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A SIMPLE NEW SYNTHESIS OF MACROCYCLIC DEHYDROANNULENONES. STEREOISOMERIC 4,5:10,11-BIS(TETRAMETHYLENE)-6,8-BISDEHYDRO[15]ANNULENONES [1]

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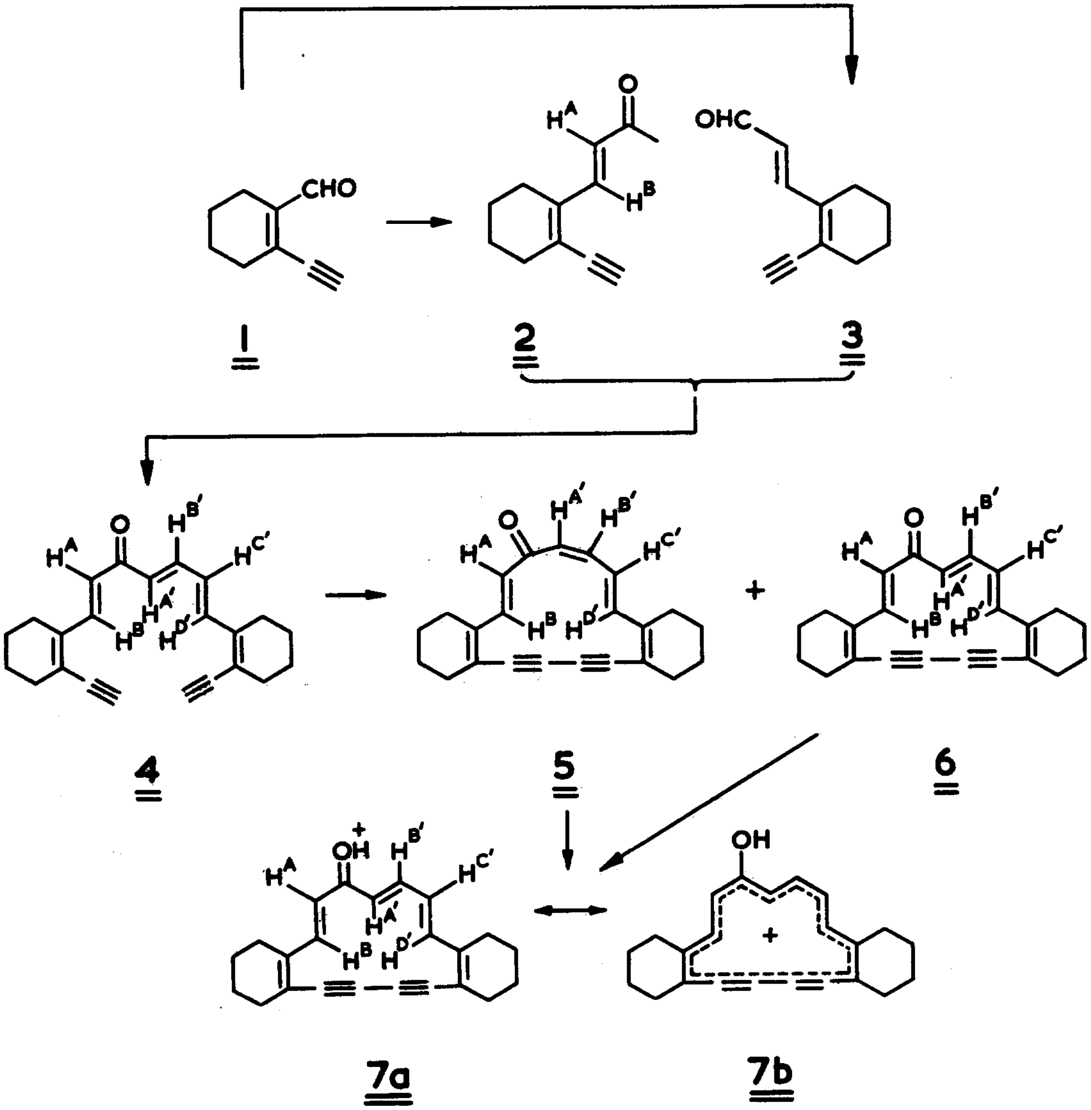
The synthesis of potentially paratropic 13- and 17-membered bisdehydroannulenones by a simple new method was reported in the preceding Communication.[1] We now describe the application of this method to the synthesis of two stereoisomers of a potentially diatropic 15-membered bisdehydroannulenone, namely 4,5:10,11-bis(tetramethylene)-6,8-bisdehydro[15]-annulenone (**5**, **6**).

