ring subunit of reserpine. Application of this general strategy to the syntheses of other alkaloid natural products is the subject of active investigations, the results of which will be described in due course.

Acknowledgment. We thank the National Institutes of Health (GM 25439) and the Robert A. Welch Foundation for generous support of this research.

Resolution, Circular Dichroism Spectrum, Molecular Structure, and Absolute Configuration of *cis,trans*-1,3-Cyclooctadiene

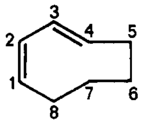
Roland Isaksson, Jan Roschester, Jan Sandström,* and Lars-Göran Wistrand

Division of Organic Chemistry 3, Chemical Center
University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Received December 21, 1984

cis,trans-1,3-Cyclooctadiene (**1**) has been known for a considerable time,[1,2] and its thermal and photochemical transformations have been carefully studied.[2-6] Models indicate that **1** is chiral and not readily racemized, but, while *cis,trans*-1,5-cyclooctadiene as well as *trans*-cyclooctene have been resolved by formation of diastereomeric metal complexes,[7,8] no resolution of **1** has been reported in spite of the inherent interest in the chiroptical properties of this nonplanar conjugated diene.

Chromatography on swollen, microcrystalline triacetylcellulose (TAC) has proven valuable for resolution of racemic compounds lacking functional groups,[9-12] and we have used this technique to resolve racemic **1**.



1

The $AgNO_3$ adduct of **1** was prepared according to Liu,[2] and the hydrocarbon was liberated with aqueous NH_3 and taken up in *n*-pentane.[2,13] Careful evaporation gave pure racemic **1**.[14] One passage of a solution of 30 mg of **1** in 12 mL of *n*-pentane through the TAC column[15] gave partial enantiomer separation, considerably improved after recycling[16] 3 times. The first eluted enantiomer has negative rotation and the eluate gave $[\alpha]^{20}_{D}$ −649°, $[\alpha]^{20}_{365}$ −2450° (*c* 0.017, ethanol),[17] and a CD spectrum with a smooth, nearly Gaussian negative band with λ_{max} 230.5 nm, $\Delta\epsilon$ −8.83, and width 61 nm at ϵ_{max}/e, followed by another negative band with $\lambda_{max} < 190$ nm (Figure 1). Since the chromatographic procedure did not give base-line separation, attempts were made to determine the enantiomeric purity by ^1H NMR spectroscopy, using $Eu(hfbc)_3$[18-20] and $Eu(hfbc)_3$ + $Ag(fod)$[21] as chiral shift reagents. However, none of these achieved splitting of the signals from racemic **1**, but computer simulation of the optical rotation chromatogram[11,15] obtained on reinjection of the resolved material on the TAC column indicates an enantiomeric excess >90%.

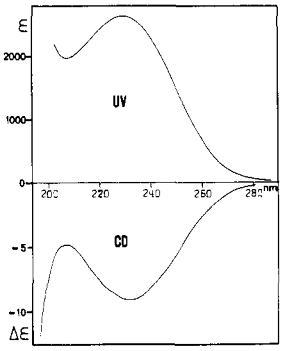


Figure 1. Ultraviolet and CD spectra of (−)-**1** in ethanol.

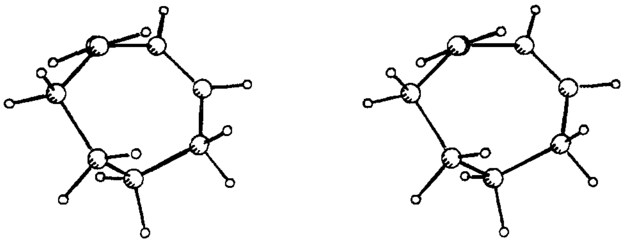


Figure 2. Stereoview of **1** along the C4–C3 bond.

Molecular mechanics calculations[22] covering all feasible combinations of the 1-2-3-4 and 5-6-7-8 dihedral angles revealed only two energy minima, with an energy difference of 2.75 kcal/mol. This corresponds to less than 1% of the minor form at room temperature, and is in agreement with the observed complete temperature independence of the CD spectrum in ethanol from +20 to −112 °C.

