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BENZ-ANNELATED BRIDGED HETERO[11]ANNULENES AND 6,7-BENZO-4,9-OXIDO[11]ANNULENYL CATION

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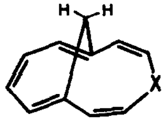
THE SYNTHESES of heteroannulenes[1] are of considerable interest, because a hetero[4n+1]annulene (1a) is expected to be isoelectronic with an aromatic [4n+2]annulene, and a hetero[4n+3]annulene (1b) is expected to be isoelectronic with a nonaromatic [4n]annulene.

Recently, 1H-azonine (aza[9]annulene)[1b,1c] and a series of methylene-bridged bisdehydroaza-[17]annulenes[1f], higher homologs of pyrrole, were reported and proved to be diatropic[1a].

In connection with these diatropic heteroannulenes, it is interesting to find out the possible paratropic[1a] homologs belonging to (1b). The only previously known paratropic member is 1-oxa[15]annulene 4:7,10:13-dioxide[1e]. 4,9-Methano-thia[11]annulene (2a) and 4,9-methano-oxa[11]annulene (2b)[2] were recently reported by E. Vogel and co-workers, and the nmr spectra of (2a) and (2b) indicated that these systems do not sustain a paramagnetic ring current.

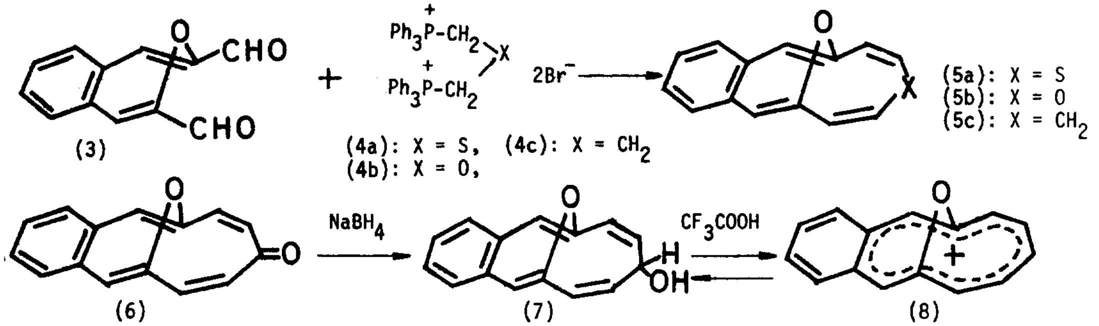


2a: X = S
2b: X = O

We now report the preparation and properties of the benz-annelated derivatives (5a and 5b), together with an aromatic [11]annulenyl cation (8), which is generated from the conjugated base (7).

A Wittig reaction between 3-benzoxepin-2,4-dialdehyde (3)[3] and dimethyl thioether α,α′-bis-(triphenylphosphonium bromide) (4a)[4] with lithium methoxide in DMF at 80° for 3 hr. gave, after chromatography on silica gel, a 12% yield of 6,7-benzo-4,9-oxido-thia[11]annulene (5a), mp 212°. The spectral data [mass spectrum m/e 226; ir (CCl_4) 1620 (vinyl sulfide), 1565, 1158, 1138 cm^{-1}; uv (EtOH) 262 nm (ε 34,400), 280 (33,000)] are in accord with the assigned structure. The nmr spectrum of (5a), recorded in Fig. 1, supported the symmetrical structure with cis-configuration at the 2,3- and 10,11-double bonds. Whilst (2a)[2] and substituted thiepins[5] easily extrude sulphur upon heating, (5a) was found to be so thermally stable that it could be purified by sublimation (230°).

