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Phenylaza- and benzoazacrown compounds with a nitrogen atom conjugated with a benzene ring

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Abstract. Data on the synthesis and properties of aza- and diazacrown compounds containing a phenyl group at a nitrogen atom or an *o*-phenylene fragment annelated to the macrocycle are generalised. The functional derivatives of these compounds and their heteroanalogues with O, S and N atoms are considered. The bibliography includes 217 references.

I. Introduction

Crown compounds bind metal cations, organic cations and neutral molecules through multidentate coordination to heteroatoms incorporated in the macrocycle. Due to this feature, they are used successfully as selective ligands,[1,2] for extraction and separation of metal cations,[3,4] for ion transport through membranes, in ion selective electrodes,[5] as phase transfer catalysts and as synzymes that simulate enzymic activity,[6] in photosensitive systems,[7–12] *etc*.

Crown ethers in which one or two oxygen atoms have been replaced by nitrogen atoms are referred to as azacrown ethers or azacrown compounds; if the number of nitrogen atoms in the macrocycle is greater than two, the latter name is used most often. In addition to the IUPAC names, two special nomenclatures are used to designate azacrown compounds. According to one of them, developed by Pedersen in 1967,[13] the total number of macrocycle units (the size) is indicated ahead of the word 'crown' and the total number of heteroatoms is indicated after this word. In the case of nitrogen analogues, the positions of nitrogen atoms are numbered separately, precede the whole compound name and are accompanied by the prefix '(di-, tri-, *etc*.) aza' (for example, 1,10-diaza-18-crown-6 ether). The second nomenclature was proposed by Busch in 1972.[14] In this case, the macrocycle size is given in square brackets, this is followed by an indication of the type of heteroatoms, with their number given as the subscript (*e.g*., [15]N_4O or [14]N_4; the last macrocycle is called cyclam).

The interest in azacrown derivatives persists, first of all, due to their extensive practical use. In particular, diazacrown compounds are important intermediates in the synthesis of cryptands. Azacrown compounds attract the attention of researchers in many fields due to their unusual complexing properties, intermediate between the properties of crown ethers, which firmly bind alkali and alkaline earth metal ions, and the properties of cyclams, which form stable complexes with heavy and transition metal ions.

Apart from the traditional applications of azacrown compounds, of special interest is the use of those fragments, in which the nitrogen atom is conjugated with the chromophore, as parts of photosensitive, chromogenic, fluorescent and photochromic ligands. These compounds can form the heart of optical sensors for metal and ammonium ions, optical information recording systems, photoswitched molecular devices and machines for molecular electronics, transporting agents for the photocontrolled membrane transport of metal cations, *etc*. For this reason, we summarise here the data on the synthesis of several classes of azacrown compounds in which the macrocycle nitrogen atom is conjugated with the benzene ring.

A number of reviews on the methods of synthesis of azacrown compounds have been published. Two of these consider crown ether analogues containing only nitrogen atoms as heteroatoms and cover a period from 1967 to 1987.[15,16] The most comprehensive data on the synthesis of azacrown compounds with different sets of heteroatoms were reported by Bradshaw *et al*. in a monograph[17] published in 1993. Among the latest studies, noteworthy is the review[18] devoted to the synthesis of fused aza- and thiaazacrown compounds. However, none of the published reviews consider specially the synthesis of azacrown compounds in which at least one nitrogen atom of the macrocycle is conjugated with a benzene ring; no systematic data are currently available on this topic.

This review is devoted to the synthesis and chemical properties of azacrown compounds based on macrocycles of various sizes (starting with the smallest, nine-membered one) containing three or more heteroatoms. A special feature of the molecules of these compounds is the presence of not more than two phenyl or annelated *o*-phenylene fragments linked to the macrocycle

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through nitrogen; the other heteroatoms may be represented by O, S and N atoms. The azacrown compounds having heteroaromatic substituents, organoelement (P-, As- and Se-containing) and organometallic derivatives or polymers containing phenylaza or benzoazacrown compounds are beyond the scope of this review. Several examples are related to the synthesis and modification of benzoannelated cryptands. The review covers the publications from the late 1960s to 2003 and includes some studies published in 2004.

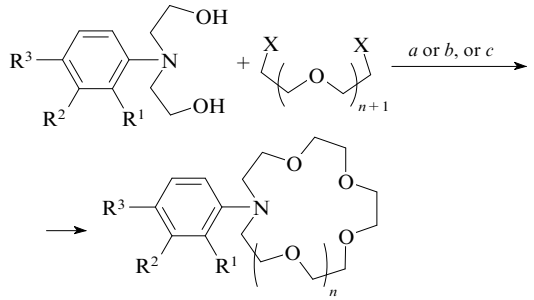
II. *N*-Phenylazacrown compounds

There are three main approaches to the synthesis of phenylazacrown compounds differing by the type of reaction used, which include the condensation of two fragments, aromatic nucleophilic substitution and cross-coupling.

1. Methods based on the condensation of two fragments

The base-induced condensation of *N*-aryldiethanolamines or their derivatives with oligoethylene glycols or their aza or thia analogues is a widely used method for the synthesis of *N*-phenylazacrown compounds. Using this method, Vögtle and Dix performed the first synthesis [19,20] of *N*-phenylaza-15(18)-crown-5(6) ethers. With dichlorides as the electrophilic component, NaOH is used most often as the base, while in the case of ditoluenesulfonate this is NaH.[19–21]

Phenylazacrown ethers **1c–i** containing Me, MeO, Cl or NO_2 groups in the *ortho*- or *para*-position of the benzene ring were prepared by condensation of *N*-aryldiethanolamine with oligoethylene glycol dimethanesulfonates (or ditoluenesulfonates) in the presence of sodium hydride [22–26] or with dichlorides in the presence of sodium hydroxide,[27–29] while 3-nitrophenylaza-15-crown-5 ether **1j** was synthesised using sodium *tert*-butoxide as the base.[30] The use of derivatives with hard oxygen-containing leaving groups (ditoluenesulfonates, dimethanesulfonates) and strong bases (sodium hydride and *tert*-butoxide) allows one to synthesise *N*-arylazacrown ether derivatives **1** in higher yields than the use of dichlorides in the presence of alkali.



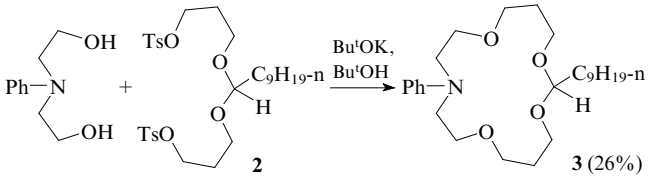
1a–j

(*a*) NaOH, dioxane; (*b*) NaH, THF; (*c*) Bu^{t}ONa, dioxane.

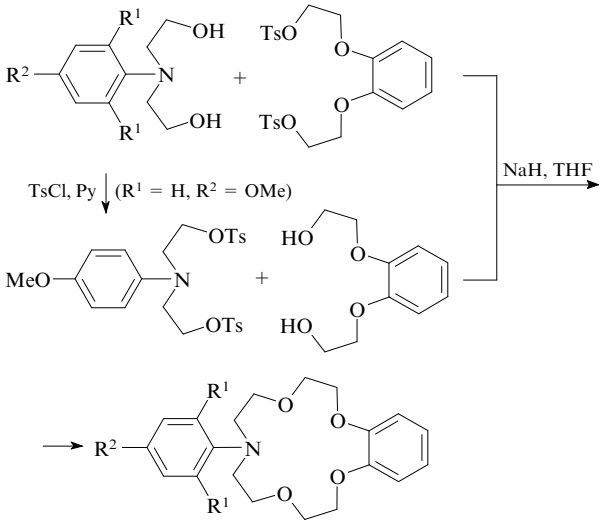
Compound **1**	X	R^1	R^2	R^3	*n*	Yield (%)
a	Cl	H	H	H	1	16
	OTs	H	H	H	1	50
b	Cl	H	H	H	2	13
c	Cl	OMe	H	H	1	16
	OMs	OMe	H	H	1	38
	OTs	OMe	H	H	1	35
d	OMs	H	H	OMe	1	30
e	OMs	OMe	H	H	2	41
f	OMs	H	H	Me	1	–
g	OMs	H	H	Cl	1	–
h	OTs	H	H	NO_2	0	55
i	OTs	H	H	NO_2	1	70
j	OTs	H	NO_2	H	1	38

Ms is $MeSO_2$, Ts is 4-$MeC_6H_4SO_2$.

The same method was utilised to obtain azacrown ether **3** with a long alkyl chain from *N*-phenyldiethanolamine and ditoluenesulfonate **2** under the action of potassium *tert*-butoxide.[31]



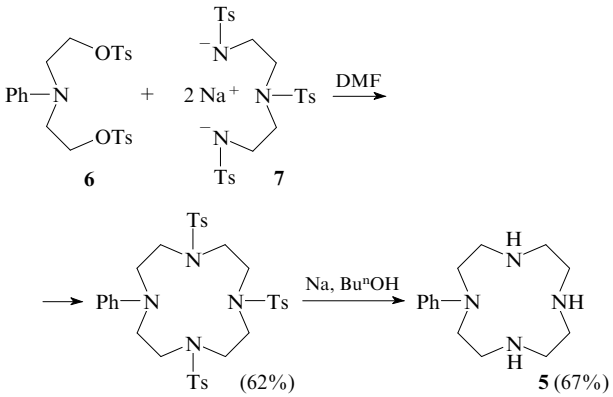
Using a similar procedure, a series of benzophenylazacrown ethers **4** have been prepared (with NaH as the base).[32] Interestingly, the methoxy derivative **4** (R^1 = H, R^2 = OMe) was also prepared using an alternative method of synthesis, namely, from *N*-aryldiethanolamine ditoluenesulfonate and the corresponding diol. The yields of products **4** were moderate in all cases.



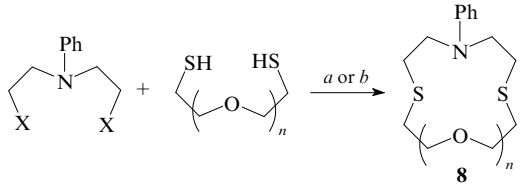
4 (30%–34%)

R^1 = H, Me; R^2 = H, OMe, Me, Bu^t.

N-Phenyltetraazacrown compound **5** was obtained by the reaction of ditoluenesulfonate **6** with the disodium salt of tritosylamide **7**. The tosyl groups were removed by refluxing with sodium metal in n-butanol.[33]



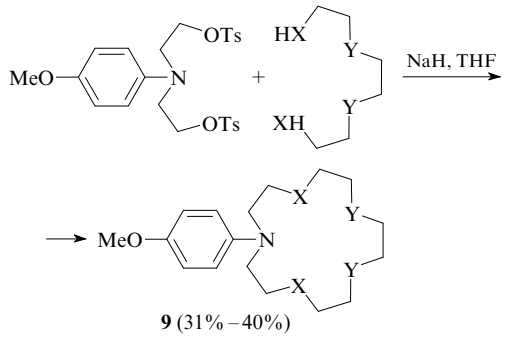
The condensation of *N*-phenyldiethanolamide dichlorides, ditoluenesulfonates or dimethanesulfonates with dithiols under the action of sodium hydroxide or potassium carbonate gave *N*-phenyldithiaazacrown compounds **8** (for the derivative with X = OMs, *n* = 1, the yield was 40%).[34–37]



8

n = 1, 2; X = Cl, OTs, OMs;
(*a*) NaOH, dioxane – Bu^{t}OH; (*b*) K_2CO_3, MeCN.

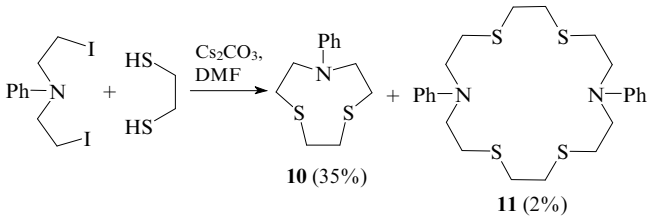
Compounds **9**, containing oxygen and sulfur atoms in various combinations in the macrocycle, have been prepared.[32] The starting compounds used for this purpose were *N*-(4-methoxyphenyl)diethanolamine ditoluenesulfonate and diols or dithiols.



9 (31% – 40%)

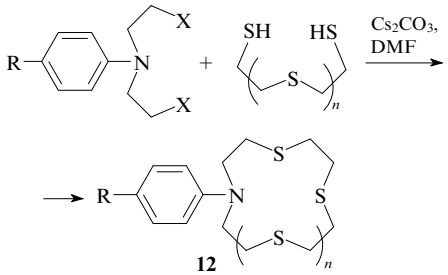
X, Y = O, S.

N-Phenylpolythiaazacrown compounds with two, three or four sulfur atoms in the macrocycle have been obtained by the reactions of dithiols with α,ω-dihalides in the presence of caesium carbonate in DMF.[38 – 40] In the synthesis of dithiaaza-9-crown-3 compound **10**, the product of [2 + 2]-condensation of both reactants, compound **11**, was also isolated, although the reaction was carried out under high dilution conditions in order to avoid the condensation.[38] Higher yields of trithiaaza-12-crown-4 and tetrathiaaza-15-crown-5 compounds **12** compared to those of macrocycle **10** were attributed to the greater steric strain in the latter compound.



10 (35%)

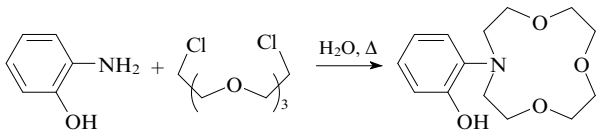
11 (2%)



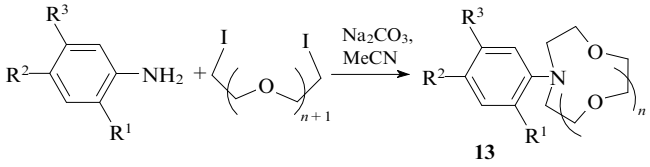
12

R	X	*n*	Yield (%)
H	I	1	52
H	I	2	61
Br	Cl	1	53

Yet another version of the condensation of two fragments is the cyclodialkylation of anilines.[22, 24, 41 – 53] This approach is usually employed to prepare *N*-phenylazacrown ethers with small rings. An early study[41] describes the synthesis (without indication of the yields) of *N*-(2-hydroxyphenyl)aza-12-crown-4 ether by the reaction of *o*-aminophenol with the dichloride prepared from tetraethylene glycol on refluxing in water.



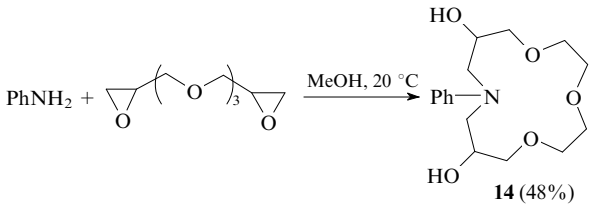
The reaction of aniline and its derivatives with the diiodides prepared from tri-, tetra- or pentaethylene glycols in the presence of sodium carbonate in acetonitrile resulted in the synthesis of arylazacrown ethers **13**.[22, 24, 42 – 50]



13

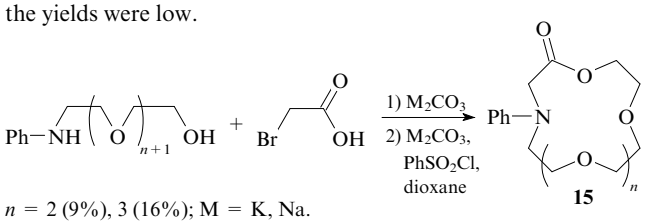
R^1	R^2	R^3	*n*	Yield (%)
H	OMe	H	1	13
H	H	H	2	51
OMe	H	H	2	26
H	H	OMe	2	40
H	CN	H	2	45
H	H	OBn	2	–
OMe	H	OMe	2	–
H	NHAc	H	2 – 3	26 – 42
H	NHAc	NHAc	2	42

N-Phenylaza-14-crown-4 ether **14**, which contains two hydroxyl groups in the macroheterocycle, is formed upon the reaction of aniline with diethylene glycol diglycidyl ether in methanol at room temperature.[51, 52]



14 (48%)

The synthesis of *N*-phenyl-3-oxoaza-15(18)-crown-5(6) ethers **15** by the two-step condensation of *N*-(polyoxyethylene)anilines with bromoacetic acid has been described;[53] first, the reaction is induced by sodium or potassium carbonate and then by the carbonate and benzenesulfonyl chloride in dioxane. However, the yields were low.



15

n = 2 (9%), 3 (16%); M = K, Na.

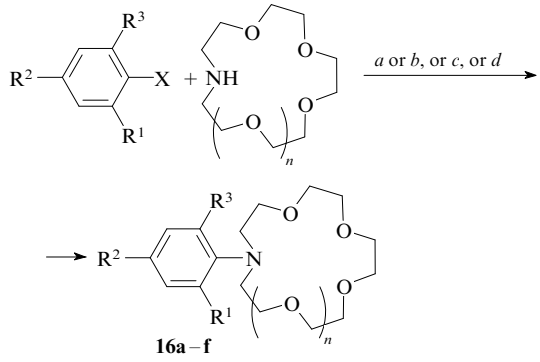
Unsubstituted *N*-phenylazacrown compounds have been used to prepare various chromo- and fluoroionophores,[54 – 57] in particular, azo dyes [20, 25, 26, 37] and squarelium dyes (squaric acid derivatives).[58]

2. The introduction of a macrocyclic fragment by aromatic nucleophilic substitution

Many derivatives of *N*-phenylazacrown compounds have been obtained by arylation of the nitrogen atom in the macrocycle. Halobenzenes containing electron-withdrawing substituents are employed most often for this purpose.

Arylazacrown ethers **16a – e** have been prepared by the reaction of aza-15-crown-5 ether with various fluoro- and

chloro-substituted benzenes (Table 1). The process conditions (heating of a reactant mixture in a polar solvent or in a neutral solvent under the action of a base) depend on the nature of the arylating reagent. Dinitrophenyl derivatives **16f** (see Table 1) with various macrocycle sizes are formed in high yields in the reaction of 2,4-dinitrochlorobenzene with *N*-unsubstituted azacrown ethers in the presence of tetrabutylammonium acetate in diethyl ether.[62, 63]

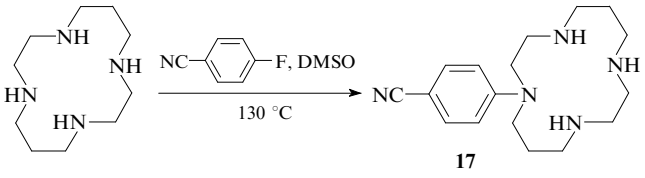


(*a*) DMSO; (*b*) Et_3N, PhH; (*c*) Py; (*d*) $AcONBu_4$, Et_2O.

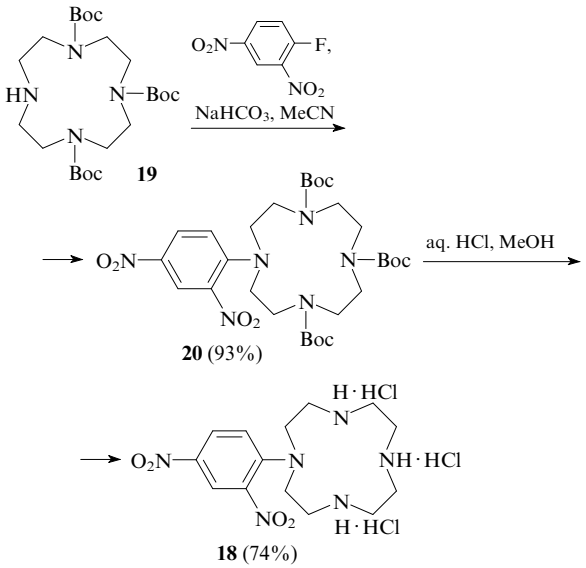
Table 1. Preparation of *N*-arylazacrown ethers by arylation.

Compound **16**	X	R^1	R^2	R^3	*n*	Reaction conditions	Yield (%)	Ref.
a	F	H	CN	H	1	*a*	70	46
b	F	H	NO_2	H	1	*a*	–	59
c	Cl	Bz	NO_2	NO_2	1	*b*	84	60
d	Cl	NO_2	CO_2Me	NO_2	1	*b*	77	60
e	Cl	CO_2H	NO_2	H	1	*c*	26	61
f	Cl	NO_2	NO_2	H	0–2	*d*	~95	62, 63

The synthesis of (4-cyanophenyl)cyclam **17** from cyclam and 4-fluorobenzonitrile has been reported;[64] however, the product yield is not indicated in the publication.



