A New Core Reagent for Dendrimer Synthesis

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Abstract:

The compound **1** is available, as 1,3,5-triaceytlbenzene, and an efficient trifunctional core reagent for synthesis of dendrimers.

In this study the triseleiolate **3** is treated with benzylic bromide **5** to give the first-generation dendrimer **6**. Similarly, the triseleiolate **3** treated with Frèchet's dendron **7** to give the second- generation dendrimer **8**.

الخلاصة

المركب (١) يعرف ب ١،٣،٥-ثلاثي أسيتايل بنزين. يعتبر المركب ر٣)الذي جرى تخليقه في هذه الدراسة مركز للتفرع الشجيري بثلاثة اتجاهات ويمكن استخدامه بكفاءة عالية لتحضير المركبات العضوية الشجرية المتناظرة .

وجرى مفاعلة المركب (٣) مع بروميد البنزايل (٥) ليعطي التوليد الاولي مكونا" المركب الشجيري (٦) ، وبنفس الطريقة حظر المركب (٨) من مفاعلة المركب المركزي (٣) مع تفرع فرنكس (٧) معطيا" التوليد الثاني (٨) .

Key words:
Dindrimer, Dendron, 1,2,3- Selenadizole, Macromolecules, triseleiolate, second generation.

Introduction

The field of cascade molecules (dendrimers) has expanded rapidly since the pioneering work of Vögtle, Tomalia and Newkome[1]. Two strategies were known as the divergent and convergent approaches. The divergent [2] starts with multifunctional initiator core on which the branches (dendron) generations are grown by repetitive steps, while in the convergent approach [3], small building block or molecular bricks are first prepared and then attached to a central core. The selection of the core is of great importance since it determines the multiplicity, shape, size and specific functions of the dendrimer.

Experimental

General

The solvents used were purified by standard procedures. The melting point (m.p) was determined on an electrothermal digital melting point apparatus and uncorrected. The (^{1}H-NMR) spectra were recorded on 400MHz (JEOL, JNM-ECP400, FT-

NMRsystem), (300MHz with AC300 instrument from Bruker company) spectrometer and ^{13}C-NMR spectra were recorded on 100MHz400MHz (JEOL, JNM-ECP400, FT-NMRsystem), (with AC300 instrument from Bruker company) spectrometers in $CDCl_3$ in the analytical laboratory of the institute of organic chemistry in the University of Maniz/ Germany. The spectral data is reported in delta (δ) units relative to TMS reference peak. Infrared (IR) spectra were recorded by using a NICOLET 410- FT-IR spectrometer (ν in cm^{-1}) in the Dep. of chemistry at Jordan University of Science and Technology.

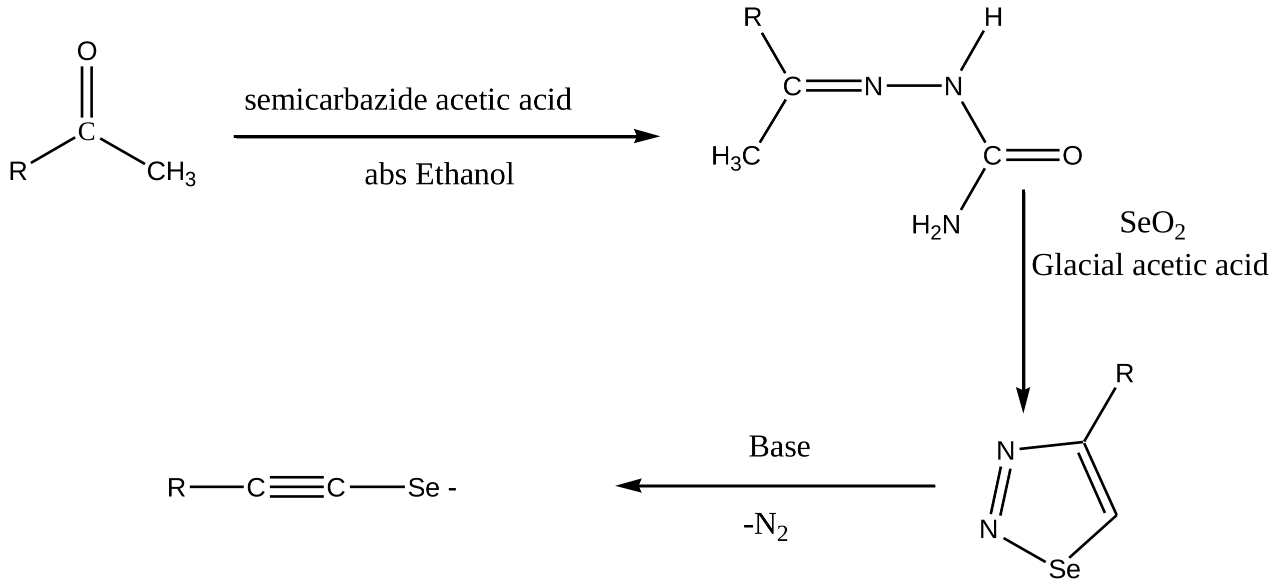
Typical procedure:

