

the silver complex suggest a greater degree of ionic bonding in the latter since the terminal B-H absorptions are at lower frequency in the silver and the bridging B-H absorptions are much higher.⁷ Both *O*-ethylboranocarbonate complexes appear to be more ionic than the corresponding BH₄⁻ complexes on the same basis. The doublet in the silver complex along with the resultant peak separation of approximately 60 cm⁻¹ indicate the presence of two terminal hydrogens;⁷ the peaks correspond to the asymmetric and the symmetric stretching modes. This assignment requires then, that the Ag-H-B complex bonding system consists of a single bridging hydrogen as compared to two bridging hydrogens in the copper complex (the analogous double bridged system is also found in the copper BH₄⁻ complex).⁸ This monodentate structure, though not established thus far for metal complexes, is analogous to the single-hydrogen-bridged structure proposed for B₂H₇⁻⁹ and (R₃B)₂H⁻^{9a,10} compounds.

The ¹¹B nmr spectra of the copper and silver complexes in CDCl₃ are identical in band shape; both consist of a broad quartet of approximate ratio 1:3:3:1 (ambient temperature, δ_{Ag complex} 33.3 ppm from BF₃OEt₂, J_{BH} = 80 Hz; δ_{Cu complex} 25.2 ppm from BF₃OEt₂, J_{BH} = 70 Hz). Although the quartet may be rationalized by splitting of the boron signal by the two different types of hydrogen attached to the boron (one terminal and two bridged or two terminal and one bridged), the best explanation perhaps is that the splitting of the boron signal and the resultant broadened peaks occur due to the presence of three equivalent hydrogens which are equivalent by virtue of an intramolecular bridge-terminal exchange process.¹¹ This explanation is not in conflict with the ir data since vibrational spectroscopy, with a faster time scale, can provide useful structural data in contrast to nmr spectroscopy which provides, in this case, useful electronic information.⁷ Broadening of the peaks could be due to a spin-lattice relaxation effect.^{11b,c} Such a "thermal decoupling" effect would be clarified by variable temperature studies, the results of which will be reported in a later paper. The difference in chemical shift values supports the difference in the singly and doubly bridged structures on an inductive basis, with the exchanging hydrogens occupying one or two coordination sites, respectively.

The ¹H nmr spectrum (ambient temperature, CDCl₃) confirms the presence of the ethyl group in the complexes (all shifts are downfield from TMS): M = Ag; δ_{CH₂} 3.84 ppm, J_{CH₂} = 7 Hz; δ_{CH₃} 0.94, J_{CH₃} = 7 Hz; M = Cu, δ_{CH₂} 3.58, J_{CH₂} = 7 Hz, δ_{CH₃} 0.89, J_{CH₃} = 7 Hz. The lack of observation of the B-H protons in the ¹H nmr supports coordination by the hydrogens of the borane group since the ethylboranocarbonate anion itself shows a fairly sharp 1:1:1:1 quartet (ambient temperature, CD₃OD, δ 0.77 ppm downfield to TMS,

(7) T. J. Marks, J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, **11**, 2541 (1972).

(8) S. J. Lippard and K. M. Melmed, *J. Amer. Chem. Soc.*, **89**, 3929 (1967); *Inorg. Chem.*, **6**, 2223 (1967).

(9) (a) Y. Matsui and R. C. Taylor, *J. Amer. Chem. Soc.*, **90**, 1363 (1968); (b) R. K. Hertz, H. D. Johnson, II, and S. G. Shore, *Inorg. Chem.*, **12**, 1875 (1973).

(10) (a) H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, **80**, 1552 (1958); (b) A. Khuri, Ph.D. Thesis, Purdue University, 1960; *Diss. Abstr.*, **21**, 55 (1960).

(11) (a) B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, **11**, 99 (1970); (b) C. H. Bushweller, H. Beall, M. Grace, W. J. Dewkett, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 2145 (1971); (c) T. J. Marks and L. A. Shimp, *ibid.*, **94**, 1542 (1972).

