reactions as in other systems since the crotylboronates are very weak (soft) nucleophiles and because the trajectory of reagent approach to the carbonyl is constrained to a considerably smaller value than in biomolecular carbonyl addition reactions.[11] Studies probing the generality of these conclusions are in progress and will be reported in due course.

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Registry No. 1, 69611-01-4; 2, 76347-14-3; 3, 69611-02-5; 4, 96041-10-0; 5, 22323-80-4; 6, 87305-35-9; 7, 88406-01-3; 7 (acetate), 96041-14-4; 8, 88424-95-7; 8 (acetate), 96094-53-0; 9, 88424-94-6; 9 (acetate), 96094-54-1; 10, 96094-43-8; 11, 96041-11-1; 11 (acetate), 96041-15-5; 12, 96094-44-9; 12 (acetate), 96094-55-2; 13, 96094-45-0; 13 (acetate), 96094-56-3; 14, 96094-46-1; 15, 96041-12-2; 15 (acetate), 96041-16-6; 16, 96094-47-2; 16 (acetate), 96094-57-4; 17, 96094-48-3; 17 (acetate), 96094-58-5; 18, 96094-49-4; 19, 96041-13-3; 19 (acetate), 96041-17-7; 20, 96094-50-7; 20 (acetate), 96094-59-6; 21, 96094-51-8; 21 (acetate), 96094-60-9; 22, 96094-52-9.

Supplementary Material Available: Spectroscopic data and physical constants for 7–17 and 19–21 (5 pages). Ordering information is given on any current masthead page.

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(12) Holder of the Firmenich Career Development Chair in Natural Products Chemistry, 1981–84; Fellow of the Alfred P. Sloan Foundation, 1982–84.

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Cascade Molecules: A New Approach to Micelles.[1a] A [27]-Arborol[1b]

Summary: The preliminary synthesis and spectral characterization of monocascade spheres (Arborols) which possess a three-dimensional microenvironment having the outer surface covered with polar functional groups is described.

Sir: In quest of novel micellar structures, we herein report a new series of micelles derived from an architectural model of trees,[2,3] specifically the Leeuwenberg model. This cascade[4] design generates a molecular structure, having an outer surface covered with polar functional groups. Since this model is based on a simple mathematical progression $[X_n = E^{n-1}]$, it denotes a new class of cascade structures.[5]

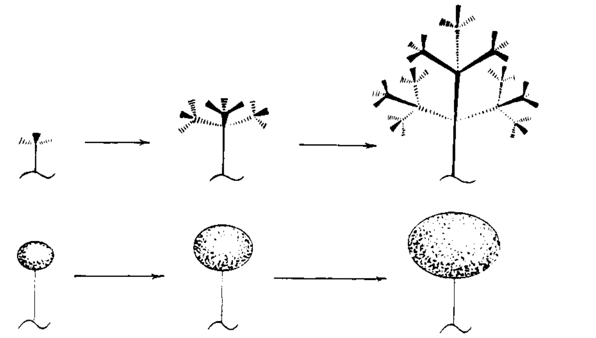
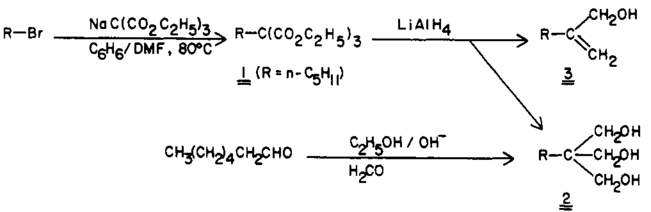


Figure 1.

Figure 1 shows the pictorial representation of the Leeuwenberg model as applied to micellar construction. The expansion of this one-directional cascade model to that of a two-directional cascade (sylvanols)[1c] affords entrance to potential "unimolecular" micelles, which possess an expandable parabolic cavity capable of surface inclusion.[14] Such a two-directional model is in essence an anticrown ether, since absorption is on the outer surface possessing the negative curvature. We herein communicate the preliminary synthesis and spectral characterization of the simplest examples of monocascade spheres.