A solution of 1,3,5-triacetylbenzene **1** (50 mmol) and semicarazide acetic acid (150mmol) in absolute ethanol (80 ml), was subjected with a continuos removal of water generated apparatus to remove the water that formed by condensation. The semicarbazone product was dissolved in glacial acetic acid (50 ml) must be very dry, with vigorous stirring and gentle heating to 40-45^{o}C. The solution was treated with selenium dioxide powder (3.0 mmol) and the mixture was kept under vigorous stirring. After 2 min the color of the mixture becomes red. Monitoring of the reaction by TLC (eluent: 1:3 ethyl acetate- hexane) showed that the reaction was complete in 30 hr. These mixtures were filtered and the filtrates poured into ice water and extracted with saturated sodium bicarbonate solution. Dried over magnesium sulphate and the solvent was removed under vacuum to afford compound **2** washed by diethyl ether and dried, red color obtained 90% yield, m.p> 220^{o}C.

Compound **2** (1.4 mmol) was suspended in dry tetrahydrofuran (50 ml) under nitrogen atmosphere and treated dropwise at 0^{o}C with 3.2equvalent of potassium *tert*-butoxide (550 mg) dissolved in THF (40 ml). After the mixture had been stirred for 8 hr at 0^{o}C, solution of the bromide **5** (6.0 mmol) in dry THF (40 ml) was added dropwise to it and the whole was stirred overnight. The reaction mixture was then diluted with water (100 ml) and extracted with $CHCl_3$ (3x150 ml). The combined organic layer was washed with water (300 ml), dried over ($MgSO_4$) and evaporated. The crude product was chromatographed on silica gel with chloroform: hexane (5:8) as eluent to give the dendrimer **6** as orange oil in 32% yield; IR: ν (cm^{-1}) 2160s and 1600s for -C≡C- and –C=C- bond respectively; ^{1}H-NMR δ 2.60 (s, 6H, C_1), δ 5.20 (s, 12H, C_2), δ 6.10 (s, 3H, C_3), δ 6.15 (s, 6H, C_4), δ 7.20 (s, 30H, C_5), δ 7.55 (s, 3H, C_6); ^{13}C-NMR δ (26.0 C_1, 77.8 C_2, 78.0 C_3, 85.0 C_4, 96.7 C_5, 107.1 C_6, 121.5 C_7, 127.3 C_8, 128.7 C_9, 135.4 C_{10}, 139.7 C_{11}, 140.9 C_{12}, 126.9 C_{13})

