

SYNTHESIS OF A BRIDGED HOMO[15]ANNULENIUM ION

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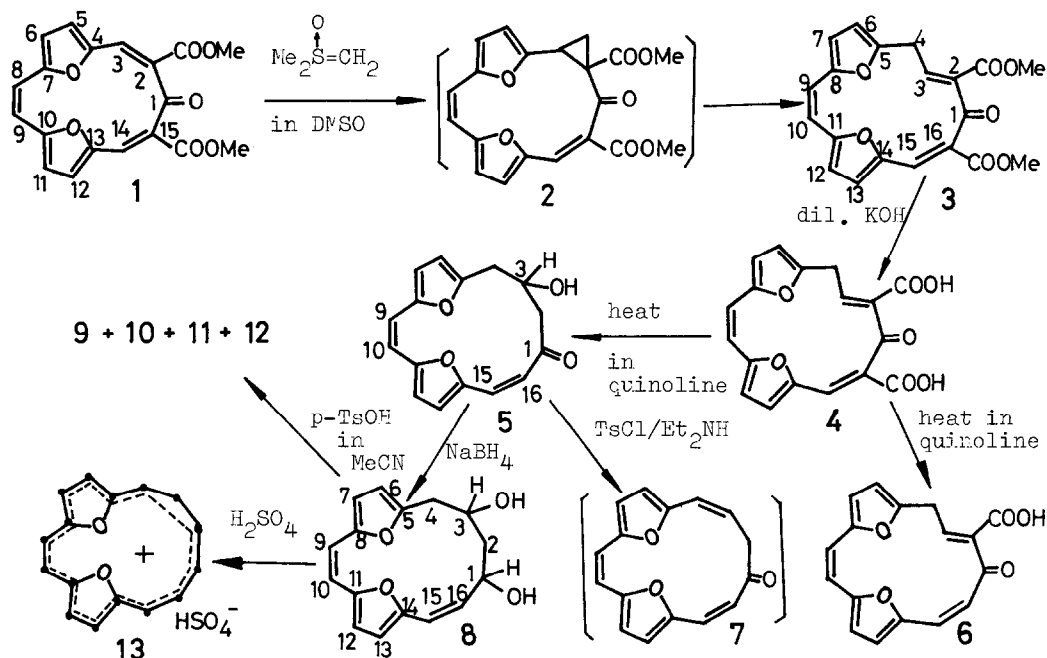
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(Received in Japan 28 September 1973; received in UK for publication 5 November 1973)

HOMOCYCLOPROPENIUM ions ( $n = 0$ ), homocyclopentadienide ions ( $n = 1$ ), homotropylium ions ( $n = 1$ ) and homocyclooctatetraene dianions ( $n = 2$ ) are well-known members of homoaromatic ions<sup>1</sup> possessing delocalizable  $(4n+2)\pi$  electrons. Similarly, higher  $[4n]$ annulenes<sup>2</sup> can be successfully converted to the corresponding homoaromatic ions  $[(4n+2)\pi$  systems ( $n = 4$ )] by acceptance<sup>3,4</sup> or by loss of two electrons.<sup>5</sup> Homo $[4n+3]$ annulenones and the corresponding alcohols are also expected to be possible precursors of these homoaromatic ions.<sup>6</sup>

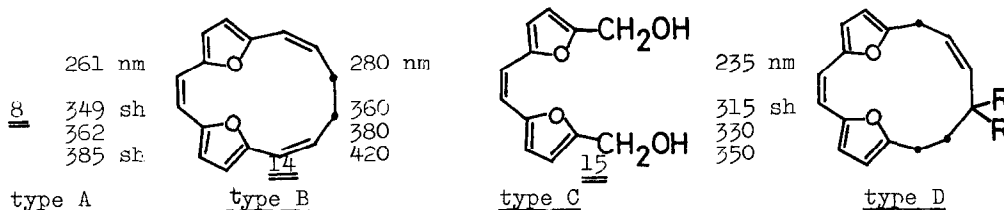
We report here spectral data supporting the formation of bridged homo[15]-annulenium ion 1, a novel  $14\pi$  homoaromatic ion, at room temperature in  $H_2SO_4$ .

