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TRIMETHYLBISDEHYDRO[23]- AND -[25]ANNULENONES

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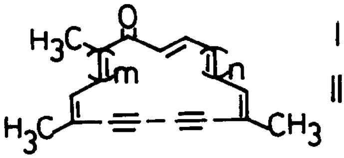
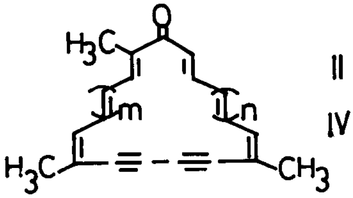
Summary: Syntheses of trimethylbisdehydro[23]- and -[25]annulenones have been described, and the examination of their ^{1}H NMR spectra suggests the diatropicity and the paratropicity of the 23-membered and 25-membered rings, respectively.

Syntheses of a series of the diatropic trimethylbisdehydro[15]-,[1] -[19]annulenone[2] of type I and the paratropic trimethylbisdehydro[17]-,[3] -[21]annulenone[4] of type II as well as α-methyl unsubstituted dimethyl compounds have been described previously. And it was shown that the trimethylbisdehydroannulenones with α-methyl substituent, formulated as I, are superior to the corresponding α-methyl unsubstituted ones for the investigation of ring current, since the annulenones with α-methyl group at C_2-position usually have higher conformational stability and molecular planarity than those with α'-methyl group or no α-methyl group.

The finding prompted us to synthesize the higher vinylogs of I and II to test the question of the limiting size for diatropicity and paratropicity in bisdehydroannulenones of these types. In this communication we wish to report the syntheses of 2,9,14-trimethyl-10,12-bisdehydro[23]-(III) and 2,11,16-trimethyl-12,14-bisdehydro[25]annulenone (IV), which are the largest-ring monocyclic annulenone derivatives to be obtained.[5]

