to record ^1H NMR spectra for IIIe and IIIg. IIIe (X = O): (CD_3CN) 5.98 (s, 2 H), 4.23 (t, 2 H, J = 6.5 Hz), 1.68 (m, 2 H), 1.31 (m, 10 H), 0.92 (t, 3 H, J = 6.2 Hz). IIIg (X = O): (CD_3CN) 5.61 (m, 1 H), 4.23 (t, 2 H, J = 6.5 Hz), 3.05 (m, 2 H), 1.67 (t, 2 H, J = 6.5 Hz), 1.34 (m, 10 H), 0.93 (t, 3 H, J = 6.5 Hz).

Preparations of *n*-Octyl Esters and Amides. Octyl Tartrate (IIIb, X = O). 1-Octanol, anhydride IId or IIe, and freshly distilled dry THF were mixed at room temperature in a dry flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet. A large-scale preparation with the TFA system used 44.9 g (285 mmol) of octanol, 40 mL of THF, and 30.8 g (95 mmol) of IId. A smaller scale reaction with the TCA system used octanol (31 mg, 0.24 mmol) and IIe (50 mg, 0.12 mmol) in 1 mL of THF. The TFA reaction was stirred at room temperature for 4 h and the TCA reaction was heated at reflux overnight. In both cases the THF was removed by vacuum. TCA hydrolysis was effected by overnight stirring in 2 mL water and both reactions were processed by adding 3 equiv of cold 3 N NaOH. The NaOH solution did not dissolve all of the white solid product. This slurry was washed 3 times with diethyl ether and lyophilized to dryness. The solid crude sodium salt was contaminated with sodium trihaloacetate which could be removed by washing with cold water followed by recrystallization from a 95/5 mixture of THF/water. The large-scale reaction gave a near quantitative yield of crude product and 88% of recrystallized material. The crude yield from the TCA preparation was 88%: ^1H NMR (D_2O) 4.49 (d, 1 H, J = 2.1 Hz), 4.25 (d, 1 H, J = 2.1 Hz), 4.09 (t, 2 H, J = 6.5 Hz), 1.53 (t, 2 H, J = 6.5 Hz), 1.17 (m, 10 H), 0.74 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (D_2O) 177.31, 174.37, 74.15, 73.23, 66.56, 32.20, 29.56 (2 C's), 28.82, 26.11, 22.93, 14.16; IR 3520–3050, 1737, 1620, 1068, 1142, 1210, 723. Conversion of the salt to the acid with dilute HCl was followed by continuous extraction into ether. After drying with $MgSO_4$, ether removal left the solid acid, mp 51–51.5 °C: $[\alpha]_D$ ($CHCl_3$, c 2.00) +7.4°; MS (70 eV, M + H) calcd $C_{12}H_{23}O_6$ 263.1495, found 263.1488.

Octyl Tartramide (IIIb, X = NH). A two-necked flask was equipped with an addition funnel, a reflux condenser, a magnetic stirring bar, and a nitrogen inlet. It was charged with IId (27.8 g, 86 mmol) in 120 mL of freshly distilled THF and cooled to −23 °C. *n*-Octylamine (44 mL, 266 mmol) was added over 10 min. The system was kept cold and stirred under nitrogen for an hour and then allowed to warm to room temperature over an additional hour. NaOH (3 N, 300 mL) was added and the THF was removed by vacuum. The resulting material was dissolved in benzene and distilled to near dryness. The gelatinous residue was recrystallized from an 84/16 THF/water mixture to yield 9.5 g of white crystalline sodium salt: ^1H NMR (D_2O) 4.33 (d, 1 H, J = 1.6 Hz), 4.20 (d, 1 H, J = 1.6 Hz), 3.10 (m, 2 H), 1.40 (t, 2 H, J = 6.5 Hz), 1.17 (m, 10 H), 0.74 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (D_2O) 178.56, 174.53, 74.03, 40.22, 32.48, 29.88 (2 C's), 29.80, 27.62, 23.21, 14.43; IR 3320, 3295, 3275, 3210, 3570–3060, 1620, 1657, 1543, 1144, 727. Concentration of the mother liquor and trituration of the residue with ether allowed recovery of another 7.5 g of product (combined yield 70%). This fraction was dissolved in 1 N HCl and the protonated form of IIIb was recovered by continuous extraction with ether, mp 150–151 °C; $[\alpha]_D$ (EtOAc, c 0.5) +32.2°; ^1H NMR (Me_2SO-d_6) 7.63 (t, 1 H, J = 6.6 Hz), 4.30 (d, 1 H, J = 2.0 Hz), 4.15 (d, 1 H, J = 2.0 Hz), 3.05 (m, 2 H), 1.42 (m, 2 H), 1.23 (m, 10 H), 0.84 (t, 3 H, J = 6.7 Hz); MS (70 eV) calcd $C_{12}H_{23}NO_5$ 261.1576, found 261.1572. The comparable TCA reaction was done with IIe (50 mg, 0.12 mmol) and *n*-octylamine (31 mg, 0.24 mmol) in 1 mL of dry THF at 0 °C. After 1 h, the reaction was warmed to room temperature (over 3 h) and 3 equiv of 3 N NaOH were added. THF was removed under vacuum and the remaining aqueous layer was stirred overnight to guarantee complete TCA removal. Following washing with diethyl ether, the aqueous solution was lyophilized to a white solid residue (55 mg) of the sodium salt of the tartramide contaminated with NaTCA. The crude yield of tartramide (corrected for NaTCA) was 71%.