According to the calculations, the stable form has a nearly planar cis double bond with the 3-2-1-8 angle 3.5° and a strongly twisted trans double bond with the 2-3-4-5 angle −133.4° (*P* helicity assumed), rather similar to the −136° found for (−)-*trans*-cyclooctene.[23-25] The dihedral angle between the double bonds (1-2-3-4) is 50.2° and the 5-6-7-8 angle is 82.4° (Figure 2). The corresponding angles for the less stable form are 9.0°, −131.9°, 67.9°, and −96.8°. Early calculations with the Hendrickson force field[26] gave four energy minima, the dihedral angles for the stable form being, in the order given above, 0°, −147.5°, 42.5°, and 84.3°, respectively.

Attempts to study the thermal racemization of **1** are likely to be thwarted by the cyclization to *cis*-bicyclo[4.2.0]oct-7-ene (**2**).[3,4]

---

(1) Cope, A. C.; Bumgardner, C. L. *J. Am. Chem. Soc.* **1956**, *78*, 2812-2815.

(2) Liu, R. S. H. *J. Am. Chem. Soc.* **1967**, *89*, 112-114.

(3) Shumate, K. M.; Neuman, P. N.; Fonken, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 3996.

(4) Bromfield, J. J.; McConaghy, J. S., Jr. *Tetrahedron Lett.* **1969**, 3723-3726.

(5) Nebe, W. J.; Fonken, G. J. *J. Am. Chem. Soc.* **1969**, *91*, 1249-1251.

(6) Padwa, A.; Koehn, W.; Masaracchia, J.; Osborn, C. L.; Trecker, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 3633-3638.

(7) Cope, A. C.; Hecht, J. K.; Johnson, H. W., Jr.; Keller, H.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1966**, *88*, 761-763.

(8) Cope, A. C.; Ganellin, C. R.; Johnson, H. W., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3191-3192.

(9) Hesse, G.; Hagel, R. *Chromatographia* **1976**, *9*, 62-68.

(10) Koller, H.; Rimböck, K.-H.; Mannschreck, A. *J. Chromatogr.* **1983**, *282*, 89-94.

(11) Isaksson, R.; Liljefors, T.; Reinholdsson, P. *J. Chem. Soc., Chem. Commun.* **1984**, 137-138.

(12) Scherübl, H.; Fritzsche, U.; Mannschreck, A. *Chem. Ber.* **1984**, *117*, 336-343.

(13) *Org. Photochem. Synth.* **1971**, *1*, 44-46.

(14) A 360-MHz ^1H NMR spectrum in $CDCl_3$ showed only signals attributable to **1** in the olefin region: δ (H1) 5.63, (H2) 6.13 ($J_{cis}{}^{3}$ = 9.2 Hz), (H3) 5.92, (H4) 5.71 ($J_{trans}{}^{3}$ = 15.8 Hz).

(15) For a description of the instrumentation, see: Isaksson, R.; Roschester, J. *J. Org. Chem.*, in press. 95% ethanol was used as eluent.

(16) Henry, R. A.; Byrne, S. H.; Hudson, D. R. *J. Chromatogr. Sci.* **1974**, 197-199.

(17) The concentration was determined from the absorbance at 230.5 nm (ϵ 2630).

(18) Fraser, R. R.; Petit, M. A.; Saunders, J. K. *J. Chem. Soc., Chem. Commun.* **1971**, 1450-1451.

(19) Goering, H. L.; Eikenberry, J. N.; Koermer, G. S. *J. Am. Chem. Soc.* **1971**, *93*, 5913-5914.

(20) Whitesides, G. M.; Lewis, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 5914-5915.

(21) Wenzel, T. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 382-388.

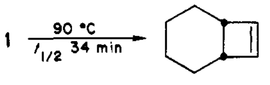
(22) MMP2 with the 1977 force field: Allinger, N. L.; Yuh, Y. H. *QCPE* **1983**, *11*, 395.

(23) Traetteberg, M. *Acta Chem. Scand., Sect B* **1975**, *B29*, 29-36.

(24) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734-5747.

(25) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121-4132.

(26) Zuccarello, F.; Buemi, G.; Favini, G. *J. Mol. Struct.* **1971**, *8*, 459-470.



