

(4,5) : (13,14)-Dibenzo-6,9,12-trioxa-3,15,21-triazabicyclo  
[15.3.1]heneicosa-(1,17,19)(18,20,21) triene 및  
Aza-Crown Polymer의 합성

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Synthesis of (4,5) : (13,14)-Dibenzo-6,9,12-trioxa-3,15,21-  
triazabicyclo[15.3.1] Heneicosa-(1,17,19)(18,20,21)  
triene and Aza-Crown Polymers

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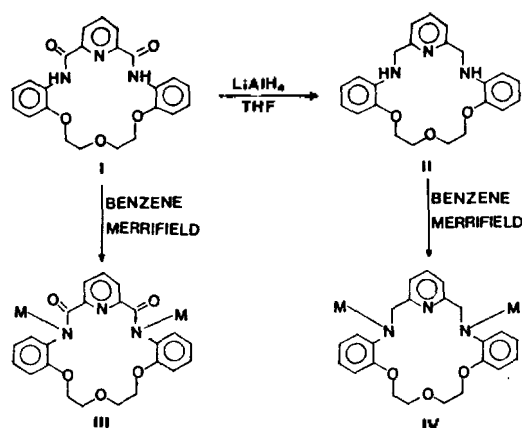
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In recent years there has been surging impetus in research on the synthesis and properties of crown ethers of various structures<sup>1</sup>. Especially, there has been many studying for the aza-crown compounds that have complexation properties that are intermediate between those of the all-oxygen crowns, which strongly complex with alkali and alkaline earth metal ions, and those of the all-nitrogen cyclans, which strongly complex with heavy-metal cations. These mixed complexation properties make the aza-crowns interesting to researchers in many areas<sup>2-5</sup>. The aza-crown have been important uses as catalysis in organic synthesis<sup>6</sup>. A great many improvements and further applications have been demonstrated in analytical chemistry, including ion selective solvent extractions<sup>7</sup>, membrane-transport procedures<sup>8</sup>, and separation by chromatographic methods<sup>9</sup>.

In the course of our studies on separation of

lithium isotopes by chromatographic method<sup>10,11</sup>, we needed to prepare new resin containing aza-crown compound. In order to use resin process, aza-crown (I)<sup>5</sup> and new aza-crown (II) containing pyridine as subcycle unit were synthesized, and they were induced to Merrifield resin. Kim *et al.*<sup>5</sup> reported that the selectivity tendency of aza-crown (I) for alkali metal ions is inconsistent with the size-fit concept<sup>1</sup>. The result of chromatographic process will be affected by this tendency.

The synthetic procedures for new triaza-crown ether and resins were outlined in Scheme 1. The products were certified by various spectroscopic methods. H-NMR spectrum was obtained with a Varian T-60 spectrometer using tetramethylsilane as an internal standard. Infrared and mass spectra were obtained with a Jasco 210A spectrometer and a GC-Mass HP 5890 II-VG TrioII, respectively. Elementary analysis was carried out with a Per-



Scheme 1.

kin-Elmer 240A.

**Synthesis of (4,5):(13,14)-dibenzo-6,9,12-trioxo-3,15,21-triazabicyclo[15.3.1] heneicosa-(1,17,19) (18,20,21)triene (II).** A 20 ml of 1.0 mole solution of  $\text{LiAlH}_4$  in THF was refluxed in a 200 ml flask under dry  $\text{N}_2$  gas. To this solution was added 0.218 g (0.52 mmole) of cyclic diamide azacrown ether (I) in small portions for ca. 30 min, and the refluxing was continued for an additional 72 hrs at  $60^\circ\text{C}$ . Into the reaction mixtures cooled with ice water was added 20 ml of ethyl acetate and 20 ml of 15% NaOH aqueous solution. After the mixtures boiled for 30 min, insoluble materials were filtered off, and the filtrate was concentrated in vacuo. Recrystallization from chloroform gave yellow-reddish crystals of products (II). Yield: 0.125 g (61%), IR(KBr);  $-\text{NH}$   $2800\sim 3400\text{ cm}^{-1}$ , aromatics  $1590\text{ cm}^{-1}$ , the carbonyl peak ( $1690\text{ cm}^{-1}$ ) of reactant disappeared. Mass;  $m_e$  391 ( $\text{M}^+$ ). H-NMR;  $\delta$  6.8 (m, 8H, benzene), 4.0 (m, 4H,  $\text{OCH}_2$ ), 4.2 (m, 4H,  $\Phi\text{-OCH}_2$ ), 7.3 (m, 3H, Pyridine), 2.8 (m, 4H,  $\text{NCH}_2$ ). mp.;  $137\sim 139^\circ\text{C}$ . Anal. Calcd.: C, 70.59; H, 6.39; N, 10.74. Found: C, 70.51; H, 6.33; N, 10.70.

**Synthesis of Polymer (III).** Into a dry 500 ml three-necked round bottom flask, equipped with a condenser, two additional funnels, and moisture protector, were placed 200 ml of dry benzene and 2 ml of triethylamine. And then 0.839 g (2 mmole) of triazacrown ether (I) in 50 ml of dry benzene

Table 1. Thermal properties of merrifield resins with aza-crowns

Polymers	Degradation temperature ( $^\circ\text{C}$ )		$T_{\text{max}}$ ( $^\circ\text{C}$ )
	initial	final	
Merrifield	320	465	375
polymer III	369	476	399
polymer IV	360	460	390

from one additional funnel and 2.94 g (4 mmole) of merrifield peptide resin in 50 ml of dry benzene from another additional funnel were added slowly. After the mixture was stirred for 72 h at  $80^\circ\text{C}$ , the residue was washed with water to remove triethylamine hydrochloride, and then was evaporated to dryness in vacuo. The product was repeatedly washed from benzene and was dried in vacuo. It gave a pale yellow powder (III). In IR(KBr) spectrum the  $-\text{CH}_2\text{-Cl}$  (s.  $690\text{ cm}^{-1}$ ) peak gave lower intensity. This results from binding between  $-\text{CH}_2\text{-Cl}$  and  $-\text{NH}$  groups (Scheme 1).

Thermogravimetric analysis was performed for the product (III) with Perkin-Elmer 7 Thermal Analysis System. In TGA thermograms, the degradation of the polymer began at  $369^\circ\text{C}$  and ended up at around  $476^\circ\text{C}$ , and  $T_{\text{max}}$  was  $399^\circ\text{C}$  (Table 1).  $T_{\text{max}}$  is a temperature at which the rate of weight loss is maximum.

**Synthesis of Polymer (IV).** This compound was prepared by the similar procedure as in the preceding method. Polymer (IV) gave a pale yellow powder. In IR(KBr) spectrum the  $-\text{CH}_2\text{-Cl}$  (s.  $690\text{ cm}^{-1}$ ) peak gave also lower intensity. The degradation of the polymer (IV) began at  $360^\circ\text{C}$  and ended up at around  $460^\circ\text{C}$ , and  $T_{\text{max}}$  was  $390^\circ\text{C}$  (Table 1).

The values of  $T_{\text{max}}$  for polymers (III and IV) were increased as compared with that of Merrifield resin. This result may be reflected by cross-linkage formation between amines or amides of aza-crowns and methyl chloride of Merrifield resin chains. We expect that this polymers can be readily applicable to separation of metal ions or isotopes.

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