

## Phosponium Cascade Molecules

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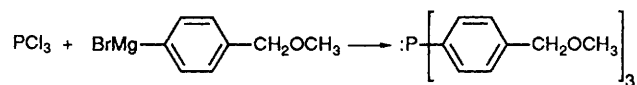
Cascade molecules have been synthesized in which the initiation core and branch points of the cascade structure are quaternary phosponium ion sites.

Recently there has developed significant interest in a category of macromolecules known as 'dendrimers' or 'cascades'.<sup>1</sup> These molecules incorporate structural repetition in an ordered manner, starting with an initiation core from which emanate two or more identical branches, each branch containing further branch sites. With successive generations of branch sites a cascade structure develops a geometry akin to that of a fractal set.<sup>2</sup>

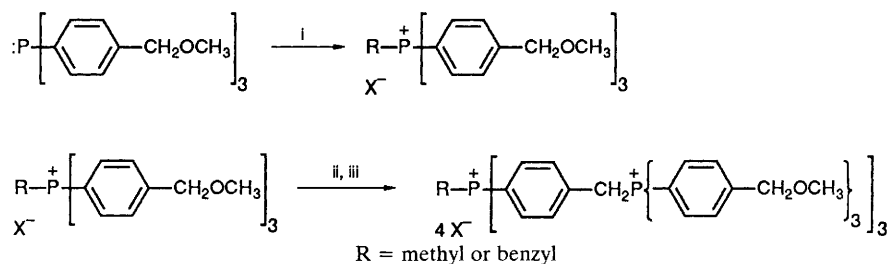
To date a variety of dendrimeric molecules have been synthesized and characterized.<sup>1,3-7</sup> These have been, without exception, species which bore no formal charge on the cascade structure. We herein report the preparation of a new category of cascade molecules in which the initiation core and subsequent branch points are quaternary phosponium ion sites. These molecules thus incorporate a large (defined) number of cationic sites within the cascade structure, having an equal number of associated anions.

Phosponium dendrimers have been prepared in which the cascade generations develop in three directions from the initiation core. The initiation core and repeating branch units are all derived from tris(*p*-methoxymethylphenyl)phosphine, synthesized in a Grignard reaction using *p*-(methoxymethyl)bromobenzene and phosphorus trichloride (Scheme 1).

After quaternization of the initiation core with an alkyl halide, successive generations of the cascade structure are introduced *via* treatment with iodotrimethylsilane followed by an excess of tris(*p*-methoxymethylphenyl)phosphine. The



Scheme 1



**Scheme 2.** i, CH<sub>3</sub>I or C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br; ii, iodotrimethylsilane; iii, tris(*p*-methoxymethylphenyl)phosphine.

reaction of iodotrimethylsilane with a benzylic alkyl ether readily generates the benzylic iodide and the alkyl trimethylsilyl ether. The benzylic iodide also readily accomplishes quaternization of the phosphine for the subsequent generation of the cascade (Scheme 2).

For each of the examples (R = methyl and benzyl), reactions ii and iii of Scheme 2 were repeated for two further generations of the cascade structure. This results in each instance in the formation of species containing forty cationic (phosphonium) sites embedded within their structures.

After each introduction of a new generation, the materials were purified and subjected to spectrometric and combustion analyses. With the initial monophosphonium salts, purification was effected by flash chromatography. Each generation of the cascade molecules was purified by passage through a Dowex 2-X8 column in the iodide form, eluting with 30% aqueous ethanol.

Each of the first two reaction sequences (ii and iii) for the introduction of further generations of the cascade provided a moderate yield (22–64%) of purified product. The initial phosphonium salts and the first two generation cascade species were all readily soluble in a wide range of solvents, including water, chloroform, acetonitrile, and ethyl acetate. Moreover, the materials were quite hygroscopic, absorbing large quantities of water upon normal exposure to moist air. The reaction sequence to form the third generation cascade materials, however, gave pure products in only poor yield (5%), and the pure materials exhibited no significant solubility in any of the aforementioned solvents, except for acetonitrile. Suitable solubility was found in [D<sub>2</sub>O]acetonitrile to allow the measurement of NMR spectra.

All the materials exhibited <sup>1</sup>H and <sup>31</sup>P NMR (IBM-Bruker: 200 MHz) spectra in accord with the proposed structures. In each instance the <sup>31</sup>P NMR signal for the initiation core phosphonium site occurred ~8 ppm downfield (28 ppm

downfield relative to external 85% phosphonic acid) from that for the phosphonium branch (21 ppm downfield relative to external 85% phosphoric acid) sites. First, second, and third generation phosphonium sites were indistinguishable from each other by their <sup>31</sup>P NMR chemical shifts. All materials exhibited combustion elemental analyses in accord with their proposed structures.

The phosphonium cascades represent a novel addition to the general class of dendrimeric molecules. A large, defined number of positively charged sites are incorporated into an organic structure at regular intervals. Numerous possibilities exist for the use of such structures in ion exchange and other supramolecular processes.

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