J_{BH} = 83 Hz). Thus, upon coordination the symmetry at the boron is changed such that the effect of extensive ¹⁰B and ¹¹B coupling to hydrogen in addition to an exchange process alluded to in the discussion of the boron nmr spectra results in the nondetection of the B-H proton absorptions.

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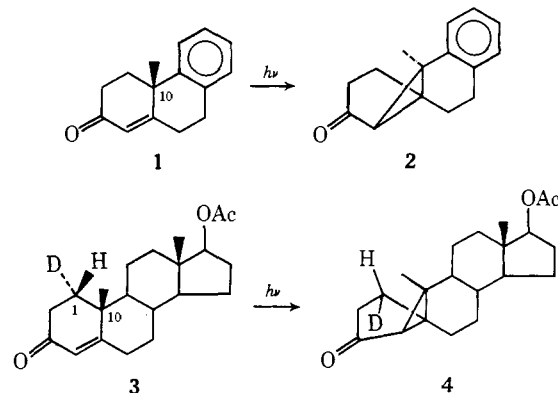
Received June 8, 1974

Absolute Stereochemistry of Photorearrangement of a Simple Chiral 4,4-Dialkylcyclohexenone¹

Sir:

The photochemical rearrangements of substituted 2-cyclohexenones continue to fascinate chemists.² Not the least of the problems which remains unresolved is the source of the extremely high inefficiency (~99%) on photoexcitation of such compounds.² Substituents on the olefinic moiety often wipe out reactivity altogether.³ We have been engaged in studies to explore the possibilities of reversible biradical formation as the source of energy wastage in these systems, using stereochemistry and kinetics as experimental probes.⁴

Prior stereochemical studies have been confined to polycyclic enones. Thus, Chapman, *et al.*, demonstrated that the photorearrangement of **1** to **2** proceeded with ≥95% retention of optical activity,⁵ while Schaffner and coworkers⁶ showed that the configuration at C₁ in **3** was retained on photorearrangement to **4**. Be-



cause of the necessary *cis* fusion of the cyclopropane to the five- and six-membered rings in **2** and **4**, the lumiketone rearrangement in both these systems^{5,6} must proceed with inversion of configuration at C₁₀. While

(1) Part XLI of a series on the photochemistry of ketones in solution. Part XL. D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **6**, 69 (1974).

(2) For a recent review and leading references, see O. L. Chapman and D. S. Weiss in "Organic Photochemistry," Vol. 3, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1973.

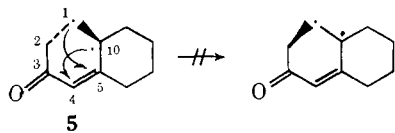
(3) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

(4) B. M. Resnick, Ph.D. Dissertation, New York University, 1974.

(5) O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Amer. Chem. Soc.*, **88**, 161 (1966).

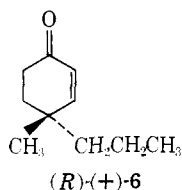
(6) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

these results rule out the intermediacy of planar achiral diradicals, they do not *require* a concerted process, as noted by us⁷ and by Chapman.² In these polycyclic systems, steric constraints operate such that a diradical **5** formed by cleavage of the C₁-C₁₀ bond would probably



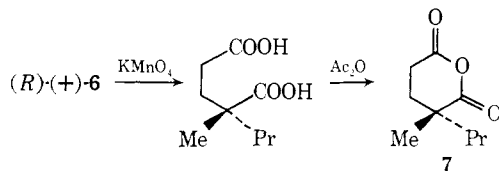
not be planar, according to molecular models. The angular methyl as well as the conformation of ring B make it likely that formation of the new C₁-C₅ bond would occur preferentially from the rear, as in **5**.⁸ Racemization in the case of **1** and steroidal enones would require rotation of the C₁-C₃ chain around to the top face of the diradical before bonding between C₁ and C₅, and models suggest that this is energetically prohibitive compared to ring closure in **5**.

