Synthesis of *N*-Pivot Lariat Ethers

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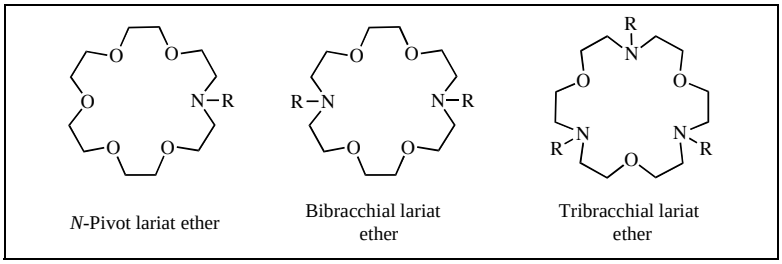

This review covers the main strategies for the synthesis of *N*-pivot lariat ethers as well as their specific syntheses.

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Contents

1. INTRODUCTION.

Since Pedersen [1] discovered crown ethers in 1967, there has been great interest in the synthesis of crown compounds in an attempt to find molecules with superior properties and proper applications in various areas. Different kinds of crown ligands have been synthesized including azacrown ethers, lariat ethers, cryptands, spherands and calixarenes and their applications have been studied and reviewed [2-10].

Our last reviews focused on the chemistry and applications of condensed azacrown ethers [11] as well as macrocyclic crown formazans [12]. This review casts light on the main strategies for the synthesis of *N*-pivot lariat ethers as well as their specific syntheses.

A number of other reviews [10,13] that have appeared concerning lariat ethers did not cover the synthesis of these compounds in an organized manner.

We have concentrated on the crown compounds containing at least 12-membered rings with at least one oxygen atom in the macro ring.

Lariat ethers are a class of macrocyclic polyether compounds having one or more donor-group-bearing sidearms [14]. Functionalization of macrocyclic polyether compounds with such additional donating centers is a good way to increase their complexing ability and selectivity [15].

Moreover, functionalization of crown ethers with ionizable sidearms opened access to switchable lariat ethers [16]. These are cation carriers that could achieve strong and selective binding of a cation and be able to release that cation rapidly enough to maintain a dynamic system through the pH control of cation complexation. Deprotonation of the ionizable group at high pH leads to strong binding to the cation due to a direct charge-charge interaction. On the other hand, lowering of the pH protonates the ionizable groups and diminishes the overall binding capacity of the system.

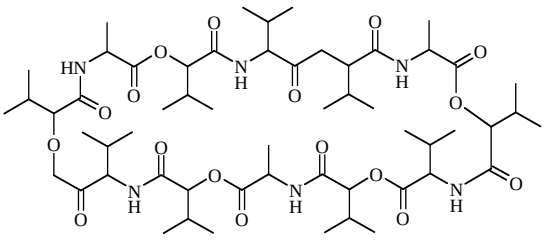
Lariat ethers with redox switchable subunits in a suitable position to interact with a ring bound cation were designed to accomplish the goal of controlling complexation and release of cations in a different technique that may be called redox switching [17]. Lariat ethers with nitrobenzene or anthraquinones sidearms are

examples of this approach. The interaction between the redox-switchable subunits and the bound cation is either weak or strong in the ground state. Oxidation will make the donor more positive and diminish its interaction with a cation. Reduction will add electron density and leads to strong interaction with a cation.

Furthermore, lariat ethers with chromogenic sidearms offer distinct advantages in detection of cations compared to the other available analytical methods. The color changes associated with complexation of different cations could make such sensors more versatile. Although change in potential or other properties could also be useful in sensing but they would be less apparent. It is noteworthy that Takagi *et al*. pioneered chromogenic lariat ether complexation [18]. Some *N*-pivot lariat ethers were reported to form luminescent complexes with divalent europium [19a]. de Silva and others reported lariat ethers that undergo fluorescence changes in the presence of alkali metal cations [19b-d].

Another stimulus for the development of lariat ethers was to mimic naturally occurring ionophores such as Valinomycin [20]. Valinomycin is one of the best K^+ complexing agents. It is a 36-membered ring with six amide and six ester carbonyl donor groups and a hydrophobic surface composed of nine isopropyl and three methyl groups. This molecule if planar (i.e. crown-like) is too large to accommodate K^+, for which it is quite selective.

Instead, the molecule folds over to create a three-dimensional cavity. In so doing, the backbone assumes "tennis-ball seam" geometry. The resulting conformation has the hydrophobic alkyl residues turned outward and a cavity that is the appropriate size for K^+. The amide donor groups are more planar than are the ester carbonyls but the latter bind the cation. This is for two reasons. First, the amides participate in transannular hydrogen bond formation that helps hold Valinomycin in the binding conformation. Second, since the amides are involved in hydrogen bonds, they can not bind to the cation.



Valinomycin

Compared to Valinomycin, cryptands had the required three-dimensionality but lacked dynamics. On the other hand the crown ethers were dynamic but lacked both the capability to envelop a cation and the requisite binding strength.

Lariat ethers should achieve a somewhat higher level of cation binding than generally observed with simple macrocyclic crown ethers by presenting a cation with a three-dimensional intramolecular array of binding sites as do the cryptands. Moreover, a higher degree of flexibility and dynamics characteristic of ionophores could be achieved. Thus, they combine characteristics of podands, corands and cryptands [11].

The concept of lariat ether now extended to encompass podands as well as macrocycles and to include molecules having sidearms that contain no donor, ionizable or chromogenic groups. In the latter case, the sidearms serve an important purpose different from bearing a Lewis basic donor group.

For example, some ligands with π-donor sidearms are prepared to explore the possible participation in cation binding [21]. Gokel *et al*. reported the synthesis of some steroidal lariat ethers, these compounds might have the appropriate balance of hydrophobicity and hydrophilicity either in neutral state or with a cation bound to form a membrane. All the systems showed a tendency to organize either into micelles or vesicles [22].

In addition some macrocyclic ligands with one or more fluorine-containing sidearms have potential applications in metal ion separations involving a fluorous phase or super critical carbon dioxide [23].

2. Nomenclature.

The physical resemblance of CPK molecular models of these compounds to rope lassoes coupled with the concept of "roping and tying" a cation suggested the name lariat ethers [14].

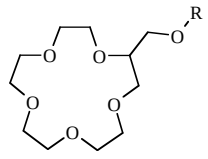
Lariat ethers are divided according to the point at which the sidearm and the macro ring meet (pivot atom), into two main classes:

i) ***C*-pivot lariat ethers I** [24].

Systems in which sidearms are attached to a carbon of the macro ring.

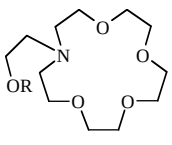
ii) ***N*-pivot lariat ethers II** [25].

Systems in which sidearms are attached to nitrogen of the macro ring.



I

A carbon-pivot lariat ether



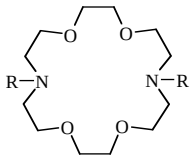
II

A nitrogen-pivot lariat ether

When more than one sidearm is attached, the number of them is designated using standard prefixed and the Latin word bracchium which means arm.

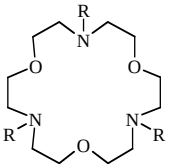
A two-armed compound **III** is thus bibracchial lariat ether and the name is abbreviated BiBLEs [26,27]. Three-

armed compound **IV** is tribracchial lariat ether and the name is abbreviated TriBLEs, etc.



III

Bibracchial lariat ether



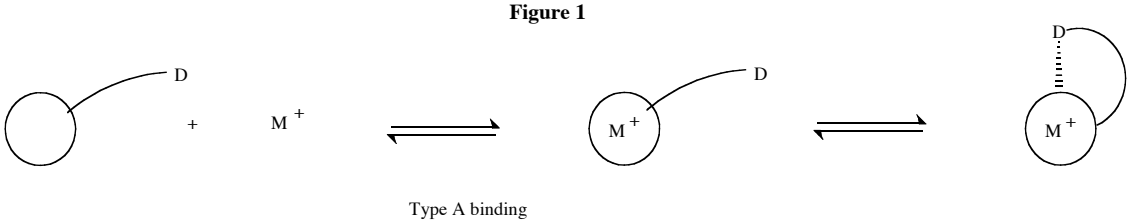
IV

Tribracchial lariat ether

3. Lariat ether complexation process.

The lariat ether idea is represented schematically in Fig. 1. The sidearm which contains one or more donor groups placed in appropriate position would provide a third dimension of solvation to a ring-bound cation (binding of Type A) [13].

Figure 1



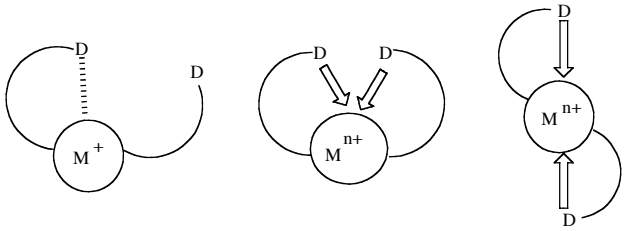
Type A binding

Two armed crown ethers have various kinds of cation binding modes (Fig. 2) [26]:

a) Only one sidearm interacts with guest metal cation (Type B).

b) Two sidearms provide coordination from the same or opposite side (Type C or Type D).

Figure 2



Type B Type C Type D

It is noteworthy to mention that carbon pivot lariat ethers proved to be more chemically stable but less dynamic than the *N*-pivot counterparts. The greater flexibility of the latter is due to the facile inversion of the nitrogen atom, a property not shared by carbon.

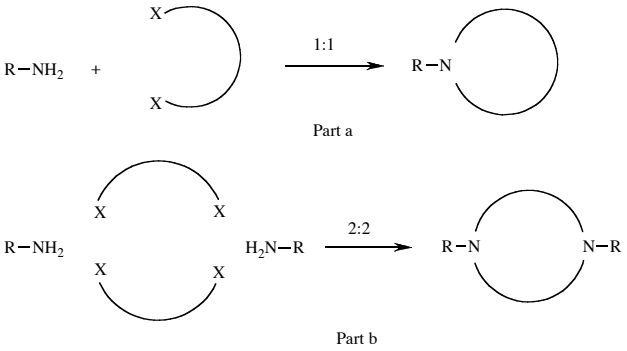
4. Main strategies for the preparation of *N*-pivot lariat ethers.

In general, the synthesis of *N*-pivot lariat ethers was performed by one of three methods:

4.1. Cyclization Reactions.

Cyclization is possible using primary or secondary amines. A primary amine can be cyclized with oligoethylene glycol dihalide or ditosylate to give a cyclic product by double alkylation of the amine group. These reactions were used mostly in 1:1 or 2:2 cyclization (Scheme 1, parts a,b).

Scheme 1

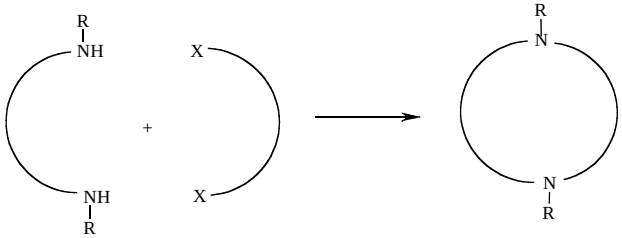


Part a

Part b

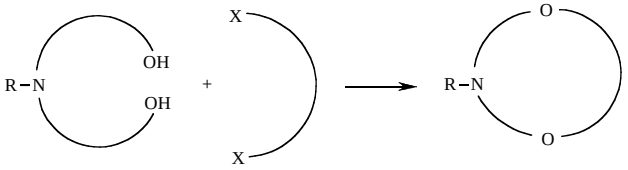
Alternatively, bis(secondary amines) can be cyclized with the appropriate dihalide or ditosylate to give the corresponding *N*,*N*-disubstituted cyclic products (Scheme 2).

Scheme 2



Cyclization is possible using other end functional groups particularly hydroxyl. For example reaction of *N*-substituted dialkanolamines with the appropriate dihalides or ditosylates in basic solution afforded the corresponding cyclic product (Scheme 3).

Scheme 3



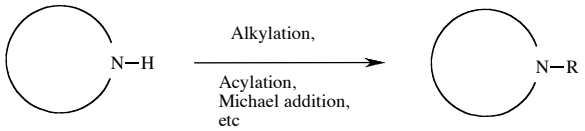
The cyclization approach requires high dilution techniques to avoid the formation of polycondensation products. In some cases the use of a metal cation as a template produced better cyclization yields [25].

Gokel *et al*. [25] classified nitrogen-pivot lariat ethers into three groups based on the cyclization yields. Lariat ethers having donor groups on flexible sidearms afforded products in good yields. Those compounds, which have sidearms incapable for geometrical reasons of coordinating a cation or lacking a donor group on the sidearm, were generally formed in low yield. Lariat ethers having relatively rigid sidearms containing ether donor groups cyclized in moderate yields. Restricted rotational freedom in the starting materials was reported to improve the cyclization yields [27].

4.2. Attachment of the sidearm by chemical modification of an amino group of azacrown ether.

In this method, the sidearms were attached to the macro ring by reaction of the secondary amine of crown rings with the appropriate reagent using some known reactions, like alkylation, acylation, Micheal addition, etc (Scheme 4).

Scheme 4

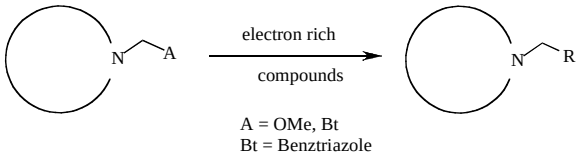


This method seems to be more effective and simpler than the cyclization process. The yields of the lariat crown are usually high and the reaction is not complicated by the formation of polymer or products of alternative cyclization. It could also be applied for the synthesis of bibracchial as well as tribracchial lariat ethers.

4.3. Electrophilic substitution reactions of N-CH_2-A containing azacrown ether (where A stands for an activation group that leave after the formation of a new bond).

This method is mostly represented by the reaction of *N*-(methoxymethyl) derivatives of azacrowns with various CH or NH active compounds and can be considered a variation of the Mannich reaction. This method was developed by Luk'yanenko *et al*. [28,29]. Moreover, Katritzky *et al*. [30] reported the synthesis of some *N*-pivot lariat ethers by the reaction of *N*-(benzotriazolylmethyl) substituted azacrown ethers with electron-rich compounds (Scheme 5).

Scheme 5



Bibracchial as well as tribracchial larait ethers can also be prepared using the above strategies.

5. General and specific synthesis of *N*-pivot lariat ethers.

5.1. Cyclization reactions.

Six approaches were reported for the formation of *N*-pivot lariat ethers by cyclization of different precursors:

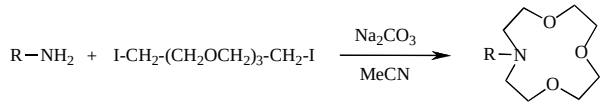
5.1.1 Cyclobis-dialkylation of a primary amine with the appropriate diiodoalkane (1+1 cyclization) (Method A).

This method is used for the synthesis of *N*-substituted monoaza-12-crown-4 and *N*-substituted monoaza-15-crown-5.

5.1.1.1. Synthesis of monoaza-12-crown-4.

Calverley and Dale [31,32] used this method for the preparation of *N*-substituted derivatives of monoaza-12-crown-4 by condensing 1,11-diiodo-3,6,9-trioxaundecane with the appropriate primary amines in acetonitrile solution containing Na_2CO_3 (Scheme 6). The reaction mechanism presumably involves two S_N2 substitution reactions of nitrogen on the diiodide [33]. Sodium carbonate deprotonates the intermediate iodoammonium salt and the Na^+ ion may also serve as a template for cyclization.

Scheme 6



It appears that the decrease in amine nucleophilicity diminishes the yield. Thus 2-methoxybenzyl amine affords the corresponding cyclic product in nearly twice the yield obtained with 2-methoxyaniline.

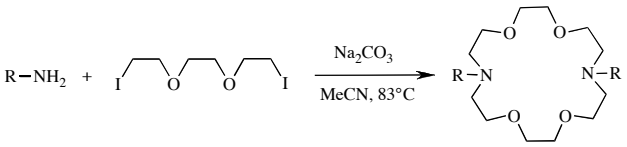
In addition, product yields appeared to be lower when nitrogen is sterically hindered. Thus 4-methoxyaniline afforded the corresponding cyclic product in nearly twice the yield obtained with 2-methoxyaniline.

5.1.1.2. Synthesis of monoaza-15-crown-5.

Bako *et al.* [34-47] reported the synthesis of some *N*-substituted chiral monoaza-15-crown-5 compounds anellated to glucose, galactose, mannose or derived from D-mannitol by cyclizing the appropriate bis-iodo derivatives with various primary amines under similar conditions to those described by Calverley and Dale [31,32] (Scheme 7).

The bis-iodo derivatives anellated to sugar units were obtained by alkylation of the appropriate diols with bis(2-chloroethyl) ethers to give the corresponding bis-chloro derivatives followed by exchange of the chlorine in the latter by iodine upon reaction with NaI in acetone.

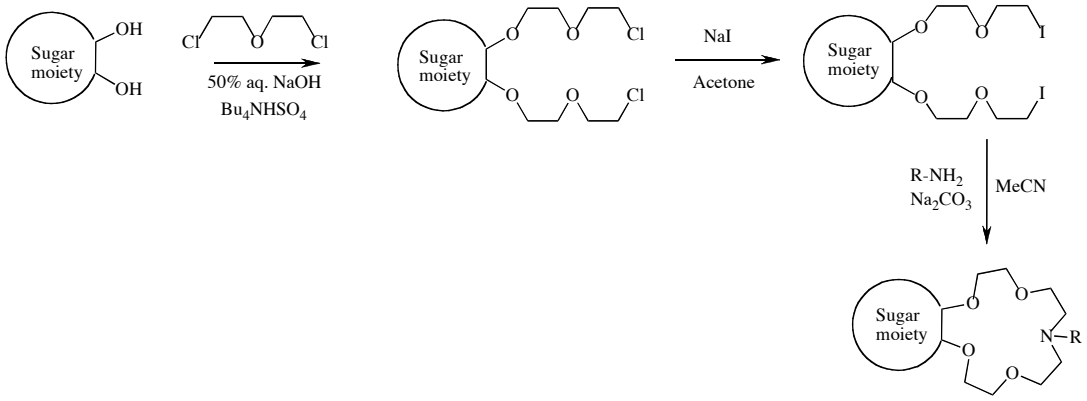
Scheme 8



This method is inappropriate for the synthesis of *N*,*N*'-disubstituted-1,7-diaza-15-crown-5. It is also not appropriate for the synthesis of symmetrical *N*,*N*'-diaryl substituted derivatives of 1,10-diaza-18-crown-6.

When *p*-anisidine was reacted with 1,2-bis(2-iodoethoxy)ethane under the same conditions used for the aliphatic amines, *N*-(*p*-methoxyphenyl)monoaza-9-crown-3 was the only cyclized product obtained from the reaction [15a] (Scheme 9). Its formation is much slower than the usual rate of dimer formation. The aniline nitrogen is less nucleophilic than aliphatic nitrogen and therefore reacts more slowly with the primary iodide. It appears that once monoalkylation occurs, cyclization to a nine-membered ring is preferred.

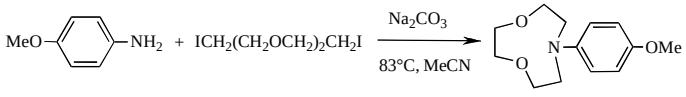
Scheme 7



5.1.2 Reaction of primary amine with 1,2-bis(2-iodoethoxy)ethane (2:2 cyclization) (Method B).

This method is used for the synthesis of *N*,*N*'-disubstituted-1,10-diaza-18-crown-6 [15b]. It involves the reaction of 1ry alkylamines with 1,2-bis(2-iodoethoxy)-ethane in the presence of Na_2CO_3 and CH_3CN [15a] (Scheme 8). This one-step cyclization method involves the formation of four new C-N bonds and an 18-membered ring so the yields (typically 20-30%) are quite acceptable. In addition the sodium complexes occasionally crystallize directly from the solution, making the work-up simple.

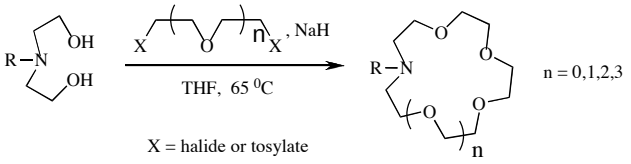
Scheme 9



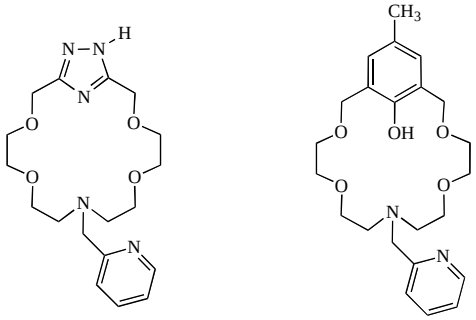
5.1.3. Cyclization of *N*-substituted dialkanolamine with the appropriate α,ω-oligo(ethylene glycol)-dihalides or ditosylates (Method C)

Cyclization of the appropriate *N*-substituted diethanolamines with the corresponding oligoethylene glycol dihalides or ditosylates in refluxing THF containing NaH is an appropriate method for the synthesis of 12-,15-,18- and 21-membered rings [25] (Scheme 10).

Scheme 10



Bradshaw *et al.* [48] demonstrated a similar approach for the synthesis of the following macrocyclic rings that contain proton ionizable subunits (triazole or *p*-cresol) as part of the cavity and a pyridine as sidearm.

