

( $C_{12}H_{10}^{++}$ ,  $4n + 2$   $\pi$ -electrons), but proton abstraction has resulted in the synthesis of heptalene ( $C_{12}H_{10}$ ,  $4n$   $\pi$ -electrons), as described in another Communication.

(9) Partial support of this work by the U. S. Army Research Office is gratefully acknowledged; D. J. B. is indebted to the Standard Oil Company (California) for a fellowship held during a portion of this research.

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### HEPTALENE

Sir:

One of the most intriguing unsolved problems in non-classical aromatic chemistry involves the synthesis, properties, and theoretical understanding of the simple members of the group of bicyclic, non-alternant,  $4n$   $\pi$ -electron hydrocarbons, pentalene and heptalene. Even though the simple valence-bond and molecular orbital methods are concordant in their predictions of appreciable delocalization energies (pentalene:  $1.09\alpha$  (32.7 kcal./mole),  $2.456\beta$  (40.5);  $1.087\gamma$  (35.9); heptalene:  $3.618\beta$  (59.7),  $1.465\gamma$  (48.3))<sup>1,2</sup> for compounds of this type, considerable doubt has arisen about the reliability of their predictions because these semi-empirical methods are discordant in their predictions of such a fundamental property as the symmetries of their ground states and some of their excited states.<sup>3</sup> Craig<sup>3a</sup> has argued on the basis of non-empirical considerations that only deductions about these compounds made by a valence-bond approach have a sound theoretical basis, and that pentalene, heptalene, and other compounds for which this method predicts a non-totally symmetrical ground state ("pseudoaromatics") should show greatly decreased  $\pi$ -electron resonance interaction and increased bond length alternation. Numerous attempts have been made to synthesize pentalene<sup>3b</sup> and heptalene<sup>3b</sup> and their only known derivatives<sup>4</sup> contain additional fused rings that obscure their most relevant properties.<sup>3d</sup> We wish to report the synthesis of heptalene (I) and some of its properties, which when augmented by results from additional studies

(1) For source references, see: B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952, pp. 226-227.

(2) Evaluated using the parameter values ( $\alpha = 30$ ,  $\beta = 16.5$ ,  $\gamma = 33$  kcal./mole) that best fit the experimental resonance energies of twelve classical benzenoid aromatic hydrocarbons; with these values only the LCAO-MO-with-overlap method, after correction for  $\sigma$ -bond skeletal strain energies, gives satisfactory predictions ( $\pm 6$  kcal./mole) of the resonance energies of the nonclassical aromatic hydrocarbons, azulene, dimethylfulvene, fulvalene, heptafulvalene (H. J. Dauben, Jr., unpublished results). Estimated strain energies of pentalene (32.0 kcal./mole) and heptalene (21.1 kcal./mole) should be subtracted from the calculated delocalization energies to give their predicted resonance energies.

(3) For cogent discussion and relevant references, see (a) D. P. Craig, and (b) E. D. Bergmann chapters in "Nonbenzenoid Aromatic Compounds" (D. Ginsburg, editor), Interscience Publishers, New York, N. Y., 1959; (c) H. C. Longuet-Higgins in "Theoretical Organic Chemistry, The Kekule Symposium," Butterworths, London, 1958; (d) M. Asgar Ali and C. A. Coulson, *Molec. Physics*, **4**, 65 (1961).

(4) (a) Dibenzo[a,e]pentalene: C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952); cf. K. Brand, *Ber.*, **45**, 3071 (1912); (b) 3,5-dimethylcyclohepta[c,d]pentalene and 3,5-dimethylcyclopenta-[e,f]heptalene: K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

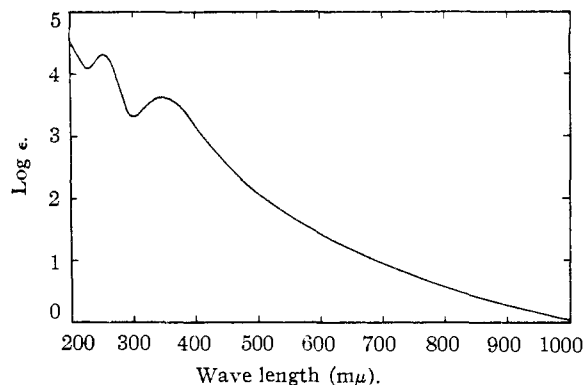
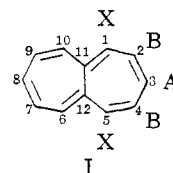


Fig. 1.—Ultraviolet-visible absorption spectrum of heptalene.

now in progress should provide an experimental answer to this theoretical enigma.



