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Synthesis of [2]rotaxanes by tritylative endcapping of in situ formed pseudorotaxanes having thiol or hydroxyl functionality on the axle termini

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Abstract—Tritylative endcapping of an in situ formed pseudorotaxane consisting of dibenzo-24-crown-8 and an axle having a thiol group at the end by treatment with trityl hexafluorophosphate at room temperature gave the corresponding sulfide-type [2]rotaxane in high yields. Treatment of the pseudorotaxane having a hydroxyl group at the axle terminal with trityl hexafluorophophate followed by addition of a base such as triethylamine afforded the corresponding ether-type [2]rotaxane in good yields. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Rotaxanes[1] are molecules that consist of dumbbell-like units threaded into wheel-like ones. They have been regarded as motifs for nano devices, such as motors, sensors, switches, amplifier, and actuators at the nanoscale level, based on their interlocked structures. One very essential feature of these molecules is that their mechanically interlocked units have a high degree of freedom in relative motion of the components. Based on this aspect, one could easily expect that polymers having rotaxane units, such as polyrotaxanes,[2] would exhibit unusual viscoelastic properties, such as a very large loss modulus, low activation energy for viscous flow, and rapid stress relaxation.[3,4]

Rotaxanes can be synthesized efficiently using template-directed protocols[5] that utilize attractive interactions, such as the coordination of heterocyclic ligands to a metal cation, a $\pi-\pi$ stacking interaction, or a hydrogen-bonding interaction. A rotaxane recognition motif, which consists of *sec*-ammonium salt centers in the rod sections of the dumbbell components encircled by crown ethers, is a well-established one.[6] Synthesis of rotaxanes using threading-endcapping methodology is attractive and it is emerging as a convenient method in recent years. However, the synthesis should be carried out under neutral or acidic conditions to keep the hydrogen-bonding interaction intact during endcapping of pseudorotaxanes.[7] [2+3]Cycloaddition reaction,[7a] oxidative coupling of thiols,[7b] conjugate addition of thiols,[7c] acylation of amines[7d] or alcohols,[7e] imine metathesis,[7f–h] thiol–disulfide interchange reaction,[7i] and the reaction of halides with phosphines[7j] have been employed for the rotaxane synthesis.

However, the synthesis of rotaxane in high yield is still a challenging task and it often relies on how exactly the endcapping is achieved. Prompted by the fact that trityl (thio)ether formation reaction can be rapidly and smoothly achieved under neutral or acidic conditions,[8] we explored the possibility of utilizing this transformation as an endcapping reaction.[9] In this paper, we report a new protocol for the synthesis of [2]rotaxanes by tritylative endcapping of the thiol or hydroxyl functionality attached to the axle units.

2. Results and discussion

A *sec*-ammonium salt having a thiol group at the end (**1**) was prepared as illustrated in Scheme 1. Treatment of 3,5-di-*t*-butylbenzoic acid[10] (**5**) with thionyl chloride followed by the reaction with 2-aminoethanthiol afforded amide (**6**). Reduction of **6** with $LiAlH_4$ yielded the corresponding amine, which was converted to **1** by treatment with hydrochloric acid followed by counteranion exchange with ammonium hexafluorophosphate. The analytical data and the spectral data of **1** were consistent with the structure.

Tritylation of the pseudorotaxane (**1**·DB24C8) formed in situ from **1** and dibenzo-24-crown-8 (DB24C8) was examined by using trityl hexafluorophosphate (Ph_3CPF_6) in dichloromethane at room temperature for 24 h (Scheme 1, Table 1). Use of three equivalents of DB24C8 gave the [2]rotaxane (**2**) in 98% yield (entry 1). A small excess of

Keywords: [2]rotaxane; tritylation; pseudorotaxane; thiol; alcohol; endcapping.

