Solid-phase synthesis of 3-hydroxy-2-methylenealkanenitriles using polymer-supported α-selenopropionitrile

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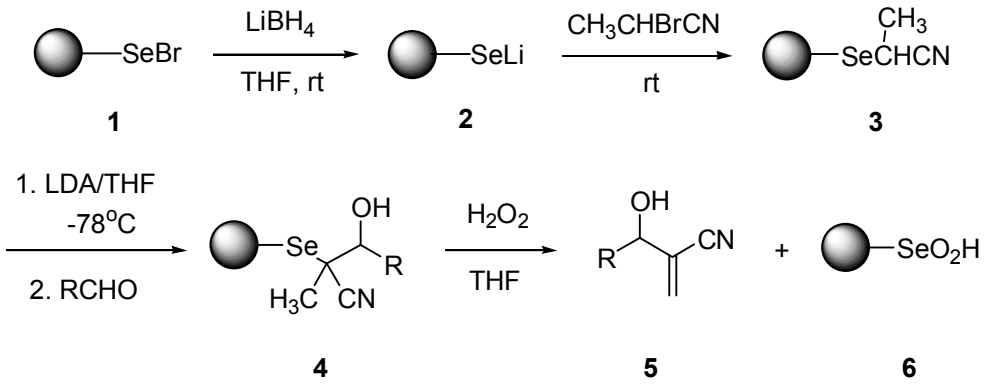
Abstract
A novel facile method for solid-phase organic synthesis of 3-hydroxy-2-methylenealkanenitriles in good yields and purities with advantages of decreased volatility and simplification of work-up procedure using polymer-supported α-selenopropionitrile is described.

Keywords: Solid-phase organic synthesis, polystyrene-supported α-selenopropionitrile, 3-hydroxy-2-methylenealkanenitrile

Introduction

Polymer-supported organic reagents and catalysts have been rapidly applied in the preparation of organic molecules. The use of polymer-supported reagents can selectively remove excess reagents and by-products through simple filtration rather than liquid-liquid extraction and chromatographic purification. In addition, polymer-supported reagents offer further advantages that include reaction of active intermediates by 'catch-and-release', selectivity and immobilization of toxic intermediates.[1] Organoselenium reagents have been increasingly used as a powerful tool for introducing new functional groups into organic substrates under extremely mild conditions.[2] For example, phenylseleno group is readily converted to a leaving group giving access to carbon-carbon double bonds *via* oxidation followed by *β*-elimination.[3] Additionally, a selenium-stabilized carbanion has played an important role in organic synthesis because of its easy availability and particularly good nucleophile, which allows the formation of new functionalized carbon-carbon bonds when it is used to react with compounds bearing an electrophilic carbon atom.[2, 4] However, organoselenium reagents always have a foul smell and are quite toxic, which is often problematic in organic synthesis. Although polymers with selenium functionalities have been known for along time,[5] there remains high interest in this kind

of solid-phase organic chemistry.[6] The Baylis-Hillman reaction has become an important tool in organic synthesis, since it allows for the formation of carbon-carbon bonds under mild reaction conditions.[7] The adducts (3-hydroxy-2-methylenealkanenitriles and 3-hydroxy-2-methylenealkanoates, *etc.*) of Baylis-Hillman reaction have recently been utilized1 as important precursors for stereoselective synthesis of different multifunctional molecules.[8] Although methods for the synthesis of 3-hydroxy-2-methylenealkanenitriles and their derivatives are well documented,[7,9] efforts are continuing for the development of more efficient methods with experimental simplicity. However, to our knowledge, solid-phase organic synthesis (SPOS) of 3-hydroxy-2-methylenealkanenitriles using selenium linkage has not been reported. In connection with our interest in solid-phase organoselenium chemistry,[10] we wish herein to report the preparation of the novel polymer-bound α-selenopropionitrile reagent and its application for the SPOS of 3-hydroxy-2-methylenealkanenitriles (Scheme 1).



Scheme 1. SPOS of 3-hydroxy-2-methylenealkanenitriles.

Results and Discussions

As shown in Scheme 1, polymer-supported α-selenopropionitrile **3** were readily prepared by treatment of a THF-swollen suspension of cross-linked (1%) polystyrene-bound selenium bromide **1** [6a] with $LiBH_4$, followed by treatment with 2-bromopropionitrile. Elemental analysis for nitrogen revealed a loading of resin **3** (1.20 mmol/g). No bromine was found by elemental analysis, indicating that the performed bromine with α-propionitrile group exchange has gone to completion. The FT-IR spectrum of the newly formed resin **3** showed a strong stretching vibration of the cyano group at 2241 cm^{-1}. A distinct advantage of the novel polymer reagents is the convenience of handling and odorless nature as compared with the nonpolymer-supported reagents.