Octyl Malate[6] (IIIc, X = O). IIf (22.4 g, 106 mmol) and 1-octanol (27.6 g, 212 mmol) were added to 100 mL of dry THF in a flask equipped with a nitrogen inlet and a magnetic stirring bar. After being stirred overnight at room temperature, the THF was removed by vacuum and cold 3 N NaOH (212 mmol) was added. This solution was washed with diethyl ether and acidified. Continuous extraction with ether afforded the acid (13.01 g, 50% yield) as a slightly colored oil: $[\alpha]_D$ ($CHCl_3$, c 5.0) −9.4°; ^1H NMR ($CDCl_3$) 5.9 (brs, 2 H), 4.49 (m, 1 H), 4.18 (t, 2 H, J = 6.6 Hz), 2.86 (m, 2 H), 1.64 (m, 2 H), 1.26 (m, 10 H), 0.86 (t, 3 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) 174.87, 173.19, 66.89, 65.99, 38.17, 31.48, 28.86 (2 C's), 28.12, 25.47, 22.33, 13.73; IR 3620–3050, 1800–1640, 1112, 1045, 960, 730; MS (70 eV, M + H) calcd $C_{12}H_{23}O_5$ 247.1546, found 247.1550. Alternatively, the sodium salt of IIIc was isolated by lyophilization after the ether wash: ^1H NMR (D_2O) 4.38 (m, 1 H), 4.03 (t, 2 H, J = 6.5 Hz), 2.48 (m, 2 H), 1.51 (m, 2 H), 1.14 (m, 10 H), 0.71 (t, 3 H, J = 6.7 Hz).

Octyl Malamide (IIIc, X = NH). IIf (22.4 g, 106 mmol) was dissolved in 100 mL of dry distilled THF in a flask equipped with a septum and a nitrogen inlet. The flask was cooled to 0 °C and *n*-octylamine (27.46 g, 212 mmol) was added over 5 min. The reaction was stirred for 1 h at 0 °C and then warmed to room temperature overnight. Solvent was removed by vacuum and cold 6 N NaOH (233 mmol) was added. The aqueous mixture was exhaustively washed with ether. The product was recrystallized from the solution that was obtained by adding 200 mL of THF to this aqueous slurry. This gave the pure sodium salt of IIIc (X = NH) as white flakes (73% yield): ^1H NMR (D_2O) 4.25 (m, 1 H), 3.06 (t, 2 H, J = 6.8 Hz), 2.39 (m, 2 H), 1.36 (m, 2 H), 1.13 (m, 10 H), 0.70 (t, 3 H, J = 6.7 Hz); ^{13}C NMR (D_2O) 179.59, 176.28, 70.57, 42.67, 40.10, 32.46, 29.88, 29.82 (2 C's), 27.56, 23.21, 14.47; IR 3430, 3330, 3300, 3230, 3240, 3207, 3180, 3150, 3550–3050, 728, 1715, 1590, 1633, 1090. A subsequent small-scale preparation using IIf gave a crude yield of 92%. The same material was made from IIg (100 mg, 0.38 mmol) and octylamine (54 mg, 0.42 mmol). The only difference in procedure was to stir the aqueous solution overnight before the ether wash to insure complete TCA removal; yield (corrected for NaTCA contamination) 81%. A sample of the protonated half acid was obtained by acidification with dilute HCl and continuous extraction into ether. After drying with $MgSO_4$, ether removal left the acid: mp 83–84 °C; $[\alpha]_D$ (EtOAc, c 2.0) −16.5°; ^1H NMR (Me_2SO-d_6) 7.80 (t, 1 H, J = 5.9 Hz), 4.18 (m, 1 H), 3.38 (brs, 2 H), 3.03 (m, 2 H), 2.45 (m, 2 H), 1.23 (m, 12 H), 0.84 (t, 3 H, J = 6.7 Hz); MS (70 eV) calcd $C_{12}H_{23}NO_4$ 245.1627, found 245.1626.

