Tetrahedron Letters No. 47, pp 4179 - 4182, 1975. Pergamon Press. Printed in Great Britain.

ANNELATED 12π-ELECTRON SYSTEMS. THE SYNTHESIS OF A DIMETHYLBENZOMONODEHYDRO[12]ANNULENE, DIMETHYLMONODEHYDRO[12]ANNULENO[c]THIOPHENE, -[c]FURAN AND -[b]FURAN [1]

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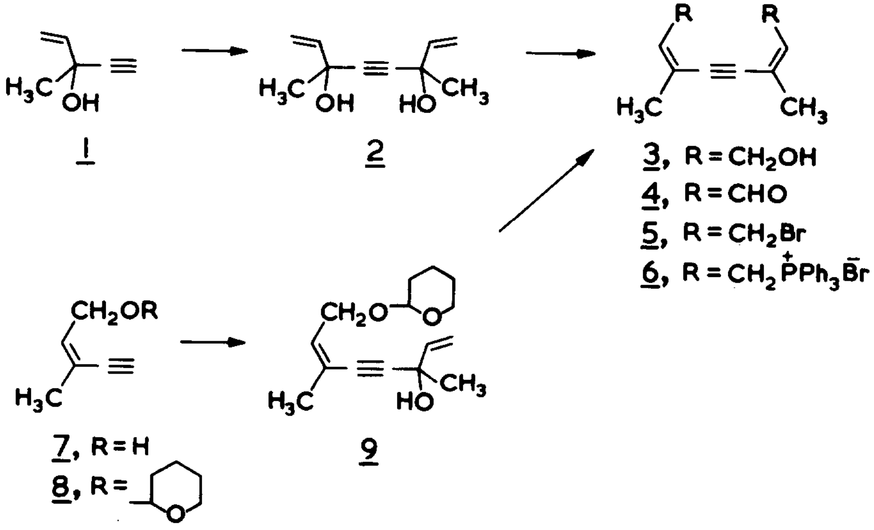
(Received in UK 6 October 1975; accepted for publication 9 October 1975)

It is interesting to study the effect produced by annelation of a 6π-ring onto macrocyclic "antiaromatic" (4*n*) and "aromatic" (4*n*+2) π-systems. We now describe syntheses of the novel annelated monodehydro[12]annulenes **10**, **11**, **12**, and **13**,[2] in which a conjugated 12-membered ring is fused to thiophene, furan and benzene. Related bisdehydro[14]annulenes are discussed in the following Communication.[3]

Treatment of 3-methylpent-1-en-4-yn-3-ol (**1**) [4] with 2 mol equiv of EtMgBr and then with 1 mol equiv of methyl vinyl ketone (MVK) in C_6H_6-Et_2O led to the crude diol **2** (stereoisomeric mixture), which was rearranged in Et_2O with 4N H_2SO_4 at 25° for 12 hr. The resulting diol **3** (*ca* 15% yield based on **1**), mp 105-106°,[5] was expected to possess the thermodynamically favoured "*cis*,*cis*" (Z,Z) stereochemistry,[6] and this was confirmed by the ¹H-nmr spectrum of the derived

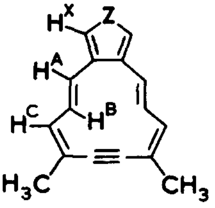


dialdehyde 4 and by its further transformations. Alternatively, the diol 3 could be obtained in *ca* 20% over-all yield from the vitamin A intermediate "*cis*"-3-methylpent-2-en-4-yn-1-ol (7)[6,7] through successive conversion to the tetrahydro-2-pyranyl ether 8, treatment with BuLi and then MVK (1 mol equiv each), reaction of the product 9 with AcOH, Ac_2O and *p*-toluenesulphonic acid[8] (20°, 90 min), and finally saponification of the resulting 3 diacetate with K_2CO_3 in MeOH.

