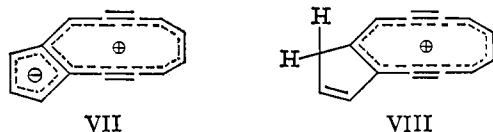


VIa (*ca.* 3:2). This assignment is based on direct comparison with authentic samples, prepared by Clemmensen reduction of the known ketones Vb and VIb.<sup>11</sup>

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.

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

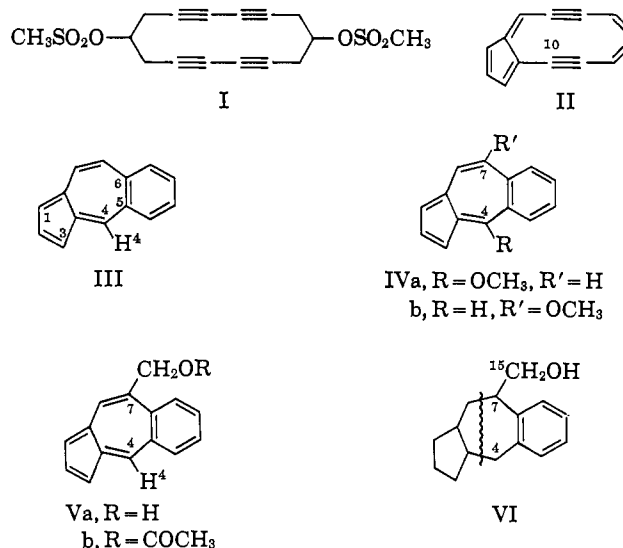
Sir:

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.

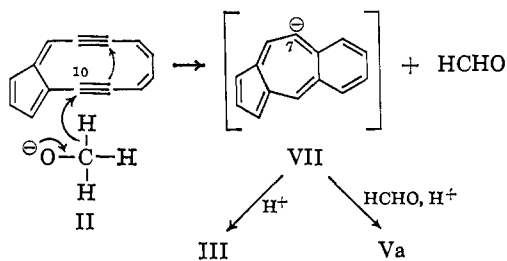
(4) P. A. Plattner, A. Fürst, and W. Keller, *Helv. Chim. Acta*, **32**, 2464 (1949); E. Kloster-Jensen, E. Kováts, A. Eschenmoser, and E. Heilbronner, *ibid.*, **39**, 1051 (1956).

(acetic anhydride, pyridine, 16 hr at room temperature) gave the acetate Vb, mp 94.5–95.5°. The nmr spectrum (60 Mcps, CCl<sub>4</sub> solution) of Vb showed a singlet at  $\tau$  1.73 (1 H, assigned to H-4), a complex multiplet at 2.03–2.92 (8 H, remaining ring protons), a singlet at 4.54 (2 H, methylene protons), and a singlet at 7.96 (3 H, methyl protons).

Catalytic hydrogenation of Va in ethanol over 5% palladium–calcium carbonate (10 hr) led to the octahydro derivative VI (presumably a stereoisomeric mixture) as a colorless liquid. The ultraviolet spectrum [ $\lambda_{\text{max}}^{\text{pentane}}$  258, 263, and 271  $\mu$  ( $\epsilon$  270, 300, and 260)] was characteristic of an *o*-disubstituted benzene.<sup>5</sup> The mass spectrum gave the expected molecular ion (23%) at  $m/e$  216 (C<sub>15</sub>H<sub>20</sub>O). The base peak was at  $m/e$  185 (C<sub>14</sub>H<sub>17</sub><sup>+</sup>), due to  $\beta$  cleavage between C-7 and C-15. There appeared also a strong peak (60%) at  $m/e$  117 (C<sub>9</sub>H<sub>9</sub><sup>+</sup>) which must be derived by  $\beta$  cleavage, as indicated in formula VI, with associated loss of the hydroxyl group.<sup>6</sup> These fragments show the hydroxymethyl group to be attached either to C-4 or C-7. The C-4 position is excluded by the nmr spectrum, leading to the 7-hydroxymethyl formulation.

Treatment of the bicyclic hydrocarbon II<sup>1</sup> under the above-described vigorous alkaline conditions led to the same three 5,6-benzazulenes III, IV (a or b), and Va, in comparable yields. The hydrocarbon II is therefore presumably an intermediate in the conversion of I to these benzazulenes.