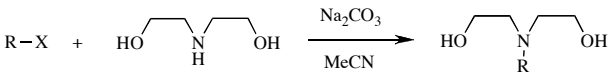


5.1.3.1 Synthesis of precursor's *N*-substituted diethanolamines.

Gokel and coworkers prepared the *N*-alkyl derivatives of diethanolamine in good yields by treating the appropriate amine with an alkyl halide using Na_2CO_3 as the base [25] (Scheme 11).

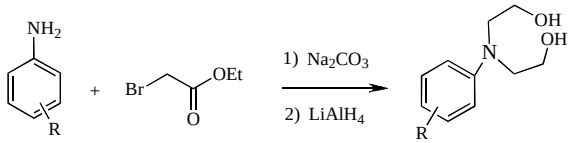
This reaction worked well when methyl 2-(2-chloroethoxy)ethyl ether was used as the alkylating agent but the products from the reaction of larger chloromethoxy derivatives bound miscellaneous salts so tightly that standard work-up techniques were not practical.

Scheme 11



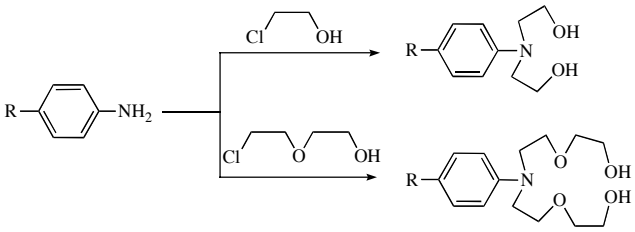
N-Phenyl substituted diethanol amines were prepared by reacting various anilines with ethyl bromoacetate followed by reduction [25] (Scheme 12).

Scheme 12



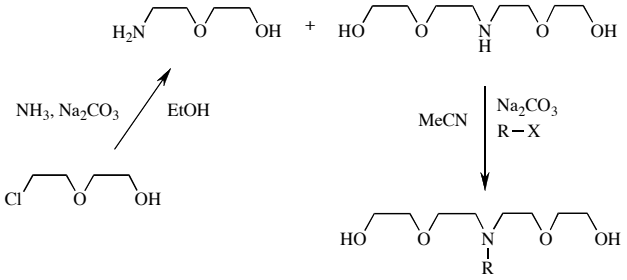
Zhang *et al.* [49] reported the synthesis of some *N*-arylsubstituted diols by the reaction of the appropriate aromatic amine with 2-chloroethanol and 2-[2-(chloroethoxy)ethanol], respectively (Scheme 13).

Scheme 13



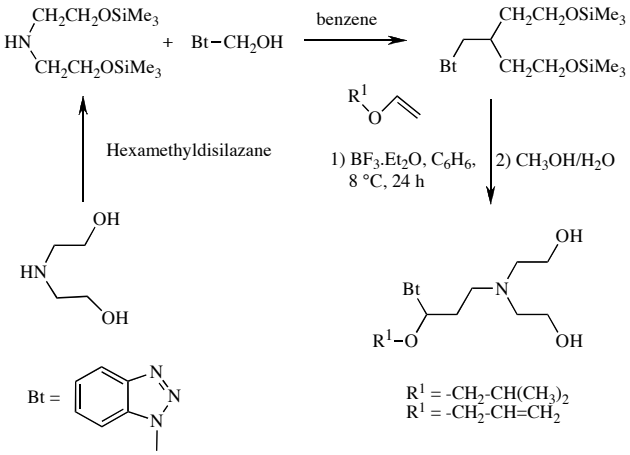
Krespan found that when 2-(2-chloroethoxy)ethanol was heated with ammonia in ethanol, a nearly equimolar mixture of 2-(2-aminoethoxy)ethanol and 6-aza-3,9-dioxaundecane-1,11-diol was isolated [50]. The latter underwent alkylation with the appropriate halo compound to give the corresponding *N*-alkyl derivatives [48] (Scheme 14).

Scheme 14



Katritzky *et al.* [51] reported the synthesis of *N*-substituted diethanolamines using a different approach as outlined in Scheme 15.

Scheme 15



Diethanol amine reacted with hexamethyl disilazane according to the general silylation method [52] to give the corresponding bis(*O*-silylated)diethanolamine in 91% yield. Subsequent reaction of the latter with 1-(hydroxymethyl)benzotriazole in benzene yielded the corresponding adducts with α-benzotriazolyl substituents which reacted with vinyl ethers to afford α-benzotriazolyl-substituted *O*-silylated ethers followed by hydrolysis with methanol-water to give the corresponding diols.

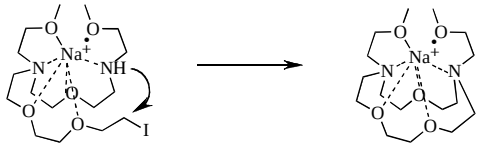
5.1.4 Cyclization of the appropriate bis(secondary amines) with the corresponding dihalides or ditosylates (Method D).

This method involves cyclization of bis(secondary amines) $(RNHCH_2CH_2)_nO$ with 1,2-bis(2-iodoethoxy)-ethane in the presence of Na_2CO_3, NaI and MeCN [15b] (Scheme 16). An important advantage of this method is that the sidearms are incorporated prior to cyclization, eliminating the need for a protection/deprotection.

When cyclization was attempted using $(CH_3OCH_2CH_2-NHCH_2CH_2OCH_2)_2$ with bis(2-iodoethyl) ether, no cyclization to the corresponding 15-membered bibracchial lariat ether was observed (Scheme 17). The failure was apparently due to competitive morpholinium salt formation.

When $(MeOCH_2CH_2NHCH_2CH_2)_2O$ was reacted with 1,2-bis(2-iodoethoxy)ethane, diaza-15-crown-5 was formed in 38% yield (Scheme 18). In the latter case, complexation of sodium (template effect) favors cyclization to the 15-membered bibracchial lariat ethers over cyclization to the nine-membered ring ammonium salt.

Scheme 18

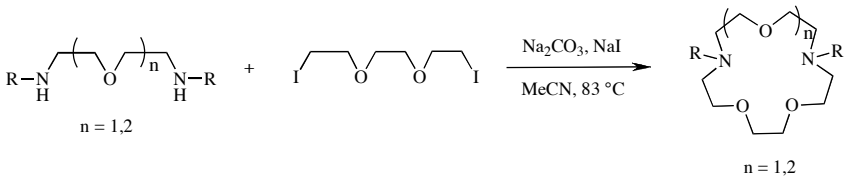


The synthesis of *N*,*N*'-disubstituted diaza-18-crown-6 compounds by method D has two advantages over their syntheses by method B: i) the yield of the product is higher compared to that obtained by method B, ii) purification of the products prepared using this method is easier than purification of the same compounds obtained from method B.

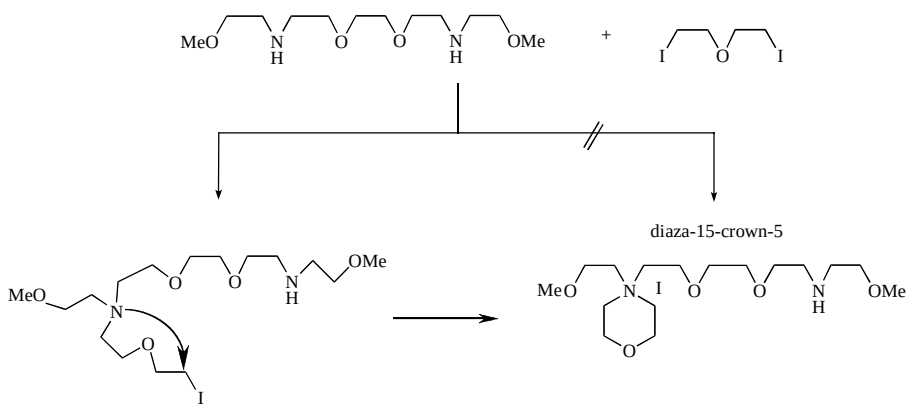
Demirel and Bulut [53] reported a similar approach (method D) for the synthesis of chiral *N*,*N*'-disubstituted benzo- and dibenzo-18-crown-6. They also studied the molecular recognition of these chiral crown ethers for amino acid K and Na salts.

Bradshaw *et al.* [54-56] reported a similar approach for the synthesis of *N*,*N*'-bis(2-hydroxyethyl)-1,4-diazacrown ethers and *N*-[(2-hydroxy-ethoxy)ethyl] substituted poly-azacrowns without the need for protecting the hydroxyl

Scheme 16

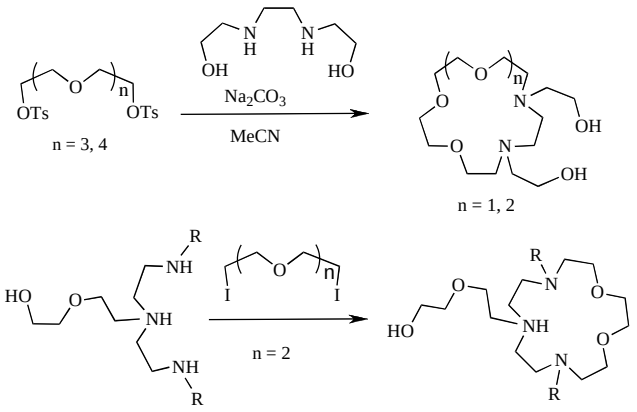


Scheme 17



group (Scheme 19). Cyclization of a hydroxyl- or dihydroxy- substituted diamine with the appropriate dihalo or ditosylate compounds took place on the two amine nitrogen atom because Na_2CO_3 which is used as a base in the reaction does not ionize the hydroxyl group.

Scheme 19



Macrocyclic diamides containing two 8-hydroxyquinolin-7-ylmethyl substituents were prepared in low yield using method D from diamines containing two 8-hydroxyquinolin-2-ylmethyl groups by reaction with the appropriate bis(α-chloroamide) in MeCN containing TEA as the base. Reduction of the resulting macrocyclic diamides by the borane-THF complex gives the corresponding tetramacrocycle in 27% yield [57,58] (Scheme 20).

The low yield (19%) of the obtained macrocyclic diamide could be due to the fact that TEA is a weak base which may not effectively remove the proton from the formed ammonium ion in the reaction intermediate (Structure a, Fig. 3). That proton could hydrogen bond with the amine function on the outer side of the pseudo macro-ring, thus reducing its nucleophilicity. It is also possible that the 8-hydroxy group of one 8-hydroxyquinoline could hydrogen bond with the amine close to the other 8-hydroxyquinoline thereby reducing its nucleophilicity (Structure b, Fig. 3) [58].

5.1.4.1 Synthesis of diamine precursors.

5.1.4.1.1 Synthesis of *N*,*N*'-symmetrical disubstituted 1,5-diamino-3-oxapentane.

N-Tosyl-substituted amines have 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 [59]. The tosyl blocking groups were removed by using sodium in isopropyl alcohol (Scheme 21). Other *N*,*N*'-dialkylamino ethers were prepared by Krakowiak and Kotelko by tosylating bis(2-aminoethyl)ether, followed by alkylation of the formed *N*,*N*'-ditosyl derivative with the appropriate alkyl halides

Scheme 20

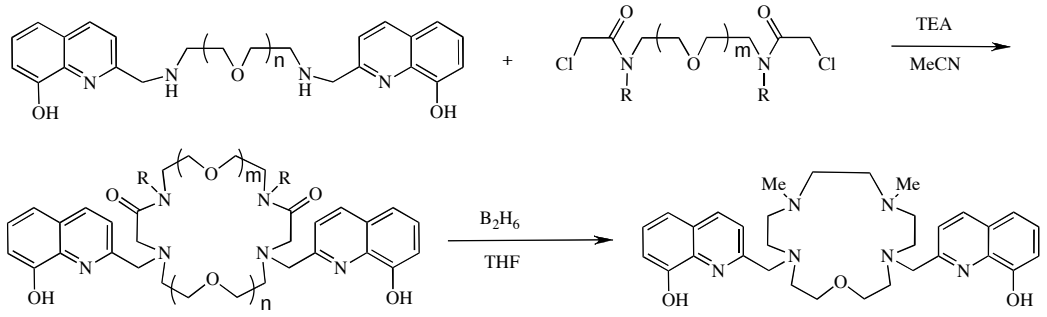
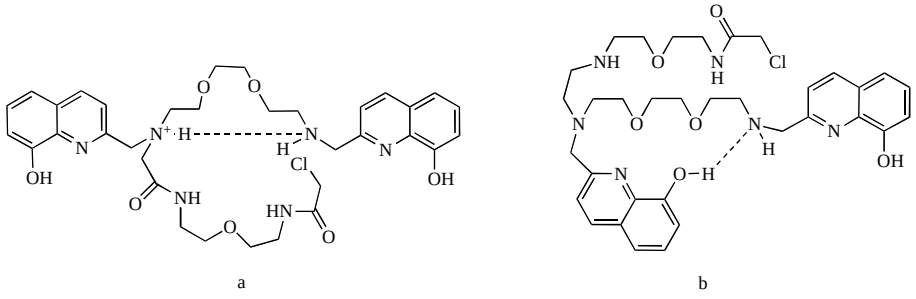
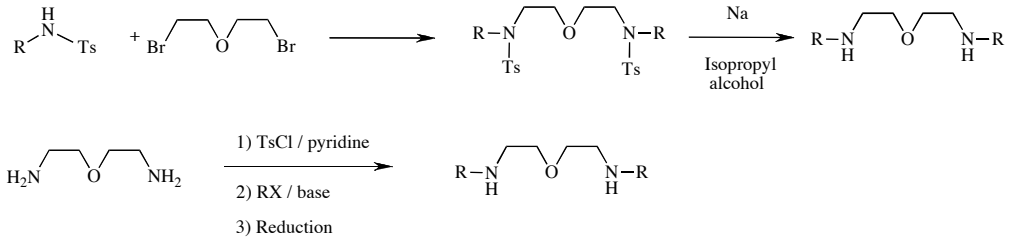


Figure 3



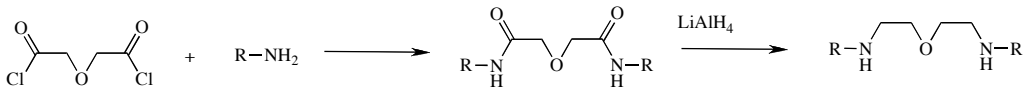
in basic solution and subsequent removing of the tosyl group by a reduction process [60] (Scheme 21).

Scheme 21



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 aluminium hydride [60] (Scheme 22).

Scheme 22



Diamines with a wide variety of alkyl substituents from methyl to 3-(*N*,*N*'-diethylamino)propyl were prepared in moderate yields using this method.

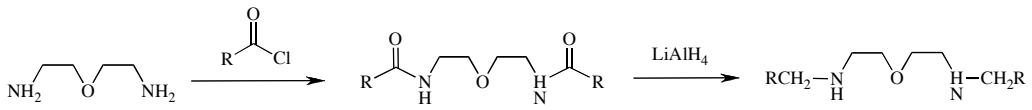
Pietraszkiewicz [61] and Gokel *et al.* [15b,62] used this procedure except borane was used as the reducing agent.

Gekel *et al.* [15b] also prepared *N*,*N*'-dialkylamino ethers by treating bis(2-aminoethyl)ether with the appropriate acid chloride followed by reduction of the resulting bis amide (Scheme 23).

Song *et al.* [58] prepared diamine containing two 8-hydroxyquinolin-2-ylmethyl groups by reductive amination of 8-hydroxyquinoline-2-carboxaldehyde with 1,5-diamino-3-oxapentane in dichloroethane containing sodium triacetoxy-borohydride (Scheme 24).

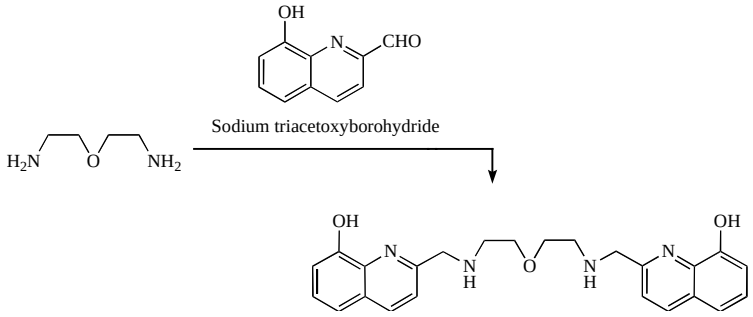
5.1.4.1.2. Synthesis of *N*,*N*'-unsymmetrical disubstituted 1,5-diamino-3-oxapentane

Scheme 23

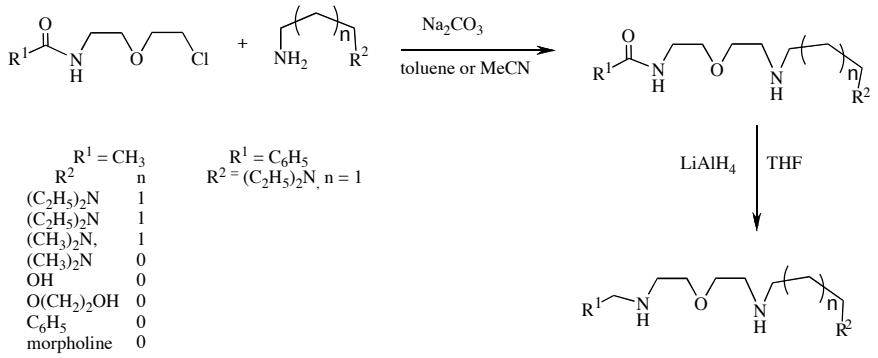


Bradshaw *et al.* [63] reported the synthesis of some bis-secondary amines that were not symmetrical by reacting *N*-[2-(2-chloroethoxy)ethyl]acetamide or its benzamide analogue with an excess of the appropriate primary amines using Na_2CO_3 as the base followed by reduction (Scheme 25).

Scheme 24



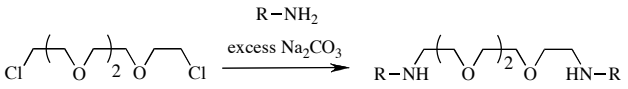
Scheme 25



5.1.4.1.3 Synthesis of *N*,*N*'-disubstituted 1,8-diamino-3,6-dioxaoctane.

A superior method to prepare the *N*,*N*'-dialkyl derivatives of 1,8-diamino-3,6-dioxaoctane uses the reaction of the readily available dichloro derivative of oligoethylene glycols with an excess of alkyl amine [15b,64,65] (Scheme 26). This process is not appropriate for the preparation of the diamino derivatives of diethylene glycol since the reaction of an amine with the dihalides yields only *N*-alkylmorpholine [15b,66].

Scheme 26



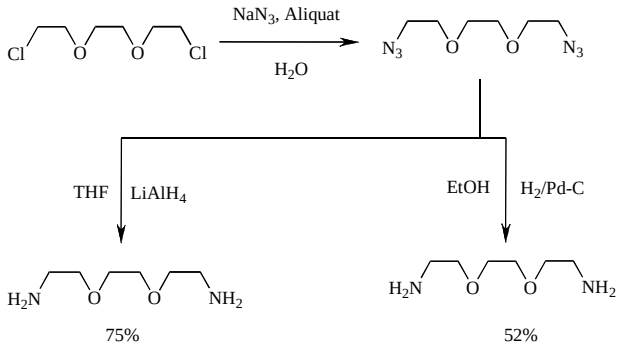
Gokel and coworkers used the more active diiodide in this reaction to prepare some *N*,*N*'-dialkylamines in better yields [15b,62].

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 the water formed in the reaction and obtained an 82% yield of the *N*,*N*-dibenzyl derivatives [65].

Demirel and Bulut [53] reported a synthesis of chiral amine precursors by the reaction of the appropriate ditosylate with *R*-(+)-1-phenylethylamine in refluxing xylene (Scheme 27).

Gokel *et al.* [15b] reported the synthesis of 1,8-diamino-3,6-dioxaoctane from the corresponding dichloride by first reaction with NaN_3 using a phase transfer reaction followed by reduction of the formed diazide with $LiAlH_4$H/THF or H_2/Pd-C/EtOH in 75% and 52% overall yields, respectively (Scheme 28).

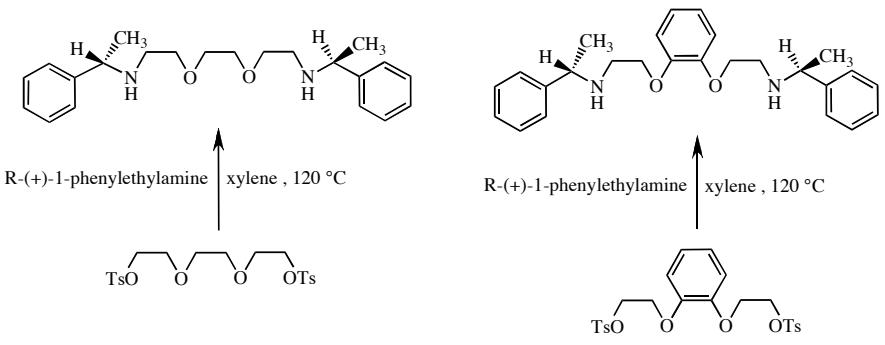
Scheme 28



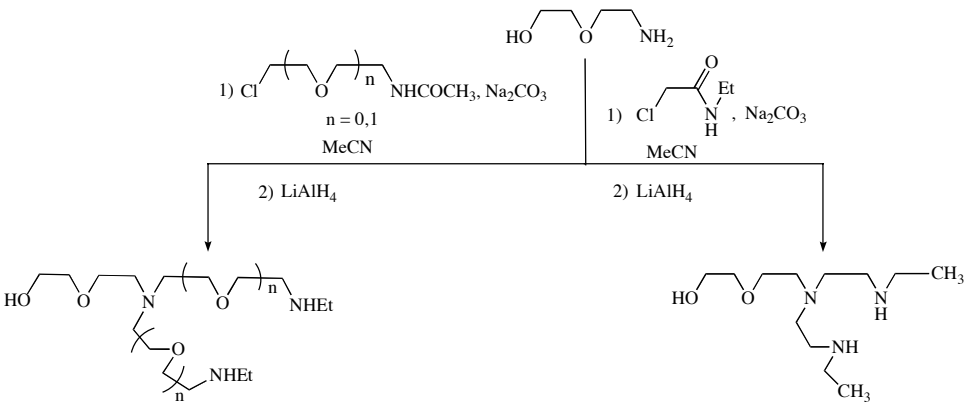
5.1.4.2 Synthesis of *N*-hydroxy-substituted diamines

Bradshaw *et al.* [54] reported the synthesis of some *N*-hydroxy-substituted diamines by alkylation of hydroxy-ethoxyethyl amine with the corresponding chloroacetamide derivatives followed by reduction with $LiAlH_4$ (Scheme 29).

