Synthetic Design of a Spheroidal C_{18}-Oxa-hexaquinane System: Model Studies for the Synthesis of Dodecahedrane

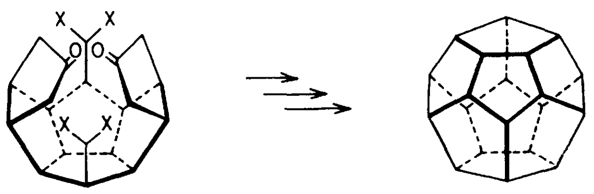
Goverdhan Mehta* and Mangalam S. Nair

School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

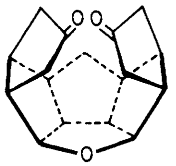
A seven-step synthesis of all-*cis*-4-oxa-octadecahydrodipentaleno[1,2,3-*cd*:1′,2′,3′-*gh*]-pentalene-2,6-dione (**3**) from the readily available hexacyclic ether (**4**) is reported.

Despite Paquette's major achievement of the synthesis of dodecahedrane (**1**),[1] more efficient, alternative syntheses of (**1**) and its precursors and congeners are still being investigated.[2,3] Our approach to (**1**) involves the intermediate (**2**), and we now report the synthesis of the model compound (**3**), which we hope will provide a short and novel access to (**1**) *via* (**2**).

Flash vacuum pyrolysis (f.v.p.; 625 °C; 7 Torr) of the readily available[4] hexacyclic ether (**4**) resulted in a facile (2 + 2) cycloreversion and furnished the C_{12}-oxa-tetraquinane (**5**), m.p. 119.5—120.5 °C, in 95% yield. Addition of a large excess of dichloroketen to (**5**) furnished the bis-adduct (**6**)† m.p. 238—240 °C (decomp.), in 35—40% yield. The dichloroketen must attack the folded (**5**) from the convex face to furnish the *exo*-addition product (**6**). Ring expansion of (**6**) with excess of ethereal diazomethane (0—5 °C; 4 h; 60%)[5] and dechlorination (Zn–NH_4Cl–MeOH; room temp.; 80%) furnished the bis-cyclopentane annelated product (**7**), $C_{17}H_{20}O_3$, m.p. 162—163 °C, ν_{max}(KBr) 1740 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 500 MHz) δ 4.35 (2H, d, J 4.3 Hz), 3.31 (2H, dd),



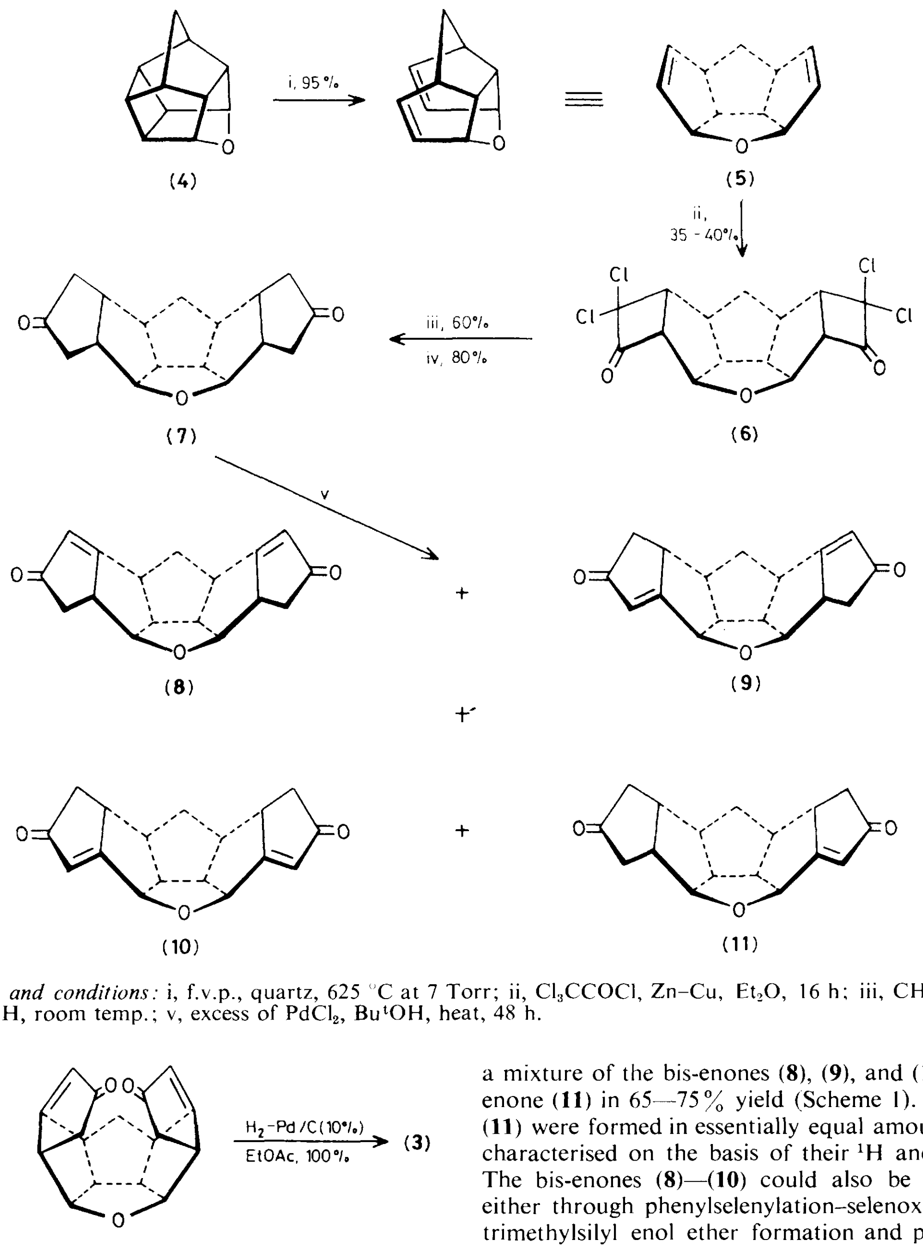
(**2**) (**1**)



