requires the use of an additional label. The appropriate system is provided by 3,7,7-trimethyltropilidene (VI).<sup>12</sup> In 40 min at 300°, VI is transformed into a mixture containing 2,7,7- and 1,7,7-trimethyltropilidenes (VII and VIII), 3- and 6-isopropenyl-1-methyl-1,4-cyclohexa-



dienes (IX and X), and *m*- and *p*-cymenes (XI and XII) in addition to recovered VI and small quantities ( $\sim 2\%$ ) of unidentified substances. Very little gas or tar is formed, the material balance being essentially quantitatively accounted for by C10H14 products. Analyses and preparative separations of the reaction mixtures are carried out by vapor chromatography. The indicated percentage composition is approximate and is not corrected for variations in thermal conductivity. Longer heating increases the proportions of the aromatic products XI and XII.

Both kinds of nonaromatizing isomerization are reversible.13

The structures of VII and VIII are assigned on the basis of elemental analyses,<sup>14</sup> ultraviolet spectra [VII,  $\lambda_{\text{max}}$  270 m $\mu$  ( $\epsilon$  3600, 95 % EtOH); VIII,  $\lambda_{\text{max}}$  278 m $\mu$ ( $\epsilon$  4400, 95% EtOH); compare VI,  $\lambda_{max}$  268 m $\mu$  ( $\epsilon$  4100, 95% EtOH) and other alkyltropilidenes<sup>15</sup>], and nuclear magnetic resonance (n.m.r.) spectra. Both VII and VIII show singlets of intensity 6 at 1.0 p.p.m. (methyl protons) and slightly broadened singlets of intensity 3 at 2.0 p.p.m. (allylic methyl protons). Compound VII shows multiplets at 6.4-6.2 p.p.m. (intensity 2), 6.1-5.7 p.p.m. (intensity 1), and 5.1-4.8 p.p.m. (intensity 2), all chemical shifts being measured at 60 Mc. downfield relative to tetramethylsilane as internal standard. Compound VIII shows multiplets at 6.4-6.2 p.p.m. (intensity 2), 6.1-5.7 p.p.m. (intensity 2), and 5.1-4.8 p.p.m. (intensity 1). The assignment of the absorptions in order of increasing field strength to the 3-4, 2-5, and 1-6 pairs of protons of tropilidenes is supported by the spectra of VI and at least 25 other tropilidenes of known structure. 15, 16

Compounds IX<sup>14</sup> and X<sup>14</sup> show only end absorption in the ultraviolet. The n.m.r. and infrared spectra strongly suggest a close structural relationship and reveal the presence of a terminal methylene group in each (infrared  $\lambda_{max}$  890 cm.<sup>-1</sup>, n.m.r. broadened singlet near 4.7 p.p.m., intensity 2). Both n.m.r. spectra show three other olefinic protons, two allylic methyl groups, two

University, 1963.

doubly allylic protons absorbing at 2.6 p.p.m., and one triply allylic proton absorbing at 3.2 p.p.m. Of the very few possible structural formulas fitting these data, mechanistic considerations<sup>13</sup> suggest IX and X as the most plausible. This guess at the structures is confirmed by partial hydrogenation and tetracyanoethylene dehydrogenation of IX to *m*-cymene (XI) and of X to o-cymene, identification of the latter substances as well as pyrolysis products XI and XII being achieved by ultraviolet and infrared spectral comparisons with those of authentic materials.17

The occurrence of the VI  $\rightleftharpoons$  VII and VI  $\rightleftharpoons$  VIII rearrangements suggests the possibility that hitherto unsuspected skeletal reorganizations may lurk beneath the apparently undisturbed aspect of tropilidene itself when it is recovered "unchanged" from pyrolyses. This is being investigated.

(17) "Catalog of Infrared Spectrograms," and "Catalog of Ultra-violet Absorption Spectrograms," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa. (18) National Institutes of Health Postdoctoral Fellow, 1964-1965.

> Jerome A. Berson, M. Robert Willcott, III<sup>18</sup> Department of Chemistry, University of Wisconsin Madison, Wisconsin Received April 17, 1965

## Skeletal Reorganization in Tropilidene Rearrangements<sup>1</sup>

Sir:

The mechanism of the isomerization of 3,7,7-trimethyltropilidene (VI)<sup>2</sup> to 2,7,7- and 1,7,7-trimethyltropilidenes (VII and VIII) is revealed by deuteriumlabeling experiments as a true skeletal reorganization of the ring carbons rather than a superficial series of methyl shifts.