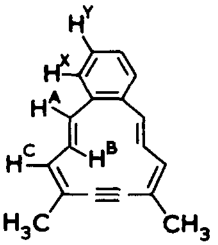
Oxidation of the diol 3 in CH_2Cl_2 with MnO_2 at 20° for 2 hr yielded 85% of the rather unstable dialdehyde 4 as pale yellow needles, mp 78-80°. Bromination of 3 in Et_2O with an excess of PBr_3 at -5° to 20° led to the dibromide 5, which on treatment with 2 mol equiv of PPh_3 in DMF at 40° for 3 hr gave the bisphosphonium salt 6 in 55% yield (based on 3) as a solvate with 2 molecules of DMF (determined from the ^{1}H-nmr spectrum).

Reaction of thiophene-3,4-bis(methylenetriphenylphosphonium bromide)[3] with BuLi (2 mol equiv) in THF at 20° for 1 hr, and treatment of the resulting bisylide with the dialdehyde 4 (1 mol equiv) at 20° for 1 hr yielded 6.5%[9] of the dimethylmonodehydro[12]annuleno[*c*]-thiophene 10[10a] as yellow plates, mp 157-158°; *m/e* 238.083 (calcd 238.082); λ_{max} (Et_2O) 248 (ϵ 13,700), 285 (28,100), *ca* 365 nm (1400); ^{1}H-nmr ($CDCl_3$, 100 MHz) τ 2.64 (dd, *J* = 16, 7.5 Hz, H^B], 2.91 (d, *J* = 16 Hz, H^A), 3.01 (s, H^X), 3.78 (d, *J* = 7.5 Hz, H^C), 8.10 (s, CH_3). Similar reaction of furan-3,4-bis(methylenetriphenylphosphonium chloride)[11] with BuLi and then with 4 led to 5%[9] of the dimethylmonodehydro[12]annuleno[*c*]furan 11[10b] as yellow needles, mp 131-132° dec; *m/e* 222.103 (calcd 222.104); λ_{max} (Et_2O) 240 (ϵ 21,900), 254sh (25,700), 271 (35,100), 333 nm (4300); ^{1}H-nmr ($CDCl_3$, 100 MHz) τ 2.11 (dd, *J* = 16.5, 8.5 Hz, H^B), 2.79 (s, H^X), 3.53 (d, *J* = 16.5 Hz, H^A), 3.72 (d, *J* = 8.5 Hz, H^C), 8.12 (s, CH_3).

Treatment of the bisphosphonium salt 6 with BuLi (2 mol equiv) in Et_2O, followed by reaction with *o*-phthalaldehyde (1 mol equiv) gave 4%[9] of the dimethylbenzomonodehydro[12]annulene 12,[10c] which could also be obtained (2.5% yield) by treatment of the dialdehyde 4 and *o*-xylylenebis-(triphenylphosphonium bromide)[12] (1 mol equiv each) with LiOEt (2 mol equiv) in EtOH. Substance 12 formed orange plates, mp 143-144°, *m/e* 232.124 (calcd 232.125), λ_{max} (Et_2O) 233sh (ϵ 14,900), 258 (34,100), 274 (39,400), *ca* 380 nm (850). The ^{1}H-nmr spectrum of 12 ($CDCl_3$, 100 MHz) was remarkably simple, consisting of a 4H two-line signal at τ 2.33, 2.36 (H^A, H^B), a 4H singlet at 2.92 (H^X, H^Y), a 2H multiplet at 3.90 (H^C), and a 6H singlet at 8.19 (CH_3). The assignments are based on the ^{1}H-nmr spectra of the dideuterio derivatives 12 (D instead of H^A)[13]



10, Z = S
11, Z = O



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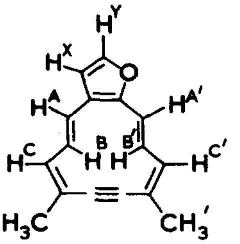

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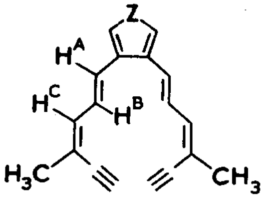
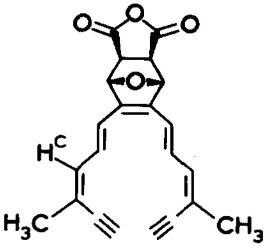
and 12 (D instead of H^B).[14] Although polybenzo[12]- and -[16]annulenes are well known,[15] 12 is the first example of a macrocyclic [4n]annulene annelated to only one benzene ring.