With resin **3** in hand, preparation of 3-hydroxy-2-methylenealkanenitriles based on resin **3** was investigated. As illustrated, reaction of the lithio derivative of resin **3** generated by treating resin **3** with lithium diisopropylamide with aldehyde furnished the resin **4**, which could not be

reliably analyzed with FT-IR. Hence next step of oxidation-elimination reaction was carried out directly with 30 % hydrogen peroxide at 0 ^{o}C and then at room temperature to afford the corresponding Baylis-Hillman products **5** in good yields (82-91 %) and purities (92-96 %). Several typical examples are described in Table 1. Seen from Table 1, the present method was effective for both aromatic (either with electron-withdrawing or electron-donating group) and aliphatic aldehydes.

Table 1. The yields and purities of 3-hydroxy-2-methylenealkanenitriles **5**

Entry	R	Product	Yield (%) [a]	Purity (%) [b]
1	C_6H_5	**5a**	90	95
2	4-$CH_3OC_6H_4$	**5b**	91	96
3	4-ClC_6H_4	**5c**	88	95
4	4-$NO_2C_6H_4$	**5d**	85	92
5	2-naphthyl	**5e**	84	95
6	2-furyl	**5f**	86	93
7	3-pyridyl	**5g**	87	95
8	*n*-C_5H_{11}	**5h**	82	92

[a]Yields were based on the functional loading of resin **3** (1.20 mmol /g). [b]Determined by HPLC of crude cleavage product.

The residual resin, polystyrene-supported phenylseleninic acid **6**, was obtained as a by-product, whose infrared data was identical to the previously reported data[11] and showed no residual cyano group absorption, which indicated the oxidative cleavage was complete. The resin **6** could be converted to selenium bromide resin **1** for recycle by treatment of it with KI/$Na_2S_2O_3$ [12] followed by bromine.[6a] To show the reactivity of the regenerated polymeric reagent, the conversion of polymeric selenium bromide **1** to target compounds **5** was repeated several times in the same reaction. For instance, 3-hydroxy-2-methylene-3-phenylpropanenitrile (**5a**) was obtained in 87% yield and with 92 % purity under the same reaction condition using the selenenyl bromide resin **1** (second run), and in 83 % yield after second recycle (i.e. third run). It was shown that recycling 2-3 times led to a gradual decrease in yield but the purity of **5a** remained almost the same as when the first prepared selenium bromide resin was used.

In summary, an efficient and convenient method for the solid-phase synthesis of 3-hydroxy-2-methylenealkanenitriles in good yields and purities employing polymer-bound α-selenopropionitrile reagent has been developed. The advantages of this method include straightforward operation, lack of odor and stability, and the polymeric reagent can be regenerated and reused for several times as environmentally benign reagent.

Experimental Section

General Procedure. Melting points were uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard. FT-IR spectra were taken on a Perkin-Elmer SP One FT-IR spectrophotometer. Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer. HPLC analysis was performed on Agilent 1100 automated system having a PDA detector (λ_{max} = 254 nm used for this study) using a gradient with CH_3CN/H_2O (1 mL/min) on a RP-18e column (150×4.6 mm). Polystyrene (H 1000, 100–200 mesh, cross-linked with 1% divinylbenzene) for preparation of selenium bromide resin [6a] was purchased from Nankai University, and the other starting materials were purchased from commercial suppliers and used without further purification. THF was stilled from sodium-benzophenone immediately prior to use.

