

## THIACROWN COMPOUNDS: SYNTHESIS AND PROPERTIES. (REVIEW)

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*Data of the last 15 years on the synthesis and properties of various thiacrown compounds containing 2-8 sulfur atoms in the ring are reviewed.*

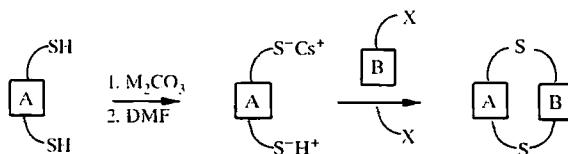
The discovery of interesting and unique complexing characteristics in crown ethers and their nitrogen and sulfur analogs is one of the most powerful achievements of modern organic chemistry. The selectivity of the macrocycle toward the ions of various metals can be controlled by the size of the ring, by the type, number, and position of the heteroatoms in the ring, and by the presence of functional groups in the ring and on its periphery. Of the many methods used in the synthesis of crown ethers and their sulfur analogs (thiacrowns) the most successful is the reaction of dihalogeno derivatives with glycols and dithiols, by means of which it is possible to influence positively the main factors determining the selectivity of the macrocycle. Methods have been developed on the basis of this reaction for the synthesis of numerous sulfur-containing heterocyclic compounds.

The various types of macroheterocycles are of great interest as reagents that make it possible to extract metals with the object of separating their mixtures and subsequently determining the individual elements. Sulfur-containing macroheterocycles and their open-chain analogs, called podands, occupy an important position in supramolecular chemistry, having the ability to connect selectively the ions of transition and heavy metals, such as Cu(II). The use of these compounds makes it possible to model the biological systems and processes in which organosulfur compounds participate. The use of macrocycles as the active components in the membranes of ion-selective electrodes and molecular receptors has proved very promising.

In the present review an attempt is made to summarize comprehensively the achievements of the last 10-15 years in the chemistry of thiacrown compounds containing only sulfur atoms as heteroatoms. The review is not concerned with the extensive material on the synthesis and properties of macroheterocycles containing nitrogen, oxygen, and other heteroatoms.

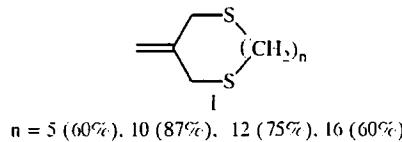
### 1. THIACROWN COMPOUNDS WITH TWO SULFUR ATOMS

The strategy for the template synthesis of thiacrown compounds, illustrated by the scheme below, gives good results when cesium is used as metal cation and DMF as solvent [1]:

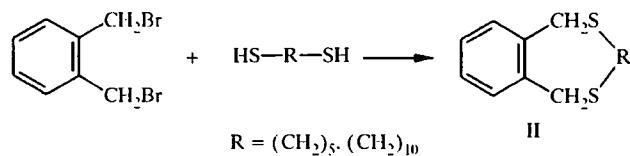


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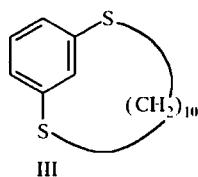
The role of the cesium cation is to accelerate the cyclization of the intermediately formed nucleophilic linear thiolates through the creation of a coordination center. This is promoted by the large radius of the cation compared with the ions of other alkali metals, by the low density of surface charge, by the high polarizability, and by the poor solvatability in DMF. This approach has been extended to the formation of macrocyclic compounds with an isobut enyl group as repeating group in the chain:



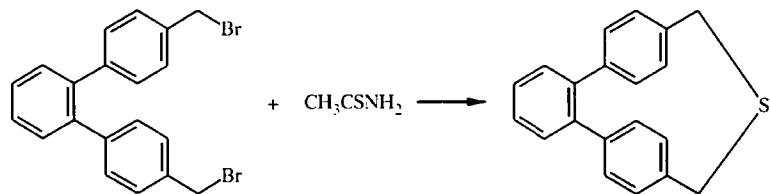
The method was also used successfully for the preparation of cyclophane compounds from xylidene dibromide [2]:



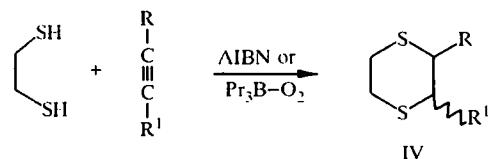
2,4-Benzo-1,5-dithiacyclopentadec-2-ene (III) was synthesized with a 95% yield from 1,3-dimercaptobenzene in the presence of cesium salts [3]:



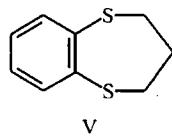
The reaction of 1,2-bis(4-bromomethylphenyl)benzene with thioacetamide in the presence of cesium carbonate leads to a cyclophane with one sulfur atom in the ring [4]:



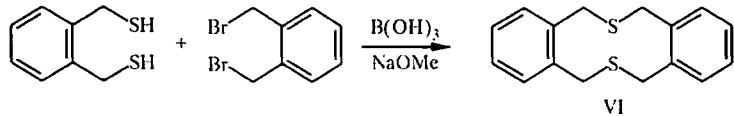
A similar method for the "assembly" of two-membered substituted thiacrown compounds is illustrated by the procedure for the construction of 1,4-dithiane rings by the homolytic cycloaddition of 1,2-ethanedithiol to alkynes [5]:



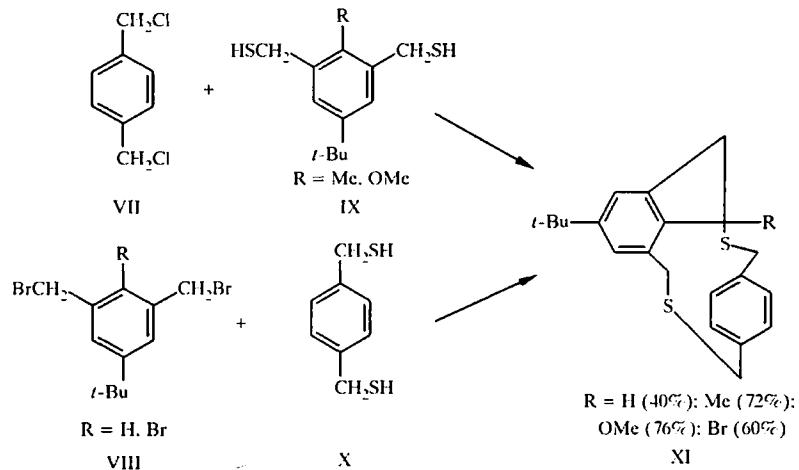
The reaction of  $\alpha,\alpha'$ -dithiocyanato-*o*-xylene with 1,3-dibromopropane in THF makes it possible to obtain a thiacrown with two sulfur atoms – 1,6-dithia-3,4-benzocyclononane (V) [6]:



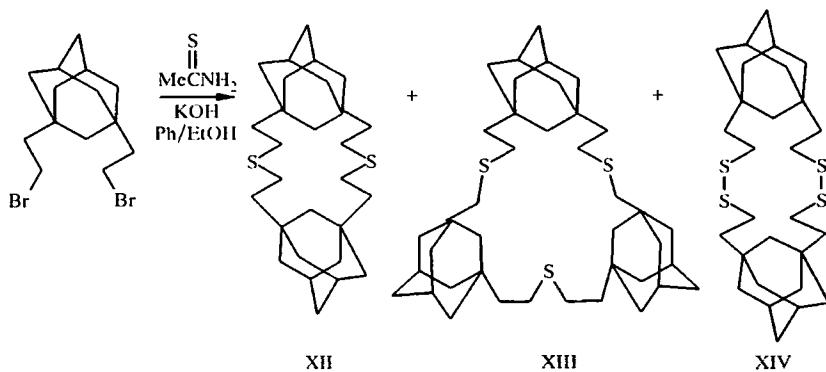
A fundamentally new method for the preparation of 3,8-dibenzo-1,6-dithiacyclodecane (VI) involves the reaction of *o*- $\alpha,\alpha'$ -xylidene dibromide with a dithiol in the presence of boric acid [7]:



The cyclocondensation of bis(halogenomethyl)benzenes VII and VIII with bis(mercaptomethyl)benzenes IX and X under conditions of high dilution in an alcohol solution of alkali in the presence of small amounts of NaBH<sub>4</sub> leads to 6-*tert*-butyl-2,11-dithia[3.3]mercaptocyclophanes XI with yields of 40-76% [8]:



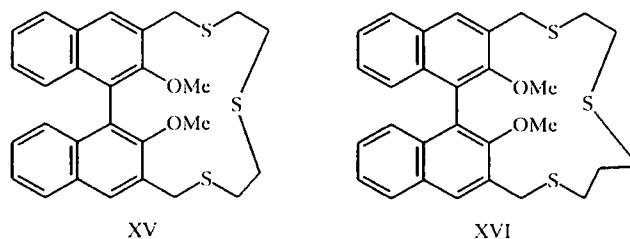
The macrocyclic compound XII with two sulfur atoms was isolated from a mixture of the thiacrowns XII-XIV, obtained as a result of the reaction between 1,3-bis(2-bromoethyl)adamantane and thioacetamide under conditions of high dilution [9]:



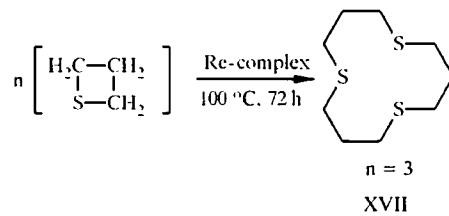
## 2. THIACROWN COMPOUNDS WITH THREE SULFUR ATOMS

The synthesis of nine-membered thiacrowns was until recently a difficult task as a result of the significant difficulties in the closure of the ring. The original synthesis of 1,4,7-trithiacyclononane proposed in [10] made it possible to obtain the compound with a yield of only 0.04%; subsequent researches increased the yield initially to 4.4% [11] and then even to 20% [12]. The described methods do not make it possible to obtain large quantities of the substances, since it is necessary to separate the 1,4,7-trithiacyclononane from its higher analogs and polymers by column chromatography. The cyclization of 2-mercaptoproethyl sulfide in the presence of  $\text{Mo}(\text{CO})_6$  leads to the desired compound with high yields; however, this process takes place in several stages and requires a large number of operations [13]. For this reason, in our opinion, the single-stage synthesis of 1,4,7-trithiacyclononane from 2-mercaptoproethyl sulfide and 1,2-dichloroethane is more attractive. It can be obtained by this method with high yields and without the use of chromatography [14]. Subsequently 9-, 10-, 11-, 12-, 14-, 16-, 18-, and 24-membered crown ethers were obtained with high yields by this method [15].