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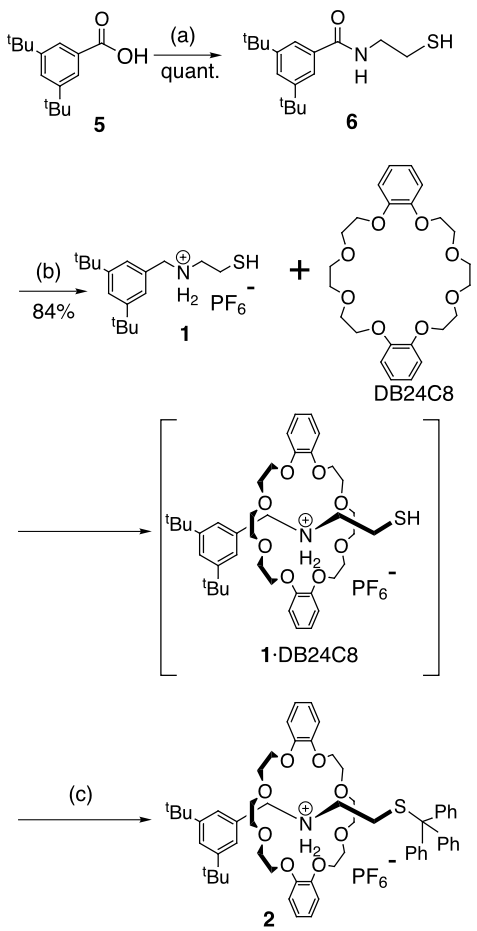
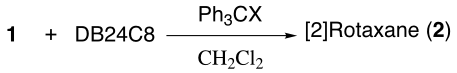


Scheme 1. *Reagents*: (a) (i) $SOCl_2$, (ii) 2-aminoethanethiol; (b) (i) $LiA1H_4$/THF, (ii) HCl/MeOH, (iii) NH_4PF_6aq; (c) PPh_3CX.

DB24C8 was enough to obtain **2** in more than 90% yield (93%, entry 2). Combination of trityl chloride and silver hexafluorophosphate, which generates trityl hexafluorophosphate in situ, also worked to give **2** in 80% yield (entry 3). When the reaction was conducted at −5°C, the yield decreased to 70% due to retarded reaction rate between the thiol group and trityl cation (entry 4). Prolonging the reaction time to 72 h hardly affected the yield (entry 5).

Solvent effects on the synthesis of **2** by tritylation were

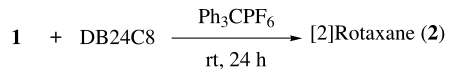
Table 1. Synthesis of sulfide-type [2]rotaxane (**2**) by tritylation of the thiol group at the axle end of **1** in the presence of DB24C8



Entry	DB24C8 (mmol)	X	Temperature	Time (h)	Yield (%)[a]
1	0.30	PF_6^-	rt	24	98 (95)
2	0.12	PF_6^-	rt	24	93 (91)
3	0.12	Cl^-[b]	rt	24	– (80)
4	0.12	PF_6^-	−5°C	24	70
5	0.12	PF_6^-	−5°C	72	74

1=0.10 mmol, Ph_3CPF_6=0.15 mmol, CH_2Cl_2=0.60 mL.
[a] Determined by ^{1}H NMR using naphthalene as an internal standard. Figures in parenthesis denote the isolated yields.
[b] An equimolar amount (0.15 mmol) of $AgPF_6$ was used to generate Ph_3CPF_6 in situ.

Table 2. Solvent effect on the synthesis of sulfide-type [2]rotaxane (**2**) by tritylation of the thiol group at the end of **1** in the presence of DB24C8