To hopefully avoid such ambiguities and gain further insight into the reaction mechanism, we have examined the absolute stereochemistry on photolysis of an unconstrained chiral cyclohexenone, **6**. In such a system,



the lumiketone rearrangement can occur *a priori* with either retention or inversion of configuration at C₄, the *only* controlling factor being the reaction mechanism. We find that the photochemical rearrangements of (+)-(R)-4-methyl-4-propyl-2-cyclohexen-1-one (**6**) are totally stereospecific within experimental error and appear to proceed *via* a completely concerted pathway.

Optically active **6**, [α]_D +4.60°, was prepared by the asymmetric induction route of Yamada and Otani.⁹ Attempts to determine the optical purity of **6** using a chiral nmr shift reagent (tris(3-(heptafluoropropylhydroxymethylene)-*d*-camphorato)europium(III)) by monitoring the 4-methyl resonance were unsuccessful. Treatment of **6** with KMnO₄ gave a diacid which was cyclized to anhydride **7**, [α]_D -3.5°, whose 2-methyl



resonance was split in the presence of the optishift reagent. Using five different optishift concentrations, the average optical purity of **7**, and hence of **6**, was 10 ± 1%.¹⁰ The *R* configuration was assigned to

(7) D. I. Schuster and D. F. Brizzolara, *J. Amer. Chem. Soc.*, **92**, 4357 (1970).

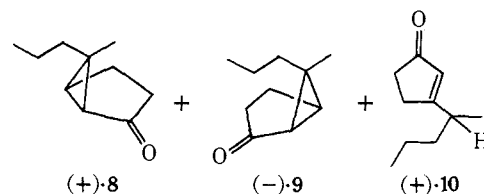
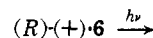
(8) This was pointed out some time ago by H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(9) S. I. Yamada and G. Otani, *Tetrahedron Lett.*, 4237 (1969). We are deeply grateful to Professor Yamada for private communication of experimental details and additional data prior to publication.

(10) The error limits reflect the statistical deviation of the ratios of the resonances of the enantiotopic methyl groups at the different concentrations of optishift reagent.

(+)-**6** on the basis of the identical sign of its long wavelength Cotton effect with that of other chiral cyclohexenones prepared by the identical asymmetric induction route,⁹ two of which have absolute configurations assigned independently and unambiguously.⁹

Photolysis of **6** in *tert*-butyl alcohol at 350 nm through Pyrex gave three primary products, isolated by preparative gas-liquid partition chromatography (glpc), assigned structures **8**, **9**, and **10**.^{11,12} The relative stereo-



chemistry (*i.e.*, *exo*-*endo* position of substituents) of **8** and **9** was assigned on the basis of (a) deshielding of the 6-methyl to a greater extent in **8** than in **9** on addition of nmr shift reagent, and (b) the nmr of benzylidene derivatives, which shows that the 6-methyl resonance in **9** is unaffected while that in **8** is shielded by 0.1 ppm after derivatization.¹³ These data all are consistent with an *endo* configuration for the 6-methyl in **8** and an *exo* configuration in **9**.

Photolysis of **6**, [α]_D +4.60°, in *tert*-butyl alcohol at 350 nm for 325 hr led to 72% conversion to products, which were collected along with residual starting material by preparative glpc. These materials were all optically active: **6**, [α]_D +4.96°; **8**, [α]_D +7.76°; **9**, [α]_D -8.35°, **10**, [α]_D +3.01°. The optical purities of **8** and **9** were found to be 10 ± 1% from splitting of the 6-methyl resonances with the nmr chiral shift reagent at several different concentrations.¹⁴ The absolute configurations of **8** and **9** were determined by circular dichroism, making use of the "inverse octant rule"¹⁵ which successfully correlates the sign of the Cotton effect with the known absolute configurations of a number of substituted bicyclo[3.1.0]hexan-2-ones and related compounds. Since (+)-**8** and (-)-**9** show, respectively, negative and positive Cotton effects centered at 292 nm, these compounds must have the absolute configurations as shown above.

