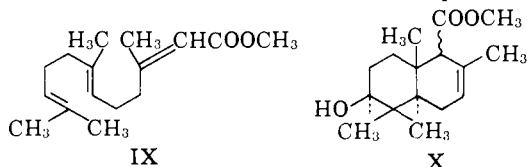
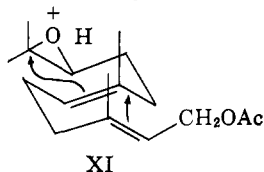


least at the site under discussion. However, when epoxide derived from *trans-trans* farnesyl acetate was cyclized by means of 85% phosphoric acid, there resulted approximately the same epimeric mixture (85% VIa; 15% IVa) as secured by cyclization of epoxide from the same geometrical isomer referred to before.¹⁰

The generality of the oxidation-cyclization sequence is suggested by preliminary experiments with methyl farnesate (IX), which, on successive treatment under appropriate conditions with (1) NBS-water-glyme and (2) phosphoric acid, is transformed into noncrystalline bicyclic hydroxy ester X, probably a mixture of carbomethoxyl epimers. The nature of this product was



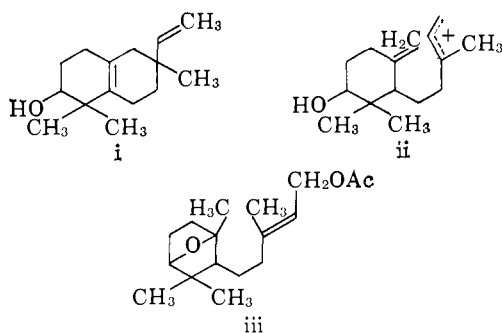
demonstrated by lithium aluminum hydride reduction to bicyclic diol from which there was isolated material of m.p. 149.5–150°, identical (infrared and m.m.p.) with diol VIb secured from farnesyl acetate as described before. Whether the formation of diol monoacetate IVa, VIa, and/or hydroxy ester X proceeds by way of a concerted pathway XI, similar to that seem-



ingly operative *in vivo*,¹¹ or through a stepwise route, is a distinction we hope to make on the basis of future studies.¹² The application of this over-all synthetic approach to other, naturally occurring systems is under investigation in this Laboratory.

Acknowledgment.—These studies were aided by a grant (AI 05102-02 MCHB) from the National Institutes of Health.

(10) Among the other products of this cyclization reaction, there is found a substance which, on the basis of its elemental analyses and infrared and n.m.r. spectral properties, appears to possess structure i. The characteristic moiety (which, interestingly enough, appears in various tricyclic diterpenes, *e.g.*



rimuene, rosenonolactone, as well as pimaric and isopimaric acids) could arise by interaction of an exocyclic methylene group in a monocyclic intermediate, as in ii, followed by proton loss to yield i. From the BF₃ etherate-benzene experiment there results still a different product, which appears, on the basis of similar evidence, to possess structure iii (*cf.* ref. 5).

(11) T. T. Tchen and K. Bloch, *J. Am. Chem. Soc.*, **78**, 1516 (1956); *J. Biol. Chem.*, **226**, 931 (1957).

(12) Full spectral and analytical data will be presented in a full publication.

(13) National Institutes of Health Predoctoral Fellow.

(14) National Science Foundation Predoctoral Fellow.

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RECEIVED AUGUST 5, 1963

The 9,10-Dihydronaphthalene-Cyclodecapentaene Valence Bond Isomer System¹

Sir:

Occupying a central position in the field of aromatic theory, the simplest $4n + 2$ π -electron homolog of benzene, cyclodeca-1,3,5,7,9-pentaene (I), has been often discussed,² but remains still only a hypothetical structure. As an original aim, we approached prepara-



tion of the parent structure by way of the valence bond isomer 9,10-dihydronaphthalene (II), which, in the reasonable assumption that the barrier for conversion would be relatively low,^{2e} should be tantamount to direct synthetic assault on the ten-membered cycle. In this Communication, we report production of *cis*-9,10-dihydronaphthalene and its apparent stability relative to the cyclodecapentaene.

The (*cis*) quinone-butadiene Diels-Alder adduct was subjected to the action of aluminum isopropoxide-isopropyl alcohol with the result that there was formed in good yield a mixture of stereoisomeric dienediols III. From the mixture there was isolated after column chromatography (Florisil) homogeneous material (m.p.



