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SYNTHESIS AND PROPERTIES OF THREE BENZANNELATED ANNULENONES

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Recently, the effect of annelation of benzenoid nuclei on the diatropicity of macrocyclic conjugated systems has been discussed on some examples.1)

Similarly, the properties of 4n π-electron systems fused by one or more benzene rings are of considerable interest.2)

We now describe syntheses and properties of three benzannelated bisdehydro[13], [17] and [21]annulenones (5) (10) (13).

Condensation of the aldehyde (1)3) with excess acetone by means of aqueous sodium hydroxide at room temperature gave 52% yield of the ketone (2) as yellow plates, mp. 64-65°;4)5)6) Mass: m/e 170 (M^+); IR (KBr): 1700, 1615, 1595 cm^{-1} (>C=0, >C=C<); UV (EtOH): $\lambda_{max}(\varepsilon)$ 230 sh (14,400), 242 (17,700), 247 (16,200), 291 nm(13,800); NMR $\tau(CDCl_3$, 60MHz): 2.02 d J=16 (1H), 2.32-2.80 m (4H), 3.33 d J=16Hz (1H), 6.57 s (1H), 7.59 s (3H).

Reaction of equimolar amounts of (2) and the aldehyde (3)7) in peroxide-free ether in the presence of methanolic potassium hydroxide for 2 hours at room temperature led to 10% yield of the ketone (4) as an unstable orange oil, IR (neat): 1660, 1615, 1600 cm^{-1} (>C=0, >C=C<); UV (EtOH): $\lambda_{max}(\varepsilon)$ 226 (11,000), 248 (9,230), 321 nm(8,830); NMR $\tau(CDCl_3$, 60MHz): 1.98 d J=17 (1H), 2.13 dd J=17, 11 (1H), 2.47-3.10 m (4H), 3.32 d J=11 (1H), 3.42 d J=17 (1H), 3.68 d J=17Hz (1H), 6.87 s (2H), 8.07 s (3H).

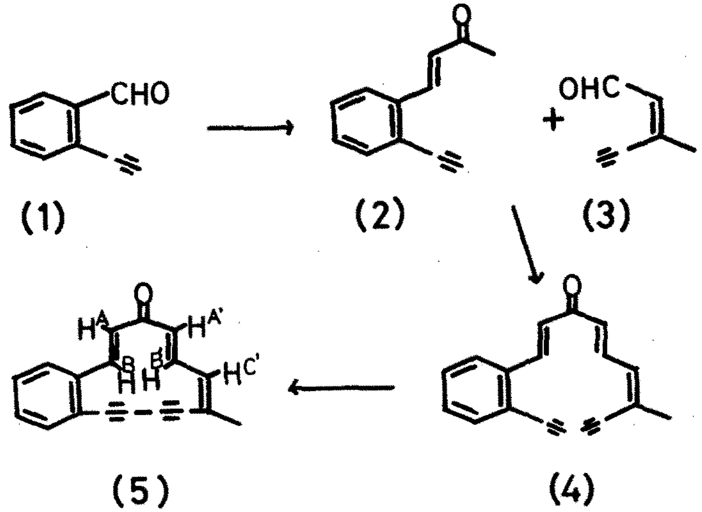
Oxidation of (4) with cupric acetate in pyridine8) at 60° yielded 20% of the monobenzobisdehydro[13]annulenone (5) as relatively stable orange needles, mp. ca. 160° (dec); Mass: m/e 244 (M^+); IR (KBr): 1630, 1610, 1590 cm^{-1} (>C=0, >C=C<); UV (EtOH); $\lambda_{max}(\varepsilon)$ 233 (9,880), 258 (15,800), 388 nm(2,100); NMR: see Table 1.

Treatment of (5) with trifluoroacetic acid gave a dark red solution, NMR τ(60MHz): 0.19 dd J=17, 11 ($H^{B'}$), 0.65 d J=17 (H^B), 2.80-2.97 (benzenoid H), 3.42 d J=11 ($H^{C'}$), 3.47 d J=17 (H^A or $H^{A'}$), 3.75 d J=17Hz (H^A or $H^{A'}$), 8.20 s (CH_3).