Reaction of 2,15-dimethoxycarbonyl[15]annulenone 4,7:10,13-dioxide 1<sup>7</sup> with one mole of dimethyloxosulfonium methylide in DMSO at room temperature gave a ring expansion product 3 in an almost quantitative yield: molecular ion at  $m/e$  368 ( $M^+ C_{20}H_{16}O_7$ ); ir (KBr) 2960 ( $\nu$   $CH_2$ ), 1695 ( $\nu$  C=O ester), 1655  $cm^{-1}$  ( $\nu$  C=O ketone); UV  $\lambda_{max}$  (MeOH) nm ( $\epsilon$ ) 221 (14,700), 260 (25,500), 270 (24,700), 390 (29,200) and 430 - 445 (9,700). The nmr spectrum of 3 gave no sign of cyclopropane ring due to structure 2. A 2H doublet at  $\tau$  5.19 ( $J = 5.5$  Hz), a 1H triplet at  $\tau$  5.78 ( $J = 5.5$  Hz) and a 1H singlet at  $\tau$  2.51 were assignable to the allylic methylene, olefinic H-3, olefinic H-15 protons of 3, respectively. The observed high field shift of the H-3 proton is presumably due to the  $\Delta^{2,3}$  trans configuration. The diester 3 was hydrolysed by dil. KOH (EtOH :  $H_2O = 1 : 1$ ) to give dicarboxylic acid 4 (orange yellow fine crystals, mp  $>300^\circ$ , 82 %). The decarboxylation of 4 in quinoline at  $170^\circ$  for 15 min. in the presence of copper chromite yielded a hardly crystallizable reddish oil 5 in ca. 60%



yield, which was purified by thin layer chromatography ( $\text{SiO}_2$ , ether).<sup>8</sup> The mass spectrum of 5 exhibited a molecular ion at  $m/e$  270 ( $\text{C}_{16}\text{H}_{14}\text{O}_4$ ), indicating one mole of  $\text{H}_2\text{O}$  was added to the expected decarboxylation product. The nmr spectrum of 5 exhibited 6H nonolefinic protons [the OH protons at  $\tau$  7.86 (s, 1H, disappeared on addition of  $\text{D}_2\text{O}$ ), the allylic protons at  $\tau$  6.30 (m, 2H) overlapped with the H-3 methine proton, and complex multiplets at  $\tau$  6.5 - 7.3 ascribable to the methylene protons (2H, m)], as well as 8H olefinic protons [furan protons at  $\tau$  3.53 and 3.63 (2H, ABq,  $J = 3.5$  Hz), furan protons at  $\tau$  3.70 and 3.75 (2H, ABq,  $J = 3.5$  Hz), the H-9, 10 protons at  $\tau$  3.98 (2H, s), and the H-15,16 protons at  $\tau$  3.63 and 4.08 (2H, ABq,  $J = 12.0$  Hz)], supporting the structure. The reduction of 5 with  $\text{NaBH}_4$  gave 8, which was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CHCl}_3$ ), and recrystallized from aq. EtOH, mp 150 - 152°, pale yellow needles (47.5%); mass spectrum:  $m/e$  272 ( $\text{M}^+$ ,  $\text{C}_{16}\text{H}_{16}\text{O}_4$ ); ir (KBr)  $3180\text{ cm}^{-1}$  ( $\nu$  OH); UV  $\lambda_{\text{max}}$  (MeOH) 261 (14,800), 345 (5,200), 364 (5,800) and 382.5 (4,700). The nmr spectrum of 8 together with the spin decoupling well confirmed the structure [OH protons of 1,3 positions at  $\tau$  6.44 (s, 2H), olefinic protons (H-6, H-7, H-9, H-10, H-12, H-13, H-15 and H-16) at  $\tau$  3.50 - 4.32 (8H),

H-4 allylic methylene protons at  $\tau$  5.94 (2H, octet), methine protons at  $\tau$  5.40 (1H, H-1, m) and 7.03 (1H, H-3, m) and H-2 methylene protons at  $\tau$  8.00 (m, 2H). The UV absorption maxima of 8 have been shifted bathochromically by about 32 - 35 nm in its main bands compared with those of model 15, while those bands have been shifted hypsochromically by 11 - 35 nm, when compared with those of model 14<sup>9</sup>. This rules out a possibility that 5 and 8 may have type D chromophores.



