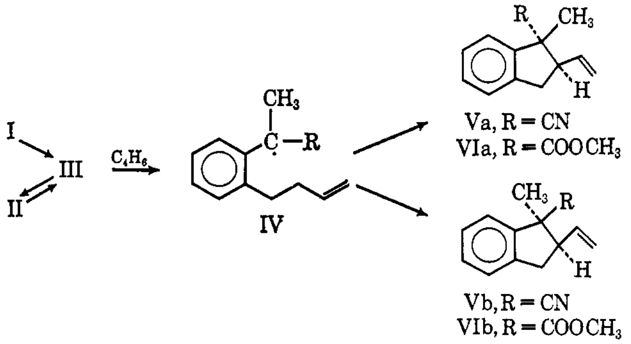
No trapping products were obtained with simple olefins such as isobutylene. The latter observation and the orientation of the butadiene addition suggest a two-step mechanism with the possible intermediacy of the resonance-stabilized diradical IV.



Benzocyclopropenes Ia–c are unstable at room temperature. Ia decomposes mostly to polymeric material, Ib gives 2-methoxy-3-methylbenzofuran and α-carbomethoxystyrene, while Ic forms quantitatively α-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.

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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.[1] Following the lead of Ziegenbein,[2] we have partially hydrogenated a sample of *trans*-2,*trans*-8-decadiene-4,6-diyne (I), prepared by the method of Bohlmann and Sinn,[4] 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-bicyclo[4.2.0]octadiene (II), 50%; $\lambda_{\max}$ 278 mμ; 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%; $\lambda_{\max}$ 260, 268, and 278 mμ; (4) deca-2,4,6,8-tetraene, 15%; $\lambda_{\max}$ 311, 296, 284, and 274 (sh) 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),[5] $\lambda_{\max}$ 227 mμ;[6] 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, $\lambda_{\max}$ 312.5, 293, 276, 261, 247, 237, 230, and 211 mu,[7] was prepared by Cadiot–Chodkiewicz coupling[8] 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, $\lambda_{\max}$ 275 mμ; 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,[6] $\lambda_{\max}$ 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[9] 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.[10] 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

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[1] Earlier reports[2,3] 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).

[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.

by nmr and mass spectrometry showed that the mixture contained 80% *n*-decane, 5% 7,8-dimethylbicyclo-[4.2.0]octane (III), 12% 1,2-dimethylcyclooctane (IV), and 3% unknown. Repetition of this sequence at room temperature gave a reference sample composition very much like the one noted above, while the completely hydrogenated product was composed of 54% *n*-decane, 20% III, and 17% IV. Finally a sample hydrogenated over the Lindlar catalyst at room temperature was heated 5 hr at 75° before being completely hydrogenated. The composition of the saturated hydrocarbon mixture was then 49% *n*-decane, 47% III, and 4% IV.

The latter results show that the reactant undergoing ring closure is an unsaturated hydrocarbon with a linear carbon skeleton and of lower oxidation state than the diendiyne. Ring closure occurs directly to the cyclooctatriene which subsequently undergoes the well-known valence isomerization[11] to the bicyclic isomer.[12] The ring-closure process is a thermal reaction in solution and does not involve the catalyst surface. These data thus provide firm support for the presumption that the reactant is a tetraene and the process involved is a thermal valence isomerization. Since it has been shown that neither the all-*trans*- nor the mono-*cis*-octatetraenes[2,13] will give cyclooctatriene on ring closure, we assume that a requirement for this process is the *cis* configuration of both central double bonds. Thus the present work shows that the cyclization of a tetraene to a cyclooctatriene is a conrotatory process and in accord with the predictions of the Woodward–Hoffmann rules.[14]

Acknowledgment. The authors are pleased to acknowledge generous financial support of this work by the National Science Foundation through Grant GP 4985. Financial assistance from the National Science Foundation for the purchase of the Varian A-60 nmr spectrometer is also gratefully acknowledged.

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[11] A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

[12] While the data do not exclude a competitive direct formation of both the cyclooctatriene and bicyclo[4.2.0]octadienes followed by the valence isomerization, the primary point of direct formation of the cyclooctatriene appears to be firmly established.

[13] W. R. Roth and B. Pelzer, *Ann.*, **685**, 56 (1965).

[14] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

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Received April 17, 1967

Book Reviews

The Organic Chemistry of Titanium. By Raoul Feld, B.Sc., Ph.D., and Peter L. Cowe, B.Sc., Laporte Titanium Ltd., Stallingborough, Grimsby, Lincolnshire. Butterworth Inc., 7300 Pearl St., Washington, D. C. 1965. viii + 213 pp. 16 × 25 cm. $9.95.

As indicated in the authors' preface, the object of this book is to present a comprehensive view of the organic chemistry of titanium and, from the standpoint of synthetic and descriptive chemistry, it appears that the authors have approached success in fulfilling this objective. The titles of the chapters are: 1. The Direct Titanium–Carbon Linkage; 2. Tetra-alkyl and Tetra-aryl Halides; 3. Alkoxy- and Aryloxytitanium Halides; 4. Chelated Compounds of Titanium; 5. Compounds of Titanium and Polyols; 6. Compounds of Titanium and Carboxylic Acids; 7. Compounds of Titanium with Other Metallic Elements; 8. Addition Compounds of Titanium Halides; 9. Compounds of the Lower Valences of Titanium; 10. Miscellaneous Compounds; 11. Organic Titanium Compounds as Catalysts in Polymerization Reactions; 12. Applications of the Organic Titanium Compounds. These chapters include numerous tables of properties, and each chapter has an extensive series of bibliographical references. Each table of references gives, in addition to the original references, also the *Chemical Abstracts* reference.

The book, however, has very little to say concerning the theoretical aspects of the subject. The electronic structures of these compounds and their use in rationalizing the properties of the compounds are virtually completely ignored by the authors, an omission which to a degree lowers the utility of the book. Furthermore, the authors make little attempt to generalize, or to state any general principles. Hence, the book has an "abstract" kind of flavor, appearing in much of its length to consist of a sequence of one- or two-sentence abstracts of papers from the literature. However, most inorganic and organic chemists will find this little volume to be a useful addition to their libraries; this will be particularly true of those interested in complex ions or in titanium compounds specifically.

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