

The data available at the present time suggest that the structure of the  $B_3H_8^-$  anion is not greatly different from that of  $B_3H_9$ . This interpretation is based on the presence of the high-field doublet in the  $^{11}B$  nmr spectrum, which is typical for "apex" type boron atoms, and on the facile reaction of the anion with HCl to regenerate  $B_3H_9$  at low temperatures. The asymmetry of the low-field group in the  $^{11}B$  nmr spectrum suggests that there are probably more than two types of "basal" boron atoms present. The exclusive formation of  $\mu$ -DB $_3H_8$  in the reaction of LiB $_3H_8$  with DCl suggests that the D $^+$  enters directly into a bridging position by a mechanism that requires minimal hydrogen rearrangement in the activated complex. These data may be interpreted in terms of three-center bond structures 2221 or 3130 suggested by Lipscomb,<sup>6</sup> though other possibilities cannot be excluded.

Further investigations of these and related systems are underway and will be reported shortly.

**Acknowledgment.** This work was supported in part by the National Science Foundation.

(6) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

Donald F. Gaines, Terry V. Iorns

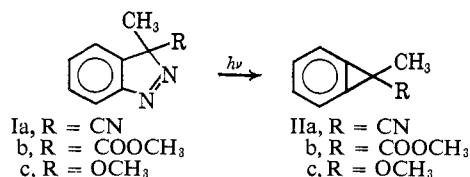
Department of Chemistry, University of Wisconsin  
Madison, Wisconsin 53706

Received April 1, 1967

### On the Mechanisms of Formation and Decomposition of Benzocyclopropenes. Electron Spin Resonance Spectral and Chemical Evidence for Triplet State Diradical Intermediates<sup>1</sup>

Sir:

The extension of the synthesis of cyclopropenes from 3H-pyrazoles<sup>2</sup> to 3H-indazoles resulted in a convenient method for the preparation of benzocyclopropene derivatives.<sup>3</sup> For example, irradiation of the 3H-indazoles Ia-c in hydrocarbon solvents at low temperatures gave the benzocyclopropenes IIa-c in satisfactory yields. We now wish to report the identification of diradicals which are probable reaction intermediates in the formation and in the thermorearrangements of IIa-c.



Ultraviolet irradiation (Pyrex filter) of Ia-c in pentane-isopentane glasses at 77°K in the cavity of an esr spectrometer produced spectra which can be assigned unambiguously to molecules in triplet states. In addition to the  $\Delta m = 2$  transitions at half-field, six maxima were observed corresponding to the extreme values of the  $\Delta m = 1$  transitions with the magnetic field vector parallel to the principal magnetic axes of the molecules.<sup>4</sup> All transitions were fitted to the usual triplet

(1) Supported by Grants NSF GP-1076 and GP-4214 from the National Science Foundation.

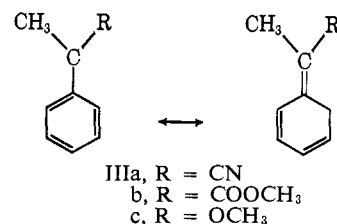
(2) G. L. Closs and W. A. Böll, *Angew. Chem.*, **75**, 640 (1963); *J. Am. Chem. Soc.*, **85**, 3904 (1963).

(3) R. Anet and F. L. Anet, *ibid.*, **86**, 525 (1964); cf. G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 64 (1966).

(4) In the spectrum obtained from Ic only four  $\Delta m = 1$  transitions

state spin Hamiltonian,  $\mathcal{H} = g \cdot H \cdot |\beta| S + DS_z^2 + E(S_x^2 - S_y^2)$ ;  $S = 1$ .<sup>5</sup> The zero-field splitting parameters for the spectra obtained from Ia-c are, respectively:  $D/hc$ ,  $0.1069 \pm 0.0005$ ,  $0.1110 \pm 0.0005$ ,  $0.1217 \pm 0.0008$  cm<sup>-1</sup>;  $E/hc$ ,  $0.0058 \pm 0.0003$ ,  $0.0069 \pm 0.0003$ ,  $0.0066 \pm 0.0003$  cm<sup>-1</sup>. All  $g$  values are close to 2.002. The spectra produced from Ia and Ib persisted with undiminished intensities for several hours after irradiation had been discontinued, but disappeared rapidly on warming above 100°K. The spectrum obtained from Ic was considerably weaker and faded in less than 1 min after irradiation was ceased, even at 77°K.

The esr data strongly suggest the formation of triplet-state molecules with structure III in which one of the unpaired electrons is essentially localized in a  $\sigma$  orbital in the benzene ring plane, while the second electron is delocalized in the  $\pi$  system.<sup>6</sup> Extended Hückel calculations<sup>7</sup> on the corresponding benzyl radicals predict spin densities at the *ortho* positions of 9.2, 8.4, and 12.2% for IIIa-c, respectively. The observed  $D$  values are in semiquantitative agreement with these calculations. The one-center dipole-dipole interaction, represented in the carbene structure of III, makes a large contribution to the zero-field splitting.