Scheme 27



Scheme 29

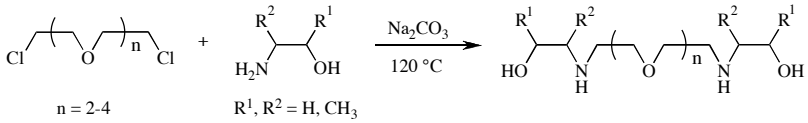


5.1.4.3 Synthesis of diamino diols

Okahara *et al.* [67] reported the synthesis of diamino diols by the reaction of the appropriate ethanol amine compounds with the dichloro derivatives of oligoethylene glycols in the presence of Na_2CO_3 as a base (Scheme 30).

Zhang *et al.* [49] reported the synthesis of *N*,*N*'-diarylsubstituted derivatives of 1,7-diaza-12-crown-4 as well as 1,10-diaza-18-crown-4 by reacting the appropriate diol with the corresponding ditosylate [68] (Scheme 32).

Scheme 30



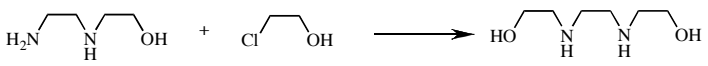
A diaminoalcohol was reacted with 2-chloroethanol under the same condition to form a diaminodiol (Scheme 31).

5.1.5 Reaction of *N*-substituted dialkanols with the ditosylate of *N*-substituted diethanolamine (Method E).

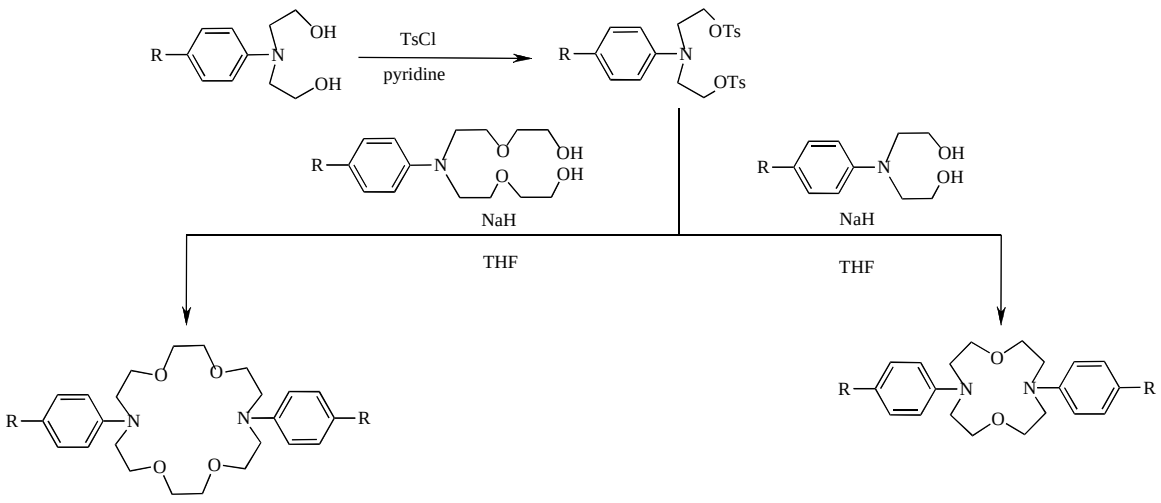
5.1.6 Reaction of primary amine with an oligoethylene glycol diglycidyl ether (Method F).

Okahara *et al.* [64,69] reported the synthesis of *N*-substituted dihydroxy-14-crown-4 by the reaction of the

Scheme 31

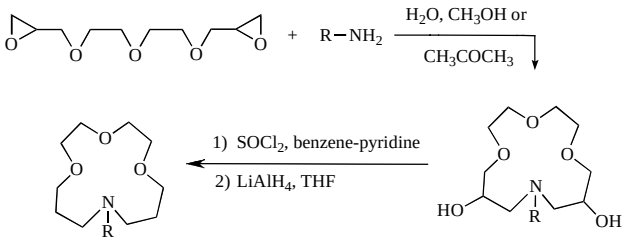


Scheme 32



appropriate oligoethylene glycol diglycidyl ethers with the corresponding primary amines in an appropriate solvent. The yields of the products were found to depend on the solvent used, the reaction temperature as well as the reaction time. Chlorination of the dihydroxy-14-crown-4 with thionyl chloride followed by reduction with $LiAlH_4$ in THF afforded the corresponding *N*-substituted monoaza-14-crown-4 ethers (Scheme 33).

Scheme 33



5.2. Attachment of the sidearm by chemical modification of an amino group of azacrown ether.

This approach involves attachment of the sidearm to the parent azacrown ethers by one of the following methods:

5.2.1. *N*-Alkylation's of the appropriate azacrown ether (Method G),

5.2.2. *N*-Acylation of the appropriate azacrown ether (Method H).

These methods involve treatment of the parent azacrown ethers with the appropriate alkylating or acylating agents in basic solution (Na_2CO_3, CH_3CN, NaH, THF,…..etc) [15b].

This approach (*N*-alkylation or *N*-acylation) represents the most popular route to the side-armed elaboration. The reactions seem to be very simple and the yields of the lariat ethers obtained by these methods are usually higher than that obtained from the cyclization reactions. However this approach is not universal because of the restricted availability of reagents used for modifications. In addition, if the sidearms are of any complexity, the described examples have required multi step procedures and complex experimental manipulation [70-72].

5.2.3. Acylation followed by reduction (Method I).

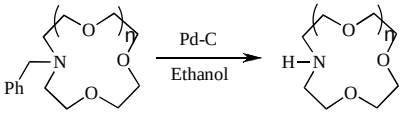
In this case, the *N*-alkyl derivatives were obtained by acylation of the appropriate azacrown ethers followed by diborane reduction.

5.2.4. Synthesis of parent monoaza-, diaza and polyazacrown precursors

5.2.4.1. Synthesis of monoazacrown ethers.

Gokel *et al.* [25] reported the synthesis of monoaza-12-, 15-, and 18-crown compounds by hydrogenolysis of the corresponding *N*-benzyl derivatives (Scheme 34).

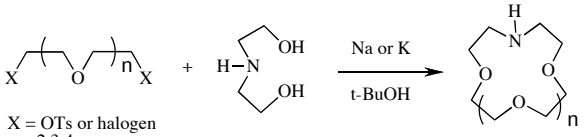
Scheme 34



n	
1	95%
2	98%
3	98%

Okahara *et al.* [73] prepared monoaza-15-, 18-, and 21-crown compounds by reacting unprotected diethanolamine with various oligoethylene glycol ditosylates or dichlorides (Scheme 35).

Scheme 35

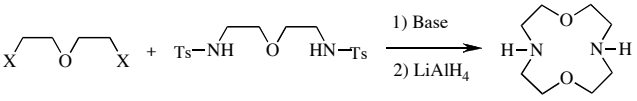


n	
2	37%
3	61%
4	35%

5.2.4.2. Synthesis of diazacrown ethers.

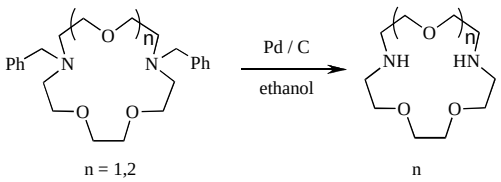
Lukyanenko *et al.* [74] reported the synthesis of diaza-12-crown-4 by reacting *N*,*N*'-bis(*p*-toluenesulfonamide) of diethylene glycol diamine with diethylene glycol ditosylate followed by removal of the *N*-tosyl group by reduction with $LiAlH_4$ (Scheme 36).

Scheme 36



Gokel *et al.* [15b] reported the synthesis of 1,7-diaza-15-crown-5 as well as 1,10-diaza-18-crown-6 by hydrogenolysis of the corresponding *N*,*N*'-dibenzyl derivatives (Scheme 37).

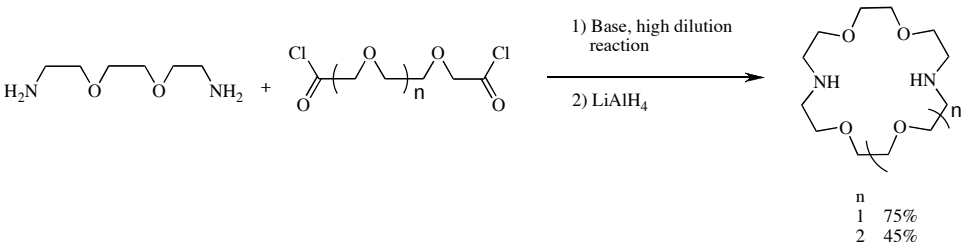
Scheme 37



n	
1	91%
2	92%

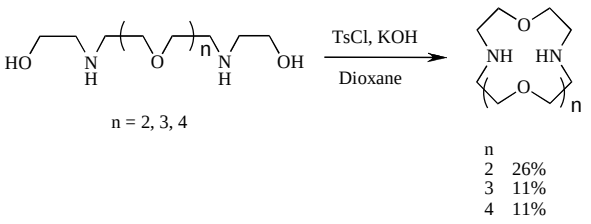
Lehn *et al.* [75] prepared 1,10-diaza-18-crown-6 and 1,10-diaza-21-crown-7 in 75% and 45% yields, respectively, by reacting 1,2-bis(2-aminoethoxy)ethane with the appropriate diacid dichloride in basic solution under high dilution conditions to give the corresponding macrocyclic diamides followed by reduction with $LiAlH_4$ (Scheme 38).

Scheme 38

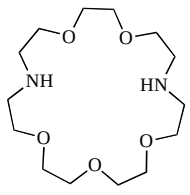


Okahara *et al*. [67] prepared 1,7-diaza-15-crown-5 (n = 2), 1,7-diaza-18-crown-6 (n =3) and 1,7-diaza-21-crown-7 (n = 3) from the appropriate oligoethylene glycols by reaction with equimolar amount of *p*-toluenesulfonyl chloride in dioxane containing KOH to give firstly mono(*p*-toluenesulfonate) derivatives followed by an intramolecular cyclization reaction to give the corresponding diazacrown compounds (Scheme 39).

Scheme 39

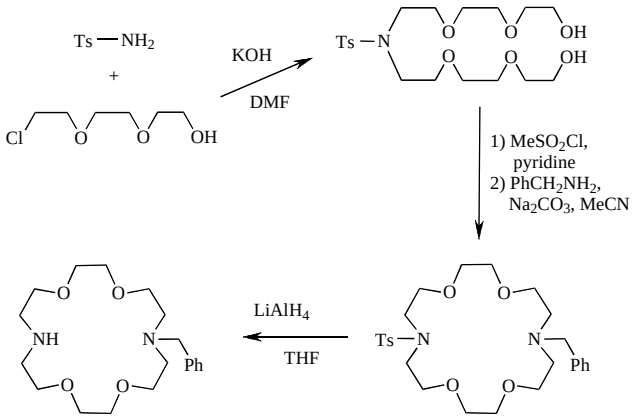


The same authors used a similar approach for the synthesis of the following 1,10-diaza-21-crown-7 in 38% from the corresponding diaminodiol.



N-Benzyldiaza-18-crown-6 was obtained in 86% overall yield from the monochloro derivative of diethylene glycol by first reaction with *p*-toluenesulfonamide in DMF containing KOH to give the corresponding diol [76]. Treatment of the latter with methanesulfonyl chloride in pyridine and subsequent cyclization with benzylamine afforded *N*-tosyl derivative. Removal of the *N*-tosyl group of the latter was accomplished by reduction with $LiAlH_4$ (Scheme 40).

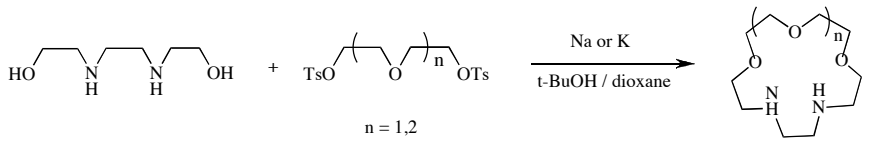
Scheme 40



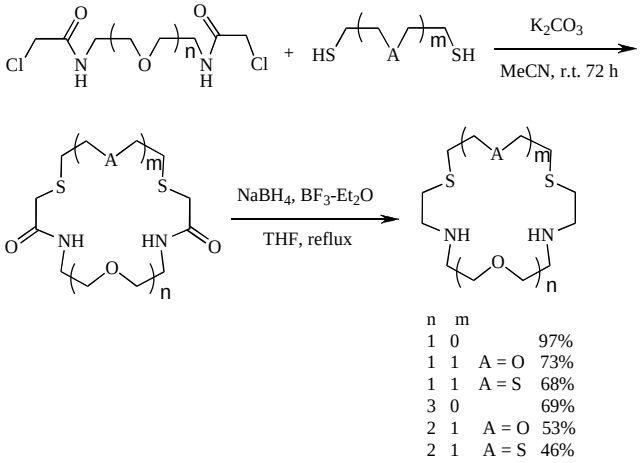
Okahara *et al.* [67] prepared a number of 1,4-diazacrown compounds by ring-closure reaction of a diazaoligoethylene glycol with the appropriate ditosylate (Scheme 41).

Song *et al.* [58] reported the synthesis of some diazadithia- and diazatrithiacrown ethers by reacting the appropriate bis(chloroacetylamino) derivatives with the corresponding dithiol in MeCN containing Na_2CO_3 to give the corresponding diamides followed by $NaBH_4$ reduction (Scheme 42).

Scheme 41

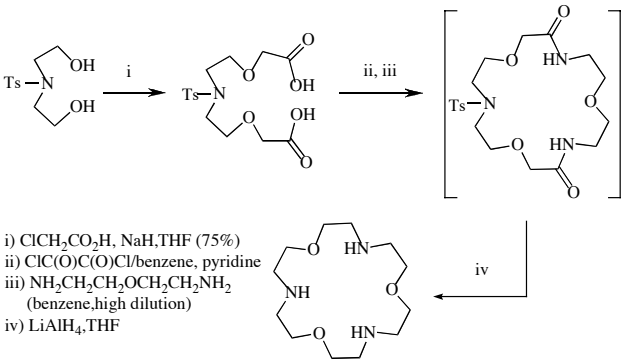


Scheme 42



n	m		
1	0		97%
1	1	A = O	73%
1	1	A = S	68%
3	0		69%
2	1	A = O	53%
2	1	A = S	46%

Scheme 43

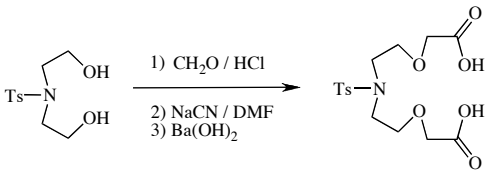


This approach is similar to that described by Lehn *et al.* [79,80] except that the formation of the diacetic acid derivative from the corresponding diol was accomplished by first conversion of the hydroxyl group into the chloromethyl ether derivative. Displacement of the chlorine by cyanide upon reaction with NaCN gave the bis(acetonitrile) derivative which was hydrolysed in basic solution to the corresponding diacetic derivative in 40% yield (Scheme 44).

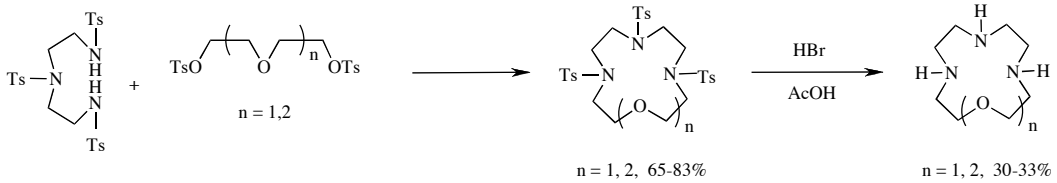
5.2.4.3. Synthesis of triazacrown ethers.

Gokel *et al.* [77,78] reported the synthesis of 1,7,13-triaza-18-crown-6 as outlined in the following scheme. *N*-Tosyldiethanolamine was reacted with sodium chloroacetate to give the corresponding diacetic acid derivative in about 80% yield. Chlorination and subsequent cyclization of the latter with bis(2-aminoethyl)ether followed by reduction with $LiAlH_4$ gave the target compound in 65% overall yield (Scheme 43).

Scheme 44



Scheme 45



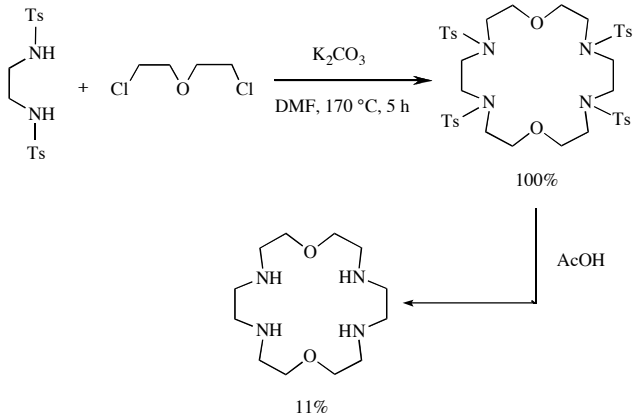
Richman and Atkin [81] reported the synthesis of triaza-12-crown-4 as well as triaza-15-crown-5 by the reaction of a tosylated triamine with the appropriate oligoethylene glycol ditosylate to give the corresponding tris(*N*-tosyl) derivatives followed by removal of the *N*-tosyl groups of the latter upon reaction with HBr in acetic acid (Scheme 45).

5.2.4.4. Synthesis of tetraazacrown ethers.

Hancock *et al.* [82] reported the synthesis of tetra-*N*-tosylaza-18-crown-6 in 100% yield by reacting bis(2-chloroethyl)ether with *N*,*N*'-bis(*p*-toluenesulfonamide) of ethylene diamine in DMF containing K_2CO_3 (Scheme 46). The high yield of the cyclized product could be explained to be a result of restricted rotational freedom in the molecule caused by the large tosyl group. 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 yield without a need for pre-organization of the starting materials [83,84].

The *N*-tosyl group of the tetra-*N*-tosylaza-18-crown-6 could be removed by reaction with HBr in acetic acid solution.

Scheme 46



5.2.4.5. Pyridinoazacrown ether.

Bradshaw *et al.* [48] prepared pyridinoazacrown ethers by reacting bis[2-(2-hydroxyethoxy)ethyl]amine with 2,6-bis(*p*-toluenesulfonyloxymethyl)pyridine in THF containing NaH (Scheme 47).

Adams *et al.* [85] prepared pyridinodibenzotriazacrown ethers in 65% yield by cyclocondensation of 1,5-bis(2-aminophenoxy)-3-azapentane with pyridine-2,6-dicarboxaldehyde in the presence of $Mn(NO_3)_3$ followed by reduction with $NaBH_4$ (Scheme 48).

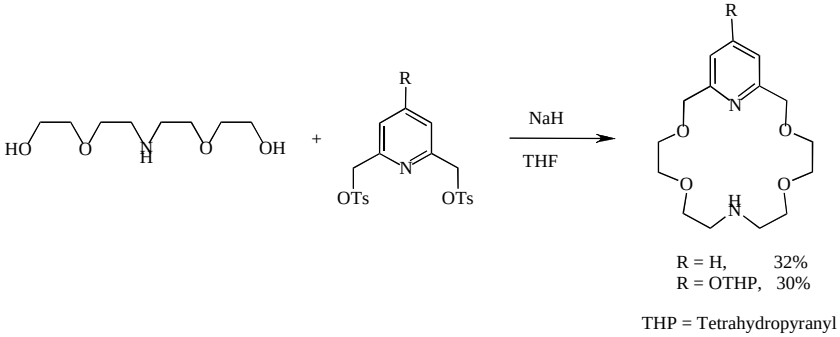
5.2.5. Ring opening of ethylene- and propylene oxide by secondary amine functions of macrocyclic polyamines (Method J).

Hancock *et al.* [82] reported the synthesis of some polyazacrown ethers containing ethanol or 2-hydroxypropane sidearms by reacting the appropriate polyazacrown compound with the equivalents of epoxide or a substituted epoxide (Scheme 49).

