per point: 0.46 Hz). For determination of chemical shifts, a Gaussian window function (LB = -2, GB = 0.2) was manipulated on FID. The ^{1}H NMR spectral data for **1a** and **2a** are listed in Table I.

Preparation of (*R*)- and (*S*)-MTPA Esters of Sipholenol-A (1). To a solution of sipholenol-A (5.2 mg, 11 μmol) and (dimethylamino)pyridine (5.4 mg, 44 μmol) in 0.3 mL of dichloromethane (distilled from P_2O_5) were added triethylamine (2.3 μL, 16 μmol) and (-)-MTPA chloride (4.1 μL, 22 μmol), and the solution was allowed to stand at room temperature for 3.5 h. 3-(Dimethylamino)propylamine (2.7 μL, 21 μmol) was added, and after 10 min, the solvent was evaporated. The residue was subjected to prep TLC [Merck, Kieselgel 60, F_{254}, hexane-EtOAc, 1:1 (v/v)], affording the pure (^{1}H NMR) (*S*)-MTPA ester (1_S) (5.9 mg, 78%): HREIMS *m/z* calcd for $C_{40}H_{59}O_6F_3$ 692.4263, found 692.4263. (*R*)-MTPA ester (1_R): HREIMS *m/z* calcd for $C_{40}H_{59}O_6F_3$ 692.4263, found 692.4278.

Preparation of Episipholenol-A (2). A solution of sipholenol-A (20.8 mg, 44 μmol) in 1.0 mL of dichloromethane (distilled from P_2O_5) was treated with pyridinium dichromate (27.5 mg, 73 μmol), and the mixture was stirred at room temperature for 7 h. After removal of the solvent, the residue was filtered through a silica gel column by using ethyl acetate to yield **3** (18.8 mg, 91% yield). The ketone **3** was dissolved in 1.5 mL of methanol, $NaBH_4$ (30.8 mg) was added, and the mixture was allowed to stand at room temperature for 1.5 h. The solvent was evaporated, and the residue was separated by prep TLC [CH_2Cl_2-EtOAc, 7:6 (v/v), 6 times development] to afford **1** (13.5 mg, 72%) and **2** (3.5 mg, 19%).

Preparation of (*R*)- and (*S*)-MTPA Esters of Episipholenol-A (2). A solution of episipholenol-A (1.6 mg, 3.4 μmol), (dimethylamino)pyridine (1.6 mg, 13 μmol), and triethylamine (0.7 μL, 5 μmol) in 0.3 mL of dichloromethane (distilled from P_2O_5) was treated with (-)-MTPA chloride (1.3 μL, 7 μmol), and the mixture was allowed to stand at room temperature for 3.5 h. 3-(Dimethylamino)propylamine (0.8 μL, 7 μmol) was added, and the residue obtained after evaporation of the solvent was applied to prep TLC [hexane-EtOAc, 2:3 (v/v)] to give pure (^{1}H NMR) (*S*)-MTPA ester (2_S) (2.5 mg, quant): HREIMS *m/z* calcd for $C_{40}H_{59}O_6F_3$ 692.4263, found 692.4267. (*R*)-MTPA ester (2_R): HREIMS *m/z* calcd for $C_{40}H_{59}O_6F_3$ 692.4263, found 692.4269.

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Registry No. 1, 78518-73-7; 2, 86783-85-9; 3, 78518-74-8.

Observation of a Transannular Cannizzaro Reaction in a Caged [7]Prismane Related System

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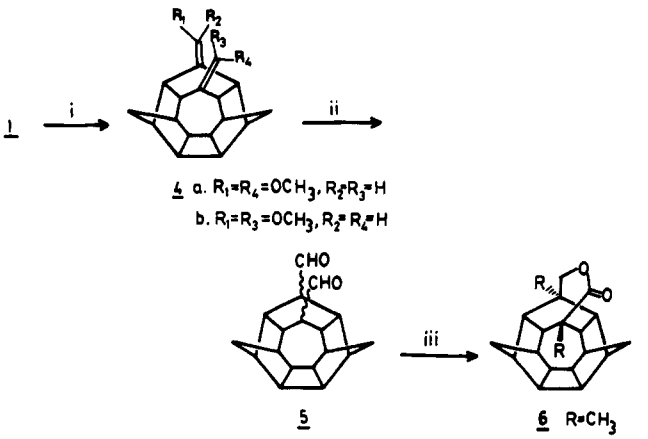
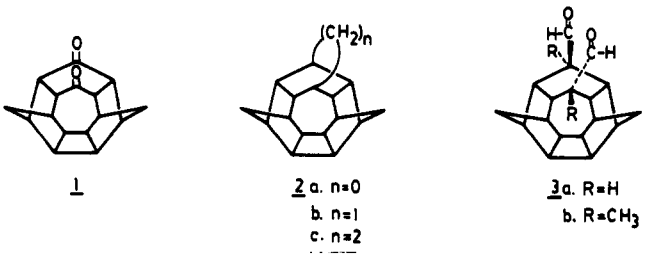
Recently, we reported a short and convenient synthesis of the caged heptacyclic dione **1** from the readily available norborneno-*p*-benzoquinone.[1] The dione **1** is formally a 1,4-bishomo-6-seco[7]prismane derivative, which we reckoned was well suited for further manipulation to [7]prismane analogues, e.g., **2**. Such an elaboration of **1** to **2** required establishment of a carbon bridge between the two transannularly located carbonyl groups. When several of our efforts to prepare **2a** and **2b** from **1**, employing a variety of tactics, failed,[2] we aimed at the synthesis of **2c** via the *endo,endo*-dialdehyde **3** in which the key step was to be a pinacolic coupling employing the methodology pioneered by McMurry.[3] However, during a base-promoted reaction proceeding via **3b**, we unexpectedly encountered a novel transannular Cannizzaro reaction, and this observation is the subject of this paper.

