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Convenient synthesis of [3]catenane by olefin metathesis dimerizations

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Dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday

Abstract—[3]Catenane **5a** and **5b** were synthesized conveniently by olefin metathesis dimerization of pseudorotaxanes **3a** and **3b**. The yields of **5a** and **5b** were influenced by concentrations of **3a** and **3b**, and a ring size of a center wheel of [3]catenane.

Topological molecules, catenanes, rotaxanes, knots[1] constitute a major research field in supramolecular chemistry. These molecules display interesting physical properties, such as photoinduced intramolecular electron transfer, electrochemically triggered molecular motions, and photochemical dethreading process.[1e,2,3] A number of these multicomponent systems have been named 'molecular machines.' Many research groups synthesized these molecules, and interesting molecular motions were found.[1e,4] Olefin metathesis has been extensively utilized for the synthesis of macrocycles, carbocycles and heterocycles.[5] Several groups showed ring-closing metathesis (RCM) was extremely useful for catenanes, rotaxanes and knots syntheses.[6] Recently Smith and co-workers reported the C_2-symmetric cyclophane skeletons by olefin metathesis dimerization.[7] Now we wish to report convenient synthesis of [3]catenane by using olefin metathesis dimerization.

Our synthetic plan of [3]catenane is outlined in Figure 1. [3]Catenanes were synthesized by several procedures.[8] However, to the best of our knowledge, there is no previous report on the synthesis of [3]catenane by olefin metathesis dimerizations. Formation of pseudorotaxane from a wheel and an axis molecule, followed by olefin metathesis dimerization should afford [3]catenane. Dimerization process consists of intermolecular olefin metathesis and ring-closing metathesis, which should occur competitively. Therefore, there is a possibility to obtain other products, such as [2]catenane, highly complicated catenanes and oligomeric compounds. In order to obtain [3]catenane efficiently, it is necessary that each step, formation of pseudorotaxane, intermolecular olefin metathesis, ring-closure olefin metathesis, were performed effectively. These steps are affected by concentrations of wheel and axis molecules. Intermolecular olefin metathesis prefers

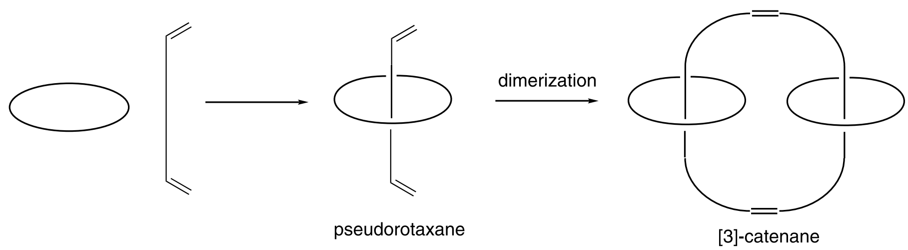

Figure 1. Outline of [3]catenane synthesis.

Keywords: ring-closing metathesis; olefin metathesis dimerization; [3]catenane.
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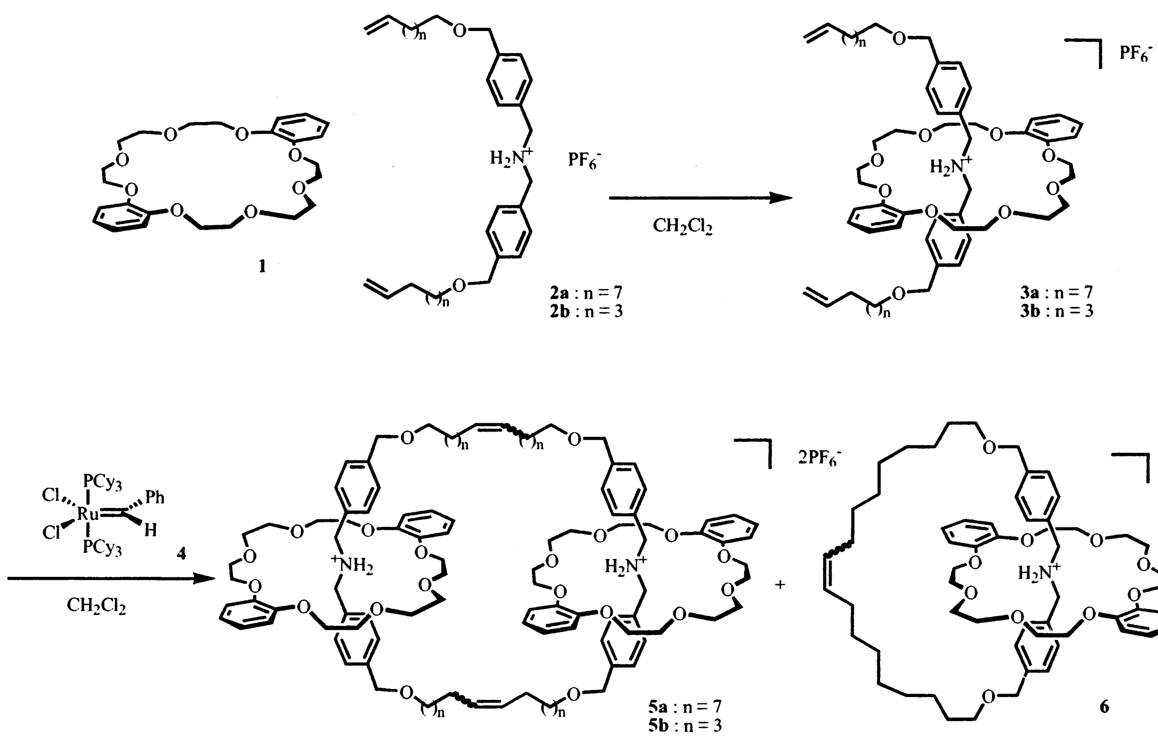

