Notes

Efficient One-pot Synthesis of Dendritic Benzyl Azides from Their Alcohols

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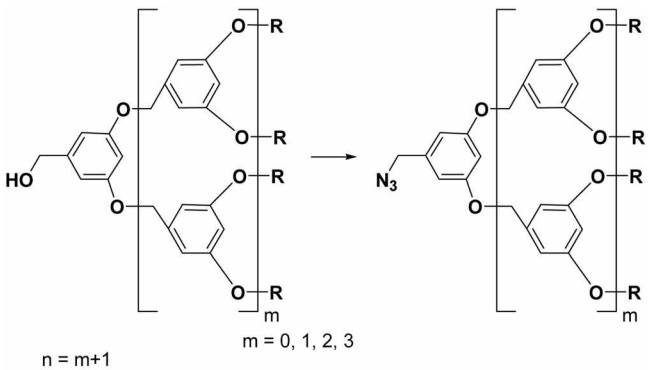
Dendrimers are prepared by repetition of a given set of reactions using either divergent or convergent strategies. The two most widely studied dendrimer families are the Frechet-type polyether and the Tomalia-type PAMAM dendrimers.[1,2] The convergent approach to dendrimer synthesis introduced by Frechet and co-workers revolutionized the synthetic approaches to monodisperse dendrimers.[2] An effective convergent synthesis requires a monomer that can undergo the activation and coupling steps in high yield. In addition, the coupling step must be very efficient to enable complete reaction. In this viewpoint, the dendritic benzylic azides are key intermediates in synthesis of the Frechet-type poly(aryl ether) dendrimers via click chemistry. In continuation with our research for the synthesis of dendrimers using click chemistry between an azide and an alkyne,[3] there is still a demand to develop a simple, convenient, and efficient method to synthesize various dendritic benzyl azides. Here, we present a successful rapid synthesis of dendritic benzyl azides from dendritic benzyl alcohols via mesylation using methanesulfonyl chloride/Et_3N and followed by in situ azidation (Scheme 1). In our method, each dendritic benzyl azide can be prepared in one pot: no isolation of intermediate mesylated dendrons is required. The key steps in the syntheses of dendritic benzyl azides were the mesylation of the hydroxymethyl group followed by the azidation with sodium azide. Furthermore, the purification of every dendritic molecule requires only solvent extraction.



1-Dn	R = CH_3	**5-Dn**	R = CH_3
2-Dn	R = $CH_2CH_2CH_2N_3$	**6-Dn**	R = $CH_2CH_2CH_2N_3$
3-Dn	R = $(CH_2CH_2O)_3CH_3$	**7-Dn**	R = $(CH_2CH_2O)_3CH_3$
4-Dn	R = $(CH_2CH_2O)_3CH_2CH_2N_3$	**8-Dn**	R = $(CH_2CH_2O)_3CH_2CH_2N_3$

Scheme 1

Experimental Section

^{1}H NMR spectra were recorded on a 300 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; quint, quintet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 75 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. EI and FAB mass spectra were obtained from Korea Basic Science Institute (KBSI) in Daegu. Analytical thin layer chromatography was performed on silica plates with F_{254} indicator and the visualization was accomplished by UV lamp or using an iodine chamber.

General procedure for the azidation of dendritic benzyl alcohols. Triethylamine (3.3 mmol) was added to a solution of dendritic benzyl alcohols (3 mmol) and methanesulfonyl chloride (3.3 mmol) in DMF (see Table 1) in an ice bath and the resulting mixture was stirred for 1 h at room temperature. Then NaN_3 (4.5 mmol) and 2-3 drops of water were added and the reaction mixture was stirred for additional 2 h at room temperature. The reaction mixture was poured into brine (100 mL) and extracted with EtOAc. The extract was washed with saturated Na_2CO_3 aqueous solution, dried over Na_2SO_4, and filtered and the filtrate was concentrated to provide the analytical pure product.

Compound 5-D1. A white liquid; 99% yield. IR 2939, 2839, 2100, 1598, 1464, 1298, 1159, 1058, 835 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 6H), 4.27 (s, 2H), 6.43 (d, J = 2.1 Hz, 1H), 6.46 (d, J = 2.1Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 137.6, 106.0, 100.1, 55.4, 54.8. MS

(EI): m/z 193 [M$^-$], 165, 151, 135. HRMS (EI) calcd for $C_9H_{11}N_3O_2$: 193.0851. found: 193.0851.