Preparation of polymer-supported selenium bromide 1

Under a positive pressure of nitrogen, to 1% divinylbenzene-styrene copolymer (2.0 g, 19.3 mequiv) swollen in dry cyclohexane (20 mL) containing 2.8 mL (18.6 mmol) of tetramethylethylenediamine (TMEDA) was added 9.5 ml of 2.50 M n-BuLi. The reaction mixture turned red gradually during 4.5 h of heating at 65 ^{o}C. After the liquid phase was removed, the resin was rinsed twice with dry cyclohexane to yield the desired lithiated resin. Then the lithiated resin was quenched by addition of a solution of dimethyl diselenide (5.0 mmol) in dry tetrahydrofuran (10 mL) with stirring at 0 ^{o}C for 30 min. The brown coloration of the resin disappeared instantly. After filtration, the resin was washed with THF, methanol, THF-water (2:1), water, THF, and finally methanol (10 mL of each). After drying in vacuo at 60 ^{o}C for 10 h, the polymer-supported methyl selenide (2.12 g) as a pale yellow resin containing 1.28 mmol Se/g was obtained. The methyl selenide resin (2.0 g) swollen in $CHCl_3$ (10 mL) was added Br_2 (0.37 g, 2.3 mmol) and the mixture was stirred at 0 ^{o}C for 10 min. After filtration, the resin was washed twice with $CHCl_3$ (2×10 mL) and then was suspended in dry ethanol (15 mL). After stirring at 70 ^{o}C for 1 h, the resin was collected on a filter and washed successively with THF, ether and finally methanol (10 mL of each). After drying, 2.05 g of a pale yellow polystyrene-supported selenium bromide resin (1.18 mmol Br/g, the loading of functional Br was analyzed by elementary analysis) was obtained. IR (KBr): ν = 3024, 2920, 1600, 1492, 1452, 1028, 757, 698, 540 cm^{-1}.

Preparation of polymer-supported α-selenopropionitrile 3

Under a nitrogen atmosphere, to polystyrene-supported selenium bromide **1** (1.0 g, 1.18 mmol) swelled in THF (10 mL) for 30 min was added $LiBH_4$ (3 mmol). After 1 h with shaking at room temperature, 2-bromopropionitrile (3 mmol) in 2 mL of THF was added slowly and the mixture was shaken for 6 h. The resin was collected on a filter and washed successively with H_2O (2×20 mL), THF (3×5 mL) and CH_2Cl_2 (3×5 mL), and then dried under vacuum overnight to afford 930 mg of resin **3** in 96 % yield with a loading value of 1.20 mmol/g (theoretical loading of the resin

1.22 mmol/g). IR (KBr): ν = 3025, 2926, 2241, 1596, 1460, 1405, 1378, 1304, 1095, 1024, 999, 740, 690, 672 cm^{-1}.

General procedure for the preparation of 3-hydroxy-2-methylenealkanenitriles (5a-5h)

To a solution of 2.0 mmol of LDA (2.2 mmol of diisopropylamine, 2.0 mmol of n-butyllithium) in anhydrous THF (10 mL) at –78 °C under nitrogen atmosphere was added resin **3** (833 mg, 1.0 mmol). After shaking at –78 °C for 1 h, the neat aldehyde (2.0 mmol in 5 mL THF) was added dropwise over ca. 5 min. Twenty minutes after addition of the aldehyde, the mixture was warmed up gradually to room temperature and kept shaking for 3 h. After neutralization with 1% hydrochloric acid, the resin **4a-4h** was collected on a filter and washed successively with H_2O (3 × 10 mL), THF (3 × 5 mL) and Et_2O (3 × 5 mL). To a suspension of the swollen resin **4a-4h** in THF (10 mL) and 0.5 mL of 30 % H_2O_2 (5.8 mmol) was added at 0 °C. The suspension was shaken at 0 °C for 0.5 h and then at room temperature for 1 h, the residual resin was collected by filtration and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was treated with saturated $NaHCO_3$ (20 mL) and washed with water, dried over magnesium sulfate and evaporated to give crude products **5a-5h**, which were further purified by chromatography [silica gel, ethyl acetate/hexane as the eluent: 1:9–1.5:8.5 (v/v)] to provide pure products for their structure analyses.

3-Hydroxy-2-methylene-3-phenylpropanenitrile (5a). Colorless oil (lit.[9a] oil). ^{1}H NMR: δ = 7.41-7.35 (m, 5 H), 6.11 (s, 1 H), 6.03 (s, 1 H), 5.28 (s, 1 H), 2.58 (br s, 1 H). ^{13}C NMR: δ = 141.3, 130.9, 128.7, 127.9, 127.5, 123.8, 118.6, 72.2. IR (neat): ν = 3345, 1630, 2225, 1250 cm^{-1}. Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.53; H, 5.82; N, 8.89.

3-Hydroxy-2-methylene-3-(4-methoxyphenyl)propanenitrile (5b). Yellow oil (lit.[9a] yellow oil). ^{1}H NMR: δ = 7.46 (d, *J* = 8.5 Hz, 2 H), 6.76 (d, *J* = 8.5 Hz, 2 H), 6.34 (s, 1 H), 6.05 (s, 1 H), 4.74 (s, 1 H), 3.74 (s, 3 H), 2.16 (br s, 1 H). ^{13}C NMR: δ = 131.2, 130.1, 123.6, 120.2, 118.9, 114.1, 113.5, 72.2, 55.2. IR (neat): ν = 3284, 2860, 2226, 1622, 1454, 1386, 1248 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.90; H, 5.95; N, 7.49.