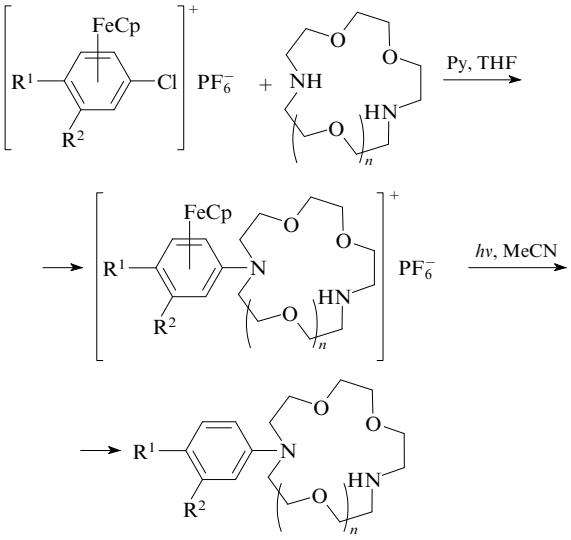
2′,4′-Dinitrophenylcyclen **18** was prepared in two stages and characterised as the trihydrochloride. The reaction of 1-fluoro-2,4-dinitrobenzene with cyclen **19** was carried out in the presence of sodium hydrogen carbonate and was followed by treatment of compound **20** with hydrochloric acid in methanol.[65]



Boc is *tert*-butoxycarbonyl.

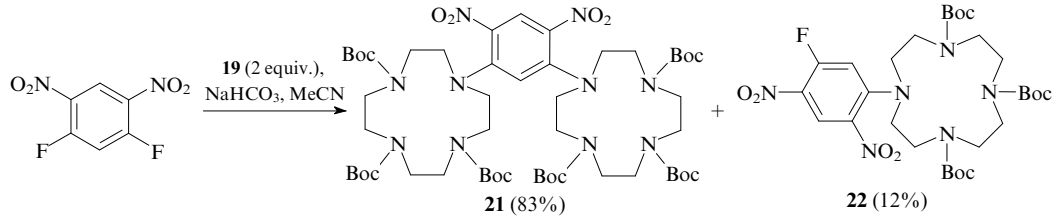
Bis(azacrown) compounds can be synthesised from dihalobenzenes. For example, the reaction of 1,5-difluoro-2,4-dinitrobenzene with two equivalents of cyclen **19** yields mainly bis(cyclen) **21**. A small amount of cyclen **22** was also isolated (Scheme 1).[66]

The *meta*- and *para*-chloro derivatives of phenyldiazacrown ethers were synthesised by the reaction of the dichlorobenzene complex with cyclopentadienyliron hexafluorophosphate and diazacrown ether. The subsequent demetallation of the compounds formed was attained by irradiation with a halogen quartz lamp (100 W).[67]

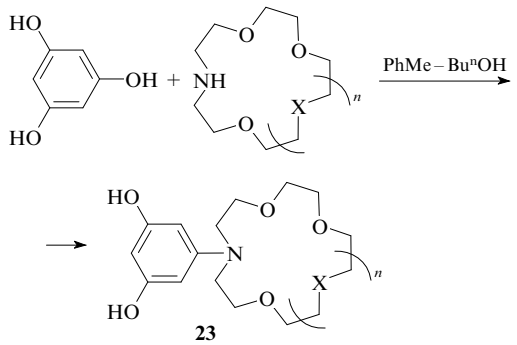


R^1	R^2	*n*	Yield (%)
H	Cl	1	68
Cl	H	1	67
Cl	H	2	77

Scheme 1



The refluxing of a mixture of aza-15(18)-crown-5(6) ethers (or diaza-15-crown-5 ether) with phloroglucinol with azeotropic removal of water gave rise to *N*-(3,5-dihydroxyphenyl)azacrown ethers **23**.[68–70]



23

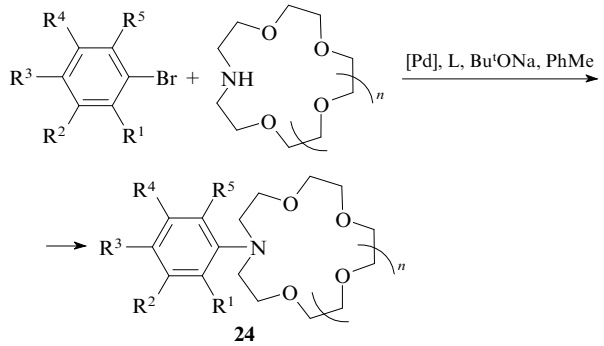
X = O: n = 1 (16%), 2; X = $NCH_2C_6H_4OMe$-2, n = 1.

Compounds **23** condense with squaric acid to give squarelium dyes.[68, 70]

3. Cross-coupling reactions

In recent years, a new approach to the preparation of the compounds in question, based on palladium-catalysed N-arylation of azacrown ethers, has been developed.[66, 71–73] The reaction is normally carried out in toluene in the presence of sodium *tert*-butoxide. The advantage of this method is the possibility of using non-activated or sterically hindered aryl halides.

The cross-coupling of azacrown ethers catalysed by systems including a palladium complex ([Pd]) and a phosphine ligand (L) was first carried out for 4-nitro- and 4-cyanobromobenzenes. Aza-18(15,12)-crown-6(5,4) ethers were used to give arylazacrown compounds **24** (Table 2, method **A**).[71] The highest product yields (57%–88%) were observed when a mixture of $Pd(OAc)_2$ and PPh_3 was used as the catalyst.

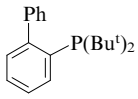
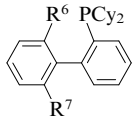


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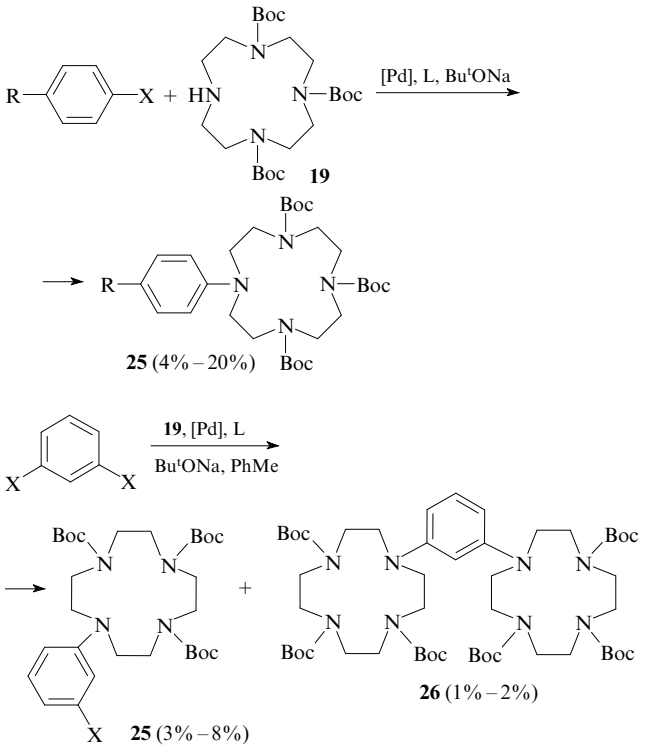
A large series of *N*-phenylaza-15-crown-5 ethers **24** with various substituents in the benzene ring have been synthesised from aza-15-crown-5 ether and aryl bromides *via* the palladium-catalysed Buchwald–Hartwig amination (see Table 2, method **B**).[72] It was demonstrated that a combination of $Pd_2(dba)_3$ and electron-excessive sterically hindered biphenyl-based phosphine is an efficient system for the catalysed coupling of aza-15-crown-5 ether with both electron-deficient and electron-excessive aryl bromides. The reaction occurs under mild conditions, the product yields being 75%–91%. Compounds **24** containing a substituent in the *ortho*-position were also prepared using this catalyst system, although the yields were lower (~40%).

The cross-coupling of cyclen **19** with mono- and dihalobenzenes resulted in the isolation of *N*-aryl-substituted (**25**) and phenylene-bridged cyclens **26** in moderate yields.[66] In the former case, toluene, THF, bromobenzene and a toluene–18-crown-6 mixture were used as solvents.

Table 2. Preparation of *N*-arylazacrown ethers by cross-coupling.

Method	[Pd]	L	R^1–R^5	n
A	$Pd(dba)_2$, $Pd(OAc)_2$	$P(Tol\text{-}o)_3$, PBu^t_3, PPh_3	$R^1 = R^2 = R^3 = R^5$ = H, $R^3 = NO_2$	0–2
			$R^1 = R^2 = R^3 = R^5$ = H, R^3 = CN	2
B	$Pd_2(dba)_3$		R^1 = H, Me, Et, OMe, CF_3, Cl; R^2 = H, Me, OMe; R^3 = H, Bu^t, OMe, CF_3, NMe_2; $R^4 = R^5$ = H, Me	1
			R^6 = H: R^7 = H, Me, Pr^i, NMe_2; $R^6 = R^7$ = Me	

(Tol-*o*) is *o*-tolyl, dba is dibenzylideneacetone, Cy is cyclohexyl.



X = I, Br; R = H, NO_2, $CH(OCH_2CH_2O)$, CHO; [Pd] = $Pd_2(dba)_3$, $Pd(OAc)_2$; L = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), 1,1′-bis(diphenylphosphino)ferrocene (DPPF), PPh_3, 2-(di-*tert*-butylphosphino)biphenyl.

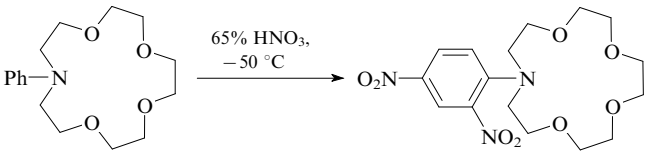
(4-Cyanophenyl)cyclam **17** (see Section II.2) is also formed upon arylation of cyclam with 4-bromobenzonitrile in the presence of the $Pd(dba)_2$–1-(*R*)-(1-methoxyethyl)-2-(*S*)-diphenylphosphinoferrocene (PPF-OMe) catalyst system and sodium *tert*-butoxide (yield 22%).[73]

III. Functional derivatives of *N*-phenylazacrown compounds

Many functional derivatives of *N*-phenylazacrown compounds are formed during the construction of the macrocycle (see Section II). An alternative way is to introduce functional groups into the benzene ring of pre-formed *N*-phenylazacrown compounds *via* electrophilic substitution or to modify the existing substituents. Reactions of this type are presented below.

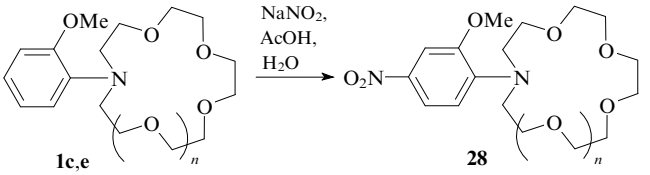
1. Nitro, nitroso and amino derivatives of *N*-phenylazacrown compounds

Direct nitration of *N*-phenylaza-15-crown-5 ether **1a** with nitric acid at low temperature resulted in the 2,4-dinitrophenyl derivative **27**.[63]



1a **27** (90%)

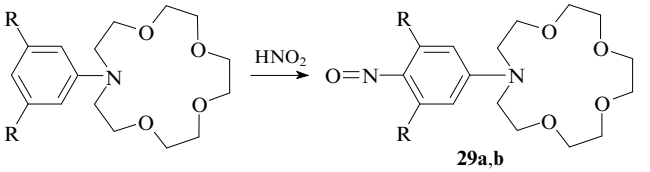
When *N*-(*o*-methoxyphenyl)aza-15(18)-crown-5(6) ethers **1c**,**e** were made to react with sodium nitrite in aqueous AcOH, nitration products **28** were isolated in high yields instead of the expected nitroso compounds.[74] The direction of substitution is determined by the aniline nitrogen atom — the nitro group enters the *para*-position with respect to this atom. The researchers suggested that nitration gives a radical cation as an intermediate. It is of interest that the use of traditional nitrating agents (HNO_3, $HNO_3 - H_2SO_4$ or NO_2BF_4) results in very low yields of nitration products in this reaction.



1c,**e** **28**

n = 1 (89%), 2 (68%).

4′-Nitroso-*N*-phenylaza-15-crown 5-ethers **29** were prepared by nitrosation of *N*-phenylaza-15-crown-5 ethers with sodium nitrite in hydrochloric acid.[20, 69]

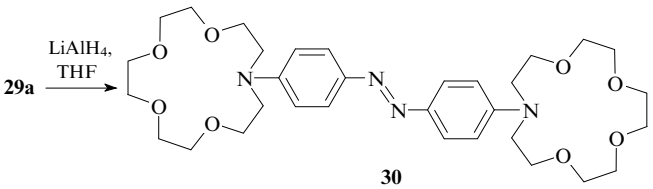


29a,**b**

R = H (**a**, 83%), OH (**b**, 40%).

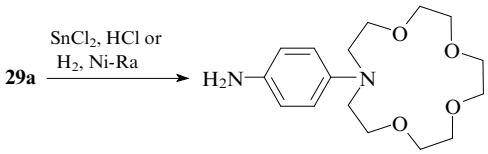
N-(4′-Nitrosophenyl)azacrown ethers condense with malononitrile and dicyanovinyl derivatives to give chromoionophoric compounds.[69, 75]

The reduction of nitroso derivative **29a** with lithium tetrahydroaluminate gives azo compound **30** and its *N*-oxide (in a 1 : 3 ratio) in a total yield of 65%.[20]

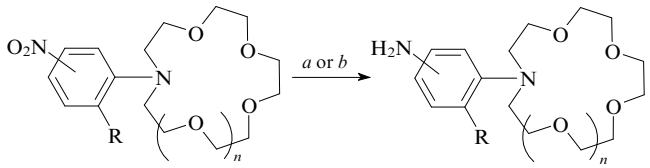


30

A major route of modification of the nitroso group in *N*-phenylazacrown ethers is reduction to the amino group. The nitroso group in **29a** was reduced with tin(II) chloride in HCl with heating (yield 87%) [20] or with hydrogen in the presence of Raney nickel (Ni-Ra) at room temperature and atmospheric pressure (the yield was not reported).[76]



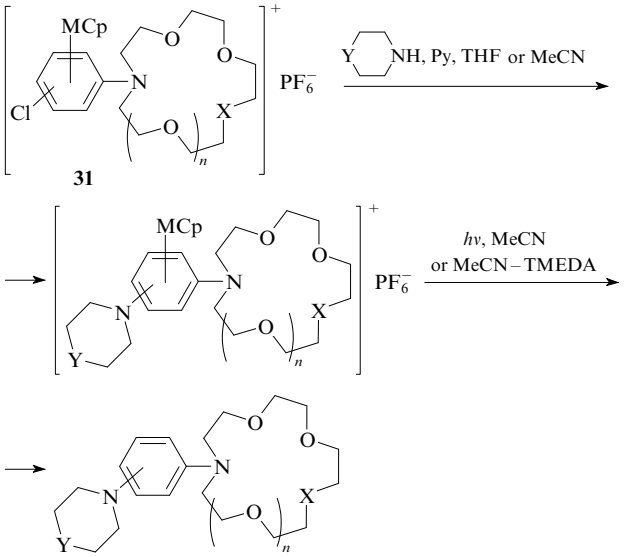
Amino derivatives of *N*-phenylazacrown ethers can also be prepared by palladium-catalysed reduction of nitro compounds with hydrogen [30, 61, 74] or by reduction with tin(II) chloride.[24]



(*a*) H_2, Pd/C, EtOH; (*b*) $SnCl_2 \cdot 2\,H_2O$, HCl, EtOAc.

Position of NO_2	R	n	Reaction conditions	Yield (%)	Ref.
4	H	0	*b*	89	24
4	H	1	*b*	85	24
4	CO_2H	1	*a*	94	61
4	OMe	1	*a*	98	74
4	OMe	2	*a*	68	74
3	H	1	*a*	85	30

A number of *para*- or *ortho*-substituted *N*-(aminophenyl)aza- and -diazacrown ethers were synthesised by nucleophilic aromatic substitution of chlorine in complexes **31**, followed by demetallation on exposure to UV light.[67, 77] The total yields of amino derivatives in relation to the starting dichlorobenzene complex with $[CpM]^+PF_6^-$ were 26% – 37% (for M = Ru) and 50% – 96% (for M = Fe).

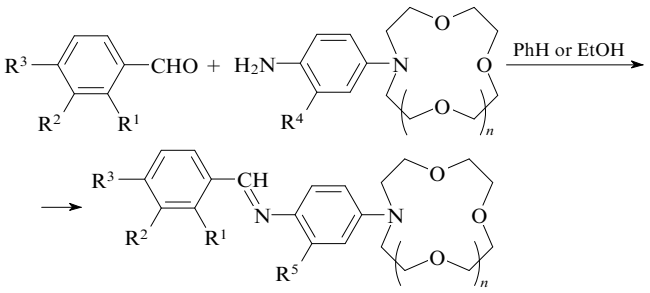


31

M = Ru: n = 1, 2; X = O; Y = CH_2; M = Fe: n = 1, 2; X = O, NH, NAc, NBz, NBn; Y = CH_2, CHOH, NH.

The obtained 4-amino- and 3,4-diamino derivatives of *N*-phenylazacrown ethers were used in condensations with various

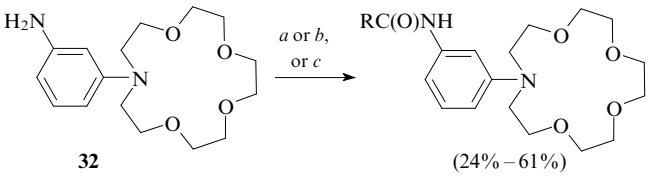
substituted benzaldehydes, giving rise to chromoionophoric Schiff's bases.[21, 50]



n = 1: R^1 = OH, R^2 = R^3 = R^4 = R^5 = H (84%); R^1 = OH, R^2 = R^3 = H, R^4 = H_2N, R^5 = N=CH–(HO-C$_6$H$_4$) (80%);

n = 2: R^1 = H, OH; R^2 = H, OMe; R^3 = H, OMe, NO_2, NMe_2; R^4 = R^5 = H (20% – 84%).

Acylation of *m*-amino-*N*-phenylaza-15-crown-5 ether **32** with acyl chlorides or acid anhydrides provided the synthesis of a series of amphiphilic azacrown ethers able to form bilayer membranes.[30, 78]



32 (24% – 61%)

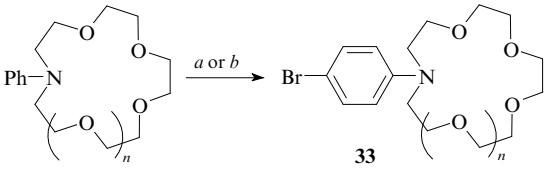
R = Me, Et, Pr^n, Pr^i, n-C_nH_{2n+1} (n = 5, 11, 13, 15, 17);
(*a*) RCOCl, KOH, PhH; (*b*) Ac_2O; (*c*) $(EtCO)_2O$.

N-(4′-Aminophenyl)azacrown ethers can add to naphthoquinones[54] and dicyanovinyl-containing heterocycles[79] to afford chromoionophoric compounds.

2. Halogen derivatives of *N*-phenylazacrown compounds

Examples of the synthesis of bromo derivatives of *N*-phenylazacrown compounds *via* electrophilic substitution are documented. Different brominating agents were used and the product yields were often high.

For example, bromination of *N*-phenylaza-15(18)-crown-5(6) ethers with tetrabutylammonium tribromide in dichloromethane[80] or with *N*-bromosuccinimide (NBS) in tetrachloromethane[81] furnishes the corresponding 4-bromophenyl derivatives **33**.

