A SIMPLE NEW SYNTHESIS OF MACROCYCLIC DEHYDROANNULENONES. 4,5:10,11-

BIS(TETRAMETHYLENE)-6,8-BISDEHYDRO[13]ANNULENONE AND 6,7:12,13-BIS-

(TETRAMETHYLENE)-8,10-BISDEHYDRO[17]ANNULENONE [1]

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Macrocyclic dehydroannulenones (conjugated cyclic enynones) containing 13-, 15- and 17-membered rings have been synthesised previously from terminal diacetylenes by condensation of the mono-Grignard derivatives with ethyl formate, followed by oxidative coupling and oxidation of the hydroxyl groups.[4] The carbonyl group in all of these compounds was flanked by acetylenic bonds on one or both sides. We now report a simple, and apparently general, new synthesis of dehydroannulenones in which the carbonyl group is flanked by ethylenic bonds on both sides. The method so far has been used for the synthesis of potentially paratropic [4] bisdehydro[13]- and bisdehydro[17]annulenone derivatives (this Communication), as well as of potentially diatropic [4] bisdehydro[15]annulenone derivatives (following Communication).

4,5:10,11-Bis(tetramethylene)-6,8-bisdehydro[13]annulenone ($\underline{3}$)

Condensation of the readily available $\underline{1}$ [5] (2 molar equiv) with acetone (1 molar equiv) by means of methanolic KOH in peroxide-free ether under N_2 for 3 hr at 20° gave 55% of $\underline{2}$ as orange-yellow needles;[6] $\underline{m/e}$ 290; IR (CCl_4): 1645s, 1605s cm^{-1}; λ_{max} (ether) 246 (ε 19,200), 343 nm (27,200); NMR ($CDCl_3$): ABq centred at τ 2.02 (H^B), 3.63 (H^A) (4H, $\underline{J}$ = 16Hz), 6.58s (2H, acetylenic), 7.45 - 7.95m (8H, allylic CH_2), 8.15 - 8.55m (nonallylic CH_2). Oxidation of $\underline{2}$ with cupric acetate in pyridine (3 hr at 60°) or with O_2, CuCl and NH_4Cl in EtOHaq and benzene (2 hr at 70°) then yielded 45-50% of $\underline{3}$ as orange crystals;[6] $\underline{m/e}$ 288; IR (CCl_4): 1655m, 1625s cm^{-1}; λ_{max} (ether) 250sh (ε 16,000), 270sh (26,800), 279 (31,000), 394 nm (1160); NMR ($CDCl_3$): ABq centred at τ 0.77 (H^B), 3.77 (H^A) (4H, $\underline{J}$ = 17Hz), 7.55 - 8.1m (8H, allylic CH_2), 8.1 - 8.6m (nonallylic CH_2).

The NMR assignments of the olefinic protons of 2 and 3 were established by condensation

of 1 with acetone-d_6 to give α,α'-dideuterio-2 [m/e 292; NMR (CDCl$_3$): Υ 2.04s (H^B) instead
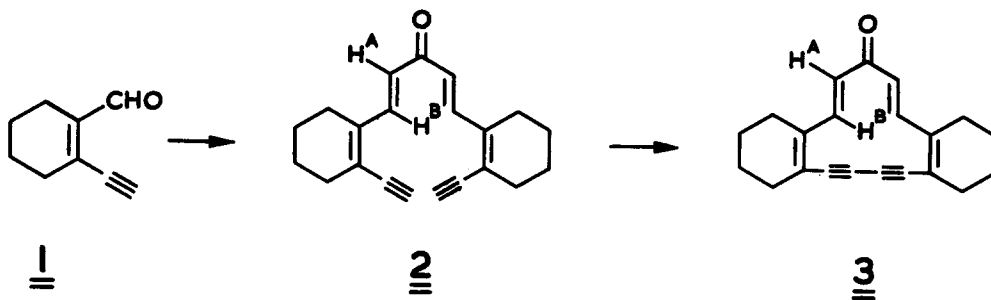
of ABq], which on coupling led to α,α'-dideuterio-3 [m/e 290; NMR (CDCl$_3$): Υ 0.78s (H^B) in-

stead of ABq]. The conformation of 3 was established by these experiments, coupled with the

finding that the Υ 3.77 (H^A) band in 3 is external (nuclear Overhauser effect, irradiation at

Υ 7.8; Eu(fod)$_3$ shift).

Comparison of the NMR spectra of 2 and 3 shows there to be little, if any, paramagnetic

ring current in 3, despite it being a potential 12 π-electron system. The downfield shift of

H^B in 3 as compared to 2 is presumably due to the anisotropy of the triple bond(s),[7] since

there is no significant corresponding upfield shift of H^A. Treatment of 3 with CF$_3$COOH gave

the corresponding carbonyl protonated species [red-brown; λ_{max} 288, 380sh, 410sh, 464sh, 501,

530sh nm, with absorption >700 nm; NMR (CF$_3$COOD): ABq centred at Υ -0.68 (H^B),[8] 3.51 (H^A) [8]

(4H, J = 16Hz), 7.4 - 8.1m (8H, allylic CH$_2$), 8.1 - 8.6m (8H, nonallylic CH$_2$)]. The fact

that the H^A and H^B resonances in the NMR spectrum of 3 in CF$_3$COOD have moved downfield as

compared to 3 in CDCl$_3$ is presumably due mainly to the positive charge, and protonated 3 also

does not seem to be significantly paratropic.

