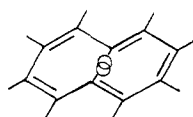
Fig. 1.—N.m.r. spectrum of *cis*-9,10-dihydronaphthalene.

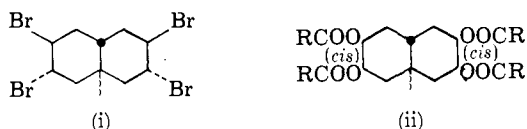
dihydronaphthalene by means of 0.5% lithium amalgam<sup>8</sup> in ether. The resulting hydrocarbon, after purification by preparative v.p.c., appeared as a colorless liquid,  $\lambda_{\text{cyclohexane}}^{\text{max}}$  247  $m\mu$  (shoulder 245  $m\mu$ ), reducible over platinum in methanol to *cis*-decalin.<sup>9</sup> The p.m.r. spectrum of the dihydronaphthalene is reproduced in Fig. 1 ( $\text{CCl}_4$  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 quinoline series,<sup>10</sup> 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)<sup>2a</sup>



VII

overshadows any supranormal stabilization that might arise from  $\pi$ -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 Tamele, P. E. Aldrich, P. Bender, and G. Miller, *Proc. Chem. Soc.*, 309 (1959).

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**Bicyclo[2.2.0]hexa-2,5-diene**

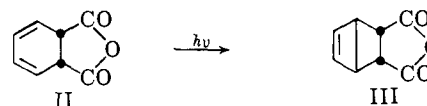
Sir:

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.<sup>1</sup>



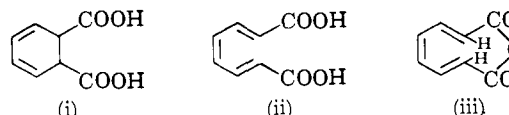
I

Ultraviolet irradiation (Hanovia lamp, Vycor filter) of *cis*-1,2-dihydrophthalic anhydride (II)<sup>2</sup> 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  $\mu$ ) and *cis*-olefinic (133  $\mu$ ) 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.

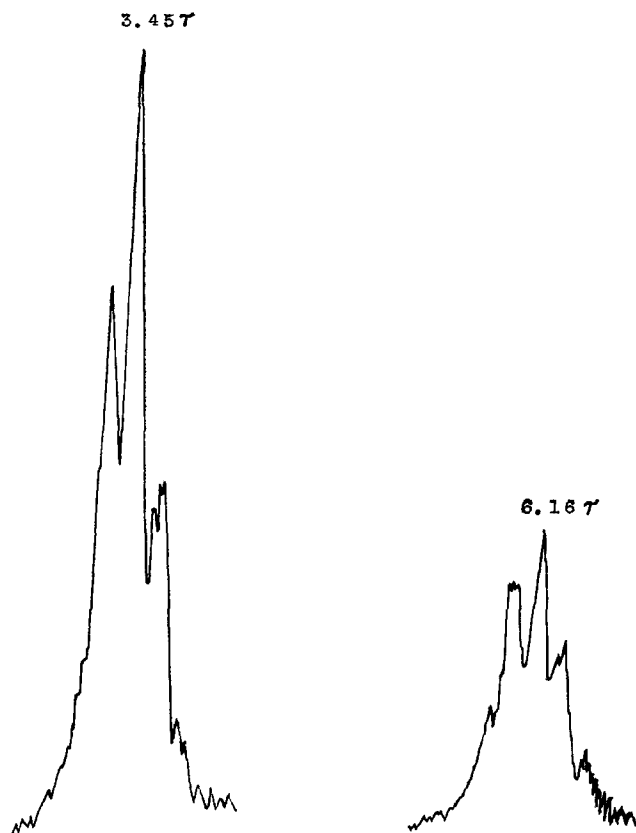
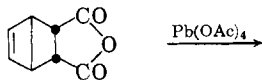


Fig. 1.—N.m.r. spectrum of bicyclo[2.2.0]hexa-2,5-diene at 60 Mc., pyridine solution with tetramethylsilane as an internal standard ( $\tau = 10.0$ ).

hydrogen, and there was produced a saturated dihydro product, m.p. 98–100°, which did not possess a C—CH<sub>3</sub> group (n.m.r.). The n.m.r. spectrum of anhydride III, possessing three peaks of equal intensity at 3.51, 6.34, and 6.58  $\tau$  (CCl<sub>4</sub> solution),<sup>3</sup> corroborates the assigned structure.<sup>4</sup>

Direct oxidative decarboxylation of photoanhydride III to the bicyclohexadiene I was accomplished by lead tetraacetate. Under rigorously controlled conditions (*inter alia*: reaction temperature 43–45°, bath 47–48°; 20-min. reaction time, reduced pressure) the anhydride in pyridine solution was treated with the aforementioned reagent, while a minimal amount of distillate was collected in a cooled receiver. Under



these conditions a pyridine solution containing an amount of "Dewar benzene" representing an approximately 20% yield could be obtained.

