Synthesis of Aza-Crown Ethers

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Contents

I. Introduction

There is a continuing interest in the synthesis of aza-crown compounds. The aza-crowns have complexation properties that are intermediate between those of the all-oxygen crowns, which strongly complex alkali and alkaline earth metal ions, and those of the all-nitrogen cyclams, which strongly complex heavy-metal cations. These mixed complexation properties make the aza-crowns interesting to researchers in many areas. The aza-crowns have important uses as synthetic receptors in molecular recognition processes[1] and, in some cases, anion complexation properties that are similar to those in certain biological systems.[2-4] They have an enhanced complexing ability for ammonium salts[5,6] and for transition-metal ions[6,7] over the all-oxygen crown compounds. In addition, the aza-crowns are important intermediates for the synthesis of cryptands (from diaza-crowns),[8,9] nitrogen-pivot lariat crown ethers,[10] and other species requiring one or two nitrogens in the macroring.[11,12] There are a number of interesting uses of aza-crowns as catalysts in nucleophilic substitution and oxidation reactions,[13,14] in the design of chromogenic reagents that are sensitive to alkali and alkaline earth metal cations,[15] and in the chromatographic separation of metal cations.[15] Certain aza-crowns have been covalently attached to silica gel or other solid supports.[16,17] The silica gel bound aza-crowns have found use for the selective separation of specific metal ions from mixtures of metal ions.[16]

An extensive number of aza-crowns have been synthesized. Several of these materials can be purchased. For example, Merck and Aldrich list a number of diaza-crowns, including 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane. These compounds are extremely expensive. A major problem is the design of new and inexpensive procedures to prepare these important ligands. A compilation of aza-crown compounds prepared prior to about 1980 is given by Gokel and Korzeniowski.[17] A number of other reviews have appeared covering the literature up to about 1982.[6,18-24] More recent reviews concerning the aza-crowns[25,26] do not cover the synthesis of these compounds in an organized manner. Other than the extensive compilation by Gokel and Korzeniowski[17] covering the synthesis of aza-crowns to 1980 and the compilation of aza-crown complexation properties by Izatt and co-workers,[6] there has been no other listing of the aza-crowns.

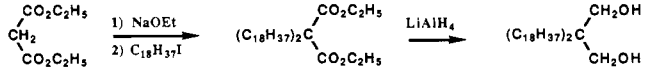
This review covers all aza-crown ethers synthesized from 1981 to 1987, aza-crowns synthesized before 1981 that were not included in ref 17, and some aza-crowns reported in 1988. We have concentrated on crowns containing at least 12-membered rings with at least one oxygen atom in the macroring. We have included the benzoaza-crowns, but crowns containing other aromatic or unsaturated or saturated subcyclic units are not included. A survey of general methods for the preparation of starting materials is also included. Specific methods for the preparation of monoaza-crowns, diaza-crowns, polyaza-crowns, and benzoaza-crowns are presented.

II. Preparation of Starting Materials

A. Diols

Most of the simple oligoethylene glycols and other diols used for the synthesis of macrocyclic compounds are commercially available. Methods for their preparation have been published.[27-36] Diols with side chains are generally not available but are very desirable since crown ethers with active side groups (hydroxy or allyl, for example) or with long-chain lipophilic groups are often needed.

Cornforth made a lipophilic diol, 2,2-dioctadecylpropane-1,3-diol, from diethyl malonate.[31] Use of this



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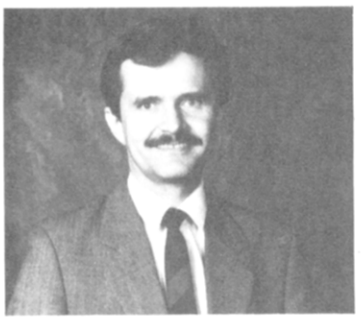
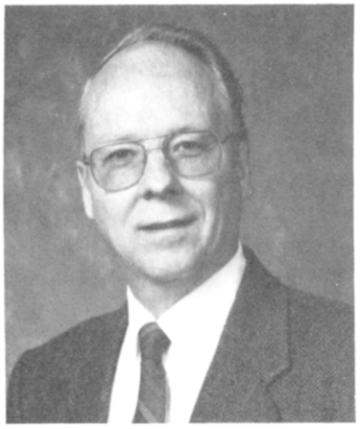


Krzysztof E. Krakowiak was born in Lodz, Poland, and received B.S. and M.S. degrees in Synthetic Fiber Chemistry from the Technical University in Lodz. He also has B.S. and M.S. degrees in Medicinal Chemistry from the School of Medicine at Lodz. He received his Ph.D. with Professor B. Kotelko on the synthesis of new 8–10-membered saturated heterocyclic compounds containing nitrogen and oxygen atoms in 1982. Since November 1986 he has held a postdoctoral position with Professor Bradshaw in the Department of Chemistry, Brigham Young University. He has published more than 40 scientific papers on new and convenient methods for the preparation of saturated heterocyclic systems, including crown ethers and cyclams. He is married and has three daughters.



Jerald S. Bradshaw was born in Cedar City, UT, and received a B.A. degree in chemistry at the University of Utah in 1955. After 4 years as an officer in the U.S. Navy, he enrolled in a Ph.D. program at UCLA. He received the Ph.D. in 1963 with Professor Donald J. Cram on electrophilic substitution at saturated carbon. He received an NSF postdoctoral fellowship for the 1962–1963 academic year to work with Professor George S. Hammond at Cal Tech. After 3 years as a research chemist at Chevron Research in Richmond, CA, he joined the faculty at Brigham Young University at Provo, UT, in 1966. He was named Professor of the Year at BYU in 1975. He was U.S. National Academy of Sciences Exchange Professor for the academic year of 1972–1973 and the Summer of 1982, working with Professor Miha Tisler at the University of Ljubljana, Yugoslavia. He also was a visiting professor with Dr. J. F. Stoddart at the University of Sheffield, England, in 1978, and a National Science Foundation Cooperative Research Fellow with Dr. L. F. Lindoy at James Cook University, Townsville, Australia, in 1988. He is a member of the American Chemical Society. His research interests are the synthesis and cation complexation properties of macrocyclic multidentate compounds, the photochemical reactions of heterocyclic compounds, and the preparation of new polysiloxanes for chromatography uses.

1,3-propanediol derivative gave crowns with a propylene bridge between the heteroatoms. Crowns with ethylene bridges form more stable complexes with metal cations than those with propylene bridges. Okahara and co-workers[37,38] developed a method to prepare substituted oligoethylene glycols using substituted ethylene oxides. The glycol containing two substituents on the first carbon was the major product of this reaction. Gandour

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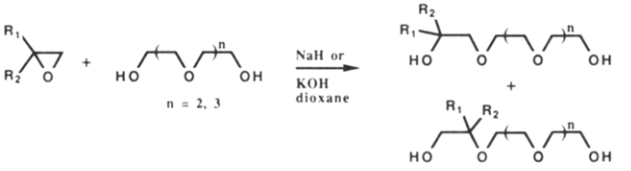
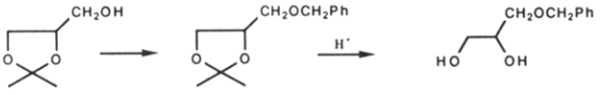
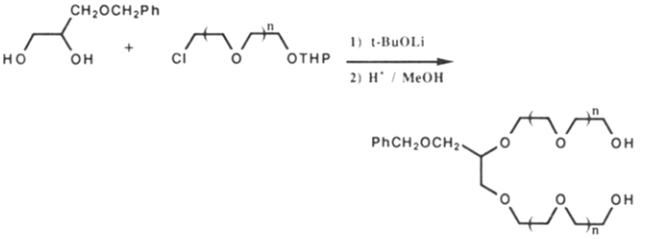
and co-workers used a similar reaction to prepare hydroxymethyl-substituted oligoethylene glycols.[39]



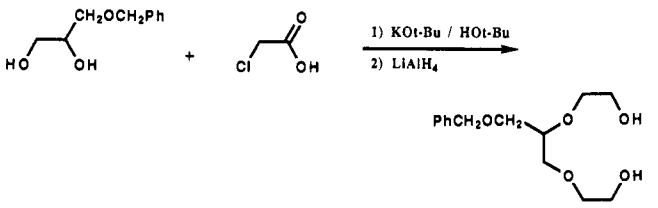
Czech first reported the synthesis of oligoethylene glycols with a (benzyloxy)methyl substituent in the middle of the molecule using (benzyloxy)methyl-substituted ethylene glycol, prepared from the 1,2-isopropylidene-blocked glycerol as shown or from epichlorohydrin.[40–43] The substituted ethylene glycol was



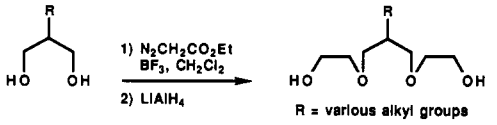
reacted with THP-blocked oligoethylene glycol monochloride followed by hydrolysis to remove the THP blocking group to form the (benzyloxy)methyl-substituted oligoethylene glycol with a greater number of ethyleneoxy units.[44,45] The benzyl portion of the (benzyloxy)methyl substituent can be readily removed by reduction to the hydroxymethyl substituent.[40–43,45,46] This process is usually done after the (benzyloxy)-methyl-substituted oligoethylene glycol has been cyclized into a crown. Thus, the (benzyloxy)methyl-substituted glycols are important intermediates for the preparation of the hydroxymethyl functionalized crowns.



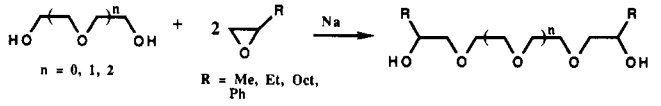
Reaction of ((benzyloxy)methyl)ethylene glycol with chloroacetic acid followed by reduction gave the substituted triethylene glycol. This latter reaction sequence, first used by Cinquini[47] to prepare didodecyltriglycolic acid, was also used with some modifications



by Bradshaw and co-workers[48,49] and Bartsch and co-workers[42,43,50] to prepare glycols containing lipophilic or (allyloxy)methyl substituents. Montanari and Tundo also used this procedure to prepare the corresponding *tert*-butoxymethyl-substituted triethylene glycol, which was used to prepare hydroxymethyl-substituted crowns and cryptands.[51] Similar glycols with a propylene bridge containing the substituent were prepared by reacting ethyl diazoacetate rather than chloroacetic acid with the starting glycol.[52]



Symmetrically substituted oligoethylene glycols with terminal alkyl substituents have been prepared by the sodium metal catalyzed reaction of a lower oligoethylene glycol with 2 equiv of a substituted epoxide.[53,54] The

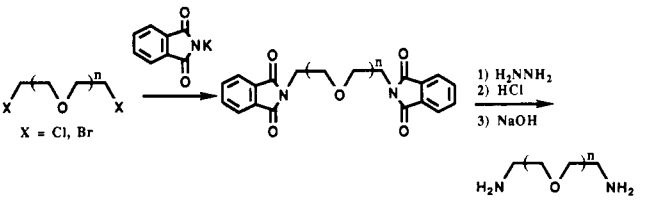


reactions generally gave good yields (30–60%) of the disubstituted oligoethylene glycols, which often could be purified by distillation. One problem with this reaction is the formation of varying amounts of 2-substituted isomer formed by attack of the alkoxide on the substituted carbon of the epoxide. The isomers can best be characterized from the NMR spectrum of their corresponding ester or tosylate derivatives. Chiral disubstituted oligoethylene glycols have been prepared by another method that requires more steps but does not give positional isomers.[55,56] Oligomerization of 1,2-propanediol also gave oligoethylene glycols where every other carbon atom contained a methyl substituent.[57]

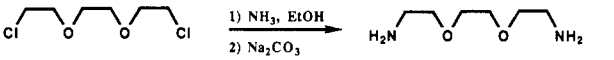
B. Diamino Aliphatic Ethers

It is important to have simple and inexpensive methods to prepare the diamine starting materials for the cyclization portion of the sequence to form diaza-crown compounds. The oligoethylene (or oligopropylene) polyamines and their *N*-methyl and *N*-ethyl analogues can be purchased. We present here some of the methods that have been used to prepare the diamino aliphatic ethers that are less available.

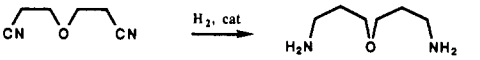
First, we report methods to prepare the primary diamino aliphatic ethers. A modified Gabriel synthesis using the reaction of potassium phthalimide with a dihalide followed by hydrolysis using hydrazine was one of the first methods to prepare the diamino ethers.[8] Krakowiak and Kotelko used this method to prepare a variety of diamino ethers containing both ethylene and propylene connecting groups.[58,59]



King and Krespan prepared 1,8-diamino-3,6-dioxaoctane by reacting the dichloride derivative of triethylene glycol with ethanolic ammonia followed by

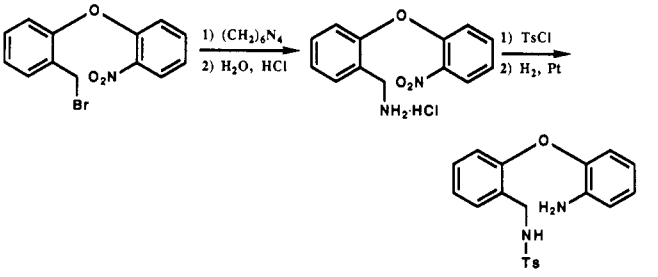


sodium carbonate.[60] Earlier, bis(3-aminopropyl) ether was prepared by a similar reaction.[61] The bis(3-aminopropyl) ether was also prepared by reducing a bisnitrile as shown.[61–64]

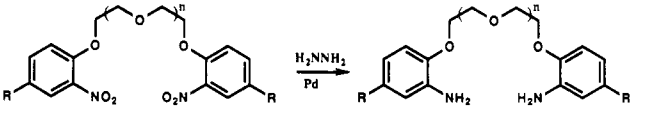


Some mixed oligo(ethyleneoxy)dipropylamines, $NH_2(CH_2)_3(OCH_2CH_2)_nO(CH_2)_3NH_2$, can be purchased from Tokyo Kassei. These materials are inexpensive and can be used to prepare similar poly(propyleneoxy)aza-crowns as shown in method AR, section IV.D.

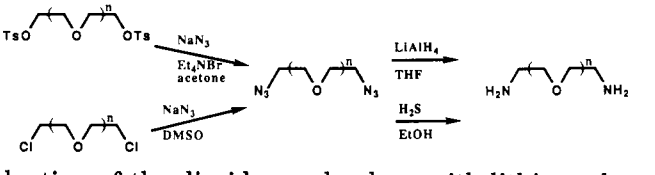
A reduction process has been used to prepare aromatic diamines from nitro- and azide-containing ethers. The preparation of an aromatic diamine using known methods was reported by Glinka, who treated an aromatic nitro halide with hexamethylenetetraamine followed by hydrolysis to give an aromatic nitro amine. The nitro amine was reduced to the diamine after tosylation to block the original amine group.[65] A palla-



dium-catalyzed hydrazine or amalgamated aluminum reduction of some bis nitro aromatic compounds appears to be a good method for the preparation of dianiline-substituted ether compounds.[66–68]



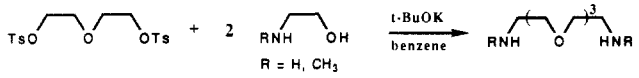
The reduction of diazido-substituted ethers to form the diamino ethers has been reported by a number of workers.[69–71] The starting diazido ethers were prepared by treating either the ditosyl or dichloro derivatives of the oligoethylene glycols with sodium azide. The re-



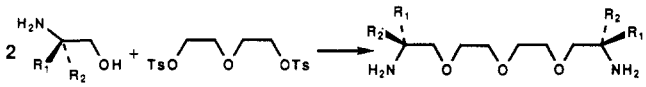
duction of the diazide can be done with lithium aluminum hydride or hydrogen sulfide in ethanol as shown.

These reactions gave an overall yield of 65–85%; however, care must be taken because the diazide can be explosive.

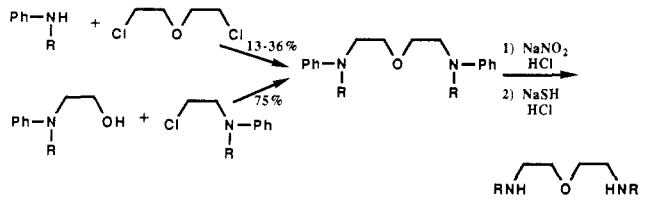
Böhmer and co-workers found that 2-aminoethanol reacted with a ditosylate using potassium *tert*-butoxide as base to form a diamino ether in a 30% yield.[72] They also prepared the *N,N'*-dimethyl derivative.



Sutherland and co-workers used this same technique to prepare a chiral diamino ether with higher yields.[73]

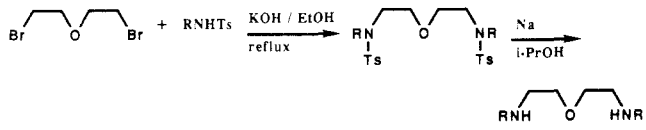


Secondary amines were prepared in much the same fashion. Boon prepared the 1,5-bis(methyl(or ethyl)-amino)-3-oxapentanes by two methods as shown.[74] The



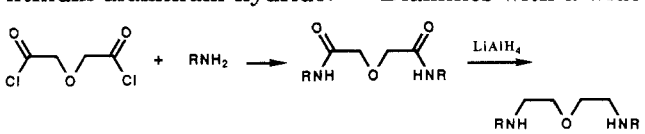
initial diamino ether contained a phenyl blocking group that required a two-step method for removal. Boon also isolated *N*-phenylmorpholine as a byproduct when the dichloride was reacted with aniline (R = H). The second method allows the preparation of unsymmetrical derivatives where the R groups substituted on each of the two nitrogen atoms are different.[74]

N-Tosyl-substituted amines have also been used to prepare secondary diamino ethers. Petranek and Ryba reacted *N*-tosylbenzylamine or the aniline analogue with the dibromo derivative of diethylene glycol to form the bis(*N*-tosylamino) derivatives.[75] The tosyl blocking groups were removed by using sodium in isopropyl alcohol. Other *N,N'*-dialkyldiamino ethers were pre-

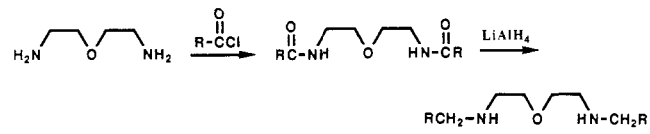


pared by Krakowiak and Kotelko by tosylating bis(2-aminoethyl) ether, subsequently alkylating the *N,N'*-ditosyl derivative in base, and removing the tosyl group by a reduction process.[76]

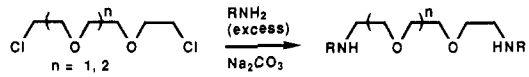
An excellent method to prepare the *N,N'*-dialkyl derivatives of 1,5-diamino-3-oxapentane involves the formation of a bisamide followed by reduction with lithium aluminum hydride.[76] Diamines with a wide



variety of alkyl substituents from methyl to 3-(*N,N'*-diethylamino)propyl were prepared in moderate yields. Pietraszkiewicz[78] and Gokel and co-workers[71,77] used this procedure except borane was used as the reducing agent. Gokel also prepared the *N,N'*-dialkyldiamino ether by treating the diamine with an acid chloride followed by reduction of the resulting bisamide.[71] This is a reasonably good method to prepare these diamines, but the starting 2,2'-bis(aminoethyl) ether is several times more expensive than diglycolyl dichloride.



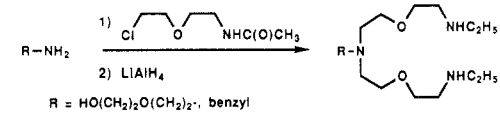
A superior method to prepare the *N,N'*-dialkyl derivatives of the oligoethylene oxide containing diamines uses the reaction of the readily available dichloro derivative of the oligoethylene glycols with an excess of alkylamine.[71,79,80] This process is not possible for the



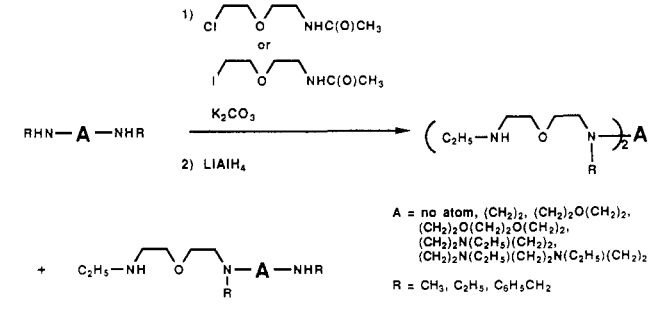
preparation of the diamine derivatives of diethylene glycol since the reaction of an amine with the dihalide yields only *N*-alkylmorpholine as mentioned above.[71,74] Gokel and co-workers used the more reactive diiodide in this reaction to prepare some *N,N'*-dialkylamines in 70–85% yields.[71,77] Bradshaw and Krakowiak have optimized the reaction with the dichloride using only a 4-fold excess of the amine in the presence of sodium carbonate and using a Dean–Stark apparatus to remove water formed in the reaction to obtain an 82% yield of the *N,N*-dibenzyl derivatives.[80]

In addition to the diamino ethers already mentioned in this section, we present here one new synthetic procedure to prepare polyamino ethers containing terminal NHC_2H_5 functions.[81,82] This procedure uses the reaction of *N*-[2-(chloroethoxy)ethyl]acetamide with an amine, diamine, or polyamine and the subsequent reduction of the amide functions as shown in the following two schemes. When the reaction to form the tetraamine (excluding any amino groups in A) was run with an excess of *N*-[2-(chloroethoxy)ethyl]acetamide in toluene or DMF, mostly the diadduct was formed. A greater amount of the monoadduct was formed when the acetamide derivative was the limiting starting material. It is possible to prepare higher order polyoxa amines if the polyamino products shown in the schemes are further reacted with *N*-[2-(chloroethoxy)ethyl]acetamide or *N*-ethylchloroacetamide followed by reduction.[82]

Triamines



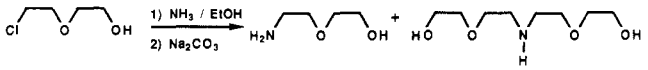
Tetraamines and Polyamines



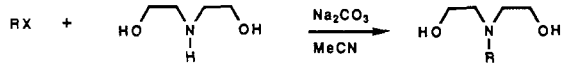
C. Amino Diols

An alternate method to the use of diamino aliphatic ethers in the cyclization reaction for the aza-crowns is to cyclize amino diols. Some of the methods to prepare the amino diols are now presented.

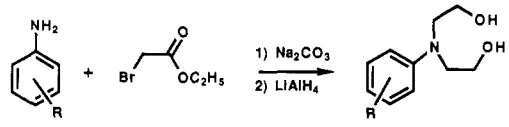
Krespan found that when 2-(2-chloroethoxy)ethanol was heated with ammonia in ethanol, a nearly equimolar mixture of 2-(2-aminoethoxy)ethanol and 6-aza-3,9-dioxaundecane-1,11-diol was isolated.[83] In addition



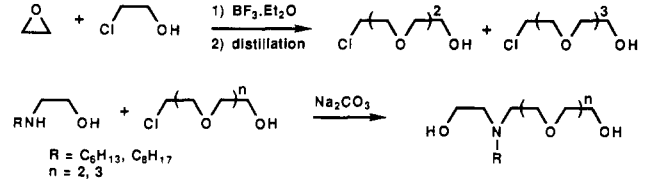
to these amino diols, King and Krespan prepared other types of amino diols starting with 2-aminoethanol or *N*-tosyl-2-aminoethanol and 1,8-dichloro-3,6-dioxaoctane or 1,5-dichloro-3-oxapentane.[60] Gokel and co-workers prepared the *N*-alkyl derivatives of diethanolamine in good yields by treating the amine with an alkyl halide using sodium carbonate as the base.[10] This reaction worked well when methyl 2-(2-chloroethoxy)ethyl ether was used as the alkylating agent but



the products from the reaction of longer chloromethoxy derivatives could not be separated from the salts so that distillation was not practical. *N*-Phenyl-substituted diethanolamines were prepared by reacting various anilines with ethyl bromoacetate followed by reduction.[10]

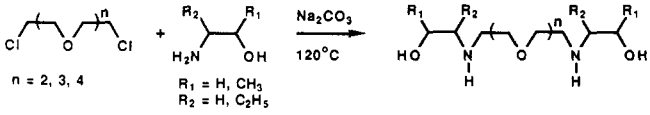


Okahara and co-workers prepared a number of *N*-alkylamino diols that were not symmetrical. They first prepared the monochloride derivative of the oligoethylene glycol by reacting ethylene oxide with 2-chloroethanol in an acidic medium.[84] The oligomers

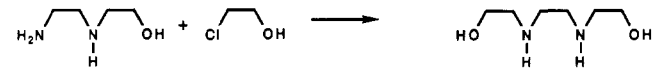


were separated by distillation. The isolated monochloro derivative was then reacted with *N*-alkylethanolamine with sodium carbonate as the base. Other alkyl-substituted compounds were prepared by first reacting the amine with an excess of monochloroethylene glycol oligomer to form an amino alcohol that was further reacted with the same or another monochloro oligomer.

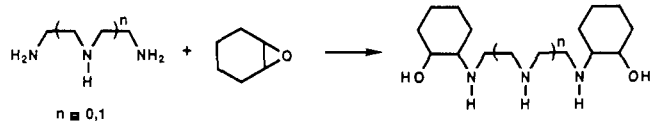
A series of diaza or triaza diols were prepared by these same workers by three different types of reactions.[85] With sodium carbonate as the base, ethanolamine compounds were reacted with the dichloro derivatives of the oligoethylene glycols.



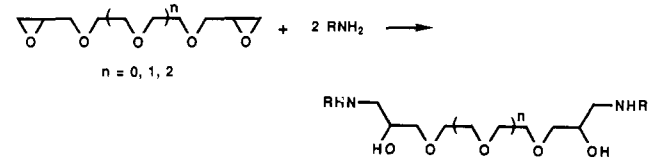
A diamino alcohol was reacted with 2-chloroethanol under the same conditions to form a diamino diol.



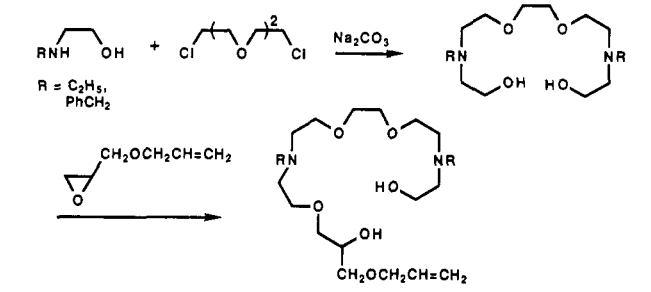
Cyclohexene oxide was heated with diaminoethane or 1,4,7-triazaheptane to form oligoaza diols containing two 2-hydroxycyclohexyl units.[85] All of these diols ring



closed to form aza-crowns when tosyl chloride was used (the Okahara procedure) as will be discussed later. Okahara and co-workers used a similar epoxide ring-opening reaction to prepare some interesting diamino diol ethers that are capable of ring closure either through the diamines or the diols.[86] A bis epoxy polyether was reacted with an excess of alkylamine to form the diamino diol material.