Thiacrown compounds with three sulfur atoms containing functional groups were obtained from 3,3'-bis(hydroxymethyl)-2,2'-dibromo-1,1'-binaphthyl and 1,4,7-trithiaheptane or 1,4,8-trithiaoctane in DMF with cesium carbonate as template agent. Good leaving groups in this case are chlorine, bromine, mesylate, and others, and this creates wide possibilities for the synthesis of new compounds [4]. The thiacrowns XV, XVI were obtained with yields of 40-74% as a result of this reaction:



A fundamentally new method for the synthesis of thiacrown compounds was developed in 1995 [16]. In the course of the reaction, catalyzed by complexes of transition metals such as rhenium, stoichiometric substitution of dithiols or dithiolates by organic halides occurs. Adams first used such a catalytic process for the synthesis of polyethers XVII with thietane as reagents [17]:

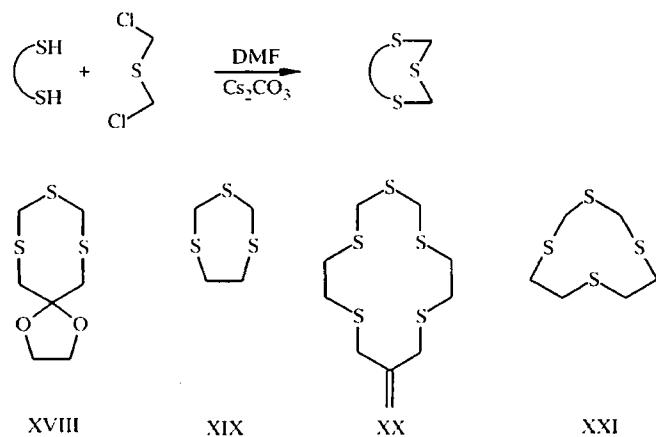


In an earlier paper [18] Adams showed that certain nucleophiles can open thietane rings, and here the sulfur atom is coordinated as a bridge between two metal atoms in a cluster complex. He also found that the complexes  $\text{Re}_3(\text{CO})_{10}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H}_3)$  [17],  $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)$  [19],  $\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H}_4)$  [20], and  $\text{W}(\text{CO})_5(\text{SCH}_2\text{CH}_2\text{CH}_2)$  [21] effectively catalyze the cyclooligomerization of thietane to polythiamacrocycles [22, 23]. The new polyselenomacrocycles 3,3,7,7-tetramethyl-1,5-diselenacyclooctane, 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane, and 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane were obtained in a similar way with the use of Re complexes [24].

The reaction of  $\text{Re}(\text{CO})_9(\text{NCMe})$  and  $\text{W}(\text{CO})_5(\text{NCMe})$  with 3-methylthiobutane ( $\text{SCH}_2\text{CHMeCH}_2$ ) gave the new compounds  $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CHMeCH}_2)$  and  $\text{W}(\text{CO})_5(\text{SCH}_2\text{CHMeCH}_2)$ , which react with 3-methylenethiobutane with the formation of 3,7,11-trimethyl-1,5,9-trithiacyclododecane with fairly high yields. The macrocyclization process includes metal-induced cyclooligomerization with ring opening in three molecules of 3-methylenethiobutane. 3,7,11-Trimethyl-1,5,9-trithiacyclododecane is formed as two isomers – *cis,trans,trans*-3,7,11-trimethyl-1,5,9-trithiacyclododecane and *cis,cis,cis*-3,7,11-trimethyl-1,5,9-trithiacyclododecane – as a result of the different orientation of the methyl substituents in the ring. Small amounts of the higher macrocycles with the general formula ( $\text{SCH}_2\text{CHMeCH}_2$ )<sub>n</sub> ( $n > 3$ ) are also formed in the reaction. Comparison of the two catalysts showed that the rhenium complex had higher activity and selectivity in the formation of 3,7,11-trimethyl-1,5,9-trithiacyclododecane than the tungsten complex [25].

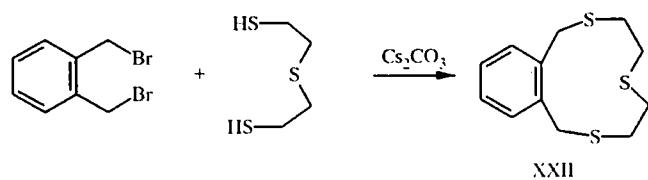
In connection with the need for a systematic study of the conformational effects in thiacycrown compounds it became necessary to develop methods for the synthesis of macrocycles containing the  $-\text{SCH}_2\text{S}-$  fragment. It is well known [26] that the presence of such one-carbon bridges imposes a certain rigidity on the system, leading preferentially to the *cis*-conformation of the sulfur atom in relation to the macrocycle. However, apart from simple systems such as 1,3,5-trithiane and 1,3-dithiane, no serious attempts have been made to obtain thiacycrons containing the  $-\text{SCH}_2\text{S}-$  fragment.

The reaction of bis(chloromethyl) sulfide with  $\alpha,\omega$ -cesium dithiolates leads to the formation of a whole series of new thiacycrons, having methylene "struts" between the heteroatoms:

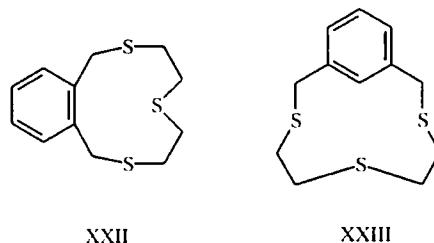


The physical characteristics of the synthesized compounds reflect well the high degree of "rigidity" of the molecules with the  $-\text{SCH}_2\text{S}-$  fragment. The low solubility of 1,3,5-trithiane and 1,3-dithiane in chloroform, methylene chloride, and ethanol also presupposes that the homologous 1,4-dithiane has low solubility in common organic solvents. By analogy compounds XIX and XXI dissolve poorly in organic solvents; moreover, the crown compound XIX decomposes at 150°C without melting. Systems with larger rings – XVIII and XX – are soluble in toluene and methylene chloride, which facilitates their chromatographic purification [27].

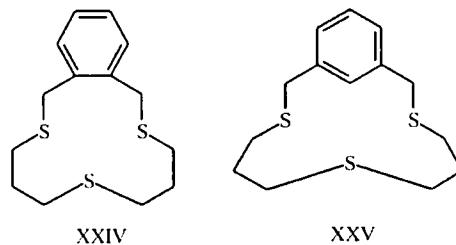
The coordination chemistry of 1,4,7-trithiacyclononane has been the subject of serious investigations, and there now a large number of this thiacycrown complexes with transition metals. Recent investigations on the synthesis of various thiacycrown compounds showed that 2,5,8-trithia[9]-o-benzophane (XXII) can be synthesized with a yield of 90% [28-30]:



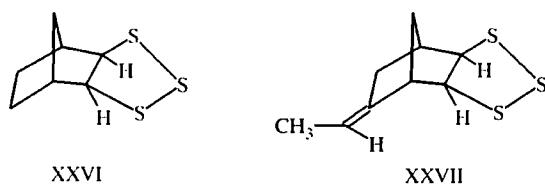
When tricyclophanes with various structures were used, thiacrowns with three sulfur atoms and with *ortho*- and *meta* XXIII substitution of the benzene ring were obtained [31]:



Although it was shown that both these molecules have an exodentate conformation, the *ortho*- and *meta*-substituted structures have different coordinating capabilities. The same authors obtained 2,6,10-trithia[11]-*o*-cyclophane (XXIV) and 2,6,10-trithia[11]-*m*-cyclophane (XXV) with yields of 80 and 90% respectively [28, 30, 33, 34]:

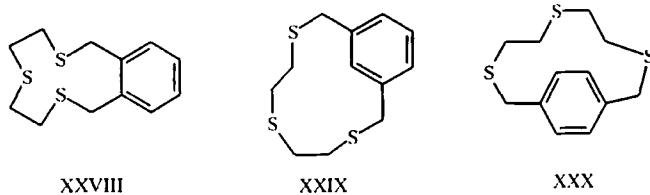
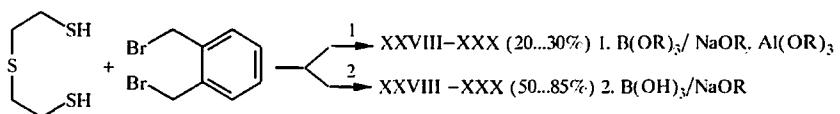


The extension of the known reaction of olefins with elemental sulfur to norbornenes and norbornadienes led to the formation of 3,4,5-trithianes XXVI and XXVII [35]:

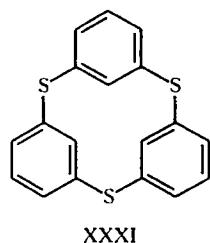


In a more recent paper [33] the reactions of various norbornenes and norbornadienes with sulfur were described. They resulted in the formation of polycyclic compounds containing three and more sulfur atoms in one ring.

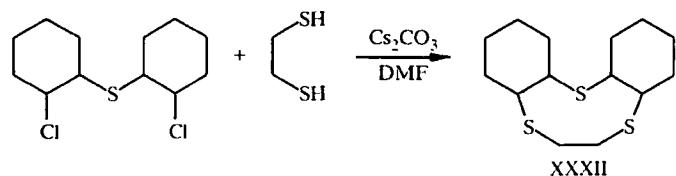
The reaction of a dithiol with  $B(OH)_3$  and a base in methanol followed by the addition of *o*-, *m*-, and *p*-xylylene dibromides led to the selective formation of the *ortho* XXVIII, *meta* XXIX, or *para*-cyclophanes XXX respectively with good yields (70-86%) [7]:



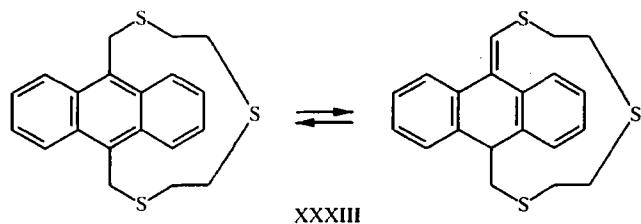
Thiacrowns with various ring sizes and with various numbers of sulfur atoms in the macrocycle were isolated as side products during the synthesis of polyphenylene sulfide from dihalogenobenzenes and sodium sulfide [37]. By the use of 1,3-dihalogenobenzenes in polycondensation it was possible to isolate the cyclic trimer XXXI:



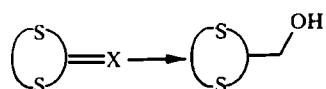
As a result of the reaction of bis(2-chlorocyclohexyl) sulfide with 1,2-ethanedithiol 2,3,8,9-dicyclohexano-1,4,7-trithiacyclononane (XXXII) was obtained [38]:



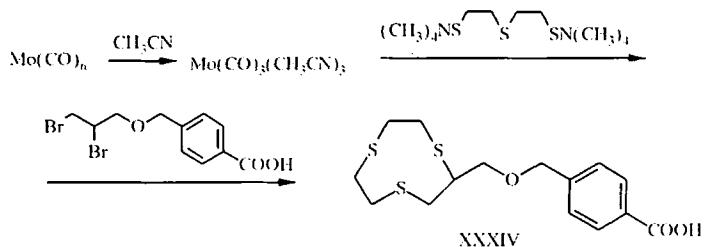
The reaction of 2-mercptoethyl sulfide with 9,10-bis(chloromethyl)anthracene gave a 54% yield of 2,5,8-trithia[9](9,10)anthracenophane (XXXIII), which exists in two tautomeric forms [39]:



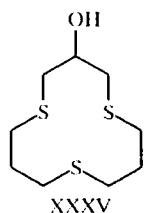
Using of the thiacrown compounds as complexing agents gives the unique possibility to functionalize the macrocycles. Thus, the introduction of alkylidene or keto groups opens up the path to hydroxyl-substituted derivatives of the thiacrowns [40]:



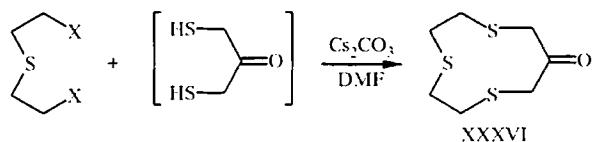
2-(4-Carboxyphenoxy)-1,4,7-trithiacyclononane (XXXIV), which was subsequently used in radiodiagnostics, was obtained with a yield of 8% by this method [41]:



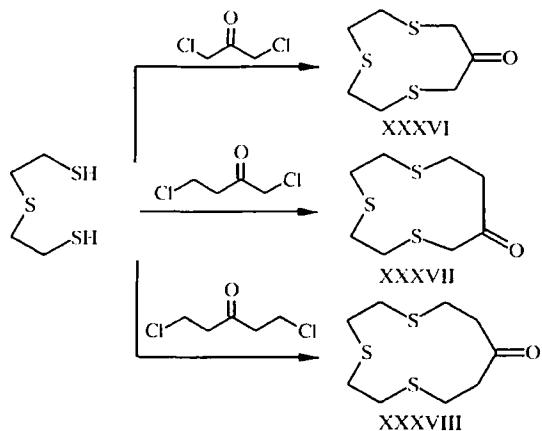
1,4,7-Trihtetan-9-ol (XXXV) was obtained with a 41% yield by the reaction of 2-mercaptoethyl sulfide with 1,3-dichloropropane [42]:



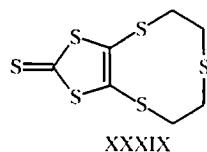
The introduction of a carbonyl group creates possibilities for the functionalization of thiacycrown compounds by means of the Wittig and Grignard reactions or by aldol condensation. Alkanone fragments were used to change the molecular periphery of the macrocycles by means of 1,3-dichloro-2-propanone, 1,4-dichloro-2-butanone, and 1,5-dichloro-3-pentanone. A substantial shortcoming of this method is the need to use a specific dithiol at the final stage of ring closure. An alternative method of introducing the 2-propanone fragment into thiacycrown compounds involves the use of 1,3-dimercaptoacetone as synthon [43]:



The same authors [40] reported a new synthesis of cyclic thiacycrons XXXVI-XXXVIII, containing various alkanone fragments:



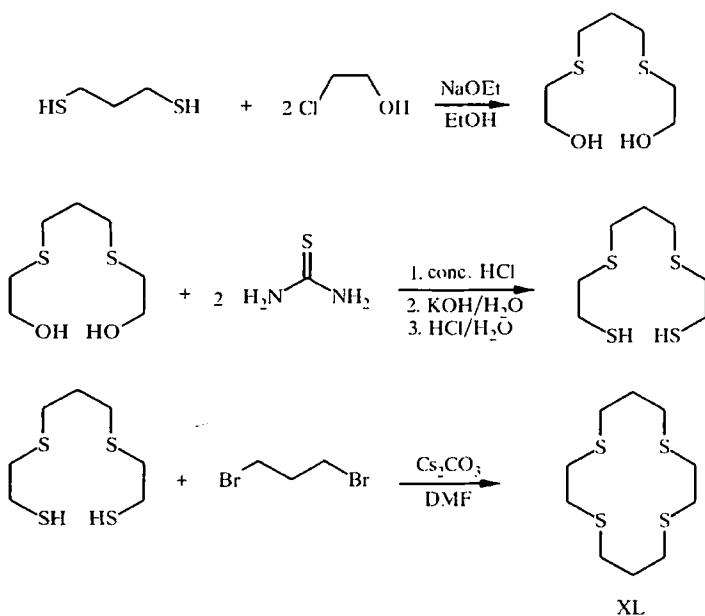
An interesting class of thiacrowns with three sulfur atoms, i.e., 2,5,8,10,12-pentathiabicyclo[7.3.0]dodec-1(9)-ene-11-thione (XXXIX), was obtained by the reaction of disodium 1,3-dithiolc-2-thione-4,5-dithiolate and bis(2-bromoethyl) sulfide [44].



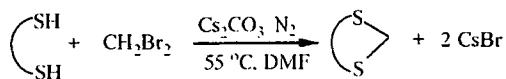
Both polar compounds (acetonitrile and methanol) and nonpolar compounds (toluene and benzene) have been used as solvents [45, 46].

### 3. THIACROWN COMPOUNDS WITH FOUR AND FIVE SULFUR ATOMS

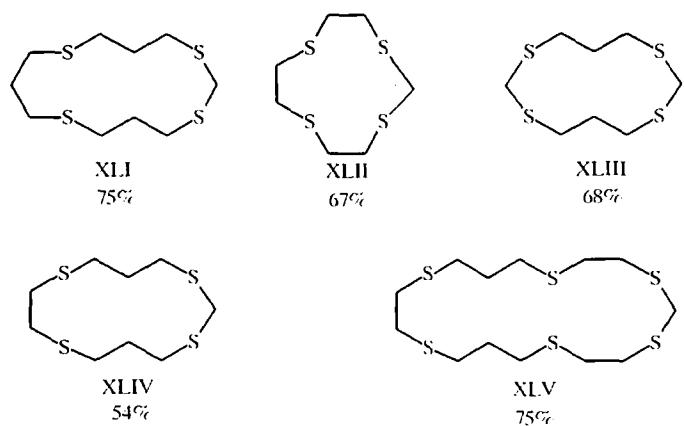
The classical method for the synthesis of macrocyclic sulfides with four sulfur atoms was first described in 1967 [47]. 1,4,8,11-Tetrathiacyclotetradecane (XL) was formed with an overall yield of 60% in three stages with cesium carbonate as template agent:



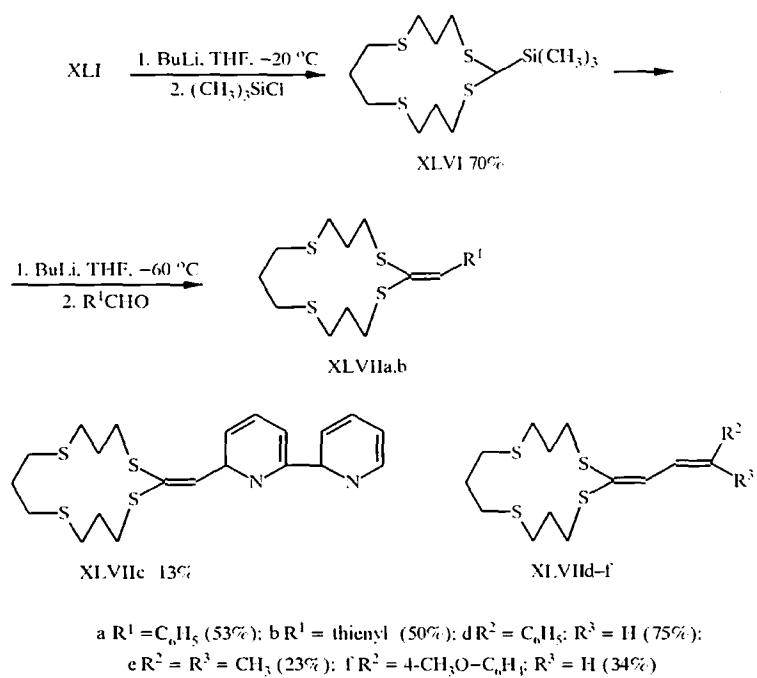
The template method was used for the synthesis of thiacrowns containing thioacetal bonds [48], and this opened up far-reaching possibilities for the functionalization of the described compounds [49]:



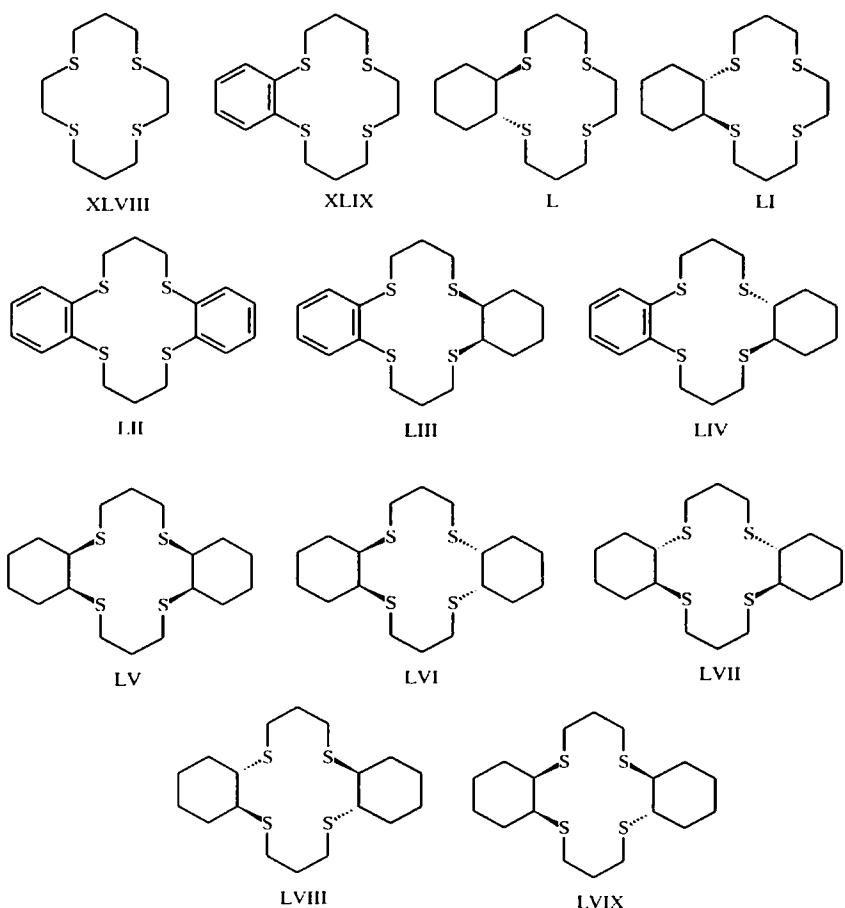
Compounds XLI-XLV were obtained according to the scheme proposed [49]:



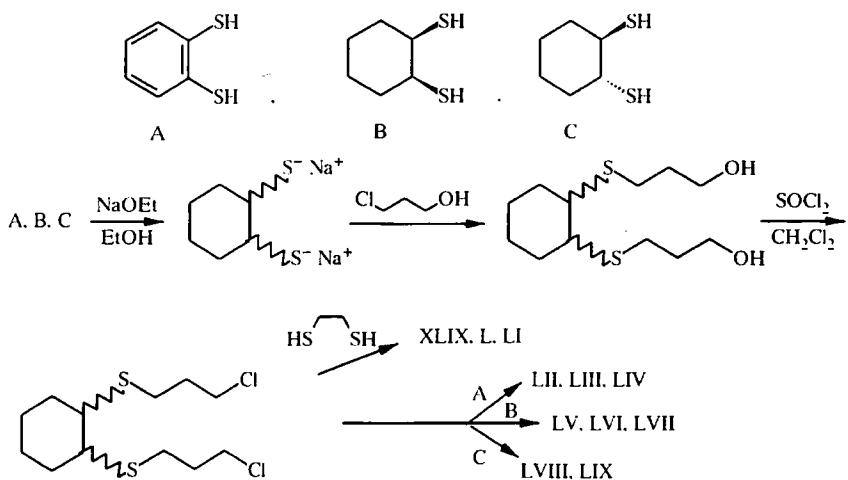
For the functionalization of the thiacrowns compound XLI was submitted to silylation and treatment with BuLi followed by the addition of aldehyde, and this led to the formation of compounds XLVIIa-e:



The work [50] was devoted to the synthesis of all 11 possible derivatives of 14-membered macrocyclic tetraethioethers of 1,4,8,11-tetrathiacyclotetradecane, in which one or both ethylene bonds are substituted by 1,2-phenylene and/or *cis*- or *trans*-1,2-cyclohexylene. All possible combinations of substituents which can promote the preferential existence of the macrocycles in the *endo* conformation XLVIII-VIX are described and characterized.



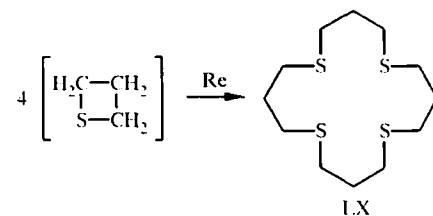
The following scheme illustrates the general strategy of the synthesis.