Scheme 1. Synthesis of [3]catenane using olefin methathesis.

highly concentrated condition; on the other hand RCM prefers high dilution condition. Also highly concentrated condition is needed for the formation of pseudorotaxane.

The synthesis of [3]catenane was performed as shown in Scheme 1. Treatment of pseudorotaxane **3a**, which was derived from dibenzo[24]crown-8 (DB24C) **1** and an equivalent of ammonium salt having two terminal olefin **2a**[9] in dichloromethane, with a catalytic amount of ruthenium carbene complex **4**[10] gave the desired catenation products **5a**,**6**[11] and oligomeric by-products. When **2b**, which had shorter alkyl chains than **2a**, was used instead of **2a**, only [3]catenane **5b** and by-products were obtained, but [2]catenane could not be find. These compounds were purified by column chromatography, GPC and HPLC analysis. ^{1}H NMR, and ESI-TOF mass spectrum[12] of the synthesized [2] and [3]catenanes were shown in Figures 2 and 3, respectively. These ^{1}H NMR show the signals of disubstituted olefin proton, which occurred olefin metathesis and crown ether and ammonium salt component. The positive-ion ESI-TOF mass gave the correspondent exact mass of each product and observed isotopic distributions of the products were similar to theoretical ones.

The yields of [3]catenane and [2]catenane are influenced by concentrations of dibenzo[24]crown-8 (DB24C) **1** and ammonium salt having two terminal olefin **2a** (Table 1). When concentration of **1** and **2a** was 0.01 M of dichloromethane solution, [2]catenane **6** was obtained in 56% yield, and [3]catenane **5a** was only in 2% yield. Increasing the concentrations, the yield of [3]catenane **5a** increased, but that of [2]catenane **6** was decreased. On the other hand, in the case of **2b**, only [3]catenane **5b** was obtained under several conditions of concentration.[13] Apparently, under high dilution condition using **2a**, ring-closing metathesis preferred to dimerization process, and then [2]catenane must be major product. As concentration of **1** and **2a** was increased, intermolecular olefin metathesis was easier to occur and the yield of [3]catenane was increased. **2b** has the axle, not long enough to form [2]catenane, therefore ring-closing metathesis would be difficult to react and the dimerization process would take priority over other processes.

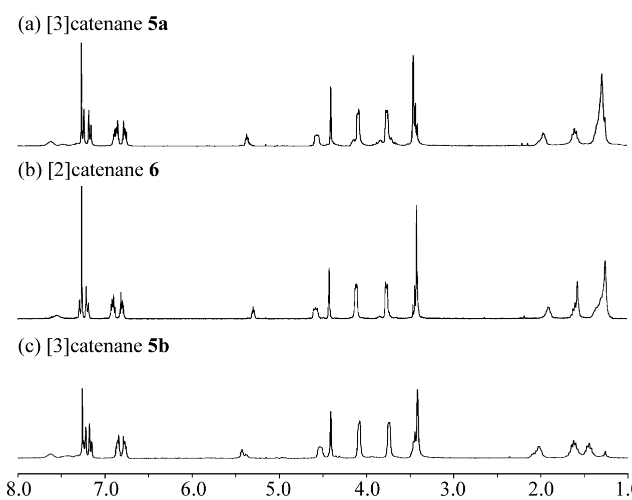

Figure 2. ^{1}H NMR spectrum of (a) [3]catenane **5a**; (b) [2]catenane **6** and (c) [3]catenane **5b**.

