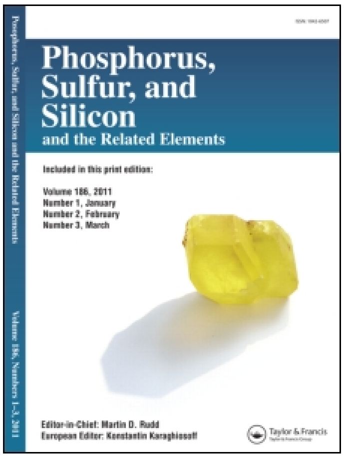


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactivity Inside a Selenophosphate Dendrimer

Grzegorz M. Salamończyk[a]
[a] Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, MLódź, Poland

To cite this Article Salamończyk, Grzegorz M.(2005) 'Reactivity Inside a Selenophosphate Dendrimer', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 3, 1051 — 1056

To link to this Article: DOI: 10.1080/10426500590906300

URL: http://dx.doi.org/10.1080/10426500590906300

Phosphorus, Sulfur, and Silicon, 180:1051–1056, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590906300

Taylor & Francis
Taylor & Francis Group

Reactivity Inside a Selenophosphate Dendrimer

Grzegorz M. Salamończyk
Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Łódź, Poland

The divergent synthesis of new series of dendrimers having phosphoryl, thiophosphoryl, and selenophosphoryl branching units has been accomplished by a concise procedure involving phosphitylation of alkanediol derivatives, followed by the corresponding chalcogen addition as the key steps. The backbone of a selenophosphate dendrimer was flexible enough to allow its chemical modification by means of the oxygenation with bulky peroxide.

Keywords Dendrimer; oxygenation; phosphoroamidite; selenium

INTRODUCTION

Dendrimers are perfectly ordered, monodisperse macromolecules exhibiting iterative architecture-branching of branches cascade. Their synthesis with precisely tuned structural components like core, branches, cavities and surface terminal functions affords material possessing particular chemical and physical properties and applications.[1–6] Modification and introduction of various functional groups to a dendrimer are of great present interest.[7] Nevertheless, most of these transformations rely on the formation of covalent or noncovalent bond to the surface. A controlled alteration of the interior of a dendrimer appears to be a much more difficult task.

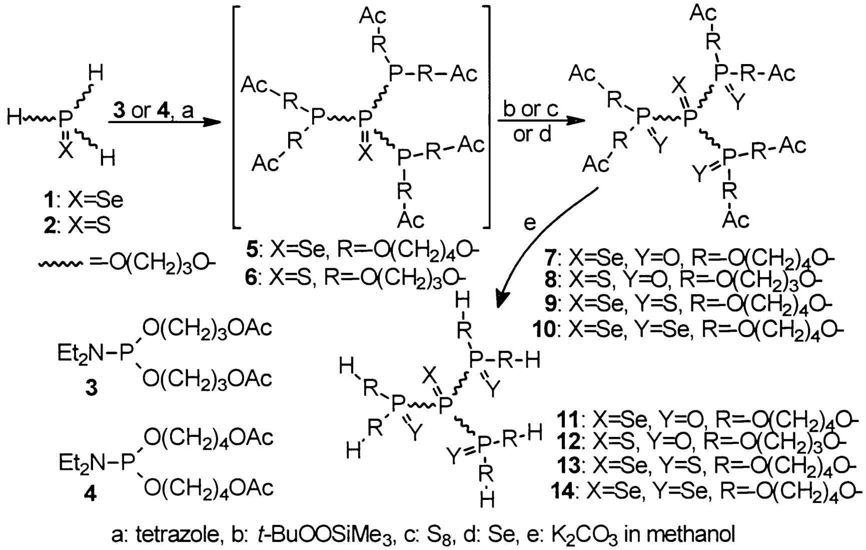
On the other hand, amidophosphite reagents now are being used widely for the synthesis of the large diversity of biologically relevant phosphates, including automated synthesis of oligonucleotides and their analogs on solid phase support.[8] In spite of this, they have not been sufficiently exploited to prove their suitability for the synthesis of phosphorus-based dendrimers.

Received January 9, 2004; accepted September 27, 2004.