The classical Williamson condensation of bis(sodiumthiolates) with 3-chloropropanol leads to bis(3-hydroxypropyl) sulfides, which are in turn transformed by the action of thionyl chloride into bis(chloropropyl) sulfides with almost quantitative yields.

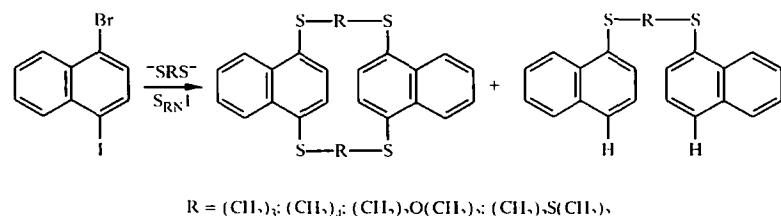
Unlike  $\beta$ -chloro sulfides, the  $\gamma$ -chloro sulfides do not have high toxicity and are significantly less reactive. This feature makes it possible to obtain macrocycles of smaller size, easily separated from high-molecular compounds by chromatography, under the conditions of a template synthesis by the reaction of 1,2-dithiols and bis(3-chloropropyl) sulfides in a large volume of DMF [51].

Another method for the synthesis of macrocycles is the transformation of thietane in the presence of rhenium catalysts [16]:

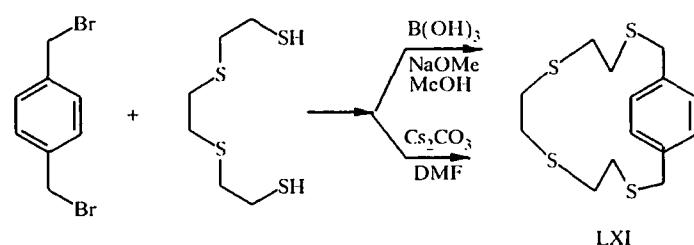


The trirhenium cluster  $\text{Re}_3(\text{CO})_{10}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H}_3)$ , which promotes the cyclooligomerization of thietane to a polythiamacrocycle, was used as catalyst. The reaction of  $\text{Re}_2(\text{CO})_9(\text{NCMe})$  with 3,3-dimethylthietane ( $\text{SCH}_2\text{CMe}_2\text{CH}_2$ ) gave the complex  $\text{Re}_2(\text{CO})(\text{CH}_2\text{CMe}_2\text{CH}_2)$ , which (as found in [52]) reacts in turn with 3,3-dimethylthietane with the formation of 3,3,7,7,11,11-trithiahexamethyl-1,5,9-trithiacyclododecane, 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane, and 3,3,7,7,11,11,15,15,19,19-decamethyl-1,5,9,13,17-pentathiacycloicosane.

A fundamentally new method for the preparation of macrocycles was proposed in 1996 [53]. Some 18-, 20-, and 22-membered heteroaromatic macrocycles were obtained in a single stage by a four-center  $\text{S}_{\text{RN}1}$  reaction between 1-iodo-4-bromonaphthalene and bidentate sulfide anions  $[\text{SRS}]^-$ :



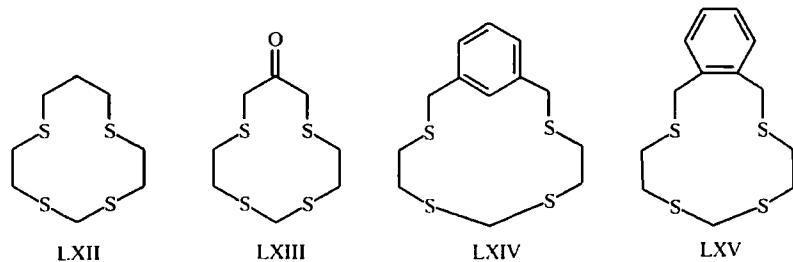
The previously unknown  $\text{S}_4$ -cyclophane LXI was synthesized with a 69% yield by the reaction of *p*- $\alpha,\alpha'$ -xylylene dibromide with 3,6-dithia-1,8-oxanedithiol. Its structure was established by comparison with the spectral data of a sample obtained by template synthesis [7]:



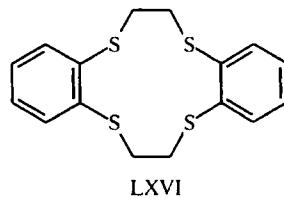
We note that in most cases the use of the template method for the synthesis of sulfur-containing macroheterocycles does not give such a great effect as in the case of oxygen- and nitrogen-containing compounds [44, 45].

Tetrathia-12-crown-4 was obtained [56] with an 84% yield by the addition of the 3,6-dithiaoctane-1,8-dithiol solution and 1,2-dibromoethane in an atmosphere of nitrogen to a suspension of cesium carbonate in DMF.

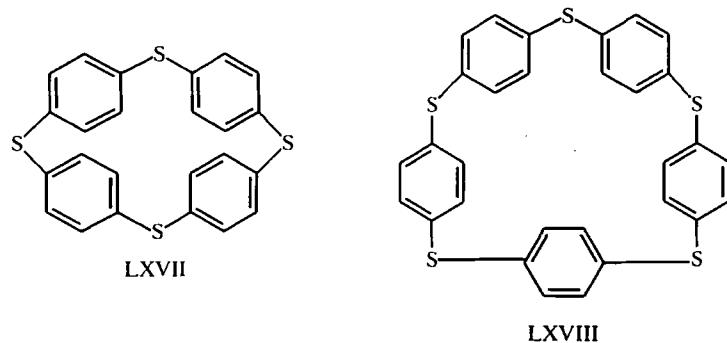
The reaction of 3,5-dithia-1,7-heptanedithiol with various  $\alpha,\omega$ -dihalogeno derivatives, catalyzed by cesium salts, led to the corresponding cyclic thioethers LXII-LXV with yields of 50-70% [57]:



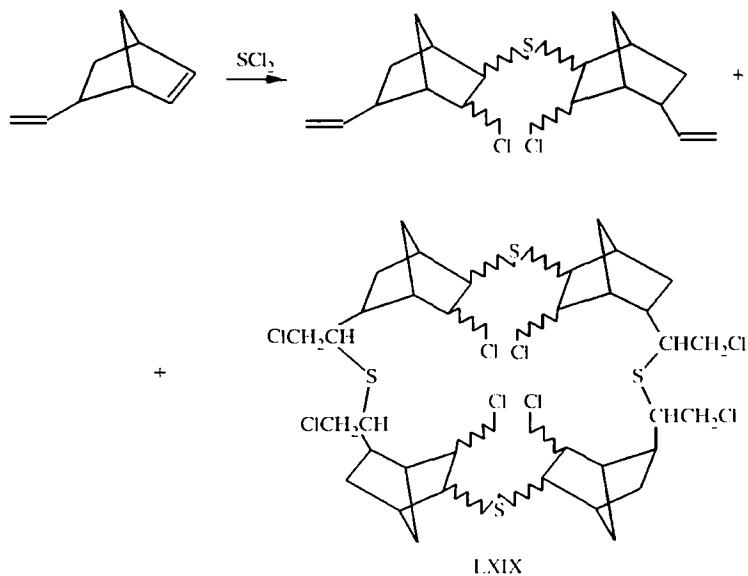
The alkylation of the complex  $[\text{Fe}(\text{CO})(\text{PMe}_3)]$  with 1,2-dithiobenzene by the action of 1,2-dibromoethane in DMF led to a mixture of thiacrown compounds with various structures, from which compound LXVI was isolated [58]:



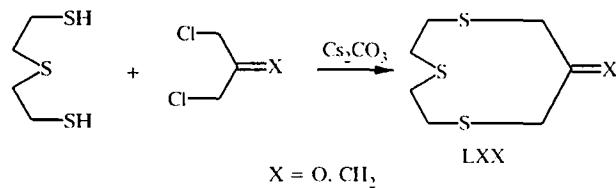
During a study of the 1,4-dichlorobenzene polycondensation with sodium sulfide the individual macrocyclic phenylene sulfides LXVII and LXVIII were isolated from the reaction mixture by fractional extraction and crystallization [37]:



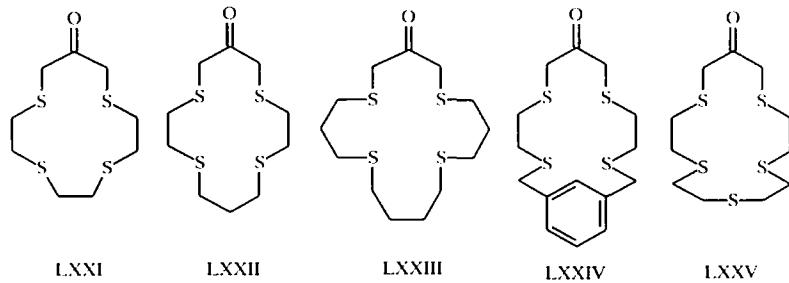
During investigation of the reaction between sulfur halides and various unsaturated compounds it was found that the addition of sulfur dichloride to endo-2-vinylnorbornene led to a mixture of compounds, one of which was a cyclooligo adduct – thiacrown LXIX [59]:



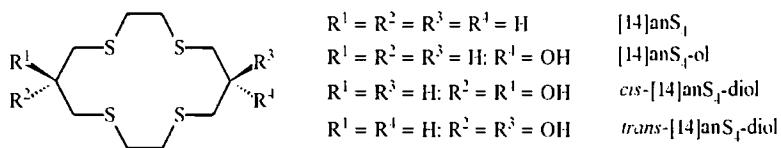
When 1,3-dichloro-2-propanone, 1,4-dichloro-2-butanone, and 1,5-dichloro-3-pentanone were used, a whole series of functionalized sulfides LXX were obtained [40]:



The thiacrowns LXXI-LXXV were synthesized according to the same scheme:

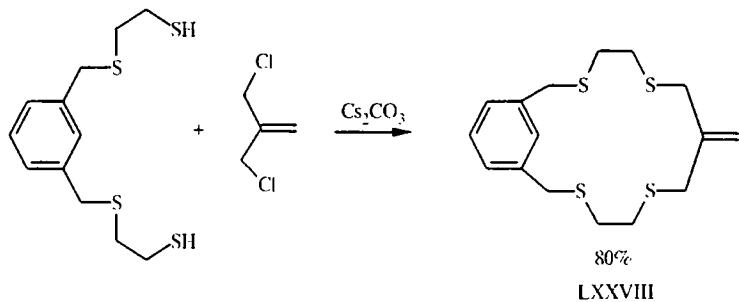


Of great interest are the water-soluble derivatives of 14-membered macrocyclic thiacrowns, such as 1,4,8,11-tetrathiacyclotetradecane. Earlier [60] it was shown that of all the aquametallic ions only Cu(II), Pd(II), Ag(I), and Hg(II) have affinity to cyclic tetrathiacrown compounds in aqueous solutions. Therefore the synthesis of 1,4,8,11-tetrathiacyclotetradecanol and the corresponding diol afford the possibility of extending the application limits of thiacrown compounds as extraction agents. The desired substances were obtained by substitution of the polypropylene bonds at the  $\beta$ -carbon atom in 1,4,8,11-tetrathiacyclotetradecane ( $[14]anS_4$ ) by a hydroxy group with the formation of  $[14]anS_4$ -ol LXXVI and  $[14]anS_4$ -diol LXXVII respectively [61]:

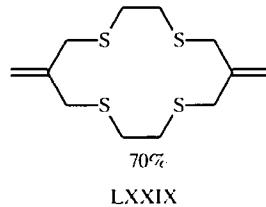


LXXVI. LXXVII

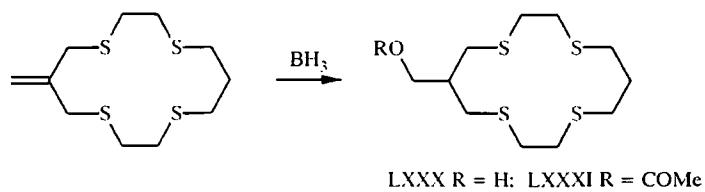
The introduction of functional groups in the synthesis of thiacrowns with four sulfur atoms opens up the way to the production of new macrocycles LXXVIII [1]:



Compound LXXIX was synthesized in the same way:

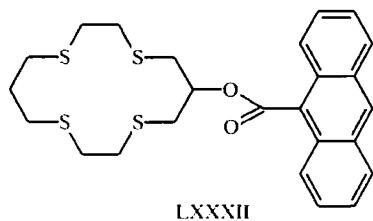


The hydroboronation of 3-methylene-1,5,8,12-tetrathiacyclotetradecane followed by oxidation with hydrogen peroxide and acetylation led to the formation of a macrocycle with a hydroxy group in the side chain LXXX and LXXXI:

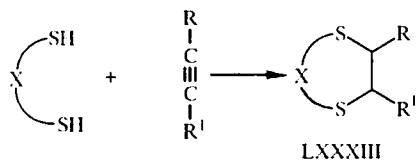


The first of the obtained alcohols has unusual properties; it is moderately soluble in water, whereas its unsubstituted analogs do not dissolve at all; the same property also applies to its salt with Cu(II). To summarize briefly the investigations in [1] and [61] it can be noted that moderate solubility in water is a common feature of hydroxy-substituted thiacrown ethers. This in turn enhances their practical importance for the extraction of the ions of heavy metals from aqueous solutions.

