

Table I. Yield and Characterization Data for $B_nC_2H_{n+2}$ Species

Compound	Mp, °C	Bp, °C (mm)	Yield, ^b %	Yield, ^c %	Analyses, %					
					Calcd			Found		
					C	H	B	C	H	B
$B_8C_2H_8(CH_3)_2$	(-40.4)-(-39.4) ^a	62 (134)	30	0	38.43	9.68	51.89	37.42	9.82	52.10
$B_7C_2H_7(CH_3)_2$	(-22)-(-21.3) ^a		7	0	35.11	9.58	55.31	35.14	9.74	55.76
1,6- $B_8C_2H_8(CH_3)_2$	1.0-1.6 ^a	73 (32)	28	41	32.32	9.49	58.18	31.97	9.69	57.84
1,10- $B_8C_2H_8(CH_3)_2$	26.5-27.5 ^a		95 ^d	..	32.32	9.49	58.18	33.35	9.67	57.63
1,7- $B_{10}C_2H_{10}(CH_3)_2$ ^e	170		0	8	27.89	9.36	62.75	27.80	9.21	62.61

^a In sealed capillary. ^b When prepared in the absence of diborane. ^c When prepared in the presence of diborane. ^d Prepared from 1,6- $B_8C_2H_8(CH_3)_2$. ^e Although several C-substituted derivatives of 1,7- $B_{10}C_2H_{12}$ have been reported [D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963)], the 1,7-dimethyl-derivative has not been previously characterized. We thank F. P. Olsen for a sample of the authentic material.

structure should contain a single methyl proton resonance. Only one line is observed at τ 7.84.

$B_7C_2H_7(CH_3)_2$. The 19.3-Mc/sec ^{11}B nmr spectrum of $B_7C_2H_7(CH_3)_2$ is presented in Figure 2. Three types of boron atoms are evident in the ratios 1:2:4. The doublet of area 1 at lowest field may be assigned to a boron atom in an apical position⁵ as in $B_{10}H_{10}^{-2}$. Such an assignment and the available data suggest the

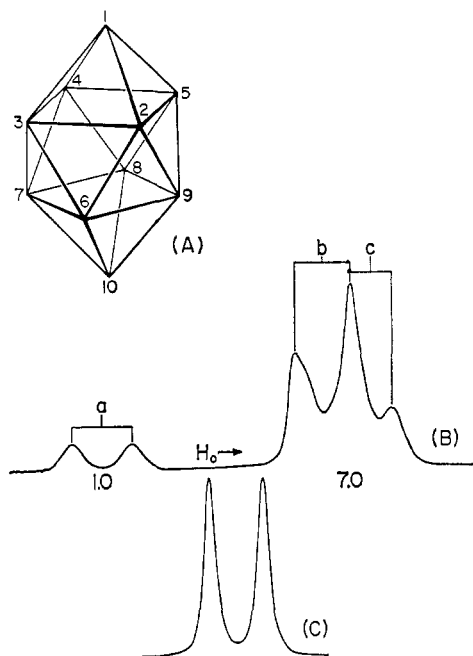


Figure 3. (A) The biccapped Archimedean antiprism geometry. (B) The 19.3-Mc/sec ^{11}B nmr spectrum of the proposed 1,6 isomer of $B_8C_2H_8(CH_3)_2$. Chemical shifts, ppm (with reference to $BF_3O(C_2H_5)_2$), and coupling constants (cps) for the indicated peaks are (a) -19.8 (178), (b) +15.3 (apparent, 167), and (c) +22.9 (apparent, 128). Integrated areas are indicated beneath the peaks. (C) The 19.3-Mc/sec ^{11}B nmr spectrum of the proposed 1,10 isomer of $B_8C_2H_8(CH_3)_2$. The chemical shift (with reference to $BF_3O(C_2H_5)_2$) and coupling constant are +10.3 ppm and 162 cps, respectively.

triccapped trigonal prism structure shown in Figure 2 with an apical boron at the 9-position. Such a structure places the two carbon atoms in nonadjacent apical positions at sites 1 and 7 with a coordination number of 5. This structure requires the two methyl group resonances to be equivalent in the proton nmr spectrum, and only one line is observed at τ 7.50.