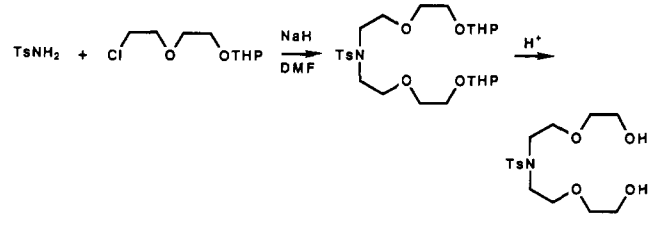


Bradshaw and Krakowiak have modified the reaction of a dihalide with *N*-ethyl- or *N*-benzyl-substituted ethanolamine in the presence of a carbonate base in toluene solvent to prepare *N,N'*-diethyl- and *N,N'*-dibenzyldiazapentaethylene glycol in high overall yields.[81]

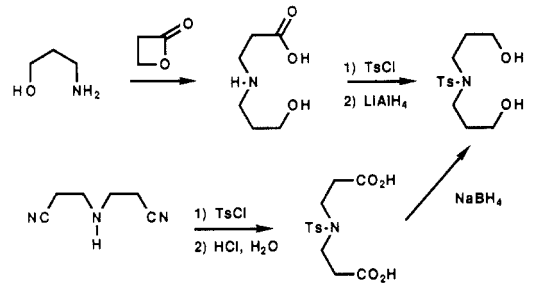


These diols were reacted with (allyloxy)methyl-substituted ethylene oxide to form the diazahexaethylene glycol containing an (allyloxy)methyl substituent. This latter diol was ring closed with tosyl chloride to form a diaza-18-crown-6, which can be attached to silica gel.[49,87]

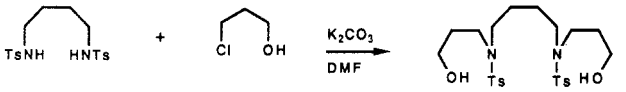
The *N*-tosylamino glycols are popular intermediates for the preparation of aza-crowns with secondary amine groups. Dale and Calverley used the reaction of *p*-toluenesulfonamide and the monochloro derivative of THP-blocked diethylene glycol to prepare the symmetrical *N*-tosylazatetraethylene glycol as shown.[88] Diols containing three *N*-tosyl nitrogens have also been prepared.[89] Lehn and co-workers prepared a number of *N*-tosylamino glycols as shown in section IV.C.



Sutherland and co-workers recently prepared diols with propylene bridges between the oxygen and nitrogen atoms using two methods shown below.[90] The second method gave the best overall yields.

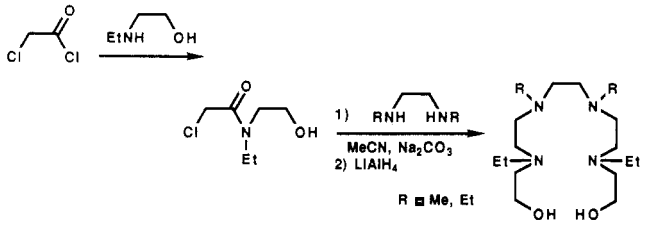


Marecek and Burrows prepared a diamino diol using *N,N'*-ditosyl-1,4-butanediamine and 3-chloro-1-propanol.[91] This diaza diol was used as a starting material to prepare a spermine macrocycle.



The tosyl groups are often difficult to remove from the final products. The yields for the reductive removal of the tosyl groups are often only moderate.[90] *N*-Tosyl groups also change the complexation properties of the aza-crowns if they are not removed. More convenient methods for preparing N-unsubstituted aza-crowns without the need to remove a blocking group are now being developed.[82]

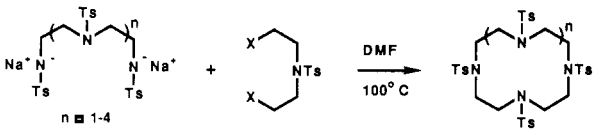
A tetraaza diol was recently prepared by first reacting chloroacetyl chloride with *N*-ethylethanolamine to form a chloro hydroxy amide.[73,82] This latter compound was reacted with *N,N'*-dimethyl- or *N,N'*-diethylethylenediamine with subsequent reduction to give the tetraaza diol.[82]



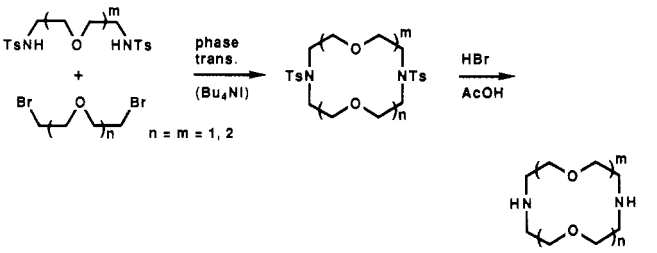
III. General Synthetic Methods Used To Prepare Aza-Crowns

A. Template Syntheses

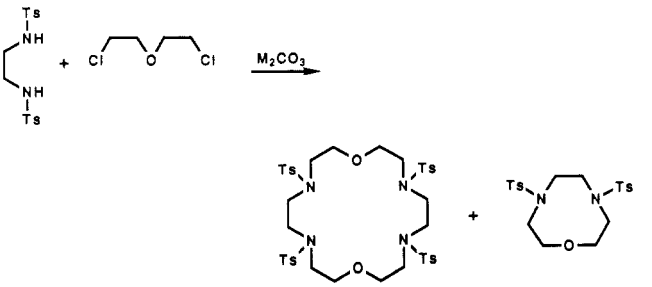
Greene observed that the formation of 18-crown-6 from a ditosylate and a diol in the presence of *tert*-butoxide salts was enhanced when a potassium cation was used.[92] This template effect was operative for the synthesis of other polyether crown compounds using alkali or alkaline earth metal cations. Template effects have also been observed for the preparation of aza-crown ethers, although the effect is less pronounced because the softer N-donor atoms form weaker complexes with the alkali metal cations.[93] Richman and Atkins reported that high-dilution techniques were not required for the cyclization reaction of a disodium salt of a pertosylated oligoamine with sulfonated diols to form medium and large polyaza-crown compounds.[94,95] When a dihalide was used in this reaction, only moderate yields of cycloaddition products were observed.[95,96] Yields were increased when cesium carbonate was used as the base. Since this effect was observed for the formation of all ring sizes, Kellogg explained this effect as a "cesium effect", not a template effect.[97,98]



It is interesting to note that replacement of the sodium cations by tetramethylammonium ion in the Richman–Atkins procedure did not inhibit the reaction as one might expect in a template reaction but only decreased the yield of the tetraaza-crown to about 50%. Gokel and co-workers suggested that the increase in the yield from 50% to 80% when sodium is used does indicate a small template effect by the sodium.[21] Bogatsky and co-workers used phase-transfer conditions[99] to obtain macrocyclic poly-*N*-tosylaza-crown compounds.[100] They reported that the yield of the cyclization step did depend on the nature of the cation. The 12-crown-4 compound formed best with lithium hydroxide while the larger crowns formed best when sodium hydroxide was used.



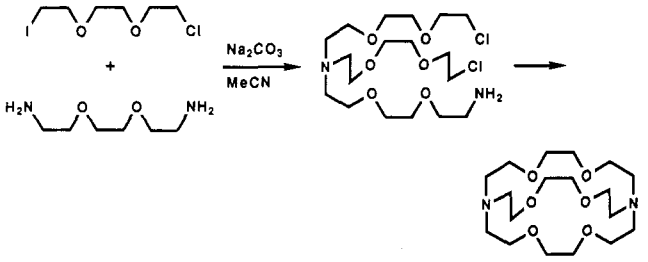
Biernat and Luboch have shown a definite template effect in the synthesis of tetra-*N*-tosylaza-18-crown-6.[101] The yields of the 18-crown-6 product were 40% with potassium carbonate but only 10% when sodium carbonate was used. The amount of 9-crown-3 byproduct was greater when sodium carbonate was used.



The diminished template effect in the formation of the poly-*N*-tosylaza-crowns with tosylate starting materials has been explained by Shaw to be a result of restricted rotational freedom in the molecules caused by the large tosyl groups.[102] As a result of the restricted rotation, there is a relatively small loss in entropy on cyclization, allowing ring closure to occur in relatively high yields without a need for preorganization of the starting materials. Rasshofer and Vögtle also explained the cyclization reactions in terms of template, steric, and entropy effects.[103]

Kulstad and Malmsten reported a remarkable synthesis of cryptand[2.2.2] and 1,10-diaza-18-crown-6 from

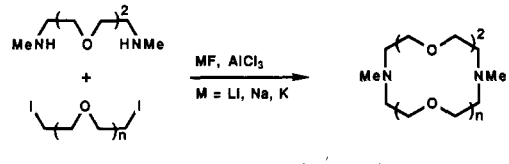
the reaction of either 1-iodo-8-chloro-3,6-dioxaoctane or 1,8-diiodo-3,6-dioxaoctane and 1,8-diamino-3,6-dioxaoctane.[70,104] The starting material gave the cryptand while the diiodo starting material gave the diaza-18-crown-6 (see method T, section IV.B). In the former case, the iodide reacted much faster than the chloride, allowing for the formation of an intermediate amine with three branches. This product then cyclized into the cryptand as shown. When the diiodo starting



material was used, the diaza-crown resulted from a simultaneous reaction with both iodides in the presence of a template cation. The formation of the cryptand was also controlled by template and solvent effects. The best solvent was found to be acetonitrile. Sodium carbonate was the best catalyst because sodium ion fits best into cryptand[2.2.2]. No significant amount of cryptand was observed when potassium carbonate was used. These authors found that variations in the combination of metal carbonate and solvent could significantly affect the yield of diaza-18-crown-6. In acetonitrile, sodium carbonate was the best catalyst followed by potassium, cesium, and lithium carbonates, which gave decreasing yields of the cyclic product. It is instructive to note that diaza-18-crown-6 yields fell to only 4% when an equimolar amount of dicyclohexano-18-crown-6 was present in the reaction mixture. Presumably the crown complexes the metal cation so that it was less available to act as a template.

Gokel and co-workers prepared a series of nitrogen-pivot lariat crown ethers (see method A, section IV.A).[10] These compounds all have side arms connected to a macroring nitrogen atom. Where a side arm was incapable of coordinating a metal ion, the ring-closure reaction occurred to give a yield of about 30% or less. Where the side arm was composed of relatively rigid aryl groups containing an ether donor oxygen atom, the ring-closure reaction occurred in about 40% yield. Cyclization yields of 50% and higher were obtained where the donor atoms were attached to a flexible side arm. In the latter case, the flexible side arm allowed the donor atom to interact with the cation in the forming macroring cavity, resulting in a more stable complex and thus a higher macroring yield.

Yamawaki and Ando have shown that crown compound synthesis can occur when a potassium fluoride coated alumina catalyst is used.[105,106] Pietraszkiewicz has found this technique useful for the preparation of diaza-crowns.[78,107] He found that the yields increased

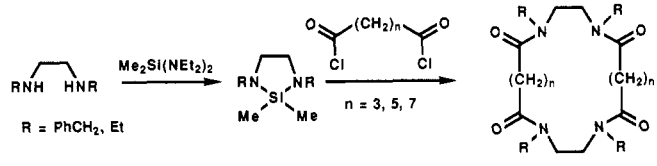


when the metal ion was changed from lithium to sodium to potassium. He explained the increase in yields as a result of greater basicity of the potassium fluoride–alumina catalyst rather than a template effect.

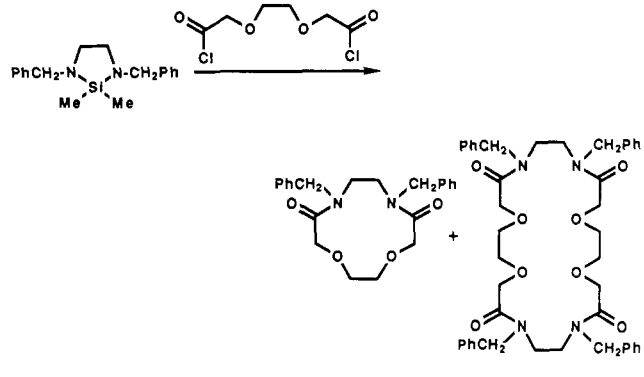
Okahara and co-workers prepared two macrocyclic monoamide compounds by heating the salt of an ω-amino acid (see method G, section IV.A).[108] No significant change in the cyclization yields was observed upon the addition of template salts such as sodium or potassium tetrafluoroborate.

Okahara and co-workers found that the oligoethylene glycols cyclized into crown ethers upon treatment with 1 mol of tosyl chloride. This method has been used to prepare many aza-crowns.[45,84,85,109–112] They determined that the best yields were obtained in either dioxane or a *tert*-butyl alcohol–dioxane mixture with an appropriate template metal hydroxide (see method F, section IV.A). Bradshaw and Krakowiak found that, in addition to tosyl chloride, ethylene glycol ditosylated or (allyloxy)methyl-substituted ethylene glycol ditosylate reacted with a diaza diol to close the ring, forming the diaza-crown. Surprisingly, the ethylene glycol ditosylate did not react to form a larger crown but reacted to give the Okahara closure type product (see method AA, section IV.B).[49,80] Unsubstituted aza-crowns have been prepared by the Okahara method, but with only moderate yields because of side reactions of the secondary amines (see method Z, section IV.B).[85]

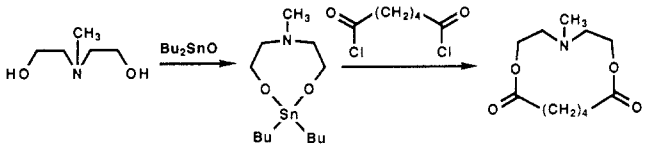
Schwartz and Shanzer have developed a new method for the preparation of cyclic tetraamides under normal reaction conditions.[113,114] First, the method involved a 1,3,2-diazasilolidine intermediate formed by the reaction of a diamine with dimethylbis(diethylamino)silane. The diazosilolidine intermediate was reacted with a diacid chloride to form the macrocyclic tetraamide.



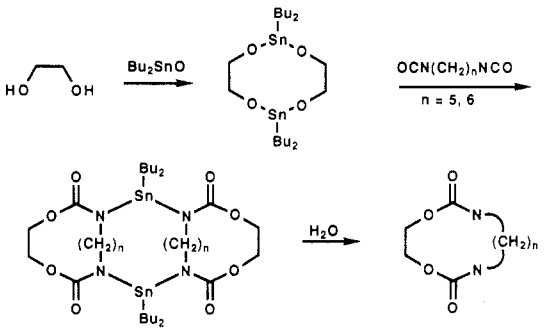
This procedure was used by other authors to prepare macrocyclic di- and tetraamides containing both nitrogen and oxygen atoms.[115]



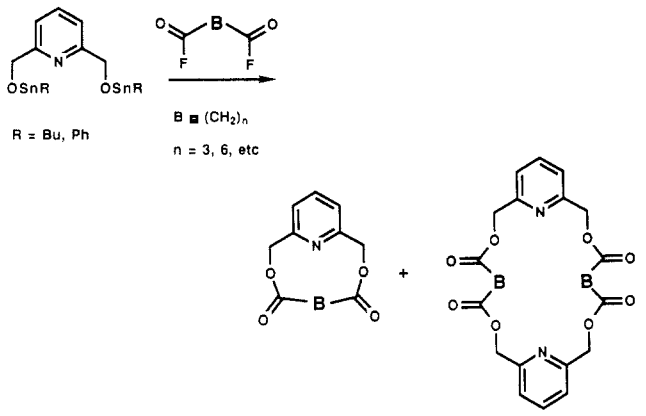
Shanzer and co-workers have studied a similar reaction using a dibutyltin derivative as an intermediate.[114,116–119] The tin intermediate acts like a template to direct the diacid chloride and diol to form a macrocyclic tetraester as the sole cyclic product. Ninagawa and co-workers used the Shanzer approach to prepare a macroring containing both oxygen and nitrogen atoms.[120]



This type of reaction has also been used to prepare a series of macrocyclic lactones and lactams.[121,122] The method can be used for the synthesis of a macrocyclic bisurethane using an activated tin derivative.[119,123]



Tisnes and co-workers reacted a diacid fluoride with a tin derivative of 2,6-pyridinedimethanol (or other diols) to prepare a macrocyclic di- and tetraesters containing the pyridine unit as the aza portion of the macroring.[124-126]

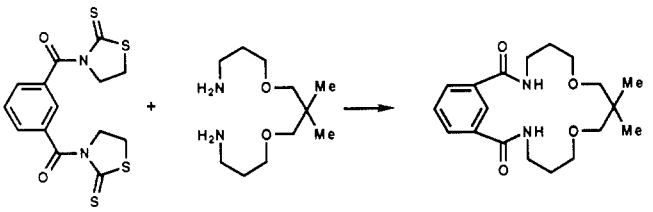


The case for template assistance in the cyclization step in the formation of polyaza-crown compounds has not been proved in many cyclization reactions. Certainly other factors such as base strength and intramolecular hydrogen bonding need to be considered.

B. Reactions of Activated Diacids with Diamines

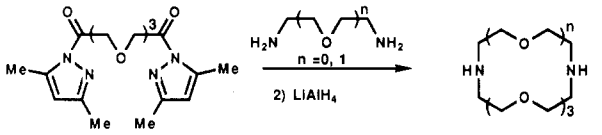
The reaction of a diacid chloride with a diamine to effect ring closure followed by reduction of the resulting diamide was the first method used to prepare the diaza-crown compounds. Stetter and co-workers were the first to make cyclic diamides by this procedure.[127] Lehn and co-workers prepared diaza-18-crown-6 by this method (see method P, section IV.B).[8,128,129] The process requires a simultaneous addition of the diamine and diacid chloride into a large volume of solvent over an extended period of time to maintain high dilution.[8,75,129-132] The intermediate macrocyclic diamides were isolated in moderate to good yields. The diamides were reduced usually by lithium aluminum hydride in THF to give high yields of diaza-crown compounds.

A number of researchers have found that if the reaction were carried out at 0 °C, a slower reaction time resulted but with higher yields.[50,132] Others have activated the diacid functional group by forming the bis(thiazolidine-2-thione) derivative by reacting the diacid with thiazolidine-2-thione in the presence of dicyclohexylcarbodiimide (DCC) together with a catalytic amount of 4-(dimethylamino)pyridine or the thalium salt of thiazolidine-2-thione. Bis(thiazolidine-2-thione) derivatives are reactive toward amines and do not yield hydrochloric acid as a byproduct.[133,134] An



excellent yield of 91% was observed for the formation of the cyclic diamides with 6% of cyclic tetraamide byproduct (result of a 2:2 cycloaddition). Isobutyl chloroformate was also reacted with a diacid to form an active derivative that was reacted with a diamine in much the same manner.[135]

Biernat and co-workers used the bis(3,5-dimethylpyrazolide) of tetraglycolic acid (prepared by reacting the crude acid with the pyrazole in the presence of *O*-ethylphosphoric acid)[101] for the preparation of the macrocyclic diamide in excellent yields and under normal reaction conditions.[101]

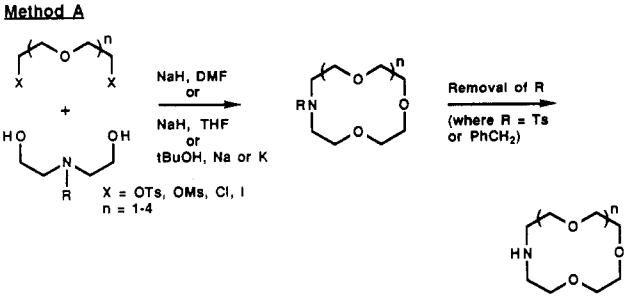


The simultaneous addition of the two starting materials over an extended time period is not convenient. Tabushi and co-workers found that high-dilution techniques were not required for the reaction of diesters (including malonates) with diamines to form the cyclic diamides (see method AH, section IV.C).[136-138]

IV. Specific Syntheses of the Aza-Crowns

A. Monoaza-Crowns (Table I)

The first monoaza-crown compounds were prepared by reacting the appropriate diethanolamine with an oligoethylene glycol ditosylate, dimesylate, or dihalide (method A).[92,139-141] This method is convenient because

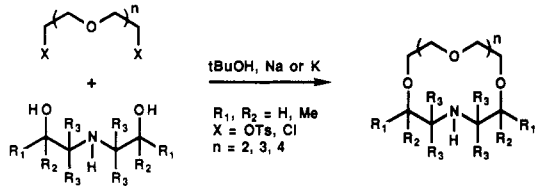


the two starting materials are readily available. The unsubstituted aza-crown can be prepared when the R group is benzyl, trityl, or tosyl. Removal of the protecting group can be achieved by acid cleavage or reduction.[140,141] The cyclization step was accomplished

by using sodium hydride in DMF or THF or in *tert*-butyl alcohol with sodium or potassium metal. The yields were moderate, depending on the size of the macroring.

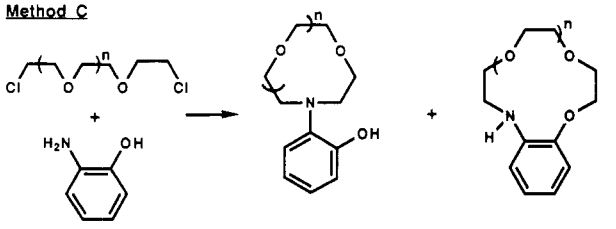
Okahara and co-workers reported a similar reaction to prepare unsubstituted aza-crowns.[142] They treated unprotected diethanolamine compounds, some of which contained methyl substituents on the carbon atoms of the molecule, with various oligoethylene glycol ditosylates or dichlorides (method B). Lai used a modification of method B to prepare similar aza-crowns in better yields.[143] Gokel and co-workers used methods A and D (see below) to prepare many of their nitrogen-pivot lariat ethers.[10,144-146]

Method B



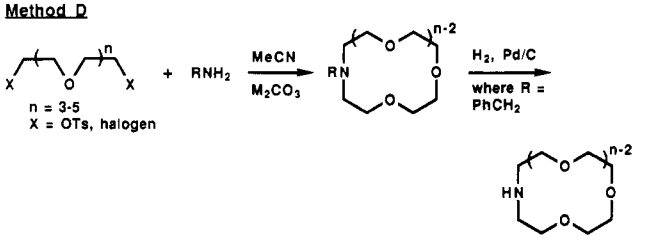
Lockhart and co-workers prepared *N*-phenyl-substituted and benzoaza-crowns by reacting 2-aminophenol with dihalides (method C).[147,148] When the reaction was carried out in water and $n = 2$, only the *N*-phenyl-substituted aza-crown was formed. In other solvents, such as DMF, and where $n > 2$, only the benzoaza-crown was formed.

Method C



Calverley and Dale reacted various aliphatic and aromatic amines with the diiodide derivative of tetraethylene glycol to prepare *N*-alkyl(aryl)-substituted aza-12-crown-4 compounds (method D).[149,150] The

Method D

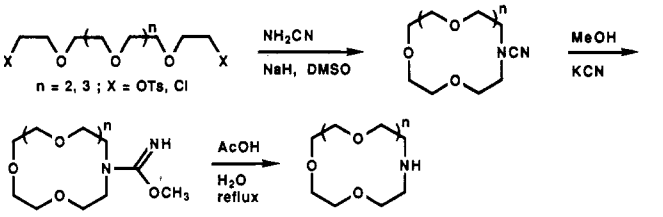


diiodide was prepared from the dichloride and sodium iodide in acetone. Shono, Kimura, and co-workers extended method D also using ditosylate starting material.[52] The unsubstituted aza-crown product could be alkylated to form other more complicated *N*-alkylaza-12-crown-4 ligands.

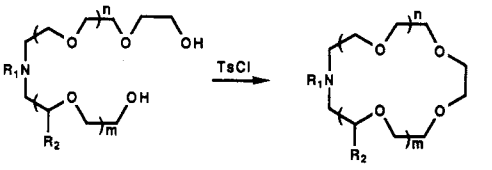
Okahara and co-workers used cyanamide to prepare some aza-crowns (method E).[151] The *N*-cyano group was converted to an imino ether that hydrolyzed to the N–H compound when treated with aqueous acetic acid.

The Okahara ring-closure reaction[8,84,85,109,112] discussed in section III.A has been used to prepare many aza-crown compounds (method F). The yields of these reactions were 50–80%, depending on ring size and the substituent on the nitrogen atom.

Method E

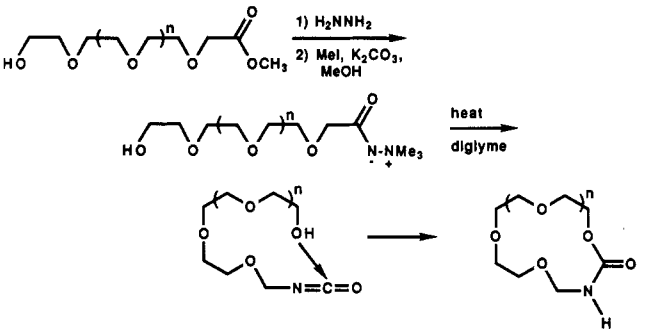


Method F



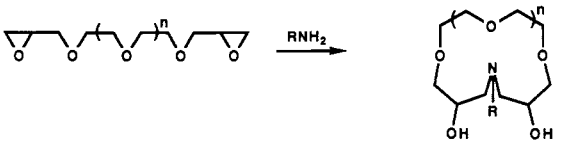
The amido crown ethers have interest as model compounds for natural ionophores.[152] The urethane-containing crown compounds were prepared because they are similar to the amido crowns (method G).[108] The reaction proceeds by a thermal rearrangement of an amino amide to an isocyanate (as shown). The ω-hydroxyl group then adds to the isocyanate.