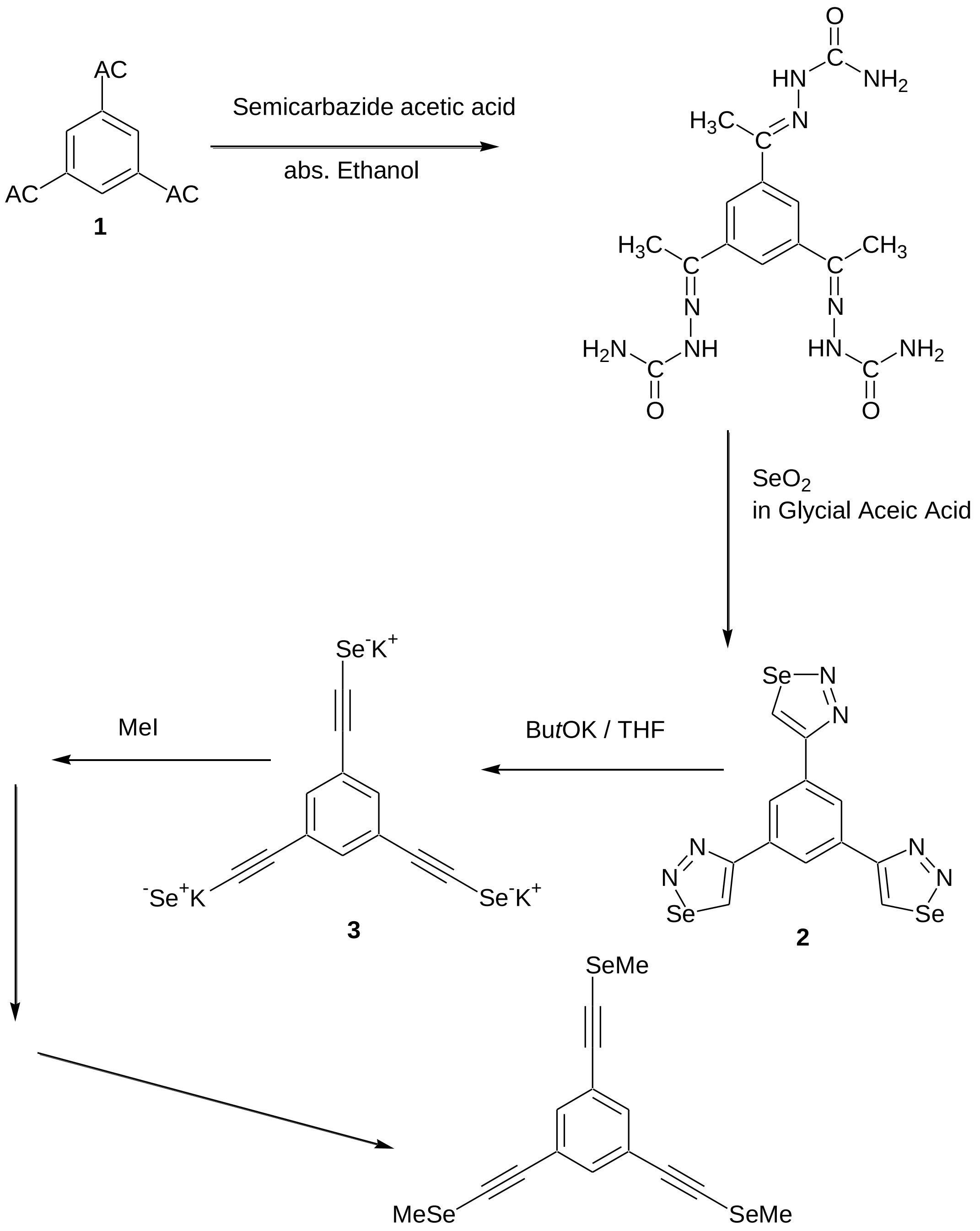
Result and Discussion

This approach is based on the knowledge that the alkyneseleniolate **3** are powerful reagent in organic synthesis [4], they are much reactive in nucleophlic displacements and sterically unhindered. An elegant method for their synthesis is the base–induced ring cleavage of 4- substituted 1,2,3-selenadiazoles [5], which themselves are easily accessible from semicarbazone compound by Lalezari method [6] (scheme 1).