Compound 5-D2. A white solid: 99% yield. m.p. 69-71 °C. IR 2937, 2839, 2100, 1597, 1458, 1298, 1155, 1055, 833 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 12H), 4.26 (s, 2H), 4.98 (s, 4H), 6.42 (d, J = 2.1 Hz, 2H), 6.55-6.57 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 160.2, 139.0, 137.7, 107.2, 105.2, 101.9, 100.0, 70.1, 55.4, 54.8. MS (EI): m/z 465 [M$^-$], 435, 286, 151. HRMS (EI) calcd for $C_{25}H_{27}N_3O_6$: 465.1900. found: 465.1900.

Compound 5-D3. A yellowish gum: 99% yield. IR 2937, 2839, 2100, 1597, 1458, 1298, 1153, 1055, 833 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 24H), 4.26 (s, 2H), 4.97 (s, 12H), 6.41 (m, 4H), 6.53-6.57 (m, 13H), 6.67 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 160.12, 160.08, 159.93, 139.3, 139.1, 139.05, 137.6, 107.2, 106.4, 105.2, 101.8, 101.6, 70.04, 70.0, 55.3, 54.8. MS (FAB): m/z 1008.5 [M$^+$], 981.6, 572.9 460.0, 391.1. HRMS (FAB) calcd for $C_{57}H_{59}N_3O_{14}$: 1009.3997. found: 1010.4075 [M$^+$ + H].

Compound 5-D4. A yellowish gum: 99% yield. IR 2937, 2839, 2100, 1597, 1458, 1298, 1155, 1053, 833 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 48H), 4.24 (s, 2H), 4.96 (s, 28H), 6.40 (m, 8H), 6.57 (m, 26H), 6.67 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 160.16, 160.09, 139.2, 139.14, 139.09, 137.7, 107.3, 106.4, 105.2, 101.8, 101.6, 100.0, 70.06, 55.3, 54.8. MS (FAB): m/z 2097.9 [M$^+$], 2069.8, 1919.6, 1646.0.

Compound 6-D1. A yellowish oil; 100% yield: IR 2935, 2879, 2098, 1597, 1454, 1296, 1169, 1064, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (quint, J = 6.2 Hz, 4H), 3.52 (t, J = 6.6 Hz, 4H), 4.04 (t, J = 5.9 Hz, 4H), 4.27 (s, 2H), 6.42 (t, J = 2.1 Hz, 1H), 6.46 (d, J = 2.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 137.6, 106.6, 101.0, 64.5, 54.7, 48.1, 28.6; MS (FAB): m/z 304.02 [M$^+$+H-N$_2$], 330.99 [M$^+$], 332.00 [M$^+$+H]; HRMS (FAB) calcd for $C_{13}H_{17}N_9O_2$: 331.1505. Found: 303.1502 [M$^-$-N$_2$], 304.1569 [M$^-$+H-N$_2$], 331.1505 [M$^+$], 322.1577 [M$^-$+H].

Compound 6-D2. A yellowish oil; 100% yield; IR 2935, 2879, 2098, 1597, 1452, 1298, 1169, 1061, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (quint, J = 6.2 Hz, 8H), 3.51 (t, J = 6.6 Hz, 8H), 4.04 (t, J = 5.9 Hz, 8H), 4.27 (s, 2H), 4.97 (s, 4H), 6.41 (m, 2H), 6.55-6.58 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 160.0, 139.1, 137.6, 107.1, 105.9, 101.8, 100.9, 69.9, 64.6, 54.7, 48.2, 28.7; MS (FAB): m/z 713.10 [M$^+$-N$_2$], 714.10 [M$^-$+H-N$_2$], 741.09 [M$^+$], 742.12 [M$^-$+H]; HRMS (FAB) calcd for $C_{33}H_{39}N_{15}O_6$: 741.3208. Found: 713.3133 [M$^-$-N$_2$], 714.3231 [M$^-$+H-N$_2$], 741.3266 [M$^+$], 742.3277 [M$^-$+H].