Method G



Functionalized aza-crown ethers are important intermediates. The dihydroxyaza-crowns, where the hydroxy groups are attached to ring carbon atoms, were prepared by reacting a primary amine with an oligoethylene glycol diglycidyl ether in protic solvents such as water or methanol (method H).[79]

Method H



Monoaza-crowns with two different functional groups were prepared by Bartsch and co-workers (method I).[45,153]

Method I

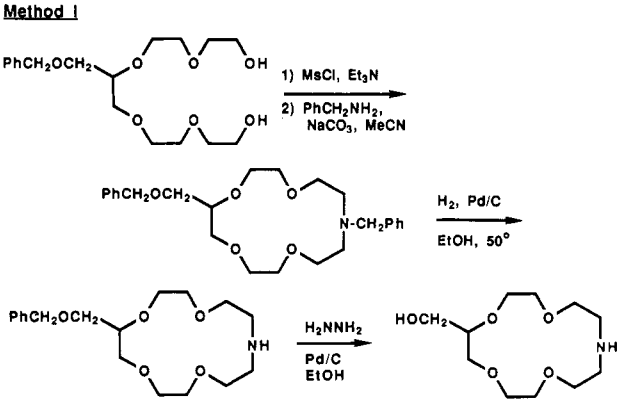
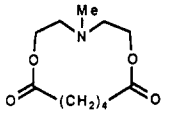
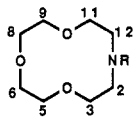


TABLE I. Monoaza-Crown Compounds

A. Aza-13-Crown-3

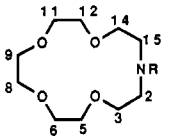
entry no.	structure	method	ref (yield)
1		other	120 (41%)

B. Aza-12-Crown-4



entry no.	R formula index	R structure	other substituents	method	ref (yield)
2	H	H		A from no. 21	141 (42%)
				B	142 (3%)
				D from no. 18	10, 146, 217 (95%); 52 (89%); 88, 150 (85%); 149
3	H	H	2,2,12,12-Me_4	B	143 (7%)
4	H	H	3-C_8H_{17}	B	218 (20%)
5	CH_3	Me		from no. 2	141 (92%)
				from no. 15	88, 150 (74%)
6	C_2H_4Cl	$Cl(CH_2)_2$		K	219 (83% HCl)
7	C_2H_4NO	$H_2NC(O)CH_2$		D	88, 150 (24%)
8	C_2H_5O	$HO(CH_2)_2$		D	52 (32%); 88, 150 (48%)
				K	142 (43%)
				N/A	219
9	C_3H_7O	$MeO(CH_2)_2$		D	10 (60%); 88, 150 (51%)
10	C_3H_7O	$HO(CH_2)_3$		D	10, 146 (56%)
11	$C_4H_7O_2$	EtO_2CCH_2		D	88, 150 (30%)
12	$C_4H_{10}N$	$Me_2N(CH_2)_2$		D	10, 146, 220 (21%)
13	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$		J	10 (66%)
14	C_6H_5	Ph		D	88, 150 (51%)
15	$C_7H_6O_2$	PhO_2C		from no. 18	88, 150
16	$C_7H_6NO_2$	2-$NO_2C_6H_4CH_2$		J	10, 146 (86%)
17	$C_7H_6NO_3$	2-OH-5-$NO_2C_6H_3CH_2$		J	221
				A	221
				N/A	222
18	C_7H_7	$PhCH_2$		D	10, 146 (53%); 52 (40%); 88, 150, 217 (54%)
19	C_7H_7O	2-$MeOC_6H_4$		D	10, 146 (26%); 220 (29%)
20	C_7H_7O	4-$MeOC_6H_4$		D	10, 146 (40%)
21	$C_7H_7O_2S$	Ts		A	141 (6%)
				D	223 (35%)
22	$C_7H_7O_2S$	Ts	3,11-$(O)_2$	other	224 (70%)
23	$C_7H_{15}O_3$	$Me(OCH_2CH_2)_3$		J	10, 146 (52%)
24	C_8H_9O	2-$MeOC_6H_4CH_2$		D	10, 146 (47%); 220 (32%)
25	$C_9H_{19}O_4$	$Me(OCH_2CH_2)_4$		J	10 (54%)
26	$C_{11}H_{21}O_4$	allyl-$(OCH_2CH_2)_4$		J	10, 146 (50%)
27	$C_{12}H_8N_3O_2$	4-(4-$NO_2C_6H_4N{=}N)C_6H_4$		from no. 18	88,, 150 (51%)
28	$C_{12}H_{25}$	$C_{12}H_{25}$		D	52 (50%)
				N/A	157, 225, 226
29	$C_{14}H_{14}P$	$Ph_2P(CH_2)_2$		from no. 6	219 (41%)

C. Aza-15-Crown-5

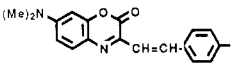
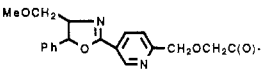
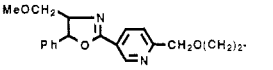
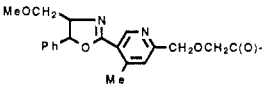
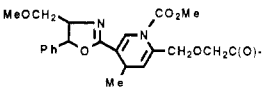


entry no.	R formula index	R structure	other substituents	method	ref (yield)
30	H	H		B from ditosyl	142 (30–37%) (GLC)
				B from dichloro	142 (1–77%) (GLC)
				B	218, 227 (37%); 228 (46%)
				D from no. 81	10 (98%); 52 (88%)
				E	151 (≈100%)
				from no. 67	229 (76% HCl)
31	H	H	3-Me	B	142 (26%)
32	H	H	3,14-Me_2	B	227 (33%)
					142 (26%); 218 (33%)
33	H	H	2,2,15,15-Me_4	B	143 (60%)
34	H	H	2-Et	B	142 (46%)
35	H	H	2,2,15-Me_3; 15-Et	B	143 (55%)

TABLE I (Continued)

entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
36	H	H	2,2-Me_2; 15,15-$(CH_2)_5$	B	143 (49%)
37	H	H	8-CH_2OH	I	45 (66%)
38	H	H	3-Ph	B	142 (33%)
39	H	H	3,14-Ph_2	B	218 (32%)
40	H	H	8-CH_2OCH_2Ph	N/A	153
				I	45 (76%)
41	H	H	3,14-$(C_8H_{17})_2$	B	218
42	H	H	3-$C_{10}H_{21}$	B	218 (41%)
43	H	H	2,3-cyclohexano	B	142 (52%)
44	CClO	ClC(O)		from no. 30	230 (78%)
45	CN	CN		E	151, 231 (33%)
46	CH_3	Me		from no. 30	10 (37%)
				other	144, 232
				N/A	233
47	CH_4O_3P	$(OH)_2P(O)CH_2$		from no. 30	234
48	C_2H_2ClO	$ClCH_2C(O)$		J	154 (90%)
49	C_2H_4Cl	$Cl(CH_2)_2$		K	154
50	C_2H_4NO	MeOC(NH)		E	151 (95%)
51	C_2H_4NO	MeNHC(O)		from no. 44	230 (90%)
52	C_2H_5O	$HO(CH_2)_2$		D	52 (19%)
				K	154 (40%); 142 (41%); 156
				from no. 87	154 (94%)
53	C_2H_5O	$MeOCH_2$		N	158 (98%)
54	C_3H_5	allyl		A	10 (61%); 145
55	C_3H_6N	aziridinyl-CH_2		from no. 53	158 (94%)
56	C_3H_6NO	$H_2NCH(Me)C(O)$		from no. 96	73 (90%)
57	C_3H_7O	$MeO(CH_2)_2$		A	10 (55%), 144, 145; 220 (69%); 231
				N/A	235
58	C_3H_8N	$H_2NCH(Me)CH_2$		from no. 56	73 (98%)
59	$C_4H_8NO_2$	$O_2NC(Me)_2CH_2$		from no. 53	158 (89%)
60	C_4H_9	*n*-Bu		A	10 (65%); 145
61	C_4H_9	*t*-Bu		A	10 (28%)
62	$C_4H_9O_2$	$H(OCH_2CH_2)_2$		J	156
63	$C_4H_9O_2$	$H(OCH_2CH_2)_2$	8-CH_2OH	from no. 109	153 (93%)
64	$C_4H_{10}N$	$MeNHCH(Me)CH_2$		from no. 108	73 (60%)
				from no. 72	73 (87%)
65	$C_5H_{10}NO$	$MeC(O)NHCH(Me)CH_2$		from no. 58	73 (84%)
66	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$		A	10 (47%), 144, 145; 220 (47%); 231
				N/A	233
67	C_6H_4NO	4-NOC_6H_4		N/A	229
68	$C_6H_4NO_3$	2-OH-4-$NO_2C_6H_3$		J	237
69	C_6H_5	Ph	3-(O)	other	236 (9%)
70	C_6H_6N	4-$NH_2C_6H_4$		N/A	229
71	$C_6H_6NO_2S$	4-$NH_2C_6H_4SO_2$		J, other	238 (64%)
72	$C_6H_{10}NO_3$	$EtCO_2NHCH(Me)C(O)$		from no. 30	73 (76%)
73	$C_6H_{11}O_2$	*t*-$BuCO_2CH_2$		J	10 (66%)
74	C_6H_{13}	C_6H_{13}		F	84 (75%)
75	C_6H_{13}	C_6H_{13}	3-(O)	other	236 (12%)
76	$C_6H_{13}O_3$	$H(OCH_2CH_2)_3$		J	156
77	C_7H_6Cl	2-$ClC_6H_4CH_2$		J	239 (72%)
78	C_7H_6Cl	4-$ClC_6H_4CH_2$		J	239 (80%)
79	$C_7H_6NO_2$	2-$NO_2C_6H_4CH_2$		J	10, 240 (35%); 239 (96%)
80	$C_7H_6NO_2$	4-$NO_2C_6H_4CH_2$		J	10, 240 (22%); 239 (85%)
81	C_7H_7	$PhCH_2$		A	10, 239 (46%) 145
				D	52
82	C_7H_7	$PhCH_2$	8-CH_2OCH_2Ph	I	45 (51%)
83	C_7H_7O	2-$OMeC_6H_4$		A	10 (38%)
84	C_7H_7O	4-$OMeC_6H_4$		A	10 (30%)
85	C_7H_7O	2-$OHC_6H_4CH_2$		J from no. 98	229 (55%)
86	$C_7H_7O_2S$	Ts	3,14-$(O)_2$	other	224 (30%)
87	$C_7H_{13}O_2$	THF-O-$(CH_2)_2$		A	154 (44%)
				J	154 (62%)
88	C_7H_{15}	C_7H_{15}		N/A	241, 242
89	$C_7H_{15}O_3$	$Me(OCH_2CH_2)_3$		A	144
				J from no. 30	10, 220 (34%); 156, 232
90	$C_8H_5N_2O_6$	2,6-$(NO_2)_2$-4-$MeCO_2C_6H_2$		J	243 (77%)
91	C_8H_6N	2-$CNC_6H_4CH_2$		J	239 (82%)
92	C_8H_6N	4-$CNC_6H_4CH_2$		J	239 (82%)
93	C_8H_8NO	$PhCH_2NHC(O)$		from no. 44	230 (90%)
94	C_8H_9O	2-$MeOC_6H_4CH_2$		A	10, 239 (40%)
95	C_8H_9O	4-$MeOC_6H_4CH_2$		J	239 (83%)
96	$C_8H_{14}NO_3$	*t*-$BuO_2CNHCH(Me)C(O)$		from no. 30	73 (80%)
97	C_8H_{17}	C_8H_{17}		F	84 (90%)
				N/A	155, 156, 244, 245, 246
98	$C_9H_9O_2$	2-$MeCO_2C_6H_4CH_2$		J	229

TABLE I (Continued)

entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
99	$C_9H_{10}NO$	PhCH(Me)NHC(O)		from no. 44	230 (87%)
100	$C_9H_{11}O$	3,5-Me_2-4-$OHC_6H_2CH_2$		from no. 53	158
101	$C_9H_{19}O_4$	$Me(OCH_2CH_2)_4$		J	10, 220 (55%); 144, 232
102	$C_{10}H_5O_2$	1,4-naphthoquinonyl		from no. 30	229 (42%)
				N/A	247
103	$C_{10}H_7$	azulenyl		from no. 30	11 (71%)
104	$C_{10}H_{13}O$	$Ph(CH_2)_2O(CH_2)_2$		N/A	242
105	$C_{10}H_{13}O_2$	$Ph(OCH_2CH_2)_2$		from no. 110	241 (30%)
106	$C_{10}H_{21}$	$C_{10}H_{21}$		F	84 (82%)
				N/A	245, 246, 248
107	$C_{10}H_{21}O$	$C_8H_{17}O(CH_2)_2$		J	155 (71%)
				N/A	244
108	$C_{11}H_{12}NO_3$	$PhCH_2CO_2NHCH(Me)C(O)$		from no. 30	73 (99%)
109	$C_{11}H_{15}O_2$	$PhCH_2(OCH_2CH_2)_2$	8-CH_2OCH_2Ph	J from no. 40	153 (76%)
110	$C_{11}H_{15}O_4S$	$Ts(OCH_2CH_2)_2$		N/A	241
111	$C_{11}H_{23}O_5$	$Me(OCH_2CH_2)_5$		J	10 (78%); 144, 232
112	$C_{12}H_8NO$	4-[4-O=C_6H_4=N]C_6H_4		N/A	229
113	$C_{12}H_{25}$	$C_{12}H_{25}$		D	52 (54%)
				F	84 (67%)
				N/A	155, 157, 225, 226, 244, 245, 246
114	$C_{12}H_{25}O_2$	$C_8H_{17}(OCH_2CH_2)_2$		J	155 (60%)
115	$C_{13}H_7N_2O_5$	2,4-$(NO_2)_2$-6-$PhCOC_6H_2$		J	243 (84%)
116	$C_{13}H_{12}P$	Ph_2PCH_2		from no. 30	249
117	$C_{14}H_6ClO_2$	8-chloroanthraquinonyl		J	229 (12%)
118	$C_{14}H_{29}O$	$C_{12}H_{25}O(CH_2)_2$		J	155 (60%)
				N/A	244
119	$C_{14}H_{29}O_3$	$C_8H_{17}(OCH_2CH_2)_3$		J	155 (61%)
120	$C_{15}H_{15}N_2O$	4-$Me_2NC_6H_4N$=C_6H_3-4-(O)-3-CH_2		from no. 85	229 (36%)
121	$C_{16}H_{10}NO_2$	naphthoquinonyl-NHC_6H_4		from no. 70	229 (56%)
122	$C_{16}H_{33}O_2$	$C_{12}H_{25}(OCH_2CH_2)_2$		J	155 (63%)
123	$C_{16}H_{33}O_2$	$HO(CH_2)_2OCH(C_{12}H_{25})CH_2$	8-CH_2OH	from no. 140	153 (58%)
124	$C_{17}H_{19}N_2O$	4-EtC_6H_4N=NC_6H_4[4-$O(CH_2)_3$]		J	250
128	$C_{17}H_{35}O_8$	$Me(OCH_2CH_2)_8$		A	10 (49%); 232
				J	144
129	$C_{18}H_{15}N_2O_2$			other	251
127	$C_{18}H_{15}Fe$	4-(ferrocenyl-CH=CH)C_6H_4		other	252
128	$C_{18}H_{17}Fe$	4-[ferrocenyl-$(CH_2)_2$]C_6H_4		other	252
129	$C_{18}H_{21}N_2O$	4-EtC_6H_4N=NC_6H_4[4-$O(CH_2)_4$]		J	250
130	$C_{18}H_{27}O_7$	3-benzo-15-crown-5-$(OCH_2CH_2)_2$		from no. 110	241 (17%)
131	$C_{19}H_{14}Fe$	4-(ferrocenyl-C(CN)=CH)C_6H_4		other	252
132	$C_{19}H_{19}N_2O_4$			from no. 48	154 (80%)
133	$C_{19}H_{21}N_2O_3$			from no. 49	154 (71%)
				from no. 132	154 (5%)
134	$C_{19}H_{23}N_2O$	4-BuC_6H_4N=NC_6H_4[4-$O(CH_2)_3$]		J	250
135	$C_{20}H_{23}N_2O_5$	3-benzo-15-crown-5-(N=N-4-C_6H_4)		other	253 (13%)
136	$C_{20}H_{25}N_2O$	4-BuC_6H_4N=NC_6H_4[4-$O(CH_2)_4$]		J	250
137	$C_{20}H_{31}O_8$	3-benzo-18-crown-6-$(OCH_2CH_2)_2$		from no. 110	241 (22%)
138	$C_{20}H_{21}N_2O_4$			from no. 132	154 (55%, 26%)
139	$C_{22}H_{25}N_2O_6$			from no. 132	154 (43%)
140	$C_{23}H_{39}O_2$	$PhCH_2O(CH_2)_2OCH(C_{12}H_{25})CH_2$		J from no. 40	153 (30%)
141	$C_{28}H_{45}O_2$	cholesteryl-C(O)		J	235 (34%)
142	$C_{29}H_{47}O_2$	cholesteryl-$COCH_2$		J	235 (68%); 254
143	$C_{29}H_{49}O_2$	dihydrocholesteryl-C(O)CH_2		J	235 (67%); 254

D. Aza-16-Crown-5

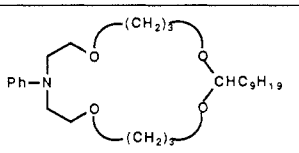
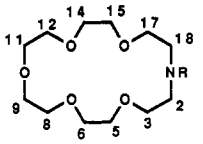
entry no.	structure	method	ref (yield)
144		A, other	255 (26%)

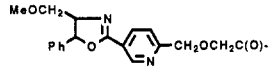
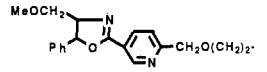
TABLE I (Continued)

E. Aza-18-Crown-6

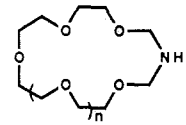


entry no.	R formula index	R structure	other substituents	method	ref (yield)
145	H	H		A from no. 171	10 (98%)
				B from ditosyl	142 (58–78%) GLC; 218, 227 (61%)
				B from dichloro	142 (27–35%) GLC; 218, 227 (35%); 228 (25%)
				D	52 (47%)
146	H	H	3-Me	B	142 (39%)
147	H	H	3,17-Me_2	B	142 (28%); 218, 227 (34%)
148	H	H	2,2,18,18-Me_4	B	143 (41%)
149	H	H	2-Et	B	142 (41%)
150	H	H	2,3-cyclohexano	B	142 (43%)
151	H	H	3-Ph	B	142 (33%)
152	CN			E	151 (17%); 231
153	CH_3	Me		from no. 145	10 (29%); 144, 232
154	CH_4O_3P	$(HO)_2P(O)CH_2$		from no. 145	234
155	C_2H_2ClO	$ClCH_2C(O)$		J	154 (93%)
156	C_2H_4Cl	$Cl(CH_2)_2$		K	154 (92%)
157	C_2H_5O	$HO(CH_2)_2$		D	52 (14%); 152
				K	142 (52%); 154 (40%); 156
				from no. 176	154 (87%)
158	C_3H_5	allyl		A	145; 220 (38%)
159	C_3H_7	Pr		J	12 (19%)
160	C_3H_7O	$MeCH(OH)CH_2$		from no. 158	220 (100%)
161	C_3H_7O	$MeO(CH_2)_2$		A	10 (53%); 144, 145; 220 (53%); 232
				N/A	235
162	$C_4H_7O_2$	$EtOC(O)CH_2$		J	12 (79%)
163	$C_4H_9O_2$	$H(OCH_2CH_2)_2$		J	156
164	$C_5H_8NO_3$	$MeOC(O)CH_2NHC(O)CH_2$		J	12 (51%)
165	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$		A	10, 220 (50%); 144, 232
166	C_6H_5	Ph	3-(O)	other	236 (16%)
167	$C_6H_6NO_2S$	$4\text{-}NH_2C_6H_4SO_2$		J, other	238 (66%)
168	C_6H_{13}	C_6H_{13}		F	84 (58%)
169	C_6H_{13}	C_6H_{13}	2-(O)	N/A	115
170	$C_6H_{13}O_3$	$H(OCH_2CH_2)_3$		J	156
171	$C_7H_6NO_3$	$2\text{-}OH\text{-}5\text{-}NO_2C_6H_4CH_2$		J	237
172	C_7H_7	$PhCH_2$		A	10 (40%)
				D	52
173	C_7H_7O	$2\text{-}OHC_6H_4CH_2$		from no. 181	229 (55%)
174	C_7H_7O	$2\text{-}MeOC_6H_4$		A	10 (41%)
175	$C_7H_7O_2S$	Ts	3,17-$(O)_2$	other	224 (37%)
176	$C_7H_{13}O_2$	THF-O-$(CH_2)_2$		A	154 (57%)
				J	154
177	C_7H_{15}	C_7H_{15}		N/A	241, 242
178	$C_7H_{15}O_3$	$Me(OCH_2CH_2)_3$		A	144
				J	10 (46%); 156, 220 (16%), 232
179	$C_8H_{14}NO_3$	$MeOC(O)CH(i\text{-}Pr)NHC(O)CH_2$		J	12 (56%)
180	C_8H_{17}	C_8H_{17}		F	84 (88%)
				N/A	155, 156, 244, 245, 246
181	$C_9H_9O_2P$	$2\text{-}MeCO_2C_6H_4CH_2$		J	229
182	$C_9H_{16}NO_3$	$MeOC(O)CH(s\text{-}Bu)NHC(O)CH_2$		J	12 (50%)
183	$C_9H_{19}O_4$	$Me(OCH_2CH_2)_4$		J	10, 220 (18%); 144, 232
184	$C_{10}H_8$	azulenyl		from no. 145	11 (54%)
185	$C_{10}H_{13}O$	$Ph(CH_2)_2O(CH_2)_2$		N/A	242
186	$C_{10}H_{13}O_2$	$Ph(OCH_2CH_2)_2$		from no. 189	241
187	$C_{10}H_{21}$	$C_{10}H_{21}$		F	84 (70%)
				N/A	245, 246
188	$C_{10}H_{21}O$	$C_8H_{17}O(CH_2)_2$		J	155 (68%)
				N/A	244
189	$C_{11}H_{15}O_4S$	$Ts(OCH_2CH_2)_2$		N/A	241
190	$C_{11}H_{23}O_5$	$Me(OCH_2CH_2)_5$		J	10 (15%); 144, 232
191	$C_{12}H_{25}$	$C_{12}H_{25}$		D	52 (35%)
				F	84 (94%)
				N/A	155, 157, 225, 244, 245, 246
192	$C_{12}H_{25}O_2$	$C_8H_{17}(OCH_2CH_2)_2$		J	155 (52%)
193	$C_{14}H_9N_2O_4$	$2,4\text{-}(NO_2)C_6H_3\text{-}4\text{-}CH{=}CHC_6H_4$		N/A	11
194	$C_{14}H_{29}O$	$C_{12}H_{25}O(CH_2)_2$		J	155 (55%)
195	$C_{14}H_{29}O_3$	$C_8H_{17}(OCH_2CH_2)_3$		J	155 (62%)
196	$C_{15}H_{15}N_2O$	$4\text{-}Me_2NC_6H_4N{=}C_6H_3\text{-}4\text{-}(O)\text{-}3\text{-}CH_2$		from no. 173	229 (36%)
197	$C_{16}H_{33}O_2$	$C_{12}H_{25}(OCH_2CH_2)_2$		J	155 (63%)
				N/A	244

TABLE I (Continued)

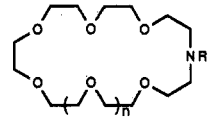
entry no.	R formula index	R structure	other substituents	method	ref (yield)
198	$C_{17}H_{36}O_8$	$Me(OCH_2CH_2)_8$		A	232
				J	10 (60%); 144
199	$C_{18}H_{27}O_7$	3-benzo-15-crown-5-$(OCH_2CH_2)_2$		from no. 189	241 (29%)
200	$C_{19}H_{19}N_2O_4$			from no. 155	154 (80%)
201	$C_{19}H_{21}N_2O_3$			from no. 156	154 (5%)
202	$C_{20}H_{31}O_8$	3-benzo-18-crown-6-$(OCH_2CH_2)_2$		from no. 189	241 (37%)
203	$C_{28}H_{45}O_2$	cholesteryl-C(O)		J	235 (52%)
204	$C_{29}H_{47}O_2$	cholesteryl-$C(O)CH_2$		J	235 (63%)
205	$C_{29}H_{49}O_2$	dihydrocholesteryl-$C(O)CH_2$		J	235 (65%)

F. Aza-16-Crown-6 and Aza-19-Crown-7



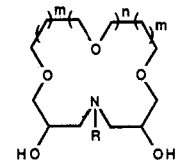
entry no.	*n*	other substituents	method	ref (yield)
206	1	2-(O)	G	108 (48%)
207	2	2-(O)	G	108 (59%)

G. Aza-21-Crown-7 and Aza-24-Crown-8



entry no.	R formula index	R structure	*n*	method	ref (yield)
208	H	H	1	A from no. 213	141 (77%)
				B	142 (33%); 218, 227 (35%)
209	H	H	2	A from no. 214	141 (66%)
210	CH_3	Me	1	from no. 208	141
211	CH_3	Me	2	from no. 209	141 (93%)
212	C_6H_{13}	C_6H_{13}	1	F	84 (79%)
213	$C_7H_7O_2S$	Ts	1	A	141 (23%)
214	$C_7H_7O_2S$	Ts	2	A	141 (17%)
215	C_8H_{17}	C_8H_{17}	1	F	84 (78%)
				N/A	245, 246
216	$C_{10}H_{21}$	$C_{10}H_{21}$	1	F	84 (61%)
				N/A	245, 246
217	$C_{12}H_{25}$	$C_{12}H_{25}$	1	N/A	245, 246

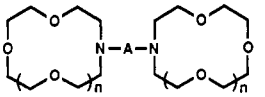
H. Aza-Crowns with Propylene Bridges



entry no.	R formula index	R structure	*m*	*n*	methods	ref (yield)
218	H	H	0	1	H	79 (31%); 256
219	C_2H_5	Et	0	1	H	79 (38%); 256
220	C_2H_5	Et	0	2	H	79 (35%); 256
221	C_2H_5	Et	0	3	H	79 (24%); 256
222	C_2H_5	Et	2	1	H	256
223	C_2H_5O	$HO(CH_2)_2$	0	1	H	79 (34%); 256
224	C_4H_9	*s*-Bu	0	1	H	79 (49%)
225	C_4H_9	*s*-Bu	0	2	H	79 (50%)
226	C_4H_9	*s*-Bu	0	1	H	256
227	C_6H_5	Ph	0	1	H	79 (48%); 256
228	$C_8H_{17}O_2$	*n*-Bu$(OCH_2CH_2)_2$	0	1	N/A	257
229	$C_{10}H_{21}$	$C_{10}H_{21}$	0	1	H	79 (50%); 248 (45%); 256
230	$C_{10}H_{21}$	$C_{10}H_{21}$	0	2	N/A	257
					H	248 (43%)
231	$C_{10}H_{21}$	$C_{10}H_{21}$	0	3	H	248 (43%)
232	$C_{12}H_{25}$	$C_{12}H_{25}$	0	1	H	248 (40%)
233	$C_{12}H_{25}$	$C_{12}H_{25}$	0	2	H	248 (44%)
234	$C_{12}H_{25}$	$C_{12}H_{25}$	0	3	H	248 (38%)

