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THE SYNTHESIS AND PROTONATION OF MONO- AND DIBENZOBISDEHYDRO[15]ANNULENONES. THE EFFECT OF BENZANNELATION ON THE DIATROPICITY OF A CONFORMATIONALLY FIXED MACROCYCLIC $(4n+2)$ π-ELECTRON SYSTEM [1]

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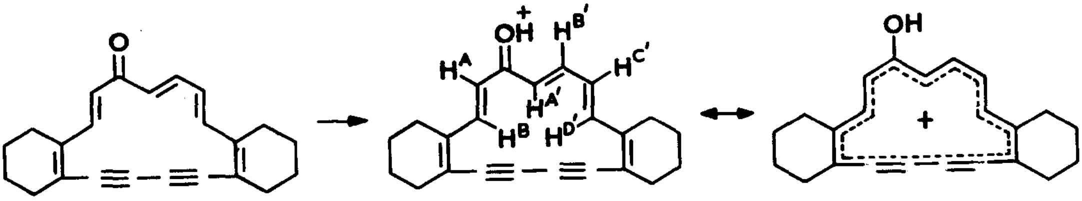
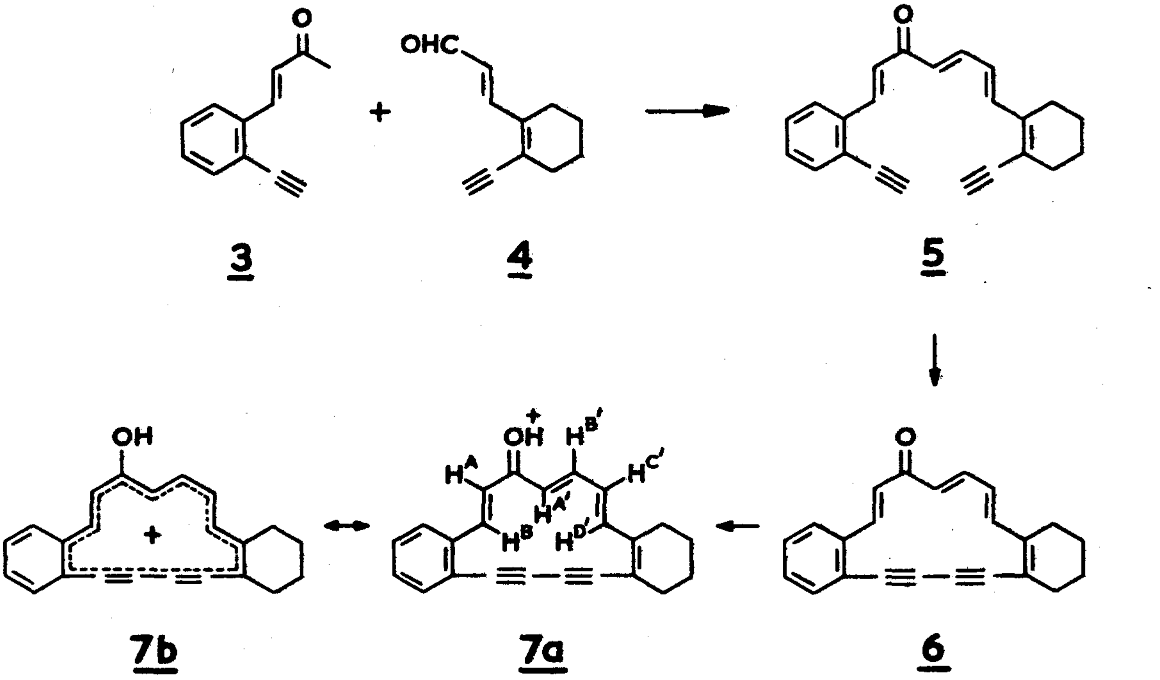
The effect on the ring current of macrocyclic conjugated systems produced by annelation of one or more benzene rings is of considerable interest.[2] In the 1,3-bisdehydro[14]annulene series, it has been shown that fusion of a benzene ring reduces the diatropicity of the macrocycle,[3] but the interpretation of the data is complicated due to the conformational mobility of the "parent" systems.[4] The bisdehydro[15]annulenone 1 and the strongly diatropic, conformationally fixed, protonated species 2 have been prepared previously.[5] We now describe syntheses of the protonated bisdehydro[15]annulenones 7 and 13, formally derived from 2 by replacement of one or of both cyclohexene rings by benzene. This has enabled us to study the effect on the ring current produced by fusion of one and of two benzene rings onto a strongly diatropic conformationally fixed macrocyclic $(4n+2)$ π-electron system, while keeping possible changes in stereochemistry to a minimum.

