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DESIGN OF A SPHEROIDAL ALL cis-C_{20}-HEXAQUINANE ON WAY TO DODECAHEDRANE

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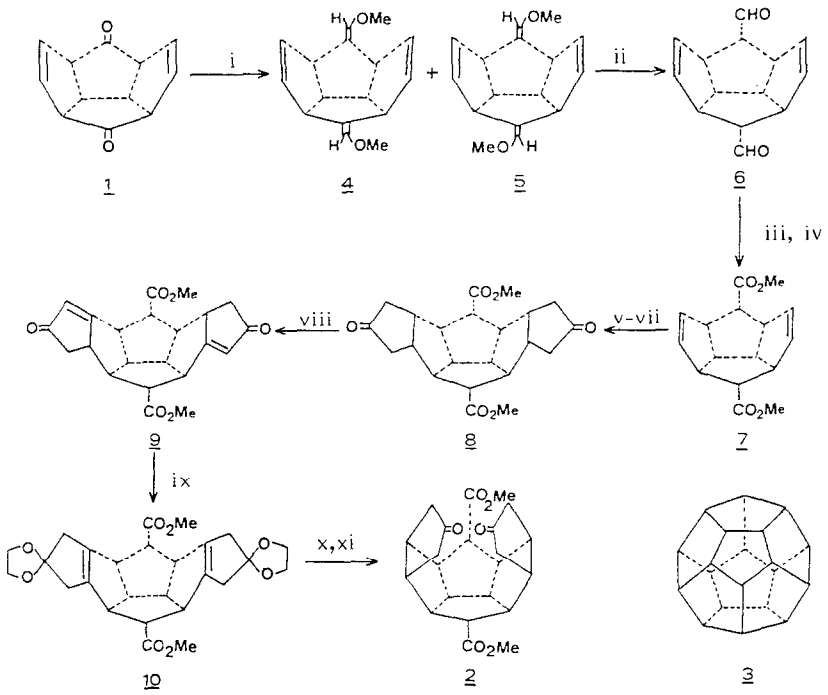
Summary: C_{12}-Tetraquinane dione 1 has been elaborated into all cis- exo, exo-C_{20}-hexaquinane dione-diester 2, the key projected precursor of pentagonal dodecahedrane 3, in eleven steps.

While the formidable synthetic challenge of undecacyclic $C_{20}H_{20}$ hydrocarbon dodecahedrane 3 has been overcome through the ingenious efforts of Paquette[1] and Prinzbach,[2] there remains considerable scope and opportunity to develop alternate synthetic strategies towards this prized molecule.[3] Sometime back, we conceived[4] an approach to dodecahedrane from the key (C_{2v})-C_{12}-tetraquinane dione 1 through the intermediacy of spheroidal C_{20}-hexaquinane dione-diester 2 and outlined[4b] a convenient synthesis of 1. In this letter, further successful elaboration of 1 to the functionalised C_{20}-hexaquinane 2, the penultimate precursor of dodecahedrane as per our theme,[4c] is reported.

To begin with, the dione 1 was subjected to a two-fold carbonyl homologation via reaction with methoxymethylphosphorane to give 4 and 5 (1 : 2 mixture). Acid hydrolysis of this mixture gave the thermodynamically stable exo, exo-dialdehyde 6.[5] Oxidation of 6 with pyridinium dichromate in DMF and esterification furnished the exo, exo-diester 7,[6] Scheme 1. The diester 7 was bis-cyclopentannulated to hexacyclic dione 8[5] in three steps involving dichloroketene addition, diazomethane ring expansion and reductive dechlorination.[4c,7] The two newly appended exo-cyclopentanone rings in 8 were now inverted and projected within the cavity of the polyquinane frame through a four-step protocol, Scheme 1. The dione 8 was regioselectively transformed into a single bis-enone 9[5] of axial symmetry (11 line ^{13}C NMR) following the Saegusa procedure.[8] Employing carefully controlled conditions and camphorsulphonic acid (CSA) catalyst, the bis-enone 9 yielded the bis-acetal 10[5] having two tetrasubstituted bridgehead double bonds. Deacetalisation and catalytic hydrogenation heralded the arrival of 2, mp 233°C, HRMS (m/z 386.1721), whose structure was secured through its ^1H NMR spectrum, ^{13}C NMR spectrum (δ219.3, 175.8, 57.4, 55.6, 52.3, 49.4, 43.0, 40.6) and single crystal X-ray diffraction studies.[9] With the firm acquisition of pivotal compound 2, we are pursuing its further evolution towards 3.