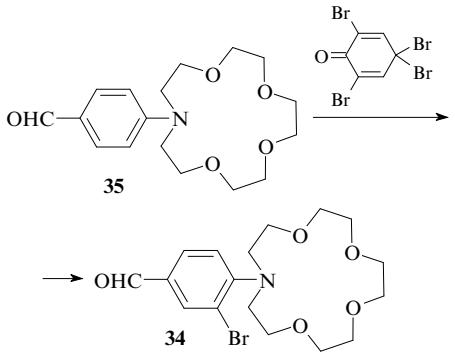


33

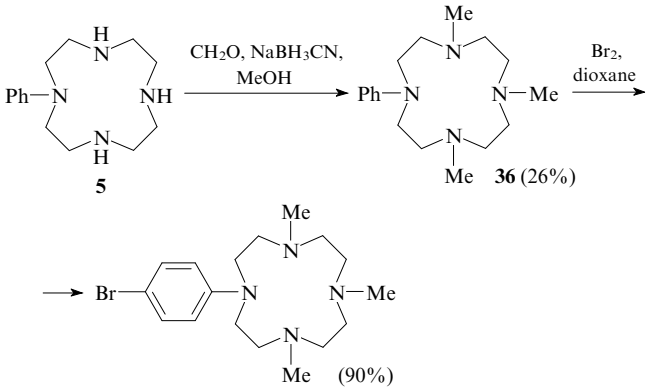
(*a*) $Bu^t_4NBr_3$, CH_2Cl_2; (*b*) NBS, CCl_4.

n	Reaction conditions	Yield (%)
1	*b*	–
1	*a*	82
2	*a*	76

The *o*-bromo derivative of *N*-(formylphenyl)aza-15-crown-5 ether **34** was prepared from aldehyde **35** using tetrabromocyclohexadienone as the brominating reagent.[82]

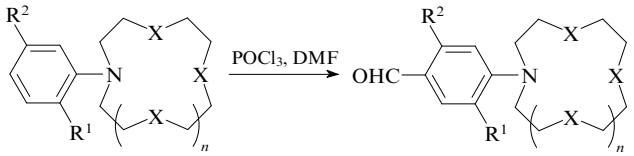


Cyclen **36**, prepared by reductive methylation of compound **5**, reacts with bromine in dioxane to give the product in a high yield.[33] In this case, bromination occurs at the *para*-position of the *N*-phenyl group.



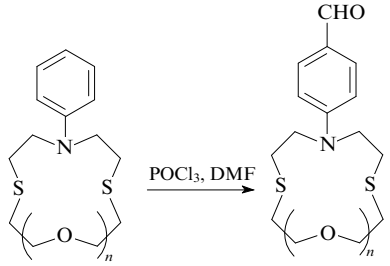
3. Formyl derivatives of *N*-phenylazacrown compounds

Numerous publications have been devoted to the introduction of a formyl group into *N*-phenylazacrown compounds. The formylation of *N*-phenylazacrown ethers[19, 20, 27–29, 49] and *N*-phenylpolythiaazacrown compounds[83, 84] has been accomplished by the Vilsmeier reaction.



X	R^1	R^2	n	Yield (%)
O	H, OMe	H, OBn, OMe	1 – 3	51 – 75
S	H	H	0 – 2	< 95

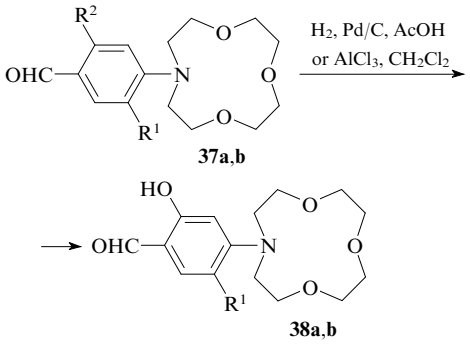
The formyl derivatives of mixed oxathiaazacrown compounds have been synthesised in a similar way.[34]



n = 1, 2.

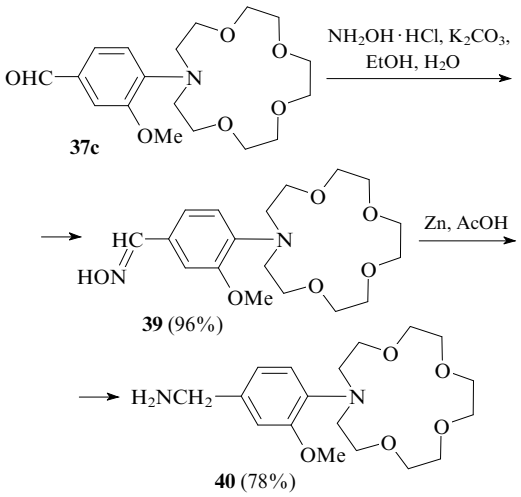
Hydrogenolysis of benzyl ether **37a** at room temperature and a pressure of 1 atm resulted in salicylaldehyde derivative **38a**.

Treatment of dimethoxy derivative **37b** with aluminium chloride in dichloromethane induces the selective demethylation of the methoxy group located in the *ortho*-position relative to the formyl group to give compound **38b**.[49] Hydroxyaldehydes **38** were used to prepare fluorophores, in particular, azacrown-containing coumarins.[49]

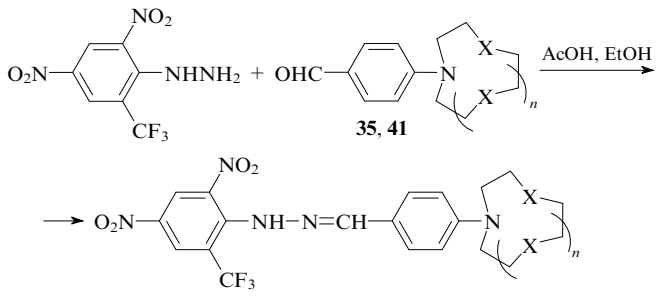


R^1 = H, R^2 = OBn (**a**); R^1 = R^2 = OMe (**b**).

The introduction of the reactive formyl group in the molecule opens the way for the preparation of other derivatives of azacrown compounds. Indeed, the reaction of aldehyde **37c** with hydroxylamine in aqueous ethanol affords oxime **39**, which is reduced by zinc in acetic acid to yield aminomethylated *N*-phenylaza-15-crown-5 ether **40**.[28,29]

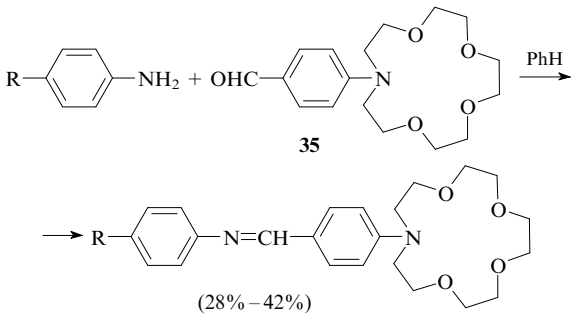


By the reaction of 2,4-dinitro-6-trifluoromethylphenylhydrazine with the formyl derivatives **35** (X = O, n = 3) and **41** (X = S, n = 1, 3), the corresponding hydrazones have been obtained.[83,85] These were used for the extraction of heavy and transition metal ions [83,85,86] and for Ag^+ transport through liquid membranes.[87]



X = O: n = 3 (49%); X = S: n = 1 (39%), 3 (52%).

The condensation of aldehyde **35** with *para*-substituted anilines provided the route to chromoionophoric Schiff's bases.[21]

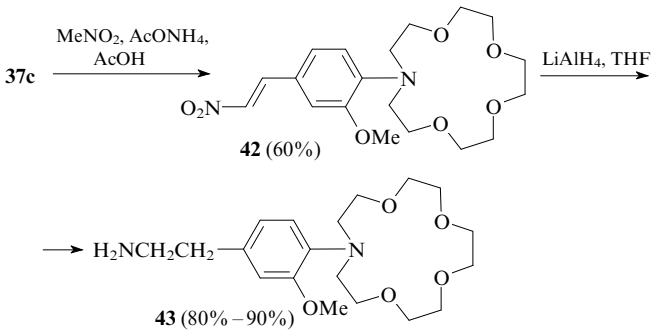


R = H, OMe, OEt, NMe_2, F, Cl, Br.

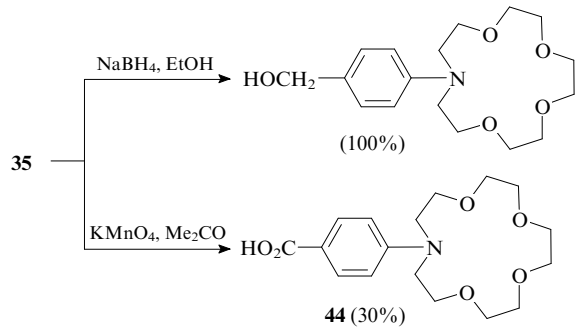
The aldehyde functional group in azacrown compounds can also be modified *via* reactions with C-nucleophiles. 4′-Formyl-*N*-phenylaza-15-crown-5 ether **35** reacts with acetone in an alkaline medium to give bis(crown ether) dibenzylideneacetone, which exhibits fluoroionophoric properties.[88]

Compounds containing an active methylene group can undergo Knoevenagel condensation with the formyl derivatives of *N*-phenylazacrown ethers. Under these conditions, 4′-formyl-*N*-phenylaza-18(15)-crown-6(5) ethers react with malononitrile to yield crown-containing benzylidenemalononitriles.[75]

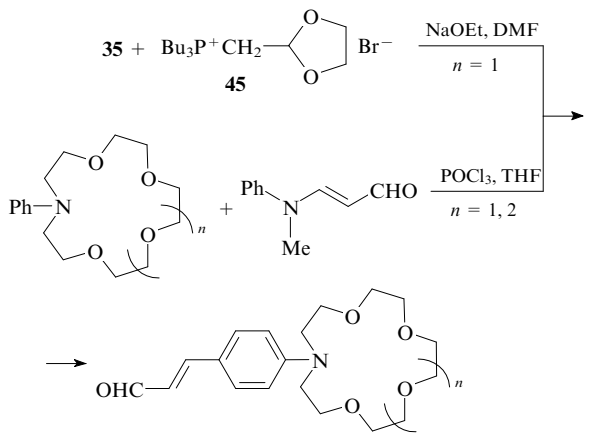
The nitroethylene derivative **42** has been prepared by the reaction of aldehyde **37c** with nitromethane in an acetic acid–ammonium acetate mixture. The reduction of this product gives azacrown ether **43**,[28,29] which has found application as an intermediate *en route* to fluorescent indicators of sodium ions.



The reduction [76] of the formyl group in *N*-phenylaza-15-crown-5 ether **35** on treatment with sodium borohydride affords the corresponding alcohol, while the oxidation of this group [89] with sodium permanganate in acetone affords crown-containing benzoic acid **44**.



Cinnamaldehydes based on *N*-phenylazacrown ethers were prepared by two routes. One employs the Wittig reaction of aldehyde **35** with phosphonium salt **45**.[82] In the alternative procedure,[90] the modified Vilsmeier reaction of *N*-phenylazacrown ethers with *N*-methyl-*N*-phenyl-3-aminoacrolein is used; the products are formed under mild conditions in 35% (n = 1) and 37% (n = 2) yields.

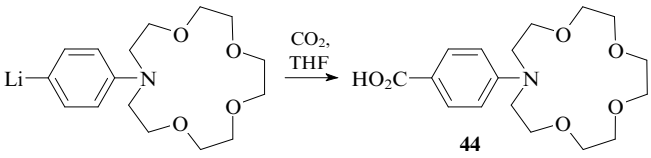


The formyl derivatives of *N*-phenylazacrown ethers are widely used in the synthesis of crown-containing stilbenes,[20, 82, 91] diphenylbutadienes,[82] hetarylphenylethylenes[92–95] and styryl,[20, 92, 93, 96–101] merocyanine[20, 93, 102–104] and butadienyl dyes.[90] These compounds have chromo- and fluoroionophore properties and are distinguished by high sensitivity and selectivity with respect to alkali and alkaline earth metal cations.[20, 82, 90–117]

4. Azacrown-containing benzoic acids

The preparation and chemical properties of azacrown compounds containing an *N*-(4-carboxy)phenyl group are considered only in two papers.[81, 89]

The synthesis of azacrown-containing benzoic acid **44** from the formyl derivative[89] has been described above (see Section III.3). The same compound is produced when carbon dioxide is passed into a tetrahydrofuran solution of the lithium derivative of *N*-(*p*-bromophenyl)aza-15-crown-5 ether.[81]



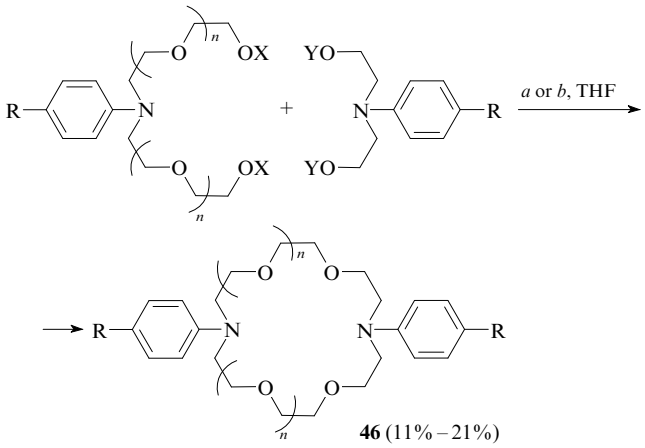
Acid **44** has been converted to give diverse derivatives, namely, the methyl ester (by the reaction with dimethyl sulfate in the presence of potassium carbonate in acetone),[81] the chloride (on treatment with $SOCl_2$ in a DMF – toluene mixture) and the amide (by the reaction of the chloride with 4-aminopyridine) (Scheme 2).[89]

IV. *N*,*N*′-Diphenyldiazacrown compounds

Generally, the routes to *N*,*N*′-diphenyldiazacrown compounds differ little from the above methods used to prepare their analogues with one nitrogen atom in the macrocycle. Diphenyldiaza derivatives are obtained most often by condensation of two fragments and by N-arylation of diazacrown ethers.

1. Routes based on the condensation of two fragments

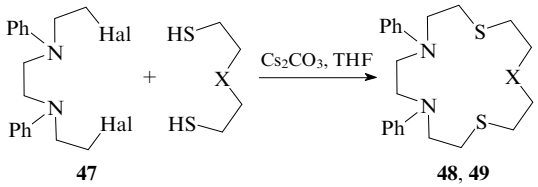
The two versions of this type of condensation (the reactions of toluenesulfonates with alcohols under the action of bases) are presented below. The reaction of *N*-phenyldiethanolamine ditoluenesulfonates with *N*-phenyldiethanolamine or *N*-phenylazatetraethylene glycol derivatives in the presence of sodium hydride resulted in *para*-substituted *N*,*N*′-diphenyldiaza-12(18)-crown-4(6) ethers **46**.[118]



X = H, Y = Ts; *n* = 0, 1; R = H, Me, OMe, Cl;
X = Ts, Y = H; *n* = 1; R = H (18%);
(*a*) NaH; (*b*) Bu^{t}OK.

In a similar method, *N*-phenylazatetraethylene glycol ditoluenesulfonate reacts with *N*-phenyldiethanolamine, which also gives *N*,*N*′-diphenyldiaza-18-crown-6 ether **46** (*n* = 1).[38] In this case, potassium *tert*-butoxide was used as the base.

The condensation of dihalide **47** with various dithiols[34, 38] affords *N*,*N*′-diphenyltetrathiadiaza-18-crown-6 ether **48** and *N*,*N*′-diphenyldiaza-15-crown-5 compound **49** containing two S atoms and one O atom in the macrocycle.

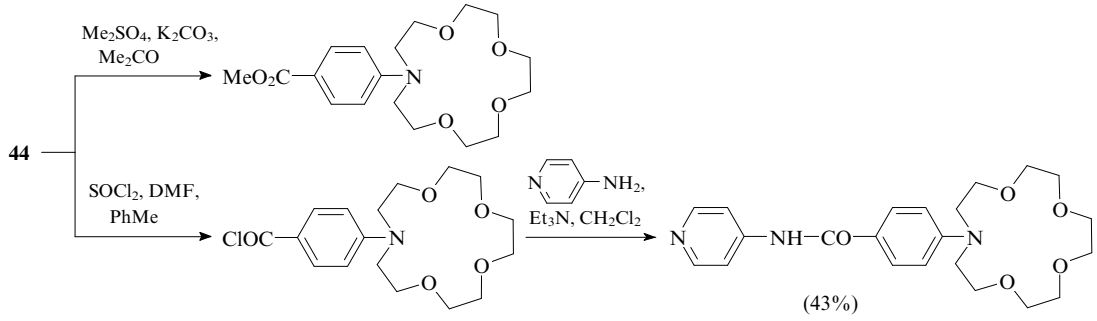


Hal = Br, X = $S(CH_2)_2S$ (**48**, 11%); X = O (**49**).

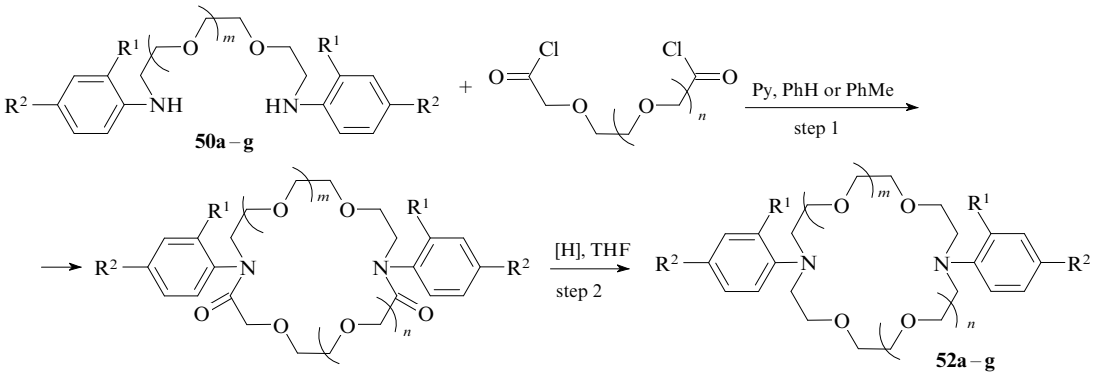
As noted above (see Section II.1), the *N*,*N*′-diphenyltetrathiadiaza-18-crown-6 compound **11**, in which the nitrogen atoms in the macrocycle are separated by three ethylene units, has been isolated as a side product in 2% yield in the synthesis of *N*-phenyldithiaaza-9-crown-3 compound **10** (see Section II.1).[38]

The condensation of diphenyldiamines **50a–g** and **51** (prepared from the corresponding anilines) (Scheme 3) with the dichlorides of dibasic carboxylic acids[74, 119–125] followed by the reduction of the obtained diamides is another method for the

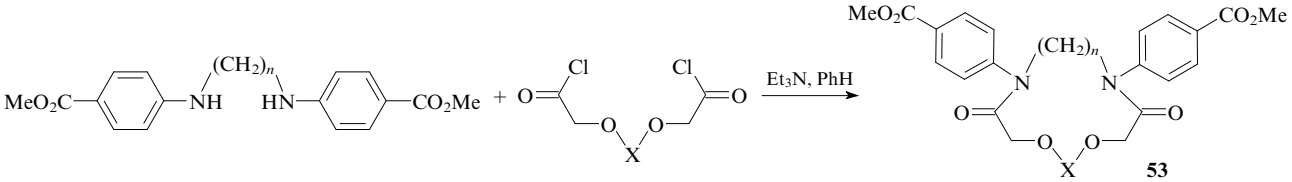
Scheme 2



Scheme 3



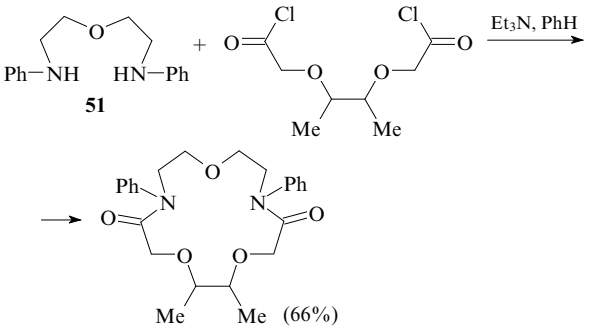
Scheme 4



X = CMe_2CMe_2: n = 6, 10, 12, 14 (61%–85%); X = $CH_2CMe_2CH_2$; n = 10 (62%), 12 (58%).

synthesis of *N*,*N*′-diphenyldiazacrown derivatives. The reactions of compounds **50a–g** were carried out in the presence of pyridine in benzene or toluene under high dilution conditions (Table 3). The reducing agents used included boron compounds (B_2H_6, BH_3 complexes with Me_2S or THF, $NaBH_4$) and lithium tetrahydroaluminate. *N*,*N*′-Diphenyldiaza-24-crown-8 ethers **52d** (n = 2, m = 2) and **52g** (R^1 = H; R^2 = Me, MeO, Br; n = 2; m = 2) were prepared in 18%–33% total yields relative to the starting 4-substituted aniline.[124]

A similar reaction of dianiline **51** was carried out in benzene under the action of triethylamine.[123]



The removal of the tosyl protective groups from the nitrogen atoms in diazacrown compound **52c** was induced by sodium naphthalenide in tetrahydrofuran under mild conditions (yield 70%).[120] Diaza-15(18)-crown-5(6) ethers **52e**,**f** were used to prepare azo dyes.[126]

A series of macrocyclic *N*,*N*′-diaryldiaza(oligomethylene)diamides **53** has been obtained by condensation of diaryldiamines containing different numbers of methylene groups with dicarboxylic acid dichlorides on treatment with triethylamine in benzene under high dilution conditions (Scheme 4).[127,128] Compounds **53**, when introduced into polyvinyl chloride membranes, have shown high selectivity for Li^+ ions.

