New Syntheses of Per-*N*-alkyl-substituted *Triaza-* and *Tetraaza*-Crown Compounds Containing an Allyloxymethyl Substituent

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Received November 28, 1988

Seven new per-*N*-alkyl-substituted *triaza-* and *tetraaza*-crown compounds have been prepared using commercially available or easily synthesized per-*N*-alkyl-substituted oligoethylene and oligopropylene polyamines, tetraazapentaethylene and tetraazaheptaethylene glycols. Five of these new polyaza-crowns have a pendant allyloxymethyl substituent.

J. Heterocyclic Chem., **26**, 661 (1989).

Introduction.

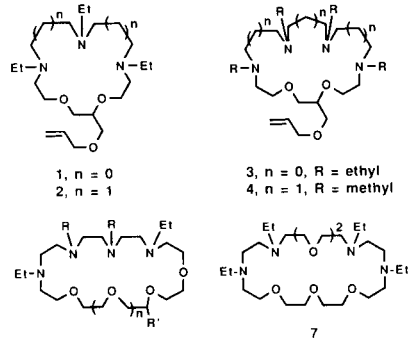
The aza-crown compounds have been studied in recent years because of their ability to complex the heavy metal ions as well as organic cations and anions [2-5]. The recent permanent attachment of diaza-crowns to silica gel *via* a hydrocarbon-ether type of linkage has made possible the design of systems capable of the selective and quantitative removal of cations from aqueous solutions [6-9]. The silica gel attachment process consists of the hydrosilylation reaction of an allyloxymethyl-substituted crown with trimethoxysilane followed by coating and heating the resulting crown-trimethoxysilane species on silca gel [6,9]. Thus, it is important to synthesize various allyloxymethyl-substituted aza-crowns so that a variety of silica gel-bound aza-crowns can be prepared for the separation of metal cations from aqueous solutions.

It is instructive to note that the complexation of metal cations by the aza-crowns with and without *N*-alkyl substituents is about the same [5]. Also, increasing the number of nitrogen atoms in the macro ring increases the affinity of a given aza-crown towards heavy metal cations [5]. Thus the triaza- and tetraaza-crowns containing a functional group capable of further reactions to bond them to silica gel should be useful in preparing silica gel-bound material capable of interesting metal ion separations.

There are many methods which have been used to prepare the aza-crown ligands [10]. The majority of the methods are for the synthesis of the non *N*-alkyl-substituted aza-crowns. These synthetic procedures require the use of *N*-blocking groups which adds steps to the process and reduces the overall yields for the aza-crown products. We desire methods to prepare the per-*N*-alkyl-substituted polyaza-crowns which require only a few steps from readily available starting materials. Allyloxymethyl-substituted diaza-crowns were prepared by us in only a few steps [9,11]. Some allyloxymethyl-substituted triaza- and tetraaza-crowns, where the macro ring nitrogen atoms were equally or nearly equally distributed around the macro ring, have also been prepared [12]. These latter compounds were prepared using *N*-[2-(2-chloroethoxy)ethyl]-acetamide as a synthon in the preparation of triaza- or tetraazaoligoethylene glycols.

This paper describes the synthesis of per-*N*-alkyl-substituted triaza- and tetraaza-crowns where the macro ring nitrogen atoms are on the same side of the macro ring (**1-6**, Figure 1). Five of these new macrocycles also contain an allyloxymethyl substituent on one of the macro ring carbon atoms. Also included is a symmetrically substituted tetraaza-27-crown-9 without an allyloxymethyl substituent, **7**. These crowns were made using readily available or easily synthesized per-*N*-alkyl-substituted oligoethylene and oligopropylene polyamines (Scheme I), tetraazapentaethylene glycols, **16**, **17**, **19** and **20** (Scheme II) or a symmetrically substituted tetraazaheptaethylene glycol, **24** (Scheme III).