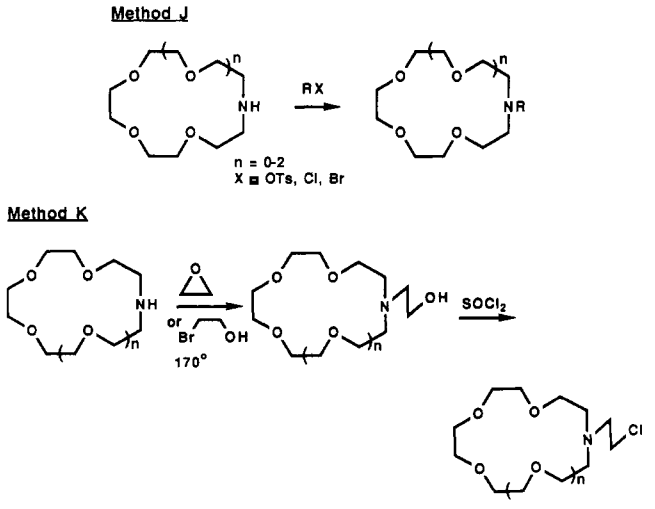
TABLE I (Continued)

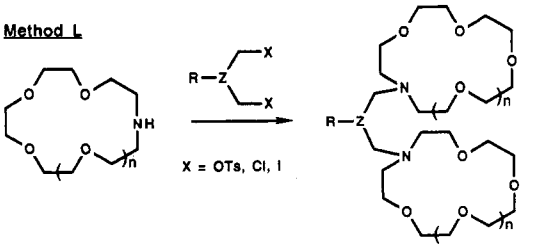
I. Bis(monoaza-crowns)



entry no.	A formula index	A structure	n	method	ref (yield)
235	C_2H_4	$(CH_2)_2$	1	L from oxalyl chloride	149 (85% overall)
				L from bis(tosylate)	149 (84%)
				L, other	88 (85%, 84%)
				N/A	258
236	C_2H_4	$(CH_2)_2$	2	O	159 (36%)
237	C_3H_6	$(CH_2)_3$	1	L	88, 149 (84%)
238	$C_4H_4O_3$	$C(O)CH_2OCH_2C(O)$	2	L	242
239	$C_4H_4O_3$	$C(O)CH_2OCH_2C(O)$	3	L	242
240	C_4H_8O	$(CH_2)_2O(CH_2)_2$	2	from no. 238	242
				N/A	259
241	$C_4H_8O_2$	$CH_2(CHOH)_2CH_2$	2	from no. 249	260 (88%)
242	C_4H_8O	$(CH_2)_2O(CH_2)_2$	3	from no. 239	242
243	$C_4H_8O_2$	$CH_2(CHOH)_2CH_2$	3	from no. 145	260 (62%)
244	$C_5H_6O_2$	$C(O)(CH_2)_3C(O)$	2	L	242
245	$C_5H_6O_2$	$C(O)(CH_2)_3C(O)$	3	L	242
246	$C_5H_8N_2O$	2-oxotetrahydroimidazol-1,3-$(CH_2)_2$-diyl	1	N	158 (95%)
247	C_5H_{10}	$(CH_2)_5$	2	from no. 244	242
248	C_5H_{10}	$(CH_2)_5$	3	from no. 245	242
249	$C_7H_{14}O_2$	2,2-Me_2-1,3-dioxolan-4,5-$(CH_2)_2$-diyl	2	L	260 (34%)
250	$C_{12}H_8O_2Fe$	C(O)-ferrocene-C(O)	2	L	261 (85%)
251	$C_{12}H_8O_2Fe$	C(O)-ferrocene-C(O)	3	L	261 (80%)
252	$C_{12}H_8O_2Ru$	C(O)-ruthenocene-C(O)	2	L	262
253	$C_{12}H_8O_2Ru$	C(O)-ruthenocene-C(O)	3	L	262
254	$C_{12}H_{22}O_5$	2-CH_2-15-crown-5-3-CH_2	2	from no. 241	260 (23%)
	$C_{14}H_{26}O_6$	2-CH_2-15-crown-6-3-CH_2	3	from no. 243	260 (21%)
255	$C_{14}H_8N_2O_2$	$C(O)C_6H_4N{=}NC_6H_4C(O)$	2	J	253 (72%)
256	$C_{14}H_{12}N_2$	$CH_2C_6H_4N{=}NC_6H_4CH_2$	2	J	253 (36%)
257	$C_{15}H_{30}$	$CH_2CH(C_{12}H_{25})CH_2$	1	L	52 (28%); 225
				N/A	157, 226
258	$C_{15}H_{30}$	$CH_2CH(C_{12}H_{25})CH_2$	2	L	52 (22%); 225
				N/A	157, 226
259	$C_{15}H_{30}$	$CH_2CH(C_{12}H_{25})CH_2$	3	L	52 (19%); 225
				N/A	157
260	$C_{19}H_{38}O_2$	$(C_{12}H_{25})CH[CH_2O(CH_2)_2]_2$	1	L	52 (36%)
				N/A	157
261	$C_{19}H_{38}O_2$	$(C_{12}H_{25})CH[CH_2O(CH_2)_2]_2$	2	L	52 (30%)
				N/A	157
262	$C_{19}H_{38}O_2$	$(C_{12}H_{25})CH[CH_2O(CH_2)_2]_2$	3	L	52 (23%)
				N/A	157
263	$C_{20}H_{36}O_4$	$(C_{12}H_{25})(Me)C[CO_2(CH_2)_2]_2$	1	M	52 (20%)
				N/A	157
264	$C_{20}H_{36}O_4$	$(C_{12}H_{25})(Me)C[CO_2(CH_2)_2]_2$	2	M	52 (21%)
				N/A	157
265	$C_{20}H_{36}O_4$	$(C_{12}H_{25})(Me)C[CO_2(CH_2)_2]_2$	3	M	52 (18%)
				N/A	157

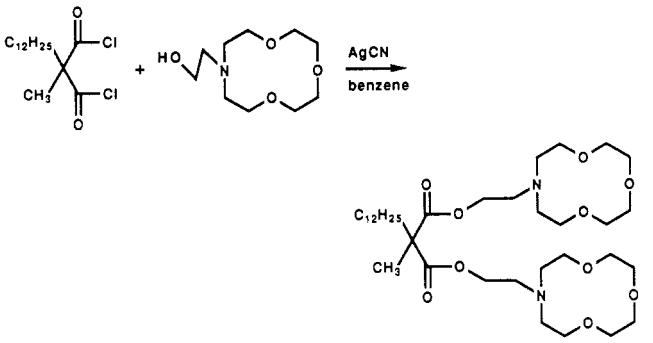
One additional method to prepare *N*-alkyl-substituted aza-crowns is the alkylation of an already cyclized aza-crown (method J).[10,144,146,154,155] Ethylene oxide or 2-bromoethanol has been used to prepare *N*-(2-hydroxyethyl)-substituted aza-crowns (method K).[83,154,156] The resulting *N*-(2-hydroxyethyl) product can be converted to the *N*-(2-chloroethyl) derivative. Dihalo or ditosyl compounds have been used to bridge two monoaza-crowns to prepare ligands with higher ion selectivities (method L).[52,149] Bridged monoaza-crowns were also prepared by reacting a bis acid chloride with *N*-(2-hydroxyethyl)aza-crown (method M),[52,157] by the reaction of a monoaza-crown with formaldehyde in methanol followed by treatment with a cyclic urea



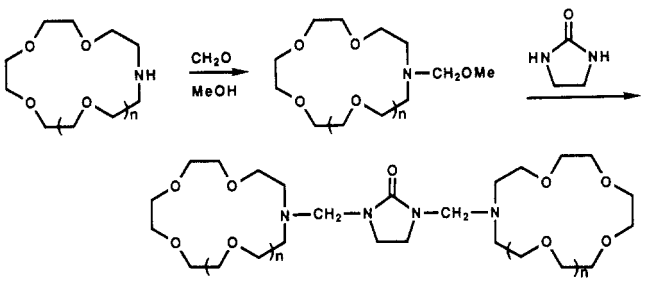


(method N),[158] and by the biscyclization of *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine with 2 mol of triethylene glycol ditosylate (method O).[159]

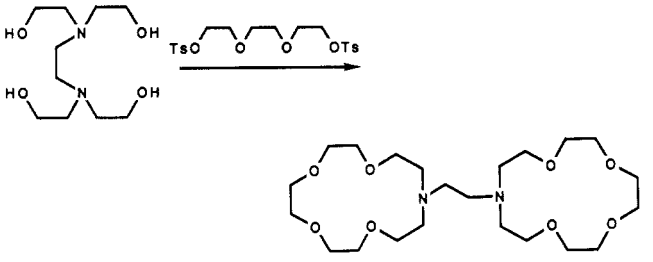
Method M



Method N



Method O



A listing of monoaza-crowns is given in Table I.

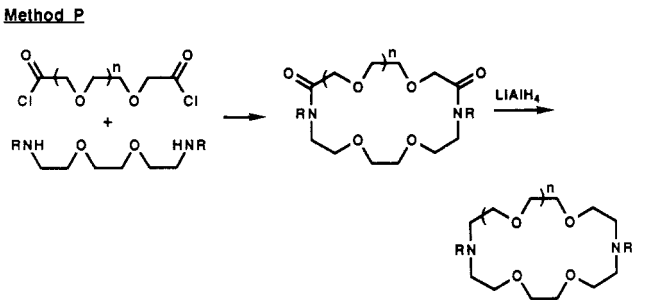
B. Diaza-Crowns (Table II)

The diaza-crowns are most important because they are key intermediates in the synthesis of cryptands and other N-substituted ligands.[8,9,128,129] The diaza-crowns also have complexing properties that are similar to those of certain biological systems.[2] Diaza-crowns that have no substituents on nitrogen or that have functional groups substituted on nitrogen are also useful for the synthesis of macrotricyclic ligands.[1,9,131] In addition, cryptands that are formed from diaza-crowns can be attached to synthetic polymers.[51,161-163] Diaza-crowns have also been attached to silica gel.[16]

Lehn and co-workers used the Stetter method (method P) to prepare the first diaza-crown compounds.[128,129] This method requires the simultaneous addition of the diacid dichloride and the diamine in the ring-closure step as was discussed in section III.B.

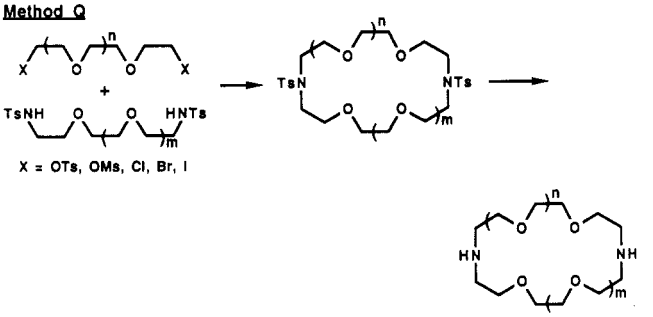
Richman and Atkins prepared the *N,N'*-bis(*p*-toluenesulfonamide) derivative of diaza-18-crown-6 by reacting the ditosyl derivative of triethylene glycol with the *N,N'*-bis(*p*-toluenesulfonamide) of triethylene glycol diamine (method Q).[94,95] The method to remove the

Method P



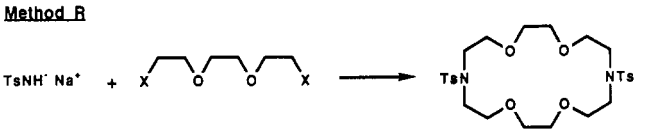
N-tosyl groups by reduction with lithium aluminum hydride is the preferred procedure to deblock the amino nitrogen atoms to prepare unsubstituted aza-crowns.[2,131,164]

Method Q



Vögtle and co-workers used the reaction of sodium *p*-toluenesulfonamide with the ditosylate (or dichloride) derivative of triethylene glycol to form the *N,N'*-ditosyldiaza-18-crown-6 (method R).[103] They compared

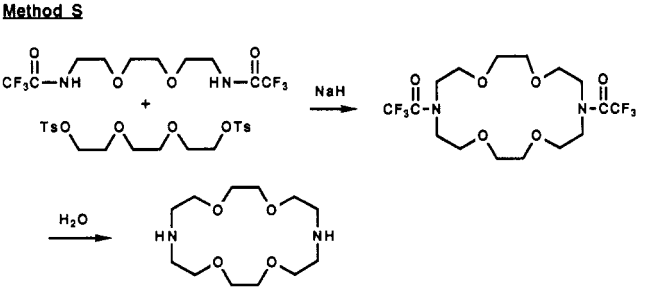
Method R



methods P, Q, and R and reported the best overall yield for method P (37%), then method Q (13%), and finally method R (9–14%). Their calculations did not include removal of the tosyl group (methods Q and R) or amide reduction (method P).

King and Krespan used the bis(trifluoroacetamide) derivatives rather than the bis(*p*-toluenesulfonamide) derivatives in their preparation of the diaza-crowns (method S).[60] The removal of the trifluoroacetyl group

Method S

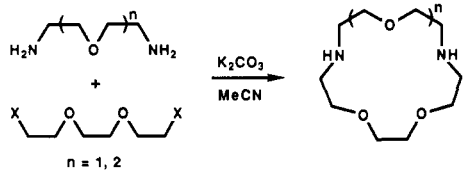


was accomplished by a simple hydrolysis step rather than the more difficult reduction process that was used to remove the tosyl protecting groups of method Q. Even with this modification, the overall yield for method S was only 3%, similar to that obtained by the same authors for a simple autoclave reaction of triethylene glycol dichloride with an excess of ammonia.[60]

Kulstad and Malmsten reported that the diaza-crowns could be prepared by reacting a diamino ether

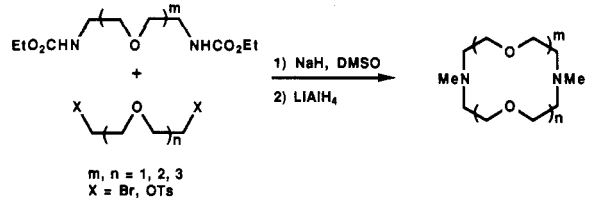
with a diiodo ether with sodium or potassium carbonate as the base (method T).[70,104] The yield was 17% for diaza-15-crown-5 but 44% for diaza-18-crown-6. The best yields were obtained when the cation size matched the cavity size.[165]

Method T



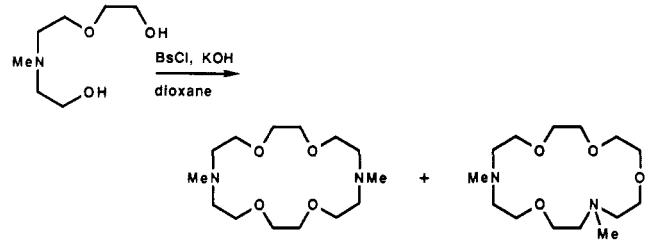
Sutherland and co-workers used ethyl carboxylate protecting groups on the diamine when they reacted an oligo(ethyleneoxy) bis(carbamate) with a ditosylate or dihalide to form an *N,N'*-bis(ethoxycarbonyl)substituted diaza-18-crown-6. The ethoxycarbonyl groups were reduced to form the bis-methyl-substituted crowns (method U).[166,167]

Method U



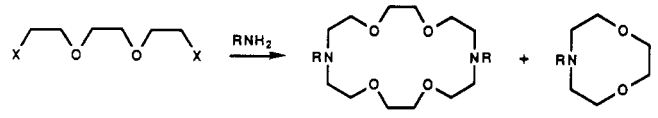
Okahara and co-workers, in an attempt to prepare aza-9-crown-3, reacted an azatriethylene glycol with benzenesulfonyl chloride. The small crown was not obtained but rather two diaza-18-crown-6 compounds (method V)[109] resulting from different dimerization pathways.

Method V



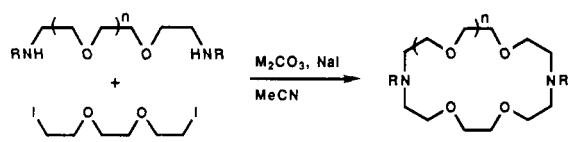
Gokel and co-workers prepared a series of N,N'-disubstituted diaza-18-crown-6 compounds by a 2:2 reaction of a primary amine with triethylene glycol dihalide (method W).[71,77,168] Only the diaza-18-crown-6

Method W



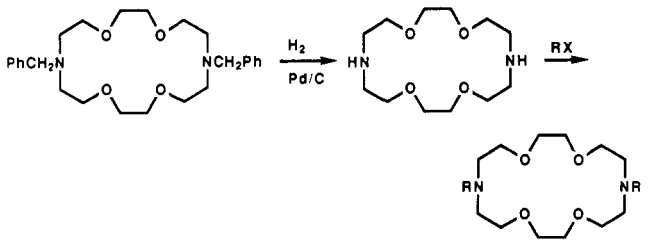
was observed when R was a benzylic or aliphatic group. When R was a 4-substituted phenyl, only the 1:1 adduct, aza-9-crown-3, was isolated. The diaza-18-crown-6 (and crown-5) compounds were prepared by these authors by a procedure similar to methods S, T, and U except they reacted an *N,N'*-dialkyl-substituted diamine with 1,8-diiodo-3,6-dioxaoctane (method X).[71,77] They found that method X gave superior overall yields. For example, *N,N'*-dibenzyldiaza-18-crown-6 was prepared in a 66% yield by method X but in only 29% yield by method W. The product was more difficult to isolate in the one-step synthesis of method W because of the many products that were formed.

Method X



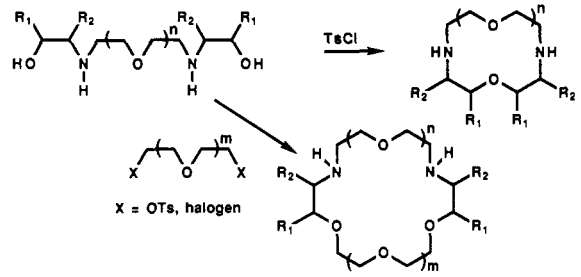
The *N,N'*-dibenzyldiaza-crowns are important because they can be readily hydrogenated to form the diaza-crowns. The diaza-crown can then be alkylated to form different *N,N'*-dialkyldiaza-18-crown-6 compounds (method Y).[71]

Method Y



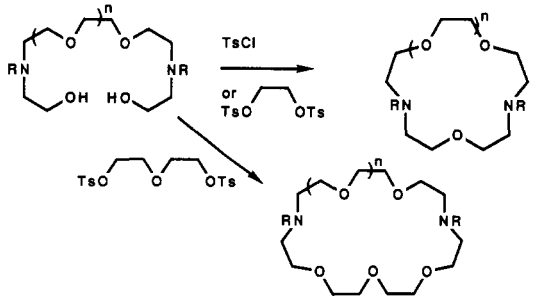
Okahara and co-workers prepared a number of diaza-crown compounds with substituents on the carbon atoms of the macroring. They used both the Okahara ring-closure reaction of a substituted diazaoligoethylene glycol with tosyl chloride and the reaction of the glycol with a ditosylate (method Z).[85,142,169]

Method Z



Bradshaw and Krakowiak prepared *N,N'*-dialkyldiaza-15-crown-5, -18-crown-6, and -21-crown-7, compounds by similar reactions except that the nitrogen atoms contained alkyl substituents (method AA).[80] They obtained excellent yields of the diaza-crowns.

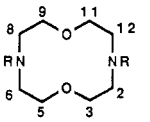
Method AA



As mentioned in section IV.A, crown ethers containing functional substituents, such as hydroxymethyl or vinyl groups, are important synthetic intermediates

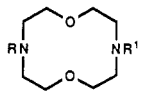
TABLE II. Diaza-Crown Compounds

A. Diaza-12-Crown-4



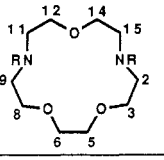
entry no.	R		method	ref (yield)
	formula index	structure		
266	H	H	Q	100 (68%); 263, 264
			N/A	219, 265, 266
267	CH_3	Me	from no. 266	266 (95%)
			N/A	141, 267
268	$C_2H_3O_2$	HO_2CCH_2	from no. 266	268, 269
269	C_2H_4Cl	$Cl(CH_2)_2$	K	219 (90% HCl); 270 (91%)
270	C_2H_5O	$HO(CH_2)_2$	K	219; 270 (94%)
			N/A	271
271	C_3H_7O	$MeO(CH_2)_2$	Y(alk)	263 (64%)
			Y(alk)	264
			N/A	272
272	$C_4H_5O_4$	$HO_2CCH_2OCH_2C(O)$	other	270 (90%); 273
273	C_4H_8ClO	$Cl(CH_2)_2O(CH_2)_2$	from no. 275	219, 270 (90%); 273
274	C_4H_8NO	Me_2NCOCH_2	Y(alk)	271 (90%)
275	$C_4H_9O_2$	$H(OCH_2CH_2)_2$	from no. 272	219 (91%); 270 (92%); 272
276	C_4H_9O	$EtO(CH_2)_2$	N/A	272
277	$C_5H_9O_2$	$BuCO_2$	from no. 266	274 (87%)
278	$C_5H_{10}NO$	$Me_2NCO(CH_2)_2$	Y(alk)	271 (86%)
279	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$	Y(alk)	263 (65%)
			Y(alk)	264
			N/A	272
280	$C_6H_{13}O$	$BuO(CH_2)_2$	N/A	272
281	$C_7H_7O_2S$	Ts	Q	100 (82%); 263
			R	223 (5%)
282	$C_7H_{15}O_3$	$Me(OCH_2CH_2)_3$	Y(alk)	263 (37%)
			Y(alk)	264
			N/A	272
283	$C_8H_{17}O_2$	$Bu(OCH_2CH_2)_2$	Y(alk)	263 (48%); 264
			N/A	272
284	$C_9H_{12}NO_2S$	$TsNH(CH_2)_2$	from no. 266	275 (91%)
285	$C_{14}H_{14}P$	$Ph_2P(CH_2)_2$	other	219 (44%); 270 (45%)
286	$C_{16}H_{18}OP$	$Ph_2P(CH_2)_2O(CH_2)_2$	from no. 273	219, 270 (45%)

B. Diaza-12-Crown-4 (R and R^1 Different)



entry no.	R	R^1	method	ref (yield)
287	H	$BuCO_2$	from no. 277	274 (68%)
288	H	$PhCH_2$	from no. 291	88, 276 (91%)
289	H	Ts	from no. 290	265 (80%)
290	$EtCO_2$	Ts	from no. 291	265 (90%)
291	$PhCH_2$	Ts	other	88 (60%); 276 (58%)
			N/A	265

C. Diaza-15-Crown-5

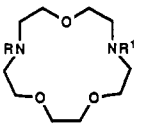


entry no.	R		other substituents	method	ref (yield)
	formula index	structure			
292	H	H		P	277 (85%)
				Q	100 (58%); 278 (47%)
				Y	71 (91%); 77 (66% overall)
				Z	85 (26%); 112 (37%); 169
				N/A	73, 266, 279
293	H	H	$12,14\text{-}Me_2$	Z	85 (17%)
294	H	H	$11,15\text{-}Et_2$	Z	85 (12%)
295	H	H	$11,15\text{-}(O)_2$	P	277 (60%)
296	H	H	$5\text{-}CH_2OH$	AE	50 (78%)
297	H	H	$2,9\text{-}(O)_2$; $5\text{-}CH_2OH$	AE	50 (74%)
298	H	H	$2,9\text{-}(O)_2$; $5\text{-}CH_2O$-allyl	AE	50 (43%)
299	H	H	$2,9\text{-}Ph_2$; $3,8,11,15\text{-}(O)_4$	other	280 (20%)

TABLE II (Continued)

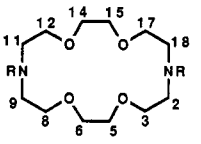
entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
300	CH_3	Me		N/A	141
				from no. 292	266 (60%)
				X, other	78 (48%)
				N/A	73, 281, 267
301	CH_3	Me	2,6,9-$(O)_3$	P	282 (35%)
302	CH_3	Me	2,6,9-$(O)_3$; 8-CH_2Ph	P	282 (34%)
303	$C_2H_3O_2$	HO_2CCH_2		Y(alk)	268, 269
				N/A	234, 283
304	$C_2H_3O_2$	$MeCO_2$		Y(alk)	71 (62%)
305	C_3H_4N	$CN(CH_2)_2$		from no. 292	281 (93%)
306	C_3H_6NO	$H_2NCH(Me)C(O)$		from no. 327	73 (95%)
307	C_3H_7O	$MeO(CH_2)_2$		X	71, 77 (38%)
				Y(alk)	278
				N/A	272
308	C_3H_8N	$NH_2(CH_2)_3$		other	281
				N/A	284
309	$C_4H_5O_4$	$HO_2CCH_2OCH_2C(O)$		from no. 292	273
310	C_4H_8ClO	$Cl(CH_2)_2O(CH_2)_2$		from no. 311	273 (80–90%)
311	$C_4H_9O_2$	$H(OCH_2CH_2)_2$		from no. 309	273 (80–90% from 292)
312	C_5H_5O	2-furanyl-CH_2		X	71, 77 (67%)
				Y(alk), other	285
313	$C_5H_9O_2$	$BuCO_2$		other	274 (45%)
314	$C_5H_{10}NO_2$	$HOCH_2CH(Me)NHCOCH_2$		Y(alk)	73 (72%)
315	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$		Y(alk)	278
				N/A	272
316	$C_6H_4NO_2$	2-$NO_2C_6H_4$		Y(alk)	71 (50%)
317	C_6H_5	Ph	5,6-Me_2; 2,9-$(O)_2$	P	75 (66%)
318	C_6H_7N	2-pyridinyl-CH_2		N/A	286
319	$C_6H_{13}O$	$BuO(CH_2)_2$		Y(alk)	278
				N/A	272
320	$C_7H_6NO_3$	2-OH-5-$NO_2C_6H_3CH_2$		Y(alk)	279, 287, 288
321	C_7H_7	$PhCH_2$		AA	49 (65%); 80 (73%, 78%)
				X	71, 77 (72%)
322	C_7H_7	$PhCH_2$	5-CH_2O-allyl	X	175 (72%)
323	C_7H_7	$PhCH_2$	5,6-Me_2; 2,9-$(O)_2$	P	75 (48%)
324	C_7H_7O	2-$OHC_6H_4CH_2$		Y(alk)	287 (64%)
325	$C_7H_7O_2S$	Ts		Q	100 (77%); 278
326	C_8H_9O	2-$MeOC_6H_4CH_2$		X	71, 77 (52%)
327	$C_8H_{14}NO_3$	$BuCO_2NHCH(Me)CO$		from no. 292	73 (77%, 95%)
328	$C_8H_{17}NO_2$	$Bu(OCH_2CH_2)_2$		Y(alk)	278
				N/A	272
329	$C_9H_{12}NO_2S$	$TsNH(CH_2)_2$		from no. 292	275 (75%); 289 (64%)
330	$C_{10}H_{12}NO_2$	$HOCH_2CH(Ph)NHCOCH_2$		Y(alk)	73 (46%)
331	$C_{11}H_{14}NO_2$	$HOCH_2CH(CH_2Ph)NHCOCH_2$		Y(alk)	73 (44%)
332	$C_{13}H_{10}N_3O_3$	5-(4-$NO_2C_6H_4N{=}N$)-2-$OHC_6H_3CH_2$		other	287 (12%)

