Design of a Key Synthon for Dodecahedrane: (C_{2v})-C_{12}-Tetraquinanedione

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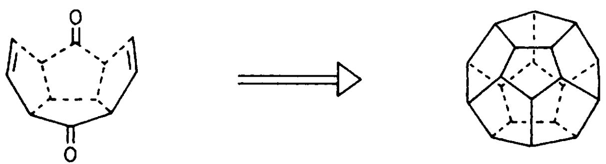
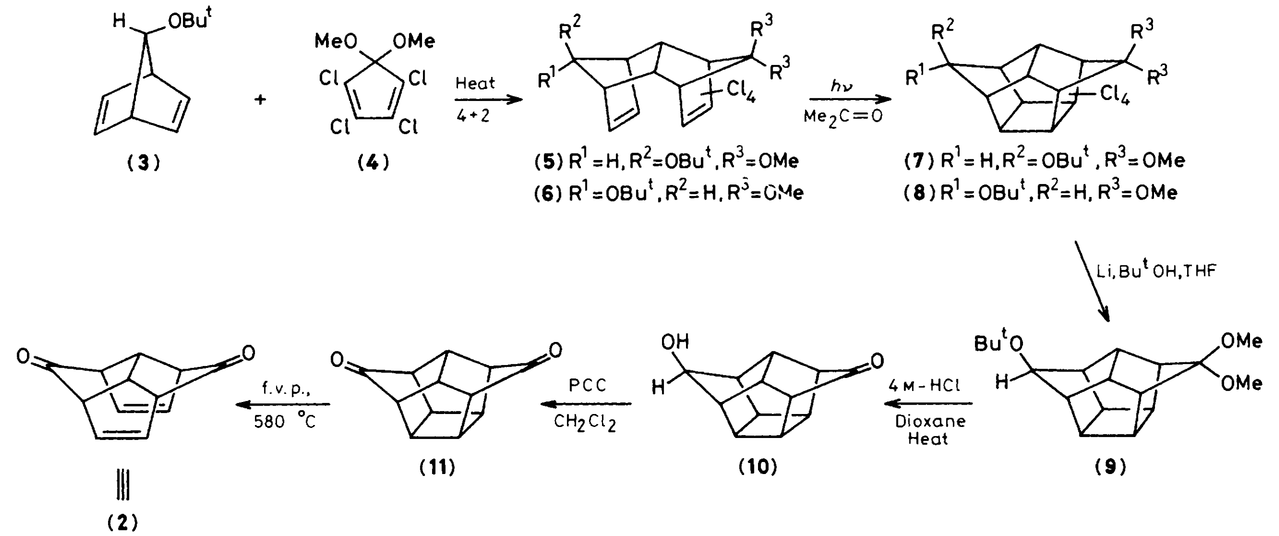
A six-step synthesis of tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene-5,12-dione (**2**) from the readily available starting materials 7-t-butoxynorbornadiene and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene is described.

In connection with our studies[1a,b] directed towards dodecahedrane (**1**), we identified the all *cis*-tetraquinane dione (**2**) with a symmetrically functionalised perimeter as the key synthon through retrosynthetic analysis,[1b] and we now describe a novel and efficient approach to (**2**).


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

Diels–Alder reaction between 7-t-butoxynorbornadiene (**3**) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**4**) furnished a mixture of three 4 + 2 addition products from