A Wittig reaction between (3) and dimethylether α,α′-bis(triphenylphosphonium bromide (4b)[6]



(3)

(4a): X = S, (4b): X = O, (4c): X = CH_2

(5a): X = S
(5b): X = O
(5c): X = CH_2

(6) (7) (8)

with lithium methoxide in DMF under a high dilution condition at 60° gave, after chromatography on silica gel, a 2.5% yield of 6,7-benzo-4,9-oxido-1-oxa[11]annulene (5b), mp 168-70°, along with other uncharacterized products. The spectral properties of (5b) [mass spectrum, m/e 210 (M^+), 181; ir (KBr) 1640 (enol ether double bond), 1252 cm^{-1}; uv (EtOH) 258 nm (ε 76,800), nmr spectrum, see Fig. 1.] are in accord with the assigned structure.

In order to obtain proper cyclic models, in which there are no ring current, 6,7-benzo-4,9-oxido-1-homo[11]annulene (5c) and 6,7-benzo-4,9-oxido-1-hydroxy-1-homo[11]annulene (7) were prepared. Compound (5c) was obtained from an analogous Wittig reaction of (3) and trimethylene bis(triphenylphosphonium bromide)[7] (4c) in 39% yield, mp 115°(n-hexane), and (7) was prepared by the $NaBH_4$ reduction of 6,7-benzo-4,9-oxido[11]annulenone (6)[3] in ethanol, mp 193°(cyclohexane) in 88% yield. The spectral data of these models are in accord with the assigned structures.

When the nmr spectra of the oxa- and thia-annulenes are compared with those of (5c) and (7), the protons exhibit practically the same chemical shifts, and no up-field shifts due to the paramagnetic ring current were observed [see Fig. 1]. Therefore, (5a) and (5b) do not possess a paratropic character, and behave only as cyclic olefins. Being the uv spectrum of (5b) with maximum at 258 nm (ε 76,800) closely similar to those of (5c) and (7), the oxa-annulene presumably has the same conformation[8]. In contrast, uv spectrum of (5a) [maxima at 262 nm (ε 34,400) and 280 (33,000)] has a close resemblance to that of the annulenone (6) [see Fig. 2 and 3].

Compound (7), upon treatment with CF_3COOH or 70% $HClO_4$, furnished a green solution, and the uv spectrum was characterized by fine absorption maxima near 610 nm, suggesting the formation of an aromatic [11]annulenyl cation (8) [see Fig. 4]. The nmr spectrum in CF_3COOH demonstrates a strong diamagnetic ring current, showing all the signals at the low field τ 0.3 - 1.5. This makes a marked contrast with an observation that protonation of (6) by CF_3COOH occurs only on the

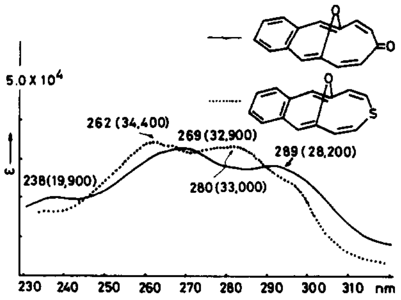


Fig. 2. Uv spectra of 6,7-Benzo-4,9-oxido[11]annulenone (6) ——— and 6,7-Benzo-4,9-oxido-thia[11]annulene (5a) ········in EtOH