D. Diaza-15-Crown-5 (R and R^1 Different)



entry no.	R	R^1	method	ref (yield)
333	H	t-$BuCO_2$	other	290
334	H	$BuCO_2$	other	274 (59%)
335	$CH_2{=}CH$	t-$BuCH_2MgO(CH_2)_2$	other	291

E. 1,10-Diaza-18-Crown-6



entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
336	H	H		Q	100 (63%)
				T	71 (30%); 263; 264; 292; 293 (30%)
				W, Y from no. 436	77 (27% overall); 168, 294 (92%); 292
				X, Y	71 (92%); 77 (63%, two steps)
				P	159 (56%)

TABLE II (Continued)

entry no.	R formula index	R structure	other substituents	method	ref (yield)
337	H	H	5-CH_2OH	AE	50 (72%)
338	H	H	5-CH_2OH; 2,9-$(O)_2$	AE	50 (77%)
339	H	H	5-CH_2O-allyl; 2,9-$(O)_2$	AE	50 (51%)
340	H	H	3-CH_2Ph; 2,5,9-$(O)_3$	N/A	295
341	H	H	5,6-$(CH_2OCH_2Ph)_2$	N/A	296
342	H	H	5,6-$(CH_2OCH_2Ph)_2$; 2,9-$(O)_2$	N/A	296
343	CClO	ClC(O)		Y(alk)	230 (69%)
344	CS_2	S_2C		other	297 (93% Et_2NH^+)
345	CH_3	Me		X, other	78 (55%)
				from no. 372	159 (91%)
				other	266 (98%)
				N/A	71, 267
346	CH_3	Me	5,6-CH_2OCH_2Ph	from no. 341	296 (98%)
347	CH_3O_3S	HO_3SCH_2		from no. 336	159 (50% Na salt)
348	CH_4O_2P	$H_2PO_2CH_2$		from no. 336	159 (74%)
349	CH_4O_3P	$H_2O_3PCH_2$		from no. 336	159 (84%)
				N/A	234
350	C_2H_2N	$CNCH_2$		Y(alk)	298 (75%)
351	C_2H_2IO	$ICH_2C(O)$		N/A	399
352	$C_2H_3O_2$	MeOC(O)		other	71 (81%)
353	$C_2H_3O_2$	HO_2CCH_2		Y(alk)	268
				from no. 392	168, 294 (81%)
				N/A	269, 283, 300
354	C_2H_4Cl	$Cl(CH_2)_2$		as K	159 (69% HCl)
355	C_2H_4NO	MeNHC(O)		from no. 343	230 (88%)
356	C_2H_4NO	$H_2NC(O)CH_2$		N/A	301
357	C_2H_4NO	$H_2NCH_2C(O)$		from no. 479	293 (92%)
358	C_2H_5	Et	5-CH_2O-allyl	AF	49 (63%); 87
359	C_2H_5O	$MeOCH_2$		from no. 336	158, 302 (82%)
				N/A	303, 304
360	C_2H_5O	$HO(CH_2)_2$		W	71, 168, 294 (28%)
				Y(alk)	305 (52%)
				as K	159 (84%), 306 (62%)
				N/A	307
361	$C_2H_5O_3S$	$HO_3S(CH_2)_2$		from no. 354	159
362	$C_2H_5O_4S$	$HO_3SO(CH_2)_2$		from no. 360	159 (79%)
363	C_2H_6N	$H_2N(CH_2)_2$		from no. 477	159 (91%); 305 (52% overall)
364	$C_2H_6O_3P$	$H_2O_3P(CH_2)_2$		from no. 354	159 (74%)
365	$C_2H_6O_4P$	$H_2O_3PO(CH_2)_2$		from no. 510	159 (74%)
366	C_3H_3	propargyl		W	71, 298 (22%)
367	$C_3H_3O_4$	$(HO_2C)_2CH$		from no. 446	159 (65%)
368	C_3H_4ClO	$ClC(O)(CH_2)_2$		from no. 373	308
369	C_3H_4N	$NC(CH_2)_2$		from no. 336	159 (99%); 308
370	C_3H_5	allyl		W	71, 168, 294, 298 (26%)
371	C_3H_5O	EtC(O)		Y(alk)	71 (100%)
372	$C_3H_5O_2$	EtO_2C		Y(alk)	159 (76%)
373	$C_3H_5O_2$	$HO_2C(CH_2)_2$		Y(alk)	309 (82%)
				from no. 369	159 (79%); 300
				from no. 394	308
				N/A	234
374	$C_3H_5O_2$	$MeOCH_2C(O)$		Y(alk)	186, 294 (80%)
375	$C_3H_5O_2$	$HO_2CCH(Me)$		Y(alk)	268
				N/A	269, 283
376	C_3H_6N	aziridinyl-CH_2		from no. 359	302 (92%)
				from no. 336	302 (94%)
377	C_3H_6Cl	$Cl(CH_2)_3$		as K from no. 382	219 (88% HCl)
378	C_3H_6NO	$H_2NC(O)(CH_2)_2$		from no. 394	159 (58%)
379	C_3H_6NO	$H_2N(CH_2)_2C(O)$		from no. 487	293 (92%)
380	C_3H_6NO	$H_2NCH(Me)C(O)$		from no. 486	293 (97%)
381	C_3H_7	Pr		Y(alk)	305 (70%)
				from no. 371	12; 71, 298 (78%)
				N/A	307
382	C_3H_7O	$HO(CH_2)_3$		from no. 410	159 (98%)
				from no. 394	219 (67%)
383	C_3H_7O	$MeO(CH_2)_2$		X	71, 77 (43%)
				Y(alk)	263 (54%); 264
				from no. 374	168, 294 (97%)
				N/A	272, 298, 301, 307
384	$C_3H_7O_4S$	$HO_3SO(CH_2)_3$		from no. 382	159 (40%)
385	C_3H_8N	$H_2N(CH_2)_3$		from no. 482	305 (45% overall)
386	$C_3H_8NO_2$	$(MeO)_2NCH_2$		from no. 359	304 (100%)
387	$C_4H_4O_3$	$HO_2CCH{=}CHC(O)$		from no. 336	159 (55%)
388	$C_4H_5N_2$	imidazolyl-CH_2		from no. 359	158 (96%)
389	$C_4H_5O_3$	$HO_2C(CH_2)_2C(O)$		from no. 336	159 (83%)
390	$C_4H_5O_4$	$HO_2CCH_2CH(CO_2H)$		from no. 336	159 (5%)

TABLE II (Continued)

entry no.	R formula index	R structure	other substituents	method	ref (yield)
391	$C_4H_5O_4$	$HO_2CCH_2OCH_2C(O)$		from no. 336	273
392	$C_4H_7O_2$	$EtOC(O)CH_2$		Y(alk)	71, 168 (92%); 12; 294 (92%)
				N/A	301
393	$C_4H_7O_2$	$HO_2C(CH_2)_3$		N/A	309
394	$C_4H_7O_2$	$MeO_2C(CH_2)_2$		from no. 336	159; 219 (78%); 308
395	C_4H_8ClO	$Cl(CH_2)_2O(CH_2)_2$		from no. 400	273 (80–90%)
396	C_4H_8NO	$H_2NCH(Et)C(O)$		from no. 492	293 (97%)
397	C_4H_8NO	$H_2N(CH_2)_3C(O)$		from no. 491	293 (91%)
398	$C_4H_8NO_2$	$O_2NC(Me)_2CH_2$		from no. 359	302 (93%)
399	C_4H_9	Bu		X	71, 77 (77%)
400	$C_4H_9O_2$	$H(OCH_2CH_2)_2$		from no. 391	273 (80–90% from no. 336)
401	$C_4H_{10}O_6S_2$	$(HO_3SCH_2)_2N(CH_2)_2$		from no. 363	159 (46%)
402	C_5H_3OS	2-thiophenyl-C(O)		Y(alk)	285, 310
403	$C_5H_3O_2$	2-furanyl-C(O)		Y(alk)	285, 310
404	C_5H_5O	2-furanyl-CH_2		W	71, 77, 168, 294 (27%)
				X	71, 77 (62%)
				from no. 403	285, 310
				N/A	286, 311, 312
405	C_5H_5S	2-thiophenyl-CH_2		from no. 402	285, 310 (60% from no. 336)
				N/A	312
406	$C_5H_6NO_2$	succinimidyl-CH_2		from no. 359	158 (90%)
407	$C_5H_6NO_3$	2,6-dioxomorpholinyl-CH_2		from no. 359	158 (86%)
408	C_5H_8NO	2-oxopyrrolidinyl-CH_2		from no. 359	158 (95%)
409	$C_5H_8NO_3$	$MeCO_2CH_2NHC(O)CH_2$		Y(alk)	12
410	$C_5H_9O_2$	$EtO_2C(CH_2)_2$		from no. 336	159 (98%)
411	$C_5H_{10}NO$	$H_2NCH(i\text{-}Pr)C(O)$		from no. 506	293 (93%)
412	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$		Y(alk)	263 (36%); 264
413	$C_5H_{12}N$	$H_2N(CH_2)_5$		from no. 505	305 (41% overall)
414	C_6H_5	Ph		P	313 (71%)
				N/A	314
415	C_6H_5	Ph	1,8-$(O)_2$	P	313 (73%)
416	C_6H_6N	(2-NH_2)C_6H_4		P from no. 503	313 (70%)
417	C_6H_6N	2-picolinyl		W	168, 294 (22% NaI)
				N/A	286
418	C_6H_6N	4-picolinyl		N/A	286
419	$C_6H_6NO_2S$	4-$NH_2C_6H_4SO_2$		Y(alk)	238
420	$C_6H_8NO_2$	glutarimidyl-CH_2		from no. 359	158 (99%)
421	$C_6H_{10}NO_3$	$MeOC(O)CH(CH_3)NHC(O)CH_2$		Y(alk)	12
422	$C_6H_{10}NO_4$	$(HO_2CCH_2)_2N(CH_2)_2$		from no. 363	159 (65%)
423	$C_6H_{12}NO$	$H_2NCH(i\text{-}Bu)C(O)$		from no. 512	293
424	C_6H_{13}	C_6H_{13}		W	71, 77 (7%)
				X	71, 77 (32%)
				Y (alk)	71 (50%)
425	C_6H_{13}	C_6H_{13}	5-CH_2OH	AE	49 (50%); 87
426	C_6H_{13}	C_6H_{13}	5-CH_2O-allyl	AE	49 (35%); 87
427	C_6H_{13}	C_6H_{13}	2,9-$(O)_2$; 5-CH_2O-allyl	AE	49 (42%); 87
428	$C_7H_3N_2O_6$	2,6-$(NO_2)_2$-4-$CO_2HC_6H_2$		Y(alk)	243 (80%)
429	C_7H_5O	PhCO		Y(alk)	315 (78%)
430	C_7H_6Cl	2-$ClC_6H_4CH_2$		Y(alk)	239 (82%)
431	C_7H_6Cl	4-$ClC_6H_4CH_2$		Y(alk)	239 (75%)
432	$C_7H_6NO_2$	2-$NO_2C_6H_4CH_2$		Y(alk)	239 (90%)
433	$C_7H_6NO_2$	3-$NO_2C_6H_4CH_2$		Y(alk)	71 (95%)
434	$C_7H_6NO_2$	4-$NO_2C_6H_4CH_2$		Y(alk)	71 (70%); 239
435	$C_7H_6NO_3$	2-OH-5-$NO_2C_6H_3CH_2$		Y(alk)	279 (90%); 288; 287 (75%)
436	C_7H_7	$PhCH_2$		W	71, 77, 168, 294 (29%)
				X	71 (66%); 78 (68%); 239 (66%)
				Y(alk)	285; 310 (60%)
				from no. 429	315 (92%)
				N/A	286, 298, 310, 311, 312, 316
437	C_7H_7	$PhCH_2$	5-CH_2OH	AE	49 (60%); 87
438	C_7H_7	$PhCH_2$	5-CH_2O-allyl	AE	49 (15%); 87
				AF	49 (62%); 87
				X	49 (80%)
				other	49 (30%)
439	C_7H_7	$PhCH_2$	5,6-Me_2; 2,9-O_2	P	76 (50%)
440	C_7H_7	$PhCH_2$	5-CH_2O-allyl; 2,9-$(O)_2$	AE	49 (40%); 87
441	C_7H_7	$PhCH_2$	5,6-$(CH_2OCH_2Ph)_2$	from no. 341	296 (64%)
442	C_7H_7O	2-$OHC_6H_4CH_2$		Y(alk)	287 (54%)
				Y	71 (85%)
				from no. 464	168, 294 (85% from no. 336)

TABLE II (Continued)

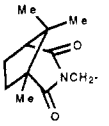
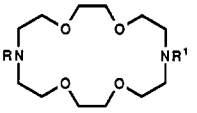
entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
443	$C_7H_7O_2S$	Ts		Q	100 (80%)
444	$C_7H_7O_2S$	Ts	3,8,12,17-$(O)_4$	other	223 (12%)
445	C_7H_9N	pyridinyl-$(CH_2)_2$		from no. 360	159 (72% HCl)
446	$C_7H_{11}O_4$	$(EtCO_2)_2CH$		Y(alk)	159 (23%)
447	$C_7H_{15}O_3$	$Me(OCH_2CH_2)_3$		Y(alk)	263 (30%); 264
				N/A	272
448	$C_8H_5N_2O_6$	2,6-$(NO_2)_2$-4-$CO_2MeC_6H_2$		Y(alk)	243 (92%)
449	$C_8H_5N_2O_6$	2,4-$(NO_2)_2$-6-$CO_2MeC_6H_2$		Y(alk)	243 (88%)
450	C_8H_6N	2-$CNC_6H_4CH_2$		Y(alk)	71 (96%); 239 (90%)
451	C_8H_6N	4-$CNC_6H_4CH_2$		Y(alk)	239 (91%)
452	$C_8H_7O_2S$	2-$SHC_6H_4OCH_2C(O)$		from no. 485	318
453	C_8H_8NO	$H_2NCH(Ph)C(O)$		from no. 521	293 (93%)
454	C_8H_8NO	$PhCH_2NHC(O)$		from no. 343	230 (94%)
455	C_8H_9O	2-$MeOC_6H_4CH_2$		W	71, 77, 168, 239, 294 (30%)
456	C_8H_9O	4-$MeOC_6H_4CH_2$		Y(alk)	239 (91%)
457	$C_8H_{10}N_5$	adeninyl-$(CH_2)_3$		Y(alk)	317 (58%)
458	$C_8H_{11}N_2O_2$	thyminyl-$(CH_2)_3$		Y(alk)	317 (49%)
459	$C_8H_{14}NO_3$	$MeO_2CCH(i\text{-}Pr)NHC(O)CH_2$		Y(alk)	12
460	$C_8H_{15}O$	$C_7H_{15}C(O)$		Y	71 (71%)
461	C_8H_{17}	C_8H_{17}		from no. 460	71 (63%)
462	$C_8H_{17}O_2$	n-$Bu(OCH_2CH_2)_2$		Y	263 (42%); 264
				N/A	272
463	$C_9H_6NO_2$	phthalimidyl-CH_2		from no. 359	158 (87%)
464	$C_9H_9O_2$	$MeCO_2C_6H_4CH_2$		Y(alk)	168
465	$C_9H_{10}NO$	$H_2NCH(CH_2Ph)C(O)$		from no. 525	293 (96%)
466	$C_9H_{10}NO$	$PhCH(Me)NHC(O)$		from no. 343	230 (89%)
467	$C_9H_{10}NO_2$	1,2,3,6-H_4-phthalimidyl-CH_2		from no. 359	158 (99%)
468	$C_9H_{12}NO_2$	$PhCH_2ON(OMe)CH_2$		from no. 359	304 (92%)
469	$C_9H_{12}NO_2S$	$TsHN(CH_2)_2$		Y(alk)	289
				from no. 336	275 (98%); 319 (99%)
470	$C_9H_{12}NO_2S$	$MeN(Ts)CH_2$		from no. 359	303 (98%)
471	$C_9H_{16}NO_3$	$MeO_2CCH(s\text{-}Bu)NHC(O)CH_2$		Y(alk)	12
472	$C_9H_{16}NO_3$	$MeO_2CCH(i\text{-}Bu)NHC(O)CH_2$		Y(alk)	12
473	$C_9H_{17}O$	$C_8H_{17}C(O)$		Y(alk)	71 (71%)
474	C_9H_{19}	C_9H_{19}		W	71, 77 (11%)
				Y(alk)	71 (45%); 285
				from no. 473	71 (63%)
				N/A	310, 312
475	$C_{10}H_8$	azulenyl		other	11 (4%)
476	$C_{10}H_8N$	2-quinolinyl-CH_2		N/A	286
477	$C_{10}H_8NO_2$	phthalimidyl-$(CH_2)_2$		from no. 354	159
				Y(alk)	305
478	$C_{10}H_{10}NO_3$	2-$(HO_2C(CH_2)_2C(O)NH)C_6H_4$		from no. 416	313 (50%)
479	$C_{10}H_{10}NO_3$	$PhCH_2O_2CNHCH_2C(O)$		N/A	320
				from no. 336	293 (95%)
480	$C_{10}H_{19}O$	$C_9H_{19}C(O)$		Y	71 (100%)
				from no. 480	71 (96%)
481	$C_{10}H_{21}$	$C_{10}H_{21}$		N/A	321
482	$C_{11}H_{10}NO_2$	phthalimidyl-$(CH_2)_3$		Y(alk)	305
483	$C_{11}H_{10}NO_4$	$MeO_2CCH_2NHC(O)C_6H_4C(O)$		from no. 336	322 (40%)
384	$C_{11}H_{11}N_2O$	$NH_2CH(indolyl\text{-}CH_2)C(O)$		from no. 526	293 (98%)
485	$C_{11}H_{11}O_3$	$PhCH_2O_2C(CH_2)_2C(O)$		N/A	320
486	$C_{11}H_{11}O_3S_2$	2-$[EtO(S)CS]C_6H_4OCH_2C(O)$		from no. 336	318
487	$C_{11}H_{12}NO_3$	$PhCH_2O_2CNHCH(Me)C(O)$		other	293 (90%, 92%, 94%)
488	$C_{11}H_{12}NO_3$	$PhCH_2O_2CNH(CH_2)C(O)$		from no. 336	293 (89%)
489	$C_{11}H_{16}NO_2$			from no. 359	158 (92%)
490	$C_{12}H_{12}NO_4$	2-$[MeO_2CCH(Me)NHC(O)]C_6H_4C(O)$		from no. 336	322 (37%)
491	$C_{12}H_{14}NO_3$	$PhCH_2O_2CNH(CH_2)_3C(O)$		from no. 336	293 (87%)
492	$C_{12}H_{14}NO_3$	$PhCH_2O_2CNHCH(Et)C(O)$		from no. 336	293 (91%)
493	$C_{12}H_{14}NO_3$	2-$[EtO(CH_2)_2NHC(O)]C_6H_4C(O)$		from no. 336	322 (56%)
494	$C_{12}H_{16}NO_4S$	$EtO_2CCH_2N(Ts)CH_2$		from no. 359	303 (87%)
495	$C_{12}H_{20}NO_3S$	camphoryl-$SO_2N(Me)CH_2$		from no. 359	303 (87%)
496	$C_{12}H_{22}O_2$	menthyl-$CH_2C(O)$		Y(alk)	296 (72%)
497	$C_{12}H_{23}O$	$C_{11}H_{23}C(O)$		Y(alk)	71 (87%)
498	$C_{12}H_{24}O$	menthyl-$(CH_2)_2$		from no. 496	296 (53%)
499	$C_{12}H_{25}$	$C_{12}H_{25}$		from no. 497	71 (45%)
				W	71 (11%)
500	$C_{13}H_7N_2O_5$	2,4-$(NO_2)_2$-6-$PhC(O)C_6H_2$		Y(alk)	243 (76%)
501	$C_{13}H_9N_4O_5$	4-[2,4-$(NO_2)_2C_6H_3N{=}N$]-2-$OHC_6H_3CH_2$		from no. 442	287
502	$C_{13}H_{10}N_3O_3$	4-[2-$NO_2C_6H_4N{=}N$]-2-$OHC_6H_3CH_2$		from no. 442	287

TABLE II (Continued)

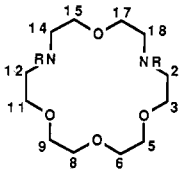
entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
503	$C_{13}H_{12}NO_2S$	2-$TsNHC_6H_4$		P from no. 504	313 (61%)
				N/A	314
504	$C_{13}H_{12}NO_2S$	(2-TsNH)C_6H_4	2,9-O_2	P	313 (62%)
505	$C_{13}H_{14}NO_2$	phthalimidyl-$(CH_2)_5$		Y(alk)	305
506	$C_{13}H_{16}O_3$	$PhCH_2O_2CNHCH(i\text{-}Pr)C(O)$		from no. 336	293 (93%)
				N/A	320
507	$C_{14}H_9BrNO_2$	2-[4-$BrC_6H_4NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (52%)
508	$C_{14}H_9ClNO_2$	2-[4-$ClC_6H_4NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (50%)
509	$C_{14}H_{10}NO_2$	2-[$C_6H_4NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (56%)
510	$C_{14}H_{14}O_4P$	$Ph_2O_3PO(CH_2)_2$		from no. 360	159 (93%)
511	$C_{14}H_{17}O_3$	$PhCH_2O_2CCH(i\text{-}PrCH_2)C(O)$		N/A	320
512	$C_{14}H_{18}NO_3$	$PhCH_2O_2CNHCH(i\text{-}Bu)C(O)$		from no. 336	293 (89%, 91%)
513	$C_{14}H_{27}O$	$C_{13}H_{27}C(O)$		Y(alk)	71 (78%)
514	$C_{14}H_{29}$	$C_{14}H_{29}$		from no. 513	71 (67%)
515	$C_{15}H_{16}NO_2S$	$PhCH_2N(Ts)CH_2$		from no. 359	303 (95%)
516	$C_{15}H_{16}P$	$Ph_2P(CH_2)_3$		from no. 377	219 (45%)
517	$C_{15}H_{18}NO_4$	2-[$MeO_2C(CH_2CH(Me)_2)$-CHNHC(O)]$C_6H_4C(O)$		from no. 336	322 (35%)
518	$C_{16}H_{14}NO_2$	2-[PhCH(Me)NHC(O)]$C_6H_4C(O)$		from no. 336	322 (57%, 53%)
519	$C_{16}H_{14}NO_3$	2-[$PhO(CH_2)_2NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (50%)
520	$C_{16}H_{14}NO_3$	2-[(4-EtO)$C_6H_4NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (43%)
521	$C_{16}H_{14}NO_3$	$PhCH_2O_2CNHCH(Ph)C(O)$		from no. 336	293 (85%)
522	$C_{16}H_{22}NO_2$	2-[$C_8H_{17}NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (53%)
523	$C_{16}H_{33}$	$C_{16}H_{33}$		Y(alk)	71 (25%)
524	$C_{17}H_{14}NO_4$	2-[4-$EtO_2CC_6H_4NHC(O)$]$C_6H_4C(O)$		other	322 (40%)
525	$C_{17}H_{16}NO_3$	$PhCH_2O_2CNHCH(CH_2Ph)C(O)$		from no. 336	293 (86%)
526	$C_{18}H_{17}N_2O_3$	$PhCH_2O_2CNHCH(indolyl\text{-}CH_2)C(O)$		from no. 336	293 (88%, 92%)
527	$C_{18}H_{35}O$	$C_{17}H_{35}C(O)$		Y	71 (100%)
528	$C_{18}H_{37}$	$C_{18}H_{37}$		from no. 527	71 (60%)
529	$C_{20}H_{14}N_3O_2$	2-[PhN=N-4-$C_6H_4NHC(O)$]$C_6H_4C(O)$		other	322 (45%)
530	$C_{20}H_{30}NO_2$	2-[$C_{12}H_{25}NHC(O)$]$C_6H_4C(O)$		from no. 336	322 (48%)

F. 1,10-Diaza-18-Crown-6 (R and R^1 Different)



entry no.	R	R^1	method	ref (yield)
531	H	HO_2CCH_2	Y(alk)	283; 323; 324 (85%)
			N/A	325
532	H	$HO_3S(CH_2)_2$	Y(alk)	325 (85%)
533	H	$HO_2C(CH_2)_2$	Y(alk)	327
534	H	$PhCH_2CO_2$	N/A	259
535	Me	$C_{12}H_{25}$	N/A	326
536	$HO_3S(CH_2)_2$	$C_{11}H_{23}C(O)$	Y(alk) from no. 532	325 (27%)
537	$HO_3S(CH_2)_2$	$(C_{16}H_{33}OCH_2)_2CHOCH_2C(O)$	Y(alk) from no. 532	325 (14%)
538	HO_2CCH_2	$C_{11}H_{23}C(O)$	Y(alk) from no. 531	323; 324 (17%); 325 (20%)
539	HO_2CCH_2	$C_{17}H_{35}C(O)$	Y(alk) from no. 531	325 (20%)
540	HO_2CCH_2	$(C_{16}H_{33}OCH_2)_2CHOCH_2CO$	Y(alk) from no. 531	325 (27%)
541	$HO_2C(CH_2)_2$	$C_{11}H_{23}C(O)$	Y(alk)	327 (18%)

G. 1,7-Diaza-18-Crown-6

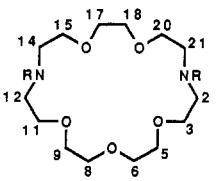


entry no.	R	other substituents	method	ref (yield)
542	H		Z	85 (11%); 112 (45%); 169
			N/A	73
			other	101
543	H	2,12-$(O)_2$	other	101
544	H	2,12-$(i\text{-}Pr)_2$	P	73 (27%); 328
545	H	2,12-$(i\text{-}Pr)_2$; 14,18-$(O)_2$	P	73 (22%); 328
546	H	2,12-Ph_2	P	73 (97%); 328
547	H	2,12-Ph_2; 14,18-$(O)_2$	P	73 (18%); 328
548	H	2,12-Ph_2; 3,11,14,18-$(O)_4$	other	280
549	H	2,12-$(CH_2Ph)_2$	P	73 (99%); 328
550	H	2,12-$(CH_2Ph)_2$; 14,18-$(O)_2$	P	73 (30%); 328
551	Me		N/A	73
552	Me	2,12-$(i\text{-}Pr)_2$	from no. 544	73 (92%); 328

TABLE II (Continued)

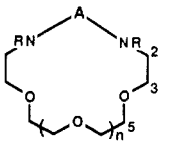
entry no.	R	other substituents	method	ref (yield)
553	Me	2,12-Ph_2	from no. 546	73 (82%); 328
554	Me	2,12-$(CH_2Ph)_2$	from no. 549	73 (99%); 328
			X	71 (63%)
555	$PhCH_2$		AA	80 (68%)
556	$PhCH_2$	2,12-(*i*-Pr)$_2$	Y(alk)	73, 328
557	$PhCH_2$	2,12-Ph_2	Y(alk)	73 (77%); 328
558	$PhCH_2$	2,12-$(CH_2Ph)_2$	Y(alk)	73 (91%); 328

