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THE SYNTHESIS OF METHANO-BRIDGED BISDEHYDRO[18]-, -[20]-, -[22]-, AND -[24]ANNULENES

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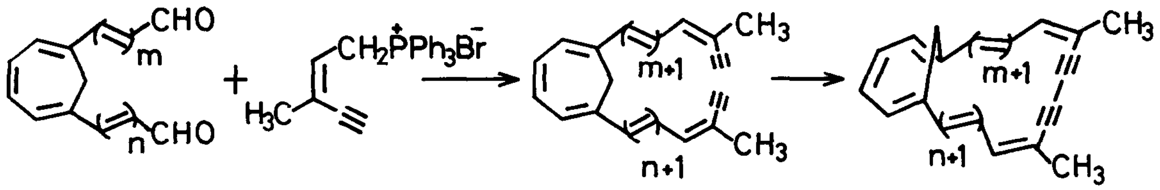
Summary: Title annulenes were synthesized by Wittig reaction of cyclohepta-1,3,5-triene-1,6-dialdehyde or its vinylogous dialdehydes with 3-methylpenten-2-yn-4-yltriphenylphosphonium bromide, followed by intramolecular oxidative couplings of the resulting acyclic compounds, and they proved to be diatropic or paratropic, corresponding to the number of peripheral π-electrons.

A number of multi-bridged annulenes have so far been synthesized, especially by Vogel.[1)] However, the monomethano-bridged annulenes over 18-membered ring have few precedents,[2)] although the monomethano-bridged aza[17]- and [21]annulenes have been synthesized by Sondheimer.[3)] We now describe a simple, and apparently general, new synthesis of dehydroannulenes which formally have a methano-bridge between 1 and 6 sites on the annulene perimeters. The method has been used for the synthesis of methano-bisdehydro[18]-, -[20]-, -[22]-, and -[24]annulenes.

The starting material was cycloheptatriene-1,6-dialdehyde (**1a**), which was converted to mono- **1b** [lemon yellow, mp 76–77°C)[4)] or bis-vinylogue **1c**[5)] by Wittig condensation with controlled quantities of [(1,3-dioxolan-2-yl)methyl]-triphenylphosphonium bromide,[6)] and LiOMe or LiOEt in DMF at 75°C, followed by hydrolysis with dilute HCl in THF at room temperature. Then the homologation for **1b** was repeated, giving rise to the bis-vinylogue **1d** (dark yellow, mp 95–