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(6) Octyl malate is mentioned in a British patent that is reported in *Chem. Abstr.* **1964**, *60*, 15741b.

Novel Polyquinanes from a Caged Hexacyclic [4.4.2]Propellane System

G. Mehta,* A. Srikrishna, K. Sambasiva Rao, and K. Raja Reddy

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

K. A. Acharya, V. G. Puranik, S. S. Tavale, and T. N. Guru Row

National Chemical Laboratory, Pune 411 008, India

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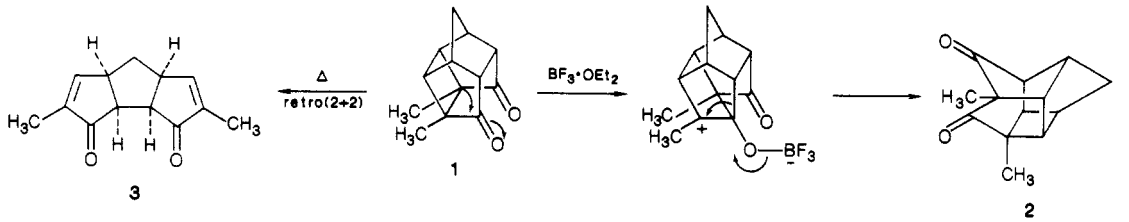
Recently, we have reported a new Lewis acid catalyzed rearrangement of the pentacyclic dione **1** to the trishomocubane system **2**.[1] Earlier we had also described the facile 2 + 2 cycloreversion of **1** to triquinane bis-enone **3** under flash vacuum pyrolysis (FVP) conditions[1b] (Scheme I). These interesting and useful observations with **1** prompted us to investigate the carbonium ion mediated

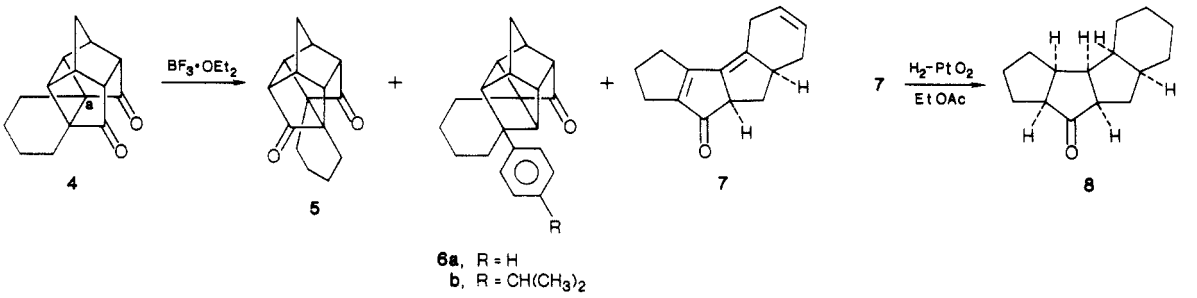
(1) (a) Mehta, G.; Reddy, A. V.; Tacreiter, W.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 441. (b) Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543. (c) Mehta, G.; Reddy, A. V.; Srikrishna, A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 291.

0022-3263/87/1952-0457$01.50/0

Scheme I



Scheme II

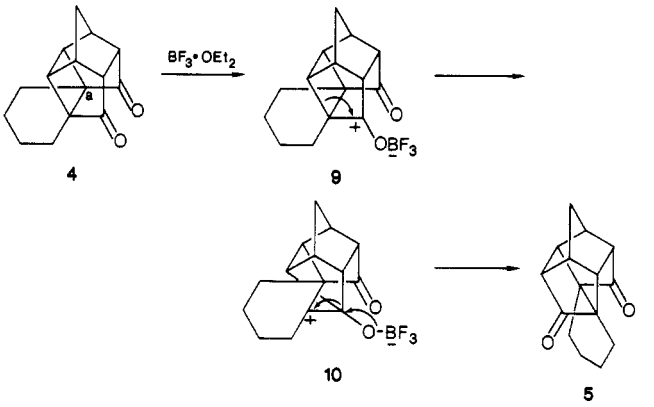


rearrangements and thermolysis under FVP conditions of an annulated, abundantly available hexacyclic derivative **4** of **1**, which also embodies a [4.4.2]propellane moiety as a part of its rigid, caged framework.[2] We find that hexacyclic propellanedione **4** responds readily to both carbonium ion and thermal rearrangements to provide novel products of mechanistic as well as synthetic interest to warrant this brief report.