Thus, formation of **8** from **6** occurs stereospecifically by movement of C₄ "up" (as drawn), bonding between C₃ and C₅ on the bottom face of the cyclohexenone, and formation of the bond between C₂ and C₄ on the top face of the cyclohexenone ring, with inversion of con-

(11) Studies as a function of time indicated that yields of each product extrapolated back to zero time. Cyclopentenone **10** is also a product of further photolysis of **8** and **9**.

(12) Compound **8**: ir (CCl₄) 1720, 1470, 1200 cm⁻¹; λ_{max} (EtOH) 207 (ε 2860) and 284 nm (ε 27.5); δ (CDCl₃) 1.07 (3 H, s) and 0.9-2.3 ppm (13 H, mult). Compound **9**: ir (CCl₄) 1710 and 1460 cm⁻¹; λ_{max} (EtOH) 207 (ε 3000) and 284 nm (ε 28); δ (CDCl₃) 1.07 (3 H, s) and 0.9-2.3 ppm (13 H, mult). Compound **10**: ir (CCl₄) 1710 and 1600 cm⁻¹; δ (CDCl₃) 1.12 (3 H, d), 0.9-1.6 (7 H, mult), 2.1-2.7 (5 H, m), 5.8 ppm (1 H, s); *m/e* 152, 110, 109, 95, and 81.

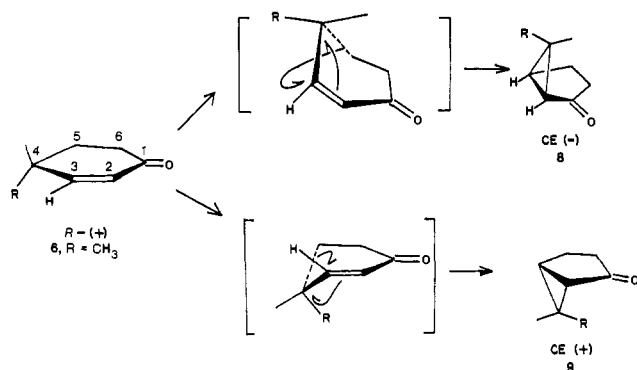
(13) Differential shielding of the *endo* compared to the *exo* methyl in the benzylidene derivative of 6,6-dimethyl-bicyclo[3.1.0]hexan-2-one has been observed: T. A. Rettig, Ph.D. Dissertation, Iowa State University, 1966; O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(14) The optical purity and absolute configuration of cyclopentenone **10** have not been determined. Experiments to accomplish this are in progress.

(15) C. Djerassi, W. Klyne, T. Norin, G. Ohloff, and E. Klein, *Tetrahedron*, **21**, 163 (1965); G. Sznatzke, *J. Chem. Soc.*, 5002 (1965).

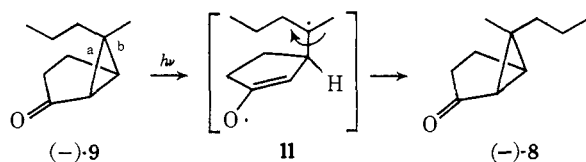
figuration at C₄ (see Scheme I). Similarly, formation

Scheme I



of **9** from **6** occurs by downward movement of C₄, bonding between C₃ and C₅ on the top face and formation of the 2–4 bond on the bottom face of the ring, once again with inversion at C₄. The results exclude the involvement of any diradical along the reaction coordinate which can undergo rotation about the former C₃–C₄ bond, since this would lead to loss of stereospecificity in lumiketone formation as well as to racemization in the route to cyclopentenone **10**.¹⁴

Photolysis of (–)-**9** at 300 nm in *tert*-butyl alcohol gives (–)-**8** as well as racemic **10**. Thus, the photochemical epimerization does not alter the configuration of the cyclopropyl ketone chromophore and must take place by cleavage of bond a in **9** and pivoting around bond b.¹⁶ Thus, the intermediate diradical in the epimerization, presumably **11**, is also specifically ex-



cluded from the pathway utilized in conversion of cyclohexenone **6** to the lumiketones **8** and **9**.