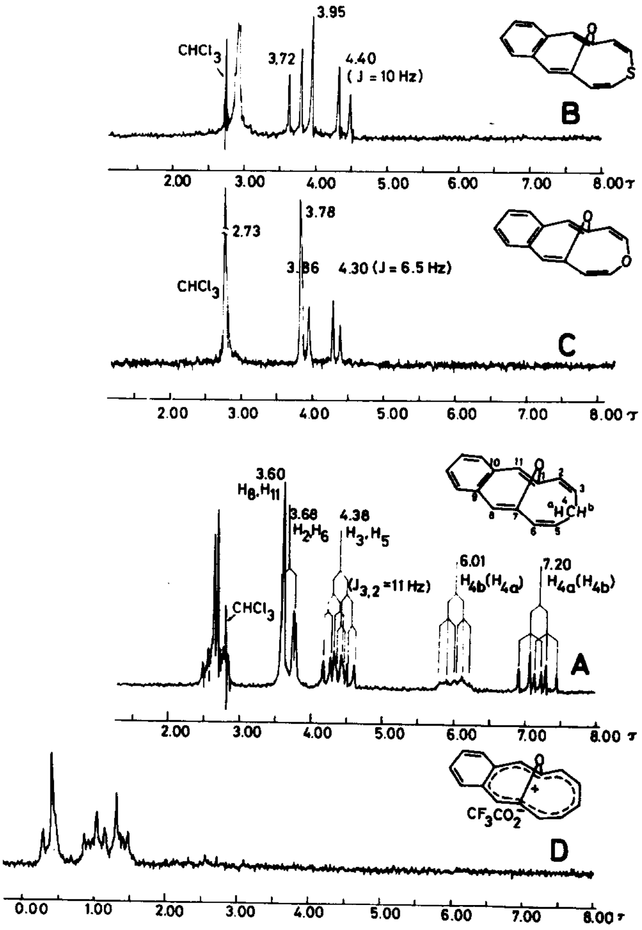


Fig. 1. NMR spectra of (A), 6,7-Benzo-4,9-oxido-1-homo[11]annulene (5c), (B) 6,7-Benzo-4,9-oxido-thia[11]annulene (5a), (C) 6,7-Benzo-4,9-oxido-oxa[11]annulene (5b) in $CDCl_3$, and (D) 6,7-Benzo-4,9-oxido[11]annulenyl cation (8) in CF_3COOH [60 MHz; TMS as internal standard]

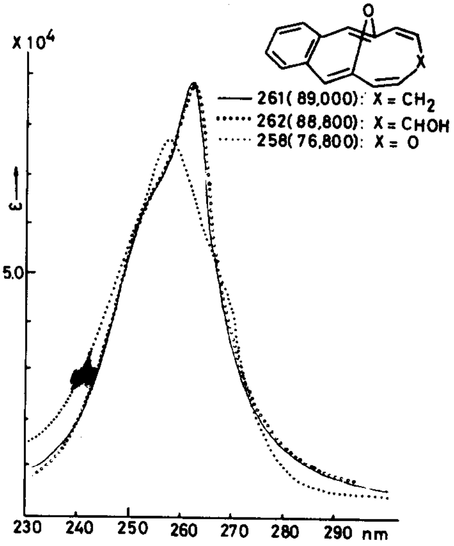


Fig. 3. Uv spectra of 6,7-Benzo-4,9-oxido-1-homo[11]-annulene (5c) ———, 6,7-Benzo-4,9-oxido-1-hydroxy-1-homo[11]-annulene (7) ••••••, and 6,7-Benzo-4,9-oxido-oxa[11]annulene (5b) ········ in EtOH

>C=O position, not causing the cyclic delocalization of the positive charge.

The pK_R+ value of (8) was obtained as - 4.1 spectrophotometrically, utilizing the acidity function $Co = pK_R+ - \log [R^+]/[ROH]$[9]. A comparison of this value with that of 1,6-methano[10]annulenyl cation[10] and 1,2:4,5-dibenz-tropylium cation[11] shows that its aromatic character is far less than that of the former (+6.2) and is comparable to that of the latter (-3.7).

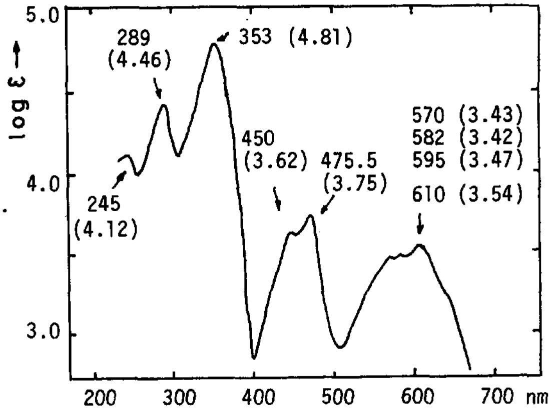


Fig. 4. Electronic spectrum of 6.7-Benzo-4,9-oxido[11]annulenyl cation (8) in 70% $HClO_4$

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