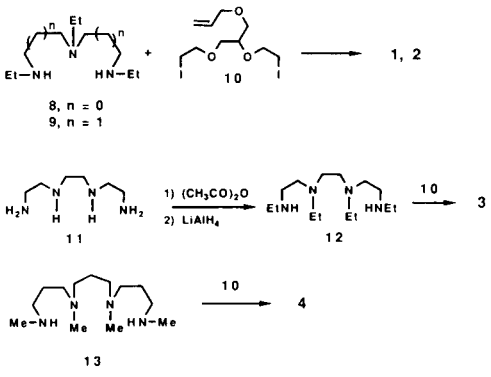
Figure 1. New Triaza- and Tetraaza-Crowns



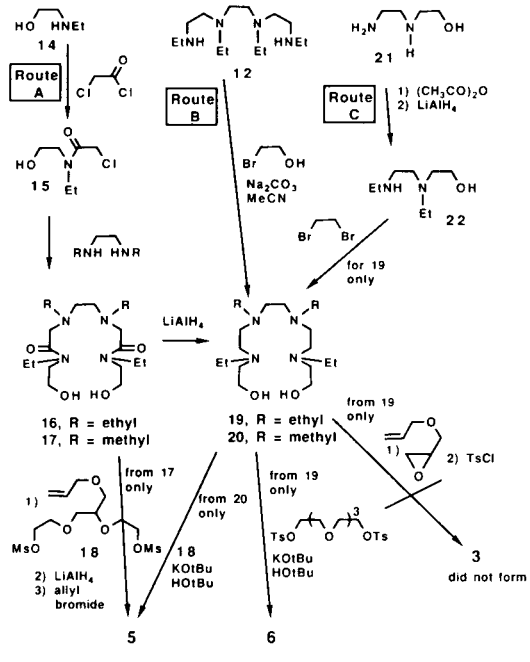
Results and Discussion.

The new polyaza-crown compounds show in Figure I were prepared as shown in Schemes I-III. The reactions shown allow for the preparation of these new macrocycles in only two or three steps from readily available starting materials and in high overall yields. Starting per-*N*-alkyl-substituted polyamines **8**, **9** and **13** were purchased and **12** was easily prepared from commercially available triethylenetetraamine (**11**), as shown in Scheme I. Diiodide **10** was

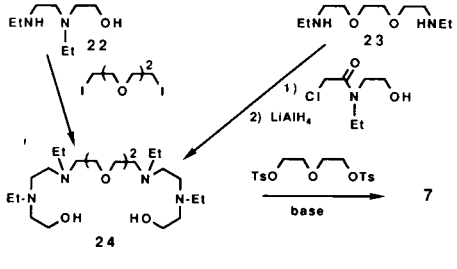
Scheme I. Preparation of Macrocycles 1-4



Scheme II. Preparation of Macrocycles 5 and 6



Scheme III. Preparation of Macrocycle 7



prepared by treating the corresponding dimesylate with sodium iodide in the presence of sodium carbonate [13]. This method to prepare **10** gave an overall higher yield than the reported method from the corresponding ditosylate [9] because the dimesylate can be prepared in a much higher yield than the ditosylate.

Macrocycles **1-6** have three or four alkyl-substituted nitrogen atoms located on the same side of the macro ring. These materials could have a somewhat different selectivity for various metal cations than similar macrocycles with symmetrically positioned ring nitrogen atoms. There are no complexation data in the literature for complexation by the different triaza- or tetraaza-crowns.

The synthetic procedures shown in Scheme I have one serious problem. Macrocycle **1** slowly decomposed over a three-month period. We suspect that traces of iodine introduced with intermediate **10** caused a slow oxidation of the polyamine. Indeed macrocycle **1**, prepared from the dichloro analog of **10**, was found to be completely stable over a four-month period. Unfortunately, the dichloride was much less reactive so that the overall yield of **1** using the dichloride analog was about half of the overall yield when **10** was used. Of course, traces of free iodine can be removed by washing the reaction mixtures with an aqueous sodium thiosulfate solution.

Three methods to prepare the larger tetraaza-crowns are shown in Scheme II. Key intermediates **19** and **20** were best prepared by the three-step Route A procedure from *N*-ethylethanolamine (**14**). Route B uses tetraamine **12** which was prepared from triethylenetetraamine (Scheme I). Purification of **19** and **20** prepared by the Route A process was straight forward. Intermediate **19** was obtained in only a 15% yield by the Route B method using 2-bromoethanol. Unfortunately, ethylene oxide could not be used for this reaction because of its hazardous label. Compound **22** was prepared in a 60% yield from **21** as shown in Route C. However, the reaction of **22** with 1,2-dibromoethane to prepare **19** is not straight forward. The reaction product was separated and then refluxed in the presence of alumina in dioxane followed by distillation to give a 30% yield of **19**. It is possible that reactions using 2-bromoethanol and, 1,2-dibromoethane gave low yields because those materials eliminate under the reaction conditions.