Lithium aluminum hydride reduction of trideuterioeucarvone (XIII)<sup>3,4</sup> followed by dehydration with sulfuric acid<sup>8</sup> gives 1,5-dideuterio-3,7,7-trimethyltropilidene  $(VI-d_2)$ . The olefinic proton region of the n.m.r. spec-



trum of undeuterated VI, which consists of a complex multiplet of intensity 3 between 5.8 and 6.3 p.p.m. and a pair of doublets of intensity 2 near 5.0 p.p.m., is replaced in VI-d<sub>2</sub> by three broadened singlets, each of intensity 1, at 6.3, 5.9, and 5.0 p.p.m.

Pyrolysis of VI- $d_2$  under the previously described<sup>2</sup> conditions gives a mixture of VI- $d_2$  with unchanged infrared and n.m.r. spectra and the dideuterated products shown. Reversibility of both types of rearrangement with complete retention of the labeling pattern is demonstrated by pyrolysis of VII- $d_2$  or X- $d_2$  and reisolation of VI- $d_2$  from the resulting product mixture. The positions of the deuteriums are assigned by n.m.r. spectros-

<sup>(12)</sup> Prepared by the method of E. J. Corey, H. J. Burke, and W. A. Remers, J. Am. Chem. Soc., 78, 180 (1956); cf. also J. R. B. Campbell, A. M. Islam, and R. A. Raphael, J. Chem. Soc., 4096 (1956).

<sup>(13)</sup> See the accompanying paper: J. A. Berson and M. R. Willcott, III, ibid., 87, 2752 (1965).

<sup>(14)</sup> All new compounds reported have correct empirical formulas by combustion analyses.

 <sup>(15)</sup> K. Conrow, M. E. H. Howden, and D. Davis, J. Am. Chem.
Soc., 85, 1929 (1963), and references cited therein.
(16) For a summary see M. R. Willcott, Ph.D. Dissertation, Yale

<sup>(1)</sup> We are indebted to the Camille and Henry Dreyfus Fund and to the Army Research Office-Durham for support of this work.

<sup>(2)</sup> J. A. Berson and M. R. Willcott, III, J. Am. Chem. Soc., 87, 2751 (1965). The numbering of structural formulas used in the companion paper is retained here.

<sup>(3)</sup> E. J. Corey, H. J. Burke, and W. A. Remers, ibid., 78, 180 (1956). (4) The n.m.r. spectrum is consistent with the previous<sup>3</sup> structural assignment.



Like VI- $d_2$ , both VII- $d_2$  and VIII- $d_2$  show three copy. broadened singlets each of intensity 1 in the olefinic region, in contrast to the patterns with intensity ratios 2:1:2 and 2:2:1 shown<sup>2</sup> by undeuterated VII and VIII, respectively. Both  $IX-d_2$  and  $X-d_2$  show intact isopropenyl and methyl group absorptions in the n.m.r., but  $IX-d_2$  has lost the absorption at 3.2 p.p.m. of the triply allylic proton as well as one olefinic proton absorption of IX; X- $d_2$  has lost half of the intensity of the doubly allylic proton resonance at 2.6 p.p.m. and one olefinic proton resonance of X. The doubly allylic proton resonance at 2.6 p.p.m. appears as a broad doublet in IX but is simplified to a slightly broadened singlet in  $IX-d_{2.5}$  These data are uniquely consistent with the formulation of  $VI-X-d_2$  as shown.

In compound XI- $d_2$ , the presence of the group  $(CH_3)_2$ -CD instead of  $(CH_3)_2$ CH is evident from the disappearance of the benzylic proton resonance and the collapse of the methyl doublet of XI (J = 7 c.p.s.) to a singlet of intensity 6. The lone methyl resonance is intact, but one-fourth of the intensity of the aromatic proton resonance is lost. The precise position of the aromatically bound deuterium of XI- $d_2$  cannot be directly deduced from the n.m.r. spectrum and is assigned here for consistency with the rest of the series. Compound XII- $d_2$  shows typical isopropyl and methyl absorptions, but the aromatic proton pattern is only half as intense as that of XII.