165.5°) which consumed two moles of hydrogen under catalysis to give a saturated diol (m.p. 154–155°).^{3,4} By means of 48% hydrobromic acid-petroleum ether mixture, the unsaturated diol III was transformed into a dibromide mixture; by direct crystallization, dibromide IV of m.p. 82–83° was secured.^{4–6} In preparation for dehalogenation to the desired hydrocarbon, the dienedibromide IV was allylically brominated by means of N-bromosuccinimide in the presence of benzoyl peroxide; the desired, oily dienedibromide (V)^{4,5} was separated from other halogenated materials⁷ by chromatography over Florisil. The penultimate intermediate was converted to *cis*-9,10-



(1) Presented at the Eighteenth National Organic Symposium, Columbus, Ohio, June 16–20, 1963.

(2) (a) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952); (b) W. Baker, in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 39; (c) V. Prelog, *ibid.*, p. 127; (d) W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 477; (e) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

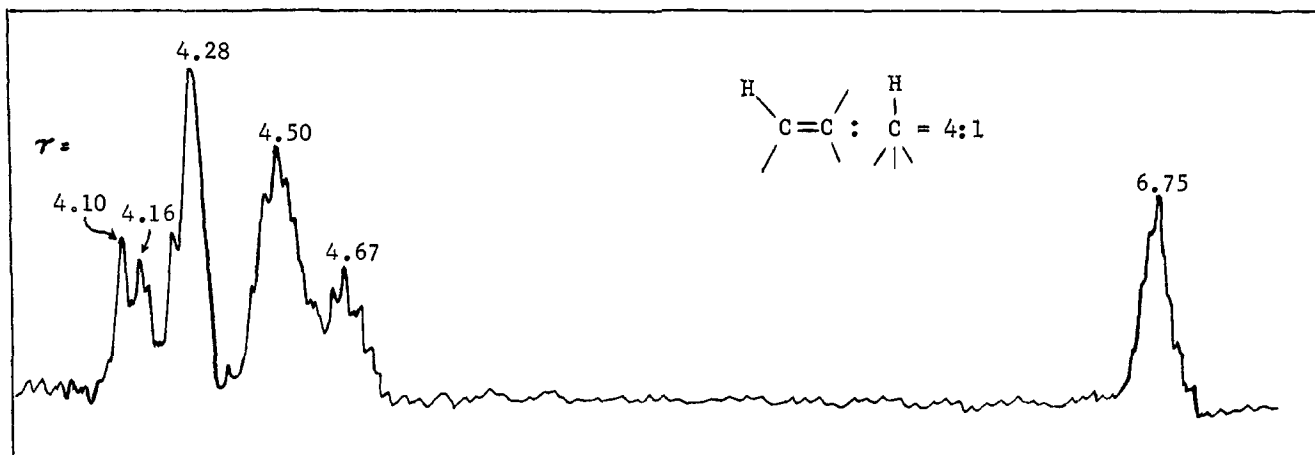
(3) Elemental analyses, carried out on all new substances described, were satisfactory.

(4) Stereochemistry of halogen and hydroxyl was not determined.

(5) The p.m.r. spectrum was in agreement with the assigned structure.

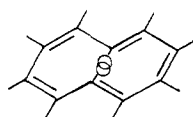
(6) In addition, a smaller amount of 1,2-dibromide, m.p. 65–67°, was isolated.⁵

(7) Crystalline hexabromide (C₁₀H₁₀Br₆), m.p. 181–182°, emerged as an easily isolable product.

Fig. 1.—N.m.r. spectrum of *cis*-9,10-dihydronaphthalene.