In the Route A process to prepare intermediates **19** and **20**, *N*-ethylethanolamine (**14**) was reacted with chloroacetyl chloride in the same manner as that described by Sutherland and his co-workers for the preparation of 2-chloroacetamido-2-phenylethanol [14]. The resulting *N*-ethylamide derivative **15** was condensed with *N,N'*-diethyl-(or dimethyl)-1,2-diaminoethane in acetonitrile in the presence of sodium carbonate to form diamides **16** and **17**. These diamides were reduced to obtain the key intermediates **19** and **20**. Diamide **17** was also reacted with dimesylate **18** followed by reduction with lithium aluminum hydride to form a hydroxymethyl-substituted tetraaza-crown. This latter compound, resulting from the reductive removal of the allyl group, was treated with allyl bromide to give **5** in a moderate yield. Macrocycles **5** and **6** were prepared from **20** and **19**, respectively, in good yields as

shown in Scheme II.

Since macrocycles **1-4**, which were prepared from diiodide **10**, were not completely stable, as discussed above, we attempted to prepare **3** from **19** (Scheme II) using a process which was successful in the preparation of an allyloxymethyl-substituted diaza-18-crown-6 [9]. Intermediate **19** was reacted with allyl glycidyl ether followed by the Okahara ring closure reaction using tosyl chloride. Macrocycle **3** could not be isolated from the reaction mixture.

The per-*N*-ethyltetraaza-27-crown-9 (**7**) with the nitrogen atoms located in a symmetrical fashion was prepared by two routes as shown in Scheme III. Tetraazaheptaethylene glycol **24** was prepared in only 20% yield from **22** (prepared by Route C in Scheme II). Product **24** was very difficult to purify when prepared from **22**. On the other hand, reaction of **23** [15,16] with *N*-ethyl-*N*-(2-hydroxyethyl)chloroacetamide in the presence of sodium carbonate in acetonitrile followed by reduction of the resulting diamide gave **24** in a 71% yield. Tetraazadiol **24** was then reacted with diethylene glycol ditosylate in a *t*-butyl alcohol-dioxane mixture in the presence of potassium *t*-butoxide to give crown **7** in a 12% overall yield.

The structures proposed for all new macrocycles are consistent with data from the nmr spectra and elemental analyses. The nmr spectra for all open chain polyaza compounds also confirmed the structures indicated. It is interesting that tetraaza compound **12** seemed to form a complex with THF. Some of the nmr spectra of **12** contained signals at δ 1.65 and 3.60 indicative of an included THF molecule.

We are reporting the synthesis of only seven new per-*N*-alkyl-substituted triaza- and tetraaza-crown compounds where the alkyl groups are ethyl and methyl. It should be recognized that these techniques can be used to prepare macrocycles substituted with long-chain alkyl, benzyl or allyl groups by using the proper *N*-substituted ethanolamine or *N,N'*-disubstituted-1,2-diaminoethane starting materials.

EXPERIMENTAL

The proton nuclear magnetic resonance (nmr) spectra were obtained on a JEOL-FX-90Q or a Varian Gemini 200 spectrometer using deuteriochloroform. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Molecular weights were determined by the electron impact method on a Finnegan 8430 High Resolution Mass Spectrometer. Starting materials were purchased from Aldrich Chemical Co. when available. Other starting materials and the macrocycles were prepared as follows:

6,9-Diethyl-3,6,9,12-tetraazatetradecane (**12**) (Scheme I).