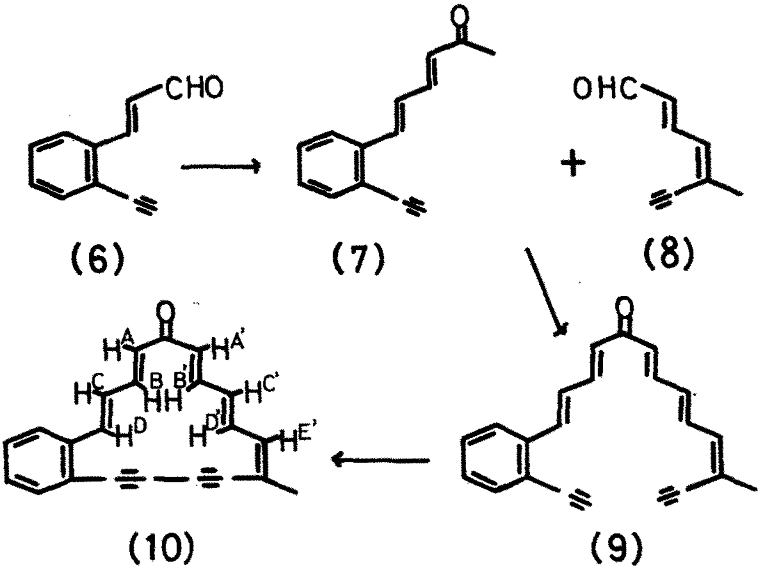
Condensation between the ketone (7) (obtainable in 80% yield from (6)9)) and the aldehyde (8)10), under the same conditions as indicated for the reaction of (2) and (3), yielded 24% of the ketone (9) as yellow-brown needles, mp. 121.5-122.5°5); Mass: m/e 298 (M^+); IR (KBr): 1660, 1605, 1600 cm^{-1} (>C=0, >C=C<); UV (THF): $\lambda_{max}(\varepsilon)$ 258 (20,200), 267 (21,800), 288 sh(18,500), 378 nm(40,700); NMR $\tau(CDCl_3$, 100MHz): 2.45 dd J=15, 11 (1H), 2.48 dd J=15, 11 (1H), 2.49 d J=15 (1H), 2.53 dd J=15, 11 (1H), 2.52-2.78 m (4H), 2.95 d J=15 (1H), 3.05 dd J=15, 11 (1H), 3.44 d J=15 (1H), 3.53 d J=15 (1H), 3.54 dd J=15, 11Hz (1H), 6.57 s (1H), 6.61 s (1H), 8.10 s (3H).

Oxidation of (9) with cupric acetate in pyridine as before afforded 12% yield of the monobenzannelated bisdehydro[17]annulenone (10) as yellow needles, mp. ca. 180° (dec); Mass: m/e

296 (M$^+$); IR (KBr): 1630, 1595 cm^{-1} ($\rangle$C=O, $\rangle$C=C$\langle$); UV (THF): λ_{max}(ε) 285 sh(28,500), 299 (35,500), 317 (30,400), 400 nm(2,760); NMR: see Table 1.



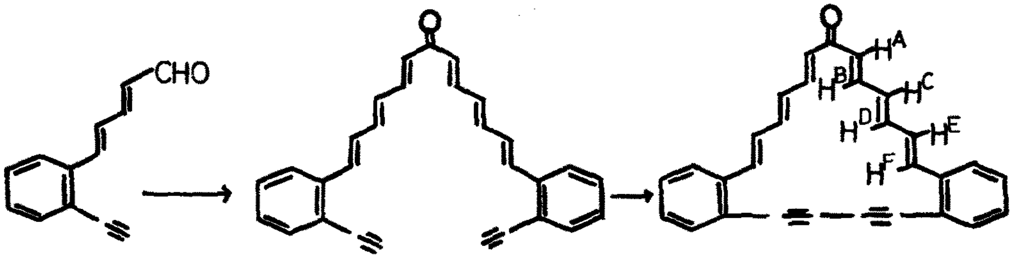
(1) (2) (3) (5) (4)