H. Diaza-21-Crown-7



entry no.	R: formula index	R: structure	other substituents	method	ref (yield)
559	H	H		Z	85 (38%); 112, 159 (85%); 169
				N/A	301
560	H	H	17-CH_2OH	AE	50 (73%)
561	H	H	17-CH_2OH; 14,21-$(O)_2$	AE	50 (81%)
562	H	H	17-CH_2O-allyl; 14,21-$(O)_2$	AE	50 (54%)
563	H	H	14,18,21-$(O)_3$	P, other	329 (35%)
564	H	H	14,18,21-$(O)_3$; 20-CH_2Ph	P	329 (28%)
565	CH_3	Me		U from no. 577	141 (58%)
566	CH_3	Me	14,18,21-$(O)_3$; 20-CH_2Ph	P	282 (30%)
567	$C_2H_3O_2$	HO_2CCH_2		Y(alk)	159 (10%)
568	C_2H_5O	$HO(CH_2)_2$	14,21-$(O)_2$; 17,18-Me_2	P	330
569	C_5H_5O	2-furanyl-CH_2		Y(alk)	285
570	C_6H_6N	2-pyridinyl-CH_2		Y(alk)	277, 286
571	C_7H_7	$PhCH_2$		AA	80 (54%)
572	C_7H_7	$PhCH_2$	5-CH_2O-allyl	other	175 (31%)
573	C_7H_7	$PhCH_2$	14,21-$(O)_2$	P	75 (63%); 331
574	C_7H_7	$PhCH_2$	14,21-$(O)_2$; 17,18-Me_2	P	75 (59%); 331
575	C_7H_7	$PhCH_2$	14,21-$(O)_2$; 17,18,18-Me_3	P	331
576	C_7H_7	$PhCH_2$	14,21-$(O)_2$; 17,17,18,18-Me_4	P	331
577	$C_8H_7O_2$	$C_6H_5CH_2CO_2$		as U	141 (34%)
578	C_8H_{17}	C_8H_{17}	17,18-Me_2	P	130 (52%)
579	C_8H_{17}	C_8H_{17}	17,17,18,18-Me_4	P	130 (43%)
580	$C_{10}H_{19}O_2$	$Me(CH_2)_6CO_2(CH_2)_2$	14,21-$(O)_2$; 17,18-Me_2	from no. 568	330

I. Diaza-Crowns with One Miscellaneous Bridge

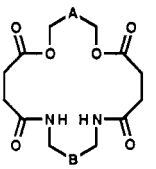


entry no.	A	R	*n*	other substituents	method	ref (yield)
581	nothing	Et	1		X, other	187 (35% overall)
					N/A	332
582	C=S	H	1		as AS	333 (34%)
					N/A	334, 335, 336
583	C=S	H	2		as AS	334 (29%)
					N/A	335
584	C=S	H	3		as AS	334
					N/A	335
585	C=S	Me	1		from no. 582	337 (49%); 338 (74%)
586	C=S	Me	2		from no. 583	338 (67%)
587	C=O	Me	1		from no. 582	339, 340 (85%)
588	C=O	Me	2		from no. 584	340 (87%)
589	$(CH_2)_2$	H	0	1,10-Ts_2	N/A	341
590	$(CH_2)_2$	H	1		Z	85 (32%)
					other	101 (50%)
591	$(CH_2)_2$	H	1	2,12-$(O)_2$	other	101 (60%)
592	$(CH_2)_2$	H	1	2,3;11,12-(cyclohexano)$_2$	Z	85 (42%)
593	$(CH_2)_2$	H	2		Z	85 (39%)
594	$(CH_2)_2$	H	2	2,3;11,12-(cyclohexano)$_2$	Z	85 (42%)
595	$(CH_2)_2$	H	3		Z	112, 169
596	$(CH_2)_2$	Me	2	8-CH_2O-allyl	AE, other	175 (62%)
597	$(CH_2)_2$	Et	2	8-CH_2O-allyl	AA	175 (22%)
598	$(CH_2)_2$	$PhCH_2$	2	8-CH_2O-allyl	AA	175 (21%)
599	$(CH_2)_2$	Ph	0	2,9-$(O)_2$	other	115 (80%)

TABLE II (Continued)

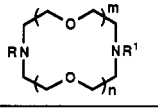
entry no.	A	R	*n*	other substituents	method	ref (yield)
600	C(O)C(O)	H	0	3,8-$(O)_2$; 2,9-Ph_2	P	342 (84%, 92%)
601	C(O)C(O)	H	1	3,11-$(O)_2$; 2,12-Ph_2	P	342 (84%, 68%)
602	C(O)C(O)	H	2	3,14-$(O)_2$; 2,15-Ph_2	P	342 (70%)
603	$C(O)(CH_2)_2C(O)$	$PhCH_2$	1		P	75 (11%)
604	$(CH_2)_2O(CH_2)_2$	H	2		Z	85 (11%); 169
605	$(CH_2)_2O(CH_2)_2$	H	3	2,6,14,18-$(O)_4$	P	329 (11%)
606	$C(O)CH_2OCH_2C(O)$	H	2		P	329 (25%)
607	$C(O)CH_2OCH_2C(O)$	H	2	3,14-$(O)_2$; 2,15-Ph_2	other	280
608	$C(O)CH_2OCH_2C(O)$	H	3	3,17-$(O)_2$; 2,18-Ph_2	other	280
609	$C(O)(CH_2)_4C(O)$	$PhCH_2$	1		P	75 (25%)
610	$CH_2(CH_2OCH_2)_2CH_2$	H	2		N/A	327
					Z	169
611	$CH_2(CH_2OCH_2)_2CH_2$	H	3		N/A	327
612	$CH_2(CH_2OCH_2)_2CH_2$	H	4	2,6,17,21-$(O)_4$	P	329 (17%)
613	$C(O)(CH_2OCH_2)_2C(O)$	H	2	3,14-$(O)_2$; 2,15-Ph_2	other	280 (42%)
614	$C(O)CH_2OCH_2CO_2CH_2C(O)$	H	2		P	329 (20%)
615	$C(O)CH_2O(CH_2)_3OCH_2C(O)$	$PhCH_2$	1		P	130 (52%)
616	$(CH_2)_2OCH_2CH(OH)CH_2O(CH_2)_2$	Et	0		from no. 628	175 (34%)
617	$(CH_2)_2OCH_2C(=CH_2)CH_2O(CH_2)_2$	H	0		AC	161 (35%)
618	$(CH_2)_2OCH_2C(=CH_2)CH_2O(CH_2)_2$	Et	0		AC	175 (67%)
619	$(CH_2)_2OCH_2C(=CH_2)CH_2O(CH_2)_2$	$PhCH_2$	0		AC	175 (63%)
620	$C(O)CH_2O(CH_2)_4OCH_2C(O)$	$PhCH_2$	1		P	130 (60%)
621	$CH_2(CH_2OCH_2)_3CH_2$	H	1		as A	141 (42%)
					N/A	327
622	$CH_2(CH_2OCH_2)_3CH_2$	Me	1		from no. 621	141 (92%)
623	$CH_2(CH_2OCH_2)_3CH_2$	Ts	1		as A	141 (10%)
624	$CH_2(CH_2OCH_2)_3CH_2$	Ts	1	3,11,15,23-$(O)_4$	other	224 (12%)
625	$CH_2(CH_2OCH_2)_3CH_2$	H	5	2,6,20,24-$(O)_4$	P	329 (19%)
626	$C(O)CH_2OCH_2C(CH_3)_2CH_2OCH_2C(O)$	$PhCH_2$	0		P	130 (43%)
627	$(CH_2)_2OCH_2CH(O\text{-allyl})CH_2O(CH_2)_2$	Et	0		other	175 (31%)
628	$(CH_2)_{10}$	C_6H_{13}	0	2,9-$(O)_2$	N/A	115
629	$CH_2(CH_2OCH_2)_4CH_2$	H	1		N/A	327
630	$CH_2(CH_2OCH_2)_4CH_2$	H	2		N/A	327
631	$CH_2(CH_2OCH_2)_4CH_2$	Ts	2	3,14,19,30-$(O)_4$	other	224 (11%)
632	$C(O)CH_2OCH(Bu)CHOCH_2C(O)$	$PhCH_2$	1		P	130 (55%)
633	$(CH_2)_{12}$	H	0		from no. 634	343 (49%)
634	$(CH_2)_{12}$	H	0	2,9-$(O)_2$	P	343 (90%)
635	$(CH_2)_{12}$	$PhCH_2$	0	2,9-$(O)_2$; 5,6-Me_2	P	75 (55%)

J. Diaza-Crowns with Butylene Bridges



entry no.	A	B	method	ref (yield)
636	CH_2	$(CH_2)_2$	P	329 (21%)
637	CMe_2	$(CH_2)_2$	P	329 (22%)
638	CH_2	$(CH_2)_4$	P	329 (25%)
639	CMe_2	$(CH_2)_4$	P	329 (23%)
640	CH_2	$(CH_2)_6$	P	329 (20%)
641	CMe_2	$(CH_2)_6$	P	329 (16%)
642	CH_2	CH_2OCH_2	P	329 (26%)
643	CMe_2	CH_2OCH_2	P	329 (19%)
644	CMe_2	$(CH_2OCH_2)_2$	P	329 (17%)
645	CH_2OCH_2	CH_2OCH_2	P	329 (31%)
646	$(CH_2OCH_2)_2$	$(CH_2OCH_2)_2$	P	329 (9%)
647	$(CH_2OCH_2)_3$	$(CH_2OCH_2)_3$	P	329 (12%)

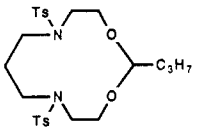
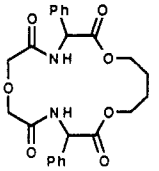
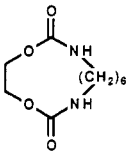
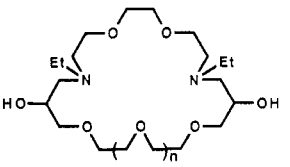
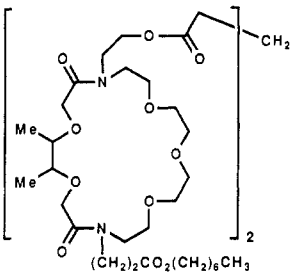
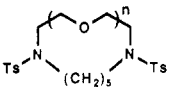
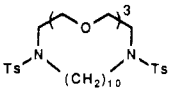
K. Diaza-Crowns (R and R^1 Different)



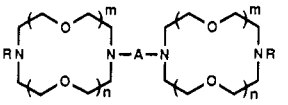
entry no.	R	R^1	*m*	*n*	other substituents	method	ref (yield)
648	$HO(CH_2)_2$	$Me(CH_2)_6CO_2(CH_2)_2$	2	3	14,21-$(O)_2$; 17,18-Me_2	from no. 568	330
649	$C_{11}H_{23}C(O)$	HO_2CCH_2	2	4		Y(alk)	327 (11%)
650	$C_{11}H_{23}C(O)$	$HO_2(CH_2)_2$	3	3		Y(alk)	327 (14%)
651	$C_6H_{13}CH(Me)C(O)$	HO_2CCH_2	3	4		Y(alk)	327 (12%)
652	$C_{11}H_{23}C(O)$	HO_2CCH_2	2	5		Y(alk)	327 (10%)
653	$C_{14}H_{29}C(O)$	$HO_2C(CH_2)_3$	4	4		Y(alk)	327 (16%)

TABLE II (Continued)

L. Miscellaneous Diaza-Crowns

entry no.	structure	n	method	ref (yield)
654			other	344 (60%)
655			other	280 (53%)
656			other	123 (35%)
657		0	AD	79 (30%)
658		1	AD	79 (22%)
659			from no. 648	330
660		2	Q	98 (76%)
661		3	Q	98 (66%)
662			Q	98 (50%)

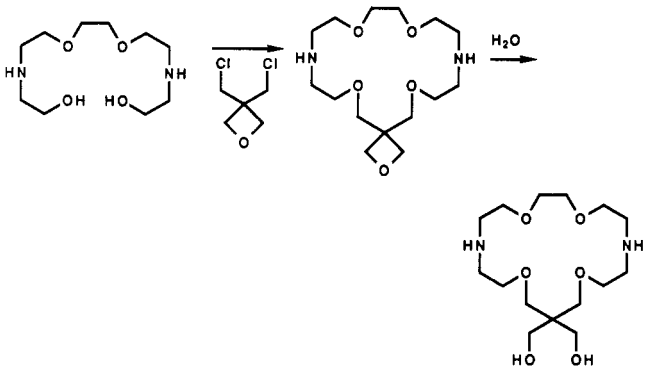
M. Bis(diaza-crowns)



entry no.	A	R	n	m	method	ref (yield)
663	$(CH_2)_2$	H	1	1	from no. 664	88 (85%)
					from no. 288	276 (85%)
664	$(CH_2)_2$	$PhCH_2$	1	1	from no. 288	88, 276
665	$(CH_2)_2$	H	1	1	from no. 666	274 (76%)
666	$C(O)(CH_2)_7C(O)$	H	1	1	from no. 667	274 (86%)
667	$C(O)(CH_2)_7C(O)$	t-BuO_2C	1	1	from no. 287	274 (74%)
668	$CH_2CH(CH_2Ph)CH_2$	H	1	1	from no. 669	265
669	$CH_2CH(CH_2Ph)CH_2$	Ts	1	1	as L from no. 289	265 (78%)
670	CH_2-4-C_6H_4-4-$C_6H_4CH_2$	H	1	1	from no. 671	274 (94%)
671	CH_2-4-C_6H_4-4-$C_6H_4CH_2$	t-BuO_2C	1	1	from no. 287	274 (23%)
672	$CH_2CH(C_{16}H_{33})CH_2$	H	1	1	from no. 673	265
673	$CH_2CH(C_{16}H_{33})CH_2$	Ts	1	1	as L from no. 289	265 (72%)
674	$CH_2(CH_2OCH_2)_2CH_2$	H	2	1	from no. 675	274 (66%); 290
675	$C(O)CH_2O(CH_2)_2OCH_2C(O)$	H	2	1	from no. 676	274 (84%)
676	$C(O)CH_2O(CH_2)_2OCH_2C(O)$	t-BuO_2C	2	1	from no. 334	274 (74%)
677	$CH_2(CHOH)_2CH_2$	H	2	2	from no. 678	260 (60%)
678	$CH_2(CHOH)_2CH_2$	$PhCH_2O_2C$	2	2	from no. 534	260 (60%)

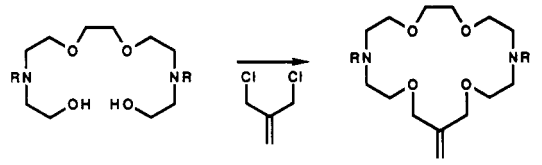
used to immobilize the crown onto silica gel[16,49,87,170,171] and to make more complex compounds such as the lariat crown ethers.[71] The easiest method to attach a functional group is through one of the ring nitrogen atoms. Those types of reactions are shown in method Y. Functionalized diaza-crowns, where the functional group is attached to a ring carbon atom, also have been synthesized. Krespan was one of the first to prepare a functionalized diaza-crown when he synthesized a bis(hydroxymethyl)diaza-19-crown-6 (method AB).[83,172]

Method AB



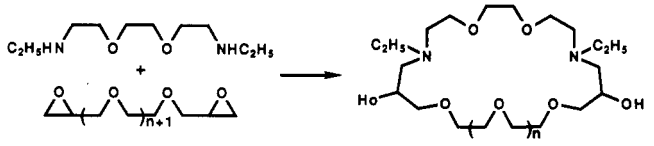
Tomoi and co-workers and, more recently, Bradshaw and co-workers have prepared similar diaza-crowns but containing an exo-methylene group (method AC),[161,162,173-175] which can be easily converted into a hydroxy compound by hydroboration.[173]

Method AC



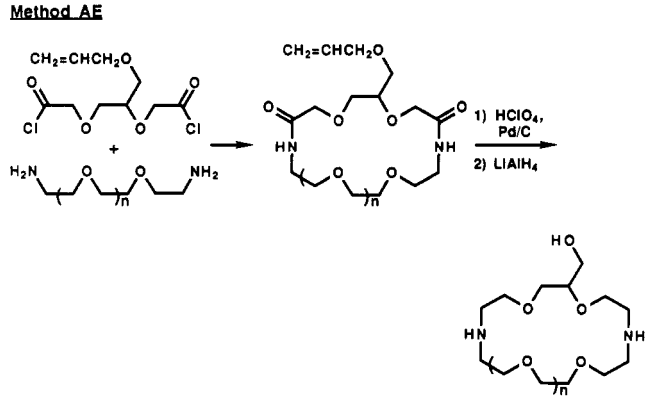
Okahara and co-workers prepared some diaza-crowns containing two hydroxy functions by reacting a diamine with a bisepoxide (method AD).[79]

Method AD



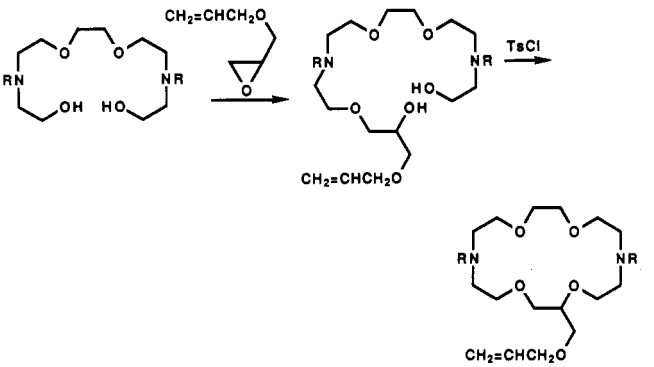
Three hydroxymethyl-substituted diaza-crown compounds were prepared by Bartsch and co-workers using method P but with an (allyloxy)methyl substituent on the diacid chloride (method AE).[50] The starting (allyloxy)methyl-substituted diacid chloride was prepared in three steps. The purification of the diacid was difficult because it polymerized during distillation. The cyclization step also required high-dilution techniques. Cinquini used methods AE and Y to prepare diaza-crowns containing long-chain lipophilic substituents on both a ring carbon and the two ring nitrogens.[47]

Method AE



Bradshaw and co-workers reported a more convenient method to prepare the (allyloxy)methyl-substituted diaza-crown compounds (method AF).[49] Their method,

Method AF



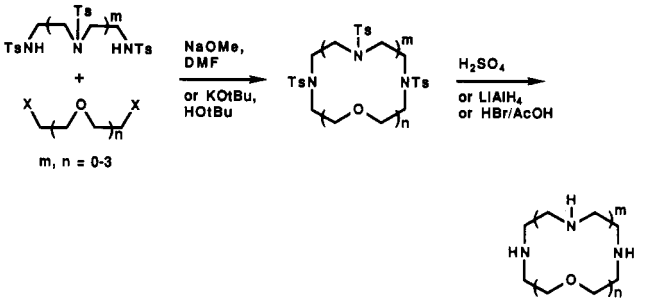
using the Okahara ring-closure procedure, gave a good overall yield of *N,N'*-dialkyl-substituted (allyloxy)-methyldiaza-18-crown-6 and can be applied to the synthesis of other similar diaza-crown ethers.[175]

A listing of diaza-crowns is given in Table II.

C. Polyaza-Crowns (Table III)

Richman and Atkins as well as Vögtle and co-workers have prepared a number of polyaza-crown compounds by reacting the appropriate per-*p*-toluenesulfonamide derivative of a polyamine with the ditosylate derivative of an oligoethylene glycol (method AG).[94,95,164,176,177]

Method AG

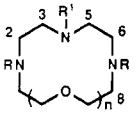


They were able to prepare polyaza-crowns with different ring sizes and numbers of oxygen and nitrogen atoms. Different methods to remove the *N*-tosyl blocking groups were tried, including HBr/phenol, H_2SO_4, $LiAlH_4$/THF, and $NaAlH_2(OCH_2CH_2OCH_3)_2$.[164] The yields of this last step varied as a function of the number of tosyl groups and the size of the macrocycle. With a triaza-12-crown-4, it was found that HBr/phenol was the best detosylating reagent followed by H_2SO_4 and $LiAlH_4$.[164]

Tabushi and co-workers reported a general synthetic procedure to prepare the polyaza-crown compounds by reacting a polyamine and the dimethyl ester of an oligoglycolic acid followed by reduction of the resulting cyclic diamide (method AH).[136,137,178] This method uses

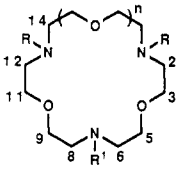
TABLE III. Polyaza-Crowns

A. 1,4,7-Triaza-Crowns



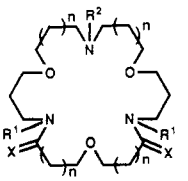
entry no.	R = R¹	R¹	other substituents	n	method	ref (yield)
679	H			1	N/A	306
680	H		8,9:17,18-(cyclohexano)$_2$	3	Z	85 (27%)
681	H		8,9:20,21-(cyclohexano)$_2$	4	Z	85 (21%)
682	Et	$(CH_2CH_2O)_2H$		2	AN	346 (68%)
683	$HO(CH_2)_2$			1	as K	306, 345
684	$MeO(CH_2)_2$			1	other	345 (20–25%)
685	Ts			1	AG	100 (65–83%)
686	Ts			2	AG	100 (80%)

B. Triaza-18-Crown-6 and Triaza-21-Crown-7



entry no.	R	R¹	other substituents	n	method	ref (yield)
687	H	H		1	AK	131 (75%)
					N/A	347
688	H	Ts		1	AK	131 (98%); 206
					N/A	182, 185
689	H	Ts	2,12-(O)$_2$	1	AK	131 (70%)
					N/A	185
690	Me	H		1	as AK	185 (90%)
					from no. 693	185
691	Me	Me		1	N/A	182, 348
					other	206
					N/A	185, 347
692	Me	Et		1	N/A	185
693	Me	Ts		1	AK	185 (90%)
					other	185
694	Me	Ts	2,12-(O)$_2$	1	AK	185 (78%)
695	Me	$Et_3{}^+NCH_2C_6H_4CH_2$		1	from no. 696	185 (15% salt)
696	Me	$Et_3{}^+NCH_2C_6H_4C(O)$		1	from no. 690	185 (50%)
697	Me	4-(tetrazac-CH_2)$C_6H_4CH_2$		1	from no. 698	185 (70%)
698	Me	4-(tetazac-CH_2)$C_6H_4C(O)$		1	from no. 690	185 (35%)
699	Et	$PhCH_2$		1	AM	81 (73%, 24% overall)
700	Et	$PhCH_2$	17-CH_2O-allyl	2	AM	81
701	HO_2CCH_2	Ts	3,11-(O)$_2$	0	as BC	198 (30%)
702	Et	$HO(CH_2)_2O(CH_2)_2$		2	AM	346 (45%)
703	Et	$HO(CH_2)_2O(CH_2)_2$	17-CH_2O-allyl	2	AM	346 (42%)
704	Et	$PhCH_2$	14,18-(O)$_2$	1	AM	81

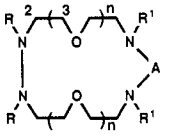
C. Triaza-Crowns with Propylene Bridges



entry no.	n	R¹	R²	X	method	ref (yield)
705	0	H	H	H_2	AR	90 (55%)
706	0	Me	Me	H_2	AR	90 (57%)
707	0	H	Ts	H_2	AR	90 (94%)
708	0	H	Ts	O	AR	90 (45%)
709	1	H	H	H_2	AR	90 (46% HCl)
710	1	Me	Me	H_2	AR	90 (42%)
711	1	H	Ts	H_2	AR	90 (96%)
712	1	H	Ts	O	AR	90 (27%)
713	1	4-$HO_2CC_6H_4C(O)$	Ts	H_2	from no. 714	90 (100%)
714	1	4-$MeO_2CC_6H_4C(O)$	Ts	H_2	from no. 711	90 (84%)
715	1	4-$ClC(O)C_6H_4C(O)$	Ts	H_2	from no. 713	90
716	1	4-$HO_2CC_6H_4C(O)$	4-$HO_2CC_6H_4C(O)$	H_2	from no. 717	90 (100%)
717	1	4-$MeO_2CC_6H_4C(O)$	4-$MeO_2CC_6H_4C(O)$	H_2	from no. 709	90 (87%)
718	1	4-$ClC(O)C_6H_4C(O)$	4-$ClC(O)C_6H_4C(O)$	H_2	from no. 716	90

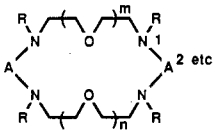
TABLE III (Continued)

D. Tetraaza-Crowns Containing the Hydrazine Moiety



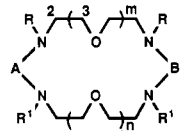
entry no.	R	R^1	A	other substituents	n	method	ref (yield)
719	Et	Et	nothing		3	other	187 (8)
						N/A	332
720	Et	Et	$C(O)CH_2OCH_2C(O)$		1	AM	187
721	Et	Et	$(CH_2)_2O(CH_2)_2$		1	AM	187 (48%); 332
722	Et	Et	$CH_2C(=CH_2)CH_2$		1	AM	187 (48%); 332
723	$PhCH_2$	Et	$CH_2C(=CH_2)CH_2$		1	AM	332 (50%)
724	Et	$PhCH_2$	$CH_2(CH_2OCH_2)_2CH_2$		1	AO	187 (71%); 332
725	Et	$PhCH_2$	$CH_2(CH_2OCH_2)_2CH_2$	2,15-$(O)_2$	1	AO	187
726	Et	Et	$(CH_2)_2OCH(CH_2O\text{-allyl})CH_2O(CH_2)_2$		1	AM	187 (50%); 332

E. Tetraaza-Crowns with Miscellaneous Bridges



entry no.	R	A	m	n	other substituents	method	ref (yield)
727	H	C=O	1	1		from no. 735	394 (87%)
728	H	C=O	2	2		from no. 739	394 (93%)
729	Me	C=O	1	1		from no. 735	340 (82%)
730	Me	C=O	2	2		from no. 739	339, 340 (81%)
731	H	C=S	0	1		AS	189 (86%)
732	H	C=S	0	2		AS	189 (80%)
733	H	C=S	0	3		AS	189 (75%)
734	H	C=S	0	4		AS	189 (65%)
735	H	C=S	1	1		AS	189 (75%)
						N/A	335, 349
						other	336
736	H	C=S	1	2		AS	189 (75%)
737	H	C=S	1	3		AS	189 (68%)
738	H	C=S	1	4		AS	189 (70%)
739	H	C=S	2	2		AS	189 (66%)
						N/A	335, 349
						other	336
740	H	C=S	2	3		AS	189 (69%)
741	H	C=S	2	4		AS	189 (47%)
742	H	C=S	3	3		AS	189 (49%)
						N/A	349
743	H	C=S	3	4		AS	189 (55%)
744	H	C=S	4	4		AS	189 (40%)
745	Me	C=S	2	2		from no. 739	337 (54%)
746	H	$(CH_2)_2$	1	1		AG	101 (25%)
						N/A	350
747	H	$(CH_2)_2O(CH_2)_2$	1	1	2,6,9,14,18,23-$(O)_6$; 8,12,20,24-(*s*-Bu)$_4$	other	351 (24%)
748	H	$(CH_2)_2O(CH_2)_2$	1	1	2,6,9,14,18,23-$(O)_6$; 8,12,20,24-$(CH_2Ph)_4$	other	344 (9%)
749	$PhCH_2$	$(CH_2)_2$	2	2	5,12,16,23-$(O)_4$	other	115 (10%)
750	$PhCH_2$	$(CH_2)_2$	1	1		AQ	188 (41%)
751	Ts	$(CH_2)_2$	1	1		AG	101 (30–40%)