Treatment of typical primary alkyl halides, for example 1-bromopentane, with $NaC(CO_2Et)_3$[15] afforded (83%) the tris-ester 1 [oil; bp 115–120 °C (3 mm); ^{13}C NMR δ 65.9



($C^{4°}$), 167.6 (CO)],[16] which can be reduced with either $LiAlH_4$ or $LiBH_4$ in ether to give triol 2 [white crystals; mp 65–65.5 °C; ^{13}C NMR δ 42.8 ($C^{4°}$), 66.7 (CCH_2O)][16] in low yield. The major unexpected product from this reduction is olefin 3 [^{13}C NMR δ 149.8 ($C{=}CH_2$), 109.4 ($C{=}CH_2$), 66.2 (CH_2O)], which arises by a facile Grob fragmentation.[17] In view of this deleterious result, a

(1) (a) Micelles. Part 1. (b) Since these cascades are based on arboreal design, they are logically called *arborols*. Sylvanols are thus the polyspherical cascade analogues. (c) Visiting Scholar from the Lanzhou Institute of Chemical Physics, Academia Sinica, China, 1983–1985.

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(4) For cascade terminology, see: Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155.

(5) There are very few examples[6] of true cascade molecules which follow such a mathematical progression. Molecules, such as polypods,[7] hydrophilic lipids,[8] octopus ["hexapus"] molecules,[9] tentacle molecules,[10] hexahosts,[11] branched polyamines,[12] and "many-armed acyclic polyethers,[13] are related to, but do not fit, a cascade formulation.

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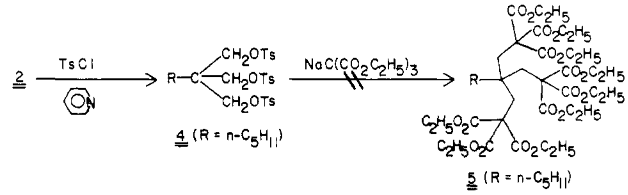
(16) Detailed synthetic, spectral, and analytical data are furnished in the supplementary material.

0022-3263/85/1950-2003$01.50/0

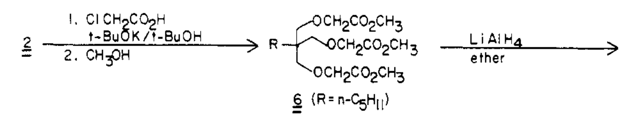
cross-Cannizzaro reaction[18] of heptanal with formaldehyde cleanly gave (60%) the desired **2**.

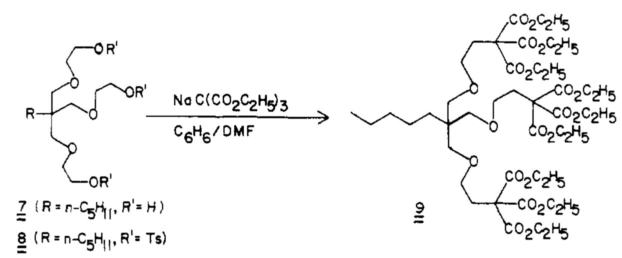
Growth of the second tier by repetition of the above sequence was envisioned, thus **2** was transformed (70%) to the tris-tosylate **4** [mp 122–123 °C; ^{13}C NMR δ 41.8



($C^{4°}$), 67.9 (CH_2O)] by standard conditions[9] using anhydrous pyridine at 0 °C. Treatment of **4** with triethyl sodiomethanetricarboxylate under diverse conditions did not generate the anticipated **5**; simple nucleophilic attack in triplicate failed probably due to the steric crowding at one or more of the terminal carbons. Circumvention of this problem in the triplication sequence utilizes an extender group.

Elongation of triol **2** with chloroacetic acid in the presence of *t*-BuOK/*t*-BuOH and subsequent esterification of the intermediate triacid with MeOH afforded (95%) **6**





[oil; bp 180 °C (0.8 mm)]. Reduction of **6** with $LiAlH_4$ in ether gave (80%) the extended triol **7** [oil; bp 180 °C (1 mm); ^{13}C NMR δ 43.2 ($C^{4°}$), 78.7 (CCH_2O), 74.1 (CH_2CH_2OH), 61.6 (CH_2OH)], which was tosylated as above to give (90%) tritosylate **8** [oil; ^{13}C NMR δ 43.2 ($C^{4°}$), 78.6 (CCH_2O)]. Without further purification **8** was treated with $NaC(CO_2Et)_3$ in C_6H_6–DMF (1:1) at 110 °C to afford (70%) the desired nonaester **9** [oil; bp 200–210 °C (2 mm); ^{13}C NMR δ 43.3 ($C^{4°}$), 78.8 (CCH_2), 67.6 (CH_2OCH_2), 34.1 (CH_2CCO), 74.0 (CCO), 166.8 (CO)]. Even though ^1H NMR is rather worthless in structural analyses of these dense cascades, ^{13}C NMR is an ideal diagnostic tool due to their inherent symmetry.