Reaction of **4**,[2] readily available from cyclopentadiene and 1,4-naphthoquinone, with $BF_3{\cdot}OEt_2$ (benzene, reflux, 90 h) and column chromatography on silica gel resulted in the isolation of three products, **5**, **6a**, and **7**, in 15%, 25%, and 20% yields, respectively (Scheme II). The structure of **5**, mp 101–102 °C, $C_{15}H_{16}O_2$, was readily derived from its simplistic ^{13}C NMR spectrum, besides other data, which showed resonances at δ 213.2 (s), 49.1 (d), 48.1 (s), 42.3 (d), 42.0 (d), 36.0 (t), 22.0 (t), and 21.8 (t) due to its symmetrical [4.3.3]propellane framework. Product **6a**, mp 107–108 °C, $C_{21}H_{22}O$, was clearly a phenylated product formed through solvent incorporation. While its ^1H NMR spectrum showed no characteristic resonances, the ^{13}C NMR spectrum displayed only one carbonyl (δ 217.0 (s)) and two quaternary carbon (δ 60.1 (s) and 54.4 (s)) resonances, suggestive of an unusual formulation. The structure was therefore solved through single crystal X-ray diffraction studies, which showed the location of the phenyl ring and quaternary C's. The last product from the reaction, **7**, viscous liquid, $C_{15}H_{16}O$, exhibited two olefinic resonances in the ^1H NMR spectrum, but its ^{13}C NMR spectrum showed the presence of seven sp^2 carbon atoms at δ 198.5 (s), 187.0 (s), 156.4 (s), 141.0 (s), 135.7 (s), 129.7 (d), and 129.1 (d), five of which were quaternary. An extensive reorganization of the carbon skeleton and generation of a condensed ring system was clearly imperative. As **7** was unsuitable for X-ray crystal structure determination, it was reduced to a crystalline perhydro derivative **8**, mp 49 °C.

X-ray crystal structure determination (see Experimental Section) on **8** showed it to possess the convoluted, all-cis tetracyclic structure. With the carbon skeleton of **7** revealed, the location of double bonds was fixed through incisive anaysis of its spectral data, in particular the ^1H NMR double resonance experiments that guided the placement of the disubstituted double bond in the cyclohexene ring.

Scheme III



We also investigated the rearrangement of dione **4** in protic acid medium, particularly in sulfuric acid, which has somehow found favor for the study of the rearrangements of propellanic systems.[3] Exposure of **4** to concentrated sulfuric acid resulted in smooth and quantitative rearrangement to the hexacyclic propellanedione **5**, thus making this novel polycycle readily available for further use.

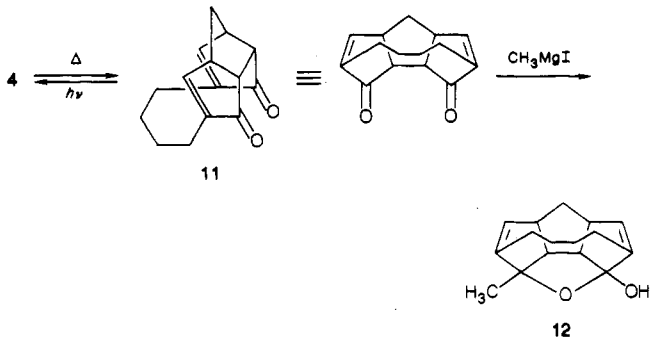
The formation of **5**, **6a**, and particularly **7**, in which the propellane moiety is lost with complete uncaging of the caged structure **4**, is indeed intriguing. Among the rearrangement products, only the genesis of hexacyclic [4.3.3]propellane derivative **5** could be readily rationalized in terms of a Cargill-type rearrangement[4] (Scheme III). In general, the driving force for the Cargill rearrangement of [*m.n.*2]propellanes is the ring expansion of the cyclobutylcarbinyl cation. However, it is noteworthy that the first step in our case is a cyclobutylcarbinyl → cyclobutylcarbinyl cation change (**9** → **10**). Formation of rearrangement products **6a** ($C_{15}H_{16}O + C_6H_6$) and **7** ($C_{15}H_{16}O$) from **4** ($C_{15}H_{16}O_2$) involves a net loss of an oxygen atom. Thus, not only a complex rearrangement sequence

(2) Kushner, A. S. *Tetrahedron Lett.* **1971**, 3275. Rao, K. S. Ph.D. Thesis, University of Hyderabad, 1984.