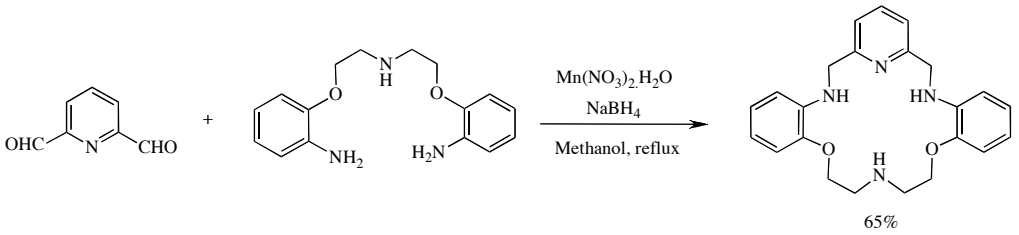
5.2.6. Ring opening of *N*-dansylaziridine by secondary amine functions of macrocyclic polyamines (Method K).

Bradshaw *et al.* [86,87] reported the synthesis of a series of novel fluorophores consisting of macrocyclic polyamines containing two dansylamidoethyl sidearms as potential zinc(II) fluoroionophores by the reaction of the appropriate macrocyclic polyamine with *N*-dansylaziridine in MeCN at reflux temperature. The starting *N*-dansylaziridine was prepared by treating aziridine with dansyl chloride (Scheme 50).

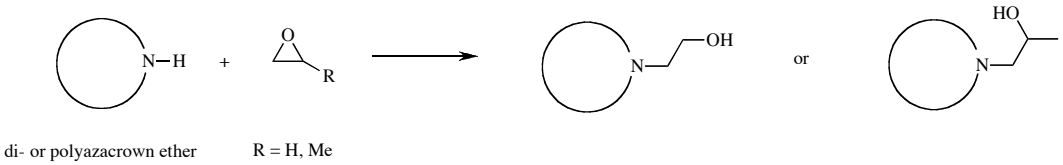
Scheme 47



Scheme 48



Scheme 49



di- or polyazacrown ether R = H, Me

5.2.7. Nucleophilic aromatic substitution (Method L).

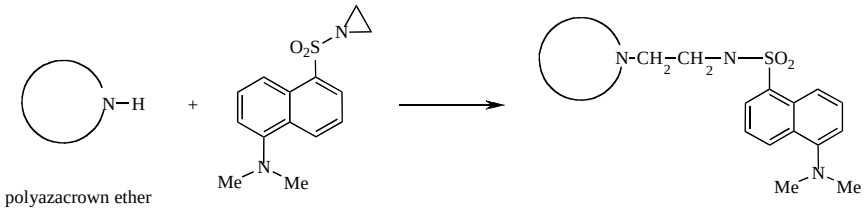
5.2.8. High pressure nucleophilic aromatic substitution (Method M).

Direct nitrogen arylation is possible but normally difficult. This has been accomplished by reaction of fluorobenzene with the appropriate azacrown ethers in basic solution [88]. Substitution on the nitrogen atom was successfully achieved by high pressure S_NAr reactions of the appropriate azacrown ethers with the corresponding haloaromatic and heteroaromatics [89,90] (Scheme 51).

5.2.9. Pd-Catalyzed *N*-arylation of azacrown ethers (Method N).

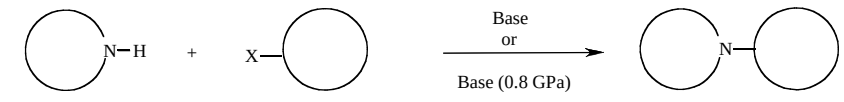
The synthesis of various *N*-arylazacrown ethers could also achieved *via* palladium catalyzed coupling of azacrown ethers with aryl chlorides, bromides and iodides. The catalytic systems consist of $Pd_2(dba)_3$ and one of the following bicyclic triaminophosphine ligands **a**, **b** or Buchwald's ligand **c** [91] (Scheme 52). The choice of the ligand depends on the nature of the aryl substituents, for example, the more constrained bicyclic triaminophosphine is useful for aryl chlorides possessing base-sensitive ester, nitro and nitrile functional groups.

Scheme 50



polyazacrown ether

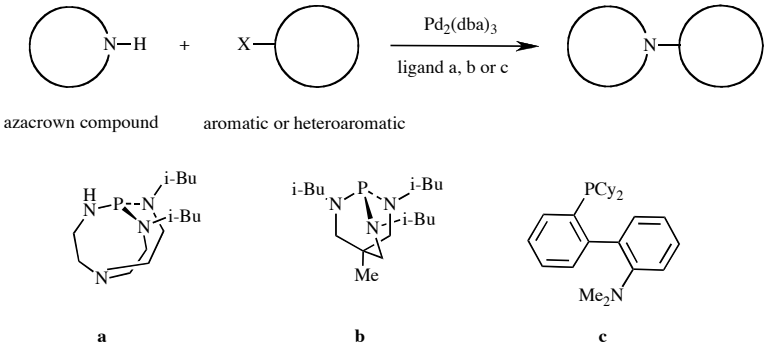
Scheme 51



azacrown compound aromatic or heteroaromatic moiety

X = Cl, Br

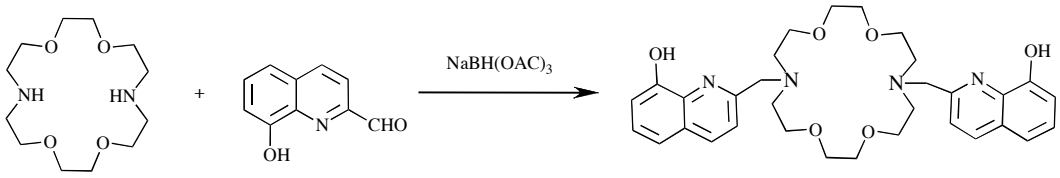
Scheme 52



5.2.10. Reductive amination of aldehydes with azacrown compounds (Method O).

Bradshaw *et al.* [57,92,93] reported the synthesis of quinoline-containing diazacrown ethers *via* reductive amination of the appropriate quinoline carboxaldehyde with the corresponding diazacrown compounds using triacetoxyborohydride as the reducing agent (Scheme 53).

Scheme 53



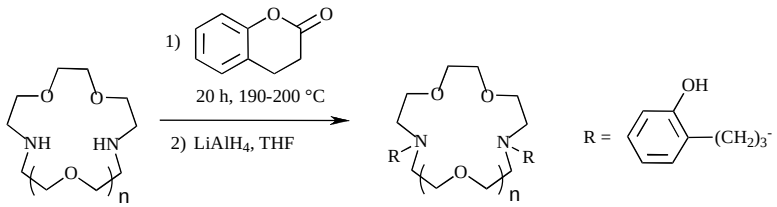
5.2.11. Fusion of azacrown compounds with coumarin followed by reduction (Method P).

Takagi *et al.* [94] reported the synthesis of diazacrown ethers with two 2-hydroxyphenylpropyl sidearms by fusion of the appropriate diazacrown ethers with 3,4-dihydrocoumarin followed by reduction with $LiAlH_4$ in THF (Scheme 54).

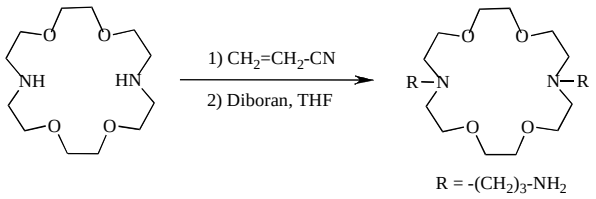
5.2.12. Michael addition (Method Q).

Beer *et al.* [78,95] synthesized primary amine functionalized azacrown ethers by reaction of the appropriate azacrown ethers with acrylonitrile followed by diborane reduction (Scheme 55).

Scheme 54



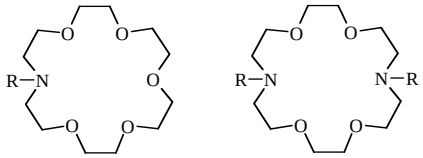
Scheme 55



5.2.13. Reaction of secondary amine functions of aza- and diazacrown ethers with carboxylic acid (Method R).

In this method the sidearms are attached to the azacrown ethers by a coupling reaction between azacrown ethers and the appropriate acid in the presence of DCC (dicyclohexylcarbodiimide) in CH_2Cl_2 or other similar reagents.

Using this approach, Gokel *et al.* [96] reported the synthesis of the following 18-membered monoaza- and diazamacrocycles with dipeptide arms.



These lariats with amide type functions have been prepared in 60-80% yields by attachment of benzyloxycarbonylglycine to nitrogen atoms of the parent aza- or diazamacrocycles either by dicyclohexylcarbodiimide (DCC) condensation or by use of Ph_3P-CCl_4-Et_3N.

Gokel *et al.* [97] have also reported the synthesis of lariat ethers with amide macro ring junction using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide and TEA or 1-benzotriazolyloxytris(pyrilidino)phosphonium hexafluorophosphate and diisopropylethyl amine.

5.3. Electrophilic substitution reactions of N-CH_2-A containing azacrown ether (where A stands for an activation group that leaves after the formation of a new bond).

5.3.1. Mannich Reaction [98,99].

The Mannich reaction, as a method for modification of azacrown macrocycles with hydroxybenzyl functions has some advantages when compared to alkylation of the azacrown by benzyl haides. Aminomethylation of the phenols allows the preparation of azamacrocycles containing both electron donating and electron withdrawing groups in the substituent phenolic rings. The preparation of such compounds by alkylation is not always convenient because of the difficulties in preparing the starting benzyl halides and the necessity of protecting the phenolic hydroxyl groups.

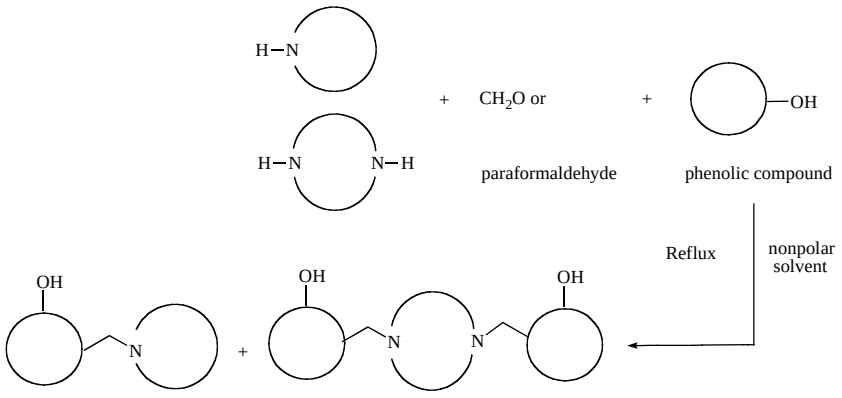
Most phenol-containing azacrown ethers synthesized by the Mannich reaction were the products of *ortho* substitution on the phenol ring. The preferential attack on the *ortho*-position is caused by formation of a six-membered transition state where the phenolic proton activates the aminomethylating reagent. When both *ortho*-positions are occupied, aminomethylation can occur in the *para*-position.

N-H acids (amides, sulfonamides, imides and azoles) are appropriate for the functionalization of azacrown ethers using the Mannich condensation.

5.3.1.1. Azacrown ethers as reagents for the Mannich condensation (Method S).

This approach uses the classical Mannich reaction in which amines (secondary amine of azacrown ethers), formaldehyde or paraformaldehyde and an appropriate receptor for aminomethylation are mixed together and heated under reflux in non-polar solvent (Scheme 56).

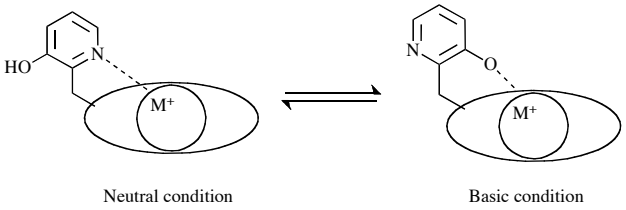
Scheme 56



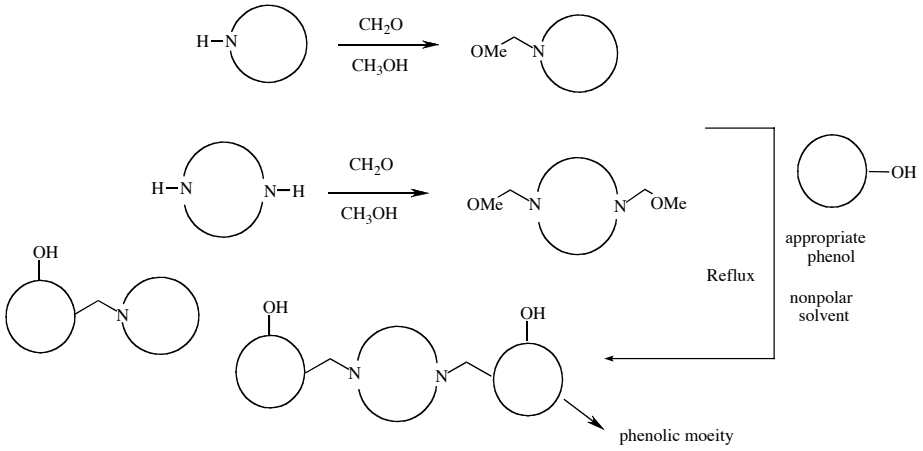
5.3.1.2. Methoxymethylazacrown ethers as reagents for the Mannich condensation (Method T).

In this case amine groups of the azacrown ethers interact with the methanol solution of formaldehyde to give the *N*-methoxymethyl substituted azacrown ethers followed by reaction with various CH and NH acids (Scheme 57). Applications of the methoxymethylamine instead of free formaldehyde and an amine has two advantages. First, it prevents the interaction of free formaldehyde with substances undergoing amino-methylation and second it allows the reaction to occur in nonpolar solvents (CCl_4, benzene and xylene). This is especially important for the self assembly cyclization process.

Scheme 58



Scheme 57



The intermediates *N*-methoxymethylazacrown ethers mentioned in this review were obtained by treatment of the appropriate mono- or diazacrown compounds with a methanol solution of formaldehyde [28,48,100-102].

Using the one step approach (Method S) or the two step approach (Method T), a variety of phenol- or naphthol-substituted monoaza-, diaza- and pyridinoazacrown ethers have been prepared.

The Mannich reaction was proved to be a good method for modification of azacrown macrocycles with a variety of phenolic sidearms. These sidearms are often composed of UV-active or fluorophoric proton ionizable materials that allow an analytical determination of certain cations by spectrophotometric methods. They also provide concomitant changes in the photophysical properties of the system upon metal ion binding while maintaining or improving the ion selectivities of the macrocycles [92].

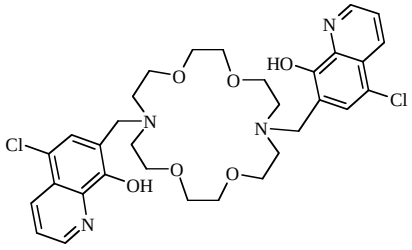
Another possible application for these phenol-derivated complexing agents prepared *via* Mannich condensation is their use as a heteronuclear metal ion receptor designed from simultaneous binding of soft-transition and hard-alkali or alkaline earth metal ions in one molecule or supramolecular aggregate [104].

Habata *et al.* [105] reported the synthesis of armed-azacrown ethers with hydroxypyridine. Since these armed-azacrown ethers have dual binding sites in the sidearm, pyridine N atom and phenolic OH group, it may be possible to control the functional group involved in complexing by changing conditions as outlines in Scheme 58.

8-Hydroxyquinoline has been used extensively as an extraction, chromogenic, and precipitation reagent in analysis. 8-Hydroxyquinoline-containing diazacrown ethers were reported to have three advantages. First, formation of a stable chelating ring between 8-hydroxyquinoline and a metal ion should stabilize the complex of the metal ion with the macrocyclic ligand. Second, the 8-hydroxyquinoline-functionalized crown ethers should improve cation selectivity. Attachement of two rigid 8-hydroxyquinoline groups to the diazacrown ring, as shown below, results in an appropriate preorganization of the ligand. Only the cation(s) whose size fits the pseudo-three dimensional cavity of the macrocycle may bring every donor site to a position where they can interact with the cation(s) without causing a large macro ring deformation. Finally, it is possible for the two 8-hydroxyquinoline moieties of the macrocyclic ligand to overlap each other through an intramolecular

interaction so that a cryptate-like structure could be formed. This effect brings a further increase in complex stability and cation selectivity [103].

Commercially available 5-chloro-8-hydroxyquinoline was used instead of 8-hydroxyquinoline because the chlorine blocks position 5 of the quinoline ring. Although attack ortho to the OH group is preferred in this electrophilic aromatic substitution reaction, the para-substituted material was used to avoid any minor products.



Habata *et al*. [106] postulated a reaction mechanism for the formation of armed-monoaza-12-crown-4 and other side reaction products by the Mannich reaction of 2,6-disubstituted phenols with *N*-methoxymethyl-monoaza-12-crown-4 ether (Scheme 59)

First, when the 2,6-disubstituted phenols which have low acidity are used, the phenols readily react with the iminium ion derived from *N*-methoxymethylmonoaza-12-crown-4 ether to give the expected Mannich product. Second, in the case of using the more acidic 2,6-disubstituted phenols, the *N*-methoxymethylmonoaza-12-crown-4 ether dissociates into formaldehyde and monoaza-12-crown-4 ether and the formaldehyde reacts with the phenols having lower electrostatic charge (higher reactivity toward formaldehyde) at the position 4 to give hydroxymethylphenol and/or hydroxymethylquinone intermediates leading to the dihydroxydiphenylmethane derivatives. Third, a very strong acid such as 2,6-dinitrophenol does not form either the Mannich or the side reaction products and instead the 2,6-disubstituted phenoxide was formed.

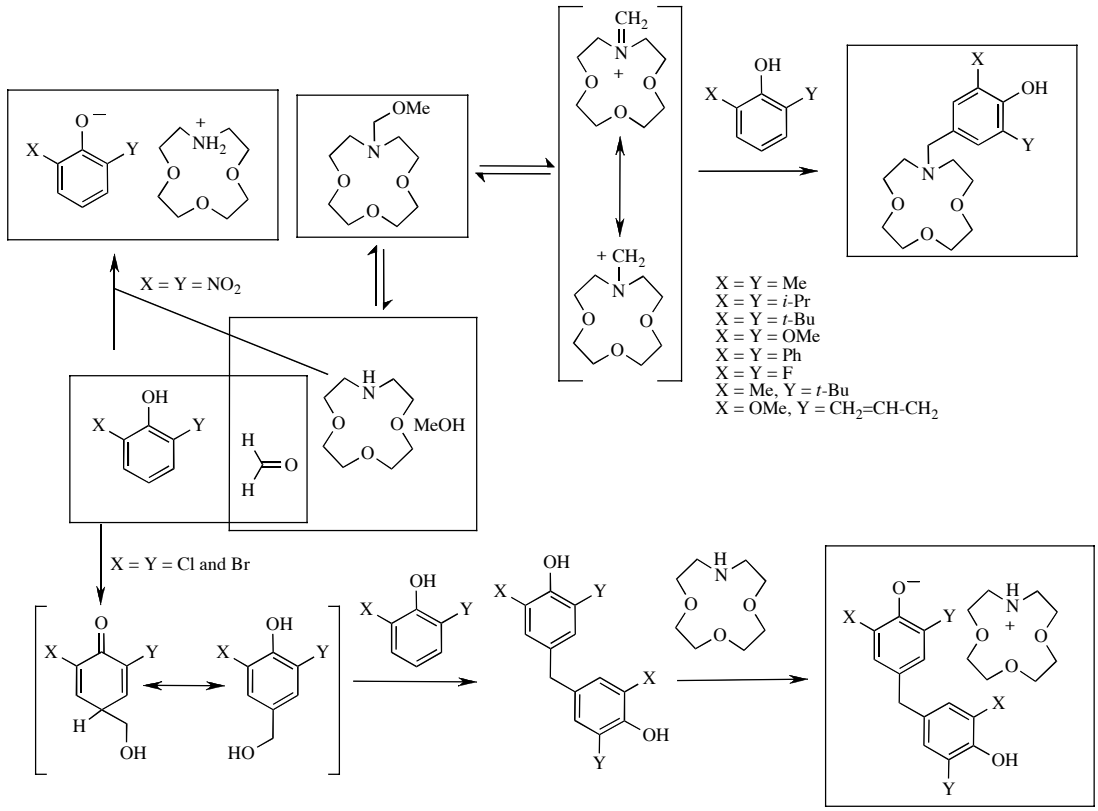
It is proposed that the acidity and the electrostatic charge of the phenols and naphthols are indications of the reactivity of the 2,6-disubstituted phenol for the Mannich reaction.

5.3.2. Reaction of *N*-(benzotriazolylmethyl)-substituted azacrown ethers with electron-rich compounds (Method U).

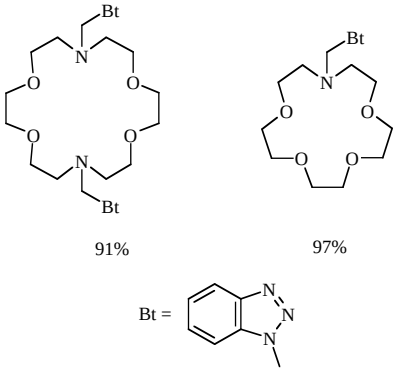
5.3.2.1. Reaction with vinyl ethers and vinyl amides.