Scheme I[a]



[a] Reagents and yield: (i) $CH_3OCH_2PPh_3Cl$, $C_5H_{11}O^-Na^+$, ether-THF, room temperature, 10 min; (ii) 35% $HClO_4$, ether, ~5 °C, 3 h, 40% (2 steps); (iii) KH, THF, -10 °C, MeI, 10 min, 40%.



Bis-homologation of the dione **1** with excess of (methoxymethyl)triphenylphosphonium chloride in the presence of a base furnished a mixture of bis-enol ethers **4a,b** (δ 5.84, s, and 3.52, s, 1:3) which was directly hydrolyzed with aqueous perchloric acid to furnish a diastereomeric mixture of *exo,exo*-, *exo,endo*-, and *endo,endo*-dialdehydes **5** (δ 9.76, 9.67, 9.40, 9.38). In order to project and lock the two aldehyde groups in the *endo,endo*-position as in **3a,b** and to obtain a single dialdehyde **3b**, **5** was treated with excess of KH and the resulting enolate anion quenched with methyl iodide. However, instead of the expected **3b**, a novel octacyclic lactone **6** was isolated in 40% yield as a very nice crystalline compound. The structure of **6** flowed mainly from the presence of mirror plane symmetry (14 ^{13}C lines) and the ^{13}C resonances due to a lactone carbonyl (δ 178.1) and oxygen attached carbon (δ 87.6). In addition, the ^{1}H NMR spectrum shows a 2 H singlet at δ 3.92 ($CH_2OC(O)$) and two 3 H singlets at δ 1.32 (CH_3C-C(O)) and 1.04 (CH_3C) in full conformity with the structure. The direct formation of a lactone moiety and the presence of two quaternary methyl groups in **6** revealed that a facile transannular Cannizzaro-type reaction[4] had taken place in the intermediate **3b** to furnish the observed product (Scheme I). The Cannizzaro reaction is perhaps occurring in the basic medium generated during the workup. It is quite apparent that this transannular Cannizzaro reaction in **5** is an outcome of the proximity of the two reacting aldehyde groups induced by the rigid caged structure.[5,6]

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(4) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: Eastern, New Delhi, 1986. (b) Geissman, T. A. *Org. React.* **1944**, *2*, 94. (c) Ashby, E. C.; Coleman, D. T. III; Gamasa, M. P. *Tetrahedron Lett.* **1983**, *24*, 851, propose a SET mechanism for the Cannizzaro reaction.

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To the best of our knowledge, the novel octacyclic lactone **6** represents the first derivative in which all carbon atoms of two seven-membered rings are joined face-to-face, albeit through bridges of various sizes. We anticipate some potential applications of the present observation in the synthesis of caged polycyclic systems.

Experimental Section

For a general write up, see ref 7.

Heptacyclo[7.6.1.$0^{2,8}$.$0^{3,7}$.$0^{4,13}$.$0^{6,12}$.$0^{10,15}$]hexadecane-11,14-dicarboxaldehyde (4a,b). (Methoxymethyl)triphenylphosphonium chloride (1.5 g, 4.37 mmol) was suspended in 5 mL of dry ether under N_2, freshly sublimed sodium *tert*-amyloxide (360 mg, 3.32 mmol) in 2 mL of dry ether was introduced, and the mixture was stirred for 5 min. To the blood red ylide that formed was added the dione **1** (200 mg, 0.83 mmol) in 2 mL of tetrahydrofuran (THF), and the reaction mixture was stirred for 10 min at room temperature and quenched by the addition of 5 mL of water. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was washed with water and dried. Removal of solvent gave a crude material which was charged on a silica gel (20 g) column. Elution of the column with hexane removed the triphenylphosphine impurities. Further elution of the column with 5% ethyl acetate–hexane furnished a viscous liquid (120 mg), which was a mixture of dienol ethers **4a,b**. IR (neat): 2950, 1660, 1210, 1120 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 5.84 (2 H, s, C=C*H*OCH$_3$), 3.54 (6 H, s, OCH_3), 3.34 (2 H, m), 2.80–2.10 (10 H, series of m), 1.80–1.0 (4 H, m). ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 142.8, 117.9, 59.3, 51.4, 48.8, 43.8, 43.5, 43.3, 43.1, 39.5, 39.4, 38.1, 37.9.