(3) (a) Kakiuchi, K.; Tsugaru, T.; Takeda, M.; Wakaki, I.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1985**, *50*, 488. (b) Smith, A. B., III; Wexler, B. A.; Tu, C.-Y.; Konopelski, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1308.

(4) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106.

Scheme IV



but also a reduction step (addition of two hydrogen atoms) prior to loss of oxygen (as H_2O) were implicated in the generation of **6** and **7**. Various probes to identify the stage at which reduction and dehydration steps occur have not revealed much, except that the source of hydrogen atoms is internal (through disproportionation) and not external (no deuterium incorporation from medium).[5] Also supporting this observation was the fact that when the BF_3·OEt_2 rearrangement of **4** was carried out in cumene, a better hydrogen donor, the product distribution between **5**, **6b**, and **7** was not significantly altered. No new products in this reaction were detected. Finally, as the formation of **7** must involve complete uncaging of the caged **4**, some fragmentation–recyclization pathway must be involved, the exact nature of which remains elusive.

Next, we turned attention to the thermally induced cycloreversions in **4**. Flash vacuum pyrolysis of **4** at 550 °C (1 torr) through a quartz tube[1b] led to smooth 2 + 2 cycloreversion, and the "belted" triquinane bis-enone **11** was obtained in 70% yield as the sole product. The structure of **11** was revealed through its eight-line ^{13}C NMR spectrum with resonances at δ 209.0 (s), 160.3 (d), and 148.2 (s) diagnostic of an α-substituted 2-cyclopentenone moiety. The proximity of double bonds and carbonyl groups in it was established through its quantitative conversion to **4** on UV irradiation and formation of oxatetraquinane derivative **12** on nucleophilic additions (Scheme IV). Both **11** and **12** are useful substrates for further elaboration into interesting spheroidal polyhedranes. In forming **11** through central bond "a" cleavage, the complex propellane **4** exhibits marked deviation from the simple [4.4.2]propellanes, which undergo peripheral cyclobutane fragmentation to ethylene and bicyclo[4.4.0]decane derivatives.[6]

Experimental Section[7]

BF_3·OEt_2-Catalyzed Rearrangement of Hexacyclo[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]pentadecane-2,8-dione (4). To a solution of hexacyclic dione (1 g, 4.38 mmol) in benzene (25 mL) was added 5 mL of BF_3·OEt_2. The resulting mixture was stirred at reflux temperature for 90 h. Then the reaction mixture was poured into saturated sodium bicarbonate solution and extracted with benzene (3 × 20 mL). The organic layer was washed with water and brine and dried over anhydrous sodium sulfate. The organic extract was concentrated in vacuo to give an oily residue, which was charged on a silica gel (30 g) column. Elution of the column with 5% ethyl acetate–hexane gave phenylated hexacyclic compound **6a** (317 mg, 25%). Recrystallization from hexane furnished an analytically pure sample of **6a**: mp 107–108 °C; IR (KBr) 3050, 1760, 1600, 1580, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 7.3 (s with structure, 5 H), 2.8–1.2 (m, 17 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 217.0 (s), 149.6 (s), 128.5 (d), 126.8 (d), 125.5 (d), 60.1 (s), 56.7 (d), 54.4 (s), 50.9 (d), 49.5 (d), 48.2, 45.2, 42.4, 42.2, 41.9, 35.0, 26.5 (t), 25.6 (t), 24.5 (t); MS, *m/e* (relative intensity) 290.3 (M^+, 38), 196.2 (100), 167.2 (19), 153.2 (12), 129.1 (20), 115 (23), 91.1 (36), 65.1 (11). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.94; H, 7.79. Continued elution of the column with the same solvent system gave hexacyclic propellanedione **5** (150 mg, 15%). Recrystallization from hexane gave an analytical sample: mp 101–102 °C; IR (KBr) 1770 (sh), 1745 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.76 (m, 2 H), 2.3 (m, 2 H), 2.13 (m, 2 H), 1.86 (m, 2 H), 1.73 (m, 2 H), 1.51 (m, 4 H), 1.14 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.0 MHz) δ 213.2 (s), 49.1 (d), 48.1 (s), 42.3 (d), 42.0 (d), 38.0 (t), 22.0 (t), 21.8 (t); MS, *m/e* (relative intensity) 228.2 (M^+, 90), 200.2 (83), 172.2 (100), 157.2 (24), 144.2 (26), 134.2 (50), 130.1 (26), 115.1 (37), 91.1 (54), 77.1 (37). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.00; H, 7.12.