2. Aromatic nucleophilic substitution reactions

Like azacrown ethers, diaza derivatives can be prepared by aromatic nucleophilic substitution in which the amino group of the crown compound attacks the carbon atom bonded to a halogen in an activated aryl halide.

N,*N*′-Diphenyldiazacrown compounds **54a–j**, containing electron-withdrawing substituents in the *para*- and *ortho*-positions of the benzene ring, have been synthesised by N,N′-diarylated diazacrown ethers.[60,61,122,129–131] The conditions of this reaction (the type of base and solvent) were mainly determined by the nature of the arylating agent. For example, the reaction of diaza-18-crown-6 ether with 2-chloro-3,5-dinitrobenzophenone

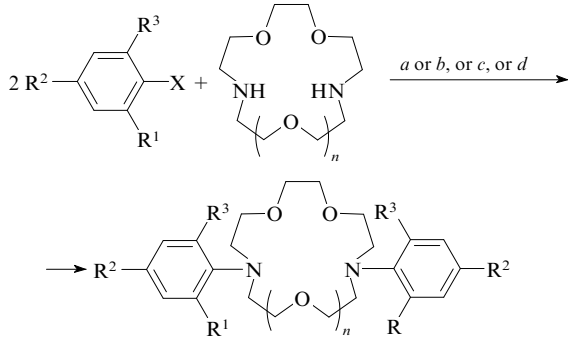
Table 3. Diphenyldiazacrown ether derivatives **52**.

Compounds **50**, **52**	R^1	R^2	m	n	Yield (%)		[H]	Ref.
					step 1	step 2		
a	H	Br	1	0	74	84	$BH_3 \cdot Me_2S$	122
b	H	Br	1	1	69	71	$BH_3 \cdot Me_2S$	122
c	NHTs	H	1	1	62	61	$LiAlH_4$	119, 120
d	H	H	1	1	73	71	B_2H_6	119, 120
	H	H	1, 2	0–2	33–71	41–50	$BH_3 \cdot THF$	125
	H	H	2	2	–	18–33[a]	$BH_3 \cdot THF$	124
e	OMe	H	1	0	67	98	$NaBH_4$	74
	OMe	H	1	0	–	–	B_2H_6	121
f	OMe	H	1	1	73	92	$NaBH_4$	74
g	H	Me, MeO, Br	2	2	–	18–33[a]	$BH_3 \cdot THF$	124

[a] The yield is given in relation to the starting 4-substituted aniline.

or with methyl 4-chloro-3,5-dinitrobenzoate in the presence of triethylamine in benzene gives compounds **54a**,**b** in high yields.[60] Compounds **54c**,**d** were prepared in a similar way.[60]

N,*N*′-Diphenyldiazacrown ethers **54e**,**f**, containing *ortho*-nitro- and *para*-trifluoromethyl groups, were prepared by the reaction of diazacrown ethers with the corresponding aryl chloride in the presence of triethylamine in THF under rigorous conditions (8 kbar pressure).[129, 130] Diaza-15-crown-5 ether reacts with 2-fluoro-5-nitroanisole[61] and diaza-18-crown-6 ether reacts with 4-fluoronitrobenzene[131] in pyridine, giving rise to *N*,*N*′-bis(nitrophenyl)diazacrown ethers **54g**,**h**. The diacyl derivatives **54i**,**j** were produced upon condensation of diaza-18(15)-crown-6(5) ethers with 4-fluoropropiophenone in the presence of tetrabutylammonium fluoride at 150 °C.[122]



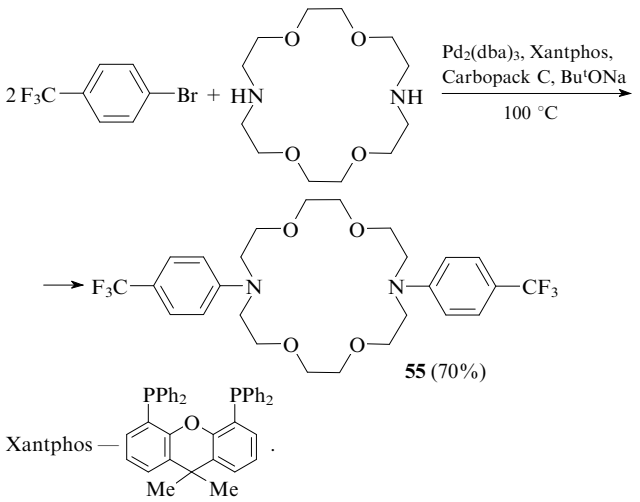
54a–**j**

(*a*) Et_3N, PhH; (*b*) Et_3N, THF, 8 kbar; (*c*) Py; (*d*) $Bu_4N^+F^- \cdot 2H_2O$, 150 °C.

Compound **54**	X	R^1	R^2	R^3	*n*	Reaction conditions	Yield (%)	Ref.
a	Cl	Bz	NO_2	NO_2	2	*a*	76	60
b	Cl	NO_2	CO_2Me	NO_2	2	*a*	92	60
c	Cl	NO_2	CO_2H	NO_2	2	*a*	80	60
d	Cl	CO_2Me	NO_2	NO_2	2	*a*	88	60
e	Cl	NO_2	CF_3	H	1	*b*	79	129, 130
f	Cl	NO_2	CF_3	H	2	*b*	92	129, 130
g	F	OMe	NO_2	H	1	*c*	23	61
h	F	H	NO_2	H	2	*c*	24	131
i	F	H	C(O)Et	H	1	*d*	25	122
j	F	H	C(O)Et	H	2	*d*	28	122

3. Cross-coupling reactions

The preparation of *N*,*N*′-diphenyldiazacrown compounds *via* cross-coupling has been reported.[132] The arylation of diaza-18-crown-6 ether with *p*-bromobenzotrifluoride catalysed by $Pd_2(dba)_3$–Xantphos in the presence of the Carbopack C graphite without a solvent resulted in compound **55**.

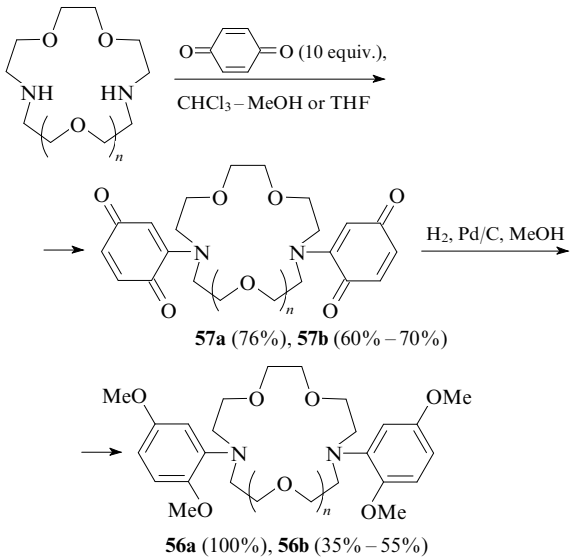


55 (70%)

4. The substitution of hydrogen by diazacrown compounds

This method for the synthesis of *N*,*N*′-diphenyldiazacrown ethers, which is seldom encountered in the literature, is based on the addition of diazacrown ethers to an activated double bond followed by oxidation of the resulting adduct with excess reagent.

N,*N*′-Diphenyldiazacrown ethers **56a**,**b**, containing *ortho*- and *meta*-methoxy groups in the benzene rings have been prepared by hydrogenation of crown-containing *p*-benzoqiuinones **57a**,**b**. The reaction takes place in MeOH under atmospheric pressure at room temperature in the presence of palladium.[61, 133, 134] Macrocycles **57** were synthesised by the reaction of *p*-benzoquinone with diazacrown ethers. Apparently, benzoquinone itself, which is used in a large excess with respect to the crown ether, acts as the oxidant in this reaction.



57a (76%), **57b** (60%–70%)

56a (100%), **56b** (35%–55%)

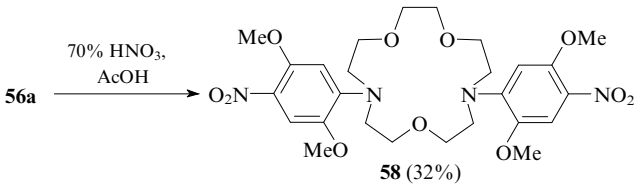
n = 1 (**a**), 2 (**b**).

V. Functional derivatives of *N*,*N*′-diphenyldiazacrown compounds

The transition from unsubstituted *N*,*N*′-diphenyldiazacrown compounds to their functional derivatives is similar to the reactions of *N*-phenylazacrown compounds.

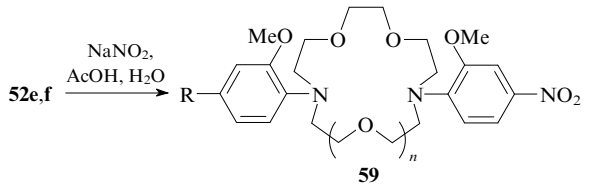
1. Nitro and amino derivatives of *N*,*N*′-diphenyldiazacrown compounds

N,*N*′-Bis(nitrophenyl)diazacrown compounds can be prepared by the nitration of the aromatic ring. Treatment of *N*,*N*′-diaryldiaza-15-crown-5 ether **56a** with an HNO_3–AcOH mixture results in 4,4′-dinitro derivative **58**.[131]



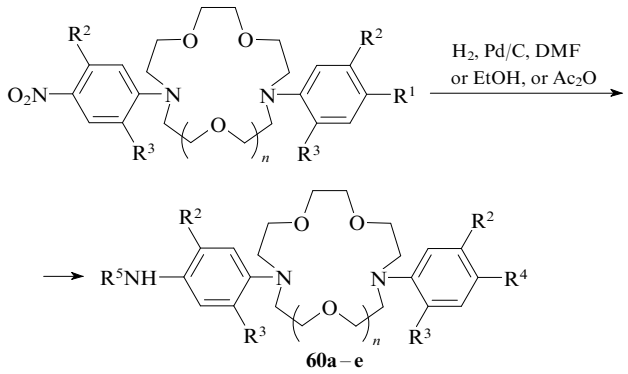
58 (32%)

N,*N*′-Bis(*o*-methoxyphenyl)diaza-15(18)-crown-5(6) ethers **52e**,**f** react with sodium nitrite in aqueous AcOH (see also Section III.1) to give compounds **59** containing one or two nitro groups, whose ratio depends on the macrocycle size.[74] The researchers noted that the use of traditional nitrating agents (HNO_3, HNO_3–H_2SO_4 or $NO_2^+BF_4^-$) results in a total yield of both mono- and dinitration products of only 5%–10%.



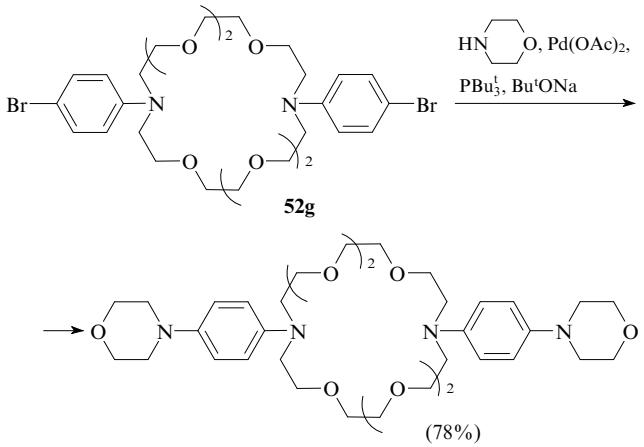
n = 1: R = H (48%), NO_2 (17%); n = 2: R = H (43%), NO_2 (36%).

Amines **60a–d** have been prepared by the reduction of nitro derivatives of N,N'-diaryldiazacrown ethers with hydrogen in the presence of a palladium catalyst in dimethylformamide or ethanol.[74, 131] Conducting the reaction in acetic anhydride gave 4,4′-diacetamide derivative **60e**.[61]

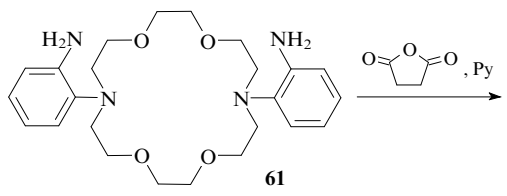


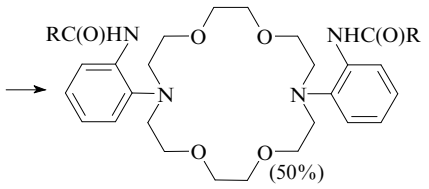
Compound **60**	R^1	R^2	R^3	R^4	R^5	n	Yield (%)
a	NO_2	H	H	NH_2	H	2	–
b	NO_2	OMe	OMe	NH_2	H	1	> 95
c	H	H	OMe	H	H	1	59
d	H	H	OMe	H	H	2	75
e	NO_2	H	H	NHAc	Ac	1	82

The bromine atom in compound **52g** is easily replaced by the morpholine residue in the presence of a palladium a catalyst.[124]



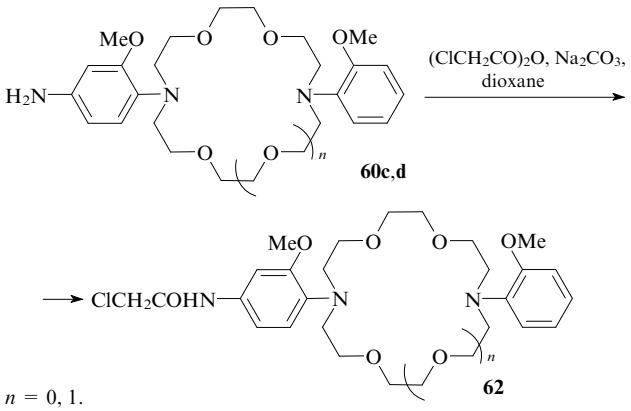
The acylation of diamine **61** with succinic anhydride in pyridine gave the corresponding disuccinic acid.[120]





R = $CH_2CH_2CO_2H$.

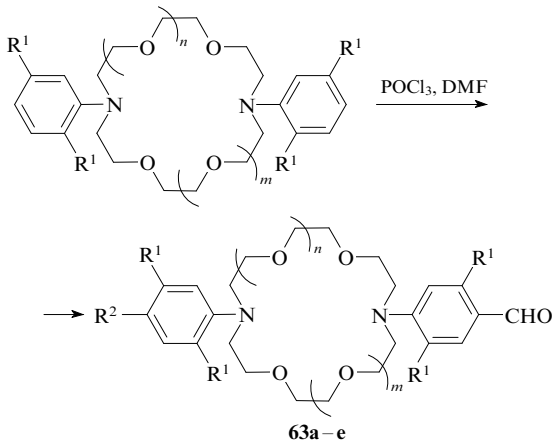
Chloroacetamides **62** were synthesised in 62% yield by the reaction of amines **60c,d** with chloroacetic anhydride under the action of sodium carbonate in 1,4-dioxane.[135]



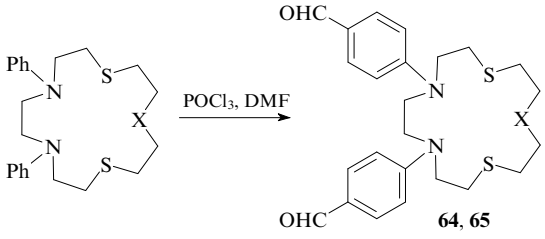
n = 0, 1.

2. Formyl derivatives of N,N'-diphenyldiazacrown compounds

The formyl derivatives of N,N'-diphenyldiazacrown ethers **63a–e**[61, 83, 125, 133, 134] and N,N'-diphenylthiadiazacrown compounds **64**[83] and **65**[34] were obtained by the Vilsmeier reaction.

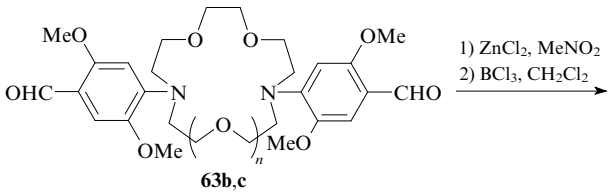


Compound **63**	R^1	R^2	m	n	Yield (%)
a	H	CHO	1	1	68
b	OMe	CHO	0	1	75
c	OMe	CHO	1	1	68
d	H	H	3	3	47
e	H	CHO	3	3	41

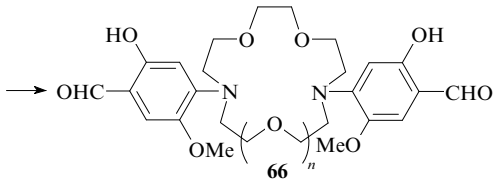


X = $S(CH_2)_2S$ (**64**), O (**65**).

On treatment with boron trichloride, compounds **63b**,**c** undergo selective demethylation of the methoxy groups that occupy the *ortho* positions with respect to the formyl functions. Dialdehyde **66** thus formed was used to prepare fluorescent reagents for Na^+ and K^+ ions.[61, 133, 134]



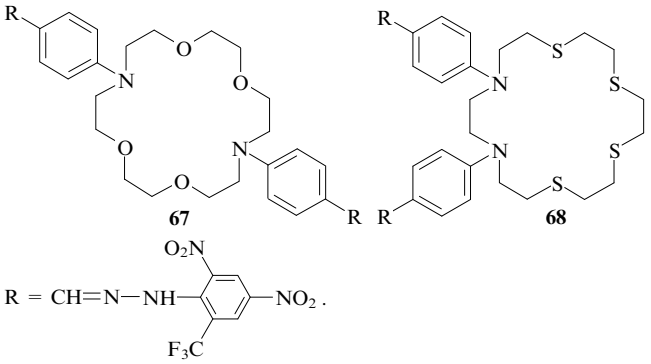
63b,**c**



66

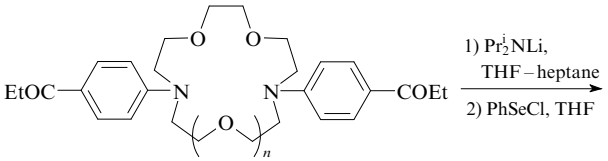
n = 1 (78%), 2 (45%).

The condensation of diformyl derivatives of *N*,*N*′-diphenyldiaza-18-crown-6 ether **63c** and *N*,*N*′-diphenyltetrathiadiaza-18-crown-6 compound **64** with dinitrotrifluoromethylphenylhydrazine affords hydrazones **67** and **68** in 68% and 52% yields, respectively.[83]

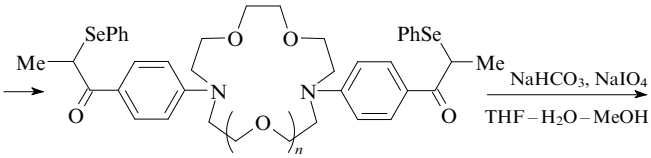


3. Acyl derivatives of *N*,*N*′-diphenyldiazacrown compounds

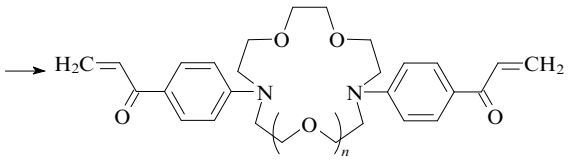
Diazacrown-containing α,β-unsaturated ketones **69a**,**b** were prepared by converting the methyl groups of the propionyl substituent of compounds **54a**,**b** into methylene groups (see Section IV.2).[122] The reaction took place *via* selenium derivatives **70a**,**b**. The enolates, obtained by deprotonation of ketones **54** under the action of lithium diisopropylamide, reacted with phenylselenenyl chloride under mild conditions. The oxidation of diselenides **70** with sodium periodate was accompanied by elimination of organoselenium residues. Compounds **69a**,**b** thus formed react with arylhydrazines to give pyrazolines that are used as fluorescent indicators for the Na^+ and K^+ ions.



54a,**b**



70a (68%); **70b** (77%)



69a (72%); **69b** (75%)

n = 1 (**a**), 2 (**b**).

