rium among the various salts had been achieved. The average of 13 integrations gave the ratio of 3.5 to 1 of aromatic protons to methoxyl protons. For structure **1** or **3** (R = *p*-anisyl) the ratio would be 3.7 to 1. For structure **4** (R = *p*-anisyl), the ratio would be 3.3 to 1. Thus, the tentative conclusion was reached that the equilibrium mixture in solution contained about 50% of **4** (R = *p*-anisyl) in this system.

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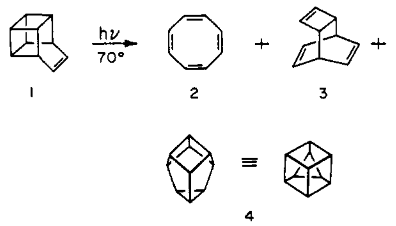
Concurrent Thermolysis and Photolysis of Basketene. Formation and the Interrelation of Some New $(CH)_{10}$ Isomers

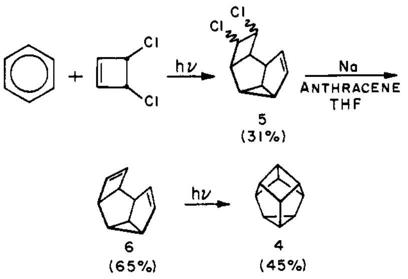
Sir:

The part of organic chemistry dealing with the $(CH)_{10}$ hydrocarbons continues to be of interest to many people.[1] Currently a large effort is being directed toward mapping of the energy surfaces and understanding what factors influence the relative positions of the minima. In this regard, we wish to report that basketene (**1**) can be converted to a new $(CH)_{10}$ isomer **4**.[2] We also describe the interrelation of some of the isomers in this new facet of $(CH)_{10}$ chemistry.

Irradiation of a 1% solution of **1**[3] in cyclohexane (Vycor tube) with 2537-Å light for 10 days at 70° produced **2** (*ca.* 2%), **3** (30–35%), and **4** (10–15%) as the major products. Compounds **2** and **3** were isolated by glpc and were identified as cyclooctatetraene and Nenitzescu's hydrocarbon,[4] respectively, by nmr spectral comparisons with authentic samples. Preparative glpc afforded a pure sample of **4**, mp 101–102° (sealed capillary). The structure assigned to **4** follows directly from the spectral data. A high-resolution mass spectrum establishes the molecular formula as $C_{10}H_{10}$ (calcd, *m/e* 130.0783; obsd, *m/e* 130.0786). The proton nmr spectrum ($CDCl_3$), which exhibits only two complex multiplets centered at τ 6.5 (6 H) and 7.4 (4 H), eliminates structures with vinyl hydrogens. The proton noise-decoupled carbon-13 nmr spectrum (C_6H_6) shows signals as singlets at 70.70 (3 C), 78.08 (3 C), 78.22 (3 C), and 96.64 (1 C) ppm upfield from benzene.[5] Off-resonance decoupling displays each signal as a doublet.[6] These data exclude all structures with trigonal carbons[7] and clearly establish that each carbon is tetrahedral and bears a single hydrogen substituent. The ir spectrum (CCl_4) is quite simple and is characterized by a 3040-cm^{-1} absorption which is diagnostic of a cyclopropane moiety.[8] Reference to Balaban's[9] and Lederberg's[10] complete lists of all the $(CH)_{10}$ isomers and examination of models singles out **4** as the only structure which fits the special requirement of four different types of carbon atoms in the ratio of 3:3:3:1 and which is consistent with all of the other observations.[11]



The structure assigned to **4** has been confirmed by independent synthesis. Photochemical addition of benzene to 3,4-dichlorocyclobutene[12] produced **5**,[13] which on treatment with sodium anthracene in tetrahydrofuran[14] gave the tetracyclodecadiene **6**.[15] Intramolecular photochemical closure of **6** led directly to **4**.