Addition of a large excess of trimethylamine in chloroform to an ice-cooled *ca.* 0.005 *M* solution of 1-heptalenium fluoroborate<sup>5</sup> in chloroform produced immediate orange coloration that darkened to red during the reaction period (20 min.); filtration yielded 82% trimethylammonium fluoroborate and a red filtrate that was concentrated, chromatographed (neutral alumina, activity II;  $CCl_4$  or cyclohexane) to give *ca.* 41% yield, evaporatively distilled (*ca.* 25° (0.4 mm.)) onto a Dry Ice-cooled condenser, rechromatographed, and concentrated to give presumably pure heptalene (I) (dark yellowish or reddish brown viscous liquid; crystallization of pure or diluted product not yet successful even at  $-78^\circ$ ; readily polymerized by oxygen or by mild warming (*ca.* 50°), moderately stable when oxygen-free either neat at  $-78^\circ$  or in dilute cyclohexane or carbon disulfide solutions at 25°; ultraviolet (cyclohexane): 256  $m\mu$  (21,400), 352  $m\mu$  (4,140), and long tail throughout the visible region, see Fig. 1; infrared (2-7.5  $\mu$  region;  $CS_2$  or  $CCl_4$ ): 3.33 s, 3.44 s, 3.52 m, 5.19 w, 5.70 w, 5.76 w, 6.08 w, 6.28 m, 6.95 m, 7.23 m; n.m.r. ( $CCl_4$ ;  $\tau(Me_4Si) = 10.00$  p.p.m.), see Fig. 2; mol. wt.: calcd. for  $C_{12}H_{10}$ , 154.2; found (mass spec.): 154; sensitivity to oxygen has precluded accurate weighings needed for carbon and hydrogen analyses.

The heptalene structure for the product is clearly delineated by the observations: (i) derivation from 1-heptalenium ion of established structure by a simple deprotonation reaction under mild conditions, (ii) reconversion to 1-heptalenium ion and no apparent other product by extraction from its cyclohexane solution by 96% sulfuric acid (method used to determine heptalene concentration in ultraviolet spectral determination), or to insoluble, crystalline 1-heptalenium hexachloroantimonate on treatment with excess hexachloroantimonic acid, (iii) rapid

(5) H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4657 (1961).

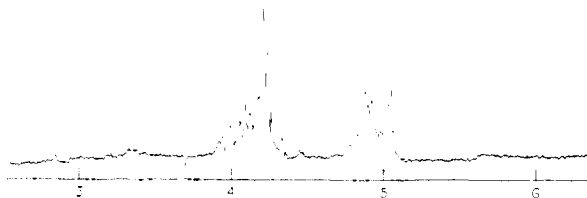


Fig. 2.—N.m.r. spectrum of heptalene.

absorption of hydrogen (PtO<sub>2</sub>, cyclohexane-ethanol, 10–12 min.) to yield *cis*(?)-bicyclo[5.5.0]dodecane (mol. wt. (mass spec.), 166), as indicated by identity of its v.p.c. retention time, infrared spectrum, and mass spectral cracking pattern with one of the *cis*, *trans* pair of products obtained from bicyclo[5.5.0]-dodeca-11-ene-1-one<sup>6</sup> on catalytic hydrogenation, tosylation, lithium aluminum hydride reduction, and (iv) especially by the n.m.r. spectrum that contains proton absorptions only in the "vinylic" region (none in the lower field "aromatic" nor in the higher field "aliphatic" regions) and exhibits the uniquely characteristic spin-spin splitting pattern (Fig. 2) of an AB<sub>2</sub>X<sub>2</sub> system (integrated intensities: A = 1.82, AB<sub>2</sub> = 5.86, X<sub>2</sub> = 4.14 protons) as expected for heptalene. In dilute carbon tetrachloride solution heptalene reacts instantaneously with bromine to give a yellow hygroscopic precipitate that is largely water-soluble; the similarity of these properties to those of tropenium bromide suggests that the major product is bromoheptalenium bromide.