Further elution of the column with 10% ethyl acetate–hexane gave tetracyclic compound **7** (186 mg, 20%). Bulb to bulb distillation at 190 °C (0.1 torr) gave **7** as a viscous, light brown liquid: UV (MeOH) λ_{max} 306 nm (ε 9600); IR (neat) 3050, 1680, 1620 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 5.88 (m, 1 H), 5.68 (m, 1 H), 3.9 (m, 1 H), 3.56 (m, 1 H), 2.96 (d, 2 H, J = 4 Hz), 2.7 (m, 2 H), 2.48 (m, 4 H), 1.8 (t, 4 H, J = 4 Hz); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 198.5 (s), 187.0 (s), 156.4 (s), 141.0 (s), 135.7 (s), 129.7 (d), 129.1 (d), 65.3 (d), 37.7 (d), 35.4 (t), 33.9 (t), 26.3 (t), 22.2 (t), 22.0, 21.9; exact mass calcd for $C_{15}H_{16}O$ *m/e* 212.1201, found 212.1188.

Catalytic Hydrogenation of 7. A solution of unsaturated compound **7** (100 mg, 0.43 mmol) in 5 mL of dry ethyl acetate was hydrogenated over preactivated platinum dioxide (5 mg) at a hydrogen pressure of 30 psi for 24 h. The reaction mixture was filtered to remove the catalyst, and the filtrate was concentrated in vacuo to afford an oily liquid, which was chromatographed on a silica gel (10 g) column. Elution with 5% ethyl acetate–hexane gave the perhydro compound **8** (56 mg, 55%) as the major product, and it was recrystallized from hexane: mp 49 °C; IR (KBr) 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 2.92 (m, 4 H), 2.1–0.6 (m, 18 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 222.1, 55.4, 54.4, 48.5, 41.6, 40.1, 29.0, 28.1, 26.8, 26.7, 26.5, 25.7, 24.3, 20.3. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.14. Found: C, 82.33; H, 9.92.

Rearrangement of Hexacyclo[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]pentadecane-2,8-dione (4) in Sulfuric Acid. To a solution of 228 mg (1 mmol) of dione **4** in 5 mL of dichloromethane was added 1 mL of 96% concentrated H_2SO_4 at ice temperature, and the reaction mixture was stirred at room temperature for 20 h. Then the reaction mixture was carefully quenched by pouring into saturated sodium bicarbonate solution and extracted with dichloromethane (3 × 10 mL). The organic layer was washed with brine and dried, and removal of solvent gave a quantitative yield of **5** as a white crystalline residue. Its melting point and IR spectrum were found to be identical with those of the material obtained in the earlier experiment.

BF_3·OEt_2 Rearrangement of Hexacyclo[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]pentadecane-2,8-dione (4) in Cumene Solvent. To 300 mg (1.31 mmol) of dione **4** in 15 mL of cumene was added 2 mL of BF_3·OEt_2. The reaction mixture was stirred at 90 °C for 40 h, and then 1 mL of BF_3·OEt_2 was added and the reaction was continued for another 20 h. Then most of the cumene was removed at reduced pressure (0.2 torr) at 70 °C. The reaction mixture was diluted with water and extracted with benzene (3 × 10 mL). The organic layer was washed with saturated $NaHCO_3$ solution and dried. Removal of solvent gave a viscous oily product, which was charged on a silica gel (20 g) column. Elution with 5% ethyl acetate–hexane gave **6b** (100 mg, 23%), which was crystallized from ethanol: mp 95–96 °C; IR (KBr) 1760, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 7.1 (s with st, 4 H), 3.1–1.3 (m, 18 H), 1.2 (d, J = 7 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 217.3, 146.8, 145.8, 126.6, 126.4, 59.8, 56.9, 54.5, 51.0, 49.4, 48.2, 42.5, 42.2, 41.9, 34.9, 33.6, 26.5, 25.6, 24.4, 24.1. Anal. Calcd for $C_{24}H_{28}O$: C, 86.74; H, 8.43. Found: C, 86.64; H, 8.45. Further elution of the column with 10% ethyl acetate–hexane gave **5** (60 mg, 20%), which was found identical by its melting point and IR comparison

(5) While reduction in BF_3–benzene medium appears improbable, instances have been recorded in literature where reduction products are obtained in a nonreducing medium through disproportionation of one of the products. See, for example: Gassman, P. G.; Olsen, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740.