Compound 6-D3. A yellowish oil; 98% yield; IR 2933, 2879, 2098, 1597, 1452, 1298, 1167, 1057, 833 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (quint, J = 6.2 Hz, 16H), 3.50 (t, J = 6.6 Hz, 16H), 4.03 (t, J = 5.9 Hz, 16H), 4.27 (s, 2H), 4.96 (s, 8H), 4.98 (s, 4H), 6.41 (m, 4H), 6.55-6.58 (m, 13H), 6.67 (d, J = 1.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.13, 160.07, 160.04, 139.2, 139.0, 137.7, 107.2, 106.4, 106.0, 101.8, 101.6, 100.9, 70.03, 69.97, 64.6, 54.8, 48.2, 28.7; MS (FAB): m/z 1534.1 [M$^-$-N$_2$], 1561.9 [M$^+$].

Compound 7-D1. A yellowish oil: 96% yield; IR 2923, 2875, 2100, 1597, 1448, 1296, 1174, 1070, 849 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38 (s, 6H), 3.53-3.56 (m, 4H), 3.64-3.75 (m, 12H), 3.84 (t, J = 4.8 Hz, 4H), 4.11 (t, J = 4.8 Hz, 4H), 4.24 (s, 2H), 6.46 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 137.0, 106.3, 100.7, 71.3, 70.2, 70.05, 69.96, 69.03, 67.0, 58.4, 54.1; MS (FAB): m/z 430.07 [M$^-$+H-N$_2$], 457.10 [M$^-$], 458.11 [M$^-$+H]; HRMS (FAB) calcd for $C_{21}H_{35}N_3O_8$: 457.2424. Found: 430.2442 [M$^-$+H-N$_2$], 457.2448 [M$^-$], 458.2506 [M$^-$+H].

Compound 7-D2. A yellowish oil; 99% yield: IR 2923, 2875, 2100, 1597, 1448, 1298, 1174, 1070, 846 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37 (s, 12H), 3.53-3.56 (m, 8H), 3.64-3.75 (m, 24H), 3.84 (t, J = 4.7 Hz, 8H), 4.11 (t, J = 4.8 Hz, 8H), 4.26 (s, 2H), 4.95 (s, 4H), 6.44 (m, 2H), 6.53-6.54 (m, 3H), 6.58 (d, J = 1.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 138.6, 137.3, 106.8, 105.6, 101.4, 100.8, 71.6, 70.5, 70.3, 70.2, 69.6, 69.3, 67.1, 58.7, 54.4; MS (FAB): m/z 966.3 [M$^+$+H-N$_2$], 994.3 [M$^+$+H]; HRMS (FAB) calcd for $C_{49}H_{75}N_3O_{18}$: 993.5046. Found: 965.5283 [M$^-$-N$_2$], 966.5078 [M$^-$+H-N$_2$], 993.5016 [M$^-$], 994.5129 [M$^-$+H].

Compound 7-D3. A yellowish oil: 99% yield; IR 2923, 2875, 2100, 1597, 1448, 1298, 1174, 1070, 845 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37 (s, 24H), 3.52-3.55 (m, 16H), 3.63-3.74 (m, 48H), 3.84 (t, J = 4.7 Hz, 16H), 4.10 (t, J = 4.7 Hz, 16H), 4.27 (s, 2H), 4.95 (s, 8H), 4.97 (s, 4H), 6.44 (m, 4H), 6.54-6.59 (m, 13H), 6.66 (d, J = 1.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 159.8, 138.8, 137.4, 107.0, 106.1, 105.8, 101.5, 101.4, 100.9, 71.7, 70.6, 70.4, 70.3, 69.8, 69.7, 69.4, 67.2, 58.8, 54.5; MS (FAB): m/z 2038.3 [M$^-$-N$_2$], 2066.4 [M$^+$].