These results, coupled with the observation of retention of configuration at C₁ in **3** → **4**,⁶ suggest that the conversion of cyclohexenones to lumiketones is a completely concerted $\sigma_{2a} + \pi_{2a}$ process.¹⁷ This is despite the fact that the reaction originates from a triplet excited state and occurs with very low quantum efficiency.¹⁸ Furthermore, energy wastage cannot be due to reversion to **6** from diradicals generated along the reaction pathway.¹⁹ All the data are consistent with a very rapid relaxation of the spectroscopic enone triplet²⁰ by torsion around the carbon–carbon double bond to give a twisted triplet,^{21,22} which partitions between

(16) This is the same route as found for interconversion of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one: H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, **90**, 4892 (1968).

(17) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH–Academic Press, 1970, p 89 ff.

(18) Φ for disappearance of **6** in *t*-BuOH at >290 nm is 0.017, and the reactions of **6** can be quenched by oxygen and by naphthalene ($k_{qT} = 7.5 \text{ M}^{-1}$).

(19) Studies to be described elsewhere indicate that reversible formation of diradicals by α -cleavage of the C₁–C₆ bond does not occur.⁴

(20) Defined as having the geometry corresponding to the minimum in the S₀ potential surface.²¹

(21) J. Michl, *Mol. Photochem.*, **4**, 243, 257 (1972).

(22) P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

decay to the ground state potential surfaces of starting material (major pathway) and products (minor pathway). One would expect that these S₀ surfaces have energy maxima in the region corresponding to the "twisted π -bond biradicaloid,"²¹ which therefore serves as an ideal point ("funnel") for crossing from T₁ to S₀. Partitioning ratios, and therefore quantum efficiencies, should depend critically on the exact shapes of the S₀ and T₁ surfaces in this region.

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MINDO/3 Study of Some Diels–Alder Reactions¹

Sir:

The mechanism of the Diels–Alder reaction has been the subject of much discussion during the last 40 years.^{2–11} Initially two limiting processes were considered, *i.e.*, a pericyclic reaction involving a more or less symmetrical cyclic transition state and a two-step process involving a biradical as a stable intermediate. In recent years it seems to have been generally agreed that the reaction is concerted, but varying opinions have been expressed concerning the symmetry of the transition state.

Problems of this kind, involving the detailed timing of individual bond forming and bond breaking processes during a reaction, are notoriously intractable to experimental solution. Equally, until very recently, no theoretical procedures were available that could give reliable predictions in such cases. The development of MINDO/3¹² seems to have met this requirement, judging by the results of a number of investigations of pericyclic and other reactions.¹⁴ We have therefore

(1) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.

(2) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

(3) A. Wassermann, "Diels–Alder Reactions," Elsevier, Amsterdam, (1965).

(4) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

(5) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).

(6) H. Wollweber in "Methoden der Organischen Chemie," Vol. V/lc, George Thieme Verlag, Stuttgart, 1970.

(7) M. J. S. Dewar and R. S. Pyron, *J. Amer. Chem. Soc.*, **92**, 3098 (1970).

(8) R. B. Woodward and T. Katz, *Tetrahedron*, **5**, 70 (1959).

(9) S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967).

(10) W. v. E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Amer. Chem. Soc.*, **94**, 3833 (1972).

(11) J. W. McIver, *J. Amer. Chem. Soc.*, **94**, 4782 (1972).

(12) MINDO/3 is an improved version of the MINDO¹³ semiempirical SCF–MO method.

(13) See N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972) and earlier MINDO papers cited there.

(14) See, *e.g.*, M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **96**, 5244, 5246 (1974), and in press; R. C. Bingham, M. J. S. Dewar, and R. C. Haddon, *ibid.*, submitted for publication; R. C. Bingham, M. J. S. Dewar, and H. W. Kollmar, *ibid.*, submitted for publication; M. J. S. Dewar and R. C. Haddon, to be published.