Katritzky *et al*. [30,51] reported the synthesis of a series

Scheme 59



of *N*-pivot lariat ethers with γ-oxy-substituted and γ-amino-substituted propylene-side-armed derivatives by reacting the appropriate *N*-(benzotriazolylmethyl)-substituted azacrown ethers with the corresponding vinyl ethers and vinyl amides, respectively, in the presence of Lewis acid catalyst followed by reduction with $LiAlH_4$ in THF. The following *N*-(Benzotriazolylmethyl)-substituted azacrown ethers were obtained by reacting the appropriate azacrown ether with *N*-(benzotriazolylmethyl)benztriazole in warm ethanol or isopropanol.



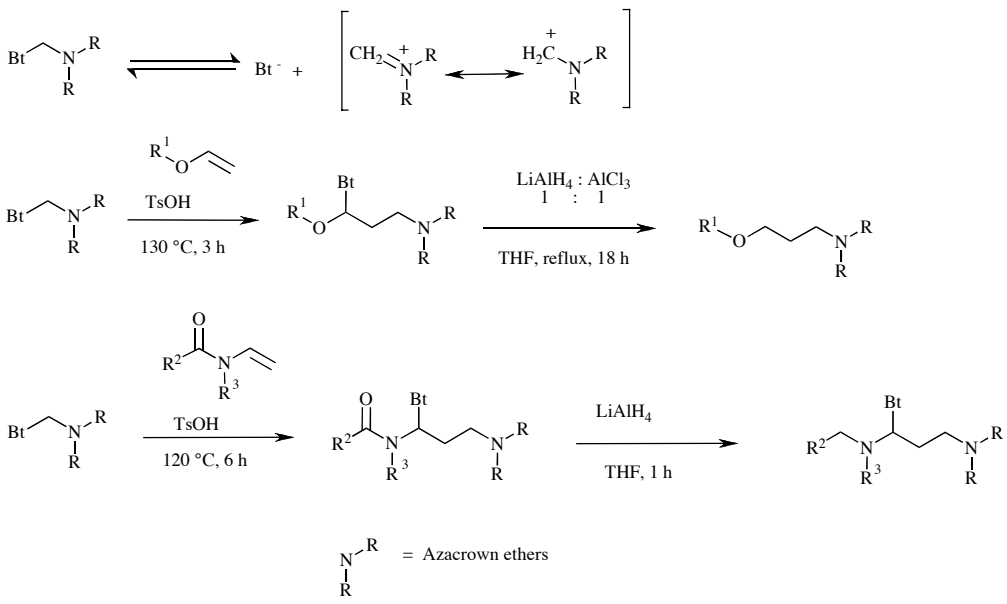
This results depend on the previously reported fact that an addition of *N*-(benzotriazolylmethyl)-substituted secondary amines to electron rich olefins (vinyl ethers or vinyl amides), catalyzed by Lewis acids, gives the corresponding Markonikov-type products in almost quantitative yields by addition of Bt^- and $R_2N^+{=}CH_2$, which are formed *in situ* under the reaction conditions, to the activated double bond. Furthermore these products were successfully reduced in order to remove the benzotriazole moiety forming 3-(amino-substituted)-propylalkyl ethers or variously substituted 1,3-diamino-propanes in quite high yields (65-94%) [51] (Scheme 60).

5.3.2.2. Reaction with metallorganic reagents [30]**.**

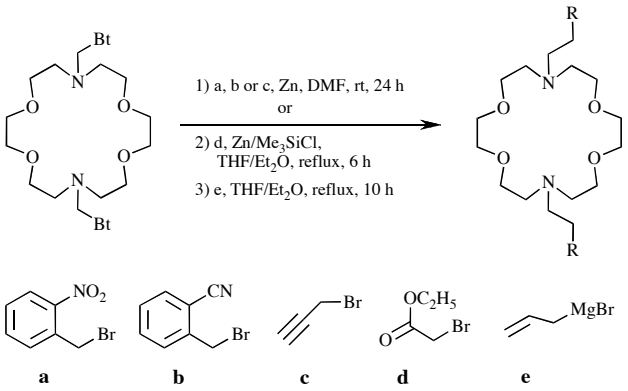
Several bibracchial lariat diazacrown ethers with terminal unsaturated groups, ester functionalities and *N,N'*-di-β-aralkyl derivatives were prepared by means of modified Reformatskii and Grignard reagent from the *N,N'*-(benzotriazolylmethyl)]-substituted diazacrown ethers (Scheme 61). Thus, modified Reformatskii reaction of the latter compound with 2-nitrobenzyl bromide as well as 2-cyanobenzyl bromides in the presence of Zn powder in DMF afforded the corresponding bis(lariat) with *N,N'*-di-β-aralkyl derivatives.

With propargyl bromide under the same conditions, the *N,N'*-(benzotriazolylmethyl)]-substituted diazacrown ethers gave bis(lariat) containing two butynyl sidearms. Moreover, the bis(lariat) with ethoxycarbonyl groups at the end of the sidearms could also prepared from β-bromo-ethylacetate by first reaction with activated (Me_3SiCl) Zn in a mixture of THF and Et_2O to give an organozinc reagent, and subsequent reaction with *N,N'*-(benzotriazolylmethyl)]-substituted diazacrown ethers. The same authors also obtained the bis-butenyl side-armed crown ether by the Grignard reaction of the *N,N'*-(benzotriazolylmethyl)] functionalized crown ether with allyl magnesium bromide.

Scheme 60

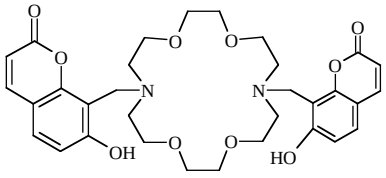


Scheme 61



5.3.2.3. Reaction with 7-hydroxycoumarin.

Reaction of *N,N'*-(benzotriazolylmethyl)]-substituted diazacrown ethers with 7-hydroxycoumarin in refluxing isopropanol in the presence of TEA was reported by Katritzky *et al.* [30] to give the following bis(lariat) with fluorescent labels on both side of the macrocycle in 31% yield. The latter compound was obtained in unspecified yield by Mannich reaction of 7-hydroxycoumarin with 4,13-diaza-18-crown-6 and formaldehyde [107].



Using this approach Katritzky *et al.* [30] prepared a series of bis(lariat)s in which the side-armed donor atoms are separated from the macro ring by three carbon atoms. This was reported to be the best distance for the interaction between a ring bound-cation and apical donor groups [13].

Preparation of such lariat ethers using either the alkylation or cyclization method is not convenient. This is because the analogs of 2-(halogen-substituted)ethylalkyl-ethers previously used for the preparation of *N*-pivot lariat ethers, 3-(halogen-substituted)propylalkylethers are not readily available [25].

Although Mannich reaction of *N*-(methoxymethyl) derivatives of azacrown ethers with phenols leads to the formation of three-carbon atom chain, this now includes two sp^2 aromatic ring carbon atoms, which diminishes the sidearm mobility [100,101].

6. Literature Survey

6.1. Introduction

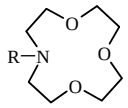
This survey of *N*-pivot lariat ethers is abstracted from the literature published from 1980 to 2005. The *N*-pivot lariat ethers are classified into 35 tables according to the ring size as well as the number of nitrogen atoms in the macro rings.

6.2. Organization of Tables

The following remarks are pertinent for the tables:

1- Each table is organized with the more simple substituents listed first.
2- The methods given in the tables are those described in section 5.
3- Many substituents were prepared by modification of the sidearms. In these cases short sentences are given to describe these changes.
4- The yields are those given in the last step in the reaction except when an overall yield was given. A range of yields indicate that the reaction was carried out more than once, giving different yields. As many of the listed publications appear as communications or letters, the yields in some cases are not mentioned and are denoted in the tables as (-).

Table 1



Aza-12-crown-4

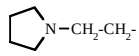
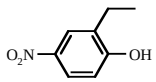
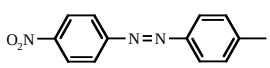
comp. no.	R	method	ref. (yield)
1	C_8H_{17}-	C	69 (38)
2	$C_8H_{17}OCH_2CH_2$-	C	69 (43)
3	$C_8H_{17}O(CH_2)_2CH_2$-	C	69 (51)
4	$CH_3OCH_2CH_2$-	A	108 (51) 109 (60)
5	$OH(CH_2)_2CH_2$-	A	108 (48) 109 (56) 110 (56)
6	$OHCH_2CH_2OCH_2CH_2$-	A	111 (25)
7	$(CH_3)_3Ge(CH_2)_2C(O)O(CH_2)_2{}^o(CH_2)_2$-	Reaction of 6 with trimethylgermylpropionic acid	111 (79)
8	$CH_3(OCH_2CH_2)_3$-	G	112 (52)
9	$CH_3OCH_2CH_2$-O-CH_2CH_2-	G	109 (66)
10	$CH_3(OCH_2CH_2)_3$-	G	109 (52), 110 (-)
11	$CH_3(OCH_2CH_2)_4$-	G	109 (54)
12	CH_2=$CHCH_2(OCH_2CH_2)_4$-	G	109 (50), 110 (-)
13	$CH_3(OCH_2CH_2)_5$-	G	109 (69), 126 (-)
14	$CH_3CH_2(OCH_2CH_2)_6$-	G	109 (68)
15	$CH_3CH_2O(CH_2)_2CH_2$-	C	51 (40)
16	$CH_3CH(CH_3)CH_2O(CH_2)_2CH_2$-	C	51 (45)
17	$CH_3CH_2OCH(Bu)CH_2CH_2$-	C	51 (54)
18	$CH_3CH(CH_3)CH_2OCH(Bu)CH_2CH_2$-	C	51 (56)
19	CH_2=$CHCH_2OCH(Bu)CH_2CH_2$-	C	51 (28)
20	$CH_3CH_2OC(O)CH_2$-	A	108 (30)
21	$NH_2C(O)CH_2$-	A	108 (24)
22	$CH_3N(CH_3)CH_2CH_2$-	A	110 (21)
23	$C_5H_{11}N(C_5H_{11})C(O)CH_2$-	G	113 (75)
24	$EtN(Et)C(O)CH_2$-	G	114 (70)
25	$EtN(Et)CH_2CH_2$-	Red of 24 (BH_3/THF)	114 (70)
26	$C_7F_{15}CH_2OCH_2C(O)$-	H	115 (78)
27	$C_7F_{15}CH_2OCH_2CH_2$-	Reduction of 26	115 (85)
28	$CNCH_2$-	G	114 (80)
29		G	114 (65)
30	$PhCH_2$-	A	108 (54) 109 (53) 110 (-)
31	Ph-	A	108 (51)
32	4-$CH_3OC_6H_4$-	A	109 (40) 110 (-)
33	2-$CH_3OC_6H_4$-	A	109 (26) 110 (-) 25 (-)
34	4-CNC_6H_4-	A	116 (45)
35	2-OHC_6H_4-	A	117 (-)
36	2-$NO_2C_6H_4CH_2$-	G	109 (86), 110 (-)
37			118 (71)
38		Coupling of *p*-nitrobenzene diazonium salt with 31	108 (51)

Table 1 (continued)

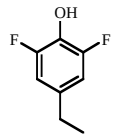
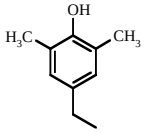
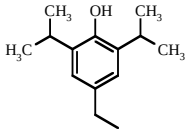
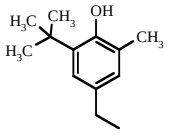
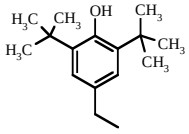
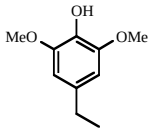
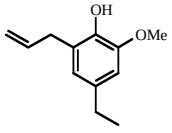
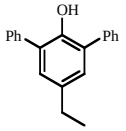
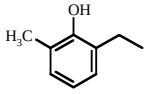
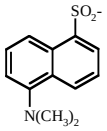
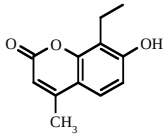
comp. no.	R	method	ref. (yield)
39		T	106 (68)
40		T	119 (35)
41		T	106 (73)
42		T	106 (68)
43		T	106 (47)
44		T	106 (47)
45		T	106 (27)
46		T	106 (36)
47		S	120 (-)
48		H	121 (69)
49		S	122 (43)

Table 1 (continued)

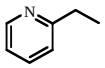
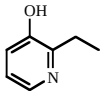
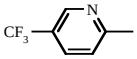
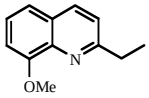
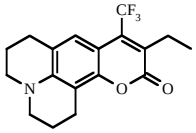
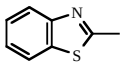
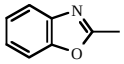
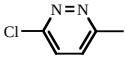
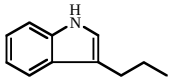
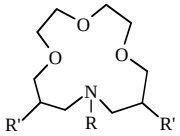
comp. no.	R	method	ref. (yield)
50		G	114 (60)
51		T	105 (74)
52		M	90 (58)
53		G	118 (62)
54		G	123 (15)
55		M	90 (64)
56		M	90 (44)
57		M	90 (57)
58		M	90 (62)
59		M	90 (74)
60		G	124 (73)

Table 2



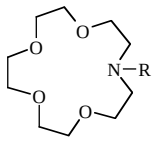
Aza-14-crown-4

comp. no.	R	R'	method	ref. (yield)
61	C_8H_{17}-	H	F	69 (72)
62	$C_8H_{17}OCH_2CH_2$-	H	F	69 (73)
63	$C_8H_{17}O(CH_2)_2CH_2$-	H	F	69 (63)
64	$C_8H_{17}O(CH_2)_2OCH_2CH_2$-	H	F	69 (73)
65	CH_3CH_2-	OH	F	64 (30-38)
66	*sec*-C_4H_9-	OH	F	64 (18-49)
67	*n*-$C_{10}H_{21}$-	OH	F	64 (6-43)
68	C_8H_{17}-	OH	F	69 (-)
69	$OHCH_2CH_2$-	OH	F	69 (34)
70	$C_8H_{17}OCH_2CH_2$-	OH	F	69 (-)

Table 2 (continued)

comp. no.	R	R'	method	ref. (yield)
71	$C_8H_{17}O(CH_2)_2CH_2$-	OH	F	69 (-)
72	$C_8H_{17}O(CH_2)_2OCH_2CH_2$-	OH	F	69 (-)
73	C_8H_{17}-	Cl	F	69 (87)
74	$C_8H_{17}OCH_2CH_2$-	Cl	F	69 (92)
75	$C_8H_{17}O(CH_2)_2CH_2$-	Cl	F	69 (51)
76	$C_8H_{17}O(CH_2)_2OCH_2CH_2$-	Cl	F	69 (72)
77	Ph-	OH	F	64 (48)

Table 3



Aza-15-crown-4

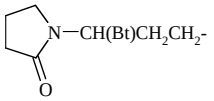
comp. no.	R	Method	Ref. (yield)
78	$CH_3(CH_2)_3CH_2$-	C	69 (38)
79	*tert*-C_4H_9-	C	69 (43)
80	*n*-C_4H_9-	C	69 (51)
81	$C_{10}H_{21}$-	G	115 (38)
82	$CH_3OCH_2CH_2$-	C	25 (55), 125, (-), 127(-)
83	$CH_3OCH_2CH_2OCH_2CH_2$-	C	125 (-), 127(-), 25 (47)
84	$CH_3(CH_2CH_2O)_5$-	G	126 (26)
85	$CH_3(CH_2CH_2O)_8$-	C	25 (49)
86	CH_2=$CHCH_2$-	C	125 (-), 127 (-)
		G	143 (82)
87	$OHCH_2CH_2$-	C	111 (82)
88	$(CH_3)_3GeCH_2CH_2C(O)OCH_2CH_2$-	Reaction of 87 with trimethylgermylpropionic acid	111 (72)
89	$C_5H_{11}NHC(O)CH_2$-	G	113 (72)
90	$C_{10}H_{21}NHC(O)CH_2$-	G	113 (76)
91	$(C_5H_{11})_2NC(O)CH_2$-	G	113 (70)
92	$(C_{10}H_{21})_2NC(O)CH_2$-	G	113 (71)
93	$CH_3CH_2O(CH_2)_2CH_2$-	C	51 (38)
94	$(CH_3)_2CHO(CH_2)_2CH_2$-	C	51 (45)
95	$CH_3CH_2OCH(Bt)CH_2CH_2$-	C	51 (50)
96	$(CH_3)_2CHCH_2OCH(Bt)CH_2CH_2$-	C	51 (62)
97	$C_6F_{13}CH_2$-CH_2-	G	115 (39)
98	$C_7F_{15}C(O)$-	H	115 (92)
99	$C_7F_{15}CH_2OCH_2C(O)$-	H	115 (85)
100	$C_8F_{17}CH_2CH_2OCH_2C(O)$-	H	115 (84)
101	$C_{10}F_{21}CH_2CH_2OCH_2C(O)$-	H	115 (70)
102	$C_7F_{15}CH_2$-	Reduction of 98	115 (90)
103	$C_7F_{15}CH_2OCH_2CH_2$-	Reduction of 99	115 (88)
104	$C_8F_{17}CH_2CH_2OCH_2CH_2$-	Reduction of 100	115 (81)
105	$C_{10}F_{21}CH_2CH_2OCH_2CH_2$-	Reduction of 101	115 (79)
106	BtCH(i-BuO)CH_2CH_2-	U	30 (-), 51(71)
107	BtCH(EtO)CH_2CH_2-	U	30 (-), 51(61)
108	*i*-$BuOCH_2CH_2CH_2$-	U	30 (-), 51 (84)
109	$CH_3CH_2OCH_2CH_2CH_2$-	U	30 (-), 51 (83)
110	$CH_3C(O)N(CH_3)CH(Bt)CH_2CH_2$-	U	30 (-), 51 (75)
111		U	30 (-), 51 (81)
112	$CH_3CH_2N(CH_3)CH_2CH_2CH_2$-	U	30 (-), 51(52)

Table 3 (continued)

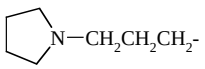
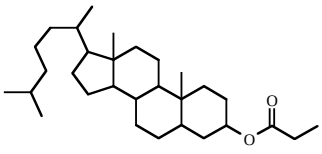
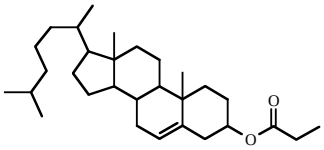
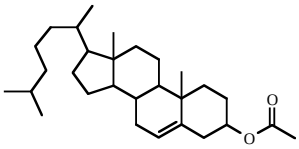
comp. no.	R	Method	Ref. (yield)
113		U	30 (-), 51(59)
114*		G	22a (67)
115*		G	22a (68) 128 (-)
116*		H	22a (34)
117	$PhCH_2$-	C	25 (46), 125(-), 127 (-)
		G	129 (9)
118	2-$CH_3OC_6H_4CH_2$-	C	25 (40)
119	Ph-	C	130 (50)
120	2-$CH_3OC_6H_4$-	C	25 (38)
121	4-$CH_3OC_6H_4$-	C	25 (30)
		**N (ligand a) / Cl	91 (50)
		**N (ligand a) / Br	91 (60)
		**N (ligand c) / Cl	91 (61)
122	4-$H(O)CC_6H_4$-	Formylation of 119	131 (75) 88 (-)
123	4-NOC_6H_4-	Nitrosation of 119	88 (-) 131 (-)
124	4-$NH_2C_6H_4$-	Reduction of 122 using $ZnCl_2$	131 (87) 88 (87)
125	2-$NO_2C_6H_4CH_2$-	G	17a (35),132 (96), 17b (-)
126	4-$NO_2C_6H_4CH_2$-	G	17a (22), 132 (85),17b (-)
127	4-CNC_6H_4-	L	116 (70)
		**N (ligand b) / Cl	91 (56)
128	2-$NO_2C_6H_4$-	L	133 (98)
129	2-$NH_2C_6H_4$-	Reduction of 128 using H_2/Pd	133 (100)
130	2-$(CH_3)_2NC_6H_4$-	Alkylation of 129 $CH_3I/CsCO_3$/MeOH	133 (90)
131	4-$CF_3C_6H_4$-	**N (ligand a) / Cl	91 (80)
132	3-$CH_3O(O)CC_6H_4$-	**N (ligand b) / Cl	91 (73)
		**N (ligand c) / Cl	91 (26)
133	4-$NO_2C_6H_4$-	**N (ligand b) / Cl	91 (81,79)
		**N (ligand c) / Cl	91 (44)
		**N (ligand b) / Br	91 (87)
134	4-$CH_3C_6H_4$-	**N (ligand a) / Cl	91 (80)
		**N (ligand c) / Cl	91 (79)
135	3-$CH_3OC_6H_4$-	**N (ligand a) / Cl	91 (66,61)
		**N (ligand a) / Br	91 (68)
136		**N (ligand a) / Cl	91 (76)
137		**N (ligand a) / Cl	91 (51)

Table 3 (continued)

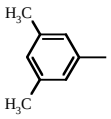
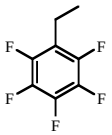
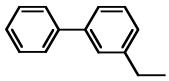
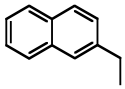
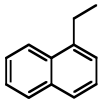
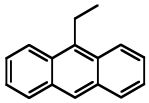
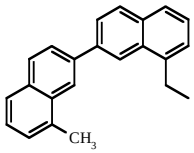
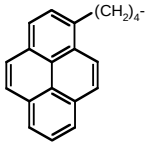
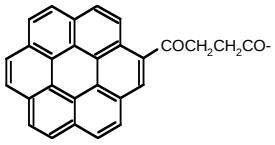
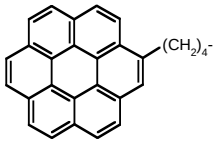
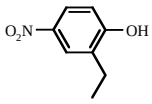
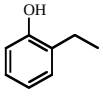
comp. no.	R	Method	Ref. (yield)
138		**N (ligand a) / Br	91 (82,81)
139		G	115 (60)
140		G	129 (9)
141		G	118 (98)
142		G	134 (-)
143		G	19b (-) 73 (-)
144		G	134 (72)
145		V	135 (-)
146		V	136 (-)
147		Reduction of 146	136 (-)
148		G	118 (91)
149		T	101 (78)