The question of the nature of the reaction pathway which leads from **1** to **4** is of special interest because of the intrinsic need of other $(CH)_{10}$ isomers in effecting the conversion. Control experiments with **1** show that thermolysis in the absence of light yields only **3** and that photolysis at 0° does not produce **4**. Photolysis of **3** at 70° also does not produce **4**. These results clearly indicate the involvement of a thermally generated intermediate which undergoes photochemical transformation. A likely candidate for this intermediate is tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (**7**), the known intermediate in the thermal isomerization of **1**

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(1) For an extensive review and list of references see L. T. Scott and M. Jones, *Chem. Rev.*, **72**, 181 (1972).

(2) The systematic name assigned to **4** by Dr. K. L. Loening, Chemical Abstracts Service, is hexacyclo[4.4.0.0^{2,4}.0^{3,9}.0^{5,8}.0^{7,10}]decane.

(3) S. Masamune, H. Cuts, and M. Hogben, *Tetrahedron Lett.*, 1017 (1966); W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966).

(4) M. Avram, E. Sliam, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636**, 184 (1960).

(5) Measured with a Varian XL-100-15 Fourier transform nmr spectrometer.

(6) W. O. Crain, W. C. Wildman, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 990 (1971).

(7) Carbon-13 signals for vinyl carbon atoms appear some 70 ppm downfield from any of the carbons in **4**. For example, the vinyl carbons of norbornene appear 6.61 ppm downfield from benzene (unpublished work in our laboratory). See also D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

(8) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

(9) A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966); **12**, 103 (1967).

(10) J. Lederberg, NASA report entitled "Dendral-64. A System for Computer Construction, Enumeration, and Notation of Organic Molecules as Tree Structures and Cyclic Graphs," NASA, Washington, D. C., 1964. We thank Professor R. Hoffmann for interpreting the program and providing us with the computer-generated data.

(11) The occurrence of the cyclopropyl proton nmr absorption below τ 8 has precedent. For example, see A. Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.*, **10**, 417 (1971); L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 6366 (1970).

(12) R. Pettit and J. Henery, *Org. Syn.*, **50**, 36 (1970).

(13) R. Srinivasan, *IBM J. Res. Develop.*, **15**, 34 (1971).

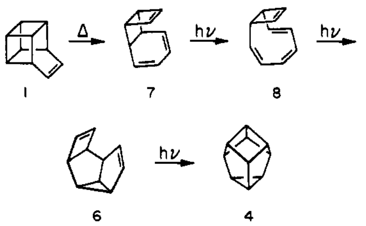
(14) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Amer. Chem. Soc.*, **94**, 4920 (1972).

(15) Compound **6** had the correct mass and nmr spectra. Its structure was established unequivocally by partial hydrogenation (Pd/C) to tetracyclo[5.3.0.0^{2,10}.0^{3,6}]dec-8-ene of known 3,6-endo configuration.[13]

into **3**.[16] We have demonstrated that **7** is formed and present under our reaction conditions by trapping it as a 1:1 adduct with maleic anhydride.[17] A search for other $(CH)_{10}$ intermediates made with glpc using capillary columns revealed that **6** was present (*ca.* 0.2%) after short irradiation times (5 hr).[18] The amount of **6** observed decreased with time, and it was not detectable after extended irradiation.

A reaction pathway which relates **6** to **7** and also accounts for the conversion of **1** into **4** is outlined in Scheme I. The photoinduced conrotatory opening of **7** to the *cis,cis,trans*-cyclooctatriene derivative **8** is a well-known phenomenon.[19–21] There is abundant precedent for photorearrangement of **8** into **6**.[19,21–24] As shown above, **6** undergoes direct photochemical closure to **4**. This (2 + 2) cyclization is a widely observed event.[20,25]

Scheme I



Additional interrelations of the isomers in this area of $(CH)_{10}$ chemistry will be reported in a subsequent paper. We also are investigating the chemistry of the new systems **4** and **6**.

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(16) H. H. Westburg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, **91**, 7512 (1969); E. Vedejs, *Chem. Commun.*, 536 (1971).

(17) E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969).