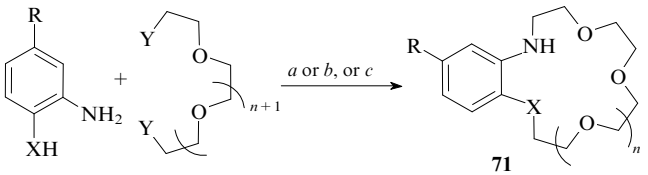
VI. Benzoazacrown compounds

Benzoazacrown compounds that contain one or two nitrogen atoms conjugated with the benzene ring are obtained most often by [1 + 1]-condensation. In some cases, intramolecular cyclisation of podands (open-chain analogues of crown ethers) is used.

1. Condensation of two fragments

One method of synthesis of benzoaza- and benzodiazacrown compounds is the reaction of 2-aminophenols or *o*-phenylenediamines with oligoethylene glycol derivatives.[41, 136–143]

Thus by condensation of 2-aminophenols and *o*-phenylenediamine with the dichlorides, obtained from oligoethylene glycols, in DMF or water, Lockhart *et al.*[41, 136, 137] performed the first synthesis of azacrown compounds **71** with different macrocycle sizes (the yields were not reported). More recently, the same researchers described the synthesis [138] of benzodiaza-15-crown-5 ether **71** by the condensation of *o*-phenylenediamine with tetraethylene glycol ditoluenesulfonate under the action of potassium carbonate in dimethylformamide on heating; however, the product yield was low.

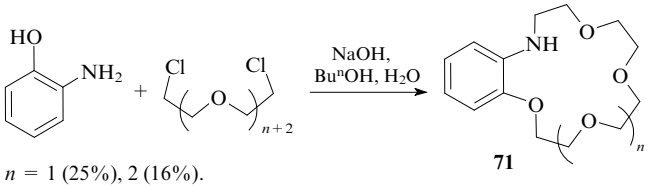


71

(*a*) DMF; (*b*) H_2O; (*c*) K_2CO_3, DMF.

Y	X	*n*	R
Cl	O	0 – 5	H
Cl	NH	0, 1	H
Cl	NH	1	Me
OTs	NH	1	H

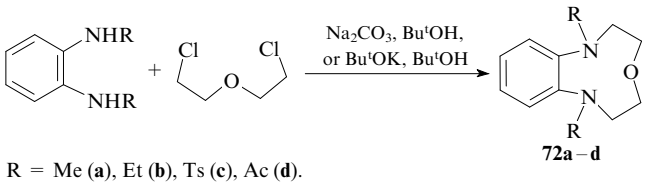
By the reaction of 2-aminophenol with the dichlorides prepared from tri- and tetraethylene glycol in aqueous butanol in the presence of sodium hydroxide, Pedersen and Bromels [139] have synthesised benzoaza-15(18)-crown-5(6) ethers **71** in moderate yields (25% and 16%, respectively). The same method [140] resulted in isolation of benzoaza-15-crown-5-ether in only 8% yield.



71

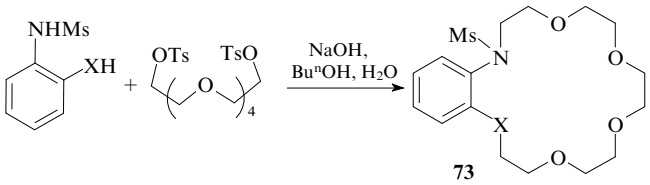
n = 1 (25%), 2 (16%).

Benzodiaza-9-crown-3 compounds **72a**–**d** have been prepared by condensation of *N*,*N*′-disubstituted *o*-phenylenediamines with chlorex.[141, 142] The tosyl groups in compound **72c** are removed by heating in concentrated H_2SO_4 (yield 48%).



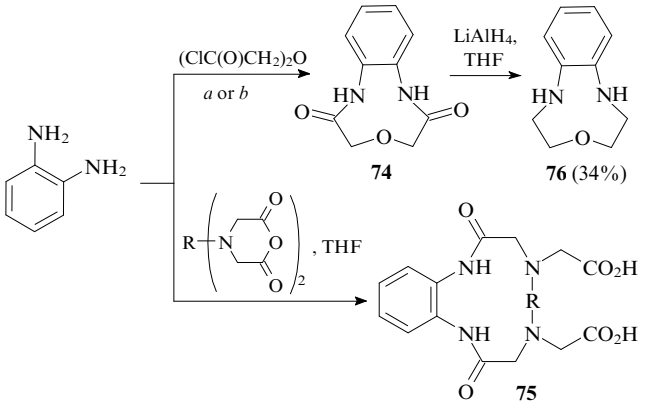
R = Me (**a**), Et (**b**), Ts (**c**), Ac (**d**).

Mesyl protection has also been used for the synthesis of nitrogen-containing benzocrown compounds **73**.[143] Mesylamides form crown compounds in higher yields than the corresponding tosylamides; however, it is difficult to prepare *N*-unsubstituted products from them. No data on the successful removal of mesyl groups from compounds **73** can be found in the literature.



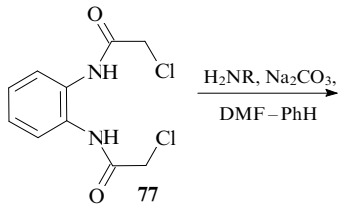
X = O (32%), NMs (5%).

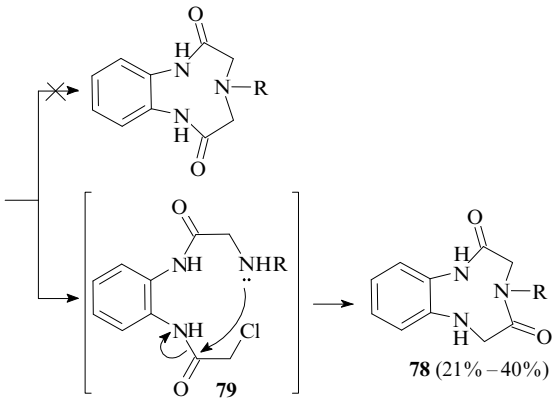
The acylation of *o*-phenylenediamine with dicarboxylic acid dichlorides [142, 144] or tetracarboxylic acid dianhydrides [145] yielded macrocyclic diamides **74** and **75**. The reduction of compound **74** with lithium tetrahydroaluminate resulted in benzodiaza-9-crown-3 compound **76**,[142] whose acylation with acetic anhydride afforded the corresponding *N*,*N*′-diacyl derivative in 25% yield.



R = CH_2CH_2 (95%), $CH_2(CH_2OCH_2)_2CH_2$ (77%);
(*a*) Na_2CO_3, xylene (62%); (*b*) Et_3N, MeCN (30%).

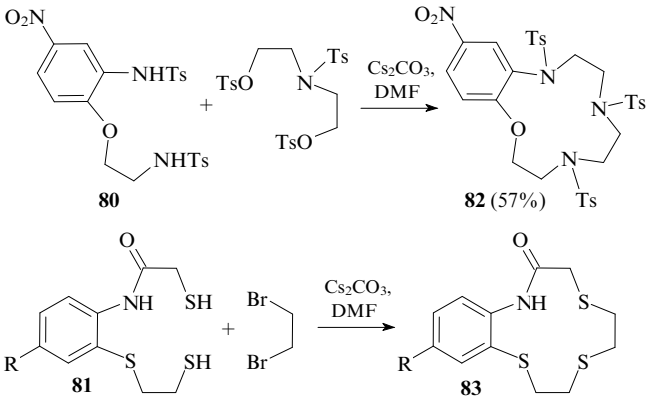
Bis(chloroacetamide) **77** reacts with primary amines to give macrocyclic amides **78**. The mechanism includes an intramolecular rearrangement of the intermediate adduct **79**.[146]





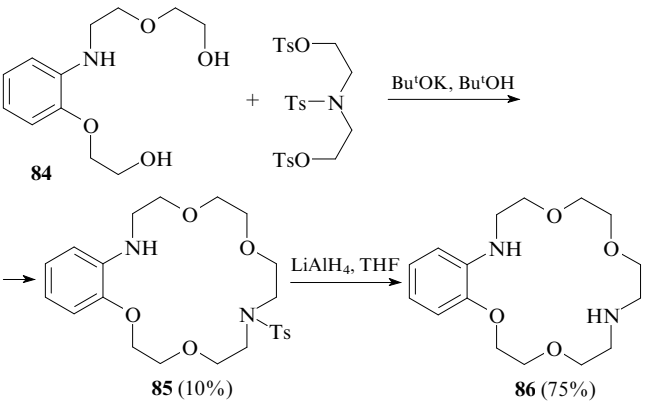
R = Bn, 4-MeC_6H_4, 2,4-$Me_2C_6H_4$, 4-$EtOC_6H_4$, 3-Br-2,4,6-$Me_3C_6HNHCOCH_2$.

Several examples of the synthesis of benzoazacrown compounds based on their linear analogues have been reported. Thus podands **80** and **81**, containing two terminal NH or SH groups, have been converted into benzopolyaza- and benzopolythiaazacrown compounds **82** and **83**.[147, 148] The removal of the tosyl groups in compound **82** was accomplished under acidic conditions as for sulfonamide **72c**, namely, by heating the compound in concentrated H_2SO_4 (yield 94%).

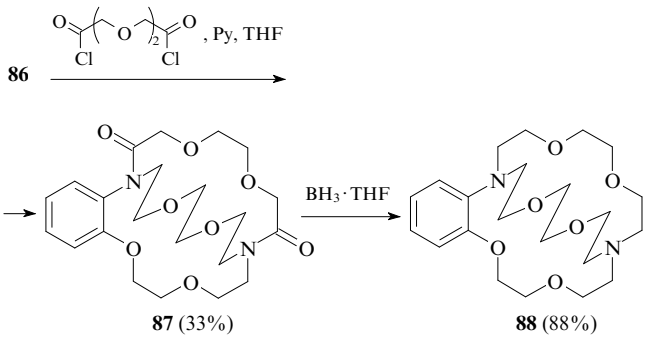


R = H (31%), OMe (17%).

The condensation of podand **84** with diethanolamine tritoluenesulfonate induced by potassium *tert*-butoxide in *tert*-butyl alcohol furnished the tosyl derivative of benzodiaza-18-crown-6 ether **85**.[149] In this case, the *N*-tosyl group was removed by treatment with lithium tetrahydroaluminate.



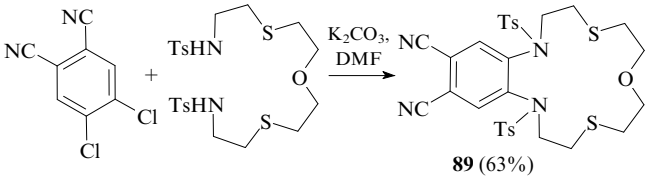
Acylation of benzodiaza-18-crown-6 ether **86** with *O*,*O*′-ethylenediglycolic acid dichloride in THF in the presence of pyridine, followed by the reduction of the resulting diamide **87** with the borane complex with THF, afforded the corresponding benzocryptand **88**.[149]



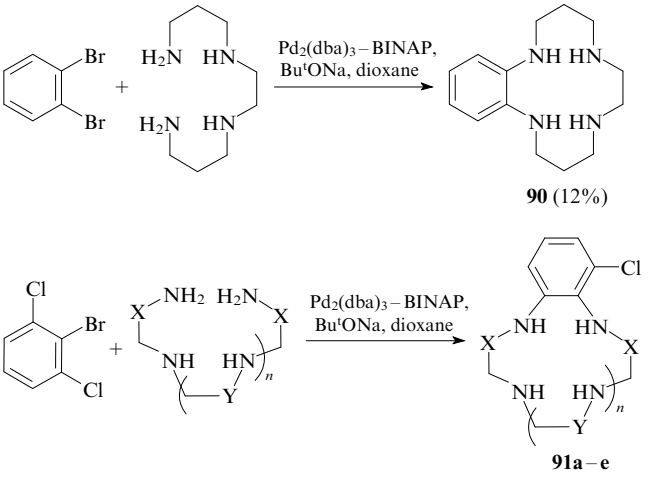
2. Arylation of α,ω-diamino compounds with 1,2-dihalobenzenes

The reactions of *o*-dihalobenzenes with diamines deserve a separate section. In these cases, the bonds between the nitrogen atoms and the benzene ring are formed as a result of nucleophilic aromatic replacement of halogen atoms in activated aryl halides or as a result of C—N cross-coupling.

The benzodithiadiazacrown compound **89**, containing two nitrile groups on the benzene ring, has been prepared by the reaction of 4,5-dichlorophthalonitrile with an acyclic ditosylamide under the action of potassium carbonate in DMF.[150]



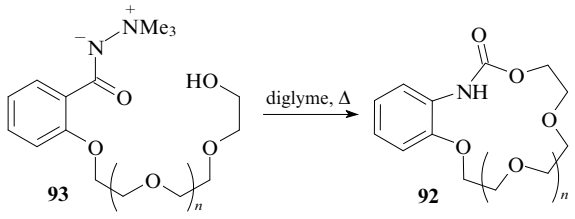
Benzocyclam **90** and benzopolyazacrown compounds **91a**–**e** with different macrocycle sizes were prepared by amination of 1,2-di- or 1,2,3-trihalobenzenes with linear polyamines in the presence of the Pd(dba)$_2$–BINAP catalyst system.[151] In addition to the macrocycles, linear products were also isolated in these reactions. The attempts to prepare benzodiaza-15-crown-5 ether derivatives from 2,6-dichlorobromobenzene and the corresponding trioxadiamine with the same catalyst system have not met with success. Only the linear product was isolated in this case.



Compound **91**	X	Y	*n*	Yield (%)
a	CH_2CH_2	CH_2	1	47
b	CH_2	CH_2	1	27
c	CH_2	CH_2CH_2	1	17
d	CH_2	CH_2	2	12
e	CH_2	CH_2	3	10

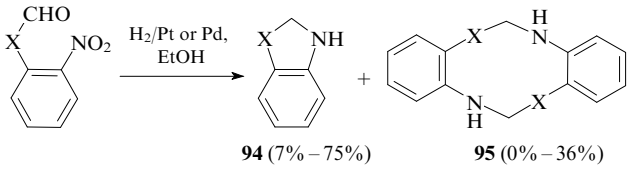
3. Intramolecular cyclisation of podands

This method of synthesis is based on the transformation of a linear molecule into a macrocycle with an annelated benzene ring. Urethane-type benzoazacrown compounds **92** are obtained from betaines **93**.[152] Under drastic conditions, these products rearrange into intermediate, readily cyclisable *N*-aryl isocyanates. The addition of template salts ($NaBF_4$, KBF_4) was found to affect only slightly the yields of these crown compounds.



n = 1 (35%), 2 (50%).

Hydrogenation of nitrobenzenes containing an aldehyde function in the peripheral substituent, over a platinum or a palladium catalyst in ethanol, furnished a large series of benzoazacrown compounds **94a**–**g**.[153] Apart from compounds **94**, the reaction mixture contained in some cases dibenzodiazacrown compounds **95b**,**e**–**g** and polymerisation products. It was shown that the formation of nine- or ten-membered macrocycles is less favourable than the formation of dimers **95** with a macrocycle comprising 18–20 units (see below, Section VIII.2.a, synthesis of compounds **95h**–**o**). After the introduction of an *N*-benzoyl group into the nitroaldehyde molecule, this reaction gives only the nine-membered compound **94a**. Monomers **94f**,**g** with a macrocycle size of 15 and 16 units are formed more readily than the corresponding dimers **95f**,**g** (30- and 32-membered rings). In these cases, the **94** : **95** ratio in the products varies from 1.5 : 1 to 3 : 1. It is noteworthy that 11-, 13- and 14-membered benzoazacrown compounds **94c**–**e** were synthesised in high yields without dimer formation (except for slight amounts of **95e**).

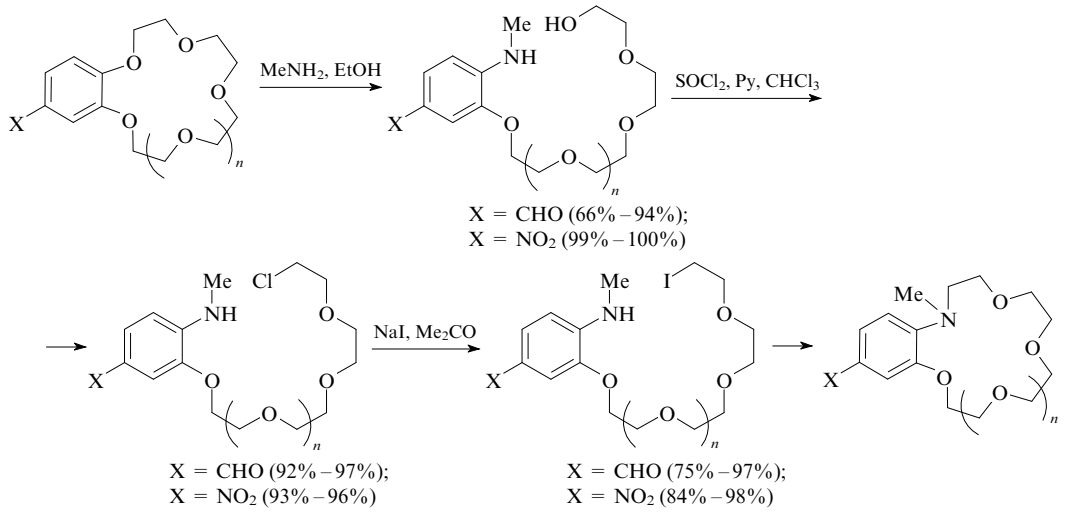


Compounds **94**, **95**	X	Catalyst	Yield (%)	
			94	**95**
a	$NBz(CH_2)_4$	Pd	22	–
b	$O(CH_2)_2O(CH_2)_3$	Pd	19	36
	$O(CH_2)_2O(CH_2)_3$	Pt	22	18
c	$O(CH_2)_2N(SO_2Me)(CH_2)_3$	Pt	36	–
d	$O[(CH_2)_2O]_2CH_2CHMe$	Pd	56	–
e	$O[(CH_2)_2O]_2(CH_2)_3$	Pd	75	6
	$O[(CH_2)_2O]_2(CH_2)_3$	Pt	58	–
f	$O(CH_2)_9CHMe$	Pt	29	18
	$O(CH_2)_9CHMe$	Pd	27	19
g	$O(CH_2)_{11}$	Pt	36	11

4. Synthesis of benzoazacrown ethers by the transformation of the benzocrown macrocycle

We proposed a new methodology for the synthesis of benzoazacrown ethers based on a stepwise ring transformation of benzocrown ethers.[154] A distinctive feature of this method is macrocycle opening upon cleavage of the Ar—O bond followed by ring closure to give the corresponding aza analogues. The starting compounds used were benzocrown ethers whose benzene ring contained an electron-withdrawing group (nitro or formyl group), which activated the regioselective macrocycle opening induced by amines.[155–158] For successful recyclisation, the hydroxyl group present in the nitrogen-containing podands thus formed was

Scheme 5

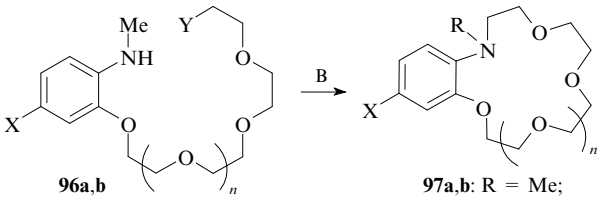


X = CHO, NO_2; n = 0 – 2.

replaced by a better leaving group such as a chlorine or an iodine atom.[159 – 164] The general pattern of the stepwise ring transformation in benzocrown ethers can be represented by Scheme 5.

The key step of this reaction sequence is ring closure in the podands to give the azamacrocycle. Several procedures differing in the reaction conditions were developed. Ring closure in the halogen derivatives of azapodands can take place both under the action of bases and without bases. Most often, iodine derivatives of azapodands are used to prepare benzoazacrown ethers.

Heating of formyl-containing iodides **96a** in the presence of alkali metal carbonates affords *N*-methylbenzoazacrown ethers **97a** [159 – 161] together with *N*-demethylated benzoazacrown ethers **98a** as side products (yields 11% – 18%). However, in the absence of bases, the reaction gives mainly (in some cases, only) *N*-demethylated benzoazacrown ethers. A drawback of the two methods of ring closure is the very long duration: the reaction does not go to completion even after 150 h. An increase in the time of heating results in a pronounced decrease in the yield of products **97a** (especially in the case of a 18-membered macrocycle) due to substantial resinification of the reaction mixture. Nitro-substituted iodopodand **96b** was converted into *N*-methylbenzoaza-15-crown-5 ether **97b**, whose yields in the presence and in the absence of potassium carbonate were 54% and 22%, respectively.[165]



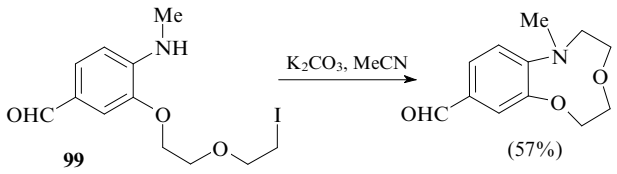
X = CHO, n = 0 – 2 (**a**); X = NO_2, n = 1 (**b**);
Y = I, Cl; B is a base.