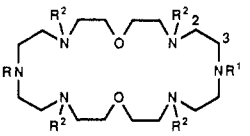
F. Tetraaza-Crowns with Miscellaneous Bridges (R and R^1 Different)



entry no.	R	R^1	A	B	m	n	other substituents	method	ref (yield)
752	Me	Ts	$(CH_2)_2$	$(CH_2)_2$	1	1		as Q	289 (52%)
753	Me	Ts	$(CH_2)_2$	$(CH_2)_2$	1	2		as Q	289 (40%)
754	Et	Me	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	2	0	5-CH_2O-allyl	AN	81 (48%, 20% overall)
755	Et	Bu	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	2	1	5-CH_2O-allyl	AN	81
756	Et	$PhCH_2$	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	2	1	5-CH_2O-allyl	AN	81
757	Et	$PhCH_2$	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	2	2	5-CH_2O-allyl	AN	81
758	OH	H	$(CH_2)_2C(O)$	$C(O)(CH_2)_2$	2	2		from no. 763	352 (25%)
759	H	Ts	$(CH_2)_2C(O)$	$C(O)(CH_2)_2$	2	2		as P	352 (56%)
760	OH	Ts	$(CH_2)_2C(O)$	$C(O)(CH_2)_2$	2	2		from no. 762	352 (6%)
761	OH	HO_2CCH_2	$(CH_2)_2C(O)$	$C(O)(CH_2)_2$	2	2		from no. 758	352 (28%)
762	$SiMe_3$	Ts	$(CH_2)_2C(O)$	$C(O)(CH_2)_2$	2	2		from no. 759	352
763	$PhCH_2O$	Ts	$(CH_2)_2C(O)$	$C(O)(CH_2)_2$	2	2		as P	352 (26%)

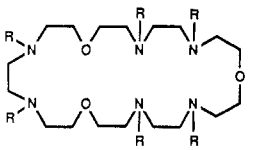
TABLE III (Continued)

G. Hexaaza-24-Crown-8



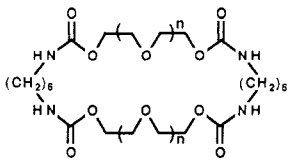
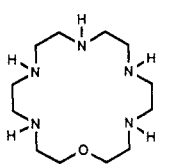
entry no.	R	R^1	R^2	method	ref (yield)
764	H	H	H	AI	183 (75%)
				AJ	183 (90%)
				N/A	179, 353, 354, 335, 356, 357, 358
765	H	H	Ts	AI	183 (75%)
				AJ	2 (56%)
				N/A	358
766	$HO(CH_2)_2$	H	H	from no. 775	2 (64%)
767	$H_2N(CH_2)_2$	H	H	from no. 777	2 (71%)
768	$HS(CH_2)_2$	H	H	from no. 781	2 (65%)
769	H_2O_3P	H	H	from no. 764	354, 357
770	H	Ts	Ts	from no. 784	2 (82%)
				N/A	179
771	9-acridinyl-$NH(CH_2)_3$	H	H	from no. 786	179 (90%)
772	Me	Me	Me	from no. 764	353 (71%)
				N/A	355
773	$HO(CH_2)_2$	$HO(CH_2)_2$	H	from no. 774	2 (61%)
774	$HO(CH_2)_2$	$HO(CH_2)_2$	Ts	from no. 765	2 (77%)
775	$HO(CH_2)_2$	Ts	Ts	from no. 770	2 (57%)
776	$H_2N(CH_2)_2$	$H_2N(CH_2)_2$	H	from no. 779	2 (72%)
777	$TsNH(CH_2)_2$	Ts	Ts	from no. 770	2 (98%)
778	$H_2N(CH_2)_3$	Ts	Ts	from no. 782	179 (61%)
779	$TsNH(CH_2)_2$	$TsNH(CH_2)_2$	Ts	from no. 765	2 (88%)
780	$HS(CH_2)_2$	$HS(CH_2)_2$	Ts	from no. 765	2 (70%)
781	$HS(CH_2)_2$	Ts	Ts	from no. 770	2 (68%)
782	$CN(CH_2)_2$	Ts	Ts	from no. 770	179 (94%)
783	PhC(O)	PhC(O)	Ts	AJ	2 (53%)
784	PhC(O)	Ts	Ts	AJ	2 (55%)
785	Ts	Ts	Ts	AJ	183
786	9-acrylidinyl-$NH(CH_2)_3$	Ts	Ts	from no. 778	179 (44%)

H. Hexaaza-27-Crown-9



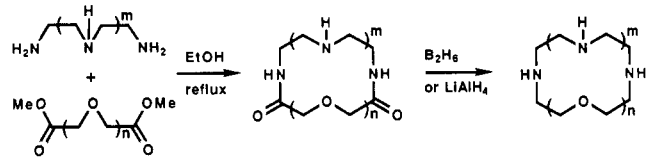
entry no.	R	method	ref (yield)
787	H	from no. 788	181 (90% HBr); 359 (90%)
		N/A	353, 355, 360
788	Ts	AG, other	181, 359 (65%)
		N/A	361

I. Miscellaneous Polyaza-Crowns

entry. no.	structure	*n*	method	ref (yield)
789		3	other	362
790		4	other	362
791			N/A	363

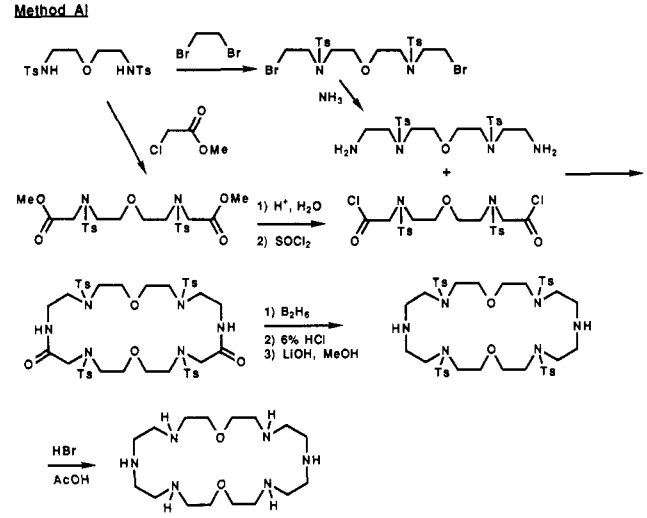
readily available starting materials and does not require high-dilution techniques.

Method AH



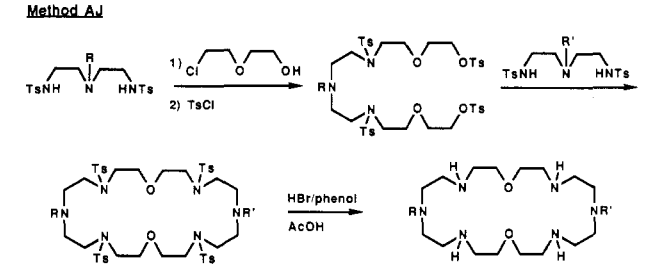
Lehn and co-workers used a number of methods to prepare some interesting polyazaoxa-crown compounds.[2,5,131,179-184] These authors used many steps to elaborate a bis(*p*-toluenesulfonamide) derivative of a diamino ether to form [24]N_6O_2 crowns (method AI).[183,184] In the process, a diacid chloride–diamine

Method AI



reaction was used to close the ring, followed by reduction and detosylation. Although the yield for each step was reasonable, the use of many steps greatly reduces the overall yield of polyaza-crowns. This procedure allows the preparation of polyaza-crowns with some of the ring nitrogen atoms blocked. A somewhat similar sequence to form the same crown by a shorter route is shown in method AJ.[183] This method does not require

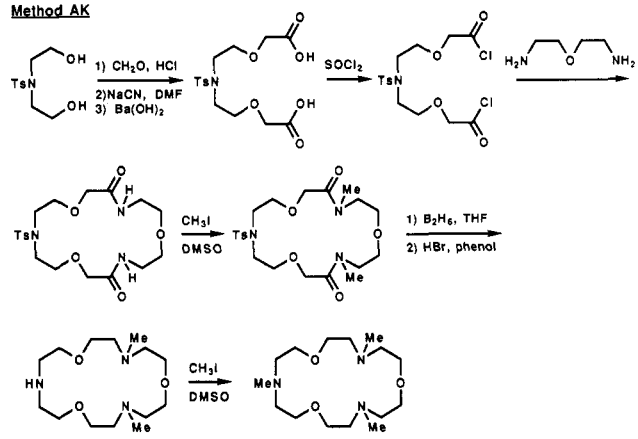
Method AJ



the cyclic diamide formation–reduction procedure of method AI but does require a detosylation step to form [24]N_6O_2 crowns. The tosyl groups greatly add to the molecular weight of the starting materials and intermediates so that large quantities (by weight) of these materials must be used to obtain reasonable amounts of the final products. These authors also prepared a [27]N_6O_3 crown by method AG.[181]

A different procedure was used by Lehn and coworkers to prepare the triaza-18-crown-6 compounds (method AK).[180] This method uses the *p*-toluene-

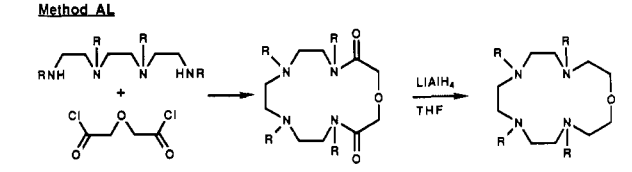
Method AK



sulfonamide derivative of diethanolamine as a starting material as shown. The methylation and reduction–detosylation steps shown in the middle of the sequence can be reversed. Schmidtchen reported the same synthesis of the [18]N_3O_3 crowns in 12 steps.[185]

Pelissard and Louis prepared *N,N',N'',N'''*-tetramethyltetraaza-15-crown-5 (or its tetraethyl analogue) by reacting the tetramethyltriethylene tetraamine (or its tetraethyl analogue) with diglycolyl dichloride followed by reduction (method AL).[186] Although this

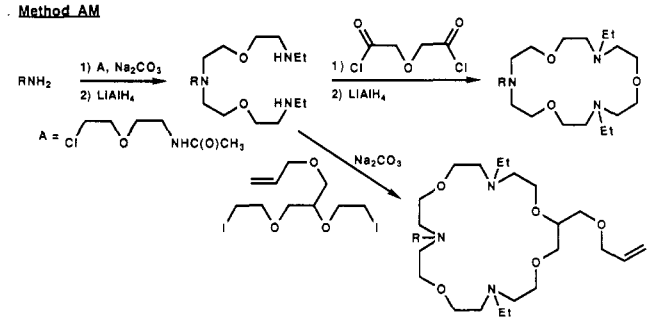
Method AL



procedure circumvents the high molecular weights and blocking group removal problems of the *N*-tosyl groups, it is still necessary to apply high-dilution techniques. The final polyaza-crowns contain *N*-alkyl groups but for many applications, the *N*-alkyl groups are useful. For example, complexation of metal and organic ammonium cations by the *N*-alkyl-substituted aza-crowns is about the same as complexation by the non-*N*-alkyl-substituted aza-crowns.[6]

Krakowiak, Bradshaw, and Izatt have developed more convenient methods to prepare the *N*-alkyl-substituted triaza- and tetraaza-crown compounds.[81,82] *N*-[2-(2-Chloroethoxy)ethyl]acetamide is the key reactant in the new methods. Method AM shows that 2 mol of the key

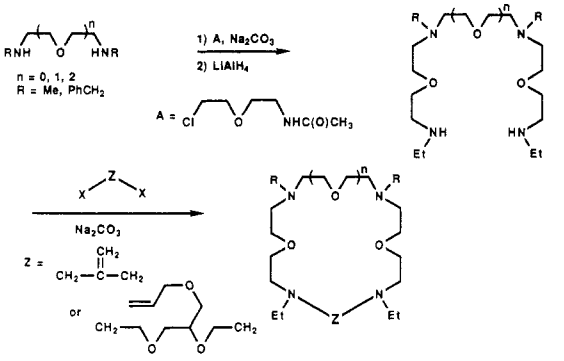
Method AM



reactant can be added to a primary amine followed by a diacid chloride and reduction to form the symmetrical triaza-18-crown-6 in four steps from compound A. The intermediate triamine of method AM can also be reacted with a dihalide to form another triaza-crown as shown. Compound A of method AM was also reacted

with *N,N'*-dialkyloligoethylenediamine to form an oligoethylenetetraamine, which was reacted with a diiodide to form a tetraaza-crown (method AN).[81] These

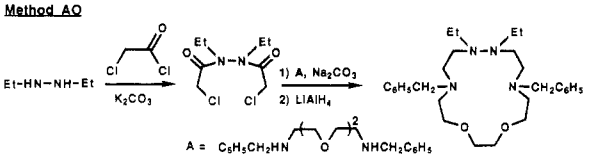
Method AN



methods allow the synthesis of tri- and tetraaza-crowns in a few number of steps with good overall yields (30–40%) and with the possibility of having two different functional groups in the macrocycle.

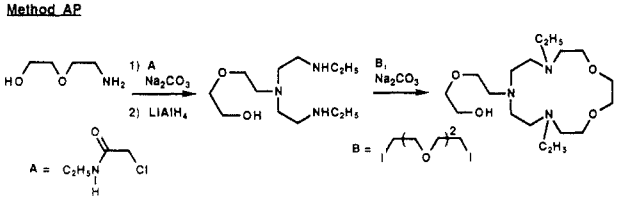
New aza-crowns containing the hydrazine moiety have been prepared by method AM except a hydrazine starting material rather than an amine was used.[187] 1,2-Diethylhydrazine was also reacted with chloroacetyl chloride followed by a diamine and reduction as another procedure to prepare the new hydrazino-crowns (method AO).[187]

Method AO



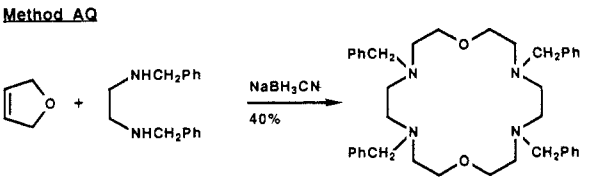
As discussed previously, monofunctionalized aza-crowns are important intermediates for bonding the aza-crowns to solid supports. A new method to prepare *N*-(hydroxyalkyl)polyaza-crowns and cyclams has been studied (method AP).[82] The pendant hydroxy groups are not ionized by the sodium carbonate base so that the nucleophilic reactions take place on nitrogen.

Method AP



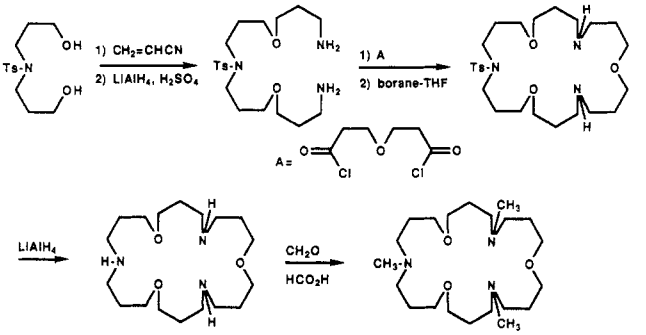
Kawaguchi and Ohashi reported a one-step procedure to prepare a symmetrical tetraaza-18-crown-6 compound (method AQ).[188]

Method AQ



Sutherland and co-workers prepared symmetrical crown ethers with propylene or mixed propylene and ethylene bridges.[90] They used an *N*-tosylamino glycol which was described in section II.C. The glycol was reacted with acrylonitrile followed by reduction to give a triamine that was used to build the crown ethers (method AR). A triaza-crown containing both ethylene

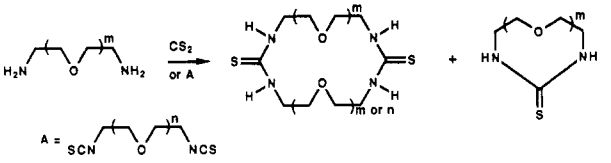
Method AR



and propylene bridges was prepared in a similar manner by using (*N*-tosylamino)diethanol rather than the (*N*-tosylamino)dipropanol and diacid chloride used in method AR.

Tetraaza-crown ethers were obtained by Bogatsky and co-workers starting from derivatives of diamines and carbon disulfide or an isothiocyanate (method AS).[189]

Method AS



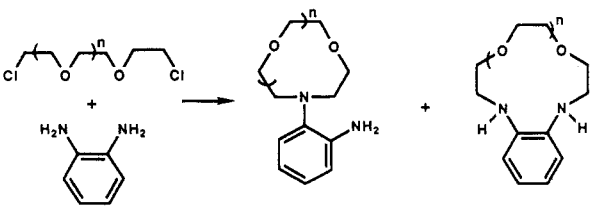
A listing of polyaza-crowns is given in Table III.

D. Benzoaza-Crowns (Table IV)

1. One Benzo Unit

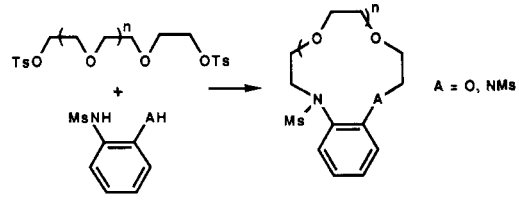
A number of benzoaza-crowns have been prepared. This section will present specific methods for the synthesis of aza-crowns with one and more benzo groups. Benzoaza-crowns with one nitrogen atom in the ring were first reported by Lockhart and co-workers in 1973[147] and by Pedersen and Bromels.[190] Lockhart reacted 2-hydroxyaniline with a series of dihalides to obtain both *N*-(2-hydroxyphenyl)aza-crowns and benzoaza-crowns (method G, section IV.A). Pedersen and Bromels, using the same starting materials, produced benzoaza-15-crown-5 and benzoaza-18-crown-6 in *tert*-butyl alcohol.[190] Lockhart and co-workers obtained both a monoaza- and a diaza-crown from 1,2-diaminobenzene (method AT).[147,148]

Method AT



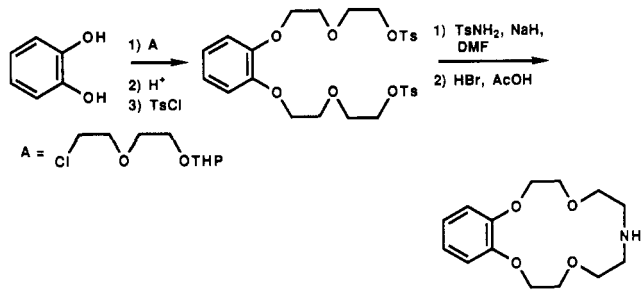
Högberg and Cram made a series of benzoaza- and benzodiaza-crowns from the methanesulfonamide derivative of 1,2-diaminobenzene or 2-hydroxyaniline (method AU).[191] The monoaza product (where A = O) was formed in 32% yield while the diaza-crown was formed in only 5% yield.

Method AU



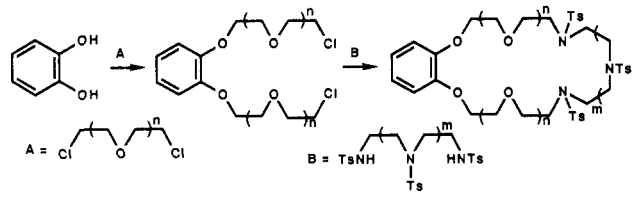
p-Toluenesulfonamide has been reacted with a bis(toluenesulfonate) derivative of a benzoglycol to form a benzoaza-crown where the benzo unit was not attached to the nitrogen atom (method AV).[191] Meth-

Method AV



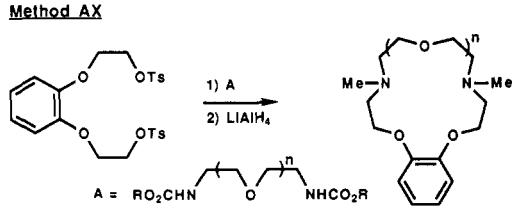
anesulfonamide gave higher yields of the *N*-mesyl-blocked product but the mesyl group was more difficult to remove. Methanesulfonamide similar sequence was reported by He and Wu for the preparation of benzopolyaza-crowns, except they used the tris- or tetrakis(*p*-toluenesulfonamide) derivative of diethylenetriamine or triethylenetetramine (method AW).[192] These researchers did not report their method for removing the tosyl groups.

Method AW

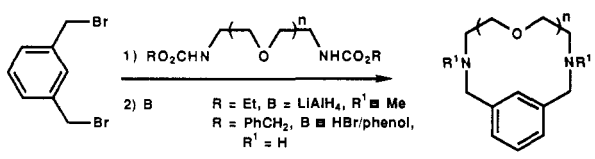


Sutherland and co-workers used several procedures to prepare a series of *o*-, *m*-, and *p*-benzodiaza-crown compounds. Three of the methods are shown here (methods AX, AY, and AZ).[167,193,194] The *p*-benzodiaza-crowns were prepared as in method AY from the corresponding *p*-bis(chloromethyl)benzene. The ring-closure steps for each of these methods gave only moderate yields.

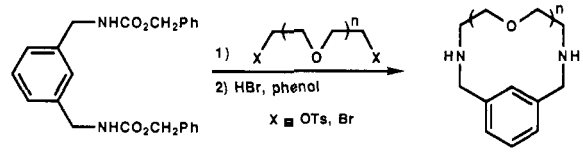
Method AX



Method AY

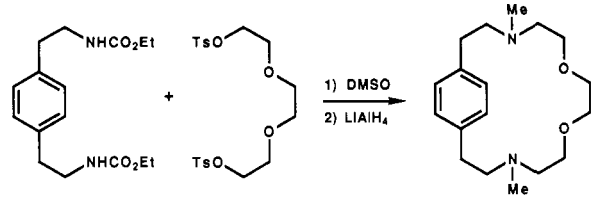


Method AZ



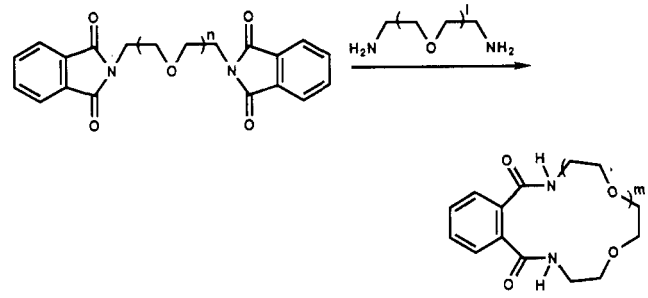
Stoddart and co-workers used a similar reaction sequence to prepare a 1,4-benzodiaza-crown ether (method BA).[195]

Method BA



Using bis(phthalimide) derivatives of the oligoethylene glycols, Komalow and co-workers prepared crown ethers containing a phthalamide moiety (method BB).[196,197] The starting bis(phthalimide) and diamine were reacted in a water–methanol mixture, and the product was isolated by chromatography.

Method BB



Other benzodiaza-crowns containing *N*-acetic acid substituents have recently been reported.[198] The synthetic procedure involved the use of ethylenediaminetetraacetic dianhydride (method BC). Bislactones have been prepared with yields in the 21–24% range. These authors also prepared a bislactam with two benzo rings starting with A plus a diamine.[198]

Method BC

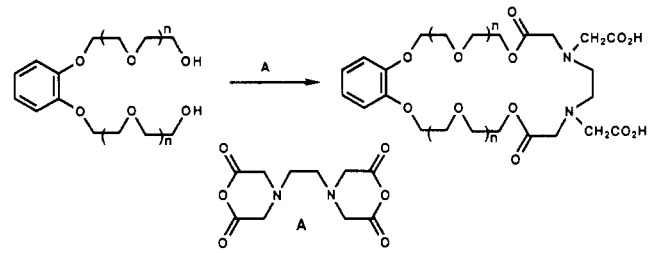


Table IV contains a listing of monobenzoaza-crowns.