(6) Ginsburg, D. *Propellanes*: Structure *and Reactions*; Verlag Chemie, GmbH: Weinheim, 1975.

(7) For a general write-up on the Experimental Section, see: Mehta, G.; Rao, K. S. *J. Org. Chem.* **1985**, *50*, 5537.

with the sample obtained in the earlier experiment. Lastly, elution with 20% ethyl acetate–hexane gave the unsaturated compound (40 mg, 14%), which was found to be identical with the sample described in the earlier experiment.

Flash Vacuum Pyrolysis of Hexacyclo[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]pentadecane-2,8-dione (4). Hexacyclic propellane 4 (2 g, 8.92 mmol) was slowly sublimed (120 °C (1 torr)) through a quartz tube (1.5 × 30 cm) packed with quartz chips, connected to a vacuum line, and provided with a collection flask and a liquid nitrogen trap. The quartz tube was heated with nichrome wire wound around it and was insulated with asbestos padding. The temperature was controlled by a Variac and was measured by a Chromel–Alumel thermocouple on a Keithley digital multimeter. The quartz tube was preheated and equilibrated at 550 °C. The solid condensate collected in the receiver was dissolved in benzene and charged on a silica gel (30 g) column. Elution with benzene removed minor impurities. Further elution of the column with 10% ethyl acetate–benzene gave 11 (1.4 g, 70%), which was recrystallized from dichloromethane–hexane: mp 158 °C; UV (MeOH) λ_{max} 224 nm (ϵ 11 035); IR (KBr) 1710, 1630 cm^{-1} (cyclopentenone); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 6.9 (s, 2 H), 3.4 (s, 4 H), 2.4–1.0 (m, 10 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 209.0 (s), 160.3 (d), 148.2 (s), 55.7 (d), 47.8 (d), 31.9 (t), 20.0 (t), 25.6 (t). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.10; H, 7.11.

Photocyclization of Tetracyclo[9.2.1.1^{3,6}.0^{4,13}]pentadeca-6(15),11(14)-diene-5,12-dione (11). A solution of 11 (228 mg, 1 mmol) in 100 mL of ethyl acetate was purged with nitrogen and irradiated with a Hanovia 450-W medium-pressure mercury vapor lamp in a quartz immersion well with use of Pyrex filter for 20 min. The TLC and IR spectrum of the product after removal of solvent were found to be identical with those of hexacyclic dione 4.

Addition of Grignard Reagent to Tetracyclo[9.2.1.1^{3,6}.0^{4,13}]pentadeca-6(15),11(14)-diene-5,12-dione (11). To the methylmagnesium iodide solution prepared from magnesium (125 mg, 5.1 mmol) and methyl iodide (2 mL) in dry ether (25 mL) was added bis-enone 11 (700 mg, 3.07 mmol) in 15 mL of THF through an addition funnel, and the reaction mixture was stirred at room temperature for 3 h. Then the reaction mixture was carefully quenched with saturated ammonium chloride solution and extracted with ether (2 × 25 mL). The organic layer was washed with brine and dried. Removal of solvent gave 12 (640 mg, 85%). Analytically pure 12 was obtained by recrystallization from hexane–carbon tetrachloride: mp 158–159 °C; IR (KBr) 3400, 3050, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 5.36 (s, 1 H), 5.12 (s, 1 H), 3.3–2.8 (m, 6 H), 2.2–1.6 (9 H), 1.4 (s, 3 H); ^{13}C NMR ($CDCl_3$, 25.0 MHz) δ 145.6, 144.5, 136.7, 133.2, 118.1, 95.4, 61.0, 59.6, 48.0, 47.1, 36.2, 29.7, 29.2, 28.8, 27.6, 25.0. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.55; H, 8.35.

Crystal Data for 6a. The crystals belong to the space group $C2/c$ with a = 20.845 (4), Å, b = 6.168 (2) Å, c = 23.320 (3) Å, and β = 90.27 (1)°. The intensity data (2419 reflections) were collected on a CAD4F-11M diffractometer with Mo Kα radiation (0.7107 Å) by using the $\omega/2\theta$ scan technique. The structure was solved by direct methods. Full-matrix refinement of scale factor, positional, and anisotropic thermal parameters (isotropic for H atoms) gave R = 0.063 for 1400 reflections with $|F_o| > 3\sigma|F_o|$.[8]

Crystal Data for 8. The crystals belong to the space group *Pbca* with a = 9.354 (1) Å, b = 11.050 (2) Å, c = 23.761 (4) Å. The intensity data (2146 reflections) were collected on a CAD4F-11M diffractometer with Mo Kα radiation (0.7107 Å) by using the $\omega/2\theta$ scan technique. The structure was solved by direct methods. Full-matrix refinement of scale factor, positional, and anisotropic thermal parameters (isotropic for H atoms) gave R = 0.047 for 1158 reflections with $|F_o| > 3\sigma|F_o|$.[8]

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(8) Further details about X-ray crystal structures can be obtained from the NCL group.