1a: m=n=0
b: m=1, n=0
c: m=n=1
d: m=2, n=1

2

3a: m=n=0
b: m=1, n=0
c: m=n=1
d: m=2, n=1

4a: m=n=0
b: m=1, n=0
c: m=n=1
d: m=2, n=1

96°C). The yields of these condensations from lower homologues were 50–90%. Reaction of **1a–d** and the salt **2**$^{7)}$ in THF with BuLi at -70°C afforded the acyclic compounds **3a–d** in 5–40% yields (**3a**: red, mp 91–92°C, ^{1}H NMR in $\mathrm{CDCl_3}$ at 200 MHz τ 2.85–3.72 (olefinic and 7-membered ring H), 6.48 ($\mathrm{-C{\equiv}CH}$), 7.15 ($\mathrm{-CH_2-}$), 8.05 ($\mathrm{CH_3}$); **3b**: red, mp 97–98°C, τ 2.85–3.73 (olefinic and 7-membered H), 6.35, 6.63 ($\mathrm{-C{\equiv}CH}$), 7.24 ($\mathrm{-CH_2-}$), 8.04 ($\mathrm{CH_3}$); **3c** (red, mp 116–117°C, τ 3.14–3.70 (olefinic and 7-membered H), 6.55 ($\mathrm{-C{\equiv}CH}$), 7.28 ($\mathrm{-CH_2-}$), 8.05 ($\mathrm{CH_3}$); **3d**: red, mp 95–96°C, τ 3.08–3.90 (olefinic and 7-membered H), 6.64, 6.66 ($\mathrm{-C{\equiv}CH}$), 7.29 ($\mathrm{-CH_2-}$), 7.99, 8.04 ($\mathrm{CH_3}$). Oxidative couplings of **3a–d** with anhydrous copper(II) acetate in pyridine-ether (3:1) under relatively dilute conditions$^{8)}$ afforded the desired bisdehydroannulenes **4a–d** as stable crystals with metallic lustre (**4a** [18]-: brown, mp 169–170°C, ^{1}H NMR in $\mathrm{CDCl_3}$ at 200 MHz τ 1.95 (d, J=15 Hz, $\mathrm{H^A}$), 2.18 (d, 10, $\mathrm{H^C}$), 2.56 (broad s, $\mathrm{H^1}$, $\mathrm{H^2}$), 7.47 (s, $\mathrm{CH_3}$), 7.97 (dd, 15, 10, $\mathrm{H^B}$), 10.45 (s, $\mathrm{-CH_2-}$), and see Fig. 1; **4b** [20]-: purple, mp 131–132°C, τ 0.25 (dd, 16, 10, $\mathrm{H^{D'}}$), 0.35 (dd, 16, 11, $\mathrm{H^B}$), 2.20 (dd, 16, 9, $\mathrm{H^{B'}}$), 2.71 (d, 16, $\mathrm{H^{A'}}$), 3.94 (dd, 16, 9, $\mathrm{H^{C'}}$), 4.01–4.11 (m, $\mathrm{H^2}$, $\mathrm{H^3}$), 4.06 (d, 10, $\mathrm{H^{E'}}$), 4.16–4.22 (m, $\mathrm{H^1}$, $\mathrm{H^4}$), 4.27 (d, 10, $\mathrm{H^C}$), 4.41 (d, 16, $\mathrm{H^A}$), 5.36 (s, $\mathrm{-CH_2-}$), 8.44 (s, $\mathrm{CH_3}$), and see Fig. 1; **4c** [22]-: brown, mp 196–197°C (dec), τ 2.50 (d, 16, $\mathrm{H^A}$), 2.51 (d, 11, $\mathrm{H^E}$), 2.54 (dd, 16, 11, $\mathrm{H^C}$), 2.81–2.85 (m, $\mathrm{H^2}$), 2.97–3.01 (m, $\mathrm{H^1}$), 6.14 (dd, 16, 11, $\mathrm{H^D}$), 6.22 (dd, 16, 11, $\mathrm{H^B}$), 7.64 (s, $\mathrm{CH_3}$), 9.19 (s, $\mathrm{-CH_2-}$), and see Fig. 1; **4d** [24]-: purple, mp 195–196°C, τ 0.76 (dd, 15, 11, $\mathrm{H^{F'}}$), 1.14 (dd, 15, 11, $\mathrm{H^D}$), 1.32 (dd, 15, 11, $\mathrm{H^B}$), 1.43 (dd, 15, 10, $\mathrm{H^{B'}}$), 1.55 (dd, 15, 11, $\mathrm{H^{D'}}$), 3.86–3.90 (m, $\mathrm{H^2}$, $\mathrm{H^3}$), 3.94 (d, 11, $\mathrm{H^{G'}}$), 4.06 (d, 16, $\mathrm{H^{A'}}$), 4.09 (dd, 16, 10, $\mathrm{H^{C'}}$), 4.15–4.20 (m, $\mathrm{H^1}$, $\mathrm{H^4}$), 4.17 (d, 10, $\mathrm{H^E}$), 4.21 (d, 15, $\mathrm{H^A}$), 4.26 (dd, 15, 11, $\mathrm{H^{E'}}$), 4.29 (dd, 15, 11, $\mathrm{H^C}$), 5.88 (s, $\mathrm{-CH_2-}$), 8.36 (s, $\mathrm{CH_3}$), 8.39 (s, $\mathrm{CH_3}$), and see Fig. 1; these assignments of **4d** were clarified by examination of two-dimensional spectrum taken at 360 MHz.

Comparison of the ^{1}H NMR chemical shifts of the various protons of the bisdehydro[18]- and -[22]annulenes **4a** and **4c** with those of the corresponding acyclic model compounds **3a** and **3c** indicates that both **4a** and **4c** are diatropic, as expected of peripheral 18π- and 22π-electron systems, respectively. This follows from the fact that all the outer protons including methyl protons in **4a** and **4c** resonate at lower field than the corresponding protons in **3a** and **3c**, respectively, whereas the inner protons including methylene protons in **4a** and **4c** resonate at higher field. On the other hand, **4b** and **4d** are paratropic, as expected of 20π- and 24π-electron systems, respectively, since the inner protons including methylene protons in **4b** and **4d** resonate at lower field than the corresponding protons in **3b** and **3d**, respectively, whereas the outer protons including methyl protons resonate at higher field.

The ^{1}H NMR spectra of the bisdehydroannulenes **4a–d** are illustrated in Fig. 1, which shows that the diatropic or the paratropic nature in **4a–d** can be deduced without having to make comparisons with the corresponding acyclic models **3a–d**, respectively. As we see from Fig. 1, although the appearance of the sharp singlet due to inner methylene protons in the spectra of **4a-d**, and the $\mathrm{H^{A'}}$, $\mathrm{H^{B'}}$

