Conjugate Addition-Approach to End-Capping of Pseudorotaxanes for Rotaxane Synthesis

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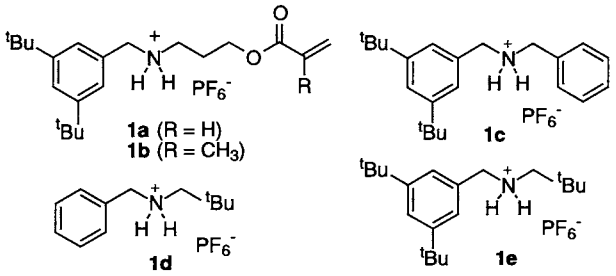
Conjugate addition of 4-*tert*-butylbenzenethiol to pseudorotaxane having terminal α,β-unsaturated ester group under radical condition afforded the corresponding aryl sulfide-capped rotaxane, while conjugate addition of sodium 4-*tert*-butylbenzenesulfinate under acidic condition also yielded aryl sulfone-capped rotaxane.

A variety of preparation methods for rotaxanes have been explored in this decade.[1-6] Among them,[4] chemical end-capping of pseudorotaxane is one of the most straightforward methods. Although some end-capping reactions of pseudorotaxanes based on "hydrophobic" interaction are possible, very limited methods are available for those based on hydrogen-bonding interaction.[7-9] The difficulty to keep hydrogen-bonding during end-capping reaction limits the variation of the hydrogen-bonding-based rotaxanes. Because of flexibility in designing the combination of ammonium salts and crown-ethers, further improvement of the end-capping of this type of pseudorotaxane would be necessary for development of rotaxanes possessing unique functionality. A promising method seems to be an end-capping through an addition reaction under radical and weakly acidic conditions, which do not affect the hydrogen-bonding interaction.[10] Thus, we have chosen α,β-unsaturated ester moiety as a suitable terminal functional group. We wish to report novel end-capping of pseudorotaxanes through conjugate addition under both radical and weakly acidic conditions.

The preparation of pseudorotaxanes from secondary benzylammonium salt and dibenzo-24-crown-8 ether (DB24C8) has been well documented.[11,12] Thus, ammonium salt **1a** possessing bulky 3,5-di-*tert*-butylphenyl and acrylate groups in both termini was prepared as an axle.[10] Its ^{1}H NMR spectra in the presence and absence of DB24C8 were measured in $CDCl_3$. In the presence of 1 eq. of DB24C8, a new set of resonances that was assignable to the crown ether-ammonium complex was observed. Analogous NMR measurements were conducted with ammonium salts **1b**, **1c**, **1d**, and **1e**. In the cases of **1b**, **1c**, and **1d**, new sets of resonances which resemble that of **1a**-DB24C8 mixture were observed, while no change was observed for **1e**-DB24C8 mixture. Thus, it is supposed that *tert*-butyl group is too bulky to thread through the ring of DB24C8,[13] and these new sets of signals can be assigned to the corresponding pseudorotaxanes. Characteristic up-field shift of *tert*-butyl proton signal (for free **1a**, 1.30 ppm; pseudorotaxane, 1.20 ppm; Figure 1) would be rationalized by the shielding effect of the benzene ring of DB24C8.[8]

Radical addition of 4-*tert*-butylbenzenethiol on **1a** was thus carried out in the presence of excess DB24C8.[14,15] The crude mixture was subjected to separation by preparative GPC to give simple addition product to **1a**, DB24C8 recovered, and 1:1:1 adduct of **1a**, thiol, and DB24C8. The composition of the adduct was confirmed by ^{1}H NMR and FAB MS. Since repeated chromatography of the adduct did not separate each component, it could be assigned as aryl sulfide-capped [2]rotaxane **2a**.[16] The *tert*-butyl proton signal observed at 1.20 ppm in the ^{1}H NMR of **2a** was well corresponded to that of the pseudorotaxane. The reaction proceeded in benzene and dichloromethane as well as



dioxane as shown in Table 1.[17] Although the importance of donation ability of solvent has been documented in pseudorotaxane formation as the solvent effect,[11,12] other polarity factors such as dielectric constant played more important role in this case. Same reaction of **1b** proceeded without difficulty to give the corresponding aryl sulfide-capped rotaxane **2b**.[15]