Treatment of 6 with BuLi (2 mol equiv) in THF, followed by reaction with furan-2,3-dicarboxaldehyde [16] (1 mol equiv) led to 0.6% [9] of the dimethylmonodehydro[12]annuleno[b]furan 13 [10d] as red crystals, mp 100-102°; m/e 222.104 (calcd 222.104); λ_{max} (Et_2O) 256 (ε 33,300), 276sh (25,500), 372 nm (1670); ^1H-nmr ($CDCl_3$, 100 MHz) τ -0.12 (dd, J=17, 10 Hz, $H^{B'}$), 1.86 (dd, J=17, 6.5 Hz, H^B), 2.22 (d, J=17 Hz, H^A), 2.91 (d, J=2 Hz, H^Y), 3.50 (d, J=17 Hz, $H^{A'}$), 3.94 (d, J=2 Hz, H^X), 4.09 (d, J=10 Hz, $H^{C'}$), 4.20 (d, J=6.5 Hz, H^C), 8.32 (broad s CH_3, CH_3'). This assignment is based on the ^1H-nmr spectrum of the monodeuterio derivative 13 (D instead of H^A), prepared from 6 and furan-2-carboxaldehyde-3-deuteriocarboxaldehyde.[17] Attempts to prepare the thiophene analogue of 13 by a similar route were unsuccessful.

We believe the trans double bonds of 10, 11, and 12 to be conformationally mobile on the ^1H-nmr time-scale, although their spectra were essentially unchanged on cooling to -60°. Support for this view is provided by the fact that both the H^A and H^B resonances are shifted downfield as compared to the "open" models 14,[3] 15,[18] and 16,[19] as would be expected for fluxional paratropi molecules. In 13, the $H^{A'}$, $H^{B'}$ trans double bond appears to be fixed in the indicated conformatio as shown by the unusually low field $H^{B'}$ resonance (τ -0.12) and the magnitude (10 Hz) of $J_{B',C'}$; the H^A, H^B trans double bond in 13 seems to be mobile, as the H^A and H^B resonances are similar and move towards each other and then cross over on cooling (-67°: H^A, τ 1.64; H^B, τ 2.32).



14, Z = S
15, Z = O
16, Z = CH═CH



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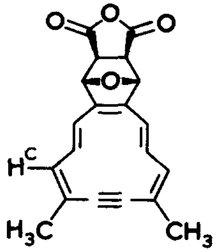

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The best ring current probe in this type of dehydroannulene is provided by the H^C and CH_3 ^1H-nmr resonances, since these protons must be external. The resonances of these protons in 10, 11, 12, and 13 are given in Table 1, together with those of the tetraalkylated monodehydro[12]annulene 18,[20] and of the "open" models 14-17.[3,18,19,20] It is evident that all the monodehydro[12]annulenes are paratropic, the ring current of the macrocycle being reduced in the order tetraalkylannulene 18 > annuleno[b]furan 13 > benzannulene 12 > annuleno[c]thiophene 10 $\simeq$ annuleno[c]furan 11. This finding, as well as the effect on the ^1H-nmr resonances of the 6π systems caused by annelation of the 12-membered rings in 10, 11, 12, and 13, are discussed in the following Communication.[3]

Acknowledgments. We thank the Science Research Council for financial support, Hoffmann-La Roche, Basel, for a gift of 7, and Mr. R.R. Jones for providing furan-2,3-dicarboxaldehyde.

Table 1. H^C and CH_3 ^{1}H-Nmr Resonances of Annelated and Alkylated Monodehydro[12]annulenes, and of their "Open" Models, in $CDCl_3$ at 100 MHz, 27° (τ Values; Internal Standard, TMS).

Compound	H^C	CH_3
18, alkyl	4.27	8.35
13, [b]furan	4.20, 4.09 ($H^{C'}$)	8.32
12, benzo	3.90	8.19
10, [c]thiophene	3.78	8.10
11, [c]furan	3.72	8.12
14-17, models	3.51 - 3.62	7.98 - 8.04

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9. Isolated by chromatography on silica gel.
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15. For references, see P.J. Garratt and K. Grohmann in "Houben-Weyl, Methoden der Organischen Chemie", Vol V, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, p.527, Table 6.
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