Compound 8-D1. A yellowish oil: 97% yield; IR 2872, 2102, 1597, 1448, 1296, 1175, 1070, 847 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38 (t, J = 4.9 Hz, 4H), 3.65-3.71 (m, 20H), 3.85 (t, J = 4.7 Hz, 4H), 4.11 (t, J = 4.7 Hz, 4H), 4.24 (s, 2H), 6.46 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 137.3, 106.7, 101.2, 70.7, 70.5, 69.9, 69.5, 67.4, 54.6, 50.5; MS (FAB): m/z 540.11 [M$^+$+H-N$_2$], 567.13 [M$^+$], 568.13 [M$^-$+H]; HRMS (FAB) calcd for $C_{23}H_{37}N_9O_8$: 567.2765. Found: 539.2770 [M$^+$-N$_2$], 540.2821 [M$^+$+H-N$_2$], 567.2820 [M$^-$], 568.2847 [M$^+$+H].

Compound 8-D2. A yellowish oil; 100% yield; IR 2872, 2104, 1595, 1448, 1298, 1175, 1068, 843 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37 (t, J = 4.9 Hz, 8H), 3.65-3.71 (m, 40H), 3.84 (t, J = 4.5 Hz, 8H), 4.11 (t, J = 4.6 Hz, 8H), 4.26 (s, 2H), 4.95 (s, 4H), 6.44 (m, 2H), 6.53-6.54 (m, 3H), 6.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.10, 160.06, 138.9, 137.6, 107.1, 106.0, 101.8, 101.1, 70.8, 70.6, 70.0, 69.6, 67.4, 54.7, 50.6; MS (FAB): m/z 1185.6 [M$^-$-N$_2$], 1213.6 [M$^+$]; HRMS (FAB) calcd for $C_{53}H_{79}N_{15}O_{18}$: 1213.5728. Found: 1185.5626 [M$^-$-N$_2$], 1186.5908 [M$^-$+H-N$_2$], 1213.5693 [M$^+$], 1214.5803 [M$^-$+H].

Compound 8-D3. A yellowish oil: 100% yield: IR 2872, 2104, 1595, 1448, 1298, 1175, 1068, 841 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (t, J = 4.8 Hz, 16H), 3.64-3.70 (m, 80H), 3.84 (t, J = 4.4 Hz, 16H), 4.10 (t, J = 4.4 Hz, 16H), 4.27 (s, 2H), 4.95 (s, 8H), 4.97 (s, 4H), 6.44 (m, 4H), 6.54

(m, 4H). 6.58 (m, 9H). 6.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 160.0, 139.0, 137.7, 107.1, 106.3, 106.0, 101.7, 101.5, 101.1, 70.8, 70.6, 70.0, 69.6, 67.4, 54.7, 50.6; MS (FAB): m/z 2480.3 [M^++2H-N_2], 2508.22 [M^+ + 2H].

Results and Discussion

Organoazides are versatile intermediates in synthetic organic chemistry, because the azide group can subsequently be converted into several other types of substituent groups.[4] Especially, dendritic azide is very useful intermediate in the construction of nanostructured materials. The dendritic benzyl azide was synthesized by the azidation of the corresponding dendritic benzyl halide. In the classical syntheses of the focal benzylic bromide functionality of dendrons, the conversion of the hydroxymethyl moiety to the bromomethyl functionality is achieved using triphenylphosphine and carbontetrabromide (or *N*-bromosuccinimide).[2a] However, this methodology often had drawback to occur the aromatic ring bromination, since the reagents above could generate bromonium ions.[5] The utilization of thionyl chloride as a chlorination agent of benzyl alcohols was reported and demonstrated that benzyl chloride is sufficient for the synthesis of aryl ether dendrimers.[6] But thionyl chloride is moisture sensitive compound and should be distillated before their use in reaction. Due to these obstacles, we have sought the effective synthesis of the dendritic benzyl azides without using the halogenated intermediate. Therefore we have designed and carried out one-pot reaction via mesylation followed by in situ azidation to obtain dendritic benzyl azides from dendritic benzyl alcohols.