3-Hydroxy-2-methylene-3-(4-chlorophenyl)propanenitrile (5c). Yellow oil (lit.[13] yellow oil). ^{1}H NMR: δ = 7.43 (d, *J* = 8.6 Hz, 2 H), 7.28 (d, *J* = 8.6 Hz, 2 H), 6.09 (s, 1 H), 6.05 (s, 1 H), 5.26 (s, 1 H), 2.32 (br s, 1 H). ^{13}C NMR: δ = 140.3, 133.5, 130.8, 128.4, 127.9, 123.8, 119.1, 72.3. IR (neat): ν = 3308, 2224, 1625, 1406 cm^{-1}. Anal. Calcd for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23. Found: C, 62.13; H, 4.24; N, 7.32.

3-Hydroxy-2-methylene-3-(4-nitrophenyl)propanenitrile (5d). Pale yellow solid; Mp 73-74 °C (lit. [13] mp 72-75 °C). ^{1}H NMR: δ = 8.25 (d, *J* = 8.6 Hz, 2 H), 7.62 (d, *J* = 8.6 Hz, 2 H), 6.19 (s, 1 H), 6.09 (s, 1 H), 5.42 (s, 1 H), 2.12 (br s, 1 H). ^{13}C NMR: δ = 147.9, 147.2, 130.7, 127.2, 126.1, 123.3, 118.6, 72.1. IR (KBr): ν = 3440, 2227, 1618, 1552 cm^{-1}. Anal. Calcd for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.95; N, 13.72. Found: C, 58.95; H, 4.04; N, 13.56.

3-Hydroxy-2-methylene-3-(2-naphthyl)propanenitrile (5e). Yellow oil (lit.[9a] yellow oil). ^{1}H NMR: δ = 7.92-7.34 (m, 7 H), 6.16 (s, 1 H), 5.85 (s, 1 H), 4.82 (s, 1 H), 2.35 (br s, 1 H). ^{13}C NMR: δ = 138.7, 133.4, 132.7, 130.9, 128.5, 128.1, 127.6, 127.1, 125.7, 125.4, 124.2, 123.4, 119.2, 72.3. IR (neat): ν = 3435, 2221, 1623 cm^{-1}. Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30;

N, 6.69. Found: C, 80.41; H, 5.44; N, 6.76.

3-Hydroxy-2-methylene-3-(2-furyl)propanenitrile (5f). Organe oil (lit.[14] oil). ^{1}H NMR: δ = 7.45 (dd, *J* = 1.7, 0.9 Hz, 1 H), 6.45 (dd, *J* = 3.2, 1.7 Hz, 1 H), 6.40 (dd, *J* = 3.2, 0.9 Hz, 1 H), 6.21 (s, 1 H), 6.16 (s, 1 H), 5.38 (s, 1 H), 2.45 (br s, 1 H). ^{13}C NMR: δ = 151.4, 143.5, 131.1, 123.6, 116.7, 110.7, 108.9, 67.7. IR (neat): ν = 3418, 2229, 1625, 1503 cm^{-1}. Anal. Calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.50; H, 4.81; N, 9.46.

3-Hydroxy-2-methylene-3-(3-pyridyl)propanenitrile (5g). Colorless oil. (lit.[9a] oil). ^{1}H NMR: δ = 8.65 (s, 1 H), 8.50 (d, *J* = 4.9 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.14 (dd, *J* = 4.9, 8.0 Hz, 1 H), 6.06 (s, 1 H), 5.84 (s, 1 H), 4.75 (s, 1 H), 5.15 (br s, 1 H). ^{13}C NMR: δ = 148.5, 148.2, 138.3, 135.1, 130.6, 124.1, 123.5, 117.8, 70.4. IR (neat): ν = 3430, 2219, 1623, 1500 cm^{-1}. Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.60; H, 5.12; N, 17.56.

3-Hydroxy-2-methyleneoctanenitrile (5h). Colorless oil (lit.[8c] oil). ^{1}H NMR: δ = 6.24 (s, 1 H), 5.83 (s, 1 H), 4.43 (t, *J* = 6.4 Hz, 1 H), 4.27 (q, *J* = 6.4 Hz, 2 H), 2.74 (br s, 1H), 1.41–1.26 (m, 6 H), 0.97 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR: δ = 134.1, 123.9, 118.6, 70.0, 33.6, 29.6, 23.5, 19.9, 12.2. IR (film): ν = 3380, 2958, 2862, 2214, 1625 cm^{-1}. Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.62; H, 9.98; N, 9.22.

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