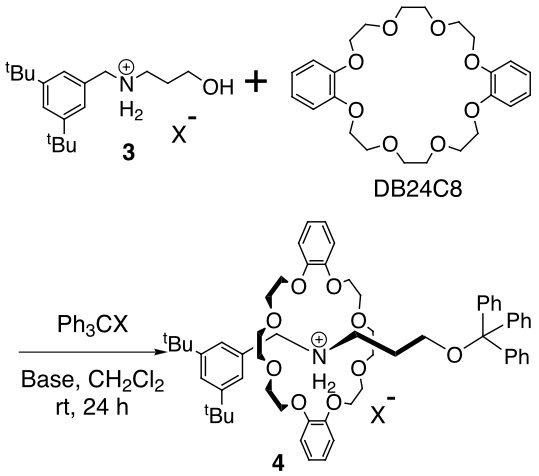
Entry	Solvent	D_N[a]	ε[a]	Yield (%)[b]
1	Toluene	0.1	2.2	80
2	CH_2Cl_2	1.0	8.9	93 (91)
3	CH_3NO_2	2.7	35.9	98
4	$CHCl_3$	4.0	4.8	88
5	CH_3CN	14.1	35.9	82 (77)
6	1.4-Dioxane	14.8	2.2	89

1=0.10 mmol, DB24C8=0.12 mmol, Ph_3CPF_6=0.15 mmol, solvent=0.60 mL.
[a] Ref. 11.
[b] Determined by ^{1}H NMR using naphthalene as an internal standard. Figures in parenthesis denote the isolated yields.

examined with respect to several aprotic solvents, and the results are summarized in Table 2. The reaction between the thiol group and trityl cation was completed in all cases. Hence, the association constants of **1** and DB24C8 would be mainly reflected in the yields of **2**. The association constants between ammonium salts and crown ethers generally increase as solvent polarity decreases, because the hydrogen-bonding interaction working between them is the main driving force for the complexation. Although solvent polarity has been evaluated by various parameters,[11] the most suitable parameter for pseudorotaxane formation has not been established. Stoddart et al. explained the association constants of pseudorotaxane formation in terms of donor numbers (D_N) of solvent: since *sec*-ammonium salts form pseudorotaxanes with crown ethers mainly by the hydrogen-bonding interaction, a solvent having a higher D_N prevents the complexation, and vice versa.[12] We have recently reported that dielectric constants (ε) of solvent also affect the association constants of pseudorotaxane formation together with D_N: since the ion–dipole interaction plays an important role for the complexation between *sec*-ammonium salts and crown ethers, a solvent having a high ε decreases the association constant.[3g] However, use of toluene having a lower D_N and an ε than those of dichloromethane resulted in a lowered yield (80%, entry 1). The highest yield was obtained by use of nitromethane (98%, entry 3). Chloroform and acetonitrile afforded **2** in lower yields than dichloromethane (entries 4 and 5). 1,4-Dioxane, which has a D_N as high as that of acetonitrile, gave **2** in 89% yield (entry 6). Thus, the effects of solvent on the yield of the tritylative endcapping are obscure at best. However, the higher yield of **2** (>80%) in all solvents that were employed is worth mentioning.

Synthesis of rotaxane by tritylation of the hydroxyl group at the end was also examined (Table 3). Tritylation of the hydroxyl group of the axle[3g] (**3**) was carried out in the presence of DB24C8 at room temperature for 24 h and afforded the [2]rotaxane (**4**) in 22% yield (entry 1). The low yield is attributed to the much slower reaction rate of the hydroxyl group than that of the thiol group, being consistent with the difference in nucleophilicity between them. In fact, **3** was recovered from the reaction mixture. Addition of triethylamine as a base to trap the hexafluorophosphoric acid formed in the reaction mixture enhanced the tritylation

Table 3. Synthesis of ether-type [2]rotaxane (4) by tritylation of the hydroxyl group at the axle end of 3 in the presence of DB24C8



Entry	Base	X	Yield (%)[a]
1	None	PF_6^-	22
2	Et_3N	PF_6^-	72
3	Pyridine	PF_6^-	74
4	DMAP	PF_6^-	67
5	Et_3N	Cl^-[b]	74

3=0.10 mmol, DB24C8=0.12 mmol, Ph_3CX=0.15 mmol, base=0.15 mmol. CH_2Cl_2=0.60 mL.
[a] Isolated yields.
[b] An equimolar amount of $AgPF_6$ was used to generate Ph_3CPF_6 in situ.

and resulted in a high yield of **4** (72%, entry 2). It should be noted here that triethylamine must be added finally, because the addition of triethylamine prior to trityl hexafluorophosphate leads to decomplexation of the pseudorotaxane. Use of other bases such as pyridine and DMAP gave **4** in similar yields (entries 3 and 4). The combination of trityl chloride and silver hexafluorophosphate also afforded **4** in 74% in the presence of triethylamine (entry 5).