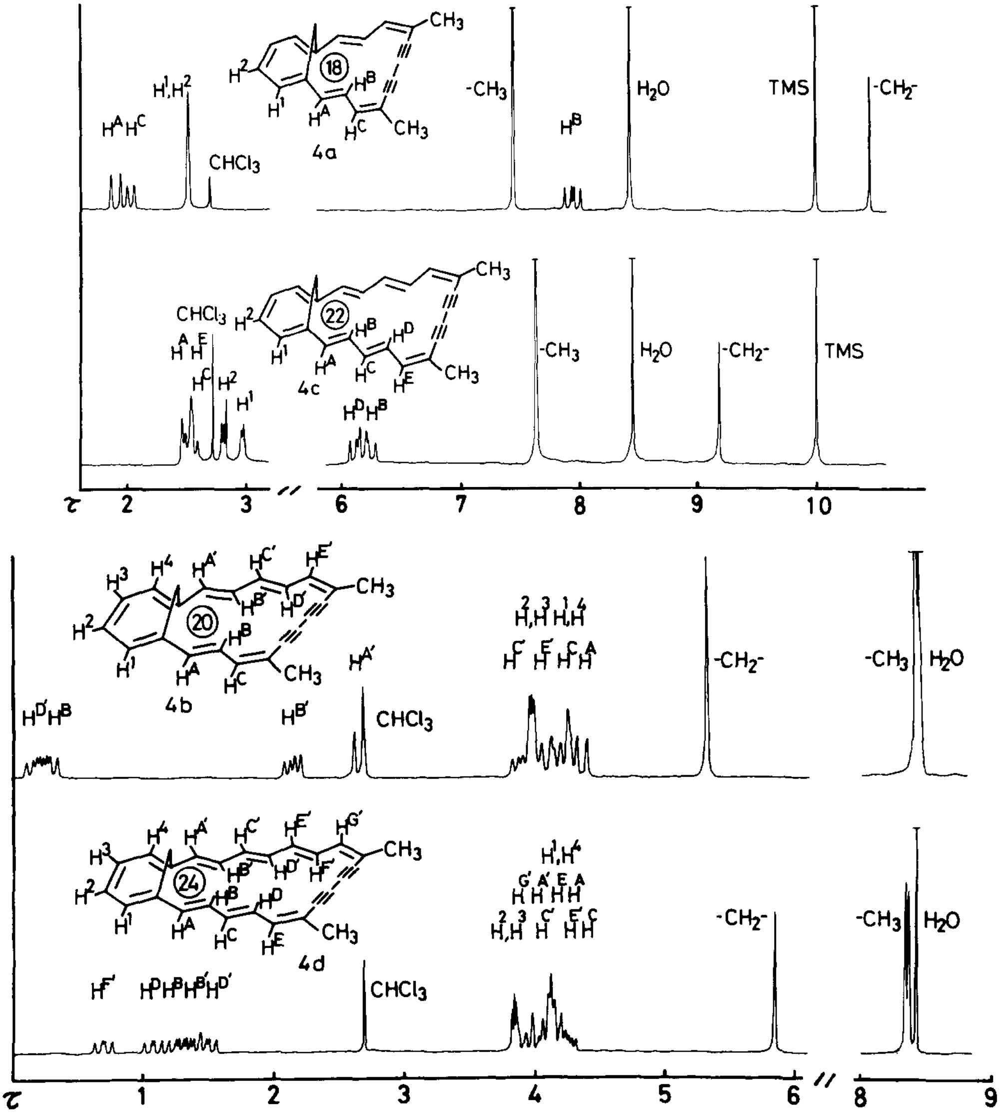


Fig. 1. The 200 MHz ^1H NMR spectra of 4a–d in $CDCl_3$

proton signals of 4b in an unexpected region, as compared with the spectra of 4a, 4c-d, require us further investigation to explain, comparison of the chemical shift differences between the olefinic inner and outer protons or of the chemical shifts of the methylene protons indicates that the diatropicity falls off in the sequence 4a > 4c, while the paratropicity falls off in the order 4b > 4d. Thus, the behaviour that both the diamagnetic ring current effect in [4n+2]π-electron system and the paramagnetic ring current effect in [4n]π-electron one become less as the ring size increases, seems to reflect both a decrease of tropicity along with an increase in ring size$^{2)}$ and an increasing flexibility of the bisdehydroannulene perimeter, albeit the annulenes 4a-d have a methano-bridge on the perimeter.

In electronic spectra, taken in THF, of the annulenes, the main maximum of the [18]annulene **4a** (343 nm) is in longer wavelength than that of the [20]annulene **4b** (324 nm), and the similar observation is made between the [22]annulene **4c** (367 nm) and the [24]annulene **4d** (355 nm). Clearly, this is due to the occurrence of the same sort of alternation between the maxima of [4n-2] and [4n]systems, as has been observed for monocyclic annulenes and dehydroannulenes [(4n-2)π systems absorbing at higher wavelengths than the (4n)π systems].9)

In addition, it is noteworthy that these annulenes **4a**-**d** are thermally stable (*vide ante*) when compared with the corresponding membered, monocyclic, annulenes and dehydroannulenes,10) presumably due to rigidity of the ring skeleton by methylene bridge.

Further progress on methano-bridged annulenes are now in progress.

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