To a solution of dienol ether mixture **4a,b** obtained above (120 mg) in 10 mL of ether cooled in an ice bath was added 1 mL of 35% $HClO_4$, and the reaction mixture was stirred for 3 h at 0–5 °C. It was then quenched with 2 mL of 10% $NaHCO_3$ and diluted with 5 mL of water. The ethereal layer was separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined ethereal layer was washed with water and dried. The residue obtained after the removal of solvent was charged on a silica gel (15 g) column. Elution with 10% ethyl acetate–hexane furnished the dialdehyde **5** (90 mg, 40% after two steps) as a mixture (3:5:12) of three isomers as revealed by the ^1H NMR spectrum. IR (neat): 2925, 2675, 1705, 730 cm^{-1}. ^1H NMR of mixture (100 MHz, $CDCl_3$): δ 9.76, 9.67, 9.40, 9.38 (all combined 1 H, singlets, C(O)*H*), 2.8 (4 H, br s), 2.65 (6 H, br s), 2.44 (4 H, br s), 1.65 (2 H, $^1/_2$ AB q, J_1 = 9 Hz), 1.23 (2 H, $^1/_2$ AB q, J = 9 Hz).

12,16-Dimethyl-14-oxaoctacyclo[8.7.1.1^{4,7}.$0^{2,9}$.$0^{3,8}$.$0^{5,16}$.$0^{6,12}$.$0^{11,17}$]nonadecan-13-one (6). Potassium hydride (~70 mg, 25% wt dispersion in oil, 0.43 mmol) was washed twice with dry hexane under N_2 to remove the mineral oil, and the residue was suspended in 2 mL of dry THF. A solution of the dialdehyde mixture **5** (50 mg, 0.186 mmol) in 1 mL of dry THF was added dropwise at −10 °C. After 2 min it was quenched with MeI (0.2 mL, freshly distilled over $CaCl_2$) and stirred further for 10 min. The reaction mixture was diluted with 5 mL of water and extracted with ethyl acetate (3 × 8 mL). The combined organic extract was washed with water and dried. Removal of solvent gave a crude material which was charged on a silica gel (5 g) column. Elution with 5% ethyl acetate–hexane furnished the lactone **6** (22 mg, 40%) which was recrystallized from dichloromethane–hexane. Mp: 240–243 °C dec. IR (KBr): 2125, 1720, 1200, 1090 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 3.92 (2 H, s, CH_2O), 2.64–2.4 (8 H, m), 2.28 (4 H, m), 1.43 (2 H, $^1/_2$ AB q, J = 10 Hz, CH_2), 1.32 (3 H, s, CH_3), 1.17 (2 H, $^1/_2$ AB q, J = 10 Hz, CH_2), 1.04 (3 H, s, CH_3). ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 178.1, 87.6, 46.8 (2 C), 46.1, 45.8 (2 C), 44.5 (2 C), 44.1 (2 C), 42.0 (2 C), 39.2 (2 C), 38.6 (2 C), 36.4, 23.2, 22.2. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.73; H, 8.18.

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(5) Base-induced intramolecular 1,6-hydride shifts[6a–d] and intramolecular Cannizzaro reactions[6e,f] have been previously observed in selected systems. We thank the reviewers for bringing the relevant references to our attention.

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4-(Benzotriazol-1-yl)-6*H*-benzo[*c*]tetrazolo[1,5-*e*][1,2,5]triazepine, a New Heterocyclic Ring System Formed by a Novel Benzotriazole Ring Opening

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We recently[1] achieved reaction between two molecules of benzotriazole (**1**) and glyoxal (**2**) to obtain the glycol **3**, which with thionyl chloride gave the dichloroethane **4**. Compound **4** proved to be an intermediate for a number of interesting structures. With the sodium salt of ethanedithiol, it gave the 1,4-dithiin **7**, and with *o*-aminothiophenol, it gave the benzo-1,4-thiazine **8**. The chlorine atoms could also be displaced by simple sodium alkoxides or sodium thioalkoxides to give the corresponding diethers and dithioethers.

Following these successful reactions, we treated the dichloroethane **4** with sodium azide in the expectation of forming the disubstituted product, the 1,2-diazido derivative of **4**, similar to the reaction of 1-(chloromethyl)-benzotriazole with sodium azide.[2] Reaction occurred smoothly in dimethyl sulfoxide at room temperature, but the product did not show the expected molecular weight or elemental analysis. These values were consistent with 4,5-bis(benzotriazol-1-yl)-1,2,3-triazole (**5**). However, the aromatic region of the 300-MHz proton spectrum showed four one-proton doublets and four one-proton triplets, initially suggesting two nonequivalent 1-benzotriazole groups. Clearly neither had isomerized to a symmetrical 2-benzotriazole, a change recently observed in several other systems.[3] No change was seen in the spectrum up to 100 °C. The 75-MHz ^{13}C NMR spectrum had 14 signals between δ 112 and 148 and no others. The clear differences between these and those of other benzotriazoles led us to perform an X-ray crystallographic analysis, which proved the structure to be 4-(benzotriazol-1-yl)-6*H*-benzo[*c*]tetrazolo[1,5-*e*][1,2,5]triazepine (**6**). A suggested mechanism

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