The transformation of II to 5,6-benzazulene (III) with base involves the addition of two atoms of hydrogen. This reaction may proceed by hydride ion transfer from methoxide, ring closure to VII, and protonation, formaldehyde being formed. The 7-hydroxymethyl-5,6-benzazulene (Va) is presumably formed by a similar mechanism, the anion VII reacting with the formaldehyde prior to protonation.<sup>7,8</sup> The finding



that the hydroxymethyl group in Va is situated at a position  $\alpha$  to the six-membered ring provides additional support for the structure (II) assigned to the green

(5) See W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959).

(6) See H. M. Grubb and S. Meyerson in "Mass Spectroscopy of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

(7) A related mechanism has been proposed by J. W. Cornforth, R. H. Cornforth, and R. Robinson (*J. Chem. Soc.*, 680, 682 (1942)) for the nuclear alkylation of indoles and phenols with sodium alkoxides, although a temperature of ca. 220° was required.

(8) It could be shown that the 7-hydroxymethyl-5,6-benzazulene (Va) was not the product of a secondary reaction of 5,6-benzazulene (III), since no Va was formed when III was treated under the basic reaction conditions in the presence of 5% aqueous formaldehyde. Moreover, reaction of III with formaldehyde is expected to occur at C-1 or C-3 (see W. Keller-Schierlein and E. Heilbronner in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter VI). In practice, Vilsmeier formylation of III and subsequent lithium aluminum hydride reduction led to two hydroxymethyl derivatives, presumably the 1 and 3 isomers, which differed from Va.

bicyclic hydrocarbon.<sup>1</sup> Moreover, the fact that the hydroxymethyl group is introduced at C-7 indicates that the C-10 position in II is the most electrophilic center.

The methoxy-5,6-benzazulene IVa or IVb can arise from II by normal nucleophilic attack by methoxide ion, again followed by ring closure and protonation. This consideration leads us to assign the 4 or the 7 position to the methoxyl group in this substance. Since the C-10 position in II appears to be the most electrophilic center, it is probable that the methoxyl group in IV is at C-4 (IVa). The 4-methoxy structure IVa is also favored by the fact that the lowest-field, one-proton nmr band appears as a multiplet, suggesting the absence of H-4 (H-4 appears as a low-field singlet in III and Vb). However, the possibility cannot be definitely excluded that the methoxy compound possesses the 7-methoxy structure IVb, and that introduction of the 7-methoxyl group into 5,6-benzazulene (III) alters the charge densities in such a way as to cause the H<sup>4</sup> singlet to appear at higher field (becoming part of the eight-proton multiplet).<sup>9</sup>

**Acknowledgment.** We are indebted to Dr. D. H. Williams (Cambridge) as well as to Professors R. Breslow and G. Stork (New York) for valuable discussions. We also thank the Royal Society for financial support.

(9) Catalytic hydrogenation of the methoxybenzazulene over a palladium–calcium carbonate catalyst and examination of the product by nmr and mass spectroscopy provided no significant structural information.

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

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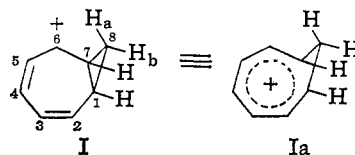
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Received November 29, 1965

## The Protonation of Cyclooctatetraene

Sir:

We have previously reported that protonation of cyclooctatetraene leads to the formation of the stable homotropylum cation (I); the hexachloroantimonate salt of I has been isolated as a yellow crystalline solid following addition of HSbCl<sub>6</sub> to cyclooctatetraene, and the same cation is quantitatively formed upon dissolution of cyclooctatetraene in concentrated H<sub>2</sub>SO<sub>4</sub>.<sup>1</sup>



The cation I, the structure of which is the subject of the following paper, displays absorptions in the nmr spectrum at  $\tau$  1.4, 3.4, 4.8, and 10.6 (areas 5:2:1:1) attributed to the protons on carbons 2–6, 1 and 7, H<sub>b</sub>, and H<sub>a</sub>, respectively. The large difference in chemical shift between the two protons H<sub>a</sub> and H<sub>b</sub> is attributed to

(1) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).