(6) (7) (8) (10) (9)

Condensation of the aldehyde (11) (2 mol) (obtainable in 49% yield from (6) by the method of Cresp et al.$^{9)11)}$ with acetone (1 mol) as indicated for the reaction of (2) and (3) gave 88% yield of the ketone (12) as orange needles, mp. 153.5-154.5°$^{5)6)}$; Mass: m/e 386 (M$^+$); IR (KBr): 1650, 1620, 1600 cm^{-1} ($\rangle$C=O, $\rangle$C=C$\langle$); UV (THF): λ_{max}(ε) 266 (21,600), 275 (22,000), 303 sh (24,100), 311 (24,500), 405 nm(72,300); NMR τ(CDCl$_3$, 100MHz): 2.34-2.65 m (7H), 3.06 dd dd J=15, 11 (1H), 3.22 dd J=15, 11 (1H), 3.54 d J=15Hz (1H), 6.62 s (1H).

Oxidation of (12) with cupric acetate in pyridine at 60° for 2 hours afforded the dibenz-annelated bisdehydro[21]annulenone (13) in 17% yield as yellow needles, mp. ca. 210° (dec); Mass: m/e 384 (M^+); IR (KBr): 1620, 1605, 1595 cm^{-1} ($>C=O$, $>C=C<$); UV (THF): $\lambda_{max}(\varepsilon)$ 283 sh (23,200), 310 nm(72,800); NMR: see Table 1.



(11) (12) (13)

Table 1. ^{1}H-nmr spectra of (5), (10), and (13) in $CDCl_3$ (τ-values, Internal standard TMS, J values in Hz in parentheses)

Proton	(5)[a]	(10)[b]	(13)[b]
H^A	3.90 d (16)[c]	4.03 d (16)[d]	3.99 d (16)
H^B	1.45 d (16)	(2.28-2.78)[e)i)]	2.64 dd (16, 11)[g]
H^C		3.51 dd (16, 11)[f]	3.39 dd (16, 11)[h]
H^D		1.94 d (16)	2.52 dd (16, 11)[g]
H^E			3.06 dd (16, 11)[h]
H^F			2.35 d (16)
$H^{A'}$	3.68 d (16)[c]	4.00 d (16)[d]	
$H^{B'}$	1.26 dd (16, 10)	2.10 dd (16, 11)[e]	
$H^{C'}$	3.60 d (10)	3.76 dd (16, 11)[f]	
$H^{D'}$		1.85 dd (16, 11)[e]	
$H^{E'}$		3.50 d (11)	
CH_3	8.17 s	8.13 s	
benzenoid H	2.73-2.92 m	2.28-2.78 m	2.7-2.8 m

a) At 60 MHz.

b) At 100 MHz.

c)d)e)f)g)h) These assignments may be reversed in each group, but most probable values are given in Table 1 by reference to the NMR spectra of the related compounds.[2]

i) This proton signal is submerged by those of benzenoid protons.

The ^{1}H-nmr spectra of the annulenones (5), (10), and (13) are given in Table 1. The monobenzannelated compounds (5) and (10) are suggested to be paratropic, as indicated by the relative chemical shifts of the inner and outer olefinic protons. By contrast, the dibenzannelated compound (13) is atropic.

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References and Notes

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2) On the syntheses of the dibenzannelated [13], [17]annulenones; J. Ojima, Y. Yokoyama, and T. Yokoyama, Chemistry Letters, 1261 (1974); J. Ojima, A. Kimura, and T. Yokoyama, ibid., 207 (1975).

3) J. Ojima, T. Yokomachi, and T. Yokoyama, Chemistry Letters, 633 (1972).

4) We reported a mistaken melting point of (2) in reference 3) by a trivial error.

5) All melting points are not corrected.

6) A satisfactory elemental analysis is obtained.

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10) (8) was prepared in 88% yield from (3) (J. Ojima and F. Sondheimer, unpublished experiment).

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