2

Attempted simulation of the racemization (MMP2) by incremental driving of the 1-2-3-4 angle in the stable form led to the cis,cis isomer with a barrier of 25.6 kcal/mol. Similar driving from the minor form led the same result with a 27.0 kcal/mol barrier. Assuming no activation entropy, this corresponds to rates similar to those for the **1** → **2** transformation. However, no complete exploration of the conformation space has been made, and lower energy paths leading to the enantiomer may exist.

Early theoretical and experimental studies of the relation between the absolute configuration and CD spectra of chiral cisoid 1,3-dienes, mostly 1,3-cyclohexadienes, led to the diene helicity rule,[27] stating that dienes with a positive dihedral angle (θ) between the double bonds (P helicity) have a positive rotational strength for the $N \rightarrow V_1$ and a negative value for the $N \rightarrow V_2$ transition. The CD spectrum of (−)-**1**, with the same sign for the first two bands, does not conform to this rule. In order to estimate to what extent the diene helicity contributes to the observed rotational strength, $|R| \geq 48 \times 10^{-40}$ cgs, for the first transition, the transition charge density was calculated by a CNDO/S-CI method[28] and scaled to conform to the oscillator strength derived from the UV spectrum. Calculation of R by the coupled oscillator model in the version of Schellman et al.[29] gave $R = 5.9 \times 10^{-40}$ cgs, positive for P helicity. With more advanced computations, Rauk and Peoples[30] obtained $R > 0$ for butadiene with P helicity but a minimum near zero for $\theta = +60°$. In a careful experimental and theoretical study of several 1,3-cyclohexadienes (θ ca. 17°), Lightner et al.[31] propose a subdivision of the rotational strength of the $N-V_1$ band into contributions from the various bonds. In this analysis the diene moiety gives a small negative contribution for P helicity, whereas an axial allylic bond gives a large positive (60×10^{-40} cgs) and the C5–C6 bond a large negative contribution (-52×10^{-40} cgs). In **1** with P helicity the C7–C8 bond is intermediate in orientation between an axial allylic and the C5–C6 bond in a 1,3-cyclohexadiene, and it can be assumed to give only a small contribution to R. Instead, the twisted trans double bond can be seen as the main source of rotational strength. The sense of twist is the same as in (−)-*trans*-cyclooctene,[32] in which the first strong transition has $R = -70 \times 10^{-40}$ cgs.[33,34] Our CNDO/S calculation supports the weight of this contribution, the transition dipole component along this bond being nearly 3 times stronger than the one along the *cis* double bond. We therefore propose that **1** with $R < 0$ for the $N \rightarrow V_1$ band, i.e., the first eluted enantiomer, has P helicity, although this admittedly is a rather crude approach. A safer assignment of the absolute configuration could be made by RPA calculations[35] or by an X-ray crystallographic study of a metal complex of **1** containing another chiral ligand of known configuration.

Acknowledgment. Financial support from the Swedish Natural Science Research Council, the National Swedish Board for Technical Development, and the Knut and Alice Wallenberg Foundation and helpful advice by Dr. T. Liljefors on the molecular mechanics calculations are gratefully acknowledged.

---

[27] See, for a review: Charney, E. "The Molecular Basis of Optical Activity"; Wiley: New York, 1979; pp 217–226.

[28] Guimon, C.; Gonbeau, D.; Pfister-Guillouzo, G. *Tetrahedron* **1973**, *29*, 3399–3405.

[29] (a) Bayley, P. M.; Nielsen, E. B.; Schellman, J. A. *J. Phys. Chem.* **1969**, *73*, 228–243. (b) Rizzo, V.; Schellman, J. A. *Biopolymers* **1984**, *23*, 435–470.

[30] Rauk, A.; Peoples, H. A. *J. Comput. Chem.* **1980**, *1*, 240–256.

[31] Lightner, D. A.; Bouman, T. D.; Gawroński, J. K.; Gawrońska, K.; Chappuis, J. L.; Crist, B. V.; Hansen, E. A. *J. Am. Chem. Soc.* **1981**, *103*, 5324–5327.

[32] Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 5626–5630.

[33] Mason, M. G.; Schnepp, O. *J. Chem. Phys.* **1973**, *59*, 1092–1098.

[34] Bouman, T. D.; Hansen, A. E. *J. Chem. Phys.* **1977**, *66*, 3460–3467.

[35] Hansen, A. E.; Bouman, T. D. *Adv. Chem. Phys.* **1980**, *44*, 545–644.