6,7:12,13-Bis(tetramethylene)-8,10-bisdehydro[17]annulenone (6)

Similar condensation of 4 (obtainable in 45% yield from 1)[1] with acetone led to 40% of 5

as orange needles;[6] m/e 342; IR (CHCl$_3$): 1635m, 1605s cm^{-1}; λ_{max} (ether) 278 (ϵ 17,100),

284 (16,400), 378nm (41,700); NMR: see Table 1. Oxidation of 5 with O$_2$, CuCl and NH$_4$Cl in

EtOHaq and benzene for 2 hr at 60° gave 6 (8.5% yield, 17% conversion) as red crystals;[6]

m/e 340; IR (CCl$_4$): 1630s, 1605s cm^{-1}; λ_{max} (ether) 283sh (ϵ 24,200), 298 (32,000), 309

(33,000), 347sh nm (7000); NMR: see Table 1. Treatment of 6 with CF$_3$COOH yielded the

corresponding protonated species [dark green; λ_{max} 333, 348, 390sh, 560sh nm with

4   **5**   **6**
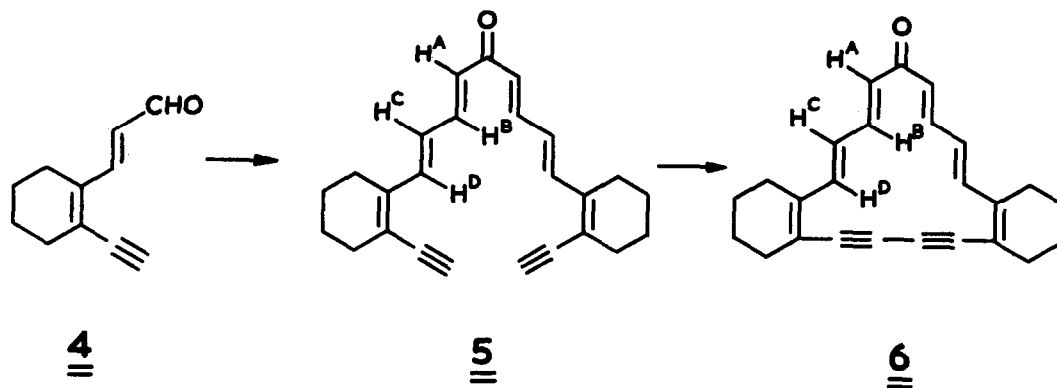
absorption >700nm; NMR (CF$_3$COOD): see Table 1].

Table 1. NMR spectra (60 MHz, γ values) of 5 and 6 [a,b]

Proton	5 (CDCl$_3$) [c]	6 (CDCl$_3$)	6 (CF$_3$COOD)
H^A	3.48d [d]	4.14d [d]	4.38d [d]
H^B	2.45dd [e]	1.42dd [e]	-2.65dd [e]
H^C	3.53dd [e]	3.92dd [e]	4.47dd [e]
H^D	2.58d [d]	1.15d [d]	-2.85d [d]
Allylic CH$_2$	7.45 - 7.9m	7.55 - 8.05m	7.95 - 8.4 m

[a] In addition, all compounds showed a multiplet at ca γ 8.1 - 8.6 (nonallylic CH$_2$).

[b] The assignments of H^A - H^D in 5 and 6, and the conformation of 6 are based on Eu(fod)$_3$ shifts.

[c] Compound 5 also showed a singlet at γ 6.65 (acetylenic protons).

[d] J = 16Hz.

[e] J = 16, 10Hz.

Comparison of the NMR spectra of 5 and 6 in CDCl$_3$ (Table 1) shows 6 to be appreciably paratropic, as expected of a potential 16 π-electron system, the H^A, H^C resonances having moved to significantly higher field, and the H^B, H^D resonances to lower field. This effect is increased in the paratropic protonated species, the upfield shift of the outer protons due to the increased paramagnetic ring current outweighing the downfield shift due to the posit- ive charge. The fact that the lower vinylogue 3 and protonated 3 are not appreciably

paratropic is presumably a consequence of their less planar structure, due to steric and/or strain effects.

REFERENCES AND NOTES

1. Unsaturated Macrocyclic Compounds XCIII. For part XCII, see R.H. McGirk and F. Sondheimer, *Angew. Chem.* in press.

2. On sabbatical leave from Michigan State University.

3. Address inquiries to this author.

4. See F. Sondheimer, *Pure Appl. Chem.* 28, 331 (1971); *Accounts Chem. Res.* 5, 81 (1972).

5. P. Schiess and H.L. Chia, *Helv. Chim. Acta* 53, 485 (1970); G.M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.* 93, 1970 (1971).

6. All new substances decomposed on attempted melting point determination.

7. See H.A. Staab and R. Bader, *Chem. Ber.* 103, 1157 (1970).

8. The assignments of H^A and H^B were established by measurement of the NMR spectrum of α,α'-dideuterio-3 in CF_3COOD.