Table 3 (continued)

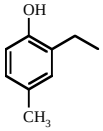
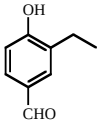
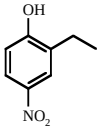
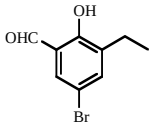
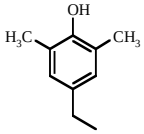
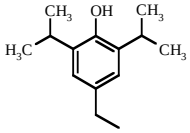
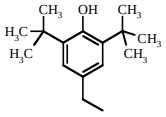
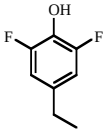
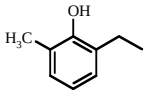
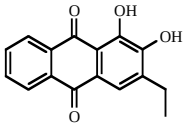
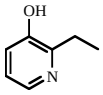
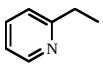
comp. no.	R	Method	Ref. (yield)
150		T	101 (74)
151		T	101 (68)
152		T	101 (73)
153		T	104 (48)
154		T	137 (-)
155		T	137 (-)
156		T	137 (-)
157		T	137 (-)
158		S	120 (-)
159		S	122 (35)
160		T	105 (89)
161		G	129 (82)

Table 3 (continued)

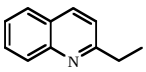
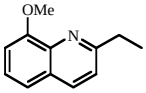
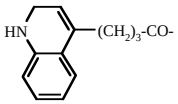
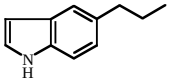
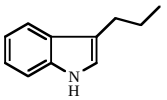
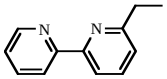
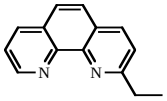
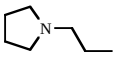
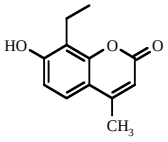
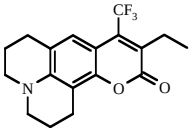
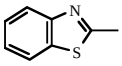
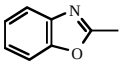
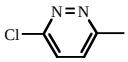
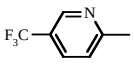
comp. no.	R	Method	Ref. (yield)
162		G	118 (83)
163		G	118 (81)
164		V	138 (48)
165		G	139 (61)
166		G	139 (93) 124 (93)
167		G	129 (93)
168		G	129 (40)
169		G	114 (40)
170		N	122 (47)
171		G	123 (15)
172		M	90 (99)
173		M	90 (99)
174		M	90 (99)
175		M	90 (96)
176		M	90 (87)
177		M	90 (88)

Table 3 (continued)

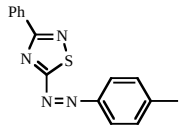
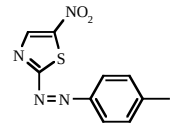
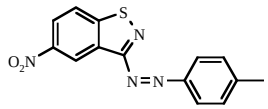
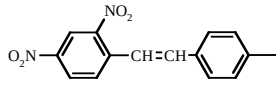
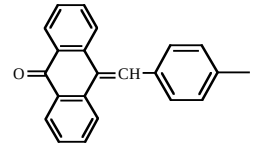
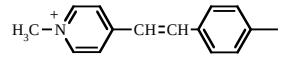
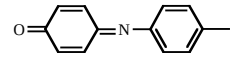
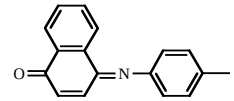
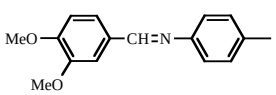
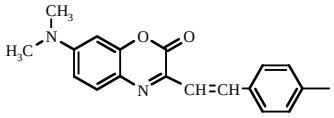
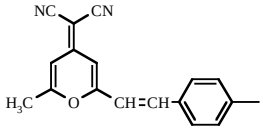
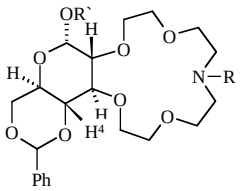
comp. no.	R	Method	Ref. (yield)
178		Coupling of the diazonium salt (obtained from 5-amino-3-phenyl-1,2,4-thiadiazole) with 119	131 (71)
179		Coupling of the diazonium salt (obtained from 2-amino-5-nitro-1,3-thiazole) with 119	131 (21)
180		Coupling of the diazonium salt (obtained from 3-amino-5-nitrobenzo[d]isothiazole with 119	131 (15)
181		Condensation of 122 with 2,4-dinitrotoluene	131 (-)
182		Condensation of 122 with anthrone	131 (40)
183		Condensation of 122 with dimethylpyridinium iodide	131 (-)
184		Condensation of 124 with phenol	131 (91)
185		Condensation of 124 with 1-naphthol	131 (65)
186	4-(PhCH=CH)C_6H_4-	Condensation of 122 with benzylphosphonium salt	88 (-)
187	4-(4-PhC_6H_4CH=CH)C_6H_4-	Condensation of 122 with 4-phenylbenzylphosphonium salt	88 (-)
188	4-(4-CNC_6H_4CH=CH)C_6H_4-	Condensation of 122 with 4-cyanobenzylphosphonium salt	88 (-)
189	4-(4-$(CH_3)_2$NC_6H_4N=CH)C_6H_4-	Condensation of 122 with 4-(dimethylamino)aniline	130 (55)
190	4-(4-$CH_3OC_6H_4$N=CH)C_6H_4-	Condensation of 122 with 4-methoxyaniline	130 (71)
191	4-(4-$C_2H_5OC_6H_4$N=CH)C_6H_4-	Condensation of 122 with 4-ethoxyaniline	130 (82)
192	4-(4-FC_6H_4N=CH)C_6H_4-	Condensation of 122 with 4-fluoroaniline	130 (70)
193	4-(4-ClC_6H_4-N=CH)C_6H_4-	Condensation of 122 with 4-chloroaniline	130 (86)
194	4-(4-BrC_6H_4N=CH)C_6H_4-	Condensation of 122 with 4-bromoaniline	130 (28)
195	4-(4-IC_6H_4N=CH)C_6H_4-	Condensation of 122 with 4-iodoaniline	130 (63)
196	4-(PhCH=N)C_6H_4-	Condensation of 124 with benzaldehyde	130 (38)
197	4-[4-$(CH_3)_2$NC_6H_4CH=N]C_6H_4-	Condensation of 124 with 4-(dimethylamino)benzaldehyde	130 (56)
198	4-(4-$NO_2C_6H_4$CH=N)C_6H_4-	Condensation of 124 with 4-nitrobenzaldehyde	130 (44)
199		Condensation of 124 with 3,4-dimethoxybenzaldehyde	130 (78)
200	4-(2-OHC_6H_4CH=N)C_6H_4-	Condensation of 124 with salicylaldehyde	130 (20)
201	4-(4-$CH_3OC_6H_4$CH=N)C_6H_4-	Condensation of 124 with 4-methoxybenzaldehyde	130 (42)

Table 3 (continued)

comp. no.	R	Method	Ref. (yield)
202		Condensation of 122 with 3-methylbenzoxazine	140 (20)
203		Condensation of 122 with 2,6-dimethyl-4-dicyanomethylene-4H-pyrane	141 (8)

*Cholesteryl 2-(*N*-aza-15-crown-15)acetate **115** and its saturated counterpart, cholestanyl 2-(*N*-aza-15-crown-5)acetate **114** were prepared in two steps. The steroidal alcohol was first treated with chloroacetyl chloride to give the ester of chloroacetic followed by reaction with aza-15-crown-5. The 15-membered ring **116** having cholesterol linked to the azacrown by a carbamate residue were prepared in a single step from commercially available cholesteryl chloroformate and the appropriate azacrown compounds. ** The abbreviation [N (ligand a, b or c) / Cl or Br] means Pd-catalyzed amination reaction of aryl chloride or bromide with azacrown ethers (Method N) in the presence of ligands a, b or c.

Table 4



Aza-15-crown-4 anellated to phenyl-α/β-D-glucopyranoside

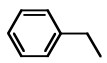
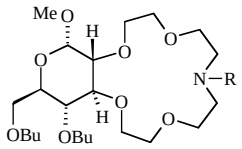
comp. no.	R	R`	Method	ref. (Yield)
204	$CH_3(CH_2)_3$-	CH_3-	A	35 (61)
205	$PhCH_2CH_2$-	CH_3-	A	35 (49)
206	$CH_3OCH_2CH_2$-	CH_3-	A	35 (75)
207	$PhCH_2$-	CH_3-	A	37 (37.7)
208	$CH_3(CH_2)_9$-	CH_3-	A	37 (40.9)
209	$CH_3(CH_2)_3$-	CH_3-	A	35 (61) 37 (68.7)
210	$PhCH_2CH_2$-	CH_3-	A	35 (48)
211	$OH(CH_2)_3$-	CH_3-	A	35 (58)
212	CH_3O-$(CH_2)_2$-	CH_3-	A	35 (44)
213	$OH(CH_2)_4$-	CH_3-	A	35 (51)
214	$CH_3(CH_2)_9$-	CH_3-	A	35 (44.3)
215	$OH(CH_2)_2$-	CH_3-	A	37 (60)
216	$CH_3O(O)CCH_2$-	CH_3-	A	37 (58.2)
217		CH_3-	A	37 (70.6)
218		CH_3-	A	37 (53.3)
219	Ph	CH_3-	A	37 (33.7)
220	α-naphthyl	CH_3-	A	37 (37)
221	$Ph_2P(O)$-CH_2-	CH_3-	A	142 (65)
222	$Ph_2P(O)(CH_2)_2$-	CH_3-	A	142 (61)
223	$Ph_2P(O)(CH_2)_3$-	CH_3-	A	142 (52)
224	$Ph_2P(O)(CH_2)_4$-	CH_3-	A	142 (58)
225	$Ph_2P(O)(CH_2)_5$-	CH_3-	A	142 (59)
226	$(EtO)_2P(O)CH_2$-	CH_3-	A	34 (40)
227	$(EtO)_2P(O)(CH_2)_2$-	CH_3-	A	34 (46)

Table 4 (continued)

comp. no.	R	R`	Method	ref. (Yield)
228	$(EtO)_2P(O)(CH_2)_3$-	CH_3-	A	34 (62)
229	$(EtO)_2P(O)(CH_2)_4$-	CH_3-	A	34 (50)
230	$(EtO)_2P(O)(CH_2)_5$-	CH_3-	A	34 (42)
231	$CH_3(CH_2)_3$-	Ph-	A	36 (43.9)
232	$CH_3(CH_2)_5$-	Ph-	A	36 (39.3)
233	$(CH_3)_2(CH)_3(CH_3)_2$	Ph-	A	36 (97.3)
234	$C_6H_{11}CH_2$-	Ph-	A	36 (32.2)
235	$OHCH_2CH_2$-	Ph-	A	36 (48)
236	$CH_3OCH_2CH_2$-	Ph-	A	36 (53.8)
237	$OHCH_2CH_2CH_2$-	Ph-	A	36 (38.4)
238	$CH_3OCH_2CH_2CH_2$-	Ph-	A	36 (66)
239	$PhCH_2$-	Ph-	A	36 (42.6)
240	$PhCH_2CH_2$-	Ph-	A	36 (71)
241	2-$CH_3OC_6H_4CH_2CH_2$-	Ph-	A	36 (52.6)
242	4-$CH_3OC_6H_4CH_2CH_2$-	Ph-	A	36 (47.6)

From comp. 204-208 ($H^4 = \alpha$); From comp. 29-242 ($H^4 = \beta$).

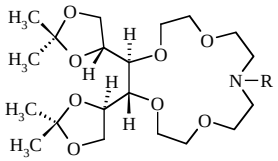
Table 5



Aza-15-crown-4 anellated to methyl 4,6-di-*O*-butyl-α-D-glucopyranoside

comp. no.	R	Method	ref. (yield)
243	$CH_3(CH_2)_3$-	A	38 (46)
244	$CH_3O(CH_2)_3$-	A	38 (42)
245	$PhCH_2$-	A	38 (40)
246	$PhCH_2CH_2$-	A	38 (45)

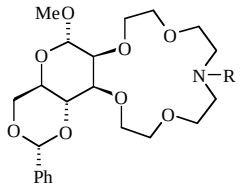
Table 6



Aza-15-crown-4 derived from D-mannitol

comp. no.	R	Method	ref. (yield)
247	$CH_3(CH_2)_3$-	A	39 (53)
248	C_6H_{11}-	A	39 (35)
249	$PhCH_2$-	A	39 (51)
250	$PhCH_2CH_2$-	A	39 (54)
251	$OHCH_2CH_2CH_2$-	A	39 (48)
252	$OH(CH_2)_4$-	A	39 (37)
253	$CH_3OCH_2CH_2$-	A	39 (48)
254	$CH_3OCH_2CH_2CH_2$-	A	39 (28)

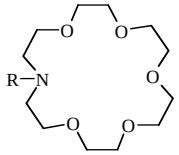
Table 7



Aza-15-crown-4 anellated to phenyl-α-D-mannopyranoside

comp. no.	R	Method	ref. (yield)
255	$OHCH_2CH_2$-	A	47 (44)
256	$OHCH_2CH_2CH_2$-	A	47 (53)
257	$OH(CH_2)_4$-	A	47 (50)
258	$CH_3O(CH_2)_3$-	A	47 (49)

Table 8



Aza-18-crown-6

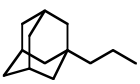
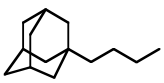
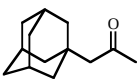
comp. no.	R	method	ref. (yield)
259	CH_2=$CHCH_2$-	C	143 (16), 125 (-), 127 (-)
260	CH_2=$CHCH_2CH_2$-	G	143 (29)
261	$CH_3CH_2CH_2$-	G	144, 145 (19)
262	$CH_3OCH_2CH_2$-	C	125 (-), 127 (-), 25 (53)
263	$CH_3(CH_2CH_2O)_2$-	C	25 (50)
264	$OHCH_2CH_2OCH_2CH_2$-	C	111 (67)
265	$(CH_3)_3Ge(CH_2)_2C(O)O(CH_2)_2O(CH_2)_2$-	Reaction of 264 with trimethylger-mylpropionic acid	111 (30.8)
266	$C_7F_{15}CH_2OCH_2CO$-	H	115 (71)
267	$C_7F_{15}CH_2OCH_2CH_2$-	Reduction of 266	115 (86)
268	$CH_3CH_2OC(O)CH_2$-	G	144 (-), 145 (79)
269	$C_{10}H_{21}OCOCH_2$-	G	113 (62)
270	$CH_3OC(O)CH_2NHC(O)CH_2$-	G	144 (-), 145 (51)
271	$C_{18}H_{37}NHC(O)CH_2$-	G	113 (60)
272	$(C_5H_{11})_2NC(O)CH_2$-	G	113 (55)
273	$(C_{10}H_{21})_2NC(O)CH_2$-	G	113 (61)
274	$CH_3OC(O)CH(Ph)NHC(O)CH_2$-	G	96 (55)
275	$PhCH_2OC(O)NHCH_2C(O)$-	R	96 (60-80)
276	$PhCH_2OCONHCH(Ph)C(O)NHCH_2C(O)$-	R	96 (50-60)
277	$CH_3OC(O)CH(Ph)NHC(O)CH_2$-	R	96 (55)
278	$(C_{18}H_{37})_2NC(O)CH_2OCH_2C(O)$-	R	97 (81)
279		C	146 (36)
		G	146 (24)
280		C	146 (21)
		G	146 (54)
281		H	146 (85)

Table 8 (continued)

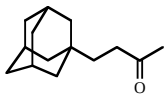
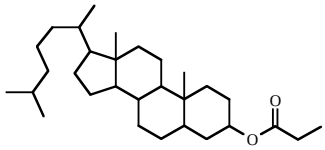
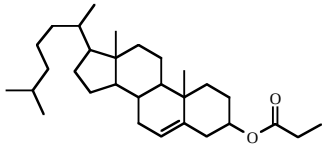
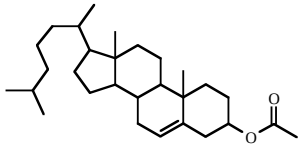
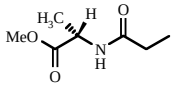
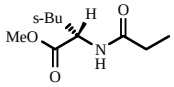
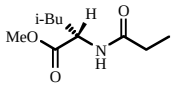
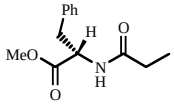
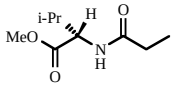
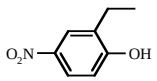
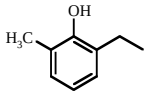
comp. no.	R	method	ref. (yield)
282		H	146 (79)
283*		G	147 (63) 128 (-) 22a (-)
284*		G	22a (65)
285*		H	22a (52)
286		G	148 (-)
287		G	148 (-) 145 (50)
288		G	145 (-)
289		G	148 (-)
290		G	148 (-) 145 (56)
291	Ph-	C	25 (41)
292	2-$CH_3OC_6H_4$-	C	131 (13) 25 (41)
293	4-$H(O)CC_6H_4$-	Formylation of 291	131 (65)
294	4-$CH_3C_6H_4$-	N (ligand a / Cl)	101 (52)
295	4-$CH_3OC_6H_4$-	N (ligand a / Cl / Br / I)	101 (51,54,55)
296	$PhCH_2$-	C	25 (40)
		G	26 (90)
297	2-$NO_2C_6H_4CH_2$-	G	132 (82)
298		G	118 (87)
299		S	120 (-)

Table 8 (continued)

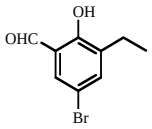
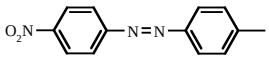
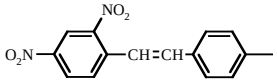
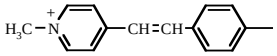
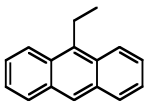
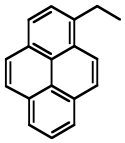
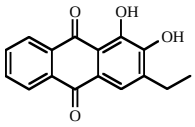
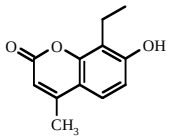
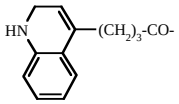
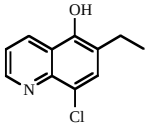
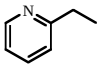
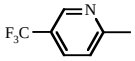
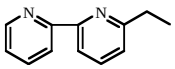
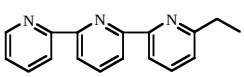
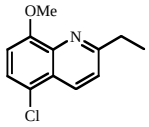
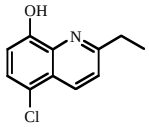
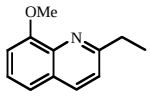
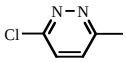
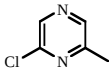
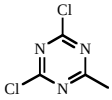
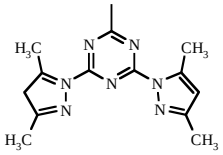
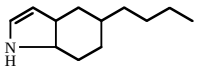
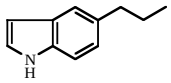
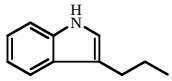
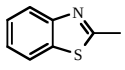
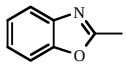
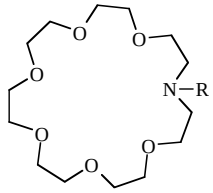
comp. no.	R	method	ref. (yield)
300		T	104 (45)
301		Coupling of 291 with *p*-nitobenzene- diazonium chloride	131 (56)
302		Condensation of 293 with 2,4-dinitrotoluene	131 (-)
303		Condensation of 293 with dimethylpyridinium iodide	131 (-)
304		C G	19b (-) 19b (-), 149 (22)
305		G	150 (90)
306		S	122 (38)
307		S	122 (62)
308		V	138 (48)
309		T	103 (56)
310		G	26 (85)
311		M	90 (92)
312		G	26 (95) 129 (88)
313		G	26 (74)

Table 8 (continued)

comp. no.	R	method	ref. (yield)
314		G	103 (74)
315		G	103 (47)
316		G	118 (76)
317		M	90 (97)
318		M	90 (89)
319		L	151 (77)
320		L	151 (12)
321		L	152 (-)
322		G	139 (67)
323		G	139 (67)
324		G	139 (73) 124 (-)
325		M	90 (92)
326		M	90 (99)
327		M	90 (96)

*Cholesteryl 2-(*N*-aza-18-crown-15)acetate **284** and its saturated counterpart, cholestanyl 2-(*N*-aza-18-crown-5)acetate **283** were prepared in two steps. The steroidal alcohol was first treated with chloroacetyl chloride to give the ester of chloroacetic followed by reaction with aza-18-crown-5. The 18-membered ring **285** having cholesterol linked to the azacrown by a carbamate residue were prepared in a single step from commercially available cholesteryl chloroformate and the appropriate azacrown compounds.