A sample of Ib which had been irradiated in a glass at 77°K and which exhibited a strong esr spectrum was warmed up and analyzed for products. Benzocyclopropene IIb was identified, suggesting, but not proving, that IIIb cyclizes on warming.<sup>8</sup>

Chemical evidence for the intermediacy of diradicals of structure III in the photolysis of indazoles was obtained when Ia was photolyzed at -70° in butadiene. Two isomeric products were isolated in 60% yield in a ratio of 1.5:1 and were assigned structures Va and Vb on the basis of mass spectral (parent peak:  $m/e$  183.1045) and nmr evidence [resonances at  $\delta$  (TMS) Va, 1.33 s (3), 2.9 m (2), 3.3 m (1), 5.3 m (2), 5.9 m (1), 7.2 m (4); Vb, 1.64 s (3), 2.7 m (1), 3.0 m (2), 5.2 m (2), 6.1 m (1), 7.2 m (4)].<sup>9</sup>

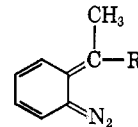
were observable. The  $S/N$  ratio of the transitions corresponding to the orientation with the greatest line separation ( $H \parallel z$ ) was too small to determine the peak positions.

(5) For a discussion of esr spectra of triplet states see: C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961); E. Wasserman, L. C. Snyder, and W. A. Yager, *ibid.*, **41**, 1763 (1964).

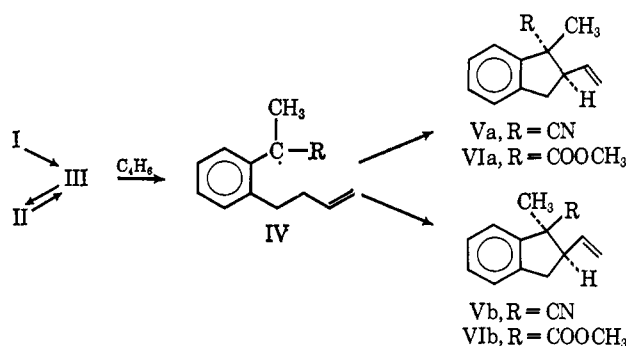
(6) No evidence is at present available on the geometries of III. While it is highly likely that the molecules are planar, it is unknown whether the methyl group in III has a *syn* or *anti* relationship to the *ortho* radical site.

(7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(8) The irradiated glasses were intensely yellow colored at 77°K and turned colorless on warming. Considering the close relationship of III with the corresponding benzyl radicals, it is very probable that the color is caused by III. The formation of III from I may well be a two step process, proceeding through an *o*-quinoid diazo compound



No trapping products were obtained with simple olefins such as isobutylene. The latter observation and the orientation of the butadiene addition suggest a two-step mechanism with the possible intermediacy of the resonance-stabilized diradical IV.



Benzocyclopropenes Ia-c are unstable at room temperature. Ia decomposes mostly to polymeric material, Ib gives 2-methoxy-3-methylbenzofuran and  $\alpha$ -carbo-methoxystyrene, while Ic forms quantitatively  $\alpha$ -methoxystyrene. All these reactions can be visualized to proceed through initial formation of diradicals of type III, formed by homolytic cleavage of the highly strained benzocyclopropene single bond. This hypothesis receives strong support from the observation that thermodecomposition of IIa in butadiene at 25° gives Va and Vb in approximately equal amounts. Similarly, the rearrangement of IIb can be intercepted by butadiene, yielding the corresponding indane derivatives VIa and VIb. The decomposition rates of IIa and IIb are not accelerated by butadiene, suggesting that a unimolecular ring opening precedes the fast addition step.

(9) The assignment of stereochemistry of the adducts is based on chemical shifts only and should be considered tentative.

(10) National Institutes of Health Predoctoral Fellow, 1965-1967.

G. L. Closs, Louise Riemenschneider Kaplan,<sup>10</sup> Victor I. Bendall  
 Department of Chemistry, The University of Chicago  
 Chicago, Illinois 60637  
 Received April 24, 1967

### Stereochemistry of Formation of Cyclooctatrienes via Valence Isomerization

Sir:

The continuing lively interest in the stereochemistry of valence isomerizations prompts us to report evidence relating to the stereochemistry of formation of cyclooctatrienes via a thermal valence isomerization.<sup>1</sup> Following the lead of Ziegenbein,<sup>2</sup> we have partially hydrogenated a sample of *trans*-2,*trans*-8-decadiene-4,6-diyne (I), prepared by the method of Bohlmann and Sinn,<sup>4</sup> over a Lindlar catalyst (2 moles of hydrogen uptake) at 0°. The mixture of products obtained could not be separated by thin layer chromatography, but glpc (Carbowax 20M column at 115°) separated five groups of products. In order of elution these were: (1) a mixture of overhydrogenated compounds (presumably dienes), 9%; (2) *trans*-7,8-dimethyl-2,4-bi-

(1) Earlier reports<sup>2,3</sup> of the formation of valence isomers from tetraenes did not provide evidence either for the route of their formation or relative to the stereochemistry.