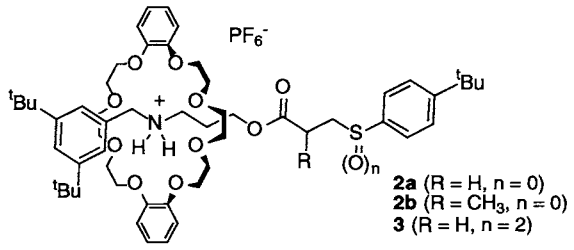


Table 1. End-capping of pseudorotaxane *via* conjugate addition

axle	DB24C8 / eq.	method[a]	solv.	temp	product	yield[b] / %
1a	10	**A**	CH_2Cl_2	r.t.	**2a**	18
1a	3	**A**	benzene	r.t.	**2a**	16
1a	3	**A**	benzene	60 °C	**2a**	17
1a	3	**A**	dioxane	60 °C	**2a**	25
1b	10	**A**	CH_2Cl_2	r.t.	**2b**	13
1a	5	**B**	CH_2Cl_2	r.t.	**3**	14

[a] **A**: radical conjugate addition (reference 15). **B**: conjugate addition of sulfinic acid (reference 19). [b] isolated yield by preparative GPC.

Further, pseudorotaxane **1a**-DB24C8 was allowed to react with sodium 4-*tert*-butylbenzenesulfinate in the presence of acetic acid to give aryl sulfone-capped [2]rotaxane **3a** in 14% yield after separation by preparative GPC.[16,18,19]

It was confirmed that radical and weakly acidic conditions did not affect the hydrogen-bonding interaction of pseudorotaxane **1**•DB24C8 during end-capping. Detailed study on this versatile end-capping approach is in progress, along with study on application to the synthesis of functionalized rotaxanes.

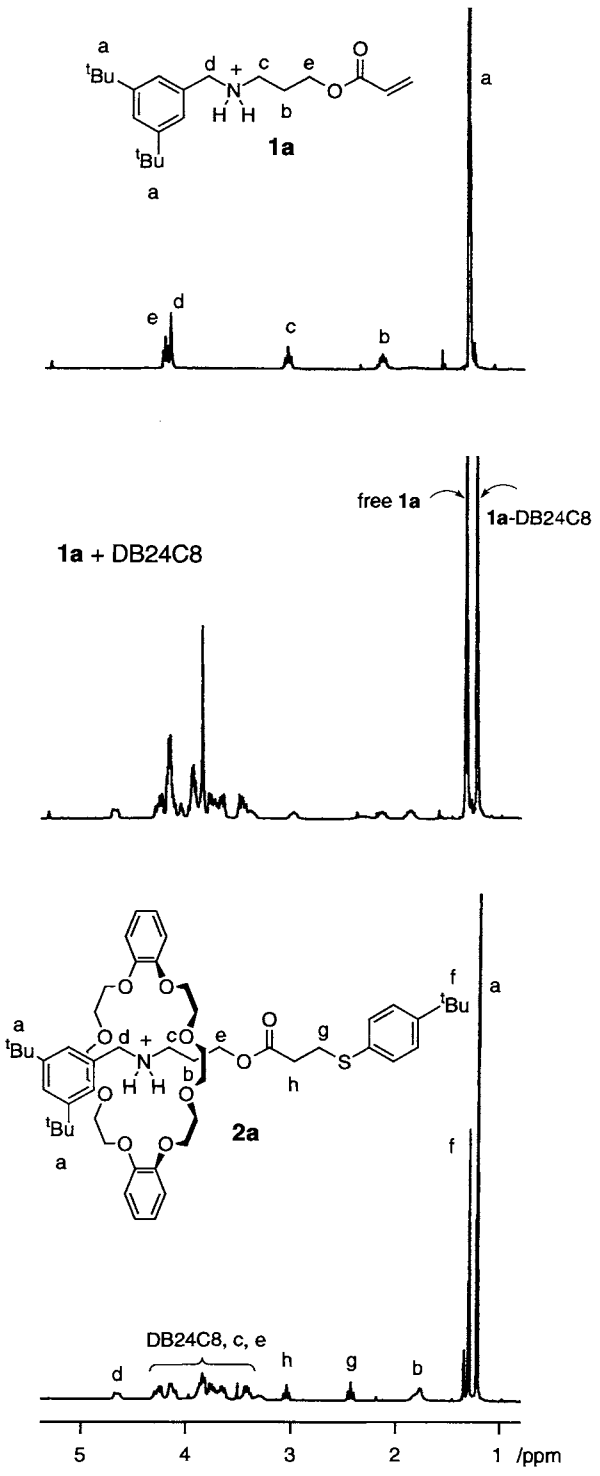


Figure 1. ^{1}H NMR spectra (270 MHz, $CDCl_3$, 298 K) of **1a**, a mixture of **1a** and DB24C8, and **2a**.