Address correspondence to Grzegorz M. Salamończyk, The Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland. E-mail: gmsalamo@bilbo.cbmm.lodz.pl

RESULTS AND DISCUSSION

In this laboratory, a novel expedient method for the synthesis of dendrimers based on phosphorus at each branching point has been designed. Our developed methodology involves applying amidophosphite chemistry in divergent synthetic approach. The dendrimer building units, the core compounds **1, 2** and phosphitylating agents **3**, **4** were prepared in high yields from appropriate alkanediol monoacetates[9] as described.[10] The key dendrimer growth step is based on acid mediated alcoholysis of amidophosphite.[13] For example, $Se{=}P[O(CH_2)_3OH]_3$ (**1**) reacts readily with an excess of $Et_2NP[O(CH_2)_4OAc]_2$ (**4**) in the presence of tetrazole to provide trisphosphite intermediate **5** and diethylammonium salt of tetrazole (Scheme 1). At this stage we faced the challenge to find a mild oxidant for the generation of the oxyphosphoryl functions in **5** and **6** without affecting the labile thiophosphate or/and the especially sensitive selenophosphate group, present in the molecule. After much experimentation we have found that *t*-butylperoxy-trimethylsilane exclusively oxidized the P(III) phosphorus atoms at peripheral branching, furnishing the first generation dendrimers **7** and **8**, in good yields.[12] It seems that even in the case of relatively small dendritic molecules, external phosphite nucleophilic centers are much better reachable for the bulky peroxide than nucleophilic selenium in the core.



a: tetrazole, b: *t*-BuOOSiMe$_3$, c: S$_8$, d: Se, e: K$_2$CO$_3$ in methanol

SCHEME 1

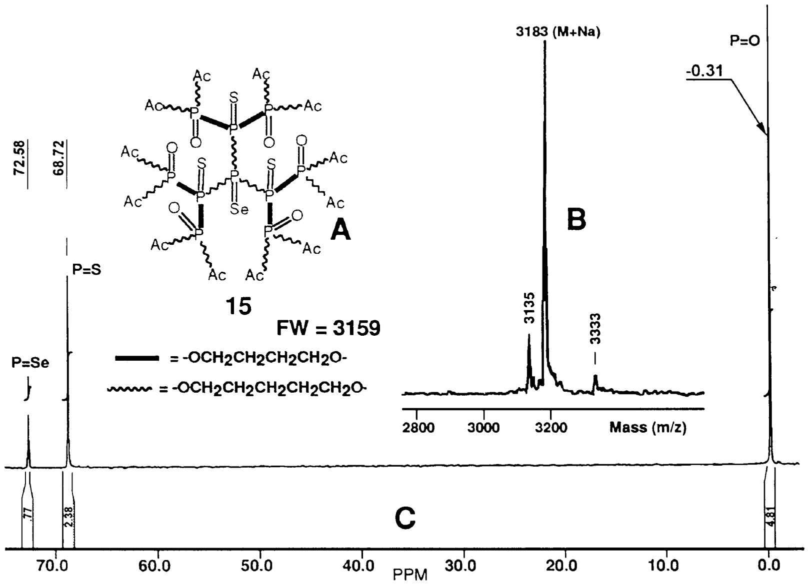


FIGURE 1 $^{31}P\{^{1}H\}$ NMR spectrum of **15**.

Addition of elemental sulfur or black selenium to crude **5** provided dendrimers **9** and **10** respectively. Cleavage of terminal acetates in **7**, **8**, **9** and **10** using K_2CO_3 in methanol afforded corresponding polyalcohols **11**, **12**, **13** and **14** in quantitative yields. The latter compounds were transformed into larger dendrimers up to generation 5 via reiteration of the synthetic strategy shown in Scheme 1. The dendrimer growth reactions can be easily monitored by $^{31}P\{1H\}$ NMR analyses. Figure 1 shows the structure of the second generation dendrimer **15** (A), as well as its MALDI TOF MS and $^{31}P\{1H\}$ NMR spectra (B) and (C), respectively. The presence of oxyphosphoryl, thiophosphoryl, and selenophosphoryl functions in one molecule gave very clear spectra compared with fully phosphorylated or thiophosphorylated dendrimer. This is due to the occurrence of signals corresponding to P=O, P=S, and P=Se in three very distinct areas.