Tetraamine **11** (as the hydrate, 15 g, 0.154 mole) in 100 ml of glacial acetic acid was slowly dripped into 70 g (0.68 mole) of acetic anhydride at 0°-5°. The mixture was stirred for 10 hours at room temperature and the solvent and excess acetic anhydride were evaporated. Toluene (30 ml) was added three times during the evaporation step to remove all of the water. The residue was recrystallized from THF to give 40 g (65%) of the tetraamide intermediate as a white solid, mp 110°-111°; ^{1}H nmr: (δ) 2.10 (m, 12 H), 3.50 (m, 12 H), 6.70 (d, 2 H). This tetraamide (11 g, 0.035 mole) was added in portions to a solution of 6 g of lithium aluminum hydride in 200 ml of THF at 0°-5°. After addition, the resulting mixture was stirred under reflux for 48 hours. After cooling, 6 ml of water, 6 ml of 15% aqueous sodium hydroxide and 15 ml of water were added successively to the stirring solution. The mixture was stirred overnight, filtered and the residue was washed with hot THF. The filtrate and washings were evaporated using two 50 ml portions of benzene to remove all solvents and water. The residue was distilled to give 7 g (77%) of **12**, bp 85°-86°/0.07 mm; ^{1}H nmr: (δ) 1.00 (t, 6 H), 1.10 (t, 6 H), 1.5 (s, 2 H), 2.60 (m, 20 H). The ^{1}H nmr spectrum of **12** often contained multiplet peaks at δ 1.65 and 3.60 indicative of complexed THF. This material was used in the next step to prepare **3** without further purification.

11-Allyloxymethyl-1,4,7-triethyl-1,4,7-triaza-10,13-dioxacyclopentadecane (**1**) (Scheme I).

A mixture of 1.87 g (10 mmoles) of 6-ethyl-3,6,9-triazaundecane (**8**), 4.7 g (0.11 mole) of **10** [9], 12 g of sodium carbonate, 0.75 g of sodium iodide and 400 ml of acetonitrile was stirred under reflux for 24 hours. The mixture was cooled, filtered and evaporated under reduced pressure. The residue was chromatographed on neutral alumina (toluene/ethanol:30/1) to give 2.42 g (65%) of **1** as an oil; ^{1}H nmr: (δ): 1.00 (m, 9 H), 2.60 (m, 18 H), 3.55 (m, 9 H), 4.00 (d, 2 H), 5.20 (m, 2 H), 5.80 (m, 1 H).

Anal. Calcd. for $C_{20}H_{41}N_3O_3$: C, 64.65; H, 11.12; mol. wt., 371.57. Found: C, 64.40; H, 11.15; mol wt., 371.

13-Allyloxymethyl-1,5,9-triethyl-1,5,9-triaza-12,15-dioxacycloheptadecane (**2**) (Scheme I).

Macrocycle **2** was prepared as above for **1** from 2.15 g (10 mmoles) of 7-ethyl-3,7,11-triazatridecane (**9**) to give 2.63 g (66%) of **2** as an oil; ^{1}H nmr: (δ) 1.00 (m, 9 H), 1.60 (m, 4 H), 2.50 (m, 16 H), 3.60 (m, 9 H), 4.00 (m, 2H), 5.20 (m, 2 H), 5.90 (m, 1 H).

Anal. Calcd. for $C_{22}H_{45}N_3O_3$: C, 66.12; H, 11.35; N, 10.52; mol. wt., 399.61. Found: C, 66.02; H, 11.30; N, 10.41; mol. wt., 399.

14-Allyloxymethyl-1,4,7,10-tetraethyl-1,4,7,10-tetraaza-13,16-dioxacyclooctadecane (**3**) (Scheme I).

Macrocycle **3** was prepared as above for **1** from 2.58 g (10 mmoles) of **12** to give a 58% yield of **3** as an oil; ^{1}H nmr: (δ) 1.00 (t, 12 H), 2.50 (m, 24 H), 3.60 (m, 9 H), 4.00 (d, 2 H), 5.20 (m, 2 H), 5.90 (m, 1 H).

Anal. Calcd. for $C_{24}H_{50}N_4O_3 \cdot 0.5\ H_2O$: C, 63.81; H, 11.36; mol. wt., 442.67. Found: C, 63.90; H, 11.14; mol. wt., 442.

17-Allyloxymethyl-1,5,9,13-tetraethyl-1,5,9,13-tetraaza-16,19-dioxacycloeicosane (**4**) (Scheme I).