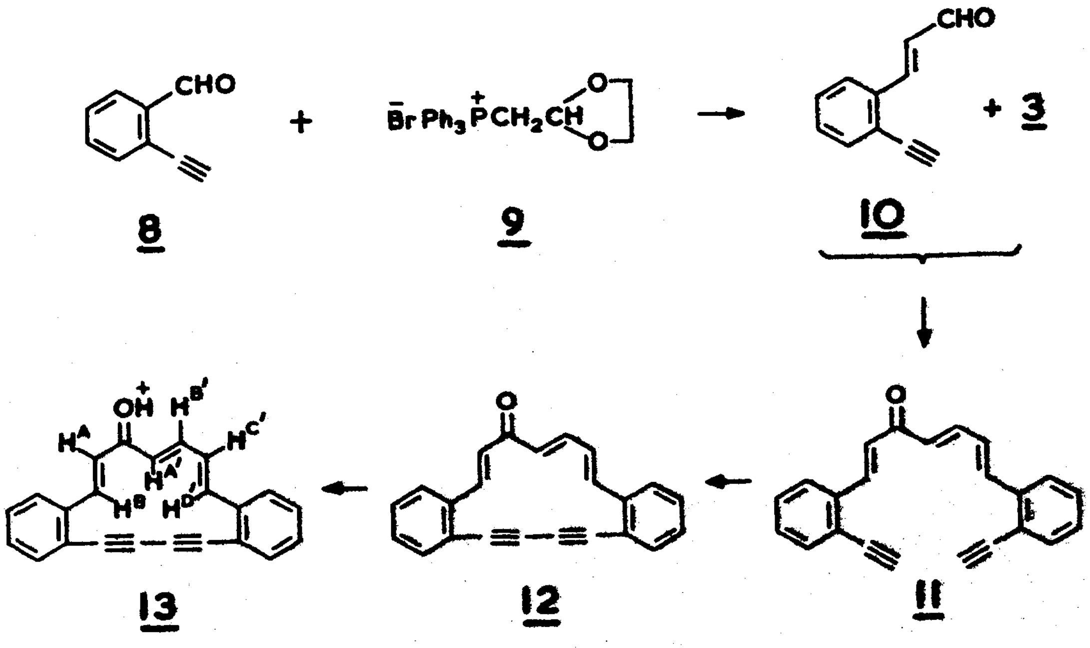


1 2a 2b

Reaction of equimolar amounts of the ketone 3 [6] and the aldehyde 4 [7] in ether in the presence of methanolic KOH under N_2 for 4 hr at -10° led to crude 5,[8a] which was coupled directly with cupric acetate in pyridine at 55°. Preparative layer chromatography on Kieselgel $PF_{254 + 366}$ then gave 11% (based on 3 and 4) of the essentially atropic monobenzobisdehydro[15]annulenone 6 as yellow crystals; decomp. ca 140°; m/e 310.135 (calcd. 310.136); ^{1}H-nmr ($CDCl_3$, 100 MHz) τ 2.07 (1H, m), ca 2.35 - 3.9 (9H, m), 7.6 (4H, m), 8.25 (4H, m); ir (KBr) 1640vs, 1605s cm^{-1}; λ_{max} (ether) 249 (ε 22,100), 280sh (32,700), 303 (38,700), 378 nm (9200). Treatment of 6 with CF_3COOH gave a violet solution of 7 (λ_{max} 373, 498, 612 nm), from which 6 could be regenerated on quenching with aqueous $NaHCO_3$.