The use of alkali metal hydroxides or NaH, which are stronger bases than alkali metal carbonates, allows selective preparation of *N*-methylated benzoazacrown ethers **97** over much shorter periods of time.[162 – 166] Indeed, sodium hydride-induced ring closure in iodopodands **96** takes place on heating for 0.5 – 2 h. The yields of the products are much higher with NaH than with hydroxides; in some cases, not only iodo but also less reactive chloro derivatives can be used. Table 4 summarises all the preparative procedures for ring closure in halopodands **96**.

Heating of iodide **99** in the presence of K_2CO_3 resulted in *N*-methylbenzoaza-9-crown-3 ether in 57% yield in relation to the converted iodide (the degree of conversion was only 23%).[166]

Table 4. Methods for the preparation of azacrown ethers **97** from halopodands.

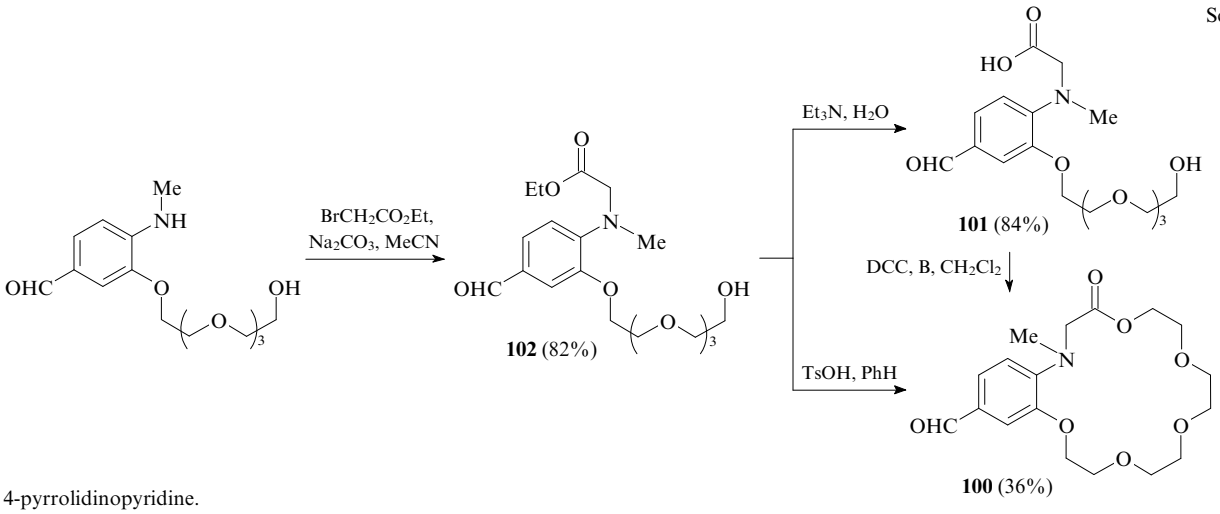
Compounds **96**, **97**	n	Y	Reaction conditions	Yield of **97** (%)	Ref.
a (X = CHO)	0	I	M_2CO_3 (M = Li, Na, K, Rb, Cs), MeCN	53 – 67	159 – 161
	0	I	NaH, THF	61 – 68	166
	1	Cl	NaH, THF	59	166
	1	I	M_2CO_3 (M = Li, Na, K, Rb), MeCN	53 – 61	159 – 161
	1	I	NaH, THF	61 – 63	166
	2	I	M_2CO_3 (M = Li, Na, K, Rb), MeCN	52 – 53	159 – 161
	2	I	NaH, THF	51 – 57	166
b (X = NO_2)	0	I	NaH, THF	36	162 – 165
	1	I	Na_2CO_3, MeCN	54	165
	1	I	NaH, THF	74 – 80	162 – 165
	2	I	NaOH, dioxane	56	162, 165
	2	I	NaH, THF	71	162 – 165



As an example of another application of podands in the synthesis of benzoazacrown ethers, one can consider the synthesis of compound **100**, which contains an ester group in the macrocycle. This azacrown ether was prepared in two ways: by intramolecular esterification of acid **101** under the action of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and by transesterification of podand **102** in the presence of *p*-toluenesulfonic acid as the catalyst (Scheme 6).[167]

The resulting *N*-methylated benzoazacrown ethers form complexes with metal cations characterised by high stability constants, due to the specific features of their conformations. The complexing properties of these compounds substantially exceed those of widely used *N*-phenylazacrown ethers (and in many cases, benzocrown ethers, too) with the same macrocycle size.[161, 165, 168] Owing to the presence of a nitro or a formyl group in the products obtained, it is possible to convert them into diverse derivatives containing benzoazacrown ether fragments. These can be used as selective ligands for metal cations, for the extraction of metal ions

Scheme 6



B is 4-pyrrolidinopyridine.

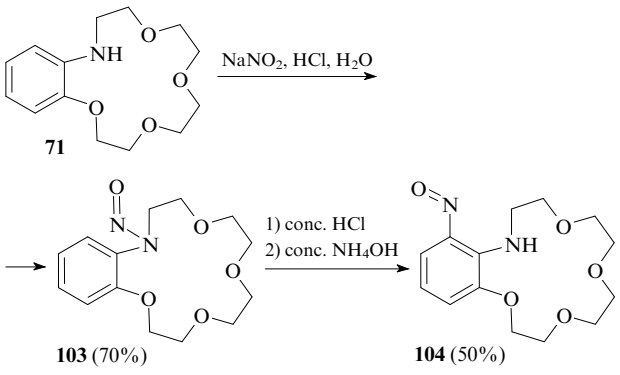
from water and for membrane transport of metal ions, as ion selective dyes and fluoroionophores, in ion selective electrodes, and as parts of polymer films and Langmuir – Blodgett films.

VII. Functional derivatives of benzoazacrown compounds

1. Synthesis of benzoazacrown compounds with substituents in the benzene ring

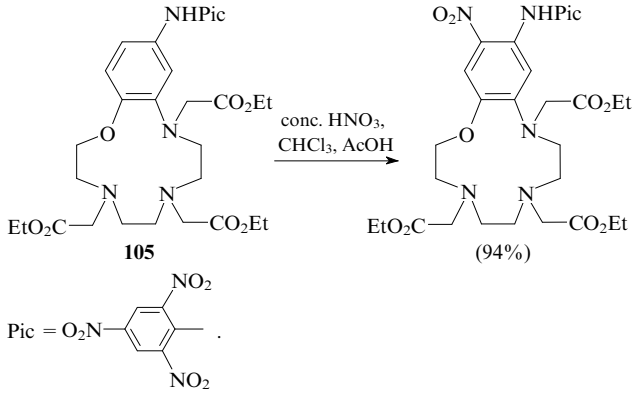
Only a few examples of the synthesis of benzoazacrown derivatives by electrophilic substitution in the benzene ring have been reported.

On treatment with sodium nitrite in hydrochloric acid under mild conditions, benzoaza-15-crown-5 ether **71** is converted into *N*-nitroso derivative **103**, which isomerises in the presence of cold concentrated HCl to give 3′-nitrosobenzo derivative **104**.[139]

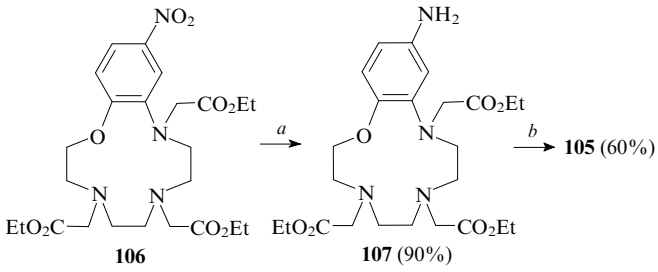


Azo coupling of benzoaza-12-crown-4 with *p*-nitrophenyldiazonium chloride leads to crown-containing azobenzene in which the substituent is in the *para*-position relative to the macrocycle nitrogen atom.[169]

Compound **105** undergoes selective nitration, under mild conditions, of the 5-position of the benzene ring annelated to the macrocycle.[147]

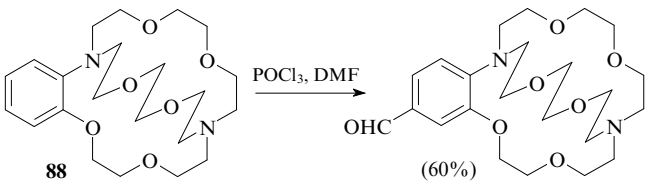


4′-Nitrobenzotriazacrown compound **106** (see below, Section VII.2) is reduced with hydrogen in the presence of a palladium catalyst to form aniline derivative **107**.[147] This product reacts with picryl chloride in the presence of potassium carbonate to afford benzotriazacrown compound **105**.[147]



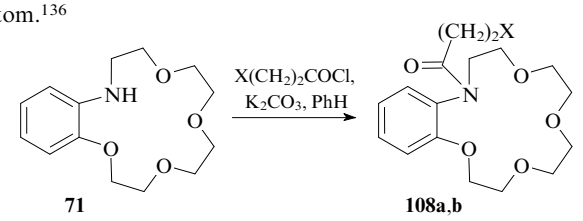
(*a*) H_2, Pd/C, TsOH, aq. EtOH; (*b*) PicCl, K_2CO_3, MeOH.

The formylation of benzocryptand **88** has been carried out by the Vilsmeier reaction.[149]



2. Benzoazacrown derivatives at the macrocycle nitrogen atom

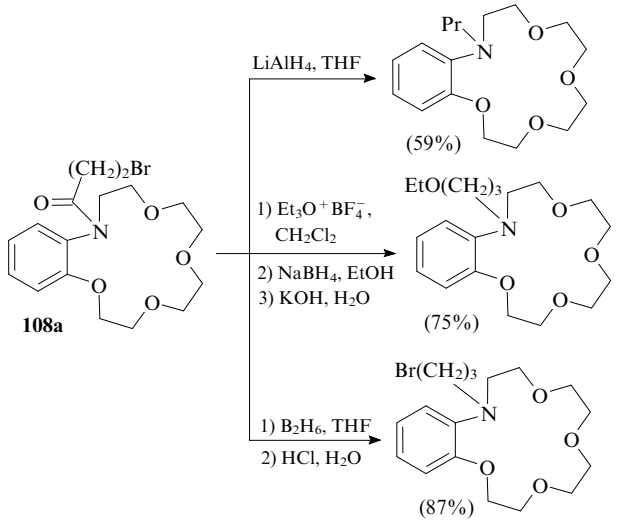
The examples of synthesis of functional derivatives at the nitrogen atom refer to benzoaza-15-crown-5 ether **71**. This compound reacts with acyl chlorides with acylation of the secondary nitrogen atom.[136]



71 **108a,b**

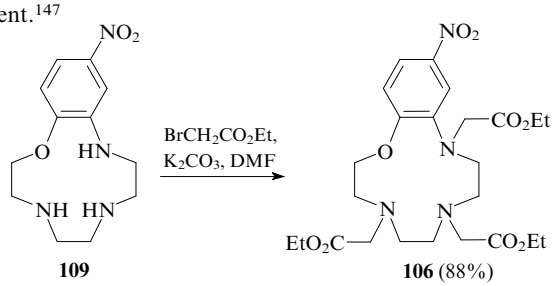
X = Br (**a**, 95%), CO_2H (**b**, 59%).

The amide bond in compound **108a** was reduced with various reagents. This gave *N*-alkylbenzoaza-15-crown-5 ethers in good yields.[136]



108a

Attempts at alkylation of benzotriazacrown compounds **109** with $ClCH_2CO_2H$ have failed. However, this reaction readily proceeds when ethyl bromoacetate is used as the alkylating agent.[147]



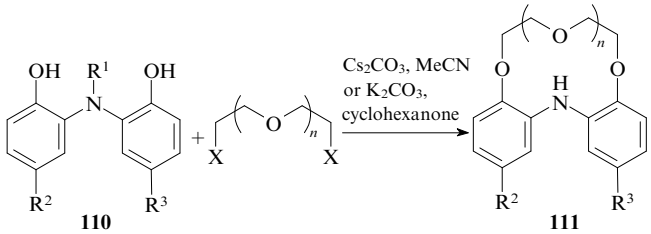
109 **106** (88%)

VIII. Dibenzoazacrown compounds

1. Dibenzomonoazacrown derivatives

The dibenzomonoazacrown ethers described in the literature, in which the nitrogen atom of the macrocycle is conjugated with two benzene rings, have been synthesised by two routes.[170, 171]

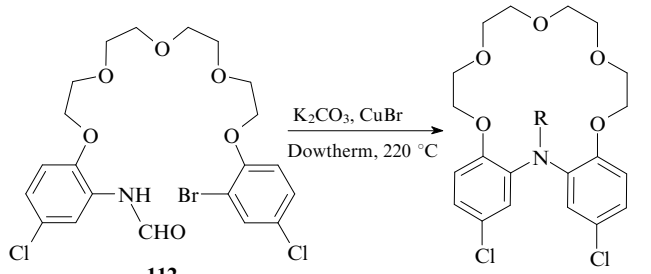
The first route involves the condensation of bisphenol **110** with oligoethylene glycol derivatives under the action of bases. The reactions with oligoethylene glycol ditoluenesulfonates (n = 2, 4) were performed in the presence of caesium carbonate in acetonitrile,[170] while the reactions with dihalides and ditoluenesulfonate (n = 3) were performed in the presence of potassium carbonate (with addition of catalytic amounts of KI in the case of dichlorides) in various solvents. The highest product yields were attained in cyclohexanone.[171] The addition of LiBr as the template salt in the synthesis of dibenzomonoaza-12-crown-4 ether increased the yield from 8% to 30%. The cyclisation of compound **110** (R^1 = CHO, Ac) is accompanied by deacylation giving rise to macrocycles **111**, which contain a secondary amino group. Subsequently, compound **111** (n = 3, R^2 = Cl, R^3 = H) was acylated. The reaction of **111** with formic acid and acetic anhydride furnished *N*-formylated and *N*-acetylated dibenzoazacrown ethers in 60% and 76% yields, respectively.



110 **111**

R^1 = R^2 = R^3 = H, X = OTs, n = 2–4 (22%–68%);
R^1 = H, CHO, Ac; R^2 = Cl; R^3 = H, Cl;
X = Cl, Br; n = 1–4 (24%–51%).

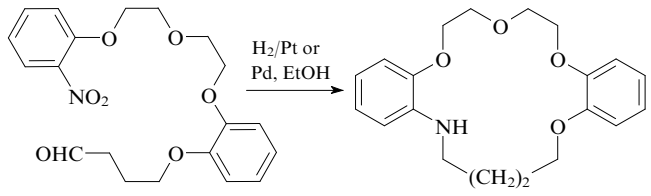
The second route to dibenzomonoazacrown ethers consists of the intramolecular cyclisation of podand **112** in the presence of potassium carbonate and copper(I) bromide under drastic conditions (Dowtherm, 220 °C).[171] Two products were isolated — compounds **113** and **114**. The latter can also be synthesised from the NH-unsubstituted derivative **113** by treatment with formic acid.



112

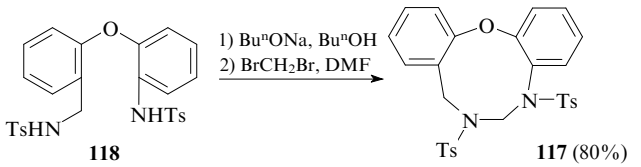
113: R = H (12%);
114: R = CHO (22%).

In some cases, podands containing two phenylene substituents are used as substrates in the synthesis of dibenzomonoazacrown ethers. Thus hydrogenation of nitroaldehyde **115** over a platinum or a palladium catalyst gives dibenzoazacrown ether **116** in 47% and 65% yield, respectively.[153]



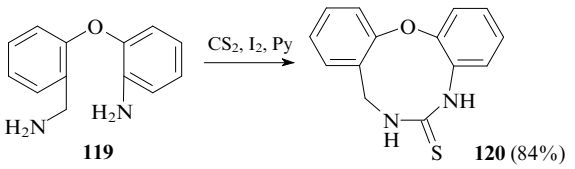
115 **116**

Examples of dibenzodiazacrown compounds in which one nitrogen atom is conjugated with the benzene ring, while the second nitrogen atom is separated from the aromatic ring by a methylene bridge are reasonably assigned to the same Section. Compound **117** was prepared by condensation of *N*,*N*′-ditosylamide **118** with dibromomethane, induced by sodium n-butoxide in DMF.[172] Attempts at detosylation by treatment with concentrated H_2SO_4 failed.



118 **117** (80%)

The reaction of diamine **119** with carbon disulfide in pyridine using iodine as the catalyst resulted in the synthesis of dibenzoazacrown compound **120**, which is a thiourea derivative.[173]



119 **120** (84%)

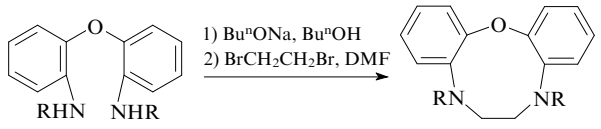
2. Dibenzodiaza- and dibenzotetraazacrown compounds

The construction of the macrocycle in the dibenzoazacrown compounds containing two or four nitrogen atoms conjugated with benzene rings is based most often on the condensation of two fragments. Only a few examples of the synthesis of dibenzotetraazacrown compounds from four fragments have been reported.

a. Syntheses based on the condensation of two fragments

The alkylation of diamines or *N*,*N*′-disubstituted analogues under the action of bases is a widely used method for the synthesis of dibenzodiazacrown compounds. The alkylating agents used include α,ω-dihaloalkanes and derivatives of oligoethylene glycols and their aza analogues.[143, 174–179]

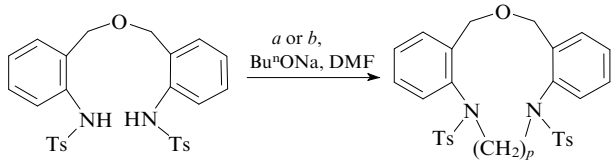
Dibenzodiazacrown compounds **121a–c** have been prepared in good yields by the reaction of *N*,*N*′-derivatives of diamines **122a–c** with dibromoethane in the presence of sodium n-butoxide.[174] The tosyl groups present in compound **121c** were removed by heating in concentrated H_2SO_4 (yield 89%).



122a–c **121a–c** (53%–65%)

R = Me (**a**), Bz (**b**), Ts (**c**).

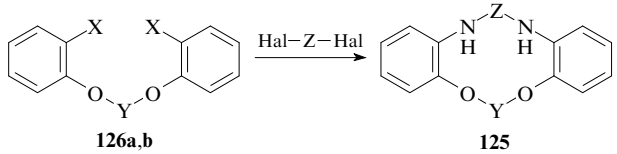
Under the same conditions, dibenzyl ether **123** was converted to **124** using dibromomethane and 1,2-dibromoethane as well as analogous *O*,*O*′-ditoluenesulfonates with longer alkylene chains as the alkylating agents.[175]



123 **124** (93%–96%)

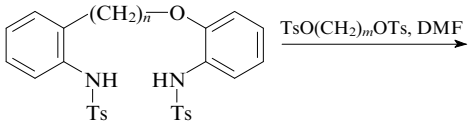
(*a*) $Br(CH_2)_nBr$ (*n* = 1, 2); (*b*) $TsO(CH_2)_mOTs$ (*m* = 3, 4); *p* = 1–4.

Dibenzodiazacrown compounds **125** (Table 5) have been prepared in moderate yields by the alkylation of either the diamine as dihydrochloride (**126a**) or the *N*,*N*′-ditosyl derivative **126b** with the corresponding dihalides under the action of alkali metal carbonates.[176] In the latter case, the tosyl groups were removed after the reaction by treatment with sodium naphthalenide in dimethoxyethane.

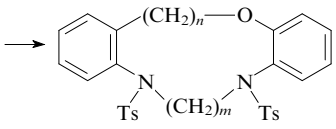


126a,b **125**

Dibenzodiazacrown compounds **127** were prepared by the reaction of the *N*,*N*′-ditosyl derivative of diamine **128** with ditoluenesulfonates of propylene or butylene glycols on heating in DMF.[177] Detosylation with concentrated H_2SO_4 was successful only for compound **127** (*n* = 1, *m* = 4).