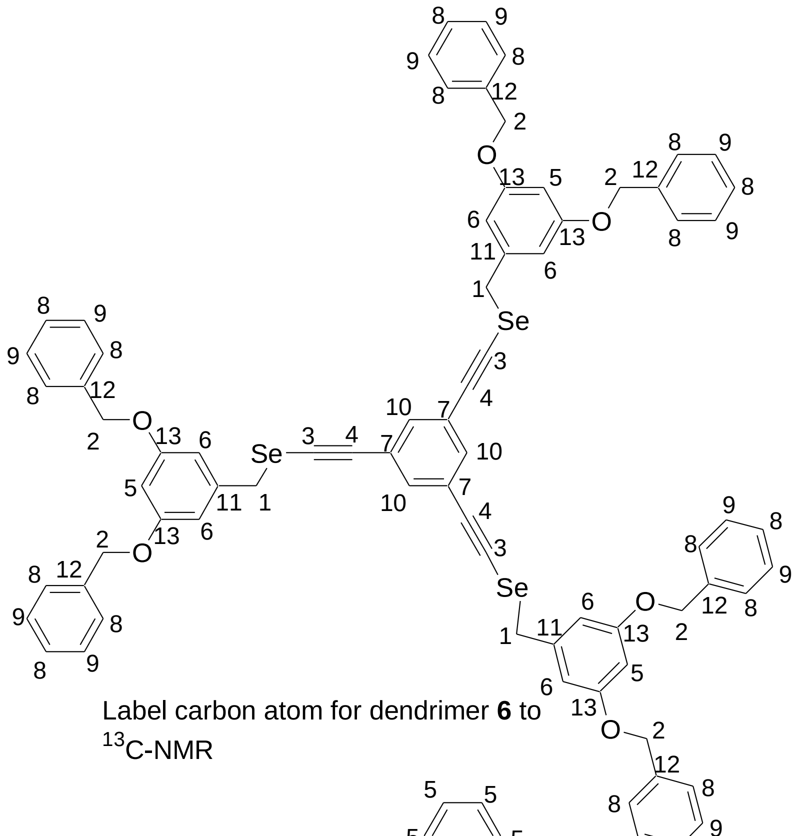


Scheme 1: General reaction for synthesis alkyne seleniolate

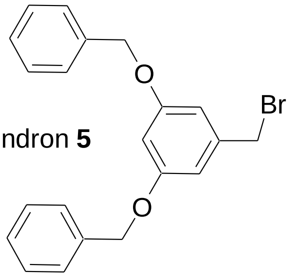
I have extended this principle with success to multifunctional compound such as 1,3,5-triacetylbenzene **1**. In particular, when the latter was treated successively with semicarbazide acetic acid and seleniumdioxide, 1,3,5-tri(1,2,3-selenadiazole-4-yl)benzene **2** was obtained in 90% overall yield (m.p>220^{o}C). In spite of the product **2** is insoluble in most known organic solvents, it decomposed smoothly when a suspension of it in dry THF was treated with potassium *tert*-butoxide at 0^{o}C, the resulting triseleniolate **3** was trapped with methyl iodide and characterized as the trimethyl derivative (45%, oil). Many attentions should be taken to work under anhydrous condition (nitrogen atmosphere) to avoid the proton-catalyzed dimerization of the alkyne seleniolate [6]. The compound **3** is a suitable core for dendrimer synthesis. The benzylicbromide **5** is combined readily with the reagent **3** at (r.t) to give the first-generation dendrimer **6** as orange oil in 32% yield after chromatographic purification. This compound showed a symmetrical structure, and confirmed by ^{13}C-NMR spectroscopic analysis (in experimental section). Similarly, the triseleiolate**3** coupled with freche's dendron[2] **7** to furnish the second-generation dendrimer **8**, obtained as orange glass in 52% yield.



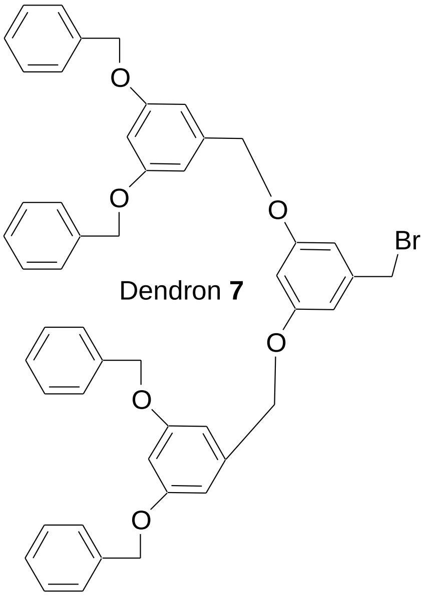
Scheme 2: synthesis of triseleniolate



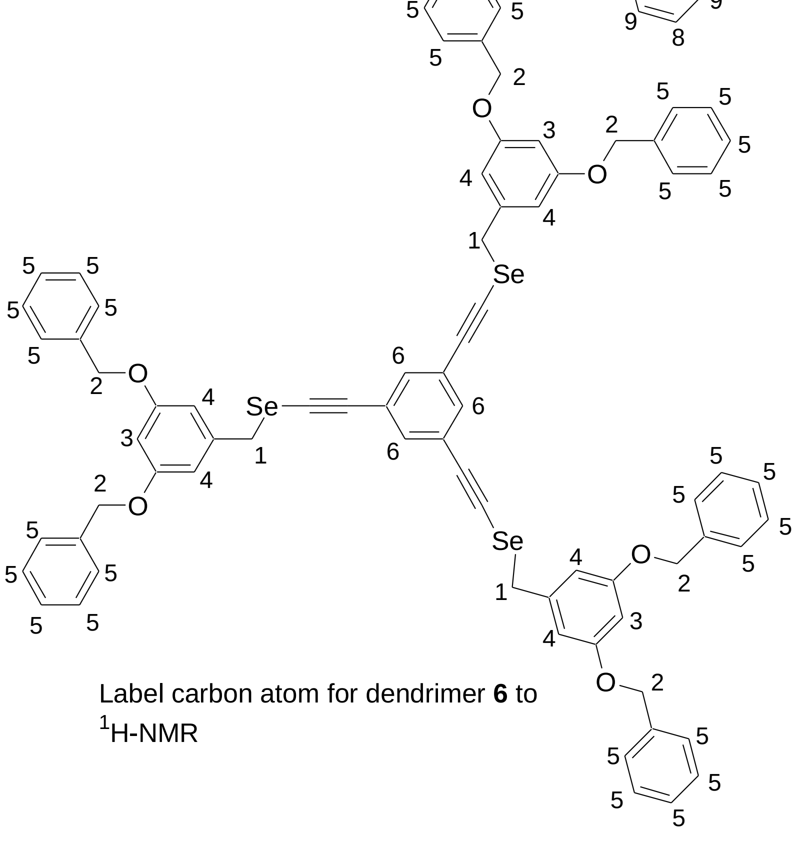
Label carbon atom for dendrimer **6** to ^{13}C-NMR