(5) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

$B_8C_2H_8(CH_3)_2$ Isomers. Figure 3 presents the 19.3-Mc/sec ^{11}B nmr spectrum (B) of the $B_8C_2H_8(CH_3)_2$ isolated from the initial pyrolysis reaction and the spectrum (C) of the isomer which results from thermal rearrangement. The low-field doublet of area 1 in spectrum B suggests a single apical boron atom⁵ and would place one carbon atom at the opposite apical position of a $B_{10}H_{10}^{-2}$ polyhedron. Since it is unlikely that the two carbon atoms are nearest neighbors, the second carbon atom may be placed in the second equatorial belt removed from the apical carbon atom. Such a 1,6 arrangement of carbon atoms should give nonequivalent methyl proton resonances as observed. The two methyl resonances appear as sharp singlets of equal intensity at τ 7.19 and 8.68.

The spectrum C (Figure 3) is a sharp doublet which suggests the equivalence of all eight boron atoms. If the $B_{10}H_{10}^{-2}$ polyhedron is again employed as the framework model, the carbon atoms are uniquely placed at the apical (1,10) positions. The methyl proton resonances were observed as one sharp singlet at τ 7.22, and this result is in agreement with the 1,10 carbon assignment. The observed thermal rearrangement thus constitutes a polyhedral rearrangement of the 1,6 isomer to the 1,10 isomer. The latter material is expected to be the most stable isomer of the $B_8C_2H_{10}$ system owing to the favorable coordination numbers of 5 and 6 for carbon and boron, respectively.¹

The work briefly described here is being extended to other members of the B_6 , B_7 , and B_8 carborane systems along with derivative and reaction chemistry.

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Concerning the Photolysis of the Sodium Salt of (Δ^2 -2,3-Diphenylcyclopropenyl)carboxaldehyde Tosylhydrazone

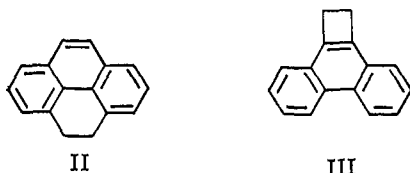
Sir:

Recently we reported that the photolysis of the title compound provided diphenyltetrahydrene in 0.1% yield.¹ However, we must retract our claim for the

(1) S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965).

synthesis of this compound (I) on the basis of the following evidence: the integral ratio of aliphatic protons (at τ 6.67) to aromatic protons of I is 1:2, different from that reported previously. The only conceivable explanation for this difference is that the purity of samples used for various spectroscopic measurements differed, and apparently that for the nmr spectrum was impure.

In view of the similarity of the ultraviolet spectrum of I to that of phenanthrene, two structures, II and III, are proposed for this $C_{16}H_{12}$ compound.² The former compound is known³ and the latter unknown. Although



the melting point and ultraviolet spectrum of II are very similar of those of I, we prefer III as the more probable structure for I. The formation of III is at least mechanistically feasible, but no reasonable pathway to II seems conceivable. A definite structure assignment will be reported.⁴

(2) Professor E. H. White, in a recent private communication, has kindly suggested III as a possibility.

(3) C. S. Marvel and B. D. Wilson, *J. Org. Chem.*, **23**, 1483 (1958). Also see N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

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The Synthesis and Properties of Diphenylcyclopropenyldiazomethane, and a Structural Reassignment for the So-called Diphenyltetrahedrane

Sir:

Theorists seem to agree that planar cyclobutadiene (I) will be unstable with respect to distortions that yield filled electronic levels that are more stable,¹ and since a bending distortion could lead to tetrahedrane II, it was of interest to examine on independent synthesis of the latter type of compound.



