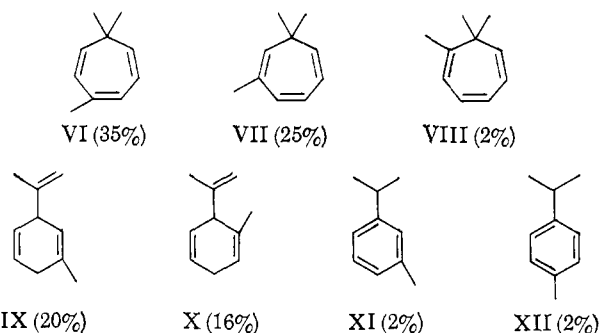


requires the use of an additional label. The appropriate system is provided by 3,7,7-trimethyltropilidene (VI).¹² In 40 min at 300°, VI is transformed into a mixture containing 2,7,7- and 1,7,7-trimethyltropilidenes (VII and VIII), 3- and 6-isopropenyl-1-methyl-1,4-cyclohexa-



diene (IX and X), and *m*- and *p*-cymenes (XI and XII) in addition to recovered VI and small quantities (~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,¹⁴ ultraviolet spectra [VII, λ_{max} 270 mμ (ε 3600, 95% EtOH); VIII, λ_{max} 278 mμ (ε 4400, 95% EtOH); compare VI, λ_{max} 268 mμ (ε 4100, 95% EtOH) and other alkyltropilidenes¹⁵], 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 IX¹⁴ and X¹⁴ 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 λ_{max} 890 cm.⁻¹, 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

(12) 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).

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

(14) All new compounds reported have correct empirical formulas by combustion analyses.

(15) 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 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 considerations¹³ 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 ⇌ VII and VI ⇌ 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 Ultraviolet Absorption Spectrograms," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

(18) National Institutes of Health Postdoctoral Fellow, 1964–1965.

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Skeletal Reorganization in Tropilidene Rearrangements¹

Sir:

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

Lithium aluminum hydride reduction of trideuterio-eucarvone (XIII)^{3,4} followed by dehydration with sulfuric acid³ gives 1,5-dideuterio-3,7,7-trimethyltropilidene (VI-d₂). 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-d₂ by three broadened singlets, each of intensity 1, at 6.3, 5.9, and 5.0 p.p.m.

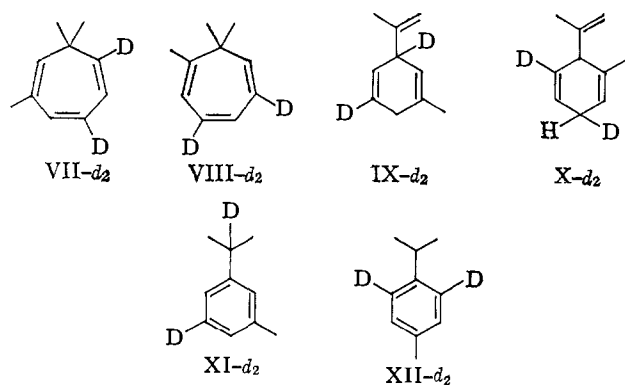
Pyrolysis of VI-d₂ under the previously described² conditions gives a mixture of VI-d₂ with unchanged infrared and n.m.r. spectra and the dideuterated products shown. Reversibility of both types of rearrangement with complete retention of the labeling pattern is demonstrated by pyrolysis of VII-d₂ or X-d₂ and resolution of VI-d₂ from the resulting product mixture. The positions of the deuteriums are assigned by n.m.r. spectro-

(1) We are indebted to the Camille and Henry Dreyfus Fund and to the Army Research Office—Durham for support of this work.

(2) 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.

(3) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).

(4) The n.m.r. spectrum is consistent with the previous³ structural assignment.



copy. Like VI- d_2 , both VII- d_2 and VIII- d_2 show three 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 shown² 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 $(\text{CH}_3)_2\text{CD}$ instead of $(\text{CH}_3)_2\text{CH}$ 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 observed⁶⁻⁹ 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 VIII- d_2 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,

(5) 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.

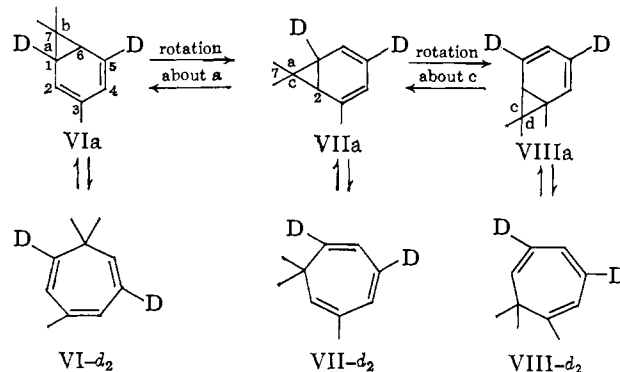
(6) W. von E. Doering and W. Grimme, unpublished observations, cited by W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); W. Grimme, *Chem. Ber.*, **98**, 756 (1965).

(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.^{10,11}



(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_2 .

(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,¹² 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, $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2^1$

Sir:

We wish to report the preparation, properties, and structure (Figure 1) of $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$, the first known example of a polyborane-transition metal carbonyl complex. This compound containing a $(\text{BH}_3)_2$ fragment with a B-B bond also represents the first known case in which all three hydrogens of a BH_3 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 systems²⁻⁵ but also confirms the

(1) H. D. K. and W. F. acknowledge the financial support of the National Science Foundation, G. P. 4175; G. R. W. and L. F. D. acknowledge the financial support of the National Science Foundation, G. P. 1523, and the use of the CDC 1604 computer at the Computing Center (University of Wisconsin).

(2) R. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).

(3) R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).

(4) R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, **3**, 1798 (1964).

(5) J. M. Davidson, *Chem. Ind. (London)*, 2021 (1964).