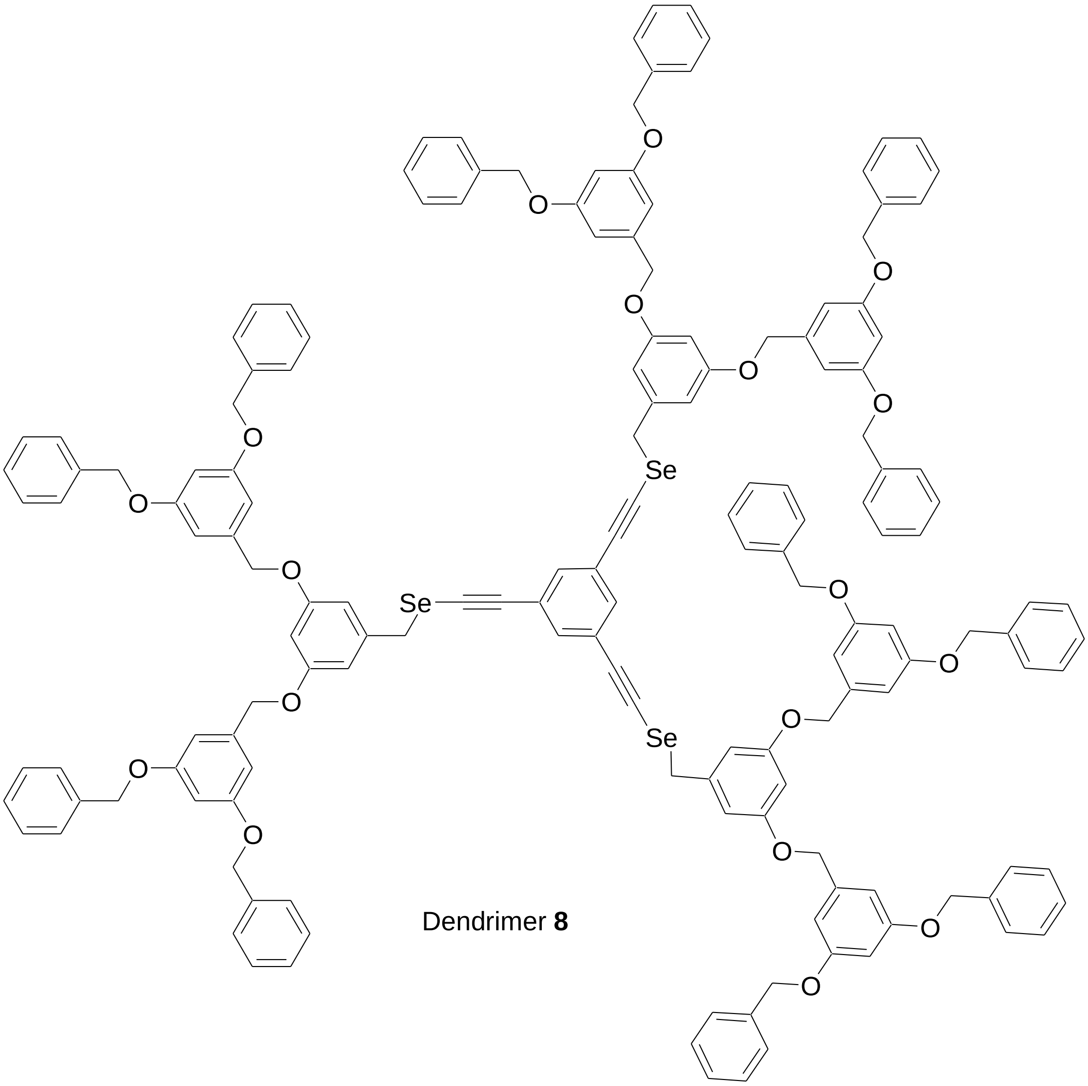
Dendron **5**



Dendron **7**



Label carbon atom for dendrimer **6** to ^{1}H-NMR



Dendrimer **8**

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