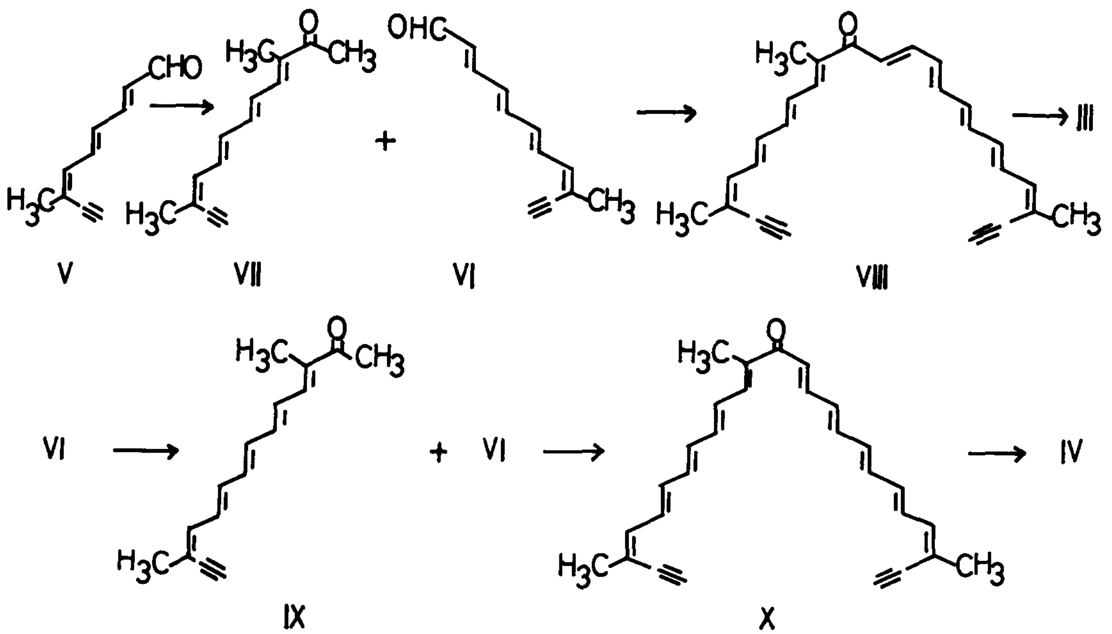


I : m=n=2
III : m=n=3



II : m=n=2
IV : m=n=3

The syntheses of the annulenones III, IV were carried out by the essentially same procedure as reported.[1–4] The Wittig condensation of 7-methyl-2,4,6-nonatrien-8-ynal (V)[6] with 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide[7] and lithium ethoxide, followed by hydrolysis with hydrochloric acid gave 9-methyl-2,4,6,8-undecatetraen-10-ynal [VI,[8] brown needles, mp 84–85°C, 60%, Mass (m/e): 172 (M^+); IR (KBr-disk): 3250 m (≡CH), 2100 w (C≡C), 1680 s (CHO), 1610 m (C=C), 995 s (*trans* -HC=CH-) cm^{-1}; UV: λ_{max}(THF) 244 (ε 5030), 253 (6430), 333 sh (32200), 349 (50700), 367 nm (47900); ^{1}H NMR ($CDCl_3$): τ 0.33 (1H, d, J=8, CHO), 2.80 (1H, dd, J=15, 11, H^7), 3.00 (1H, dd, J=15, 11, H^3), *ca.* 3.1–3.7 (4H, m, H^4, H^5, H^6, H^8), 3.80 (1H, dd, J=15, 8, H^2), 6.53 (1H, s, ≡CH), 7.98 (3H, s, CH_3)]. Condensation of the ketone VII,[2] which has been prepared by acid-catalysed condensation of V with 2-butanone, with VI in the presence of ethanolic sodium ethoxide in ether for 8 h at 2–3°C gave the acyclic ketone [VIII, brown needles, mp 92°C (dec), 66%, Mass (m/e): 354 (M^+); IR (KBr-disk): 3300 m (≡CH), 2100 w (C≡C), 1635 s (C=O), 1595 s



(C=C), 1010 s, 990 s (*trans* -HC=CH-) cm^{-1}; UV: λ_{max}(THF) 286 sh (ε 11100), 340 sh (29900), 355 sh (33800), 372 sh (35600), 400 sh (44600), 418 (50600), 445 sh nm (38700); ^{1}H NMR (CDCl$_3$): τ 2.52–3.85 (15H, m, olefinic H), 6.59 (1H, s, $\equiv$CH), 6.62 (1H, s, $\equiv$CH), 8.00 (9H, s, CH$_3$)]. Oxidative coupling of VIII with anhydrous copper(II) acetate in pyridine and dry ether[9] for 6 h at 50°C yielded the annulenone [III, red cubes, mp 163°C (dec), 6.6%, Mass (m/e): 352 (M$^+$); IR (KBr-disk): 2150 w (C$\equiv$C), 1635 s (C=O), 1620 s (C=C), 980 s (*trans* -HC=CH-) cm^{-1}; UV: λ_{max}(THF) 237 (ε 13400), 283 (24800), 299 (24700), 362 (102000), 456 sh nm (11400) and see Fig. 2; ^{1}H NMR: see Table 1 and Fig. 1]. The acid-catalysed condensation of the aldehyde VI with 2-butanone afforded the ketone [IX, orange needles, mp 98–99°C, 28%, Mass (m/e): 226 (M$^+$); IR (KBr-disk): 3280 m ($\equiv$CH), 2100 w (C$\equiv$C), 1670 s, 1660 s (C=O), 1620 m (C=C), 1005 s (*trans* -HC=CH-) cm^{-1}; UV: λ_{max}(THF) 245 sh (ε 51900), 251 (61300), 255 (60400), 262 sh (46200), 277 sh (10400), 339 sh (39900), 378 (58500), 400 nm (54800); ^{1}H NMR (CDCl$_3$): τ 2.60–3.85 (8H, m, olefinic H), 6.60 (1H, s, $\equiv$CH), 7.64 (3H, s, CH$_3$), 8.02 (3H, s, CH$_3$), 8.08 (3H, s, CH$_3$)]. The condensation of VI with IX as that with VII afforded the acyclic ketone [X, brown cubes, mp 146°C (dec), 88%, Mass (m/e): 380 (M$^+$); IR (KBr-disk): 3300 m ($\equiv$CH), 2100 w (C$\equiv$C), 1635 s (C=O), 1605 s (C=C), 1005 s, 990 s (*trans* -HC=CH-) cm^{-1}; UV: λ_{max}(THF) 256 (ε 6170), 346 sh (42800), 366 (49800), 387 sh (53900), 418 (69600), 432 (72700), 456 sh nm (58800); ^{1}H NMR (CDCl$_3$): τ 2.47–3.75 (17H, m, olefinic H), 6.60 (2H, s, $\equiv$CH), 8.00 (9H, s, CH$_3$)]. Oxidative coupling of X as before yielded the annulenone [IV, purple needles, mp 145°C (dec), 5.0%, Mass (m/e): 378 (M$^+$); IR (KBr-disk): 2100 w (C$\equiv$C), 1640 m (C=O), 1615 s, 1595 s (C=C), 1000 s (*trans* -HC=CH-) cm^{-1}; UV: λ_{max}(THF) 268 (ε 11800), 338 sh (65700), 355 (96300), 371 (106000), 494 sh nm (4310) and see Fig. 2; ^{1}H NMR: see Table 1 and Fig. 1].