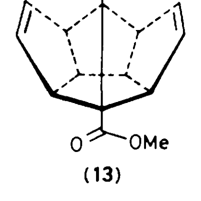
(**3**)

---

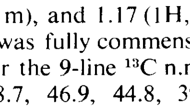
† The regiochemical assignment to the dichloroketen adduct (**6**) is only tentative, but this does not affect the subsequent transformations.



Scheme 1. *Reagents and conditions:* i, f.v.p., quartz, 625 °C at 7 Torr; ii, Cl_3CCOCl, Zn–Cu, Et_2O, 16 h; iii, CH_2N_2–Et_2O, 0—5 °C; iv, Zn–NH_4Cl, MeOH, room temp.; v, excess of $PdCl_2$, Bu^tOH, heat, 48 h.



(12)



(13)

3.03—2.8 (4H, m), 2.45—2.33 (6H, m), 2.23 (2H, d), 2.1 (1H, td), 1.87—1.82 (2H, m), and 1.17 (1H, d with fine structure). The structure of (**7**) was fully commensurate with its spectral data and in particular the 9-line ^{13}C n.m.r. spectrum (δ 218.8, 91.4, 57.0, 54.1, 48.7, 46.9, 44.8, 39.8, and 37.5 p.p.m.) showed that it had a mirror plane of symmetry.

The next steps involved the inversion of the two newly appended cyclopentane rings so that they projected within the interior of the developing sphere. Reaction of (**7**) with excess of $PdCl_2$ in Bu^tOH (reflux; 48 h)[6] transformed it into a mixture of the bis-enones (**8**), (**9**), and (**10**) and the mono-enone (**11**) in 65—75% yield (Scheme 1). Compounds (**8**)—(**11**) were formed in essentially equal amounts and were fully characterised on the basis of their ^1H and ^{13}C n.m.r. data.‡ The bis-enones (**8**)—(**10**) could also be obtained from (**7**) either through phenylselenylation–selenoxide elimination[7] or trimethylsilyl enol ether formation and palladium-mediated