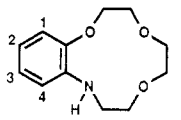
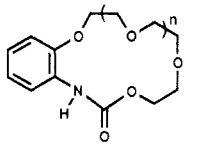
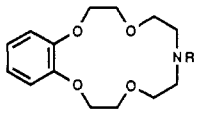
2. *Two Benzo Units*

An early synthesis of a dibenzodiaza-crown was reported by Wudl and Gaeta.[199] They used optically active proline to obtain a macrocycle containing two benzo and two pyrolidine rings (method BD). These researchers also prepared a macrocycle from D-ephedrine.[199]

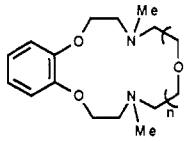
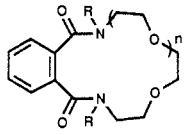
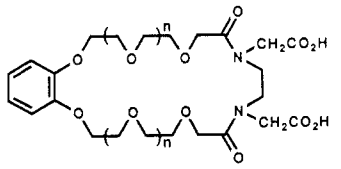
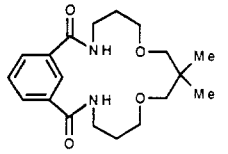
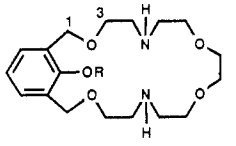
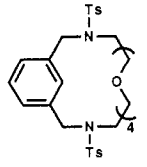
TABLE IV. Monobenzoaza-Crowns

1. One Benzo Unit

A. Benzoaza-Crowns

entry no.	structure	R	*n*	other substituents	method	ref (yield)
792					N/A	200
793				2-(N=NC$_6$H$_4$-4-NO$_2$)	from no. 792	200 (36%)
794			1		as G	108 (35%)
795			2		as G	108 (50%)
796		MeO(CH$_2$)$_2$			as B	364
797		BuO(CH$_2$)$_2$			as B	364
798		Me(CH$_2$CH$_2$O)$_2$			as B	364
799		Ts			as B	223

B. Benzodiaza-Crowns

entry no.	structure	R	*n* or other substituents	method	ref (yield)
800			1	other	266 (95%)
801			2	N/A	267, 365
802		H	1	BB	196, 197 (38%)
803		H	2	BB	196, 197 (7%)
804		H	3	BB	196, 197 (9%)
802		Me	2	as P	75 (37%)
806			0	BC	198 (24%)
807			1	BC	198 (22%)
808				other	134 (91%)
809		H		from no. 810	132 (79%)
810		Me	4,15-(O)$_2$	as P	132 (40%)
811				as Q	98 (46%)

C. Benzotriaza(tetraaza)-Crowns

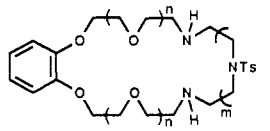
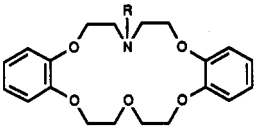
entry no.	structure	*n*	*m*	method	ref (yield)
812		1	1	AW	192 (75%)
813		2	1	AW	192 (71%)
814		3	1	AW	192 (65%)
815		1	2	AW	192 (64%)
816		2	2	AW	192 (55%)
817		3	2	AW	192 (46%)

TABLE IV (Continued)

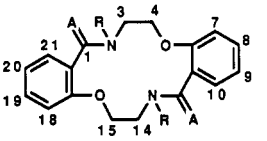
2. Two Benzo Units

A. Dibenzomonoaza-Crowns



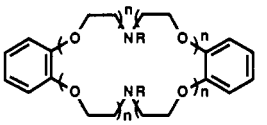
entry no.	R: formula index	R: structure	method	ref (yield)
818	C_3H_5	allyl	BH	203
819	C_3H_7O	$MeO(CH_2)_2$	BH	203
			N/A	366
820	C_4H_9	*n*-Bu	BH	203
			N/A	366
			N/A	363
821	C_4H_9O	$EtO(CH_2)_2$	BH	203
			N/A	366, 367
822	C_5H_{11}	C_5H_{11}	BH	203
			N/A	366
823	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$	BH	203
			N/A	366
824	$C_6H_{13}O$	$BuO(CH_2)_2$	BH	203
			N/A	366
825	C_7H_7	$PhCH_2$	BH	203
			N/A	366
826	$C_8H_{17}O_2$	$Bu(OCH_2CH_2)_2$	BH	203
			N/A	366

B. Dibenzodiaza-Crowns with Methylenyl Bridges and *o*-Benzo Groups



entry no.	R	A	other substituents	method	ref (yield)
827	H	H_2		BO	214
				BP	215 (82–84%)
828	H	H_2	3,14-Me_2	BP	215 (75%)
829	H	H_2	3,14-(*i*-Pr)$_2$	BP	215 (70%)
830	Me	H_2	2,13-Me_2; 3,14-(*i*-Pr)$_2$	from no. 829	215 (40%)
831	MeCO	H_2	2,13-$[CH_3C(O)]_2$	from no. 827	215 (70%)
832	H	O		BP	215 (62%)
833	H	O	3,14-Me_2	BP	215 (69%)
834	H	O	3-(*i*-Pr)	BP	215 (40%)
835	H	O	3-(*i*-Pr); 14-Me	BP	215 (41%)
836	H	O	3,14-(*i*-Pr)$_2$	BP	215 (72%)
837	H	O	3,14-(*s*-Bu)$_2$	BP	215 (60%)
838	H	O	3-$(CH_2)_2SMe$	BP	215 (45%)
839	H	O	3,14-$[(CH_2)_2SMe]_2$	BP	215 (57%)
840	H	O	3,14-$(CH_2SCH_2Ph)_2$	BP	215 (70%)
841	H	O	3-Me; 4-Ph	BP	215 (62%)
842	H	O	3,14-Me_2; 4,15-Ph_2	BP	215 (62%, 25%)

C. Dibenzodiaza-Crowns with *o*-Benzo Groups



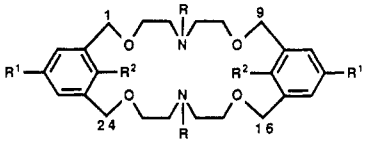
entry no.	R: formula index	R: structure	*n*	method	ref (yield)
843	H	H	2	from no. 859	368 (66%)
844	CH_3	Me	1	other	266 (92%)
845	CH_3	Me	2	from no. 847	368 (76%)
846	C_3H_5	allyl	1	BH	366, 203
				N/A	367
847	$C_3H_5O_2$	EtO_2C	2	from no. 843	368 (65%)
				N/A	369
848	C_3H_7O	$MeO(CH_2)_2$	1	BH	203, 366
849	$C_4H_7O_2$	EtO_2CCH_2	2	from no. 843	368
				N/A	370
850	C_4H_9	*n*-Bu	1	BH	203, 366
851	C_4H_9O	$EtO(CH_2)_2$	1	N/A	367
			1	BH	203, 366

TABLE IV (Continued)

C. Dibenzodiaza-Crowns with *o*-Benzo Groups

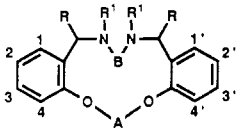
entry no.	R		*n*	method	ref (yield)
	formula index	structure			
852	C_5H_{11}	C_5H_{11}	1	BH	203, 366
				N/A	367, 371
853	$C_5H_{11}O_2$	$Me(OCH_2CH_2)_2$	1	BH	203
854	C_6H_5	Ph	1	BH	372 (10%)
855	$C_6H_{13}O$	$BuO(CH_2)_2$	1	BH	203, 366
856	C_7H_7	$PhCH_2$	1	BH	372 (34%)
				from no. 843	367
857	C_7H_7	$PhCH_2$	2	from no. 843	368
858	C_7H_7O	4-$MeOC_6H_4$	1	BH	372 (64%)
				other	372 (57%)
859	$C_7H_7O_2S$	Ts	2	other	368 (23%)
				N/A	369
860	C_8H_9O	4-$MeOC_6H_4CH_2$	2	from no. 843	368 (71%)
861	$C_8H_{17}O_2$	$Bu(OCH_2CH_2)_2$	1	BH	203, 366

D. Dibenzodiaza-Crowns with Methylenyl Bridges and *m*-Benzo Groups



entry no.	R	R^1	R^2	other substituents	method	ref (yield)
862	Me	H	H		BI	141 (11%)
863	Me	Me	OMe		BI	205
864	Et	Cl	OMe		BI	205
865	*n*-Bu	Me	OMe		BI	205
866	*n*-Bu	Cl	OMe		BI	205
867	C_8H_{17}	Me	OMe		BI	205
868	C_8H_{17}	Cl	OMe		BI	205
869	Ts	H	OMe	1,9,16,24-$(O)_4$	BI	204 (4%)
870	Ts	Me	OMe		BI	205
871	Ts	Cl	OMe		BI	205

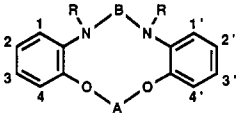
E. Dibenzodi(tri)aza-Crowns with Aza Groups Two Atoms Removed from the Benzo Units



entry no.	A	B	R	R^1	other substituents	method	ref (yield)
872	$(CH_2)_2$	$(CH_2)_2$	H	H		N/A	373, 374, 375
873	$(CH_2)_2$	$CH_2CH(Me)$	H	H		N/A	375
874	$(CH_2)_2$	$(CH_2)_3$	H	H		N/A	373, 374, 375
875	$(CH_2)_2$	$(CH_2)_3$	H	H	2,2′-Cl_2	N/A	373, 375
876	$(CH_2)_2$	$(CH_2)_3$	H	H	4,4′-OMe_2	N/A	373
877	$(CH_2)_2$	$(CH_2)_3$	H	Me		N/A	373, 375
878	$(CH_2)_3$	$(CH_2)_3$	H	H		N/A	373, 374, 375
879	$(CH_2)_4$	$(CH_2)_3$	H	H		N/A	373, 375
880	$(CH_2)_2$	$CH_2CHOHCH_2$	H	H		N/A	375
881	$(CH_2)_2$	$CH_2CHOHCH_2$	H	Me		N/A	374
882	$(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	H	H		N/A	376
883	$(CH_2)_2$	$(CH_2)_2NH(CH_2)_2$	H	H		BN	212 (40%)
						N/A	374, 376–380
884	$(CH_2)_2$	$CH(Me)CH_2NHCH(Me)CH_2$	H	H		N/A	379, 380
885	$(CH_2)_2$	$CH(Me)CH_2NHCH_2CH(Me)$	H	H		BN	212 (50%)
						N/A	379, 380
886	$(CH_2)_2$	$(CH_2)_2NH(CH_2)_3$	H	H		BN	212 (55%)
						N/A	378
887	$(CH_2)_2$	$(CH_2)_2NH(CH_2)_4$	H	H		N/A	378
888	$(CH_2)_2$	$(CH_2)_3NH(CH_2)_3$	H	H		N/A	378
889	$(CH_2)_2$	$(CH_2)_3N(Me)(CH_2)_3$	H	H		N/A	378
890	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2$	H	H		BN	213 (58%)
891	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2$	Me	H		BN	213 (96%)
892	$(CH_2)_2O(CH_2)_2$	$(CH_2)_3$	H	H		BN	213 (75%)
893	$(CH_2)_2O(CH_2)_2$	$(CH_2)_3$	Me	H		BN	213 (90%)
894	$CH_2(CH_2OCH_2)_2CH_2$	$(CH_2)_2$	H	H		BN	213
895	$CH_2(CH_2OCH_2)_2CH_2$	$(CH_2)_3$	H	H		BN	213

TABLE IV (Continued)

F. Dibenzodi(tri,tetra)aza-Crowns with Aza Groups next to the Benzo Units



entry no.	A	B	R	other substituents	method	ref (yield)
896	$(CH_2)_2$	$(CH_2)_2$	H		BF, other	101 (3%, 6%)
897	$(CH_2)_2$	$(CH_2)_3$	H		BF, other	101 (9%)
898	$(CH_2)_3$	$(CH_2)_2$	H		BF, other	101 (1%, 7%)
899	$(CH_2)_3$	$(CH_2)_3$	H		BF, other	101 (4%)
900	$(CH_2)_2$	$(CH_2)_5$	H		BG	201 (80%)
					N/A	202
901	$(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	H		BG	201 (84%)
					N/A	202
902	$(CH_2)_2$	$C(O)CH_2OCH_2C(O)$	H		BG, other	201 (87%)
903	$(CH_2)_2$	$C(O)(CH_2)_3C(O)$	H		BG, other	201 (50%)
904	$(CH_2)_2$	$(CH_2)_2N(Ts)(CH_2)_2$	H		N/A	202
905	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2$	H		BF, other	101 (8%)
					BG	200 (77%)
906	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2$	H	$3,3'$-$(4\text{-}NO_2C_6H_4N{=}N)_2$	from no. 905	200 (11%)
907	$(CH_2)_2O(CH_2)_2$	$C(O)C(O)$	H		BG	200 (54%)
908	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	H		BG	200 (71%)
909	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	H	$3,3'$-$(4\text{-}NO_2C_6H_4N{=}N)_2$	from no. 908	200 (32%)
910	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	MeC(O)		other	66 (11%)
911	$(CH_2)_2O(CH_2)_2$	$C(O)CH_2OCH_2C(O)$	H		BG	200 (40%)
					BG, other	66 (41%)
912	$(CH_2)_2O(CH_2)_2$	$C(O)CH_2N(Me)CH_2C(O)$	H		BG, other	66 (10%)
913	$(CH_2)_2O(CH_2)_2$	$CH_2(CH_2OCH_2)_2CH_2$	H		BF, other	101 (12%)
914	$CH_2(CH_2OCH_2)_2CH_2$	$(CH_2)_2$	H		BF, other	101 (8%)
915	$CH_2(CH_2OCH_2)_2CH_2$	$C(O)CH_2OCH_2C(O)$	H		BG, other	66 (14%)
916	$(CH_2)_2O(CH_2)_2$	$[C(O)CH_2N(CH_2CO_2H)CH_2]_2$	H		BC, other	198 (55%)
917	$CH_2(CH_2OCH_2)_2CH_2$	$[C(O)CH_2N(CH_2CO_2H)CH_2]_2$	H		BC, other	198 (42%)

G. Miscellaneous Dibenzoaza-Crowns

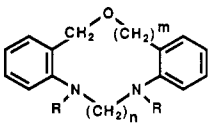
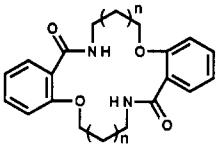
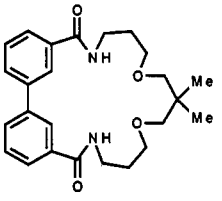
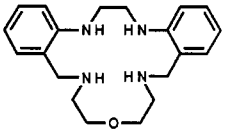
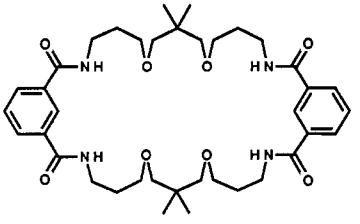
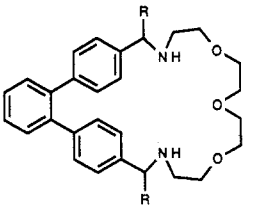
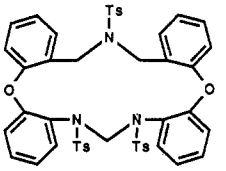
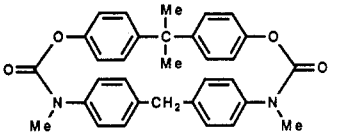
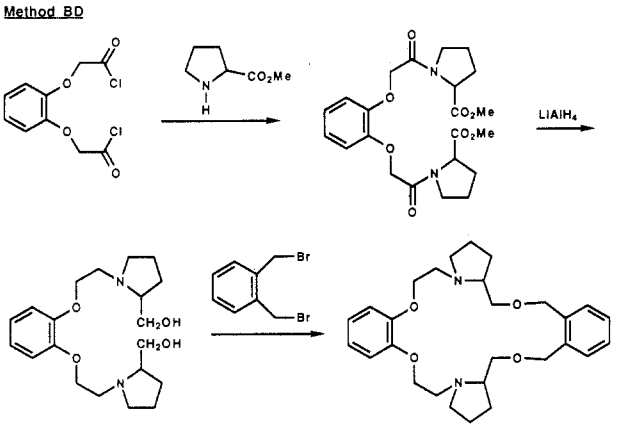
entry no.	structure	m	n	R	method	ref (yield)
918		0	4	H	BF, other	381 (26%)
919		1	3	Ts	BF, other	382 (93%)
920		1	4	Ts	BF, other	382 (95%)
921		0	4	Ts	BF, other	381 (35%)
922			1		BP	215 (45%)
923			2		BP	215 (38%)
924					other	134 (76%)
925					N/A	376
926					other	134

TABLE IV (Continued)

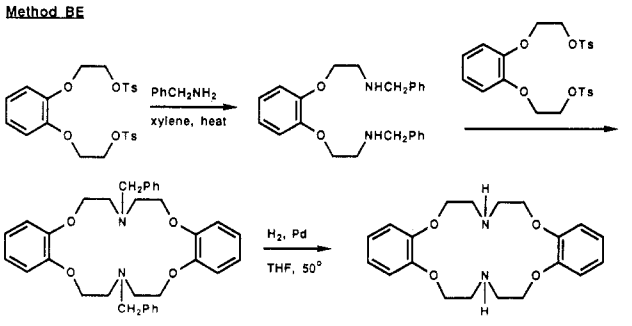
3. Three or Four Benzo Units

A. Miscellaneous

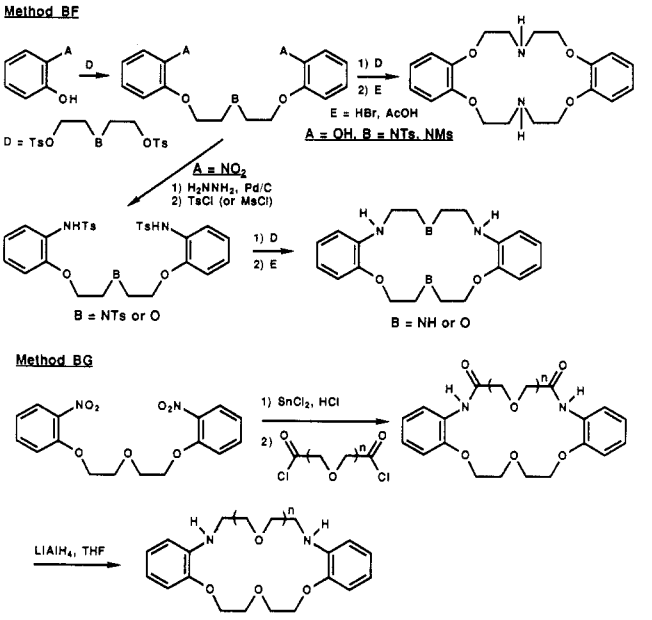
entry no.	structure	R	method	ref (yield)
927		H	from no. 928	343 (32%)
928		O	as P	343 (80%)
929			other	65 (31%)
930			other	378



Pedersen prepared one dibenzodiaza-crown by a three-step process (method BE).[190]

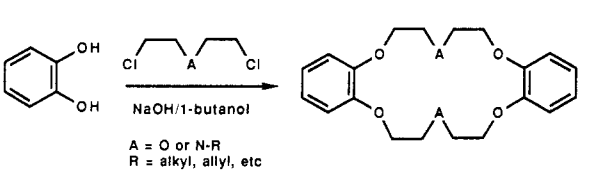


Högberg and Cram prepared the same dibenzodiaza-crown by a different procedure (method BF).[191] This procedure allows the synthesis of dibenzo-crowns containing from two to four nitrogen atoms, depending on the nature of A and B in the starting materials. The small amount of benzene ring bromination product in this reaction was removed by reduction with hydrazine and palladium on carbon. Lockhart and Thompson used a similar approach to prepare a dibenzodiaza-crown except they used a triglycolyl dichloride in the ring-closure step followed by reduction (method BG).[148] This latter method, (method BG), using the Stetter



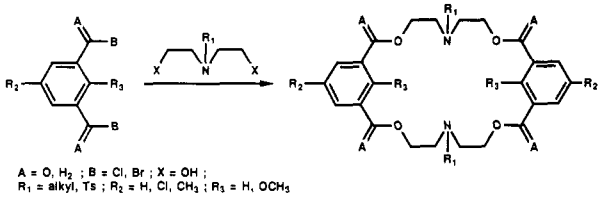
bis(amide) synthesis for ring closure, has been used by other researchers in the preparation of dibenzodiaza-crowns.[200-202] Biernat and co-workers have prepared a series of dibenzodiaza-crowns by methods BF and BG except that some of their macrocycles contained propylene bridges and they used dichlorides as well as activated diacid intermediates as discussed in section III.B.[66,101]

As would be expected, the dibenzodiaza-crowns have been prepared by a one-pot synthesis using catechol and *N*-alkyl-substituted bis(2-chloroethyl)amine (method BH).[203] These authors patterned their work after



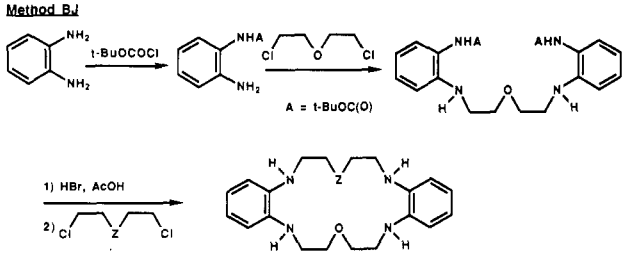
Pedersen's patent for dibenzoaza-18-crown-6.[190] A similar synthesis used either isophthaloyl dichloride or *m*-bis(bromomethyl)benzene to form dibenzodiaza macrocycles (method BI).[141,204,205]

Method BI



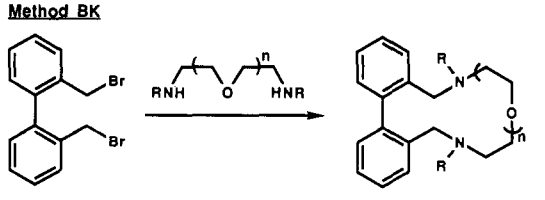
1,2-Diaminobenzene has been used to prepare dibenzoaza-crowns (method BJ).[190] One of the amino nitrogens was blocked with *tert*-butoxycarbonyl chloride, which was readily removed in a later step. Unfortunately, the experimental procedure is not fully described in the patent.

Method BJ

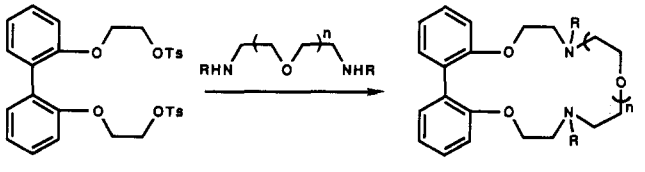


Sutherland and co-workers have prepared some interesting biphenyl-containing diaza-crowns (methods BK and BL).[206] The R group was (benzyloxy)carbonyl,

Method BK

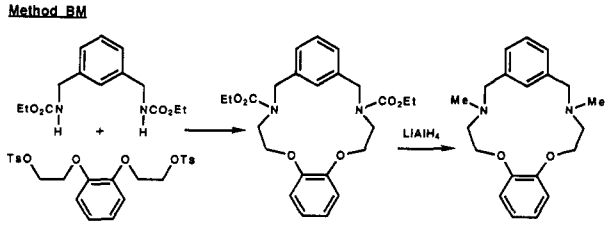


Method BL



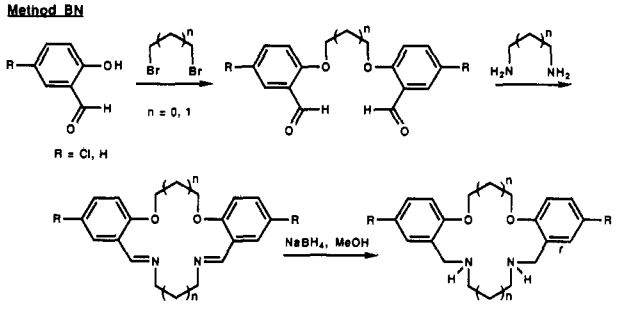
which could be reduced to give methyl substituents or could be hydrolyzed with HBr/AcOH to give the bis-NH crown. A mixed 1,2-benzo- and 1,3-benzodiaza-crown system was prepared by the same researchers (method BM).[194] In another paper, these authors reported the preparation of bis(1,2-benzodiaza-crowns) using this same method.[167]

Method BM



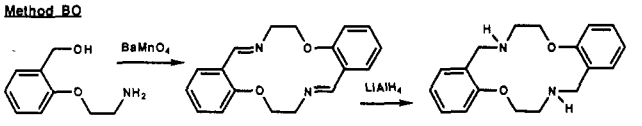
The synthesis of a variety of dibenzo-containing aza-crowns from salicylaldehyde or its derivatives has been reported by Lindoy and co-workers.[207-212] The salicylaldehyde was first reacted with a dihalide followed by condensation with a diamine to form an imine, which was reduced as shown (method BN). These workers also reversed the process by first reacting the salicylaldehyde with the diamine followed by the dihalide. Kodera and co-workers used the same method to prepare a series of diamino-crowns except they also used $LiAlH_4$ in the reduction step.[213]

Method BN



Wild and co-workers prepared a dibenzodiaza-14-crown-4 with a trans arrangement of the N_2O_2 donor groups (method BO).[214] The hydroxymethyl group of

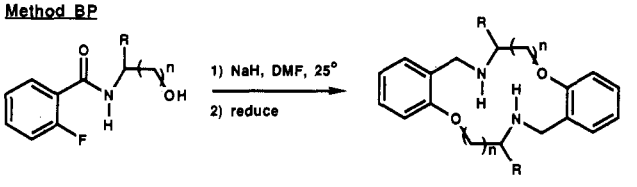
Method BO



the starting material was first oxidized to the aldehyde, which condensed with the primary amine of another molecule of starting material. The resulting bis Schiff base was reduced to form the final dibenzodiaza-crown.

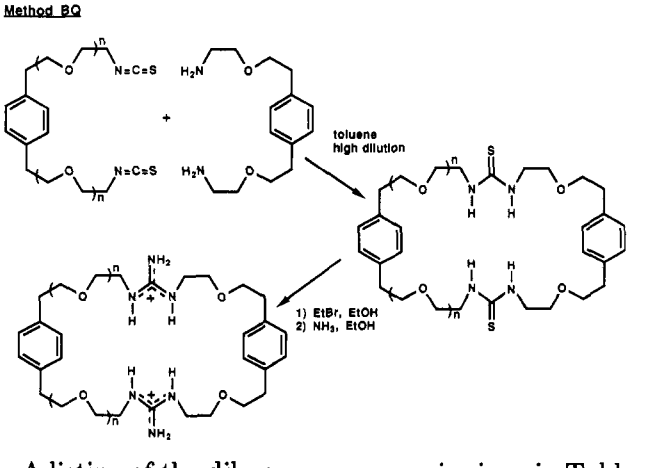
Recently, Schultz and co-workers reported a new procedure to prepare dibenzo N_2O_2 macrocycles.[215] They used the bimolecular cyclization reaction of *o*-fluorobenzamide derivatives (method BP).

Method BP



Lehn and co-workers prepared some macrocycles that incorporate two guanidinium groups into the macroring (method BQ).[216] A bis(isothiocyanate) was reacted with a diamine in the ring-closure step, followed by conversion of the bis(thiourea) into the bis(quanidinium) material.

Method BQ



A listing of the dibenzoaza-crowns is given in Table IV.

V. Organization of Tables

Tables I–IV give listings of the aza-crowns synthesized since 1981. The following remarks are pertinent for the tables.

Formula Index. This is the molecular formula for the substituent R groups. This allows for a more rapid search of the substituted aza-crown ethers. Each table is organized with the more simple substituents listed first, starting with the smaller number of carbons and then hydrogen, halogen, nitrogen, phosphorus, oxygen, and sulfur atoms.

Structure. Standard abbreviations for the various alkyl and aryl groups are used. In the case of substituted phenyl groups, a number is placed before the substituent to indicate its position on the benzene ring. In general, parentheses indicate that a group is attached to the preceding atom. For example, in $H_2NCH(Me)$-CH_2-, the Me group is attached to the preceding carbon atom. An (O) indicates a carbonyl oxygen atom.

Methods. The methods given in the tables are those shown in section IV. The symbol N/A indicates that a specific method was not given in the reference. The term "as K" indicates that the method used was similar to method K. Many substituted aza-crowns were prepared by modifying another aza-crown. In those cases, the tables shows a "from no. xxx" in the methods column. The term "Y(alk)" shows that the alkylation part of method Y was used. The term "X, other" indicates that the method was comparable to method X but some modifications were used in the reference. "Other" means that the method used was given in the reference but it was a "one of a kind" procedure and is not otherwise listed in this review.

Yields. The yields are those given for the last step in the reaction except where an overall yield was given. A yield given after two or more reference numbers means that the same reaction yield was reported in two or more references. The "% HCl" etc. indicates that the yield was for a salt of the aza-crown. A range of yields indicates that the reaction was carried out more than once, giving different yields. Some yields were determined by GLC and are so indicated.

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