Table 9



Aza-21-crown-7

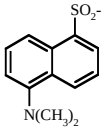
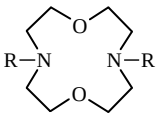
comp. no.	R	Method	ref. (yield)
328	CH_2=$CHCH_2$-	C	143 (1)
329		H	121 (60)

Table 10



Diaza-12-crown-4

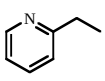
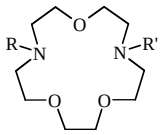
comp. no.	R	Method	ref. (Yield)
330	$OHCH_2CH_2$-	J	153 (-)
331	$PPh_3CH_2CH_2$-	Chlorination of 330 with $SOCl_2$ followed by reaction with K-diphenylphosphine in 1,4-dioxane	153 (44)
332	$OHCH_2CH_2$-OCH_2CH_2-	I	153 (91)
333	$PPh_3CH_2CH_2OCH_2CH_2$-	Chlorination of 332 with $SOCl_2$ followed by reaction with K-diphenylphosphine in 1,4-dioxane	153 (45)
334	$(CH_3CH_2)_2NC(O)CH_2$-	G	154 (70)
335	$(CH_3CH_2)_2NCH_2CH_2$-	Reduction of 334 (BH_3)	154 (40)
336	$(CH_3CH_2)_2OC(O)CH_2$-	G	154 (80)
337	Ph-	E	49 (16)
338	$PhCH_2$-	G	154 (60)
339	4-$CH_3C_6H_4$-	E	49 (18)
340	4-$CH_3OC_6H_4$-	E	49 (15)
341	4-ClC_6H_4-	E	49 (11)
342		G	154 (60)

Table 11



Diaza-15-crown-5

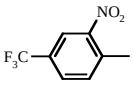
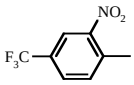
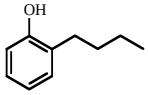
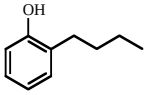
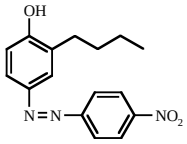
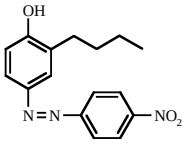
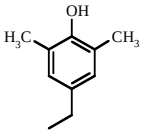
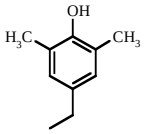
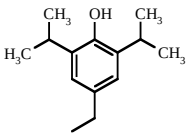
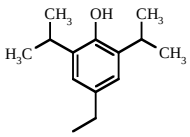
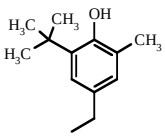
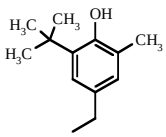
comp. no.	R	R`	Method	ref. (yield)
343	CH_3CH_2-	$(CH_3)_2NCH_2CH_2$-	D	63 (49)
344	CH_3CH_2-	$(CH_3)_2N(CH_2)_2CH_2$-	D	63 (21)
345	CH_3CH_2-	$(CH_3CH_2)_2NCH_2CH_2$-	D	63 (71)
346	CH_3CH_2-	$(CH_3CH_2)_2N(CH_2)_2CH_2$-	D	63 (72)
347	CH_3CH_2-	$OHCH_2CH_2$-	D	63 (52)
348	CH_3CH_2-	$OH(CH_2)_2OCH_2CH_2$-	D	63 (81)
349	CH_3CH_2-	$PhCH_2$-	D	63 (62)
350	CH_3CH_2-	Morpholin-CH_2CH_2-	D	63 (67)
351	$PhCH_2$-	$(CH_3CH_2)_2N(CH_2)_2CH_2$-	D	63 (80)
352	$CH_3OCH_2CH_2$-	$CH_3OCH_2CH_2$-	D	62 (38), 15b (-)
353	$CH_3CH_2OCH_2CH_2$-	$CH_3CH_2OCH_2CH_2$-	G	155 (56)
354	$PhCH_2OCH_2CH_2$-	$PhCH_2OCH_2CH_2$-	G	155 (77)
355	$OHCH_2CH_2$-	$OHCH_2CH_2$-	Pd/C reduction of 354	155 (82)
356	$PhCH_2$-	$PhCH_2$-	D	62 (72), 15b (-)
357	2-$CH_3OC_6H_4$-CH_2-	2-$CH_3OC_6H_4$-CH_2-	G	156 (52)
			D	62 (52), 15b (-)
358	2-$NO_2C_6H_4CH_2$-	2-$NO_2C_6H_4CH_2$-	G	17b (-), 157 (-)
359	2-$NH_2C_6H_4CH_2$-	2-$NH_2C_6H_4CH_2$-	Pd/C hydrazine reduction of 358	157 (61)
360			M	89 (95)
361			M	89 (92)
362			P	94 (68)
363			P	94 (53)
364			T	102 (49)
365			T	102 (74)
366			T	102 (59)

Table 11 (continued)

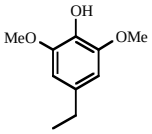
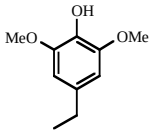
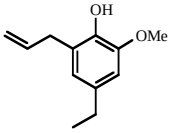
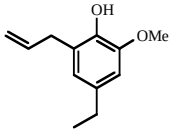
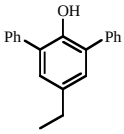
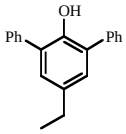
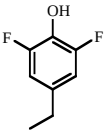
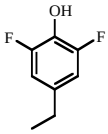
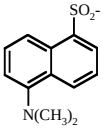
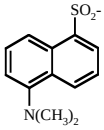
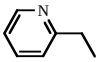
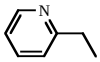
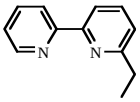
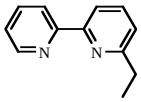
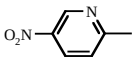
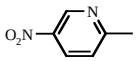
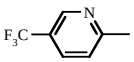
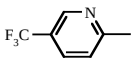
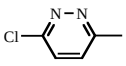
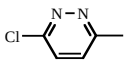
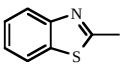
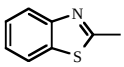
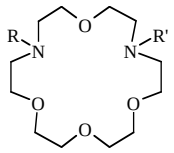
comp. no.	R	R`	Method	ref. (yield)
367			T	102 (25)
368			T	102 (20)
369			T	102 (21)
370			T	102 (30)
371			H	121 (15)
372			G	158 (-), 159 (55)
373			G	129 (46)
374			M	89 (95)
375			M	89 (83)
376			M	89 (82)
377			M	89 (80)
378			D	62 (67), 15b (67)
379			M	89 (89)
380			M	89 (95)

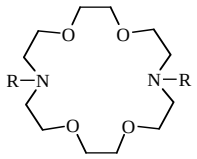
Table 12



1,7-Diaza-18-crown-6

comp. no.	R	R`	Method	ref. (yield)
381	CH_3CH_2-	$(CH_3)_2NCH_2CH_2$-	D	63 (47)
382	CH_3CH_2-	$(CH_3)_2N(CH_2)_2CH_2$-	D	63 (33)
383	CH_3CH_2-	$(CH_3CH_2)_2NCH_2CH_2$-	D	63 (44)
384	CH_3CH_2-	$(CH_3CH_2)_2N(CH_2)_2CH_2$-	D	63 (33)
385	CH_3CH_2-	$OHCH_2CH_2$-	D	63 (62)
386	CH_3CH_2-	$OH(CH_2)_2OCH_2CH_2$-	D	63 (73)
387	CH_3CH_2-	Morpholin-CH_2CH_2-	D	63 (55)
388	$PhCH_2$-	$(CH_3CH_2)_2N(CH_2)_2CH_2$-	D	63 (68)

Table 13-1



1,10-Diaza-18-crown-6

comp. no.	R	method	ref. (yield)
389	$CH_3CH_2CH_2$-	I	144 (78), 145 (-)
390	$CH_3(CH_2)_2CH_2$-	D	62 (77)
391	$CH_3(CH_2)_3CH_2$-	U	30 (-), 51 (94)
392	$CH_3(CH_2)_4CH_2$-	B	62 (7)
		D	62 (32)
393	$CH_3(CH_2)_7CH_2$-	B	62 (11)
394	$CH_3(CH_2)_8CH_2$-	G	115 (92)
395	$CH_3(CH_2)_{10}CH_2$-	B	15b (11)
396	CH_2=$CHCH_2$-	G	143 (35)
		B	15a (25), 15b (26)
397	CH_2=$CHCH_2CH_2$-	U	30 (70)
398	HC≡CCH_2-	B	15b (22)
399	HC≡CCH_2CH_2-	U	30 (36)
400	$OHCH_2CH_2$-	B	15a (28), 160 (-), 161 (24) 111 (20)
		D	160 (-), 161 (32-41)
401	$(CH_3)_3GeCH_2CH_2C(O)OCH_2CH_2$-	Reaction of 400 with trimethylgermylpropionic acid	111 (43.5)
402	$OHCH_2CH_2CH_2$-	Q	153 (81)
403	$PPh_3CH_2CH_2CH_2$-	Chlorination of 402 with $SOCl_2$ followed by reaction with K-diphenylphosphine in 1,4-dioxane	153 (45)
404	$OHCH_2CH_2OCH_2CH_2$-	B	82 (7.2)
405	$CH_3OCH_2C(O)$-	H	15a (80)
406	$CH_3OCH_2CH_2$-	D	62 (43)
		I	15a (76)
		G	155 (42), 162 (29)
		Diborane reduction of 405	15a (97)
407	$CNCH_2$-	G	163 (75)
408	$CNCH_2$-CH_2-	G	78 (80-94)

Table 13-1 (continued)

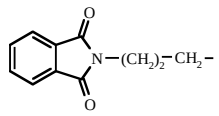
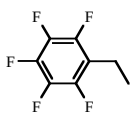
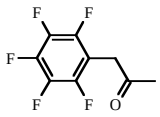
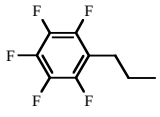
comp. no.	R	method	ref. (yield)
409		G	78 (97)
410	$NH_2(CH_2)_2CH_2$-	Hydrazinolysis of 409	78 (97)
		Reduction of 409	95 (-), 78 (84-98)
411	$CH_3OC(O)CH_2$-	G	145 (92)
412	$CH_3CH_2OC(O)CH_2CH_2$-	U	30 (76)
413	$CH_3CH_2OC(O)CH_2$-	G	144 (-), 145 (79)
			15a (92)
414	$CH_3CH_2OC(O)CH_2CH_2$-	G	15d (70)
415	$CH_3CH_2OC(O)CH_2CH_2CH_2$-	G	15d (65)
416	$NH_2C(O)CH_2$-	G	145 (61)
417	$CH_3OC(O)CH_2NHC(O)CH_2$-	G	144 (-), 145 (58)
418	$CH_3OC(O)CH(CH_3)NHC(O)CH_2$-	G	144 (-), 145 (50), 148 (-),164(-)
419	$CH_3OC(O)CH(i\text{-}Pr)NHC(O)CH_2$-	G	144 (-), 145 (59), 148 (-), 145 (-)
420	$CH_3OC(O)CH(sec\text{-}Bu)NHC(O)CH_2$-	G	144 (-), 145 (60), 148, 164(-)
421	$CH_3OC(O)CH(i\text{-}Bu)NHC(O)CH_2$-	G	144 (-), 145 (51), 148 (-), 164(-)
422	$CH_3OC(O)CH(PhCH_2)NHC(O)CH_2$-	G	144 (-), 145 (-), 148 (-), 164(-)
423	$(C_5H_{11})_2NC(O)CH_2$-	G	113 (-)
424	$(C_2H_5)_2NC(O)CH_2CH_2$-	G	15d (60)
425	$CH_3OC(O)CH(Ph)NHC(O)CH_2$-	G	96 (61)
426	$(C_{18}H_{37})_2NC(O)CH_2OCH_2C(O)$-	R	97 (44)
427	$OHC(O)CH_2$-	Aqueous hydrolysis of 413	15a (81)
428	$C_6F_{13}CH_2CH_2$-	G	115 (14)
429	$C_8F_{17}CH_2CH_2$-	G	115 (16)
430	$C_7F_{15}C(O)$-	H	115 (86)
431	$C_7F_{15}CH_2OCH_2C(O)$-	H	115 (95)
432	$C_8F_{17}CH_2CH_2OCH_2C(O)$-	H	115 (83)
433	$C_{10}F_{21}CH_2CH_2OCH_2C(O)$-	H	115 (78)
434	$C_7H_{15}CH_2$-	BH_3/HF reduction of 430	115 (80)
435	$C_7F_{15}CH_2OCH_2CH_2$-	BH_3/HF reduction of 431	115 (80)
436	$C_8F_{17}CH_2CH_2OCH_2CH_2$-	BH_3/HF reduction of 432	115 (81)
437	$C_{10}F_{21}CH_2CH_2OCH_2CH_2$-	BH_3/HF reduction of 433	115 (70)
438		D	53 (48)
439	$PhCH_2$-	D	62 (68), 15b (66)
		B	62 (29), 165 (67)
		I	166a (60)
		G	158 (-), 166b (-)
440	$PhCH_2OC(O)NHCH_2C(O)$-	R	96 (60-80)
441	$PhCH_2OC(O)NHCH(Ph)C(O)NHCH_2CO$-	R	96 (50-60)
442	$CH_3OC(O)CH(Ph)NHC(O)CH_2$-	R	96 (61)
443	4-ClC_6H_4-	E	49 (18)
444	4-$CH_3C_6H_4$-	E	49 (16)
445	4-$CH_3OC_6H_4$-	E	49 (21)
446		G	115 (63)
447		H	167 (70)
448		Reduction of 447	167 (70)

Table 13-1 (continued)

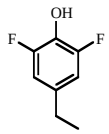
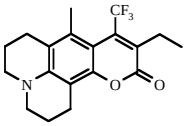
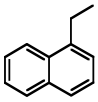
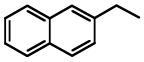
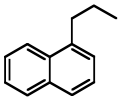
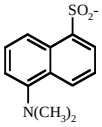
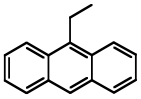
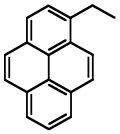
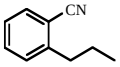
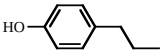
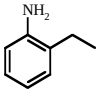
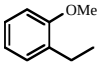
comp. no.	R	method	ref. (yield)
449		T	102 (29)
450		G	123 (10)
451		G	168 (-), 169 (-)
452		G	169 (76), 170 (76), 26 (98)
453		G	167 (61)
454		H	121 (30)
455		G	171 (68),171 (68), 172 (90)
456		G	150 (95), 173 (-)
457		U	30 (62)
458		U	30 (95)
459		G	15a (85)
460		B	167 (14)
461		G	17b (90), 174 (-), 157 (-)
462		Reduction of 461 by Pd/C- hydrazine in ethanol	174 (48)
463		B	62 (30)

Table 13-1 (continued)

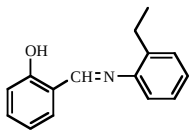
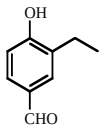
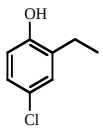
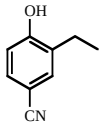
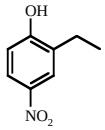
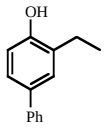
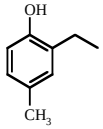
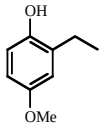
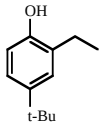
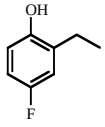
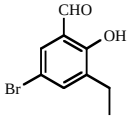
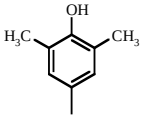
comp. no.	R	method	ref. (yield)
464		Condensation of 462 with salicylaldehyde	174 (55)
465		G	175 (29)
466		T S	103 (77) 176 (-), 177 (77)
467		S	177 (50)
468		S	177 (15)
469		S	177 (91)
470		T S	178 (84) 179 (-), 177 (85)
471		S	178 (61), 177 (87)
472		S	180 (-), 177 (70)
473		S	177 (75)
474		T	104 (52)
475		T	119 (53)

Table 13-1 (continued)

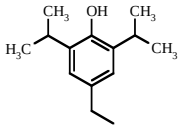
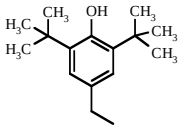
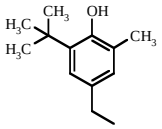
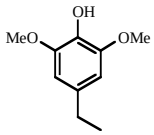
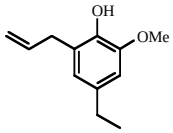
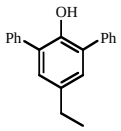
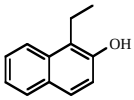
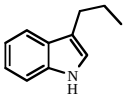
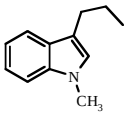
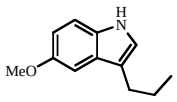
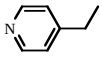
comp. no.	R	method	ref. (yield)
476		T	102 (86)
477		T	102 (68)
478		T	102 (79)
479		T	102 (48)
480		T	102 (31)
481		T	102 (29)
482*		T	178 (79)
483		D B G I	62 (62) 62 (27) 158 (-), 166b (-) 166a (50)
484		G I	181 (-) 166a (60)
485		G	167 (53)
486		G	167 (46)
487		B	167 (6)
488		B G G	15a (22) 158 (-) 159 (60)
489		G	158 (-), 159 (72)

Table 13-1 (continued)

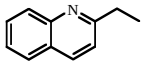
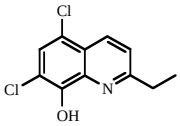
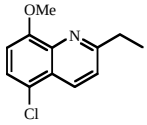
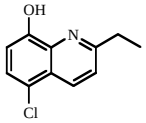
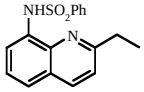
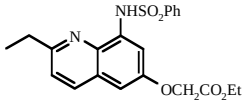
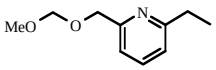
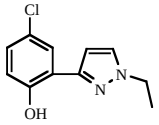
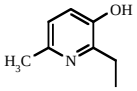
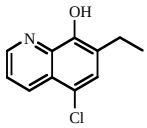
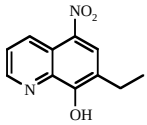
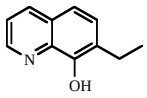
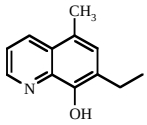
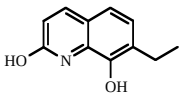
comp. no.	R	method	ref. (yield)
490		G	158 (-), 159 (45)
491		G	92 (48)
492		G	103 (61) 176 (-)
493		Reaction of 492 with LiCl in DMF	103 (48), 176 (-), 26 (94)
494		K	182 (85)
495		K	182 (78)
496		G	26 (94)
497		T	92 (98)
498		S	183 (45)
499		S	103 (67), 92 (68)
500		S	92 (85)
501		S	92 (60)
502		S	92 (55)
503		S	92 (24)

Table 13-1 (continued)

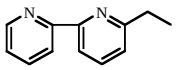
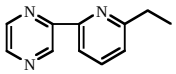
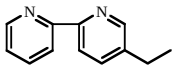
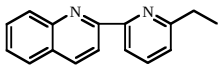
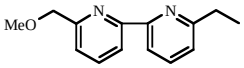
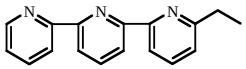
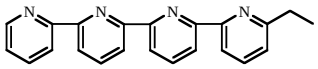
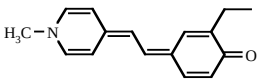
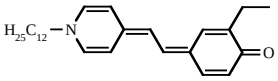
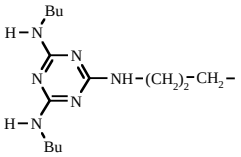
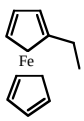
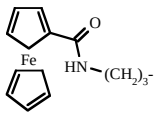
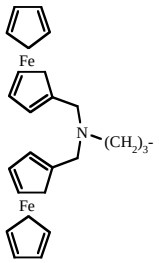
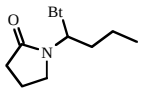
comp. no.	R	method	ref. (yield)
504		G	26 (95), 129 (-), 184 (80)
505		G	26 (76)
506		G	26 (53)
507		G	26 (63)
508		G	26 (75)
509		G	26 (74)
510		G	185 (60)
511		Reaction of 465 with 1,4-dimethylpyridinium iodide in EtOH containing piperidine	175 (70)
512		Reaction of 465 with 1-dodecyl-4-methylpyridini-um iodide in EtOH containing piperidine	175 (27)
513		G	78 (46)
514		G	78 (70)
515		Acylation of 410	78 (65)
516		Acylation of 410	78 (92)
517		U	30 (-), 51 (91)

Table 13-1 (continued)

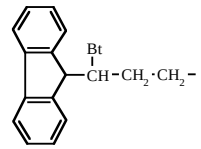
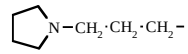
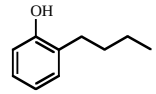
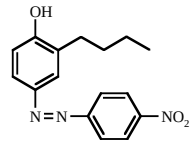
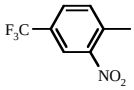
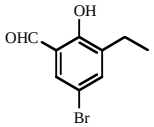
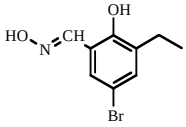
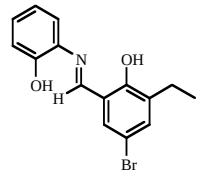
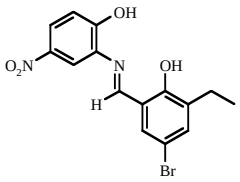
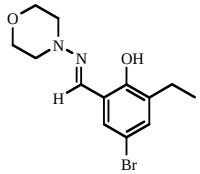
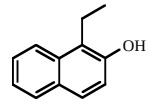
comp. no.	R	method	ref. (yield)
518		U	30 (-), 51 (97)
519		U	30 (-), 51 (76)
520	Ph-	E	49 (19)
521		P	94 (67)
522		P	94 (30)
523		M	186 (79)
524		T	104 (52)
525		Condensation of 524 with hydroxylamine	104 (57)
526		Condensation of 524 with 2-aminophenol	104 (95)
527		Condensation of 524 with 4-nitro-2-aminophenol	104 (72)
528		Condensation of 524 with *N*-aminomorpholine	104 (97)
529		T	178 (79)

Table 13-1 (continued)

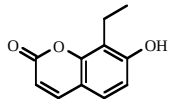
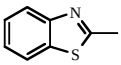
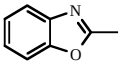
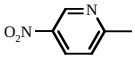
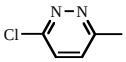
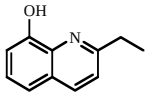
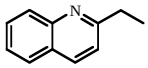
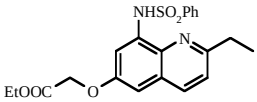
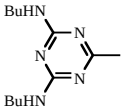
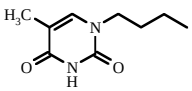
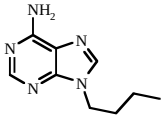
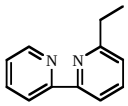
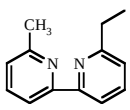
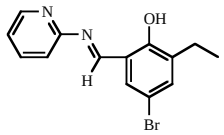
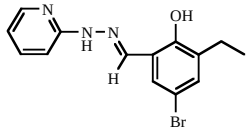
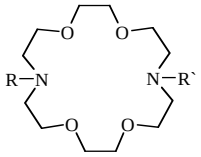
comp. no.	R	method	ref. (yield)
530		U T	30 (31) 58 (-)
531		M	186 (51)
532		M	186 (74)
533		M	186 (64)
534		M	186 (77)
535		M	186 (100)
536		M	186 (86)
537		M	186 (81)
538		O	92 (77)
539		O	92 (85)
540		O	93 (78)
541		L	78 (53)
542		G	187 (67)
543		G	187 (24)
544		G	178 (80)
545		G	178 (77)

Table 13-1 (continued)

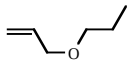
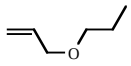
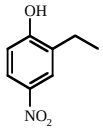
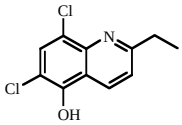
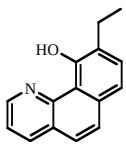
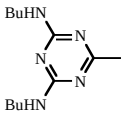
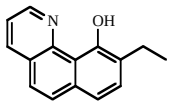
comp. no.	R	method	ref. (yield)
546		Condensation of 524 with 2-aminopyridine	104 (74)
547		Condensation of 524 with 2-hydrazinopyridine	104 (75)

* Compound **482** could also obtained by aminomethylation of β-Naphthol or 1,1'-methylenebis-2-naphthol with 18-crown-6. In the last case the reaction proceeded on already occupied position of the naphthol ring followed by loss of the benzyl group.