Condensation of the readily available **1** [4] with excess acetone by means of aqueous NaOH under N_2 for 90 min at 20° gave 60% of **2**, mp 44-45°; _m/e_ 174; IR (CCl_4): 1665s, 1595s cm^{-1}; λ_{max} (pentane) 293 (ϵ 23,200), 305 nm (20,800); NMR (CCl_4): τ 1.25d (1H, _J_ = 16Hz, H^B), 2.95d (1H, _J_ = 16Hz, H^A); 6.60s (1H, acetylenic), 7.45 - 8.0m and 7.75s (total 7H, allylic CH_2 and methyl), 8.0 - 8.5m (4H, nonallylic CH_2). Reaction of equimolar amounts of **2** and **3** (obtainable in 45% yield from **1**) [5] in peroxide-free ether in the presence of methanolic KOH under N_2 for 2 hr at 20° led to 65% of **4** as yellow needles, which decomposed at _ca_ 150° on attempted mp determination; _m/e_ 316; IR (CCl_4): 1645m, 1605s cm^{-1}; λ_{max} (ether) 362 nm (ϵ 31,800); NMR: see Table 1. The all-_trans_ stereochemistry of **4** follows from the NMR spectrum in the presence of $Eu(fod)_3$, which showed four 1H doublets and two 1H double doublets, all with _J_ = 16Hz.

Oxidative coupling of **4** with O_2, CuCl and NH_4Cl in EtOHaq and benzene for 2 hr at 60-65°, followed by chromatography on silica gel, gave successively unchanged **4** (45%), the mono-_cis_ bisdehydro[15]annulenone **5** (6%), and the all-_trans_ isomer **6** (15%). Substance **5** formed orange-yellow crystals, mp 116-118° dec; _m/e_ 314; IR (CCl_4): 1645s, 1590s cm^{-1}; λ_{max} (ether) 315 (ϵ 29,800), _ca_ 390sh nm (9100); NMR: see Table 1. Substance **6** formed orange-red crystals, which decomposed at _ca_ 140° on attempted mp determination; _m/e_ 314; IR (CCl_4):



1645s, 1610m, 1600m cm^{-1}; λ_{max} (ether) 312 (ε 35,900), ca 390sh nm (13,400); NMR: see Table 1. The all-trans stereochemistry of 6 (no conformation implied) again follows from the NMR spectrum in the presence of Eu(fod)$_3$, which showed four 1H doublets and two 1H double doublets, all with J = 16Hz. On the other hand, in the NMR spectrum of 5 in the presence of Eu(fod)$_3$, the two lowest field bands were 1H doublets with J = 16Hz (H^A) and 10Hz (H$^{A'}$), showing the carbonyl group to be flanked by a trans and a cis double bond. Examination of

Table 1. NMR spectra (60 MHz, τ values) of 4, 5, 6 and 7

Proton	4 ($CDCl_3$)[a]	5 ($CDCl_3$)	6 ($CDCl_3$)	7 (CF_3COOD)
H^B	1.85 - 3.90m	2.40 - 3.95m	2.25 - 4.55m	9.61d [b]
$H^{A'}$				9.76d [b]
$H^{D'}$				9.88d [b]
H^A				1.49d [b]
$H^{B'}$				0.37dd [c]
$H^{C'}$				1.45dd [c]
Allylic CH_2	7.4 - 8.0m	7.3 - 7.85m	7.25 - 7.9m	6.2 - 6.8m
Nonallylic CH_2	8.0 - 8.55m	8.0 - 8.5m	8.0 - 8.5m	7.3 - 7.9m

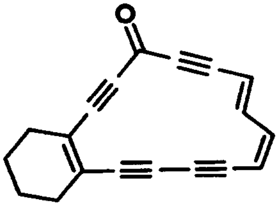
[a] Compound 4 also showed 1H singlets at τ6.55 and 6.60 (acetylenic protons).

[b] J = 15Hz.

[c] J = 15, 7Hz.

molecular models indicates configuration 5 (no conformation implied) to be the most likely, although the alternative structure in which the double bond on the other side of the carbonyl group possesses the *cis* configuration cannot be excluded with certainty.

Comparison of the NMR spectra of 5 and 6 with that of the acyclic analogue 4 shows that neither 5 nor 6 is diatropic, despite their being potential 14 π-electron systems. By contrast, 4,5-tetramethylene-2,6,8,14-tetradehydro[15]annulenone (8), formally derived from 5 or 6 by replacement of the α,α'-ethylenic bonds by acetylenes (and removal of a tetramethylene substituent) has been found to be diatropic.[6] This difference is presumably a consequence of the fact that 5 and 6 are less planar than 8, due to steric



8

and/or strain effects.

On the other hand, the protonated species 7 (violet; λ_{max} 375, 518, 569nm with absorption >700nm), obtained by treatment of either 5 or 6 with CF_3COOH, proved to be strongly diatropic. This follows from the NMR spectrum in CF_3COOD (Table 1), the inner olefinic protons having moved to very high field, and the outer olefinic, allylic and non-allylic protons to low field (this downfield shift is much greater than could be accounted for by the positive charge). Structure 7 follows from an analysis of the NMR spectrum, and was confirmed by quenching with water, when 6 was obtained, irrespective whether 7 had been formed from 5 or 6. It is interesting that 7 is more diatropic than protonated 8, while 5 and 6 are less diatropic than 8, and this is presumably a consequence of the greater number of acetylenes in 8.

REFERENCES AND NOTES

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