Well-separated resonance lines gave also the $^{31}P\{1H\}$ NMR and $^{77}Se\{1H\}$ NMR spectra of dendrimers having P=Se functions at each branching point. For example, $^{31}P\{^{1}H\}$ NMR spectrum of somewhat large 4th generation selenophosphate dendrimer (theor. FW = 15275) showed five distinct resonance lines with accurate integration: $\delta = 73.99$(1P, core), 73.72(3P), 73.57(6P), 73.54(12P), 73.41(24P) ppm. All signals displayed satellite side bands with the splitting of

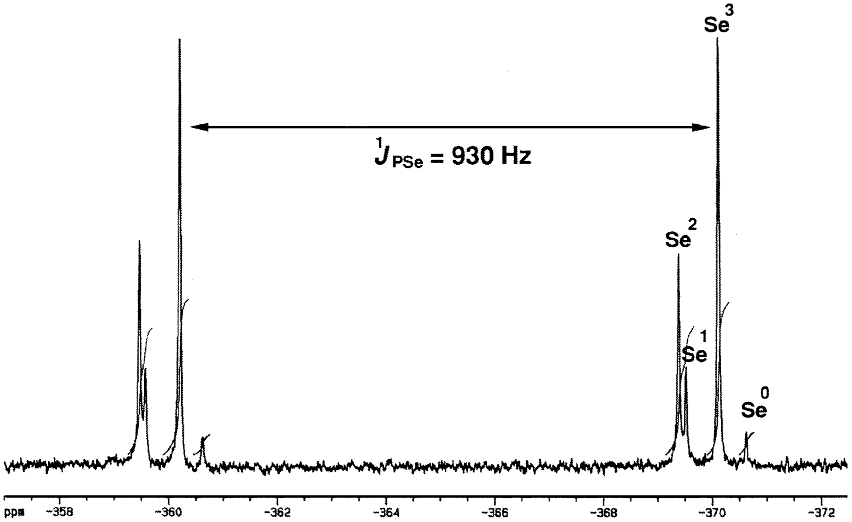
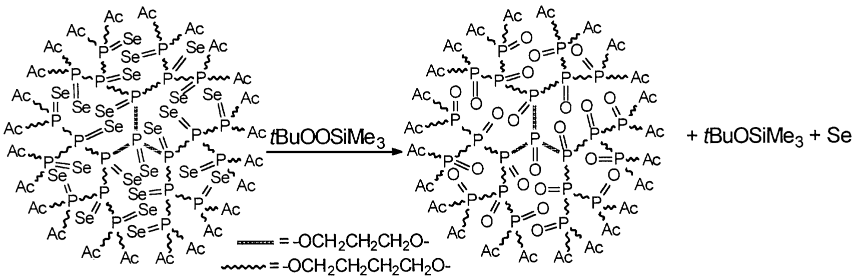


FIGURE 2 ^{77}Se{^{1}H} NMR spectrum of **16**.

931 Hz due to ^{31}P-^{77}Se coupling. Figure 2 shows the ^{77}Se{1H} NMR spectrum of third generation selenophosphate dendrimer **16** (Scheme 2) having three and four carbon chains in its scaffold. The spectrum displays clearly four doublets with the same $^1J_{P,Se}$ = 930 Hz. The selenium atoms (22) at each generation are undoubtedly detected, including selenium at the core (the lowest resonance lines, Se^0).

The chemical behavior of selenophosphate dendrimers was found to be rather intriguing.[11] Oxidation of thio- and selenophosphates with peroxides to their corresponding oxo compounds is documented and proceeds presumably via addition-elimination mechanism with formation of pentacovalent phosphorus intermediates.[16,17] Treatment of



16 **17**

SCHEME 2

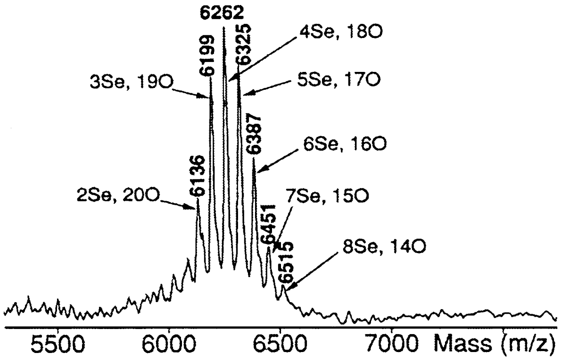


FIGURE 3 MALDI TOF spectrum of **17**.