A third tier construction utilizes amide formation. Treatment of **9** with tris(hydroxymethyl)aminomethane (**10**) at 70 °C in Me_2SO generates (90%) the [27]-arborol **11** [oil; ^{13}C NMR δ 44.5 (CH_2CCH_2), 62.5 (HNC), 65.1 (CH_2OH), 75.2 (CCO), 171.6 (CO)], which is infinitely water soluble even though the molecular weight is >1600.

This communication describes only the preliminary methodology and work is currently in progress in our laboratories to delineate the synthetic as well as the physical properties of these novel cascade molecules.

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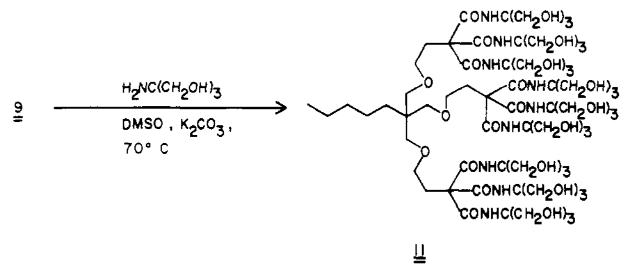

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Registry No. 1, 20484-14-4; 2, 20762-79-2; 3, 64251-19-0; 4, 96150-67-3; 5, 96150-68-4; 6, 96150-69-5; 7, 96150-70-8; 8, 96150-71-9; 9, 96150-72-0; 10, 77-86-1; 11, 96150-73-1; $BrCH_2(CH_2)_3CH_3$, 110-53-2; $NaC(CO_2Et)_3$, 68922-87-2; $CH_3(CH_2)_5CHO$, 111-71-7; HCHO, 50-00-0; $ClCH_2CO_2H$, 79-11-8.

Supplementary Material Available: Experimental details of synthesis and characterization (7 pages). Ordering information is given on any current masthead page.

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Stereoselective Syntheses of Alkenyl-Substituted 1,3-Dioxolanes or 4,7-Dihydro-1,3-dioxepins or an (*E*)-α,β-Unsaturated Aldehyde from (*Z*)-2-Butene-1,4-diols

Summary: Treatment of (*Z*)-2-butene-1,4-diols with boron trifluoride etherate in acetone solvent affords stereodefined alkenyl-substituted 1,3-dioxolanes or 4,7-dihydro-1,3-dioxepins or an (*E*)-α,β-unsaturated aldehyde, depending on the reaction temperature and time.

Sir: In connection with ongoing work, our need for ready access to isopropylidene derivatives of (*Z*)-2-butene-1,4-diols prompted us to explore methods for their preparation. In the course of these investigations we observed that treatment of the diol **1a** in acetone with boron trifluoride etherate at 50 °C did not afford the anticipated acetal **4a** but instead produced the (*E*)-α,β-unsaturated aldehyde **2a**. To delineate the scope of this interesting stereoselective transformation as well as to find conditions for the formation of the acetal **4a**, the reactions of a variety of (*Z*)-2-butene-1,4-diols **1a–d** with boron trifluoride etherate in acetone solvent were investigated.

We now report that the natures of the products derived from (*Z*)-2-butene-1,4-diols and boron trifluoride etherate in acetone are remarkably dependent upon the conditions under which the reaction is carried out. Thus, treatment of **1a**[1] (1 mmol) in acetone (2 mL) at 0 °C with $BF_3{\cdot}OEt_2$ (1 equiv) followed by warming the reaction mixture at 50 °C for 1 h furnished, by GLC analysis, a 77% yield of the *E* aldehyde **2a**.[2-4] On the other hand, when the reaction was performed at 25 °C for 1 h, the GLC chromatogram

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