Scheme 1



Reagents & Yields : (i) $Ph_3P^+CHOCH_3Cl^-$, $NaOC_5H_{11}$, THF, 0°C, 30 min, 85%; (ii) 35% $HClO_4$, ether, 12h, 68%; (iii) PDC, DMF, 12h, 68%; (iv) CH_2N_2, ether, 0°C, 70%; (v) Cl_3CCOCl, Zn(Cu), ether, 16h; (vi) CH_2N_2, ether, MeOH, 0°C, 30 min; (vii) Zn, NH_4Cl, MeOH, 30 min, 7 to 8 overall yield 35%; (viii) LiHMDS, THF, TMSCl, -78°C ; $Pd(OAc)_2$, CH_3CN, 1h, 72%; (ix) $HOCH_2CH_2OH$, benzene, CSA, Δ , 1h, 55%; (x) 20% HCl, THF, 8h; (xi) H_2 - 10% Pd/C, 45 psi, 2h, 60% from 10.

References:

1. R.J. Ternansky, D.W. Balogh, L.A. Paquette, J. Am. Chem. Soc., 1982, 104, 4503; L.A. Paquette, R.J. Ternansky, D.W. Balogh, G. Kentzen, ibid, 1983, 105, 5446.
2. W-D. Fessner, B.A.R.C. Murthy, J. Worth, D. Hunkler, H. Fritz, H. Prinzbach, W.D. Roth, P.v.R. Schleyer, A.B. McEwen, W.F. Maier, Angew. Chem. Intl. Engl. Ed., 1987, 26, 452 and references cited therein.
3. For leading references in the area, see, E. Carceller, M.L. Garcia, A. Moyano, M.A. Pericas, F. Serratosa, Tetrahedron, 1986, 42, 1831.
4. (a) G. Mehta, M.S. Nair, J. Chem. Soc., Chem. Commun., 1983, 439. (b) idem., 1985, 629. (c) G. Mehta, M.S. Nair, J. Am. Chem. Soc., 1985, 107, 7519.
5. Compound 8 : IR(KBr): 2950, 1730, 1220 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 3.7 (6H, s), 3.48 - 1.8 (20H, series of m); ^{13}C NMR (25 MHz, $CDCl_3$): δ 218.9, 174.9, 58.2, 55.3, 52.3, 48.1, 44.3. 9 : IR(KBr): 1730, 1710, 1630, 1280 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 5.9 (2H, d, J = 3 Hz), 3.68 (6H, s), 3.4 - 1.3 (14H, series of m); ^{13}C NMR (25 MHz, $CDCl_3$): δ 208.9, 186.9, 173.2, 125.5, 58.1, 54.0, 51.6, 50.7, 48.5, 47.4, 46.6. 10 : IR(KBr): 1730, 1620, 1300 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 3.9 (8H, s), 3.66 (6H, s), 3.4 - 3.1 (4H, m), 2.86 (2H, s), 2.4 - 2.1(10H, m); ^{13}C NMR (25 MHz, $CDCl_3$): δ 176.5, 143.5, 120.8, 64.5, 64.2, 58.5, 52.8, 51.9, 47.2, 40.4.
6. L.A. Paquette, M.J. Wyvratt, H.C. Berk, R.E. Moerck, J. Am. Chem. Soc., 1978, 100, 5845.
7. A.E. Greene, J.P. Depress, J. Am. Chem. Soc., 1979, 101, 4003.
8. Y. Ito, T. Hirao, T. Saegusa, J. Org. Chem., 1978, 43, 1011.
9. We thank Dr. T.N. Guru Row and his colleagues at the National Chemical Laboratory for the crystal structure determination of 2.

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