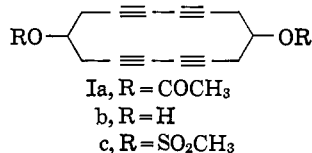


**1,5,9-Tridehydro[14]annulene and Bicyclo[9.3.0]tetradeca-1,5,7,11,13-pentaene-3,9-diyne, an Acetylenic Homolog of Azulene Containing Fused Five- and Eleven-Membered Rings<sup>1</sup>**

Sir:

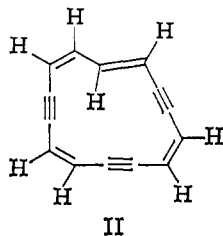
We have studied the base-induced elimination of 3,5,10,12-cyclotetradecatetrayne-1,8-diol dimethanesulfonate (Ic; mixture of isomers, explosion point *ca.* 210°)<sup>2</sup> as a new synthetic route to dehydro[14]annu-



lenes.<sup>4,5</sup> Although this objective could be realized, extensive transannular bond formation occurred and the reaction led mainly to the unusual bicyclic compound III, as well as to tricyclic derivatives.<sup>6</sup>

The dimethanesulfonate Ic in a small volume of dimethyl sulfoxide was treated with 2% potassium hydroxide in 97% aqueous methanol at 15–20° for 1 hr, and the product was chromatographed on alumina impregnated with silver nitrate.<sup>7</sup>

The first substance to be eluted (*ca.* 1.1% yield)<sup>8</sup> was the rather unstable 1,5,9-tridehydro[14]annulene (II). This compound formed red plates, which decomposed on attempted melting point determination; mol wt 176 (C<sub>14</sub>H<sub>8</sub>, determined by mass spectroscopy); λ<sub>max</sub><sup>pentane</sup> in mμ (ε) 246 (5380), 251 (5860), 258 (6120), 305 (137,000),



348 (3180), 375 (5370), 387 (8200), 393 (8550), 406 (26,600), 448 (150), 463 (150), 497 (370), 517 (320), 523 (340), 535 (290), 548 (370), and 558 (2790); acetyl-

(1) Part XXXVIII in the series Unsaturated Macrocyclic Compounds. For part XXXVII, see R. Wolovsky, *J. Am. Chem. Soc.*, **87**, 3638 (1965).

(2) This substance was prepared from the previously described diacetate Ia (mixture of isomers)<sup>3</sup> by saponification to the diol Ib and subsequent treatment with methanesulfonyl chloride and pyridine.

(3) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **81**, 6301 (1959).

(4) See F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).

(5) This approach was investigated, after we had found that the corresponding "monomer," 1,6-heptadiyn-4-ol methanesulfonate (mp 42–43°), undergoes very ready elimination and rearrangement with potassium hydroxide at room temperature to give the allene 1,2,4-heptatrien-6-yne in high yield. For the elimination of *p*-toluenesulfonates of β,γ-acetylenic alcohols, see G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

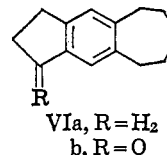
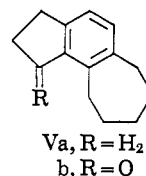
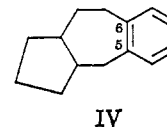
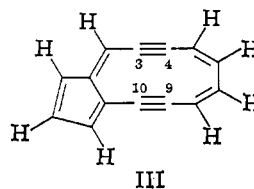
(6) The tricyclic compounds are discussed in the following communication (J. Mayer and F. Sondheimer, *J. Am. Chem. Soc.*, **88**, 603 (1966)).

(7) See Wolovsky (ref. 1) and references cited there.

(8) The reported yields were estimated spectroscopically before chromatography, since the compounds decomposed in part on chromatography.

ene band at 4.65 μ in the infrared (CHCl<sub>3</sub>). The nmr spectrum (100 Mcps, CCl<sub>4</sub> solution) consisted of two sets of low-field multiplets at τ 0.53–0.81 (2 H) and 1.46–1.92 (5 H) assigned to the outer protons, as well as a high-field signal (approximate triplet) at τ 14.96 (1 H) assigned to the inner proton. The positions of these bands show the substance to be aromatic,<sup>4</sup> in agreement with the presence of 14 out-of-plane π-electrons. Full hydrogenation of II in acetic acid over platinum gave cyclotetradecane as the sole product (analysis by gas-liquid partition chromatography).