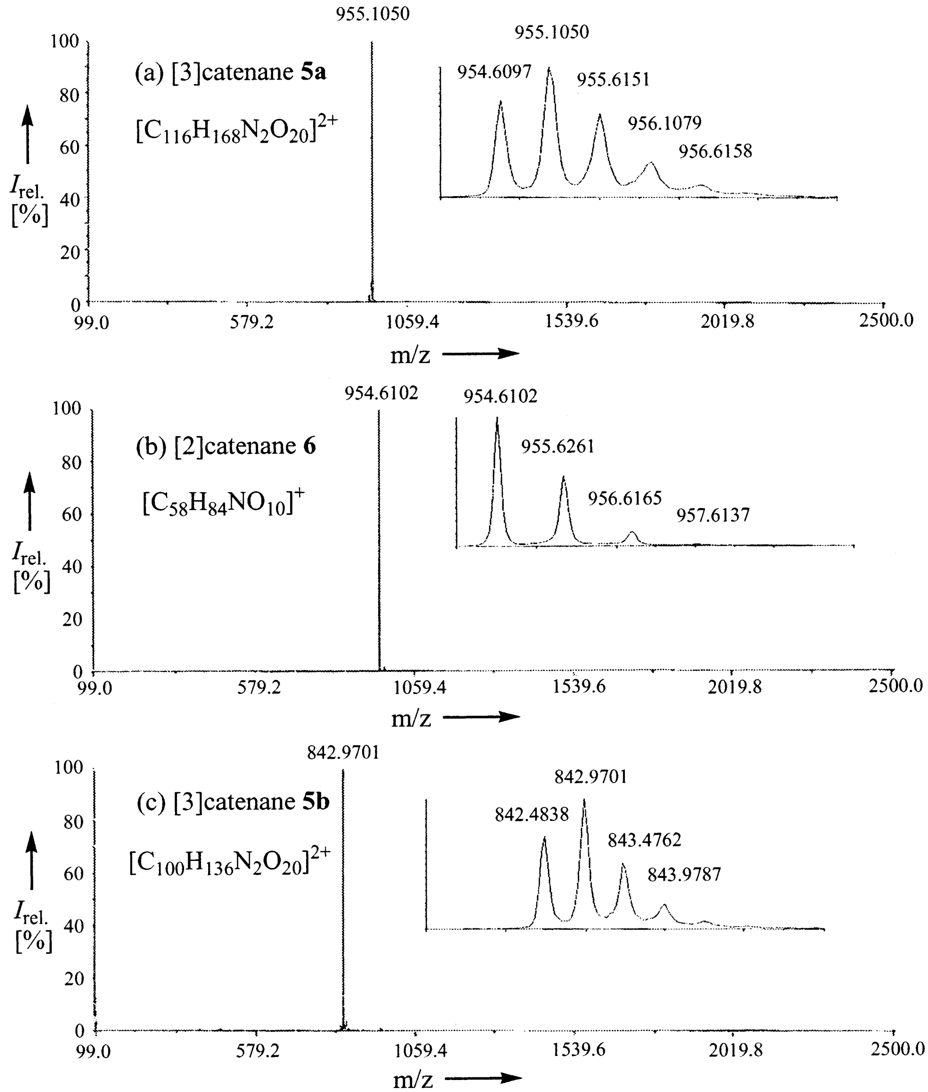

Figure 3. ESI-TOF mass spectrum of (a) [3]catenane **5a**; (b) [2]catenane **6** and (c) [3]catenane **5b**.

Table 1. Yields of [3]catenanes **5a** and **5b**, and [2]catenane **6**

Alkyl chain length n	Concentration [M][a]	Yield	
		[3]Catenane (%)	[2]Catenane (%)
7 (**2a**)	0.002	2	56
	0.01	16	41
	0.02	20	31
3 (**2b**)	0.002	25	0
	0.01	33	0
	0.02	35	0

[a] Both of dibenzo[24]crown-8 (DB24C) **1** and ammonium salt **2a** and **2b** were prepared as the same concentration.

In conclusion, we have developed a convenient method of synthesis of [3]catenane by olefin metathesis dimerization. The method was affected by a concentration of the substrates, and the size of center wheel of [3]catenane made by olefin metathesis dimerization.

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11. Compounds **5a**,**b**, **6** were obtained as mixtures of isomers *E* and *Z* olefin, which could not be separated. Oligomeric by-products were not purified, therefore not identified.
12. ESI-TOF mass were carried out on a AppliedBioSystems coupled to a Mariner TK-3500 BioSpectrometry Workstation. The samples were dissolved in 1% AcOH in MeCN/1% AcOH in $H_2O=50/50$, and Bradykinin, Angiotensin I and Neurotensin were used as internal standards for obtaining high-resolution mass spectral data.
13. The higher concentrations more than 0.02 M did not give sufficient yields of [3] and [2]catenane, and oligomeric by-products were increased.