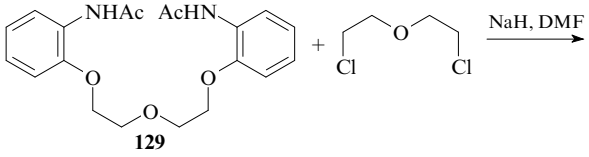
128



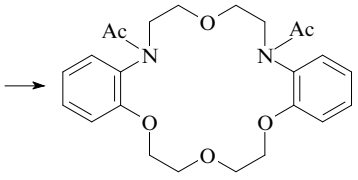
127 (26%–37%)

n = 0, 1; *m* = 3, 4.

The sodium hydride-induced condensation of diamine **129**, containing *N*-acetyl protective groups, with the dichloride prepared from diethylene glycol affords dibenzodiaza-18-crown-6 compound **130**.[178]

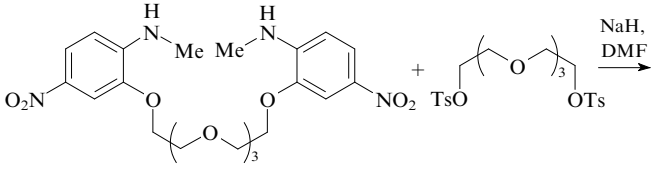


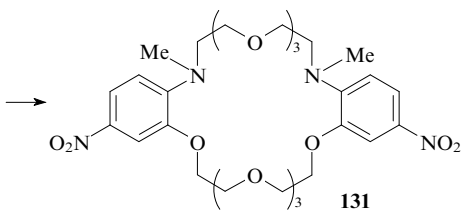
129



130 (11%)

Dinitrodibenzodiaza-30-crown-10 ether **131**, with *N*-methyl substituents, has been obtained under similar conditions using appropriate reagents.[179]





131

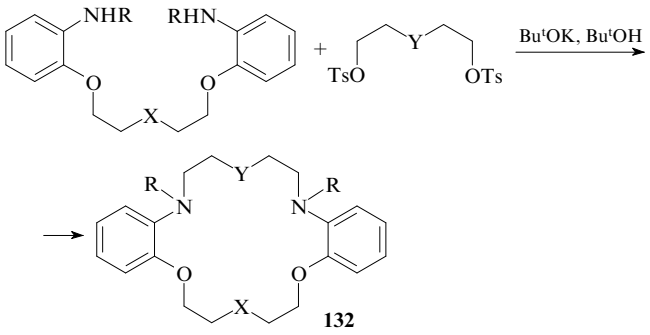
In an early study,[143] dibenzodiaza-, triaza- and tetraaza-18-crown-6 compounds **132** were synthesised by condensation of *N*-tosyl- or *N*-mesyldiamines with appropriate ditoluenesulfonates. The reaction proceeds in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol. The removal of the sulfonyl groups from the macrocycle nitrogen atoms is best accomplished by the heating of compounds **132** with an AcOH (glacial)–HBr–PhOH mixture (the yields of the NH derivatives were 30%–82%). Minor amounts of benzene ring bromination products were also isolated;

Table 5. Synthesis of dibenzodiazacrown compounds **125**.

Compound **126**	X	Y	Z	Hal	Reaction conditions	Yield (%)
a	$NH_2 \cdot HCl$	$(CH_2)_n$, n = 2, 3; $(CH_2)_2O(CH_2)_2$	$(CH_2)_n$, n = 2, 3	Br	K_2CO_3, DMF	1–9
	$NH_2 \cdot HCl$	$(CH_2)_2O(CH_2)_2$	$CH_2(CH_2OCH_2)_2CH_2$	I	K_2CO_3, DMF	12
b	NHTs	$(CH_2)_n$, n = 2, 3; $CH_2(CH_2OCH_2)_2CH_2$	$(CH_2)_n$, n = 2, 3	Br	1) Na_2CO_3, DMF; 2) $C_{10}H_8Na$, DME [a]	4–8

[a] DME is 1,2-dimethoxyethane.

the bromine atoms were removed by treatment with hydrazine on a Pd catalyst.

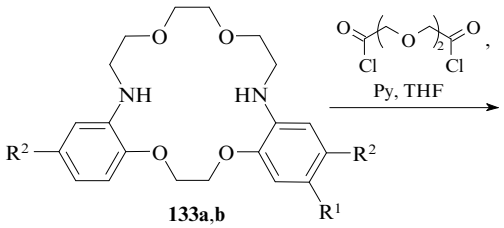


R = Ms: X = Y = O (40%);
R = Ts: X = NTs; Y = O (54%), NTs (20%).

Yet another method used rather widely to prepare dibenzodiazacrown compounds is acylation of the corresponding bridged bis(anilines) with dicarboxylic acid derivatives. Most often, this process is induced by bases and is carried out under high dilution conditions.[136, 144, 169, 178, 180–194] The diamides formed are subsequently reduced by lithium tetrahydroaluminate or diborane.[136, 169, 180–183, 185–193]

Dibenzodiazacrown compounds with different macrocycle sizes **133** have been obtained by the acylation of diamines **134** with oxalic and di- or triglycolic acid dichlorides (Scheme 7, Table 6).[136, 169, 180–183] Compounds **133** with m = 1 were used in Pb^{2+} extraction experiments and that with R^2 = Bu^t was also employed to study Pb^{2+} ion transport through plasticised cellulose triacetate membranes.[181]

Dibenzodiazacrown compounds **133a**,**b** were employed in the preparation of benzoannelated cryptands **135a**,**b**.[180, 182] The substrates **133a**,**b** were acylated with triglycolic acid dichloride under high dilution conditions, and the subsequent reduction of the resulting amides **136a**,**b** was carried out with a solution of diborane in THF. The yields were reported only for R^1 = H, R^2 = OBn: **136b**, 43%; **135b**, 88%.[182]



Scheme 7

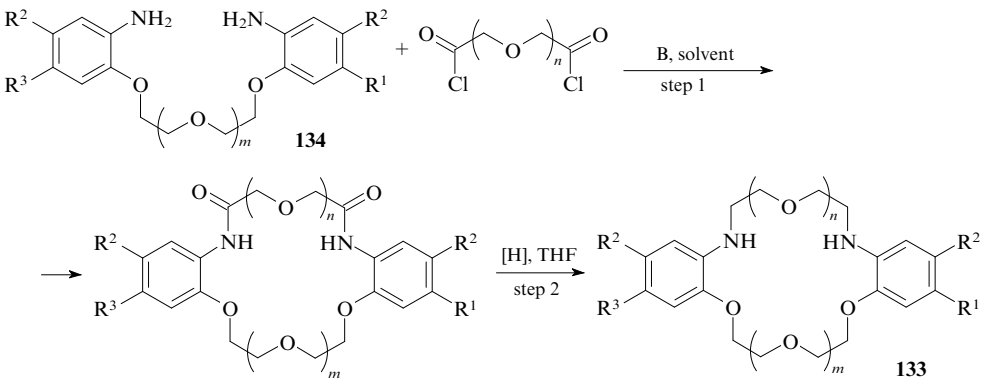
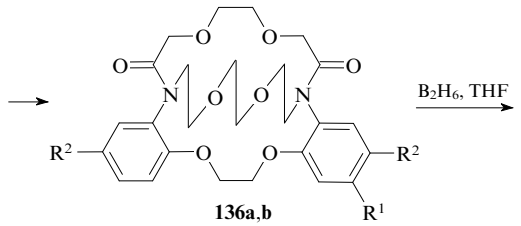


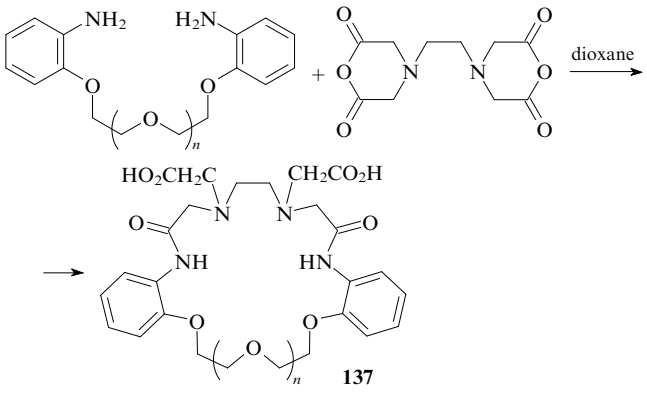
Table 6. Synthesis of dibenzodiazacrown compounds **133**.

R^1	R^2	R^3	m	n	Step 1			Step 2		Ref.
					B	solvent	yield (%)	[H]	yield (%)	
H	H	H	1	0	Py	benzene	54	$LiAlH_4$	77	169
H	H	H	1	0	Et_3N	toluene	61	$LiAlH_4$	60	181
H	H	H	1	1	Et_3N	toluene	88	$LiAlH_4$	98	181
H	H	H	1	1	Py	benzene	40	$LiAlH_4$	71	169
H	H	H	1	2	excess **134**	benzene	88	$LiAlH_4$	62	136
H	Bu^t	H	1	1	Et_3N	toluene	63	$LiAlH_4$	80	181
H	OBn	H	0	2	Et_3N	THF	60	$LiAlH_4$	77	182
Me	H	H	0	2	–	–	–	$LiAlH_4$	–	180
F	H	F	0	1	Py	CH_2Cl_2	40	B_2H_6	92	183



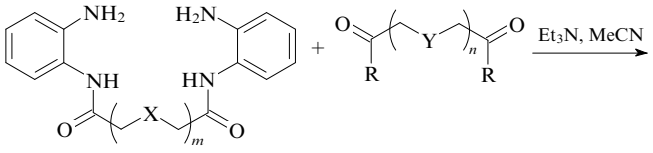
R^1 = Me, R^2 = H (**a**); R^1 = H, R^2 = OBn (**b**).

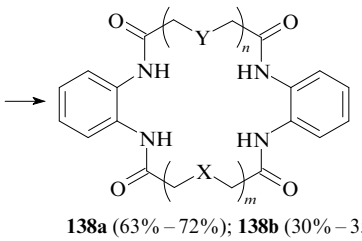
N,*N*′-Dicarboxymethyldibenzotetraazacrown compounds **137** have been obtained from diamines and ethylenediaminotetraacetic acid dianhydride in dioxane.[184]



n = 1 (55%), 2 (42%).

Macrocyclic 18–24-membered dibenzotetraaza- (**138a**) and dibenzopolyazatetralactams (**138b**) are formed in the reaction of diamines with derivatives of dicarboxylic acids under the action of triethylamine. The reaction occurs in highly diluted solution in the case of oxygen-containing compounds **138a** (X = Y = O) and without dilution in the case of polyazacrown compounds **138b** (X = NBoc, NCbz; Y = NBoc).[144]



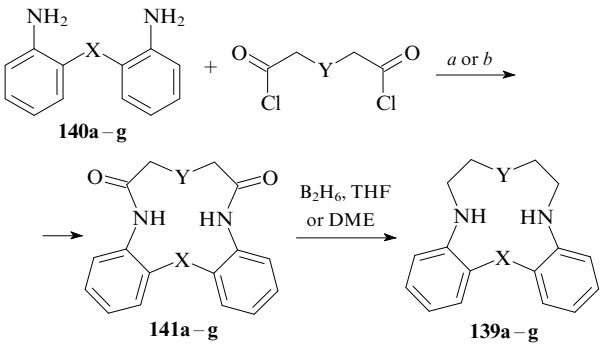


138a (63%–72%); **138b** (30%–35%)

n = *m* = 1, 2; X = Y = O; R = Cl (**a**);
n = 2; *m* = 1, 2; X = NBoc; Y = NBoc, NCbz; R = PivO (**b**);
Boc is *tert*-butoxycarbonyl, Cbz is benzyloxycarbonyl,
Piv is *tert*-butylcarbonyl

A series of 15- and 18-membered dibenzodiaza- (**139a**,**b**) and dibenzodithiadiazacrown compounds (**139c**–**e**) (Table 7), containing one or two O, S or N atoms in the macroheterocycle in addition to the two N atoms, have been synthesised from diamines **140a**–**e** and dichlorides of dibasic acids (glutaric, diglycolic, thiodiglycolic and *N*-tosyliminodiacetic). Pyridine was used as the base and the condensation was carried out in a highly diluted benzene solution. The subsequent reduction of the carbonyl groups in the resulting diamides **141a**–**e** was performed by treatment with a solution of borane in THF or dimethoxyethane.[185–193]

Amides **141e** were prepared by condensation in dichloromethane in the presence of KF and catalytic amounts of Bu_4NHSO_4.[194] An attempt to reduce amides **141a**–**c** with lithium tetrahydroaluminate was successful only for **141a** with Y = CH_2 (yield 77%).[185] The tosyl group in compounds **139b** (Z = NTs; Y = CH_2, O, NTs) was removed by treatment with an AcOH–HBr–PhOH mixture (yields up to 60%), whereas in compound **139b** (Z = O, Y = NTs), the removal took place only on treatment with sodium in boiling n-butanol (yield 67%).[186]



(*a*) Py, PhH; (*b*) KF, $Bu^n_4N^+HSO^-_4$, CH_2Cl_2.

A number of 16–18-membered dibenzodiazacrown compounds **139f**, containing polymethylene chains (3 to 5 units) and additional donor atoms (O, S and N) in the macrocycles, have been synthesised by acylation of the corresponding diamines with

Table 7. Synthesis of dibenzodithiadiazacrown compounds **139**.

Compounds **139**–**141**	X	*n*	Y	Reaction conditions	Yield (%)		Ref.
					141	**139**	
a	OCH_2CH_2O	–	CH_2, O, S, NTs	*a*	50–87	75–84	185, 192
b	$O(CH_2)_2Z(CH_2)_2O$; Z = O, S, NTs	–	CH_2, O, S, NTs	*a*	28–96	38–95	186–188
c	SCH_2CH_2S	–	CH_2, O, S	*a*	70–90	78–95	185
d	$S(CH_2)_2Z(CH_2)_2S$; Z = CH_2, O, S	–	CH_2, O, S, NTs	*a*	19–90	44–88	189–191
e	$SCH_2(CH_2OCH_2)_nCH_2S$	1–3	S	*b*	68–80	–	194
f	$O(CH_2)_nO$	3–5	CH_2, O, S, NTs	*a*	20–92	28–85	186, 195
g	$OCH_2CH(OAc)CH_2O$ [a]	–	CH_2, O, S, NTs	*a*	18–95	41–95	196

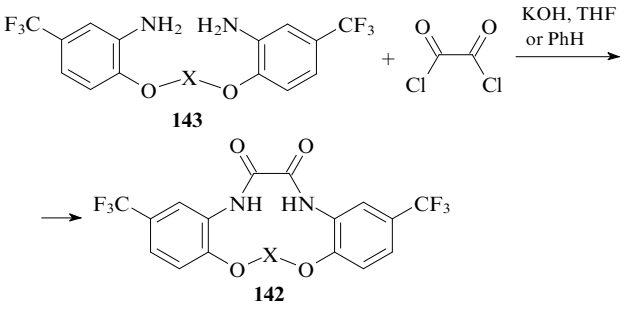
[a] For compound **139g**, X = $OCH_2CH(OH)CH_2O$.

dicarboxylic acid dichlorides under similar conditions (see Table 7).[186, 195] The tosyl group from **139f** (n = 5; Y = NTs) was removed by treatment with an AcOH – HBr – PhOH mixture (yield 71%).

The macrocyclic 15-membered compounds **139a**,**c** and 16 – 20-membered compounds **139b** (Z = O, NTs; Y = CH_2, O, NTs), **139f** (n = 3 – 5: Y = S; n = 5: Y = CH_2, O, NTs) and **139e** were used in experiments on extraction and membrane transport of heavy and transition metal ions.[192 – 194, 197 – 199]

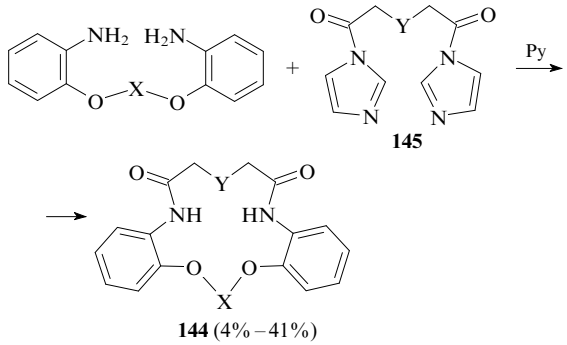
The acylation of acetoxy-substituted aromatic diamine **140g** with glutaric, diglycolic, thiodiglycolic and *N*-tosyliminodiacetic acid dichlorides in the presence of pyridine in benzene gave 16-membered acetoxy-substituted crown lactams (see Table 7). The reduction of these products with diborane in dimethoxyethane to give macrocyclic diamines **139g** is accompanied by elimination of the acetyl group.[196] On attempted reduction in THF, only extremely stable complexes of compounds **139g** with the solvent and, perhaps, with boron hydride were isolated.

Macrocyclic diamides **142**, containing trifluoromethyl groups, have been prepared by acylation of diamines **143** with oxalyl chlorides.[200]



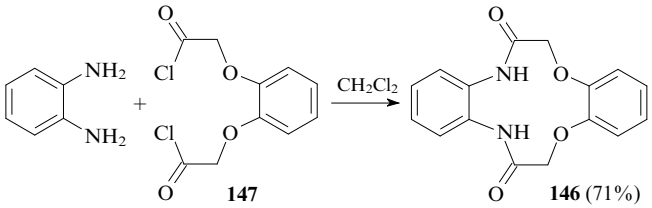
X = CH_2CH_2 (50%), $(CH_2)_2S(CH_2)_2$ (79%).

In the synthesis of compounds **144**, diimidazolides **145** were used as acylating agents.[178] The reaction takes place on heating of the reactants in pyridine, but the product yields are relatively low.

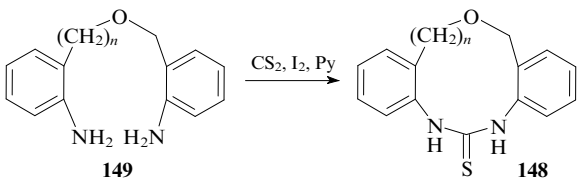


X = $(CH_2)_3$, $CH_2(CH_2OCH_2)_nCH_2$ (n = 1, 2); Y = O, S, NMe.

o-Phenylenediamine diamide **146** has been prepared by condensation of *o*-phenylenediamine with dichloride **147** at room temperature.[201]

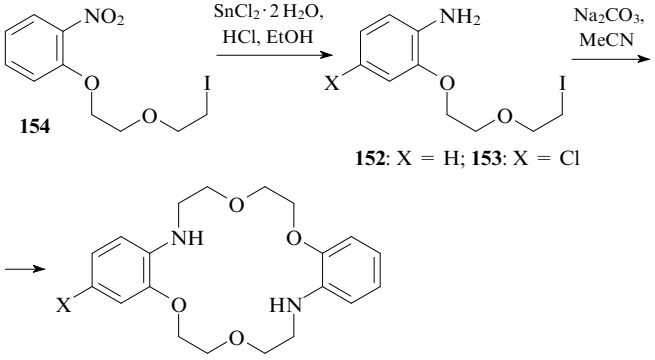


Macrocyclic derivatives of *N*,*N*′-diphenylthiourea **148** were obtained by the reaction of bis(anilines) **149** with carbon disulfide in pyridine in the presence of iodine as the catalyst.[173]

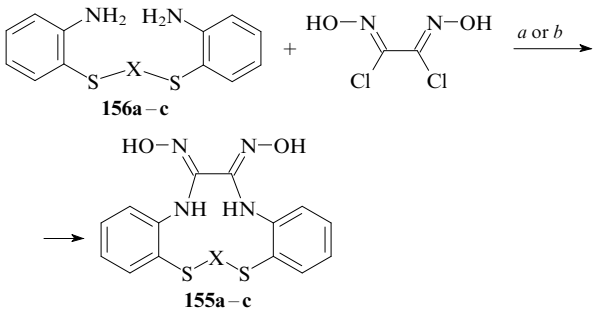


n = 0 (88%), 1 (85%).

Dibenzodiaza-18-crown-6 ether **150** and its chloro derivative **151** are formed upon intramolecular alkylation of aromatic amines **152** and **153** in the presence of sodium carbonate.[202] Amines **152**, **153** were formed in a 10 : 1 ratio upon the reduction of nitro compound **154**. Due to their low stability, they were not separated but used in the condensation as a mixture. The yields of products **150** and **151** are given in relation to the starting nitro compound **154**.