In order to find the best reaction conditions, we first investigated the solvent effect for the mesylation of 3,5-dimethoxybenzyl alcohol **1-D1** as a model compound using methanesulfonyl chloride (MsCl) and Et_3N at room temperature. From the reactions of **1-D1** in THF or EtOAc in the presence of MsCl and Et_3N at room temperature, the only mesylated product was obtained. The reactions of **1-D1** in CH_2Cl_2 or DMF in the presence of MsCl and Et_3N at room temperature provided the mesylated product as well as chlorinated product which were detected by TLC runs of the reaction mixture. The latter is produced from the chlorination of the mesylated product by the generated triethylammonium chloride.[7] Considering the next one-pot azidation reaction, we tried to find the reaction condition with DMF as a solvent at room temperature. It was observed that the mesylation reaction of 3,5-dimethoxybenzyl alcohol **1-D1** was finished within 1 h in 1.0 M solution of DMF. Then sodium azide, for azidation of the mesylated product in one-pot, was added to the resulting mixture obtained from the reaction of 3,5-dimethoxybenzyl alcohol **1-D1** and MsCl in DMF in the presence of Et_3N. The azidation reaction was completed after 2 h at room temperature which was observed from TLC analysis of the reaction mixture.

The optimal condition for obtaining the dendritic benzyl azides from dendritic benzyl alcohols consists of the mesylation of hydroxyl group with MsCl (1.1 equiv.) and Et_3N (1.1 equiv.) in DMF followed by the azidation with sodium azide (1.5 equiv.). The appearance and disappearance of mesylated product were observed from TLC analysis of the reaction mixture. It was found that the azidation is more effective by adding several drops of water due to increasing the solubility of sodium azide.

Table 1. Synthesis of dendritic benzyl azides

entry	SM[a]	Solvent[b]	Temperature[c]	Reaction period[d]	Product	Yield (%)[e]
1	**1-D1**	DMF (1M)	r.t./r.t.	1 h / 2 h	**5-D1**	99
2	**1-D2**	DMF (1M)	r.t./r.t.	1 h / 2 h	**5-D2**	99
3	**1-D3**	DMF (1M)	r.t./r.t.	1 h / 2 h	**5-D3**	99
4	**1-D4**	DMF (1M)	r.t./r.t.	1 h / 2 h	**5-D4**	99
5	**2-D1**	DMF (1M)	r.t./r.t.	1 h / 2 h	**6-D1**	quant
6	**2-D2**	DMF (1M)	r.t./r.t.	1 h / 2 h	**6-D2**	quant
7	**2-D3**	DMF (1M)	r.t./r.t.	1 h / 2 h	**6-D3**	98
8	**3-D1**	DMF (1M)	r.t./r.t.	1 h / 2 h	**7-D1**	96
9	**3-D2**	DMF (1M)	r.t./r.t.	1 h / 2 h	**7-D2**	99
10	**3-D3**	DMF (1M)	r.t./r.t.	1 h / 2 h	**7-D3**	99
11	**4-D1**	DMF (1M)	r.t./r.t.	1 h / 2 h	**8-D1**	97
12	**4-D2**	DMF (1M)	r.t./r.t.	1 h / 2 h	**8-D2**	quant
13	**4-D3**	DMF (0.1M)	r.t./r.t.	4 h / 5 h	**8-D3**	quant

[a]SM means starting material. [b]parenthesis is molar concentration of starting substrate. [c,d]first one is for mesylation step and second one is for azidation step. [e]isolated yield and quant means quantitative yield.

With this optimal condition, we tried to demonstrate the validity of the chemistry in the synthesis of various dendritic benzyl azides, as shown in Scheme 1. The reaction conditions including solvent, time, and concentration was summarized in Table 1, together with the isolated yields of the dendritic benzyl azides. The purification of the resulting compounds was achieved by normal aqueous work-up. The methyloxy-terminated dendritic benzyl azides (entries 1-4) and azidopropyloxy-terminated dendritic benzyl azides (entries 5-7) as well as the PEG-terminated dendritic benzyl azides (entries 8-13) were obtained in excellent yields. The structures of the dendritic benzyl azides were confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectra. Therefore we found the optimized conditions for the quantitative conversion of the focal benzylic alcohol functionality into the focal benzylic azide in dendrons without any problems. To the best of our knowledge, this is the first systematic investigation to synthesize dendritic benzyl azide from their alcohol. This method can be easily applied for the conversion of benzylic and allylic alcohols to their azides. We are currently investigated the synthesis of functional dendrimers using these peripherally modified dendrons.

In summary, a one-pot and efficient synthesis of dendritic benzyl azides was demonstrated from the corresponding alcohols which was achieved by the conversion of the hydroxyl group into the mesylated group followed by the azidation with sodium azide in one flask. The pure dendritic azides were obtained from only normal aqueous work-up.

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