References and Notes

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15 A typical procedure (Method A): A solution of **1a** (100 mg, 0.21 mmol), DB24C8 (283 mg, 0.63 mmol), 4-*tert*-butylbenzenethiol (350 mg, 2.1 mmol), and AIBN (1 mg, 6.3 μmol) in dioxane (1 mL) was sealed under vacuum and heated at 60 °C for 20 h. After evaporation of the solvent, the crude product was separated by preparative GPC to give amorphous solid **2a** (58 mg, 25 %) as the highest molecular weight fraction.
16 **2a:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55-7.24 (7H, m, Ar*H*), 6.94-6.86 (8H, m, Ar*H* of DB24C8), 4.73-4.56 (2H, m, $ArCH_2NH_2$), 4.35-4.02 (8H, m, CH_2 of DB24C8), 3.95-3.60 (14H, m, CH_2 of DB24C8 and $NH_2CH_2CH_2CH_2$), 3.47-3.20 (6H, m, CH_2 of DB24C8 and $OCH_2CH_2CH_2$), 3.02 (2H, t, J = 7 Hz, $ArSCH_2CH_2$), 2.42 (2H, t, J = 7 Hz, $ArSCH_2CH_2$), 1.90-1.60 (2H, m, $CH_2CH_2CH_2$), 1.29 (9H, s, $tC_4H_9C_6H_4S$), 1.21 (18H, s, 3, 5-$(tC_4H_9)_2C_6H_3$; FAB-MS (matrix: mNBA) m/z 947 [$(M\text{-}PF_6)^+$], 498 [$(M\text{-}DB24C8\text{-}PF_6)^+$]. **2b:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38-7.22 (7H, m, Ar*H*), 6.95-6.84 (8H, m, Ar*H* of DB24C8), 4.72-4.58 (2H, m, $ArCH_2NH_2$), 4.30-4.20 (8H, m, CH_2 of DB24C8), 3.92-3.58 (14H, m, CH_2 of DB24C8 and $NH_2CH_2CH_2CH_2$), 3.50-3.26 (6H, m, CH_2 of DB24C8 and $OCH_2CH_2CH_2$), 3.09 (1H, dd, J = 13 Hz, 8 Hz, $ArSCH_2CH(CH_3)$), 2.82 (1H, dd, J = 13 Hz, 7 Hz, $ArSCH_2CH(CH_3)$), 2.60-2.44 (1H, m, $ArCH_2CH(CH_3)$), 1.90-1.74 (2H, m, $CH_2CH_2CH_2$), 1.28 (9H, s, $tC_4H_9C_6H_4S$), 1.20 (18H, s, 3, 5-$(tC_4H_9)_2C_6H_3$), 1.15 (3H, d, J = 7 Hz, CH_3CH)); FAB-MS (matrix: mNBA) m/z 961 [$(M\text{-}PF_6)^+$], 412 [$(M\text{-}DB24C8\text{-}PF_6)^+$]. **3:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 8 Hz, $tC_4H_9C_6H_4SO_2$), 7.57 (2H, d, J = 8 Hz, $tC_4H_9C_6H_4SO_2$), 7.40-7.28 (3H, m, Ar*H*), 6.98-6.86 (8H, m, Ar*H* of DB24C8), 4.73-4.60 (2H, m, $ArCH_2NH_2$), 4.35-4.05 (8H, m, CH_2 of DB24C8), 3.95-3.60 (16H, m, CH_2 of DB24C8 , $NH_2CH_2CH_2CH_2O$, and $NH_2CH_2CH_2CH_2O$), 3.45-3.35 (4H, m, CH_2 of DB24C8), 3.31 (2H, t, J = 7 Hz, $ArSO_2CH_2CH_2$), 2.56 (2H, t, J = 7 Hz, $ArSO_2CH_2CH_2$), 1.90-1.75 (2H, m, $CH_2CH_2CH_2$), 1.34 (9H, s, $tC_4H_9C_6H_4S$), 1.21 (18H, s, 3, 5-$(tC_4H_9)_2C_6H_3$)); FAB-MS (matrix: mNBA) m/z 979 [$(M\text{-}PF_6)^+$], 530 [$(M\text{-}DB24C8\text{-}PF_6)^+$].
17 Radical conjugate addition of benzenethiol to acrylate generally gives addition product in moderate yield (Ref. 14). Low yield of **1a** seems to come from both low *Ka* in **1a**-DB24C8 system (Ref. 10) and low efficiency of radical conjugate addition.
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19 A typical procedure (Method B): To a solution of **1a** (200 mg, 0.42 mmol), DB24C8 (940 mg, 2.1 mmol), and acetic acid (40 mg, 0.67 mmol) in CH_2Cl_2 (5 mL) was added portionwise sodium 4-*tert*-butylbenzenesulfinate (100 mg, 0.50 mmol) over a period of 9 days, and the mixture was stirred for additional 1 day. After usual work-up, the crude product was separated by preparative GPC to give **3** (67 mg, 14 %) as a pale yellow oil.