(2) W. Ziegenbein, *Chem. Ber.*, **98**, 1427 (1965).

(3) H. Meister, *ibid.*, **96**, 1688 (1963).

(4) F. Bohlmann and H. Sinn, *ibid.*, **88**, 1869 (1955).

cyclo[4.2.0]octadiene (II), 50%;  $\lambda_{\text{max}}$  278 m $\mu$ ; nmr (ppm) multiplet (4 H) at 5.3-6.0, multiplet (1 H) at 2.8-3.2, multiplet (3 H) at 2.1-2.6, doublet (3 H) at 1.09 ( $J = 6.5$  cps), doublet (3 H) at 1.01 ( $J = 6.5$  cps); (3) deca-2,4,6-trienes, 13%;  $\lambda_{\text{max}}$  260, 268, and 278 m $\mu$ ; (4) deca-2,4,6,8-tetraene, 15%;  $\lambda_{\text{max}}$  311, 296, 284, and 274 (sh) m $\mu$ ; (5) unknown, 13%. This hydrogenation mixture was heated for 2 hr at 75° and then treated with dimethyl acetylenedicarboxylate at 100° for 15 hr under nitrogen. Pyrolysis of the oily adduct at 200° and removal of the volatile products in a stream of nitrogen gave *trans*-2,*trans*-4-hexadiene (57% based on the amount of I in the mixture),<sup>5</sup>  $\lambda_{\text{max}}$  227 m $\mu$ ; nmr (ppm) multiplet at 5.1-6.2, doublet at 1.7 ( $J = 6.5$  cps). The presence of two types of methine protons in a 3:1 ratio and of two nonequivalent methyl groups in the bicyclic diene, coupled with the isolation of a hexadiene with two equivalent methyls, provides reasonable evidence for the *trans* orientation of the methyl groups in the ring-closure product.

A sample of *cis*-2,*trans*-8-decadiene-4,6-diyne,  $\lambda_{\text{max}}$  312.5, 293, 276, 261, 247, 237, 230, and 211 m $\mu$ ,<sup>7</sup> was prepared by Cadiot-Chodkiewicz coupling<sup>8</sup> and reduced over a Lindlar catalyst as described above. The mixture was analyzed by glpc and shown to contain ca. 45% of *cis*-7,8-dimethyl-2,4-bicyclo[4.2.0]octadiene,  $\lambda_{\text{max}}$  275 m $\mu$ ; nmr (ppm) singlet (4 H) at 5.63, broad multiplet (4 H) at 2.4-2.8, doublet (6 H) at 1.03 ( $J = 7.0$  cps). The mixture was treated with dimethyl acetylenedicarboxylate and the resultant material pyrolyzed as before. The major volatile product (68% of the volatile material) was *cis*-3,4-dimethylcyclobutene,<sup>6</sup>  $\lambda_{\text{max}}$  end absorption only; nmr (ppm) singlet (2 H) at 6.0, broad multiplet (2 H) at 2.8-3.2, doublet (6 H) at 1.0 ( $J = 7.0$  cps). A second fraction (22%) contained a mixture of hexadienes.

These experiments establish the stereochemistry of the ring-closure product for two separate cases. All attempts<sup>9</sup> to separate from the partial hydrogenation mixture and to identify directly the reactant which leads to the ring-closed product have so far proved unsuccessful. The following experiments were designed to provide indirect evidence about the mechanism of the formation of the bicyclic dienes. Partial hydrogenation of I at ca. -40° followed by glpc analysis of an aliquot indicated that 48% of II and ca. 37% of under- and overhydrogenated products were identified by the detector.<sup>10</sup> The main hydrogenation mixture was separated from the Lindlar catalyst in the cold and immediately completely hydrogenated over platinum oxide at ca. -40°. Analysis followed by preparative glpc separation and identification of the products

(5) D. A. Bak and K. Conrow, *J. Org. Chem.*, **31**, 3958 (1966).

(6) A conrotatory ring opening of the intermediary 3,4-dimethylcyclobutene is to be expected. R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965), reports the *trans*-3,4-dimethylcyclobutene isomerizes to *trans*-2,*trans*-4-hexadiene at 175°.

(7) Extinction coefficients are not reported since this material was contaminated with about 10% of the di-*trans* isomer. Preparation of a pure sample is underway.

(8) See G. Eglinton and W. McCrae, "Advances in Organic Chemistry: Methods and Results," Vol. 4, Interscience Publishers, New York, N. Y., 1963, pp 253-274.

(9) Studies aimed at finding a substituted tetraene which will permit the isolation of the reactant are in progress.

(10) The peaks indicated by the glpc detector and identified after trapping do not, of course, prove that these materials were originally present in the mixture put on the column. In the present case the data described show clearly that the component of interest II was formed on the column.