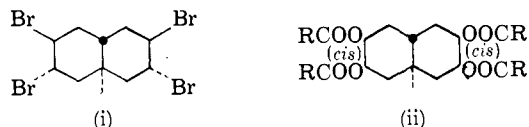
dihydronaphthalene by means of 0.5% lithium amalgam⁸ in ether. The resulting hydrocarbon, after purification by preparative v.p.c., appeared as a colorless liquid, $\lambda_{\text{cyclohexane}}^{\text{max}}$ 247 $m\mu$ (shoulder 245 $m\mu$), reducible over platinum in methanol to *cis*-decalin.⁹ The p.m.r. spectrum of the dihydronaphthalene is reproduced in Fig. 1 (CCl_4 solution at 60 Mc., relative to tetramethylsilane at $\tau = 10.0$).

cis-9,10-Dihydronaphthalene (IIa) is, for all practical purposes, stable at room temperature. Upon being heated under nitrogen in a carbon tetrachloride solution (sealed tube) for 10 min. at specific temperatures in the range 150–200°, IIa was transformed to naphthalene, the only detectable organic product. Ultraviolet irradiation (Hanovia lamp, Vycor filter) served to convert IIa in ether to a distillable product mixture possessing only end absorption in the ultraviolet spectrum. Attempts to prepare from IIa a cyclodecapentaene- $\text{Mo}(\text{CO})_6$ complex were unsuccessful. Thus, here, as in the quinolizine series,¹⁰ there is no overt tendency for cyclodecapentaene formation, and it thus appears that steric interference of (potential) opposed 1,6-hydrogens on the *trans* double bonds (VII)^{2a}



VII

overshadows any supranormal stabilization that might arise from π -orbital overlap in a planar, or even a somewhat distorted, cyclodecapentaene. Whether cyclodecapentaene exists in equilibrium with II, but to an extent undetected by the spectra tools so far employed, is a question we hope to investigate by appropriate, more subtle means.

(8) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).(9) In an endeavor to obtain *trans*-9,10-dihydronaphthalene (IIb), the tetrabromide i was dehydrohalogenated with potassium *t*-butoxide; how-

ever, only 1,2-dihydronaphthalene was isolated from this reaction. Attempts to produce IIb by pyrolysis of tetraester ii were also unrewarding (H. Winicov, University of Wisconsin).

(10) E. E. van Tameelen, P. E. Aldrich, P. Bender, and G. Miller, *Proc. Chem. Soc.*, 309 (1959).

Acknowledgment.—This research was supported by the Petroleum Research Fund (Grant 589-C).

(11) Stanford University, Department of Chemistry.

(12) National Science Foundation Fellow, 1961–1962.

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RECEIVED AUGUST 5, 1963

Bicyclo[2.2.0]hexa-2,5-diene

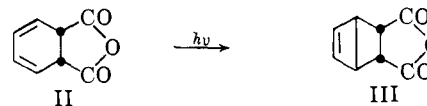
Sir:

We wish to announce the preparation and identification of bicyclo[2.2.0]hexa-2,5-diene, the nonplanar species corresponding to the Dewar representation (I) for benzene.¹



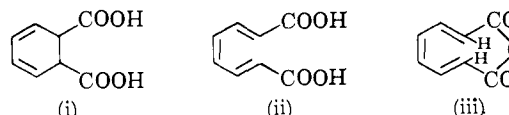
I

Ultraviolet irradiation (Hanovia lamp, Vycor filter) of *cis*-1,2-dihydrophthalic anhydride (II)² in ether resulted in formation of bicyclo[2.2.0]hexa-5-ene-2,3-dicarboxylic acid anhydride (III), m.p. 162–163°



(C, 64.08; H, 3.96). Molecular weight determination (150, mass spectrometric; 161 and 166, Rast) indicated the new substance to be monomeric. In the ultraviolet region of the spectrum, only end absorption was observed (>215 $m\mu$), while the infrared spectrum featured normal anhydride carbonyl (5.4 and 5.6 μ) and *cis*-olefinic (133 μ) absorption. The photoanhydride can be hydrolyzed to diacid, m.p. 205–207°, which is convertible at 100° to starting anhydride. On catalytic reduction, anhydride III consumed one mole of

(1) Presented at the Eighteenth National Organic Symposium, Columbus, Ohio, June 16–20, 1963.

(2) Photolysis of 1,2-dihydrophthalic acid (*cis* or *trans*) (i) did not lead to cyclobutene compounds, but directed starting diene to material absorbing at 300 $m\mu$, possibly the triene acid (ii), which, on further irradiation, was con-

verted to product exhibiting only end absorption. Photolytic ring opening was avoided by use of anhydride II, in which case formation of monocyclic triene (iii) is thwarted, presumably by virtue of the potential 3,8-hydrogen steric interaction in that hypothetical structure.