3. Conclusion

Tritylative endcapping of the in situ formed pseudorotaxane having a thiol moiety at the axle end was carried out simply by treating a solution of the pseudorotaxane with tritylhexafluorophophate at room temperature to give the corresponding sulfide-type [2]rotaxane in high yields. Tritylation of the pseudorotaxane having a hydroxyl group at the axle terminus was achieved by treatment with trityl hexafluorophophate followed by addition of a base such as triethylamine to afford the corresponding ether-type [2]rotaxane in good yields. This protocol has been demonstrated to be effective for the synthesis of [2]rotaxanes, since it is simple, high-yielding, and tolerant to various solvents.

4. Experimental

4.1. General

Melting points were measured on a Yanagimoto micro melting-point apparatus and were uncorrected. IR spectra were recorded on a JASCO FT-IR model 230 spectrometer. ^1H NMR were performed on JEOL JNM-GX-270 and JNM-L-400 spectrometers in $CDCl_3$ with tetramethylsilane as an internal reference. FAB-MS measurements were performed on a Finnigan TSQ-70 instrument. For preparative HPLC, a JAICO LC-908 system using columns JAIGEL 1 (∅ 20 mm×600 mm) and JAIGEL 2 (∅ 20 mm×600 mm) was used.

4.1.1. Synthesis of amide (6). A solution of 3,5-di-*t*-butylbenzoic acid[10] (**5**, 5.56 g, 23.7 mmol) in $SOCl_2$ (13 mL) was stirred overnight at 50°C. Then, the mixture was concentrated in vacuo. The remaining $SOCl_2$ was removed as an azeotropic mixture with benzene to give the corresponding acid chloride. To a solution of 2-aminoethanethiol (2.26 g, 29.3 mmol) and Et_3N (4.2 mL, 30 mmol) in CH_2Cl_2 (115 mL) was slowly added a solution of the acid chloride in Et_2O (15 mL). The mixture was stirred for 1 h at room temperature, washed with 1 M HCl (20 mL×3) and successively with brine, anhydrous $MgSO_4$, and evaporated to dryness to give amide (**6**) as a white solid (6.6 g, 94%). **6** was used in the next step without further purification. Mp 180–183°C; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.60–7.58 (m, 3H, Ar*H*), 6.55 (br s, 1H, CON*H*), 3.65 (dt, J_1=J_2=6.3 Hz, 2H, CH_2S), 2.81 (dt, J_1=8.6 Hz, J_2=6.3 Hz, 2H, CH_2N), 1.42 (t, J=8.6 Hz, 1H, S*H*), 1.35 (s, 18H, *t-Bu*); IR (KBr) 1633 cm^{-1} ($\nu_{C=O}$).