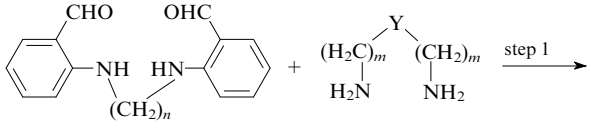
Dibenzodithiadiazacrown dioximes **155a**,**b** were synthesised from diamines **156a**,**b** and oxalyldihydroxymoyl chloride in an aqueous solution of sodium carbonate at low temperature.[203, 204] Dibenzodithiadiaza-12-crown-4 tetraoxime **155c** was prepared from dioxime **156c** in ethanol in the presence of sodium hydrogen carbonate.[205]

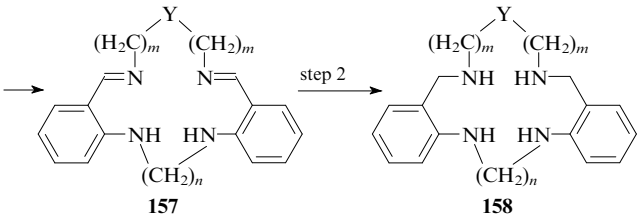


X = CH_2CH_2 (**a**, 27%), $CH_2(CH_2OCH_2)_3CH_2$ (**b**, 63%); C(=NOH)C(=NOH) (**c**, 65%);
(*a*) Na_2CO_3, H_2O, CH_2Cl_2; (*b*) $NaHCO_3$, EtOH.

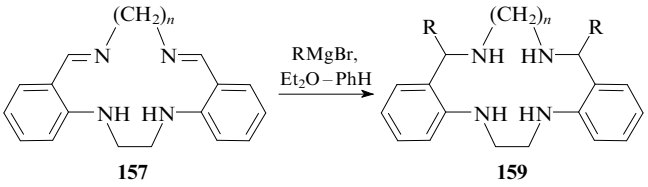
The macrocyclic diimines obtained by condensation of aliphatic diamines with the corresponding dialdehydes are important precursors of dibenzotetraazacrown compounds. [206, 207]

The reduction of diimines **157** yields dibenzotetraazacrown compounds **158** (Table 8).[207 – 209] Schiff's bases **157** (Y = O, S, NH) were synthesised in the presence of *p*-toluenesulfonic acid, which served as the catalyst.[207]



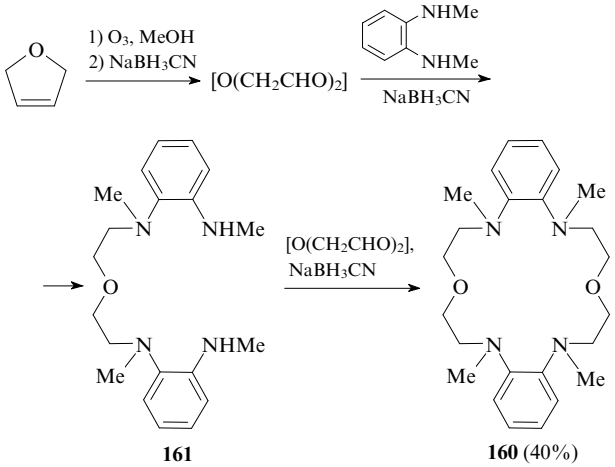


The reactions of diimines **157** ($n = 2$; $m = 1, 2$; Y is none or CH_2) with Grignard reagents have produced tetraazacrown compounds with alkyl substituents in the macrocycle **159**.[208, 210]



$n = 2-5$, R = Et (87%–94%); $n = 3$, R = Pr^n (80%), Bu^n (71%).

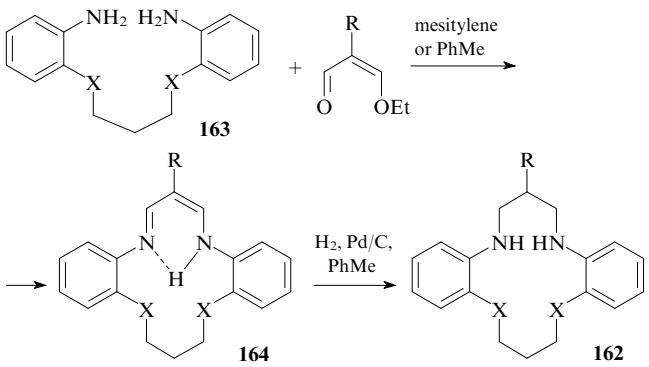
An unusual procedure has been developed for the synthesis of symmetric dibenzotetraazacrown compounds **160**.[211] Dihydrofuran was used as the reagent; first, it was ozonised and then reduced with sodium cyanoborohydride to dialdehyde. The product was used, without isolation, in the reductive alkylation of *N*,*N*′-dimethyl-*o*-phenylenediamine. The resulting diamine **161** was converted into dibenzotetraazacrown compound **160** using a similar reaction sequence. The yield of product **160** is given in relation to *N*,*N*′-dimethyl-*o*-phenylenediamine.



Dibenzodiaza- and tetraazacrown compounds **162** were prepared from diamines **163** and 2-alkyl-3-ethoxyacroleins.[208, 212, 213] The condensation products **164** thus formed, which contain C=C and C=N double bonds, were reduced with hydrogen over a Pd catalyst.[208, 212]

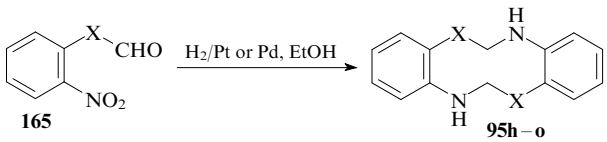
Table 8. Synthesis of dibenzotetraazacrown compounds **158**.

n	*m*	Y	Step 1		Step 2	
			conditions	yield (%)	conditions	yield (%)
2	1	$(CH_2)_{0-2}$	EtOH	86–94	$NaBH_4$, EtOH	–
2	2	O, S, NH	*p*-TsOH, EtOH	71–96	$LiAlH_4$, THF or Et_2O	20–58
3	3	NH	*p*-TsOH, EtOH	62	$LiAlH_4$, THF	59



X	R	Yield (%)	
		164	**162**
O	H	37	86
O	Me	26–41	84
NH	Me	40	57

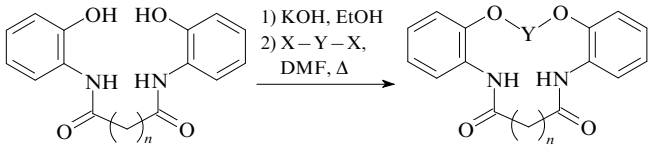
Hydrogenation of aldehydes **165** containing an *o*-nitrophenylene substituent has yielded a series of 16-, 18- and 20-membered dibenzodiazacrown compounds **95h–o**.[153] It is noteworthy that no formation of monomers (benzoazacrown compounds) was observed in the synthesis of 18- and 20-membered macrocycles **95h,j–m,o** (see Section VI.3, the synthesis of compounds **94a–g**).



Compounds **95**	X	Catalyst	Yield (%)
h	$O(CH_2)_2CHMe$	Pd	30
i [a]	$O(CH_2)_3$	Pd	8
j	$O(CH_2)_4$	Pd	64
	$O(CH_2)_4$	Pt	75
k	$O(CH_2)_3CHMe$	Pd	62
l	$CH_2O(CH_2)_3$	Pd	23
m	$O(CH_2)_2OCHMe$	Pd	58
	$O(CH_2)_2OCHMe$	Pt	47
n [b]	$O(CH_2)_5$	Pd	20
o	$O(CH_2)_2OCH_2CHMe$	Pd	37

[a] The major product is monomer **94i** (35%); [b] Monomer **94n** (7%) was also formed.

Thirteen- to sixteen-membered diamines **166** have been prepared from bis(phenols).[214] First, bis(phenols) were treated with an ethanolic solution of potassium hydroxide and the resulting phenolates were made to react with dihalides or ditoluenesulfonates on heating in DMF.

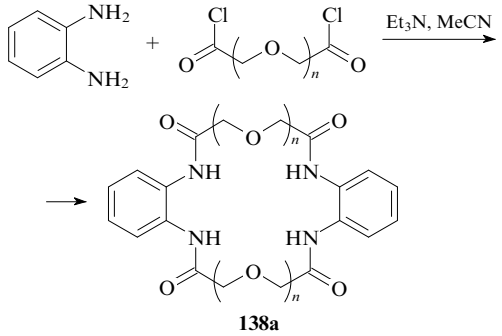


$n = 0, 1$; X = Cl, Br, OTs;
Y = $(CH_2)_m$, $m = 2-5$; $CH_2C(=CH_2)CH_2$; $(CH_2)_2O(CH_2)_2$.

b. Condensation of four fragments

Macrocyclic dibenzotetramides **138a** are formed as side products (yields < 5%) in the reaction of *o*-phenylenediamine with di- and triglycolic acid chlorides in the presence of triethylamine under high dilution conditions in MeCN.[144] The reaction gave benzodi-

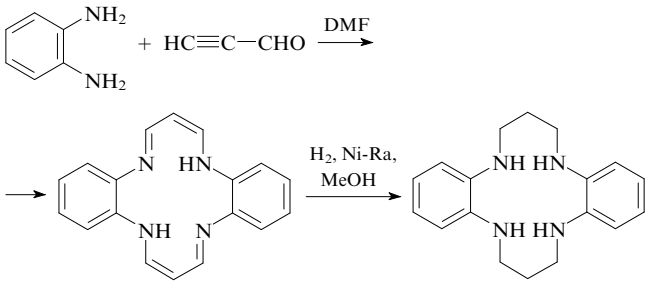
lactam monomers (yield 30% for benzodilactam **74** with $n = 1$, see Section VI.1) or oligomers as the major products.



138a

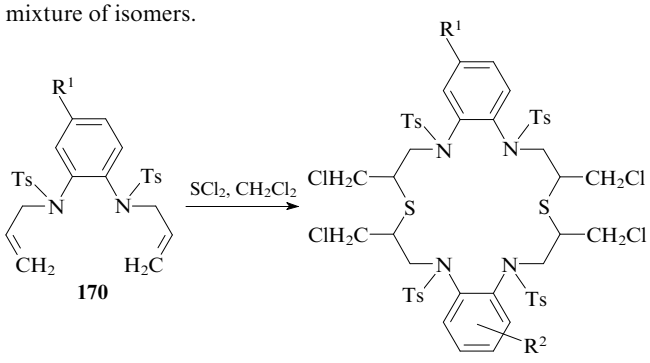
$n = 1, 2$.

Tetraaza[14]annulene **167** has been prepared by the condensation of *o*-phenylenediamine with propiolaldehyde; the catalytic reduction of this product with hydrogen in the presence of Raney nickel gives dibenzocyclam **168**.[215]



167 (27%) **168** (34%)

Dibenzodithiatetraazacrown compounds **169** were obtained in high yields by treatment of *N*,*N*′-diallyl-*N*,*N*′-ditosyl-*o*-phenylenediamines **170** with sulfur(II) chloride.[216] In the case of substituted *o*-phenylenediamine **170** (R^1 = Me), this reaction gives a mixture of isomers.



170 **169** (91% – 97%)

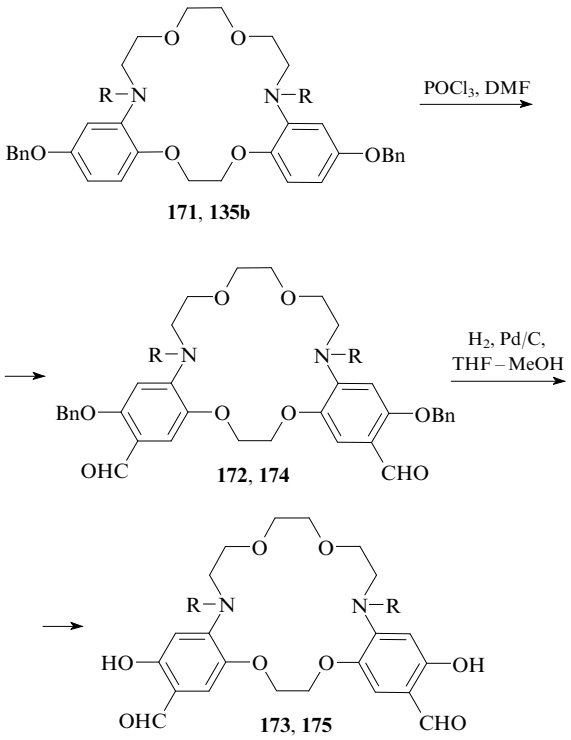
$R^1 = R^2 = H$; R^1 = Me: R^2 = 4-Me, 5-Me.

IX. Functional derivatives of dibenzoazacrown compounds

1. Dibenzoazacrown derivatives at the benzene ring

The number of functional derivatives of dibenzoazacrown compounds at the benzene ring reported in the literature is relatively small. These compounds were mainly prepared during the dibenzoazacrown ring construction by condensation of reactants already containing the required substituents (see Section VIII.2). Some examples of the synthesis of functional derivatives of dibenzoazacrown compounds by electrophilic aromatic substitution have been reported.

For example, formylation of dibenzodiazacrown compound **171** by the Vilsmeier reagent gave dialdehyde **172** (yield 77%). The removal of the benzyl protective groups in the aryl substituents by hydrogenolysis gave rise to the desired product **173** (yield 97%).[182]



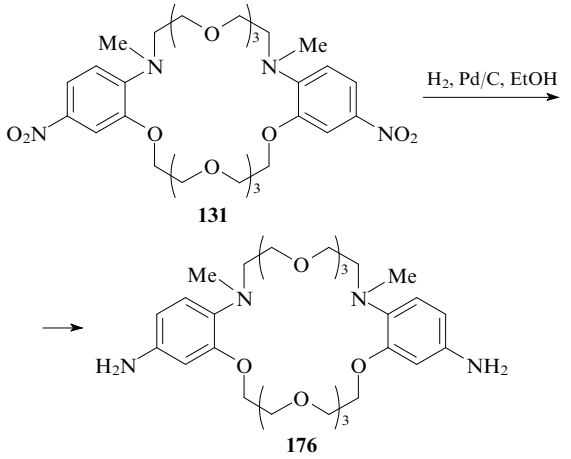
171, **135b** **172**, **174** **173**, **175**

R = CH_2CO_2Me (**171**, **172**, **173**);
R – R = $CH_2(CH_2OCH_2)_2CH_2$ (**135b**, **174**, **175**).

A similar formylation of benzoannelated cryptand **135b**, followed by reductive elimination of the benzyl groups in compound **174**, resulted in the formation of compound **175** in an overall yield of 71%.[182] Macrocycles **173** and **175** were used to prepare crown-containing coumarins, which are fluorescent reagents for alkali and alkaline earth metal ions.

Dibenzodiazacrown compounds easily enter into azo coupling with *p*-nitrophenyldiazonium chloride.[169]

Reduction of the dinitro derivative of *N*,*N*′-dimethyldibenzodiaza-30-crown-10 compound **131** with hydrogen over a palladium catalyst gave diamine **176**. This product reacts with methyl isothiocyanate to give a crown-containing thiourea derivative (yield 40% in relation to the starting compound **131**).[179]



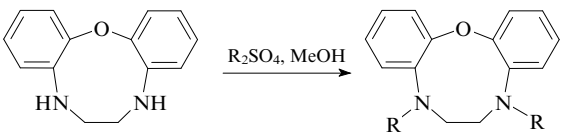
131 **176**

2. Derivatives of dibenzoazacrown compounds at the macrocycle nitrogen atom

N-Substituted dibenzoazacrown compounds are often formed upon cyclisation or condensation of fragments (see Section

VIII.2). In addition, these compounds can be obtained by direct alkylation of pre-formed macrocycles; however, only a few such examples are known.

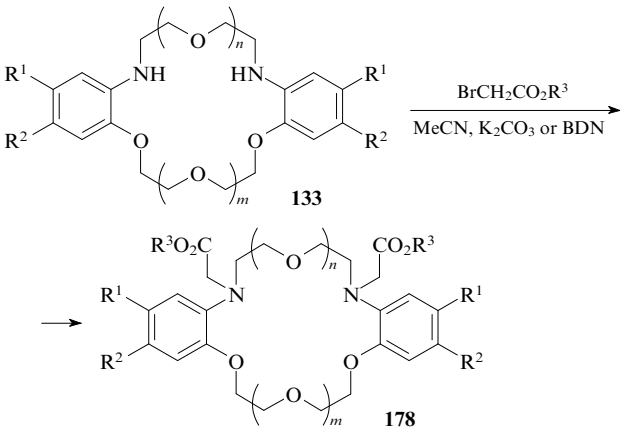
The reaction of compound **177** with dialkyl sulfate in methanol gave *N*,*N*′-dialkyl derivatives **121**.[175]



177 **121**

R = Me (56%), Et (62%).

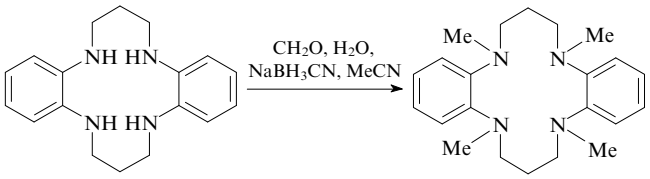
Derivatives **178** have been prepared in a similar way.[181–183] Alkylation of dibenzodiazacrown compounds **133** with ethyl or methyl bromoacetate proceeds in the presence of potassium carbonate or 1,8-bis(dimethylamino)naphthalene (BDN). Compound **178** ($n = m = 1$) has been used as an extractant for Pb^{2+} ions and in Pb^{2+} transport through plasticised membranes based on cellulose triacetate.[181]



133 **178**

R^1	R^2	R^3	*m*	*n*	Yield (%)
H	H	Et	1	1	71
H	F	Et	0	2	54
OBn	H	Me	0	2	91

The reductive alkylation of dibenzocyclam **168** with an aqueous solution of formaldehyde and sodium cyanoborohydride in acetonitrile yielded the tetramethyl derivative of dibenzocyclam **179**.[217]



168 **179**

X. Conclusion

The data presented in the review were classified according to the chemical type of the synthesised structures. To sum up, it is pertinent to present a brief systematisation of the data in terms of the synthetic methods used, as shown in Table 9. It can be seen that, despite the diversity of approaches, [1 + 1]-condensation of two acyclic fragments still remains the key route to azacrown compounds. Nucleophilic aromatic substitution is widely used to prepare *N*-phenylaza- and *N*,*N*′-diphenyldiazacrown compounds, which is attributable to the ready availability of the starting compounds. The other methods for the synthesis of azacrown compounds are encountered much more rarely in relevant publications. Meanwhile, more and more publications deal with the synthesis of such compounds by C–N cross-coupling. Of the most recent publications on this topic, of special interest in our opinion are the studies on the synthesis of benzodiazacrown compounds started not long ago.[151]

It should also be noted that the synthesis of functional derivatives of *N*-phenylaza- and *N*,*N*′-diphenyldiazacrown compounds is documented rather extensively. The number of known derivatives of annelated azacrown ethers is much smaller. The chemistry of benzoazacrown compounds has been poorly developed until recently because the synthesis of these compounds by condensation of two fragments is complicated and the podands needed for intramolecular condensation are difficult to obtain. We proposed a new methodology for the synthesis of functional derivatives of benzoazacrown ethers by the stepwise

Table 9. Brief characteristics of the main methods of synthesis of azacrown compounds (as presented in this review).

Reaction type	Desired products	Features of the method	Range of yields (%)	Number of references
[1 + 1]-Condensation	*N*-phenylazacrown compounds	relatively cheap	6–70	36
	N,*N*′-diphenyldiazacrown compounds	the same	11–85	13
	benzoazacrown compounds	"	5–95	15
	dibenzoazacrown compounds	"	1–95	47
Nucleophilic aromatic substitution	*N*-phenylazacrown compounds	the use of commercially available azacrown compounds	12–95	13
	N,*N*′-diphenyldiazacrown compounds	the same	23–92	6
	benzoazacrown compounds	poor availability of the starting compounds	63	1
Cross-coupling	*N*-phenylazacrown compounds	high cost of reagents and catalysts	4–91	4
	N,*N*′-diphenyldiazacrown compounds	the same	70	1
	benzoazacrown compounds	"	10–47	1
Intramolecular cyclisation of podands	benzoazacrown compounds	poor availability of the starting podands	7–75	2
	dibenzoazacrown compounds	the same	12–65	2
Macrocycle transformation in benzocrown ethers	benzoazacrown compounds	the use of commercially available benzocrown ethers	36–80	10
[2 + 2]-Condensation	dibenzoazacrown compounds	applicable only in particular cases	5–97	3
Other methods	*N*,*N*′-diphenyldiazacrown compounds	—	21–80	3

transformation of readily available oxygen-containing analogues, which appears a promising alternative to the existing approaches.

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