The formation of the cyclohexadienes IX and X from norcaradiene intermediates would be analogous to previously observed<sup>6-9</sup> reactions of 1-alkyl-2-vinylcyclopropanes, although direct hydrogen transfers from one of the pair of geminal methyl groups to C-4 in the stable nonplanar form of any of the tropilidenes also could lead to IX and X with the proper labeling pattern.

The changes leading from VI- $d_2$  to VII- $d_2$  and VIIId<sub>2</sub> are encompassed by a formalism in which C-1 and C-6 are joined and the isopropylidene group consisting of C-7 and its pair of methyls is allowed to wander over the six-membered ring. Reattachment at C-1–C-2 or C-4–C-5 (numbering as in VI) generates VII- $d_2$ , at C-2–C-3 or C-3–C-4 generates VIII- $d_2$ , and at C-1– C-6 or C-5–C-6 regenerates VI- $d_2$ . In detail, this might well involve the corresponding norcaradienes (VIa,

(7) W. R. Roth, Ann., 671, 10 (1964).

(8) D. S. Glass, J. Zirner, and S. Winstein, Proc. Chem. Soc., 276 (1963).

(9) R. J. Ellis and H. M. Frey, *ibid.*, 221 (1964).

VIIa, VIIIa) as intermediates which are interconverted by a sequence in which rupture of one of the cyclopropane bonds alternates with a pivoting motion around the unbroken bond and recyclization at the next available site.<sup>10,11</sup>



(10) The possibility that the rearrangements involve an intermediate in which both isopropylidene ring bonds are weakened (for example, some kind of complex between dimethylcarbene and the aromatic ring cannot be excluded formally, but seems unlikely). In this connection, W. G. Woods (J. Org. Chem., 23, 110 (1958)) has considered the possibility that toluene is formed from cycloheptatriene or norbornadiene by dissociation and reinsertion of CH<sub>2</sub>.

(11) Whether these acts are concerted or stepwise cannot yet be answered, nor can a decision yet be reached on whether the rotations occur in a specific direction. If the symmetry of the highest occupied molecular orbital (HOMO) is as influential here as in the cases of electrocyclic additions,<sup>12</sup> and if it is permissible to use as a crude model of the process VIa  $\rightarrow$  VIIa a transition state in which the C-2-C-6 system is treated as a pentadienyl radical, a concerted change would require that bond c in VIIa be formed between C-2 and the same face of C-7 as was used to form bond b in VIa, since the HOMO has two nodes. Corollary conclusions are that the norbornadiene  $\rightarrow$  norcaradiene and vinylcyclopropane  $\rightarrow$  cyclopentene rearrangements are stepwise. Although these considerations must be taken as merely suggestive at present, it will be of interest to observe the extent of their concordance with more detailed calculations or experiment.

(12) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).

(13) National Institutes of Health Postdoctoral Fellow, 1964-1965.

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## A New Type of Electron-Deficient Compound. A Polyborane Hydridomanganese Carbonyl, $HMn_3(CO)_{10}(BH_3)_2^{1}$

## Sir:

We wish to report the preparation, properties, and structure (Figure 1) of  $HMn_3(CO)_{10}(BH_3)_2$ , the first known example of a polyborane-transition metal carbonyl complex. This compound containing a  $(BH_3)_2$ fragment with a B-B bond also represents the first known case in which all three hydrogens of a BH<sub>3</sub> group are coordinated to other atoms *via* three-center bonds. The X-ray structural determination not only substantiates the existence of transition metal-hydrogen-boron bridging systems<sup>2-5</sup> but also confirms the

<sup>(5)</sup> The triply allylic proton resonance at 3.2 p.p.m., which appears as a broad doublet in X, is still a doublet in  $X-d_2$ , apparently because of long-range coupling.

<sup>(6)</sup> W. von E. Doering and W. Grimme, unpublished observations, cited by W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); W. Grimme, *Chem. Ber.*, **98**, 756 (1965).

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<sup>(2)</sup> R. Noth and R. Hartwimmer, Chem. Ber., 93, 2238 (1960).

<sup>(3)</sup> R. B. King, Z. Naturforsch, 18b, 157 (1963).

<sup>(4)</sup> R. K. Nanda and M. G. H. Wallbridge, Inorg. Chem., 3, 1798 (1964).

<sup>(5)</sup> J. M. Davidson, Chem. Ind. (London), 2021 (1964).