The dehydration of 5 by TsCl/Me<sub>2</sub>NH gave a small amount of dehydrated product [ $m/e$  252 (M<sup>+</sup>, C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>); ir (KBr) 3440 ( $\nu$  OH), 1680 cm<sup>-1</sup> ( $\nu$  C=O); UV  $\lambda_{max}$ (MeOH) 342 and 362 nm], but this compound was exceedingly unstable and polymerized rapidly on exposure on light and air. We tentatively assigned this compound to have structure 7. On the other hand, dehydration of 8 with a small amount of p-TsOH in MeCN at 60° for 6 min. proceeded quite easily to give a mixture of products, each of these were separated pure by thick layer chromatography on silica gel (ether). Four products (9, 10, 11 and 12) were obtained, all of which exhibited same molecular ions at  $m/e$  254 (C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>), indicating all of these are the monodehydrated products of 8.

The fastest moving band furnished a yellow oil 9, which showed  $\nu$  C-O<sub>asym.</sub> at 960 cm<sup>-1</sup>, and no  $\nu$  OH band, suggesting the formation of an oxetane ring, whereas the latter three well separated crystalline substances (10, 11, and 12) showed  $\nu$  OH absorptions at near 3430 cm<sup>-1</sup> [total yield ca. 85%, isomer ratio, 3.5:1.3:1.0:1.3, respectively], showing each of these is isomeric monodehydrated 16-membered heptaene alcohol [for UV data, see Table 1].

On dissolving the diol 8 in conc. H<sub>2</sub>SO<sub>4</sub>, a deep blue colour developed, showing sharp absorptions at 334 (30,400) and 349 nm (33,000) [see, Figure 1b]. The UV spectrum of this solution had a close resemblance with that of diatropic [15]annulenium tetrafluoroborate 16<sup>10</sup>. This seems to give a strong support for the existence of a homo[15]annulenium ion 13. It is of interest to note that

13 exists stably only when it was produced in highly diluted concentrations. An attempt to take a well resolved nmr spectrum of this cation 13 has so far been unsuccessful due to the formation of an unidentified polymeric material.

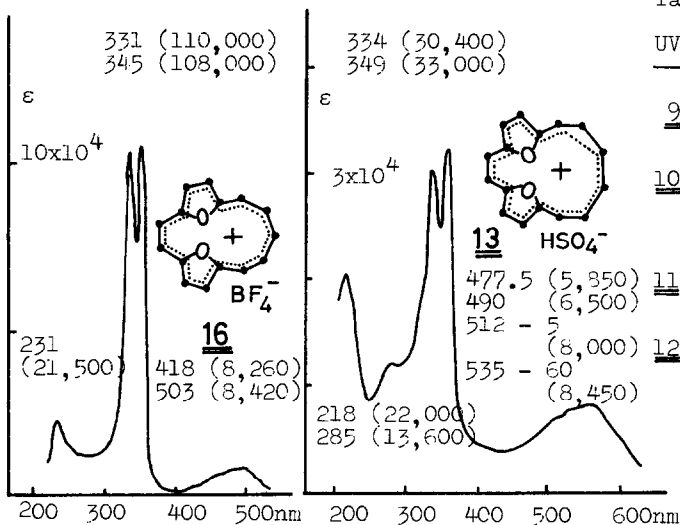


Figure 1a. Electronic Spectrum of 16 in 30%  $H_2SO_4$

Figure 1b. Electronic Spectrum of 13 in conc.  $H_2SO_4$

Table 1

UV Spectral Data in MeOH

<u>9</u>	261 nm	(28,500)
	375	(10,000)
<u>10</u>	261	(21,100)
	362.5	(8,320)
	375	(8,050)
	262.5	(18,800)
<u>11</u>	360	(9,100)
	261	(13,700)
<u>12</u>	360	(7,100)
	385 sh	(4,840)

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