

Ammonium Cascade Molecules

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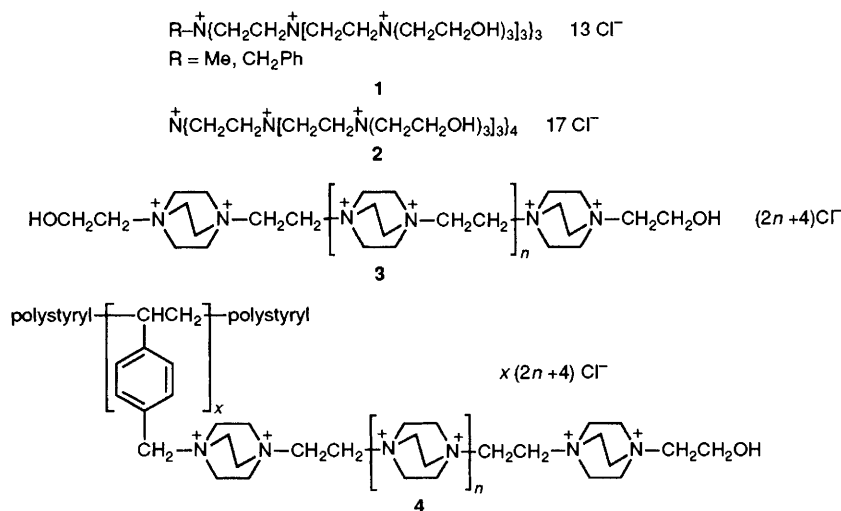
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New categories of cascade molecules have been synthesized in four general structural categories (balloons, stars, strings and combs) in which the core and branching points are ammonium ion sites.

Recently there has developed an interest in the synthesis and investigation of cascade molecules, or dendrimers. These are species which incorporate the structural features of a 'core', and several branches emanate from that core, each branch having a reiterative structural component allowing the introduction of additional branches in a controlled and systematic

manner. The geometry of such species may be described as three-dimensional chemical fractals. Developments in this area of chemical study have been reviewed recently.¹

Efforts of this laboratory have been directed toward the preparation of a variety of cascade molecules, particularly those bearing multiple cationic phosphonium ion sites within



the covalent structure, with freely associated anions.²⁻⁵ We herein report on the preparation of a new series of cationic cascade species based on an ammonium ion core and branch points with geometries represented by 'balloons' **1**, 'stars' **2**, 'strings' **3** and 'combs' **4**.

Balloons incorporate a core from which emanate three branching arms and one simple alkyl group. Stars differ from balloons in that all four arms emanating from the core are branched. Strings are a linear array of reiterative structural units devoid of branching. Combs are species in which numerous core sites are present along a polymeric backbone bearing balloon or string type arms. The species **4** illustrated has string type arms.

The syntheses of these materials proceeds easily using repetitive sequences of reactions. For **1** and **2**, triethanolamine is alkylated by heating with an excess of the appropriate alkyl halide in acetonitrile solution. Stars **1** have been prepared using methyl iodide and benzyl bromide as quaternizing agents for the core site of triethanolamine. For **2**, the alkyl halide used was 2-chloroethanol, allowing all four arms to be branched. Upon concentration of the reaction mixture under reduced pressure the crystalline salts were isolated in excellent yields (>95%). The salts were poorly soluble in most organic solvents, except for methanol and ethanol, but readily soluble in water. The ¹H NMR (D₂O, 200 MHz) and IR spectra, and combustion analyses were in accord with the proposed structures for these simple salts. For the introduction of further generations of branch sites about the core and the elaboration of the arms of the dendrimers, the simple salts were tosylated using an excess of tosyl chloride with pyridine in acetonitrile. The resultant polytosylates exhibited spectra in accord with the proposed structures, but were not subjected to combustion analyses as they deteriorated rapidly on standing and were highly hygroscopic. Rather, these materials were immediately treated with an excess of triethanolamine in acetonitrile using the same procedure as for the initial quaternization, the salts being isolated upon concentration under reduced pressure in good yield (>90%) and high purity as indicated by ¹H NMR (D₂O, 200 MHz) and IR spectra, and combustion analyses. The addition of further generations was accomplished by repetition of the tosylation and alkylation steps. The species elaborated through three generations were produced for both types of dendrimers. An alternative procedure which has been used in the elaboration of the arms of comb species involves conversion of the free hydroxy to a chloride using an excess of phosgene in a pyridine-toluene mixture, followed by reaction with triethanolamine.

The preparation of string species was accomplished in an analogous manner. 1,4-Diazabicyclo[2.2.2]octane (dabco) was dialkylated in benzene solution using 2-chloroethanol to produce the 1,4-bis(β-hydroxyethyl)-1,4-diazabicyclo[2.2.2]-

octane dichloride. The resultant salt was tosylated with tosyl chloride in pyridine yielding, after evaporation of the pyridine under reduced pressure, the ditosylate, which was extremely hygroscopic and was used in reaction with an excess of dabco (acetonitrile solution) immediately upon isolation. The material isolated by evaporation of the solvent was purified using a DOWEX 2-X8 column eluting with water and was alkylated using 2-chloroethanol to give the string species **3** wherein *n* = 1. Further generations of **3** were prepared by subsequent iteration of the tosylation and displacement steps. Again, yields were extremely high for the individual steps (>90%). As with the balloon and star species, an alternative approach involved conversion of the free hydroxy sites to chloride using phosgene, followed by reaction with dabco. Species elaborated through three generations were produced. All materials exhibited ¹H NMR and IR spectra in accord with the proposed structures and the non-tosylate salts exhibited satisfactory combustion analyses.

Comb species were prepared using both the tosylation and phosgene activation procedures, in a manner completely analogous to that noted for balloons and strings, using Merrifield's peptide resin (2% crosslinked chloromethylated styrene-divinylbenzene copolymer) as the backbone. Species elaborated through three generations were produced with each of the dabco and triethanolamine extension units. These materials and their intermediates were completely insoluble in the entire range of solvents used, both aqueous and organic. Using triethanolamine, the initial alkylation proceeded at only ~55% of the nominally available reactive benzylic sites. Using dabco, a higher level of incorporation could be attained (~80%), but there remained unreacted sites. Upon elaboration of the arms, appropriate increases in the nitrogen content could be observed by combustion analyses. These materials have proven to serve quite efficiently as high capacity ion exchange materials.

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