Assignment of structure rests on the following observations. On being heated at 90° for 30 min., the new hydrocarbon in pyridine solution was converted quantitatively to benzene (analytical v.p.c.); at room temperature the hydrocarbon in pyridine exhibits a half-life of about 2 days, again forming benzene. The benzene precursor itself can be successfully chromatographed in the vapor phase (Ucon polar column at 45°); its retention time (2.7 min.) is of the order expected for a hydrocarbon in the C<sub>6</sub>-range (cyclohexene 3.3 min., bicyclo[2.2.0]hexane 3.7 min., benzene 5.7 min.). Small amounts of material trapped from the v.p.c.

(3) Measured by means of a Varian A-60 instrument, chemical shifts expressed relative to internal tetramethylsilane at  $\tau = 10.0$ .

(4) For previous photochemical conversions of 1,3-dienes to cyclobutenes, see (a) W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 4060 (1959); (b) O. L. Chapman and D. J. Pasto, *Chem. Ind. (London)*, 53 (1961).

column exhibited only end absorption in the ultraviolet. The n.m.r. spectrum, measured on a pyridine solution of hydrocarbon I, is reproduced herewith. The olefinic and methine protons, appearing in the ratio of 2:1, exhibit splitting with apparent  $J = 0.7$  c.p.s. for each interaction (see Fig. 1). Olefinic hydrogen (3.45  $\tau$ ) is split by the nearer as well as the farther methine hydrogen and, thus, appears as a triplet; in turn, methine hydrogen is acted upon by the four olefinic hydrogens, and, thus, reveals itself as a quintuplet (6.16  $\tau$ ). Thus, the n.m.r. data are consistent with structure I and moreover constitute powerful support for the assignment.

Substantiation by way of chemical behavior was found during the course of reduction experiments. Diimide (generated by decarboxylation of azodicarboxylic acid in the manner previously described<sup>5</sup>) hydrogenation of hydrocarbon I in pyridine–water–acetic acid solution was carried out. The product was identified as bicyclo[2.2.0]hexane, by comparison with an authentic sample,<sup>6a,b</sup> as well as by pyrolysis to biallyl, known to be formed when bicyclo[2.2.0] is heated.<sup>6a</sup>

In view of the fact that 1,2,5-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-diene was recently made in this Laboratory<sup>7</sup> by photolysis of the isomeric benzenoid, the chemistry reported herein represents preparation of the second known "Dewar benzene" as well as the second type of synthetic route to a member of this class.

**Acknowledgment.**—For financial support, the authors are indebted to the Petroleum Research Fund (Grant 589-C) and to the National Institutes of Health for a graduate fellowship (1960–1962). Thanks are due also to Mr. G. Zimmerman and Dr. H. Budzikiewicz (Stanford University) for technical contributions.

(5) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961). See also E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Letters*, No. 11, 347 (1961); S. Hünig, H. R. Müller, and W. Thien, *ibid.*, No. 11, 353 (1961).

(6) (a) S. Cremer and R. Srinivasan, *ibid.*, No. 21, 24 (1960); (b) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

(7) E. E. van Tamelen and S. P. Pappas, *ibid.*, **84**, 3789 (1962).

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### Optical Activity and the Conformation of Polynucleotides

Sir:

Comparatively few studies have been devoted to optical rotatory properties of polynucleotides and nucleic acids,<sup>1–3</sup> in contrast to relatively well developed experimental and theoretical studies on polypeptides and proteins.<sup>4</sup> In order to find a basis for an empirical relation between helical conformation and optical rotatory power, circular dichroism (c.d.) measurements were applied to the studies of homopolyribonucleotide model compounds of relative structural simplicity. Several polyribonucleotides have been shown to exist in a helical conformation in the solid state, and there is indirect evidence which suggests that in solution these compounds retain the same conformation under certain conditions.<sup>5,6</sup>

(1) J. R. Fresco, *Tetrahedron*, **13**, 185 (1961).

(2) J. R. Fresco, A. M. Lesk, R. Gorn, and P. Doty, *J. Am. Chem. Soc.*, **83**, 3155 (1961).

(3) P. O. P. Ts'o, G. K. Helmkamp, and C. Sander, *Biochem. Biophys. Acta*, **55**, 584 (1962); G. K. Helmkamp and P. O. P. Ts'o, *ibid.*, **55**, 601 (1961).

(4) Summarized in P. Urnes and P. Doty, *Advan. Protein Chem.*, **16**, 401 (1961); E. Blout in "Optical Rotatory Dispersion," C. Djerassi, Ed., McGraw-Hill Book Co., New York, N. Y., 1960; J. A. Schellman and P. Oriol, *J. Chem. Phys.*, **37**, 2114 (1962).