Dioxa-1,3-bishomopentaprismane: Synthesis and Transformations

Goverdhan Mehta* and K. Raja Reddy

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

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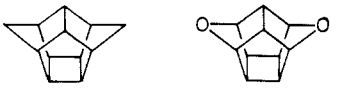
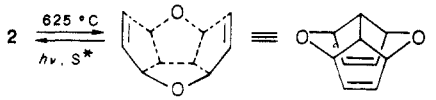
Heterocaged systems have received attention in recent years from synthetic as well as mechanistic considerations.[1] The main motivation for these studies has been the desire to compare the reactivity pattern of carbon caged compounds with their heterologues. We have been investigating the chemistry of bishomopentaprismane (1) and its derivatives[2] and in this context became interested in its dioxa-analogue 2. Herein, we report the synthesis of hexacyclic diether 2 and describe its transformations to some new and structurally related polycyclic diethers.



1 2

Readily available[3] hexacyclic keto ether 3 on treatment with aqueous alkali furnished the hexacyclic carboxylic acid 4 in good yield through Haller–Bauer cleavage and sequential intramolecular displacement of two chlorine atoms with the carboxylate oxygen.[3,4] Hunsdieker reaction on 4 proceeded readily to the bromo-compound 5 (85%). Reductive dehalogenation of 5 with Li–THF–*t*-BuOH[5] proceeded as expected to furnish the dioxabishomopentaprismane 2, mp 271–273 °C, in 70% yield, Scheme I. The structure and C_{2v} symmetry of 2 were clearly revealed through its three-line ^{13}C NMR spectrum with diagnostic resonances at δ 83.5, 56.4, and 41.9.

In view of the previous interesting observations[2,6] with 1 and its derivatives, the dioxa-analogue 2 was also subjected to thermally induced cycloreversion reaction. Flash vacuum pyrolysis (FVP) of 2 through a quartz column at 625 °C led to facile and regioselective fragmentation of the cyclobutane ring, and dioxatetraquinane 6 was obtained in 70% yield. The structure of 6 followed from its spectral characteristics (vide Experimental Section) and in particular through its ^{13}C NMR resonances at δ 134.7, 88.7, and 53.0. On irradiation with UV light, the proximate



6

double bonds of 6 underwent photocycloaddition back to 2. The dioxatetraquinane 6 appeared to be a good source of novel pentacyclic diethers related to heterodiamantanes via transannular bonding of its cyclopentane double bonds.

(1) (a) Sasaki, T.; Eguchi, S.; Kiriyama, T.; Hiroaki, O. *Tetrahedron* **1974**, *30*, 2707. (b) Singh, P. *J. Org. Chem.* **1979**, *44*, 843. (c) Dekker, J.; Dekker, J. J.; Fourie, L.; Dekker, T. G.; Pachler, K. G. R.; Wessels, F. L. *Tetrahedron Lett.* **1976**, 1613. (d) Barborak, J. C.; Khoury, D.; Maier, W. F.; Schleyer, P. V. R.; Smith, F. C.; Smith, W. F.; Wyrick, C. *J. Org. Chem.* **1979**, *44*, 4761. (e) Ammann, W.; Jaggi, F. J.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 2019. (f) Ammann, W.; Ganter, C. *Helv. Chim. Acta* **1981**, *64*, 996. (g) Hirao, K.; Kajikawa, Y.; Yonemitsu, O.; Osawa, E. *Heterocycles* **1982**, *17*, 63. (h) Mehta, G.; Rao, H. S. P. *J. Chem. Soc., Chem. Commun.* **1986**, 472.

(2) Mehta, G.; Nair, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 7519.

(3) Marchand, A. P.; Chou, T.-C. *Tetrahedron* **1975**, *31*, 2655.

(4) Dauben, W. G.; Reitman, L. N. *J. Org. Chem.* **1975**, *40*, 841.

(5) Bruck, P.; Thomson, D.; Winstein, S. *Chem. Ind. (London)* **1960**, 405.

(6) Fukunaga, T.; Clement, R. A. *J. Org. Chem.* **1977**, *42*, 270.

0022-3263/87/1952-0460$01.50/0