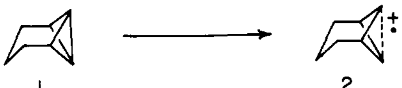
Alkyl Group Migration in Photoinduced Cation Radical Reactions

Paul G. Gassman* and Bruce A. Hay

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received January 21, 1985

Recently, we have discussed in detail the ease with which an electron could be removed from the HOMOs of certain highly strained polycyclic molecules.[1,2] Electrochemical oxidations[1,2] and photosensitized single electron transfer reactions[3,4] proved to be very efficient in the conversion of highly strained saturated hydrocarbons into their corresponding cation radicals. Both experimental[1,3] and theoretical[2] studies of derivatives of bicyclo[1.1.0]butane indicated that removal of an electron from the HOMO of this system involved the central bond of the bicyclo[1.1.0]butane moiety. This was exemplified by the conversion of **1** to **2**. It was of interest that **2**, although extremely reactive, appeared to be relatively stable structurally.[5] In order to see if a major rearrangement[6] of a photogenerated cation radical could be induced on a preparative scale, **3** was prepared[10] and subjected to the conditions required for a photosensitized single electron transfer reaction. We now wish to report that **3** rapidly undergoes rearrangement to **4** under a variety of conditions which have previously been employed for the conversion of **1** to **2**.



1 2

Irradiation of a solution containing 1.35 g (7.5 mmol) of **3**, 0.76 g (5.0 mmol) of 1-cyanonaphthalene (1-CN), and 0.50 g of decane (as an internal GC standard) in 5.0 L of deoxygenated, dry tetrahydrofuran for 5 days in a Pyrex apparatus with a 450-W Hanovia medium-pressure mercury lamp gave a 58% yield of pure **4**.[11,12] The structure of **4** was established on the basis of spectral data and through independent synthesis from **7**. The ^{1}H NMR

---

[1] Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

[2] Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793. Richtsmeier, S. C.; Gassman, P. G.; Dixon, D. A. *J. Org. Chem.* **1985**, *50*, 311.

[3] Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. Gassman, P. G. Olson, K. D. *Ibid.* **1982**, *104*, 3740.

[4] Roth, H. D.; Schilling, M. L. M.; Gassman, P. G.; Smith, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2711.

[5] For preliminary indications that isomerization of **2** might occur; see ref 4.

[6] Numerous examples of photoinduced valence tautomerism via cation radical intermediates are known (e.g., quadricyclane to norbornadiene,[7] Dewar benzene to benzene[8]). However, we are aware of only one example of a major alkyl group migration and this involves a 1–3 allylic shift.[9a] For a recent example of a fragmentation reaction and leading references to electron transfer sensitized C–C bond cleavage, see ref 9b.

[7] Jones, G., II; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805 and references contained therein.

[8] Jones, G., II; Chiang, S.-H. *Tetrahedron* **1981**, *37*, 3397 and reference contained therein.

[9] (a) Padwa, A.; Chou, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555. (b) Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968.

[10] The synthesis of **3** involved (a) the reaction of [(trimethylsilyl)methyl]magnesium chloride with 3-bromocyclohexene to yield 3-[(trimethylsilyl)methyl]cyclohex-1-ene (**5**, 81% yield), (b) addition of dichlorocarbene to **5** to give *trans*-7,7-dichloro-2-[(trimethylsilyl)methyl]bicyclo[4.1.0]heptane (**6**, 69%), and (c) treatment of **6** with *n*-butyllithium to produce 2-[(trimethylsilyl)methyl]tricyclo[4.1.0.0^{2,7}]heptane (**3**, 56%). Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds. All compounds prepared had ^{13}C NMR, ^{1}H NMR, and IR spectra that were consistent with the assigned structures.

[11] The use of either benzene or methanol as solvent also resulted in the formation of **4**. No trapping of intermediates by methanol was observed.

[12] Careful monitoring of yields by GC analysis showed that the yield of **4** was a function of the concentration of both **3** and 1-CN. When a tetrahydrofuran solution that was 1.31×10^{-3} M in **3** and 1.00×10^{-3} M in 1-CN was irradiated under the conditions indicated, an 82% yield of **4** was observed by GC analysis. Increasing the concentration of either **3** or 1-CN resulted in a systematic decrease in yield.