---

‡ Compound (**8**): m.p. 217 °C (decomp.), M^+ m/z 268; ν_{max}(KBr) 1705 and 1640 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 500 MHz) δ 5.86 (2H, d), 4.52 (2H, m), 3.62—3.43 (6H, m), 2.86 (1H, d), 2.82 (1H, d), 2.51 (1H, td), 2.27 (1H, d), 2.24 (1H, d), and 1.86 (1H, td); ^{13}C n.m.r. ($CDCl_3$, 25.0 MHz) δ 208.9, 186.9, 125.1, 91.4, 60.2, 50.2, 49.3, 42.2, and 38.2 p.p.m.; (**9**): m.p. 215 °C (decomp.), M^+ m/z 268; ν_{max}(KBr) 1700 and 1630 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 500 MHz) δ 5.97 (1H, d), 5.83 (1H, d), 5.1 (1H, d), 4.5 (1H, dd), 3.62—3.43 (4H, m), 3.23 (1H, m), 2.84—2.78 (2H, m), 2.72 (1H, td), 2.54 (1H, m), 2.27 (1H, dd), 2.16 (1H, dd), and 1.82 (1H, td); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 214.8, 208.9, 189.1, 184.8, 125.4, 124.8, 90.8, 84.4, 61.0, 51.3, 50.0, 49.5, 49.0, 43.9, 42.0, and 40.9 p.p.m.; (**10**): m.p. 216—218 °C (decomp.), M^+ m/z 268; ν_{max}(KBr) 1702 and 1620 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 100 MHz) δ 6.0 (2H, d), 5.06 (2H, d), 3.6—3.2 (4H, m), 2.84 (1H, d), 2.70 (1H, d), and 2.6—1.6 (6H, m); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 210.0, 183.8, 125.7, 83.1, 60.2, 51.9, 47.7, 43.5, and 29.7 p.p.m.; (**11**): m.p. 148 °C, M^+ m/z 270; ν_{max}(KBr) 1740, 1715, and 1640 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 500 MHz) δ 5.95 (1H, d), 4.87 (1H, d), 4.58 (1H, d), 3.48—3.33 (3H, m), 2.99—2.94 (2H, m), 2.76 (1H, dd), 2.47—2.3 (5H, m), 2.16—2.09 (2H, m), and 1.93—1.80 (2H, m); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 218.0, 210.2, 184.8, 124.9, 92.7, 81.1, 60.2, 58.1, 54.3, 51.3, 49.1, 47.3, 47.2, 44.7, 43.3, 39.2, and 36.9 p.p.m.

dehydrosilylation[8] but these routes offered no substantial advantage over the direct $PdCl_2$-dehydrogenation.[6]

The bis-enone (**8**) on exposure to 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) smoothly epimerised to furnish the bis-enone (**12**) in 90% yield. Its ^1H and ^{13}C n.m.r. signals at δ 209.7, 189.9, 125.6, 81.6, 58.5, 51.3, 46.9, 37.8, and 33.5 p.p.m. established its close structural identity with its precursor (**8**). Catalytic hydrogenation of (**12**) on 10% Pd/C yielded the spheroidal oxa-hexaquinane dione (**3**) in near quantitative yield. The 9-line ^{13}C n.m.r. spectrum (δ 220.2, 87.7, 57.5, 50.1, 43.4, 43.2, 40.4, 38.4, and 32.3 p.p.m.) of (**3**) and the multiplicity of the proton attached to the ether oxygen atom [δ 4.39, dd, J 5.3 Hz; *cf.* δ 4.35, d, J 4.3 Hz for (**7**)] in its 500 MHz ^1H n.m.r. spectrum fully established its formulation.

Finally, repetition of this synthetic sequence with the Hedaya–Paquette tetracyclic diester (**13**)[9] proved efficacious and opened the way to the key precursor (**2**). These results will be published elsewhere.[10]

We thank Dr. A. Srikrishna for 500 MHz ^1H n.m.r. spectra.

Received, 5th January 1983; Com. 025

References

1 R. J. Ternansky, D. W. Balogh, and L. A. Paquette, *J. Am. Chem. Soc.*, 1982, **104**, 4503; L. A. Paquette, R. J. Ternansky, and D. W. Balogh, *ibid.*, p. 4502; L. A. Paquette, D. W. Balogh, R. Usha, D. Kountz, and G. G. Christoph, *Science*, 1981, **211**, 575; L. A. Paquette and D. W. Balogh, *J. Am. Chem. Soc.*, 1982, **104**, 774.

2 P. E. Eaton, *Tetrahedron*, 1979, **35**, 2189, provides an authoritative summary of results in the area; L. A. Paquette, *Top. Curr. Chem.*, 1979, **79**, 41; W. P. Roberts and G. Shoham, *Tetrahedron Lett.*, 1981, 4895; M. A. McKervey, P. Vibuljan, G. Ferguson, and P. Y. Siew, *J. Chem. Soc., Chem. Commun.*, 1981, 912; G. Mehta, K. S. Rao, K. Venkatesan, and M. M. Bhadbhade, *ibid.*, p. 755.

3 See *e.g. Chem. Eng. News*, 1982, Aug. 16, p. 25.

4 G. Mehta, A. Srikrishna, A. V. Reddy, and M. S. Nair, *Tetrahedron*, 1981, **37**, 4543.

5 A. E. Greene and J. P. Depres, *J. Am. Chem. Soc.*, 1979, **101**, 4003.

6 E. Mincione, G. Ortaggi, and A. Sirna, *Synthesis*, 1977, 773.

7 H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, 1975, **97**, 5434.

8 Y. Ito, T. Hirao, and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011.

9 D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropoulos, and E. Hedaya, *J. Am. Chem. Soc.*, 1974, **96**, 4673; L. A. Paquette, M. J. Wyvratt, H. C. Berk, and R. E. Moerck, *ibid.*, 1978, **100**, 5845.

10 M. S. Nair and K. S. Rao, unpublished results.