The FT ^{1}H NMR spectra of III and IV are indicated in Fig. 1. Essentially temperature independent ^{1}H NMR spectra of III and IV in the range of -60 to 60°C were observed. The ^{1}H

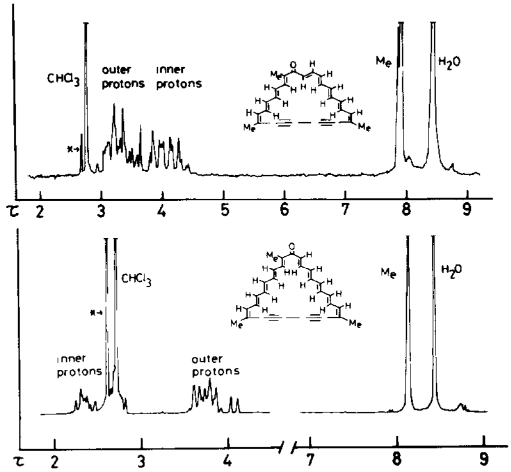
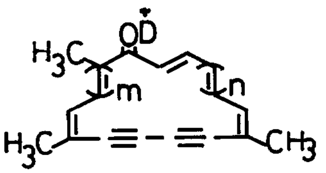
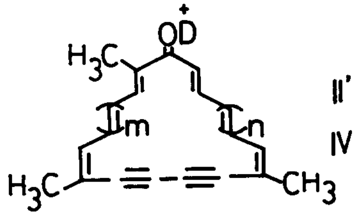


Fig. 1. The FT ^{1}H NMR spectra of III (at 100 MHz) and IV (at 200 MHz) in $CDCl_3$ at 22°C (*: The signal due to benzene used as recrystallization solvent)



I': m=n=2
III': m=n=3



II': m=n=2
IV': m=n=3

NMR chemical shifts of the olefinic and methyl protons of the annulenones III, IV, altogether with those of their respective lower vinylogs I, II, are listed in Table 1. The chemical shifts of the protons of the deuteronated species I'–IV' which were obtained by dissolving in deuteriotrifluoroacetic acid, are also given in Table 1.