4.1.2. Synthesis of axle (1). To a suspension of $LiAlH_4$ (80%, 1.30 g, 27.4 mmol) in THF (10 mL) was added a mixture of **1** (1.45 g, 4.94 mmol) and THF (20 mL) under Ar atmosphere. The mixture was refluxed for 20 h. A saturated aqueous solution of Na_2SO_4 was added to the reaction mixture to form a white precipitate, which was removed by suction filtration. The filtrate was poured into a mixture of conc. HCl (2 mL) and MeOH (50 mL). The resulting solution was evaporated to dryness. The residue was dissolved in MeOH (15 mL). To this solution was added a solution of NH_4PF_6 (1.93 g, 11.8 mmol) in H_2O (10 mL) to form a white precipitate. Water was added until no further precipitate was formed. The precipitate was collected by suction filtration, washed with water, dried in vacuo, and recrystallized from H_2O/EtOH to afford axle (**1**) as a white solid (1.0 g, 7.2%). Mp 180–182°C; ^1H NMR (CD_3CN, 270 MHz) δ 7.55 (t, J=1.6 Hz, 1H, Ar*H*), 7.32 (d, J=1.6 Hz, 2H, Ar*H*), 4.17 (s, 2H, ArCH_2), 3.16 (t, J=7.3 Hz, 2H, CH_2N), 2.80 (t, J=7.3 Hz, 2H, CH_2S), 1.33 (s, 18H, *t*-Bu) (the signals of the S*H* and NH_2 were not observed probably due to fast exchange process); Found: C, 47.92; H, 7.00; N, 3.20%. Calcd for $C_{17}H_{30}F_6NPS$: C, 47.99; H, 7.11; N, 3.29%.

4.1.3. Representative procedure for the preparation of sulfide-type [2]rotaxane (2). To a solution of thiol (**1**) (43 mg, 0.10 mmol) and DB24C8 (54 mg, 0.12 mmol) in dichloromethane (0.60 mL) was added trityl hexafluorophosphate (59 mg, 0.15 mmol). The reaction mixture was stirred at room temperature for 24 h and then partitioned between $CHCl_3$ (3 mL) and H_2O (3 mL). The organic layer was washed with H_2O (3 mL×1), dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was purified with preparative HPLC to afford the sulfide-type [2]rotaxane (**2**) in 91% yield. Mp 76.2–77.0°C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (br t, 1H, axle-Ar*H*), 7.25–7.13

(m, 19H, axle-Ar*H* and NH_2), 6.92–6.79 (m, 8H, wheel-Ar*H*), 4.49 (m, 2H, ArCH_2NH$_2$), 4.15–3.30 (m, 26H, crown-CH_2 and ArCH$_2$NH$_2$CH_2), 2.21 (t, J=7.8 Hz, SCH_2), 1.16 (s, 18H, t-C$_4H_9$); FAB-MS (matrix: mNBA) $[M-PF_6+H]^+$ 970.5; Found: C, 63.89; H, 7.01; N, 1.32%. Calcd for $C_{60}H_{76}F_6NO_8PS\cdot(H_2O)_{0.5}$: C, 64.04; H, 6.90; N, 1.24%.

4.1.4. Representative procedure for the preparation of ether-type [2]rotaxane (4). To a solution of alcohol[3g] (**3**) (42 mg, 0.10 mmol) and DB24C8 (54 mg, 0.12 mmol) in dichloromethane (0.60 mL) was added trityl hexafluorophosphate (59 mg, 0.15 mmol). Then Et_3N (21 μL, 0.15 mmol) was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 24 h and then partitioned between $CHCl_3$ (3 mL) and H_2O (3 mL). The organic layer was washed with H_2O (3 mL×1), dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was purified with preparative HPLC to afford the ether-type [2]rotaxane (**2**) in 72% yield. Mp 165–166°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4–7.2 (m, 20H, axle-Ar*H* and NH_2), 6.95–6.85 (m, 8H, wheel-Ar*H*), 4.66 (m, 2H, ArCH_2NH$_2$), 4.30–3.30 (m, 28H, axle-CH_2 and wheel-CH_2), 2.97 (t, J=5.8 Hz, 2H, ArCH$_2$NH$_2$CH_2), 1.75 (m, 2H, CH$_2$CH_2CH$_2$), 1.18 (s, 18H, t-C$_4H_9$); FAB-MS (matrix: mNBA) $[M-PF_6+H]^+$ 968.5; Found: C, 65.18; H, 6.91; N, 1.26%. Calcd for $C_{61}H_{78}F_6NO_9P\cdot(H_2O)_{0.5}$: C, 65.23; H, 7.09; N, 1.25%.

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