 cation followed by a stereospecific migration of an adjacent methyl or hydrogen to give a new tertiary cation which then ultimately loses a proton from the $\alpha$-methyl grouping to give the observed exocyclic olefin. Internal hydride migration was confirmed for the cis-dimethyloctalin 13 by means of a deuterium-labeling experiment. The photochemical isomerizations of the 10-methyl-1(9)-octalins are contrasted with their behavior in strong acid and a scheme is presented which accommodates the observed reactions in terms of cationic intermediates.

Recent studies have shown that cyclohexenes exhibit rather unusual behavior upon photosensitized irradiation in protic solvents insofar as products which appear to arise *via* ionic reaction pathways are produced. For example, 1-methylcyclohexene (1a) and 1-menthene (1b) yield the corresponding alcohols (2, R′ = H), ethers (2, R′ = CH$_3$ or C$_2$H$_5$), acetates (2, R′ = CH$_3$CO$_2$), and exocyclic olefin isomers (3) upon irradiation with ultraviolet light in water, alcohols, or acetic acid in the presence of aromatic hydrocarbons such as benzene, toluene, or xylene.[2] Deuterium-labeling experiments indicate that both the addition and isomerization reactions proceed through a common intermediate resulting from proton transfer to the olefin by the protic solvent.[2c] These findings as well as the stereochemical outcome of additions to 1-menthene[2b] can all be understood in terms of a photochemically derived cationic intermediate.

Since acyclic olefins, cyclopentenes, and cyclooctenes



1a, R = H
b, R = i-Pr

2

3

and larger ring olefins fail to undergo analogous addition and isomerization reactions, some special significance must be placed on the ring size. Kropp and Krauss[2c] have attributed the unique photochemistry of cyclohexenes and cycloheptenes to ring strain. They propose that upon excitation these olefins afford orthogonal triplets possessing appreciable, albeit not prohibitive, steric strain. Conceivably this strain factor imparts unusual reactivity to these triplet states enabling them to abstract a proton from even such weak acids as alcohols and water thereby leading to cationic species. Alternatively, the orthogonal triplets could play their usual role as intermediates in cis-trans isomerization

(1) (a) Fellow of the Alfred P. Sloan Foundation, 1966–1968. (b) National Institutes of Health Predoctoral Fellow, 1965–1968.

(2) (a) P. J. Kropp, *J. Am. Chem. Soc.*, 88, 4091 (1966); (b) J. A. Marshall and R. D. Carroll, *ibid.*, 88, 4092 (1966); (c) P. J. Kropp and H. J. Krauss, *ibid.*, 89, 5199 (1967).