Table 13-2

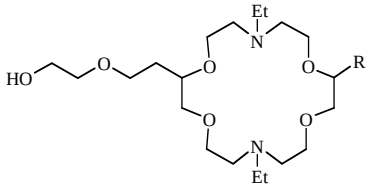


1,10-Diaza-18-crown-6 (R and R' are different)

comp. no.	R	R`	Method	ref. (yield)
548		Tetrahydrofuryl-OCH_2CH_2-	*	160 (74)
549		$(CH_3)_3CCH_2CH_2OCH_2CH_2$-	*	160 (85)
550	Ph-CH_2-	$(C_{18}H_{37})_2NC(O)CH_2OCH_2C(O)$-	R	30 (46)
551			**	92 (63)
552	H		T***	92 (25)
553	$PhCH_2$-		L	78 (55)
554	H		T	92 (25)

*Compounds **548**, **549** were obtained by controlled etherization of *N*,*N*'-bis(2-hydroxyethtyl)-4,13-diaza-18-crown-6 **400** with allyl bromide and NaH to give first *N*-(2-allyloxy)ethyl-*N*'(2-hydroxyethyl)-4,13-diaza-18-crown-6 in a good yield followed by reaction of the latter with sodium hydride and tetrahydrofurfuryl chloride or 3,3-dimethylbutyl tosylate in THF. **The unsymmetrically substituted diaza-18-crown-6 Compound **551** was obtained by first treatment of diaza-18-crown-6 with a lower amount of 5,7-dichloro-2-iodomethyl-8-quinolinol to give mono-5,7-dichloro-8-hydroxyquinaldinyl-substituted diaza-18-crown-6 and subsequent treatment of the latter with α-bromo-4-nitro-*o*-cresol. *** The mono-10-hydroxybenzoquinoline (HBQ)-substituted diaza-18-crown-6 **552** was obtained even in the presence of 2.2 equiv. of HBQ. It is possible that one attached HBQ prevents the second HBQ from reacting through steric hindrance or by intramolecular hydrogen bonding between the nitrogen atom of HBQ and the NH of the crown ether.

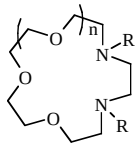
Table 14



1,10-Diaza-18-crown-6 with substituents on the ring carbons

comp. no.	R	method	ref. (yield)
555	H	D	54 (45)
556	CH_2=$CHCH_2OCH_2$-	D	54 (42)

Table 15



1,4-Diaza-15-crown-5, 1,4-Diaza-18-crown-5 and 1,4-Diaza-21-crown-7

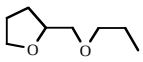
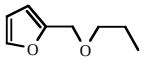
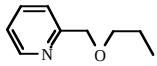
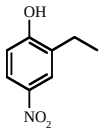
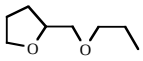
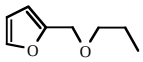
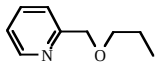
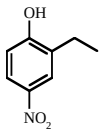
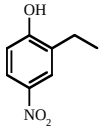
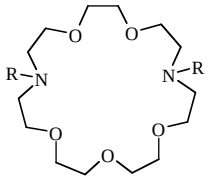
comp. no.	N	R	method	Ref. (yield)
557	1	$OHCH_2CH_2$-	D	55 (-), 56 (97)
558	1	$OHCH_2CH_2OCH_2CH_2$-	G	55 (33), 56 (-)
559	1	$CH_3OCH_2CH_2OCH_2CH_2$-	G	55 (77), 56 (-)
560	1		G	55 (72), 56 (-)
561	1		G	55 (55), 56 (-)
562	1		G	55 (48), 56 (-)
563	1		G	94 (50)
564	2	$OHCH_2CH_2$-	D	55 (66), 56 (-)
565	2	$OHCH_2CH_2OCH_2CH_2$-	G	55 (29), 56 (-)
566	2	$CH_3OCH_2CH_2OCH_2CH_2$-	G	55 (71), 56 (-)
567	2		G	55 (67), 56 (-)
568	2		G	55 (50), 56 (-)
569	2		G	55 (40), 56 (-)
570	2		G	94 (48)
571	3		G	94 (71)

Table 16



1,10-Diaza-21-crown-7

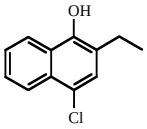
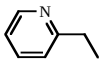
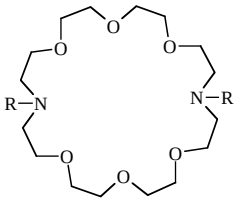
comp. no.	R	method	ref. (yield)
572		T	103 (54)
573		G	158 (-), 159 (45)
574		M	89 (92)

Table 17



1,13-Diaza-24-crown-8

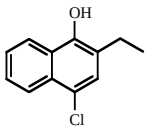
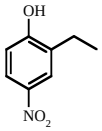
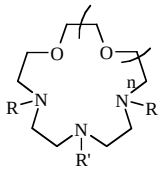
comp. no.	R	Method	ref. (yield)
575	$OHCH_2CH_2OCH_2CH_2$-	B	111 (5)
576	$(CH_3)_3GeCH_2CH_2C(O)OCH_2CH_2$-	Reaction of 575 with trimethylgermylpropionic acid	111 (87)
577		T	103 (45)
578		G	94 (8)

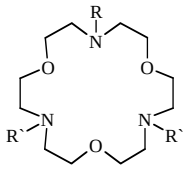
Table 18



1,4,7-Triaza-12-crown-4 and 1,4,7-Triaza-15-crown-5

comp. no.	n	R	R'	method	ref. (yield)
579	0	$OHCH_2CH_2$-	$OHCH_2CH_2$-	J	188 (-), 189 (-)
580	1	$CNCH_2$-	$CNCH_2$-	G	190 (-), 191 (56)
581	1	$NH_2CH_2CH_2$-	$NH_2CH_2CH_2$-	Reduction of 580 (BH_3)	190 (-), 191 (75)
582	1	$CH_3CH(OH)CH_2$-	$CH_3CH(OH)CH_2$-	J	82 (47.7)
583	0	$CH_3CH(OH)CH_2$-	$CH_3CH(OH)CH_2$-	J	82 (-)
584	1	CH_3CH_2-	$OH(CH_2)_2O(CH_2)_2$-	D	54 (68)

Table 19



1,7,13-Triaza-18-crown-6

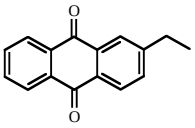
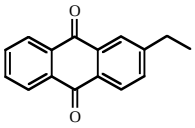
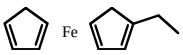
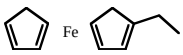
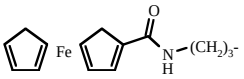
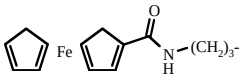
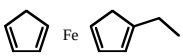
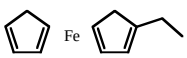
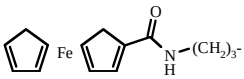
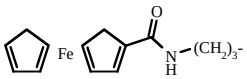
comp. no.	R	R`	method	ref. (yield)
585	$CH_3(CH_2)_5$-	$CH_3(CH_2)_5$-	G	192 (51)
586	$HC\equiv CCH_2$-	$HC\equiv CCH_2$-	G	192 (36)
587	$CNCH_2CH_2$-	$CNCH_2CH_2$-	Q	78 (80-94)
588	$NH_2(CH_2)_2CH_2$-	$NH_2(CH_2)_2CH_2$-	Q	95 (-),78 (80-94)
			$LiAlH_4$ reduction of 587	78 (85-97)
589	$OHCH_2CH_2$-	$OHCH_2CH_2$-	G	192 (78)
590	$CH_3OCH_2C(O)$-	$CH_3OCH_2C(O)$-	U	192 (44)
591	$CH_3OCH_2CH_2$-	$CH_3OCH_2CH_2$-	BH_3 reduction of 590	192 (31)
592	$CH_3CH_2OC(O)CH_2$-	$CH_3CH_2OC(O)CH_2$-	G	192 (30)
593	$PhCH_2$-	$PhCH_2$-	G	192 (91)
594	2-$NO_2C_6H_4CH_2$-	2-$NO_2C_6H_4CH_2$-	G	192 (50)
595			G	78 (55)
596			G	78 (86)
597			G	95 (-), 78 (59-69)
598	Ts		G	78 (87)
599	H		$LiAlH_4$ reduction of 598	78 (94)
600			Acylation of 588	78 (69)

Table 19 (continued)

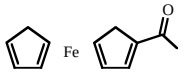
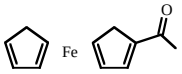
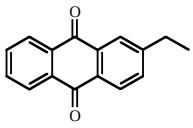
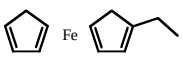
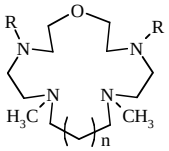
comp. no.	R	R`	method	ref. (yield)
601			H	78 (76-85)
602			G	78 (38)

Table 20



1,4,7,10-Tetraaza-15-crown-5 (N-4 and N-7 are substituted with methyl groups)
and 1,4,8, 11-Tetraaza-16-crown-5

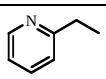
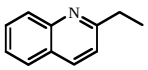
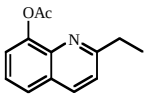
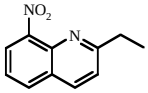
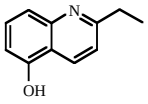
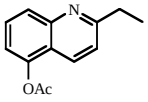
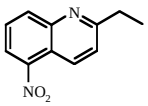
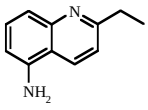
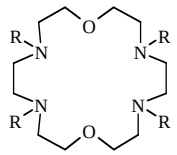
comp. no.	n	R	method	ref. (yield)
603	0		O	57 (87)
604	0		O	57 (82)
605	0		O	57 (82)
606	0		O	57 (55)
607	1		O	57 (94)
608	1		O	57 (85)
609	1		O	57 (52)
610	1		O	57 (81)

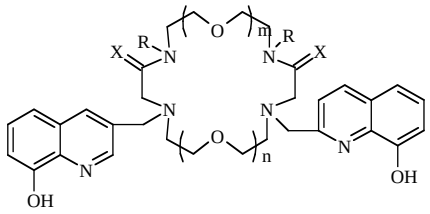
Table 21



Tetraaza-18-crown-6

comp. no.	R	Method	ref. (yield)
611	$OHCH_2CH_2$-	J	82 (80)
612	$CH_3CH(OH)CH_2$-	J	82 (100)

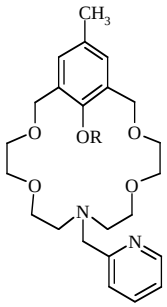
Table 22



1,4,7,10-Tetraaza-15-crown-5 (with two amide linkages) and 1,4,10,13-Tetraaza-21-crown-7

comp. no.	R	n	M	X	Method	ref. (yield)
613	CH_3	1	0	O	D	57 (-)
614	H	2	1	O	D	57 (19)
615	CH_3	1	0	H_2	Reduction of 614 (B_2H_6 / THF)	57 (27)

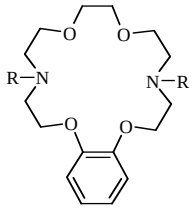
Table 23



Benzoaza-crowns with methylene bridges and *m*-benzo group

comp. no.	R	Method	Ref. (yield)
616	CH_3	C	48 (42)
617	H	Reaction of 616 with LiI in refluxing pyridine	48 (31)

Table 24



Benzodiaza-crowns

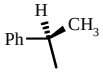
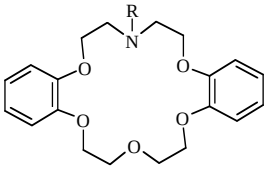
comp. no.	R	Method	ref. (yield)
618	$CH_3CH_2OC(O)CH_2$-	G	15d (80)
619	$CH_3CH_2OC(O)CH_2$-CH_2-	G	15d (60)
620	$CH_3CH_2OC(O)(CH_2)_2CH_2$-	G	15d (60)
621	$CH_3OCH_2CH_2$-	G	15d (45)
622	$(CH_3CH_2)_2C(O)CH_2$-	G	15d (60)
623		D	53 (54)

Table 25



Dibenzoaza-crowns

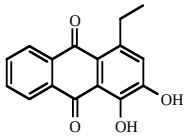
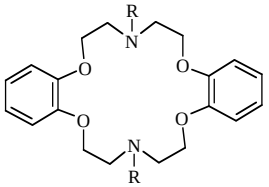
comp. no.	R	method	ref. (yield)
624		O	193 (68)

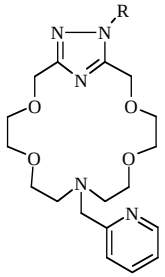
Table 26



Dibenzodiaza-crowns

comp. no.	R	method	ref. (yield)
625		D	53 (45)

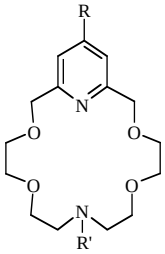
Table 27



Triazoloaza-crowns

comp. no.	R	method	ref. (yield)
626	THP	C	48 (29)
627	H	C	48 (22)

Table 28



Pyridinoaza-crowns

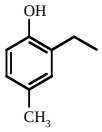
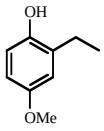
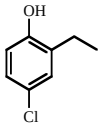
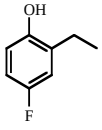
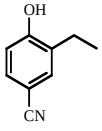
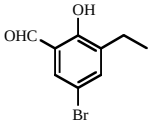
comp. no.	R	R'	Method	ref. (yield)
628	H		T	48 (51)
629	H		T	48 (55)
630	H		T	48 (56)
631	H		T	48 (15)
632	H		T	48 (20)
633	H		T	48 (61), 104 (61)

Table 28 (continued)

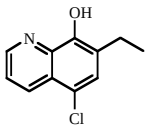
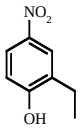
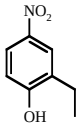
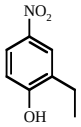
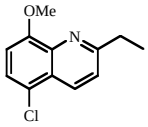
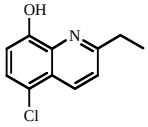
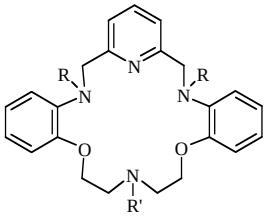
comp. no.	R	R'	Method	ref. (yield)
634	H		T	48 (58)
635	H		G	48 (85)
636	OTHP		G	48 (-)
637	OH		Reaction of 636 with CH_3OH	48 (21)
638	H		G	48 (79)
639	H		Reaction of 638 with LiCl in DMF at 130^0C	48 (48)

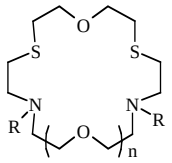
Table 29



Dibenzopyridinoaza-crowns

comp. no.	R	R`	Method	ref. (yield)
640	H	4-$NO_2C_6H_4CH_2$-	G	194 (-)
641	4-$NO_2C_6H_4CH_2$-	4-$NO_2C_6H_4CH_2$-	G	194 (83)
642	H	$CNCH_2$-	G	194 (58)
643	H	4-$NH_2C_6H_4CH_2$-	Reduction. of 641 Pd/C	194 (60)

Table 30



Diazadithia-18-crown-6, 1,7-Diaza-10,16-dithia-21-crown-7, Diazadithia-24-crown-8

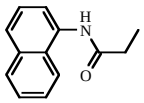
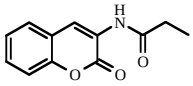
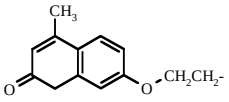
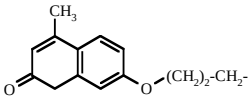
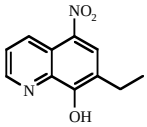
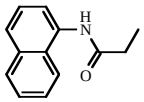
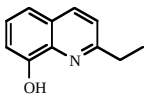
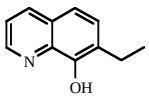
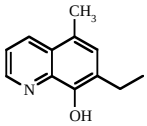
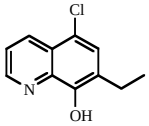
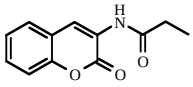
comp. no.	n	R	method	ref. (yield)
644	1		G	195 (32)
645	1		G	195 (31),
646	1		G	195 (31)
647	1		G	195 (43)
648	1		S	58 (28)
649	2		G	195 (53)
650	2		O	58 (48)
651	2		S	58 (65)
652	2		S	58 (51)
653	2		S	58 (64)
654	3		G	195 (31)

Table 30 (continued)

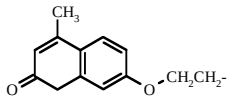
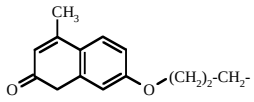
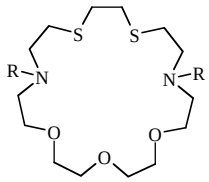
comp. no.	n	R	method	ref. (yield)
655	3		G	195 (43)
656	3		G	195 (54)

Table 31



1,10-Diaza-4,7-dithia-21-crown-7

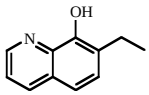
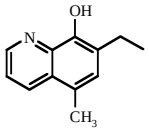
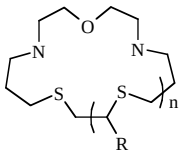
comp. no.	R	method	ref. (yield)
657		S	58 (57)
658		S	58 (57)

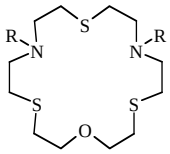
Table 32



Diazadithia-17-crown-5 and Diazatrithia-20-crown-6

comp. no.	n	R	method	ref. (yield)
659	1	H	K	86 (-), 87 (81)
660	1	$HOCH_2$-	K	86 (-), 87 (86)
661	2	H	K	86 (-), 87 (80)

Table 33



1,7-Diaza-4,10,16-trithia-18-crown-6

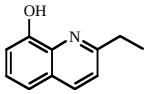
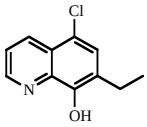
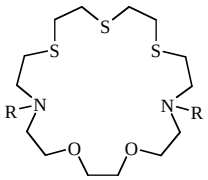
comp. no.	R	method	ref. (yield)
662		O	196 (75)
663		S	196 (75)

Table 34



Diazatrithia-21-crown-7

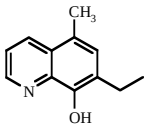
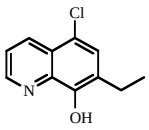
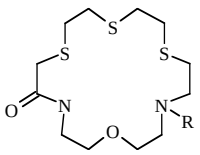
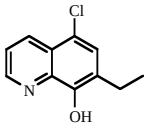
comp. no.	R	method	ref. (yield)
664		S	58 (66)
665		S	58 (76)

Table 35



1,7-Diaza-10,13,16-trithia-18-crown-6

comp. no.	R	method	ref. (yield)
666		S	58 (60)

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