Macrocycle **4** was prepared as above for **1** from 2.44 g (10 mmoles) of 6,10-dimethyl-2,6,10,14-tetraazapentadecane (**13**) to give 1.93 g (45%) of **4** as an oil; ^{1}H nmr: (δ) 1.50 (m, 6 H), 2.10 (s, 6 H), 2.15 (s, 6 H), 2.30 (m, 12 H), 2.50 (m, 4 H), 3.50 (m, 9 H), 3.95 (d, 2 H), 5.10 (m, 2 H), 5.80 (m, 1 H).

Anal. Calcd. for $C_{23}H_{48}N_4O_3$: C, 64.44; H, 11.29; mol. wt., 428.65. Found: C, 64.34; H, 11.40; mol. wt., 428.

N-Ethyl-*N*-(2-hydroxyethyl)chloroacetamide (**15**) (Scheme II).

A vigorously stirred mixture of 27 g (0.3 mole) of *N*-ethylethanolamine (**14**), 180 ml of water and 50 ml of methylene chloride at 0° was treated successively with 25 ml portions of a solution containing 36 ml of chloroacetyl chloride in 214 ml of methylene chloride followed after five minutes with a 45 ml portion of 1 *M* aqueous sodium hydroxide. Ten such additions were made over a 95 minute period. The volume of the mixture was reduced by evaporation and the aqueous residue was extracted three times with 500 ml portions of ethyl acetate. The combined organic extracts were washed successively with aqueous sodium bicarbonate and water and then dried over anhydrous magnesium sulfate. The mixture was filtered and evaporated under reduced pressure to give 40 g (68%) of **15** as an oil; ^{1}H nmr: (δ) 1.10 and 1.20 (two t, 3 H), 3.40 (m, 5 H), 3.70 (s, 2 H), 4.10 and 4.20 (two s, 2 H). This material was used without further purification to prepare **16** and **17**.

3,6,9,12-Tetraethyl-3,6,9,12-tetraazatetradecane-4,11-dione-1,14-diol (**16**) (Scheme II).

A mixture of 1.90 g (0.02 mole) of *N,N'*-diethylethylenediamine, 6.8 g (0.04 mole) of **15**, 20 g of sodium carbonate and 100 ml of acetonitrile was stirred under reflux for 16 hours. The mixture was cooled, filtered and evaporated under reduced pressure to give 7.3 g (97%) of **16** as an oil; ^{1}H nmr: (δ) 1.05 (m, 12 H), 2.60 (m, 8 H), 3.40 (m, 14 H), 3.70 (m, 4 H). This material was used without further purification to prepare **19**.

6,9-Dimethyl-3,12-diethyl-3,6,9,12-tetraazatetradecane-4,11-dione-1,14-diol (**17**) (Scheme II).

Diol **17** was prepared as above for **16** from 1.76 g (0.02 mole) of *N,N'*-dimethylethylenediamine, 6.8 (0.04 mole) of **15** and 20 g of sodium carbonate to give 6.74 g (97%) of **17** as an oil; ^{1}H nmr: (δ) 1.00 (m, 6 H), 2.20 (m, 6 H), 2.50 (m, 4 H), 3.15 (m, 4 H), 3.40 (m, 10 H), 3.60 (m, 4 H). This material was used without further purification to prepare both **5** and **20**.

3,6,9,12-Tetraethyl-3,6,9,12-tetraazatetradecane-1,14-diol (**19**) (Scheme II).

Compound **16** (7.8 g, 0.054 mole) in 50 ml of THF was slowly dripped into a stirred mixture of 2.7 g of lithium aluminum hydride in 50 ml of THF at 0°-5°. The resulting mixture was cooled and 3 ml of water, 3 ml of 15% aqueous sodium hydroxide and 6 ml of water were successively added. The resulting mixture was filtered, washed several times with hot THF and evaporated. The residue was distilled to give 4.33 g (60%) of **19**, bp 166-169°/0.06 mm; ^{1}H nmr: (δ) 1.05 (t, 12 H), 2.60 (m, 24 H), 3.55 (t, 4 H), 4.70 (broad, 2 H). This material was used without further purification to prepare **6**.

6,9-Dimethyl-3,12-diethyl-3,6,9,12-tetraazatetradecane-1,14-diol (**20**) (Scheme II).