(18) Compound **6** was identified by comparison of retention times and by enrichment of the photolysis mixtures with authentic **6** on two different 500 ft × 0.03 in. open tubular capillary columns (95% OV-101, 5% Igepal, and Carbowax 20M). A regular 15 ft × $^{1}/_{8}$ in. 20% SE-30 on Chromosorb W column also gave similar results.

(19) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *J. Amer. Chem. Soc.*, **94**, 4285 (1972).

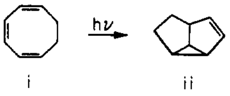
(20) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(21) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **89**, 1755 (1967); **88**, 2850 (1966).

(22) See A. Padwa, L. Brodsky, and S. Clough, *ibid.*, **94**, 6767 (1972), for a list of pertinent references.

(23) J. Zirner and S. Winstein, *Proc. Chem. Soc., London*, 235 (1964); O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964); W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 969 (1970).

(24) In this regard, it is interesting that irradiation of *cis,cis,cis*-cyclooctatriene (i) under conditions similar to ours produces ii as one of the products.[23] The formation of ii is not predicted on the basis of orbital symmetry considerations. This suggests that the reaction either involves an undetected cis–trans isomerization or proceeds in a stepwise fashion *via* radical intermediates. In the case of **8**, the stereochemistry is proper for an allowed closure.



(25) R. N. Warrener and J. B. Bremmer, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

(26) National Science Foundation Trainee, 1969–1973.

Facile Reaction of Alkyl- and Aryldichloroboranes with Organic Azides. A General Stereospecific Synthesis of Secondary Amines

Sir:

Alkyldichloroboranes,[1,2] $RBCl_2$, as well as aryldichloroboranes,[3] react readily with organic azides, $R'N_3$, in benzene solution, producing an intermediate, $RR'NBCl_2$, readily converted by alkaline hydrolysis to the corresponding secondary amines, $RR'NH$, in yields of 84 to 100% (eq 1). The reaction possesses wide generality and proceeds with retention of stereochemistry of the alkyl group in the alkyldichloroborane. Consequently, this development provides a new, simple route to secondary amines far more general than any method now available.

$$RBCl_2 + R'N_3 \xrightarrow{-N_2} RR'NBCl_2 \xrightarrow[H_2O]{NaOH} RR'NH \qquad (1)$$

Trialkylboranes react with a variety of organic azides in refluxing xylene.[4] Basic hydrolysis produces the secondary amine. Unfortunately, this reaction is relatively slow and very sensitive to steric requirements. Recently, we discovered that the dialkylchloroboranes circumvent these problems.[5,6] However, this procedure suffers from a further significant disadvantage—only one of the two alkyl groups on boron is utilized in the synthesis.

This development suggested that alkyldichloroboranes might not only give a fast reaction with organic azides, but also provide for complete utilization of the alkyl groups. Indeed, when *n*-butyldichloroborane (5 mmol) was placed in 5 ml of benzene and *n*-butyl azide (5 mmol) was added dropwise at room temperature, gas (presumably nitrogen) was vigorously evolved. The solution was heated briefly to reflux to ensure completion of the reaction, cooled to room temperature, and hydrolyzed with base. Analysis by glpc indicated an 84% yield of di-*n*-butylamine. These results were encouraging. Consequently, a representative series of alkyldichloroboranes was synthesized, and the reactions with representative organic azides were investigated. These results are summarized in Table I.

The following procedure for the preparation of *N*-cyclohexylaniline is representative. A dry 250-ml flask equipped with a septum inlet, reflux condenser, and

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(1) H. C. Brown and A. B. Levy, *J. Organometal. Chem.*, **44**, 233 (1972).

(2) H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **95**, 2396 (1973).

(3) Phenyldichloroborane is available from Ventron Corp. Others may be prepared by the method of Hooz: J. Hooz and J. G. Calgada, *Org. Prep. Proced.*, submitted for publication.

(4) A. Suzuki, S. Sono, M. Itoh, H. C. Brown, and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 4329 (1971).

(5) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **94**, 2114 (1972).

(6) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **94**, 3662 (1972).