o-Ethynylbenzaldehyde (8)[6] was converted to the vinylogue 10 by the method of Cresp et al.[9] Reaction of 8 and the salt 9[9] in DMF with ethanolic LiOEt at 90°, followed by hydrolysis with conc HCl in THF at room temperature, gave 70% of 10[10] (isolated by chromatography on Al_2O_3) as needles, mp 94–95°;[8b,11] λ_{max} (ether) 241 (ε 29,500), 247 (28,000), 289 nm (27,000). Condensation between 3 and 10, essentially as indicated for the reaction of 3 with 4, yielded



60% of 11 (isolated by chromatography on Al_2O_3) as yellow needles, mp ca 112-116° decomp;[8c,11] ir (CCl_4) 1655m, 1620s, 1590s cm^{-1}; λ_{max} (ether) 345 nm (ε 40,300). Oxidative coupling of 11 to 12 proved troublesome, but this reaction could be carried out in low yield with cupric acetate in DMF at 50°; chromatography on Al_2O_3 and then on SiO_2 yielded 7.5% of the atropic dibenzobisdehydro[15]annulenone 12 as bright yellow crystals; decomp ca 150°; m/e 306.103 (calcd. 306.104); ^{1}H-nmr ($CDCl_3$, 100 MHz) τ 2.0 - 3.3 (complex m); ir (KBr) 1650s, 1625m, 1580s cm^{-1}; λ_{max} (ether) 300 (ε 50,500), ca 350sh nm (13,800). Finally, treatment of 12 with CF_3COOH gave a dark red solution of 13 (λ_{max} 340sh, 370sh, 530 nm), from which 12 could be regenerated by quenching with aqueous $NaHCO_3$.

The ^{1}H-nmr parameters of the protonated ketones 2, 7 and 13 (in CF_3COOD) are given in Table 1. The monobenzannelated compound 7 is clearly still diatropic, as indicated by the relative chemical shifts of the inner and outer olefinic protons, the low-field allylic and non-allylic proton resonances (normal values, ca τ 7.7 and 8.3, respectively), as well as the low-field benzenoid resonances.[12,13] However, comparison with the chemical shifts of the corresponding protons in 2 show that 7 is considerably less diatropic than 2. By contrast, the dibenzannelated compound 13 is atropic, all the protons resonating at τ 2.1 - 3.2. Replacement of one of the cyclohexene rings of 2 by benzene therefore reduces the diamagnetic ring current, whereas replacement of both cyclohexene rings by benzene eliminates it.

Table 1. ^{1}H-Nmr Parameters of 2, 7, and 13 in CF_3COOD (τ Values; Internal Standard, TMS; J Values in Hz in Parentheses).

Proton	2[a]	7[b]	13[b,c]
H^B	9.61d (15)	5.71d (16)	2.1 - 3.2m
$H^{A'}$	9.76d (15)	6.14d (16)	
$H^{D'}$	9.88d (15)	6.52d (16)	
H^A	1.49d (15)	1.94d (16)	
$H^{B'}$	0.37dd (15, 7)	1.24dd (16, 7)	
$H^{C'}$	1.45dd (15, 7)	2.14dd (16, 7)	
Benzenoid H	-	1.25 - 1.5m (1H) 1.75 - 2.15m (3H)	
Allylic H	6.5m	7.1m	-
Nonallylic H	7.6m	8.0m	-

[a] At 60 MHz (see reference 5).

[b] At 100 MHz.

[c] At -10° using a time-averaged computer.

The nmr sample of 13 in CF_3COOD was considerably less stable than that of 2 or 7 (appreciable decomposition was observed after several hours at room temperature), and this is in accord with its "non-aromaticity".

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9. T.M. Cresp, M.V. Sargent, and P. Vogel, *J. Chem. Soc. Perkin I*, 37 (1974).
10. Dr. J. Ojima has informed us that he and his coworkers have independently converted **8** to **10** by the same method (J. Ojima, A. Kimura, Y. Yokoyama, and T. Yokoyama, *Bull. Chem. Soc. Japan*, in press).
11. A satisfactory elemental analysis was obtained.
12. See D. Cremer and H. Günther, *Liebigs Ann. Chem.*, **763**, 87 (1972).
13. The small downfield shift of all of the protons expected to be caused by the positive charge does not significantly affect the argument.