The limited data available allow only tentative conclusions to be made about the nature of the heptalene system. Its facile reactions with catalytic hydrogen, oxygen, acids and bromine, and the greater stability of 1-heptalenium ion than 1-azulenium ion,<sup>5</sup> indicate that heptalene is a very reactive compound, and both more reactive and more basic than azulene. Preferential protonation at the 1-position<sup>5</sup> shows that nucleophilic localization energy is lowest at this position, and the higher field positions of the n.m.r. absorptions of X<sub>2</sub> protons that of A or B<sub>2</sub> protons suggests that electron densities are highest at the 1, 5, 6, and 10 positions. The location of all proton absorptions at the high field end of the "vinylic" region probably is attributable to the lack of appreciable aromatic ring current.<sup>7</sup> Its ultraviolet absorption maxima occur at much shorter wave lengths (256, 352 mμ) than those predicted by the simple molecular orbital method for a fully conjugated system, but are in good agreement with those approximated by the weakly-interacting independent-systems method of Simpson<sup>8</sup> (245, allowed; 387 mμ, allowed and forbidden); the long tail through the visible region may arise from a forbidden transition becoming partially allowed by molecular vibrations or twisting, from transitions according to the Franck-Con-

(6) G. Büchi and O. Jeger, *Helv. Chim. Acta*, **32**, 538 (1949); we are grateful to Professor A. G. Anderson, Jr., for the 5-(1'-cycloheptenyl)-pentanoic acid used in this synthesis.

(7) G. Berthier, B. Pullman and J. Baudet, *J. Chim. Phys.*, **49**, 641 (1952), predicted a pronounced diminution of diamagnetic susceptibility in heptalene (and pentalene), in contrast to the exaltations found in azulene and benzenoid aromatic compounds.

(8) W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 6164 (1955); we are indebted to Professor Simpson for this suggestion and for the calculation of these values.

don principle from a ground state with a single or double potential energy minimum, or from limited resonance splitting of N and/or E states.<sup>8</sup> Provided these initial deductions are correct, heptalene more resembles a weakly-interacting cyclic polyene than a strongly-interacting aromatic system, presumably because of theoretical reasons or non-planarity.

(9) Acknowledgment is gratefully made to the U. S. Army Research Office for partial support of this work, and to the Standard Oil Company of California for a fellowship held by D. J. B. during a portion of this research.

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#### THE CONFIGURATIONS OF LEVOPIMARIC ACID AND $\alpha$ -PHELLANDRENE; INTERPRETATION OF THEIR ROTATORY DISPERSIONS

Sir:

Levopimaric ( $\Delta^{6,8(14)}$ -abietadienoic) acid (I) has been assigned the  $\beta$ -configuration at C-13 (steroid numbering, C-9) by Klyne<sup>1</sup> from a comparison of its [M]<sub>D</sub> with that of 2,4-cholestadiene (II) (cf. 589 mμ region of Fig. 1). Recently, however, Schuller and Lawrence<sup>2</sup> have presented strong chemical

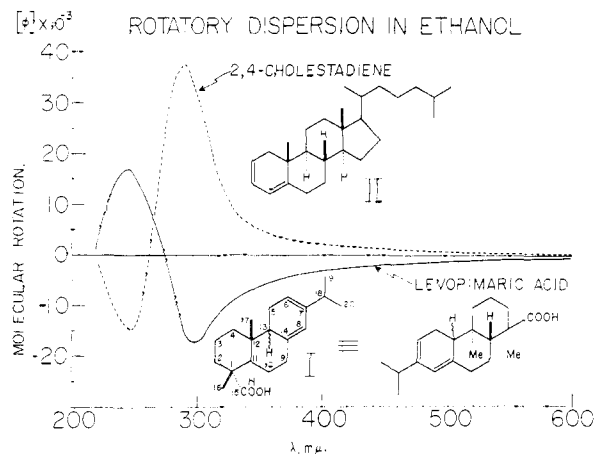


Fig. 1.

evidence for the  $\alpha$ -orientation at this center. In addition, other facts, such as formation of a common hydrogenation product<sup>3</sup> from both I and neoabietic ( $\Delta^{7(13),8(14)}$ -13 $\alpha$ -abietadienoic) acid<sup>4</sup> can be viewed as favoring the  $\alpha$ -configuration at C-13 in I.<sup>5</sup>

We have measured the complete Cotton-effect curves of I, II, and several related compounds, and have observed an antipodal relationship between those of I and II (Fig. 1). Although at first sight this result would seem to confirm the 13 $\beta$ -assignment, we wish to suggest an alternative interpreta-

(1) W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(2) W. H. Schuller and R. V. Lawrence, *Chemistry & Industry*, 105 (1961); *J. Am. Chem. Soc.*, **83**, 2563 (1961); cf. also W. D. Lloyd and G. W. Hedrick, *J. Org. Chem.*, **26**, 2029 (1961).

(3) Cf. J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4762 (1960).

(4) Proof of configuration: C. Djerassi, R. Riniker and B. Riniker, *ibid.*, **78**, 6365 (1956).

(5) Epimerization of an unstable  $\beta$ -configuration at C-13 during hydrogenation would, of course, invalidate this particular argument.