The bicyclic compound III (isomeric with II) was eluted next, in the form of intensely dark green solutions (*ca.* 15–20% yield).<sup>8</sup> Evaporation to dryness gave a dark green solid which decomposed rapidly, and all determinations therefore had to be carried out with solutions; λ<sub>max</sub><sup>pentane</sup> in mμ (ε)<sup>9</sup> 300 (49,900), 312 (47,700), 324 (44,600), *ca.* 340 sh (30,600), *ca.* 393 sh (3240), *ca.* 415 sh (2450), 428 (1490), 457 (815), 558 (340), 578 (380), 605 (415), 630 (425), 656 (400), 695 (320), 732 (265), and 773 (87); unusually strong acetylene band at 4.67 μ in the infrared (CHCl<sub>3</sub>). In the nmr spectrum (60 or 100 Mcps, CCl<sub>4</sub> solution), all the protons appeared as a complex multiplet in the region τ 2.1–3.2, and no



significant structural information could be obtained.

Full hydrogenation of III in acetic acid over platinum gave a mixture, which contained no significant quantity (<1%) of cyclotetradecane (mass spectroscopy, glpc) but a considerable amount of C<sub>14</sub>H<sub>26</sub> material (mass spectroscopy). A bicyclic formulation was therefore indicated. Partial hydrogenation of III in benzene over 5% palladium-calcium carbonate (interrupted after 2–3 min) led to 5,6-benzazulene<sup>6</sup> in *ca.* 15% yield.

Hydrogenation of III in ethanol over 5% palladium-calcium carbonate (12 hr) resulted in a mixture, from which three consecutive peaks [A (8%), B (24%), and C (68%)] could be isolated by preparative glpc. Peaks A (liquid) and B (mp 48–49°) were the *cis* and *trans* isomers of octahydro-5,6-benzazulene (IV)<sup>10</sup> and were identified with authentic samples obtained by similar hydrogenation of 5,6-benzazulene.<sup>6</sup> Peak C proved to be an unresolvable mixture of the hydrocarbons Va and

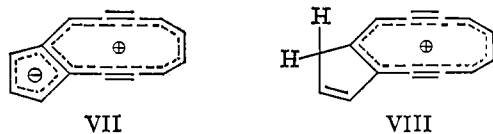
(9) The ε data are approximate and represent minimum values; sh = shoulder.

(10) No specific stereochemical assignment could be made. The octahydro-5,6-benzazulene (IV, mp 29–30°) reported previously (J. W. Cook, N. A. McGinnis, and S. Mitchell, *J. Chem. Soc.*, 286 (1944)) is presumably a mixture of stereoisomers.

VIa (*ca.* 3:2). This assignment is based on direct comparison with authentic samples, prepared by Clemmensen reduction of the known ketones Vb and VIb.<sup>11</sup>

The fact that the green substance is bicyclic and that transannular addition of hydrogen gives rise to the three carbon skeletons present in IV, Va, and VIa leads to structure III. Bond formation between C-4 and C-9 results in IV, between C-4 and C-10 gives Va, while bond formation between C-3 and C-9 results in VIa. Further support for structure III is given in the following communication.<sup>6</sup>

Substance III is a homolog of azulene, formally derived from this compound by insertion of two acetylenes into the seven-membered ring. In analogy to azulene, III may be regarded as a cyclopentadienyl anion (six  $\pi$ -electrons) fused to a bisdehydrocycloundecapentanyl cation (ten  $\pi$ -electrons), each ring representing a cyclic  $(4n + 2)$   $\pi$ -electron system (see formula VII). Substance III should therefore represent an aromatic system. The positions of the nmr bands of III indeed show the compound to be aromatic, in the same way as



azulene (which shows a complex nmr band at 1.67–3.14).<sup>12</sup> Another similarity to azulene is found in the observation that III is extracted reversibly from organic solvents with strong acids (85% phosphoric acid, 97% sulfuric acid),<sup>13</sup> presumably due to the formation of a cation such as VIII.

**Acknowledgment.** We are indebted to the Royal Society for financial support, to Professor R. Granger (Montpellier) for kindly providing samples of Vb and VIb, and to Varian Associates Ltd. (Walton-on-Thames), for determination of the 100-Mcps nmr spectra.

(11) R. Granger, H. Orzalesi, and A. Muratelle, *Compt. Rend.*, **255**, 720 (1962).

(12) Measurement (60 Mcps, CCl<sub>4</sub> solution) made in our laboratory; see also W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Am. Chem. Soc.*, **80**, 3497 (1958).

(13) Extensive decomposition occurred during these manipulations.

(14) Taken from a Ph.D. thesis submitted by J. Mayer to the Weizmann Institute of Science, Sept. 1965.