Diol **20** was prepared as above for **19** from 7.4 g (0.054 mole) of **17** to give a 62% yield of **20**, bp 158°-162°/0.07 mm; ^{1}H nmr: (δ): 1.05 (t, 6 H), 2.20 (s, 6 H), 2.50 (m, 20 H), 3.50 (t, 4 H), 4.80 (broad, 2 H). This material was used without further purification to prepare **5**.

17-Allyloxymethyl-4,7-dimethyl-1,10-diethyl-1,4,7,10-tetraaza-13,16,19,22-tetraoxacyclotetracosane (**5**) from **20** (Scheme II).

Dimesylate **18** [13] (3.76 g, 0.01 mole) was slowly dripped into a stirred solution of 3.18 g (0.01 mole) of **20** in 300 ml of *t*-butyl alcohol containing 1 g of dissolved potassium metal at 65°. This mixture was refluxed for 24 hours, cooled, filtered and the solvent was evaporated under reduced pressure. The residue was chromatographed on neutral alumina (toluene/ethanol:30/1) to give a 36% yield of **5** as an oil; ^{1}H nmr: (δ) 1.05 (t, 6 H), 2.30 (s, 6 H), 2.65 (m, 20 H), 3.60 (m, 17 H), 4.00 (m, 2 H), 5.20 (m, 2 H), 5.90 (m, 1 H).

Anal. Calcd. for $C_{26}H_{54}N_4O_5$: C, 62.12; H, 10.83; mol. wt., 502.65. Found: C, 62.37; H, 10.89; mol. wt., 502.

Compound **5** from **17** (Scheme II).

Compound **17** (2.3 g, 5 mmoles) in 50 ml of dioxane and 2.7 g (6.7 mmoles) of **18** in 50 ml of dioxane were simultaneously dripped into a stirred solution of 500 ml of *t*-butyl alcohol containing 0.8 g of dissolved potassium metal at 60°. The resutling mixture was stirred under reflux for 24 hours. The mixture was cooled, filtered and the solvents were removed under reduced pressure. The residue was chromatographed on neutral alumina (toluene/ethanol:30/1) to give a 31% yield of the cyclic diamide; ^{1}H nmr: (δ) 1.20 (m, 6 H), 2.30 (m, 6 H), 2.60 (m, 4 H), 3.60 (m, 25 H), 4.00 (d, 2 H), 5.20 (m, 2 H), 5.90 (m, 1 H); M^+ 530. This cyclic diamide (2.65 g, 5 mmoles) in 25 ml of dry THF was slowly dripped into 0.8 g of lithium aluminum hydride in 30 ml of dry THF at 0°. The resulting mixture was refluxed for 24 hours. The mixture was filtered, the residue was washed with hot THF and the solvents were evaporated from the filtrate solution under reduced pressure. The residue was chromatographed on neutral alumina (toluene/ethanol:25/1) to give a 55% yield of the hydroxymethyl analog of **5**; ^{1}H nmr: (δ) 1.00 (t, 6 H), 2.20 (s, 4 H), 2.60 (m, 20 H), 3.70 (m, 18 H); M^+ 462. Allyl bromide (0.6 g, 5 mmoles) and 0.55 g (5 mmoles) of potassium *t*-butoxide were added to 1 g (2.2 mmoles) of the hydroxymethyl analog of **5** in 50 ml of *t*-butyl alcohol. The resulting mixture was stirred at room temperature for 48 hours. The mixture was filtered, evaporated and the residue was chromatographed on neutral alumina (toluene/ethanol:15/1) to give a 75% yield of **5** which had the same spectral properties as reported above.

1,4,7,10-Tetraethyl-1,4,7,10-tetraaza-13,16,19,22,25-pentaoxacycloheptacosane (**6**) (Scheme II).

Tetraethylene glycol ditosylate (3.76 g, 7.5 mmoles) in 100 ml of dioxane was slowly dripped into a stirred solution of 2.6 g (7.5 mmoles) of **19** in 300 ml of *t*-butyl alcohol containing 0.8 g of potassium metal at 65-70°. This mixture was stirred under reflux for 24 hours. The mixture was cooled, filtered and the solvents were evaporated under reduced pressure. The residue was chromatographed on neutral alumina (toluene/ethanol:50/1) to give a 19% yield of **6** as an oil; ^{1}H nmr: (δ) 1.05 (m, 12 H), 2.60 (m, 24 H), 3.60 (m, 20 H).