Comparison of the chemical shifts of various olefinic protons of the [23]annulenone III and the [25]annulenone IV with those of the corresponding acyclic ketones VIII and X is difficult owing to overlapping peaks. However, the methyl protons of III (τ 7.86, 7.91) resonate at a slightly lower field than those of the corresponding acyclic model VIII (τ 8.00), whereas the methyl protons of IV (τ 8.15) resonate at a slightly higher field than those of the corresponding acyclic model X (τ 8.00), suggesting that III is diatropic, as might be expected of 22π-system, while IV is paratropic, as might be expected of 24π-system.

The support for this interpretation follows from the systematic examination of both the ^{1}H NMR spectra (Table 1, Figure 1) and the electronic spectra (Figure 2) of the compounds I–IV, with reference to the results obtained previously.[10]

It is evident that in the spectra of [23]annulenone III, the inner protons resonate at higher

Table 1. The ^{1}H NMR data of I–IV (in $CDCl_3$) and I'–IV' (in CF_3COOD) at 22°C (τ values)

Trimethylbisdehydro[n]annulenone		inner H	outer H	CH_3
I	-[19]-	3.87–4.48	2.87–3.40	7.79, 7.83
I'		7.12–9.54	0.84–2.90	6.84, 6.94
II	-[21]-	1.92–2.32	3.63–4.07	8.18
II'		-1.17– -1.98	4.23–4.55	8.28, 8.49
III	-[23]-	3.70–4.29	2.95–3.56	7.86, 7.91
III'[a)]		6.84–7.85	1.30–2.15	7.08, 7.12, 7.24
IV	-[25]-	2.24–2.82	3.60–4.10	8.15
IV'		-0.33– -1.43	3.97–4.76	8.23, 8.49

a) Keeping the species III' resulted in a change (under investigation).

field than the outer protons, while in the spectra of [25]annulenone IV, the inner protons resonate at lower field than the outer protons. The simplest test for the nature of the ring currents is provided by the chemical shifts of the methyl protons, since these must be external in these compounds I–IV and can readily be recognized. The alternation of the methyl proton resonances between III (relatively low field) and IV (relatively high field) is seen, as has been observed between I and II.[10] And it is seen that the ring currents of the deuteronated species I'–IV' are larger than those of the annulenones I–IV, since the alternation of the methyl proton resonances in I'–IV' is considerably greater than in I–IV.

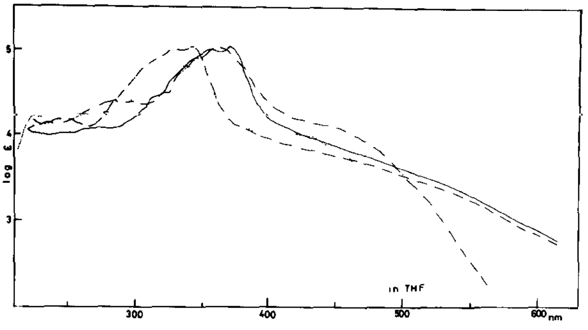


Fig. 2. The UV spectra of I (-·-·-·-·-), II (—·—·—·), III (—··—··), and IV (———)

The electronic absorption spectra of the trimethylbisdehydroannulenones I–IV are illustrated in Figure 2. Although the main maxima of these annulenones exhibit a bathochromic shift as the ring size increases, this shift is very small between the [23]- III and the [25]annulenone IV, as is seen between the [19]- I and [21]annulenone II.[10] This is considered to be due to the occurrence of the same sort of alternation of the main maxima of (4n-2) and 4n systems, as has been observed for the annulenes and dehydroannulenes.[11] Also, it is noted that the alternation of the main maxima in trifluoroacetic acid is observed, the main maxima of [19]- I, [21]- II, [23]- III, and [25]annulenone IV in trifluoroacetic acid occurring at 406, 376, 438, and 417 nm, respectively.

Thus, the results obtained above suggest that the limiting size of the diatropicity and paratropicity of the bisdehydroannulenones of these types lies above 23-membered and 25-membered rings, respectively.

References and Notes

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