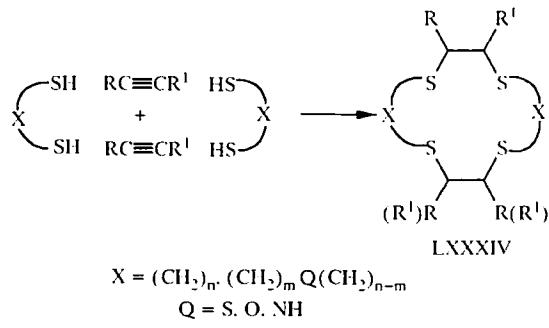
A new type of thiacrown compound with an ester group in the side chain was obtained by the treatment of 1,4,8,11-tetrathiacyclotetradecan-6-ol with sodium hydride in DMF followed by the addition of anthracene-9-carbonyl chloride. 1,4,8,11-Tetrathia-6-cyclotetradecylanthracene-9-carboxylate (LXXXII) was obtained with a 44% yield [62]:



A new approach to the construction of thiacrowns, based on the simple single-stage "assembling" of such compounds from dithiols and alkynes through homolytic cycloaddition [64] was recently proposed [63]. It was found that the heterocyclization of alkynes with 1,2-, 1,3-, and other  $\alpha,\omega$ -dithiols in the presence of free radical initiators gave 6- and 7-membered [65], 8-membered [66], and 9-membered [67] 1,4-dithiacyclanes:

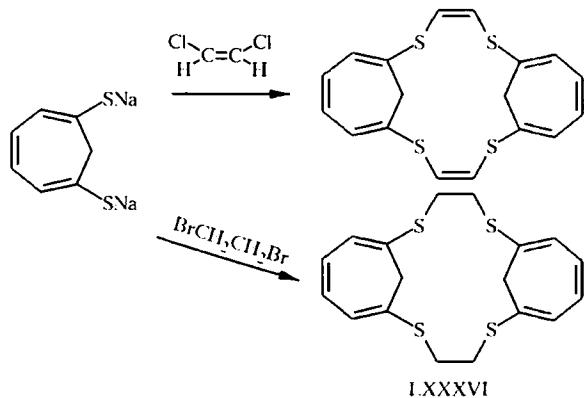


This approach was extended successfully to the "assembling" of thiacrowns differing in the size of the ring, the number and type of heteroatoms (sulfur, oxygen, nitrogen), and their mutual arrangement. 12-Membered thiacrown ethers were obtained [68] according to the scheme given above, in which 14-membered [69], 16-membered [66], and 18-membered [67] macro compounds LXXXIV were formed as the products of homolytic [2+2]-cycloaddition:

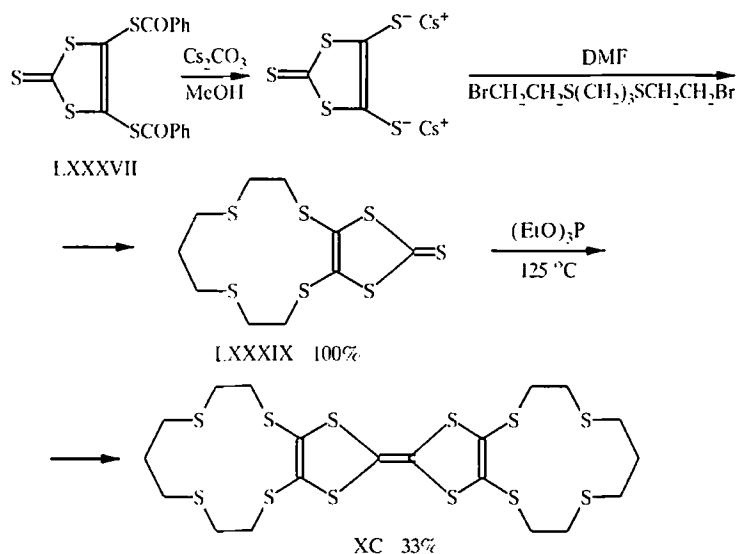


The mechanism of the free radical addition of thiols to alkynes was discussed in detail [70].

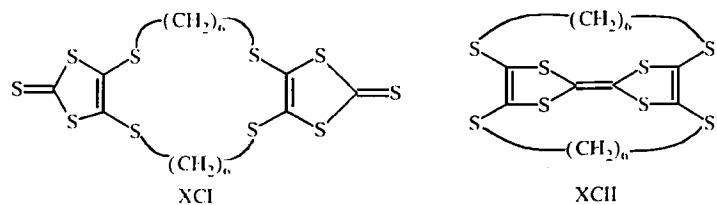
Thiacrown compounds containing cyclopentatriene fragments were first obtained from dithiocyanate, reduced to dithiolate, which reacts with *cis*-1,2-dichloroethylene and 1,2-dibromoethane, forming 2,5,12,15-tetrathia[4.4.1.1<sup>6,11</sup>]docosa-3,6,8,10,13,16,18,20-octaene (LXXXV) and 2,5,12,15-tetrathia[4.4.1.1<sup>6,11</sup>]docosa-6,8,10,16,18,20-hexaene (LXXXVI) with yields of 13 and 7% respectively:



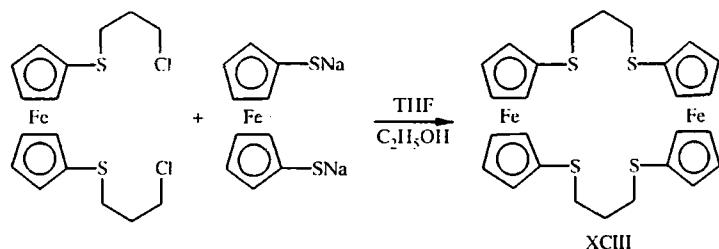
Treatment of the dithiolate dianion LXXXVIII with 1,2-dibromo-3,7-dithianone gave 8H-5,6,9,10,12,13-hexahydro-1,3-dithiolo[4,5-*e*][1,4,7,10]tetrathiacyclotridecene-2-thione (LXXXIX), which can be converted into the tetrathiifulvalene derivative – bis(8H-5,6,9,10,12,13-hexahydro-1,3-dithiolo[4,5-*e*]-[1,4,7,10]tetrathiacyclotridecen-2-ylidene) (XC) [72].



The thione XCI was obtained in a similar way, and its intramolecular cleavage led to compound XCII [73]:

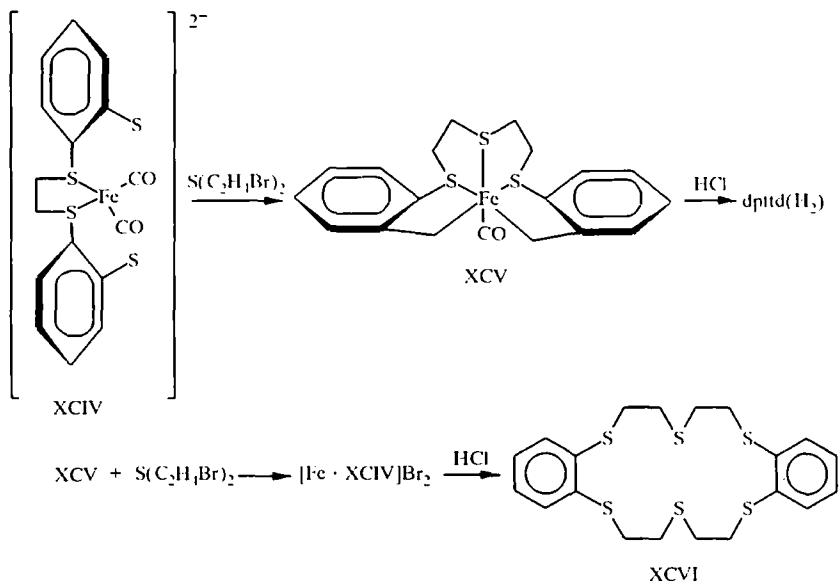


The complexes of transition metals with thioether ligands are of great interest in connection with coordination chemistry. In coordination and organometallic chemistry special attention has been paid to the complexes of the metals with macrocyclic polythioethers, in which an additional transition metal is included in the main chain [74, 75]. Such organometallic ligands provide a good starting material for the synthesis of heterobimetallic complexes, having different catalytic activity and unique reactivity. Thiamacrocycles condensed with two ferrocenes are of undoubtedly interest in the investigation of metal–metal interactions. One such macrocycle was obtained by the addition of sodium ferrocene-1,1'-dithiolate and 1,1'-bis(3-chloropropylthio)ferrocene solutions in THF with the same rates to a large quantity of boiling ethanol. After treatment of the reaction mixture 1,5,16,20-tetrathia[5.5]ferrocenophane (XCII) was obtained with a yield of 40% [76]:

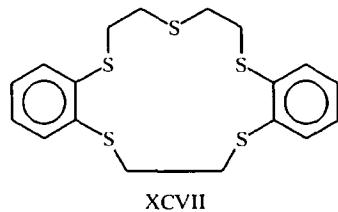


#### 4. THIACROWN COMPOUNDS WITH SIX AND MORE SULFUR ATOMS

The methods for the synthesis of 18- and 24-membered thiacrowns containing six sulfur atoms are similar to those described earlier for the production of the compounds containing two, three, and four sulfur atoms. It is necessary to mention especially the method proposed in 1988 [77], from which it follows that the treatment of *cis*-[Fe(CO)<sub>2</sub>(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> (XCIV) with dibromoethyl sulfide in THF leads to [Fe(CO)(dpttd)] (XCV), where dpttd = 2,3,11,12-dibenzo-1,4,7,10,13-pentathiatridecane(2-). Further alkylation with S(C<sub>2</sub>H<sub>4</sub>Br)<sub>2</sub> leads after hydrolysis to dibenzo-18-crown-S6 (XCVI) with a yield of 68%:



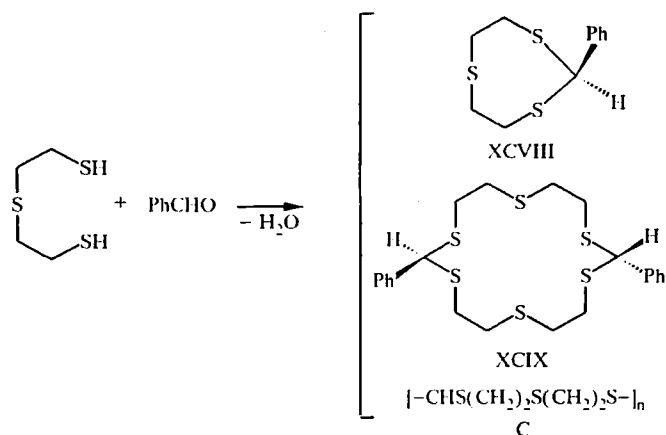
The alkylation of [Fe(CO)<sub>2</sub>dttd] [dttd<sup>2-</sup> = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2-)] by the action of S(C<sub>2</sub>H<sub>4</sub>Br)<sub>2</sub> with boiling leads to the formation of dibenzo-15-crown-S5 (XCVII) with a yield of 20%:



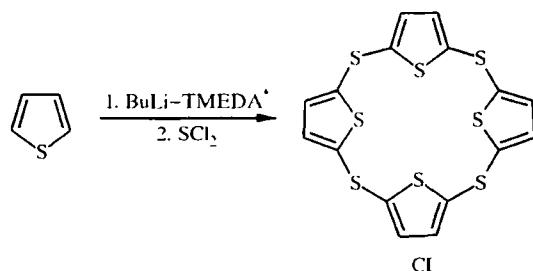
Thiacrown compounds containing thioacetal bonds are of great practical interest. Only the "mini" ring of 1,3,5-trithiane has been studied comprehensively [78]. 1,3,6,9,11,14-Hexathiacyclohexadecane and 1,3,5,7,9,11-hexathiacyclododecane are typical examples of the macrocycles [79]. The synthesis of 1,3,5-trithiacycloheptane and its analogs using cesium thiolates, where the thioacetal group is transformed into a component of the chain, was described [80]. The presence of the thioacetal group opens up the way to further functionalization of the ring using carbanion chemistry [81, 82].

When 2,2'-thiodiethanethiol and benzaldehyde were boiled in benzene with TsOH the polymer C, the monomer XCVIII, and the dimer XCIX were obtained with yields of 81, 9, and 10% respectively.

It is possible to increase the yield of the reaction products (18-membered thiacrowns) substantially by conducting a stage synthesis, including compounds containing a hydroxyl group and chlorine as intermediates. The thiacyclophanes 2,5,8,17,20,23-hexathia[9.9]-*m*-cyclophane and 2,5,8,17,20,23-hexathia[9.9]-*o*-cyclophane were obtained as a result of this process with yields of 81 and 92% respectively [83].

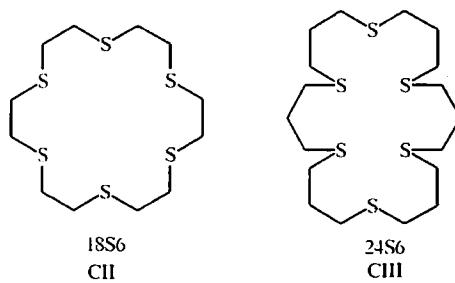


An interesting type of compound similar in structure to the thiacrowns is the thiocalixarenes. The first thiocalix[4]arene Cl was isolated in small amounts from the reaction products of thiophene with sulfur dichloride [84]:



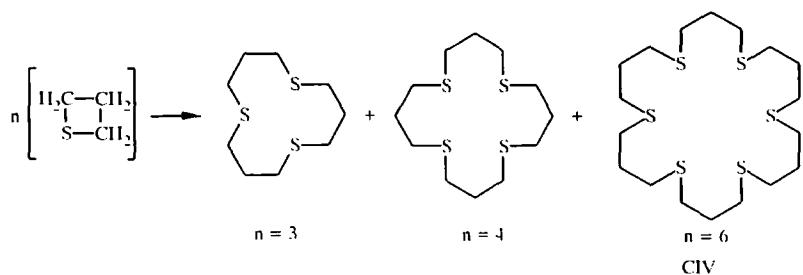
The process of the development of a reliable method for the synthesis of 18-membered thiacrowns with good yields has gone through several stages. In 1934 an 18-membered thiacrown compound was obtained with a yield of 2% [85]. In 1974 the yield was increased to 33%, but this method required the use of yperite [86]. Since cesium salts began to be used for cyclization in the synthesis of thiacrowns, the methods proposed in [87] have brought a turn around in the strategy for the preparation of 18-membered thiacrown ethers.

The slow addition of the 3-thiapentane-1,5-dithiol solution and 1,11-dichloro-3,6,9-trithiaundecane to a suspension of cesium carbonate in DMF gave the thiacrown CII with a yield of 80%; the thiacrown CIII was obtained similarly with a good yield [88]:

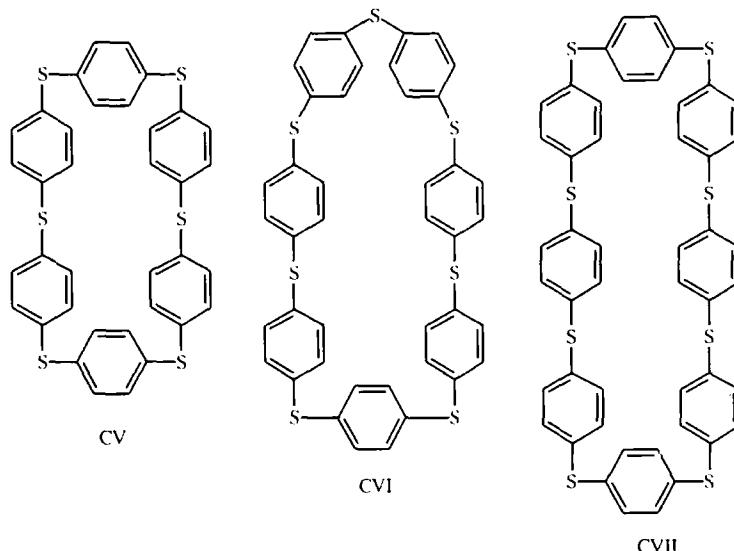


As already mentioned [57], if thietanes are used as reagents with metal-complex catalysts it is possible to obtain thiacrown compounds with various structures, including those of the CIV type:

\* TMEDA is tetramethylethylenediamine.

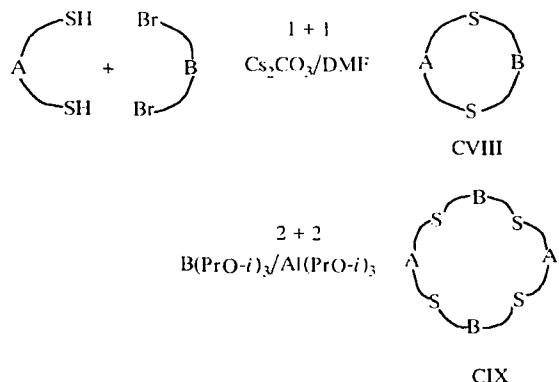


The individual macrocyclic phenyl sulfides CV-CVII were isolated as a result of the polycondensation of 1,4-dichlorobenzene with sodium sulfide followed by fractional extraction and crystallization [37]:



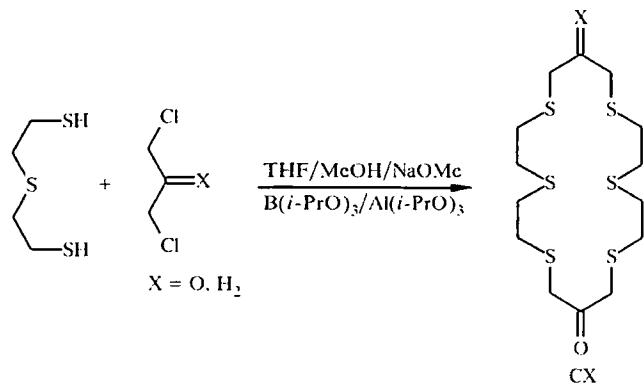
The predominant compound in the macrocyclic fraction was a hexameric ring.

As already mentioned above, the reaction of a dithiol with various dihalide derivatives in the presence of cesium carbonate (in some cases sodium carbonate) gives rise to the formation, mainly, of [1+1]-cyclic polyethers CVIII [47, 48]. In the presence of  $(i\text{-PrO})_3\text{B}/(i\text{-PrO})_3\text{Al}$ , however, the products of [2+2]-cyclization CIX are formed in some cases. Apart from the high yields, the advantage of these methods is the possibility of using them for the synthesis of complex molecules containing carbonyl groups or double bonds [7]:

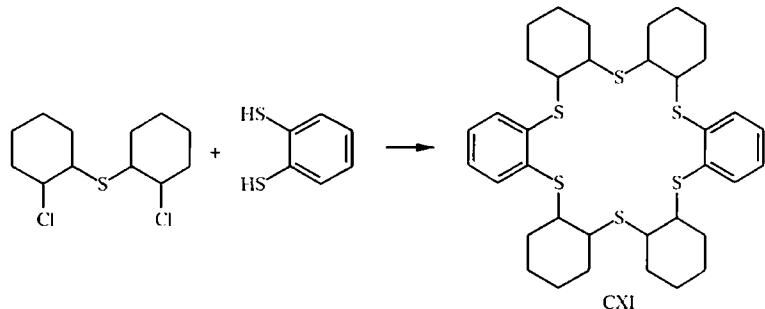


The region for application of the [2+2] model is fairly narrow and is restricted to the use of molecules containing two or three carbon atoms. Thus, the reaction of 3-thiapentane-1,5-diol with 1,3-dichloroacetone or 1,3-dibromopropane by the action of a 5:1  $(i\text{-PrO})_3\text{B}/(i\text{-PrO})_3\text{Al}$  mixture leads to the formation of

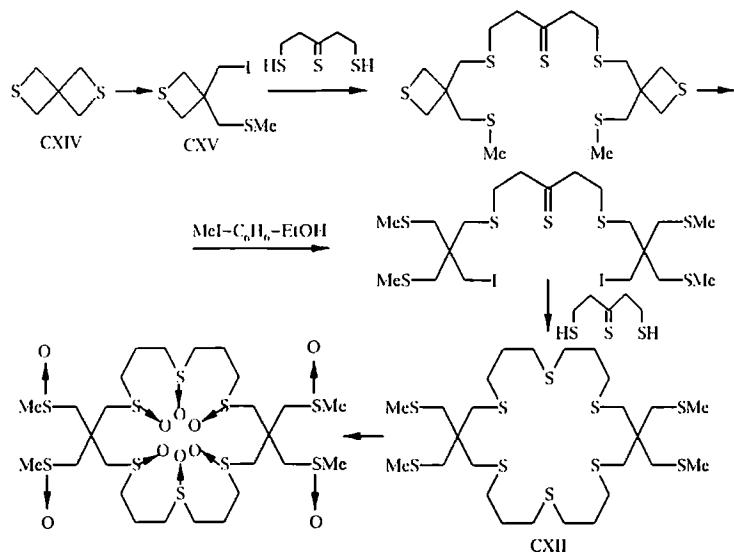
1,4,7,11,14,17-hexathia-3,13-dioxooctadiene and 1,4,7,11,14,17-hexathiaoctadiene respectively. The [1+1]-cyclization products CX were found in amounts of less than 5%:



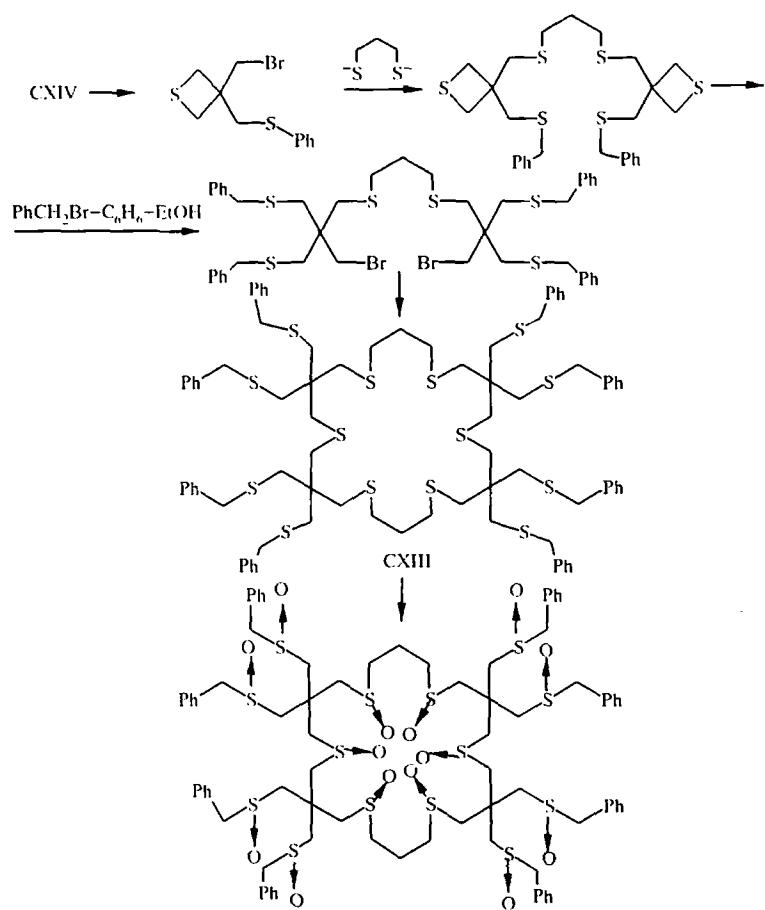
In the reaction of bis(chlorocyclohexyl) sulfide with 1,2-dimercaptobenzene 2,3,8,9,11,12,17,18-tetracyclohexano-5,6,14,15-dibenzo-1,4,7,10,13,16-hexathiacyclooctadecane (CXI) was isolated with a yield of 19% [38]:



To obtain polysulfoxides from macrocyclic thiacrowns it was proposed to use the standard method for the oxidation of sulfur compounds – with 30% hydrogen peroxide in acetic acid [89]. An alternative method for the synthesis of macrocyclic thiacrown compounds with side functional groups can be illustrated by the following scheme:

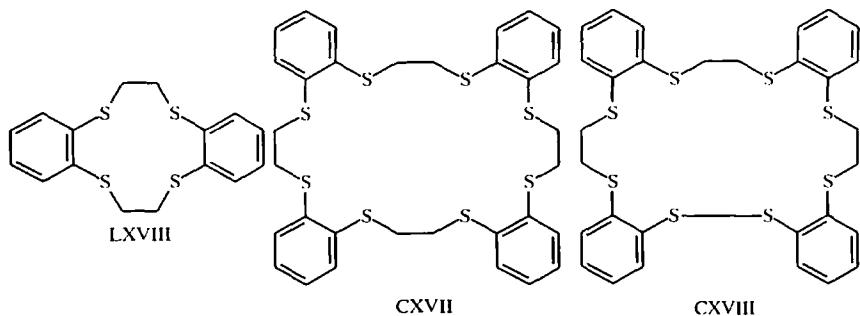


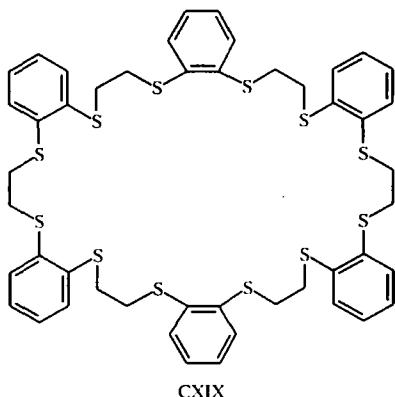
New macrocyclic polythioethers with side alkylthio groups CXII and CXIII were obtained through the thietanes CXV and CXVI, starting from 2,6-dithiaspiro[3.3]heptane CXIV, which is easily formed [89] in the reaction of 1,3-dibromo-2,2-bisbromomethylpropane with sodium sulfide.



The macrocyclic polythioether CXIII was also obtained starting from the spiroheptane CXIV and benzyl bromide.

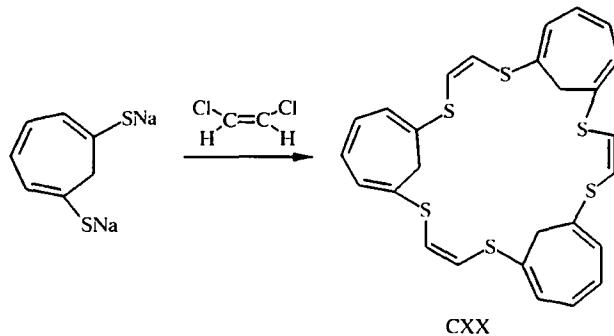
A mixture of sulfur-containing macrocycles with a large number of sulfur atoms is formed during the alkylation of  $[\text{Fe}(\text{CO})\text{P}(\text{Me})_3\text{S}_4]$  with 1,2-dibromoethane in DMF [48]:



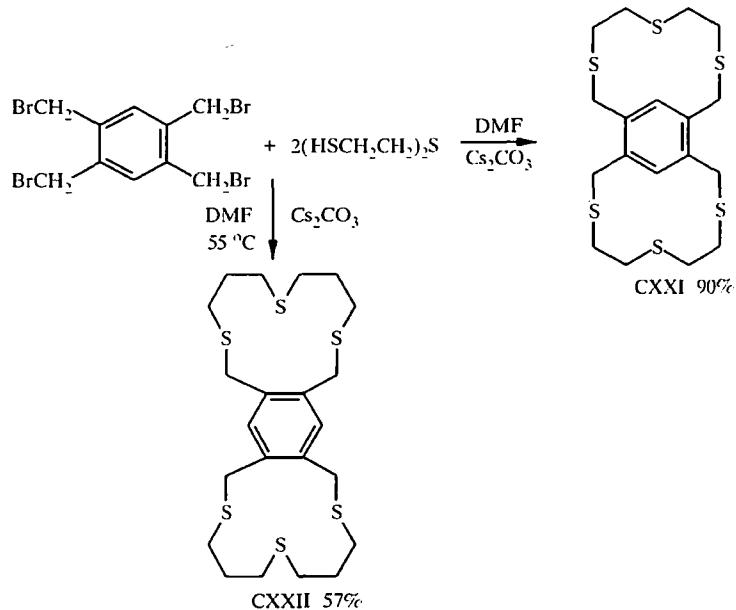


In this case the metal-carbonyl fragment acts as template agent.

As already mentioned the first thiacrown compounds containing cycloheptatriene blocks were obtained by the reaction of cycloheptatriene dithiocyanate, reduced to the dithiolate, with *cis*-1,2-dichloroethylene [72]. As a result of this reaction 2,5,12,15,22,25-hexathiatetracyclo[24.4.1<sup>6,11</sup>]tritriaconta-3,6,8,10,13,16,18,20,23,26,28,30-dodecane (CXX) was obtained with a yield of 11%:

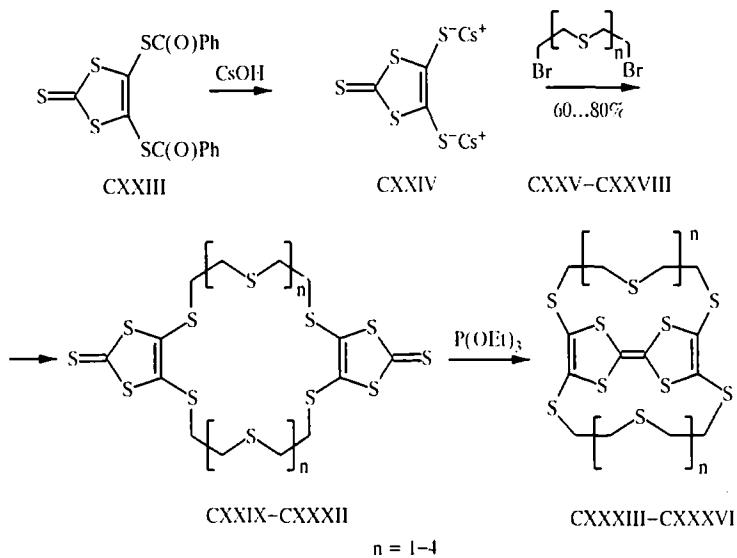


The bisthiacrown compound CXXII was obtained as a result of the reaction of one mole of the tetrabromide with two moles of the dithiol under the conditions of high dilution in DMF [34]:

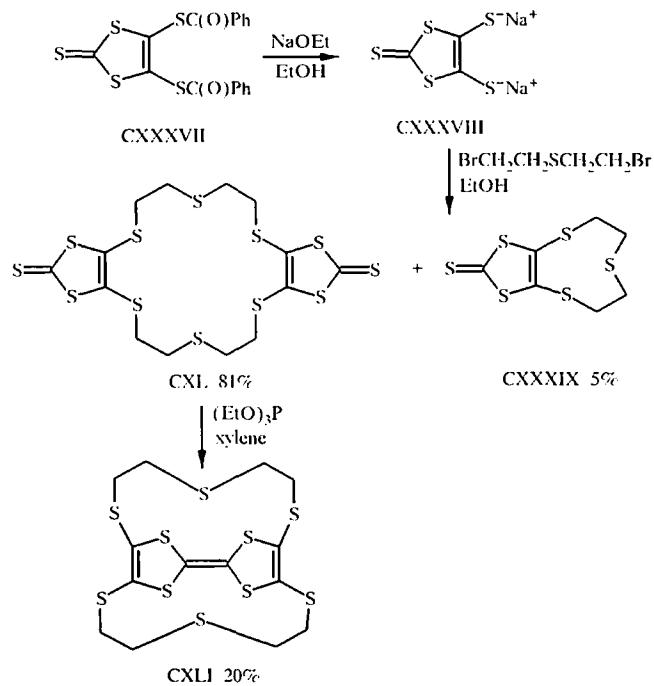


In another paper [90] these authors reported on the selectivity of the reaction, which leads exclusively to the thiacrown CXXI.