which the two required *endo,endo*-adducts (**5**) (40%) and (**6**) (20%) were readily separated.[2] Acetone-sensitised photolysis of (**5**) and (**6**) furnished the corresponding hexacyclic caged compounds (**7**)† and (**8**)† in 95 and 75% yield, respectively. At this stage the redundant chlorine atoms were removed and treatment of the *syn*-isomer (**7**) with Li–Bu^{t}OH in tetrahydrofuran (THF) furnished (**9**)† in 85% yield. One-step deprotection of the ether and the acetal functionality in (**9**) was effected with 4 M-HCl in refluxing dioxane to furnish (**10**), m.p. 182—184 °C (80%). Oxidation of the hydroxy-ketone (**10**) with pyridinium chlorochromate (PCC)–molecular sieve in dichloromethane furnished the hexacyclic dione (**11**)†‡ (80%) whose four-line ^{13}C n.m.r. spectrum illustrated its symmetry. The hexacyclic dione (**11**) could also be obtained from the *anti*-isomer (**8**) through the same three-step sequence. Flash vacuum pyrolysis (f.v.p.) (580 ± 10 °C, quartz column)[3] of (**11**) proceeded cleanly to furnish (**2**)† (70% yield after 2 cycles) *via* cyclobutane fragmentation and without any interference from concomitant decarbonylation. The diagnostic ^{13}C n.m.r. resonances at δ 214.2, 133.5, 62.7, and 43.2 fully established the structure of (**2**) and, with ready access to it established, efforts are underway to elaborate it to (**1**) through our 'molecular stitching' strategy.[1]

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† Compound (**7**): m.p. 156 °C, ^{1}H n.m.r. (CDCl$_3$, 100 MHz) δ 4.0—3.9 (1H, m), 3.64 (3H, s), 3.36 (3H, s), 3.36—3.2 (2H, m), 3.0—2.86 (2H, m), 2.8—2.6 (2H, m), and 1.44 (9H, s); ^{13}C n.m.r. (CDCl$_3$, 25.0 MHz) δ 105.8 (s), 80.8 (d), 79.4 (s), 79.1 (s), 73.9 (s), 55.9 (d), 51.7 (q), 51.1 (q), 49.9 (d), 48.3 (d), and 28.3 (q); (**8**): m.p. 140—141 °C; ^{1}H n.m.r. (CDCl$_3$, 100 MHz) δ 4.16 (1H, br. s), 3.6 (3H, s), 3.55 (3H, s), 3.2 (2H, m), 2.88 (2H, m), 2.7 (2H, m), and 1.4 (9H, s); ^{13}C n.m.r. (CDCl$_3$, 25.0 MHz) δ 105.0, 80.2, 80.1, 74.6, 72.7, 52.2, 51.8, 50.6, 49.9, 47.8, and 27.2; (**9**): m.p. 117—118 °C, ^{1}H n.m.r. (CDCl$_3$, 100 MHz) δ 4.0—3.88 (1H, m), 3.28 (3H, s), 3.18 (3H, m), 3.0—2.86 (2H, m), 2.84—2.64 (2H, m), 2.64—2.40 (2H, m), 2.2—2.04 (2H, m), and 1.16 (9H, s); ^{13}C n.m.r. (CDCl$_3$, 25.0 MHz) δ 120.2 (s), 82.8 (d), 72.9 (s), 50.9 (d), 50.4 (q), 49.3 (d), 48.3 (d), 42.8 (d), 40.5 (d), and 28.6 (q); (**11**): m.p. 227—228 °C, $\nu_{\text{max.}}$ (KBr) 1770, 1190, 1160, and 1130 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$, 100 MHz) δ 3.2 (4H, m), 3.05 (2H, m), and 2.15 (4H, m); ^{13}C n.m.r. (CDCl$_3$, 25.0 MHz) δ 210.0, 48.8, 42.4, and 41.8; (**2**): m.p. 173—175 °C, $\nu_{\text{max.}}$ (KBr) 1720, 1630, 1180, and 730 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$, 100 MHz) δ 5.64 (4H, s) and 4.0—4.34 (6H, m); ^{13}C n.m.r. (CDCl$_3$, 25.0 MHz) δ 214.2, 133.5, 62.7, and 43.2.

‡ After the completion of this work, we learnt that the hexacyclic dione (**11**) has also been prepared by G. Sedelmeier and H. Prinzbach, personal communication. We are grateful for this information.