Joseph Mayer,<sup>14</sup> Franz Sondheimer  
Daniel Sieff Research Institute  
Weizmann Institute of Science, Rehovoth, Israel  
and the University Chemical Laboratory  
Cambridge, England

Received November 29, 1965

## 5,6-Benzazulene and Derivatives from Cyclic Polyacetylenes<sup>1</sup>

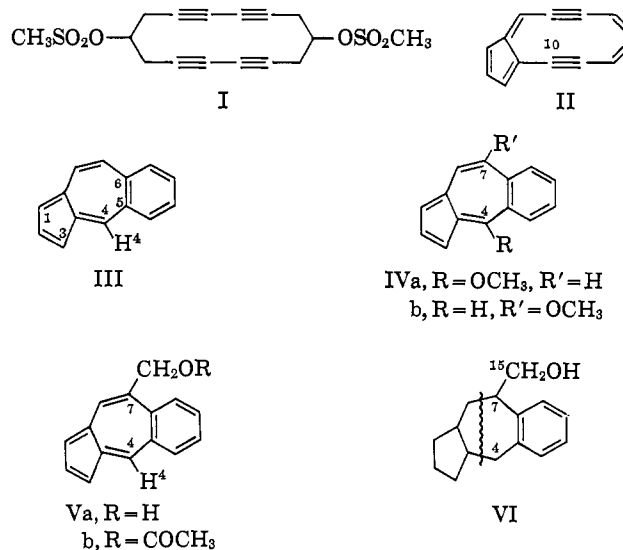
Sir:

The conversion of the dimethanesulfonate I under comparatively mild basic conditions to 1,5,9-tridehydro[14]annulene and the bicyclic hydrocarbon II has been reported in the preceding communication.<sup>1</sup> When this reaction was carried out under more vigorous conditions (I in a small volume of dimethyl sulfoxide

(1) Part XXXIX in the series Unsaturated Macrocyclic Compounds. For part XXXVIII, see J. Mayer and F. Sondheimer, *J. Am. Chem. Soc.*, **88**, 602 (1966).

boiled under reflux with 7% potassium hydroxide in 95% aqueous methanol for 15 min), neither of these substances was obtained, but the three tricyclic 5,6-benzazulene derivatives III, IV (a or b), and Va were isolated.<sup>2</sup> These were separated by chromatography on basic alumina.<sup>3</sup>

The first substance to be eluted (*ca.* 34% yield determined spectroscopically, 25% isolated) proved to be the known 5,6-benzazulene (III).<sup>4</sup> It formed dark



violet plates, mp 164–165°; mol wt 178 (C<sub>14</sub>H<sub>10</sub>, determined by mass spectroscopy). The ultraviolet and infrared spectra were identical with those reported.<sup>4</sup> The nmr spectrum (60 Mcps, CCl<sub>4</sub> solution) showed a singlet at  $\tau$  1.67 (1 H) assigned to H-4, as well as a complex multiplet at  $\tau$  2.02–2.96 (9 H) due to the remaining protons.

The next compound eluted (*ca.* 5% yield, determined spectroscopically) was either 4-methoxy-5,6-benzazulene (IVa) or 7-methoxy-5,6-benzazulene (IVb): dark violet crystals, mp 92–93°; mol wt 208 (C<sub>15</sub>H<sub>12</sub>O, determined by mass spectroscopy; this spectrum also gave a strong peak at *m/e* 207); no hydroxyl band in the infrared (KBr). The very detailed ultraviolet spectrum was very similar to that of 5,6-benzazulene (III), and quite different from that of the other two possible benzazulenes.<sup>4</sup> The nmr spectrum (100 Mcps, CCl<sub>4</sub> solution) consisted of a multiplet at  $\tau$  1.50–1.60 (1 H; collapses to a singlet when the spectrum is recorded with simultaneous irradiation at  $\tau$  2.58), a multiplet at 2.32–3.03 (8 H), and a singlet at 5.92 (3 H, methoxyl protons).

The third compound to be eluted (*ca.* 9% yield, determined spectroscopically) was 7-hydroxymethyl-5,6-benzazulene (Va). It formed dark violet needles, mp 127–128° dec; mol wt 208 (C<sub>15</sub>H<sub>12</sub>O, determined by mass spectroscopy); hydroxyl band at 3.10  $\mu$  in the infrared (KBr). The ultraviolet spectrum was again very similar to that of 5,6-benzazulene. Acetylation

(2) These three compounds were also formed under the original milder conditions, but in reduced yield. They were not obtained when methanol was omitted.

(3) This adsorbent was used, since the previously employed silver nitrate impregnated alumina<sup>1</sup> caused practically complete decomposition of these 5,6-benzazulenes.

(4) P. A. Plattner, A. Fürst, and W. Keller, *Helv. Chim. Acta*, **32**, 2464 (1949); E. Kloster-Jensen, E. Kováts, A. Eschenmoser, and E. Heilbronner, *ibid.*, **39**, 1051 (1956).