3rd generation dendrimer **16** [theor. mol. weight 7398 (M + Na)] with *tert*-butylperoxy trimethylsilane (8 equiv.) resulted in regioselective oxygenation of phosphorus atoms at peripheral branching and extrusion of red selenium, which precipitated from reaction medium. The $^{31}P\{^{1}H\}$NMR spectra proved that on average 6 out of 12 phosphorus atoms at peripheral branching were regioselectively oxygenated.

Next, the addition of identical quantity of peroxide to the reaction mixture shifted the degree of oxygenation to about 70%. At this stage the MALDI TOF spectral analysis supplied definitive information about the reaction course (Figure 3). All peaks differ in mass exactly 63 amu due to replacement of selenium (79) by oxygen (16). Major products (central peak) contain 4 selenophosphate and 18 phosphate functions suggesting that the majority of remaining selenium is placed in the core and at first sphere. Evidently no degradation of dendrimer skeleton has taken place. Successive addition of the final amount (8 equiv.) of organic peroxide completed the conversion (Scheme 2) of hydrophobic dendrimer **16** into water-soluble polyphosphate **17** in quantitative yield. Interestingly, the entire dendritic structure was sufficiently flexible to allow bulky peroxide to penetrate the depth of the macromolecule. Moreover, during the reaction time, all branching units and the core must have changed their geometry from tetrahedral to trigonal bipyramidal and back to tetrahedral. It is also worthy to mention that the analogous thiophosphate dendrimer did not react in these mild conditions.

We have synthesized highly pure, novel heteroorganic dendrimers via simple one-pot phosphitylation and chalcogen addition reactions. In addition, selenophosphate dendrimer served as a macromolecular substrate for partial or complete oxygenation. The oxygenation reaction cleanly proceeded. In the beginning, peroxide reagent oxidized peripheral branching, then it was capable of penetrating deeper into the internal structure. The dendrimer was adaptable enough to make possible the modification in the core.

REFERENCES

[1] G. R. Newkome, C. N. Moorefield, and F. Vögtle, *Dendrimers and dendrons: Concepts, Syntheses, Applications*, (Wiley-WCH: Weinheim 2001).

[2] J. M. J. Fréchet and D. Tomalia, *Dendrimers and other dendritic polymers,* (John Wiley and Sons, 2001).

[3] J. P. Majoral, A. M. Caminade, and V. Maraval, *Chem. Commun.*, 2929 (2002).

[4] J. P. Majoral and A. M. Caminade, *Top. Curr. Chem.*, **223,** 111 (2002).

[5] Astruc and D. Chardac, F. *Chem. Rev.*, **101,** 2991 (2001).

[6] S. M. Grayson and J. M. J. Fréchet, *Chem. Rev.*, **101,** 3819 (2001).

[7] S. Hecht, J. M. J. Fréchet, *Angew. Chem. Int. Ed.*, **40,** 74 (2001).

[8] S. L. Beaucage and P. R. Iyer, *Tetrahedron*, **49,** 10441 (1993).

[9] T. Nishigushi and H. J. Taya, *J. Am. Chem. Soc.*, **111,** 9102 (1989).

[10] G. M. Salamończyk, M. Kuźnikowski, and A. Skowrońska, *Tetrahedron Lett.*, **41,** 1643 (2000).

[11] G. M. Salamończyk, M. Kuźnikowski, and E. Poniatowska, *Chem. Commun.*, 2202 (2001).

[12] G. M. Salamończyk, M. Kuźnikowski, and E. Poniatowska, *Tetrahedron Lett.*, **43,** 1747 (2002).

[13] M. D. Matteucci and M. H. Caruthers, *J. Am. Chem. Soc.*, **103,** 3185 (1981).

[14] L. J. McBride and M. H. Caruthers, *Tetrahedron Lett.*, **24,** 245 (1983).

[15] S. L. Beaucage, *Tetrahedron Lett.*, **25,** 375 (1984).

[16] W. J. Stec, A. Okruszek, and J. Michalski, *J. Org. Chem.*, **41,** 233, (1976).

[17] N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, *J. Chem. Soc. Chem. Commun.*, 714 (1971).