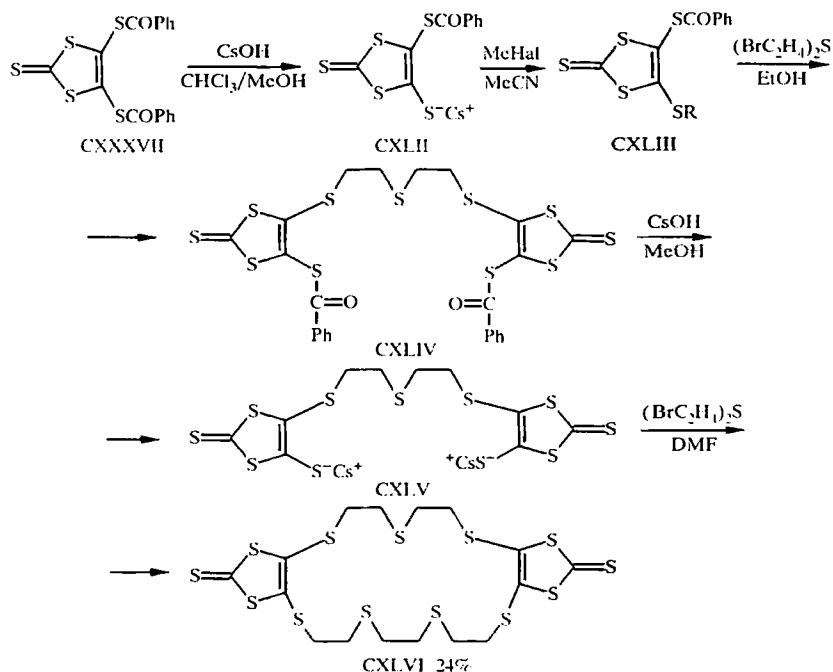
In 1979 the synthesis of a benzoyl thioether by the reduction of carbon disulfide by an alkali metal in DMF was described [91]. The reaction of dicesium 1,3-dithiole-2-thione-4,5-dithiolate (CXXIV), formed during cleavage of compound CXXIII by cesium hydroxide [92], with the dibromides CXXV-CXXVIII in DMF quickly gives a reaction product in the form of the yellow thiacrown compounds CXXXIX-CXXXII with yields of 60-80%. The intermolecular cleavage of the dithiones CXXIX-CXXXII in pure triethyl phosphite leads to the tetrathiafulvalene derivatives CXXXIII-CXXXV with moderate yields and trace quantities of compound CXXXVIII [93]:



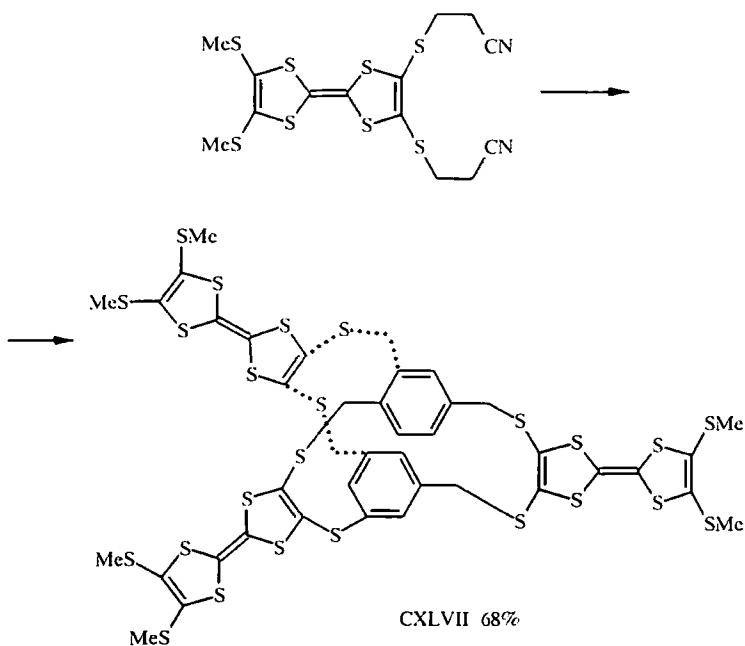
The condensation of the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion CXXXVIII with 1,5-dibromo-3-thiapentane gave the macrocycle CXL, which can be converted into the tetrathiafulvalene macrocycle CXLI by treatment with triethyl phosphite [94]:



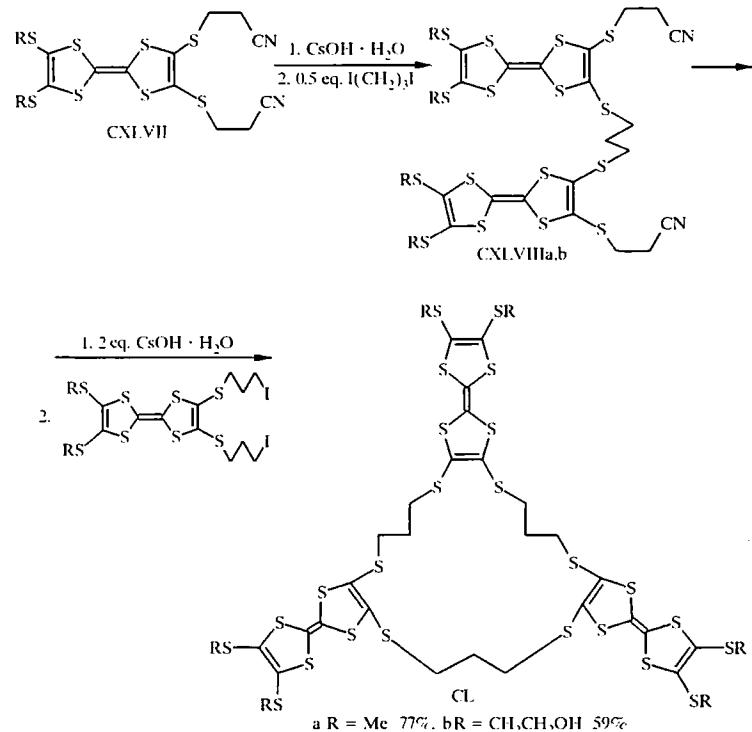
A new type of tetrathiafulvalene was synthesized from 1,3-dithiole-2-thione-4,5-dithiolate [95]. The addition of alkyl dihalides, such as 1,5-dibromo-3-thiapentane, to an alcohol solution of compound CXLII led to the formation of compound CXLV, the treatment of which with cesium hydroxide in methanol led smoothly to the thiacrown CXLVI with a yield of 76%. On account of the good solubility of the salt CXLVI in water, methanol, ethanol, and acetonitrile and high reactivity its use opens up the way to the synthesis of new thiacrown compounds [96, 97] and bioinorganic model compounds [98].



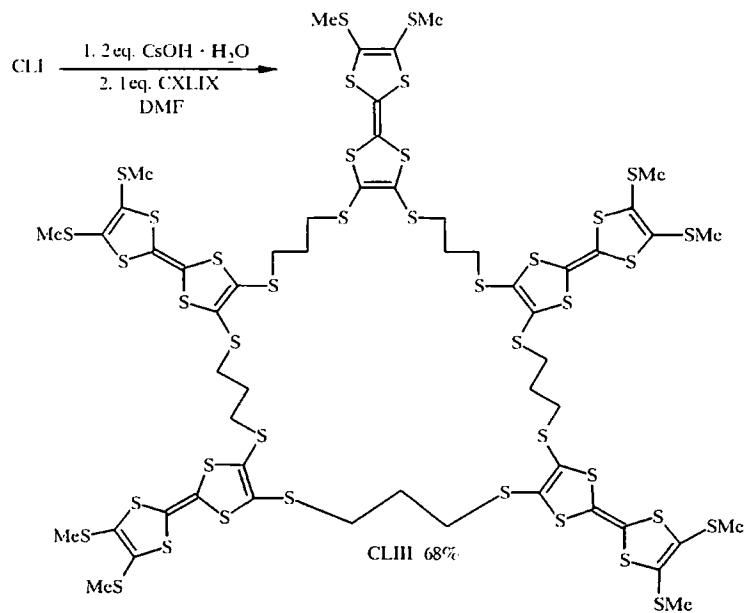
A series of new macrocyclic tetrathiafulvalenes with three tetrathiafulvalene bridges was obtained under the conditions of high dilution using selective protection of the tetrathiafulvalenethiolates by cyanoethyl groups, which were subsequently removed. The reaction was carried out by a one-pot process [99]:

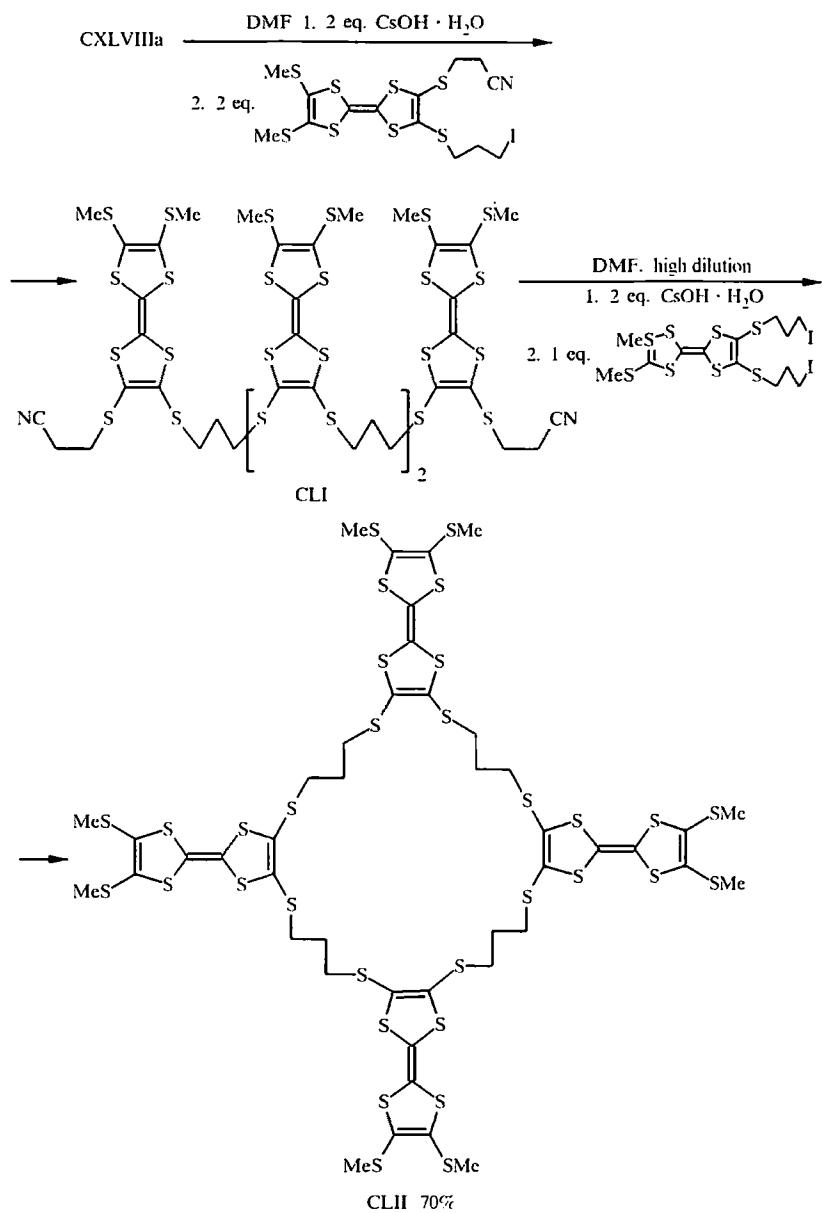


Macrocyclic tetrathiafulvalene derivatives containing more than one tetrathiafulvalene fragment have attracted great interest from investigators in recent years on account of their possible use in materials science. This proposal was motivated by the fact that tetrathiafulvalene derivatives with two or more donating atoms facilitate the formation of charge-transfer complexes and give the possibility to control the stoichiometry of the reaction. The properties of tetrathiafulvalene as a mobile, stable, and electron-donating particle make it possible to include it in macrocyclic systems that can act as receptors for electron-deficient compounds. Tris(tetrathiafulvalenes) CL were synthesized from compound CXLVII by the standard procedure for the preparation of thiacrowns [100]:



Tetrakis(tetrathiafulvalene) CLII and pentakis(tetrathiafulvalene) CLIII were obtained in a similar way with high yields:





The presented material shows that there are various approaches to the synthesis of thiacrown compounds with various macrocycle sizes and various number of sulfur atoms. Such a multitude of methods makes it possible to select the optimum method for each specific case to secure the synthesis of a macrocycle with good complexing characteristics.

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