Anal. Calcd. for $C_{26}H_{54}N_4O_5$: C, 61.85; H, 11.19. Found: C, 61.62; H, 11.07.

3,6,15,18-Tetraethyl-3,6,15,18-tetraaza-9,12-dioxacosane-1,20-diol (**24**) from **22** (Scheme III).

A mixture of 3.4 g (0.02 mole) of **22**, 3.7 g (0.01 mole) of 1,8-diiodo-3,6-dioxaoctane and 8 g of anhydrous sodium carbonate was refluxed in 50 ml of acetonitrile for 24 hours. The mixture was evaporated under reduced pressure. The residue was mixed with 50 ml of dioxane and filtered. Neutral alumina (10 g) was added to the dioxane solution and the resulting mixture was refluxed for two hours. The mixture was cooled, filtered and distilled twice to give 0.86 g (20 %) of **24**, bp 195°-197°/0.07 mm; ir: 3400 and

1100 cm^{-1}; ^1H nmr: (δ) 1.00 (m, 12 H), 1.80 (b, 2 H), 2.60 (m, 24 H), 3.60 (m, 12 H). This material was used without further purification to prepare **7**.

3,6,15,18-Tetraethyl-3,6,15,18-tetraaza-9,12-dioxacosane-1,20-diol (**24**) from **23** (Scheme III).

A mixture of 3 g (0.015 mole) of **23** [11,15], 5.0 g (0.036 mole) of *N*-ethyl-*N*-(2-hydroxyethyl)chloroacetamide and 15 g of anhydrous sodium carbonate was stirred at room temperature in 100 ml of acetonitrile for 12 hours. The mixture was then refluxed for 6 hours, filtered and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (isopropyl alcohol then ethanol) to give 3.4 g (50%) of the intermediate diamide; ir: 3400, 1680, 1100 cm^{-1}; ^1H nmr: (δ) 1.00 (m, 12 H), 1.50 (b, 2 H), 2.60 (m, 8 H), 3.50 (m, 22 H) 5.80 (b, 2 H).

The diamide was reduced to form **24** as follows: The diamide (3.0 g, 0.064 mole) in 50 ml of THF was slowly dripped into 50 ml of THF containing 1.5 g of lithium aluminium hydride at 5°. The mixture was allowed to warm to room temperature and then refluxed for 24 hours. The resulting mixture was cooled to 5°-10° and 3 ml of water and 3 ml of 50% sodium hydroxide were successively added. The resulting mixture was filtered and the residue was washed several times with hot THF. The solvent was evaporated under reduced pressure from the filtrate and the residue was distilled to give 2.0 g of **24** (71%) which had the same bp, ir and nmr properties as reported above.

1,4,13,16-Tetraethyl-1,4,13,16-tetraaza-7,10,19,22,25-pentaoxacycloheptacosane (**7**) (Scheme III).

Compound **24** (2.17 g, 0.05 mole) was added to 200 ml of *t*-butyl alcohol in which 0.78 g of potassium metal was dissolved. Into this solution at 60°, 1.07 g (0.05 mole) of diethylene glycol ditosylate in 100 ml of dioxane was slowly added. The resulting mixture was stirred under reflux for 48 hours. The mixture was evaporated under reduced pressure and the residue was added to 50 ml of chloroform. The chloroform mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was chromatographed on neutral alumina (toluene/ethanol:50/1 and then on silica gel (methanol) to give 0.4 g (16%) of **7** as an oil; ^1H nmr: (δ) 1.00 (t, 12 H), 2.60 (m, 24 H), 3.60 (m, 20 H).

Anal. Calcd. for $C_{26}H_{56}N_4O_5$: C, 61.87; H, 11.18. Found: C, 61.68; H, 11.40.

Acknowledgement.

The authors thank the Center of Excellence Program of the State of Utah and Serpentix Conveyor Corporation, Westminster, CO, for funding this research. J. S. B. thanks the Department of Chemistry, James Cook University, Townsville, Australia for the use of their facilities while writing this paper.

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