We have prepared diphenylcyclopropenyldiazomethane (III) in the hope that thermally or on irradiation it would yield either an isolable tetrahedrane (IV)² or else, in view of the expected lability of this intermediate, dimeric products³ derived from 1,3-diphenylcyclobutadiene.

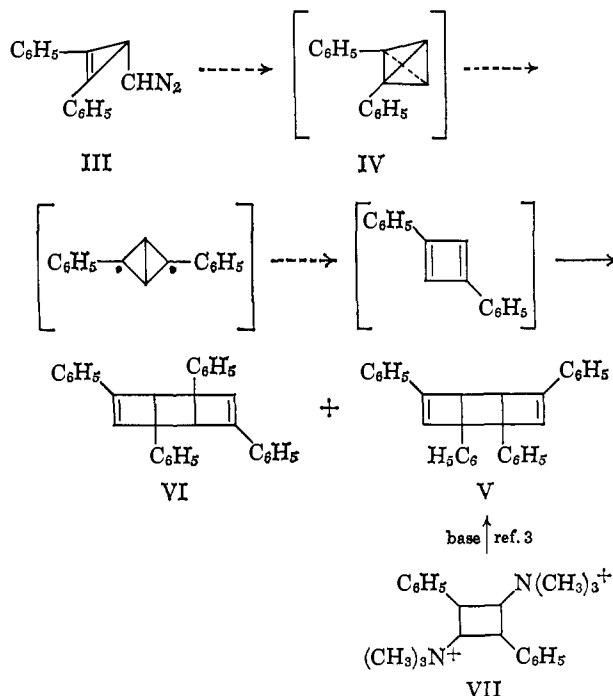
1,2-Diphenylcyclopropenyldiazomethane (III) was prepared in seven steps from 1,2-diphenylcyclopropenyl-3-carboxylic acid (see Table I for experimental details).⁴ All of the compounds cited in Table I

(1) W. N. Lipscomb, *Tetrahedron Letters*, No. 18, 20 (1959).

(2) A related cyclopropane synthesis is given by G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961).

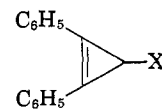
(3) E. H. White and H. C. Dunathan, *ibid.*, **86**, 453 (1964).

(4) R. Breslow, R. E. K. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).



gave satisfactory elemental analyses and showed fine structure in the ultraviolet characteristic of the diphenylcyclopropenyl system.

Table I. Preparation of



Compd	X	Reagents	Mp, °C
VIIIa	CO ₂ H		209 (lit ⁴ 209-211)
b	COCl	SOCl ₂ (25°)	100.7-101.2
c	CO ₂ NH ₂	NH ₃ (25°)	276
d	CN	Tosyl chloride + pyridine (0°)	117
e	CH ₂ NH ₂ ·HCl	LiAlH ₄ (-30°)	222-224 dec
f	CH ₂ NHCO ₂ CH ₃	CH ₃ OCOC (-15°)	107
g	CH ₂ N(NO)CO ₂ CH ₃	N ₂ O ₄ (-75°); NH ₃ to destroy excess	82-84
h	CH ₂ OH		68.3-69.6
i	CH ₂ OCOC ₆ H ₃ - (NO ₂) _{2-3,5}		154-154.5

The cyclopropenyldiazomethane was usually prepared at 0° by the reaction of compound VIIIg with solid sodium methylate still containing some methanol of solvation. The reaction was rapid and, judging from the intensity of the diazo peak in the infrared at 4.88 μ (2050 cm^{-1} in CCl₄), yields of about 80% were obtained. The diazo compound III proved to be abnormally sensitive to protic compounds (water, methanol, etc.) and therefore the diazo compound could not be separated from the other products of the reaction. Furthermore, the compound was also very sensitive to oxygen, and the syntheses were therefore carried out in evacuated systems. In dilute solution (oxygen-free) the compound had a half-life of about 30 min at 25°. In concentrated solutions the diazo group was lost rapidly, and for this reason the nmr spectrum could not be taken. The infrared spectra