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SYNTHESIS OF OXATHIACROWN COMPOUNDS BY THE REACTIONS OF SULFUR DICHLORIDE WITH UNSATURATED COMPOUNDS AND THEIR EXTRACTION CHARACTERISTICS. (REVIEW)*

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Published data of the last 10-15 years on the use of the reactions of sulfur dichloride with various unsaturated compounds for the synthesis of oxathia- and thiacrown compounds and study of their extraction characteristics toward various transition and heavy metals are reviewed. Some previously unpublished results and associated experimental data are also included.

Keywords: sulfur dichloride, oxathiacrown compounds, metals, extraction.

Crown ethers and their heteroanalogs have been subjects of intense study by chemists over the last 30 years. This interest is due not only to the fact that such compounds present a variety of structural possibilities but also to their great potential as molecular receptors during the transport of ionic particles and organic molecules in living organisms and also as active components of ion-selective electrodes. Sulfur-containing macrocycles and their open-chain analogs, called podands, occupy a special position among such substances on account of their unique ability to act as ligands for selective complexation with transition and heavy metals such as Cu(II) [1]. Such characteristics of these compounds create excellent potential for modelling biological systems and processes involving organosulfur compounds.

From the time of the first papers by Pedersen, published in 1967 [2], various approaches have been proposed for the production of oxathia- and thiacrowns, and the most widely used of them is the reaction between dihalogen derivatives and the corresponding glycols and dithiols or their tosylates [3-6]. Three methods are used most often in the synthesis of macrocycles. The first (the template method), in which the metal cation serves a matrix for the assembly of the macrocycle from the initial fragments, gives good results in the production of crown ethers. The Cs^+ cation is used as alkali-metal cation, and DMF is used as solvent [7, 8].

Another widely used method of "assembly" of a sulfur-containing macrocycle is the high dilution method, in which the lowest concentration of reagents with which it is possible to direct the process toward intramolecular cyclization and to suppress intermolecular interactions is created during the reaction [9]. The method can only be used for rapid processes, and highly active reagents are therefore used for it.

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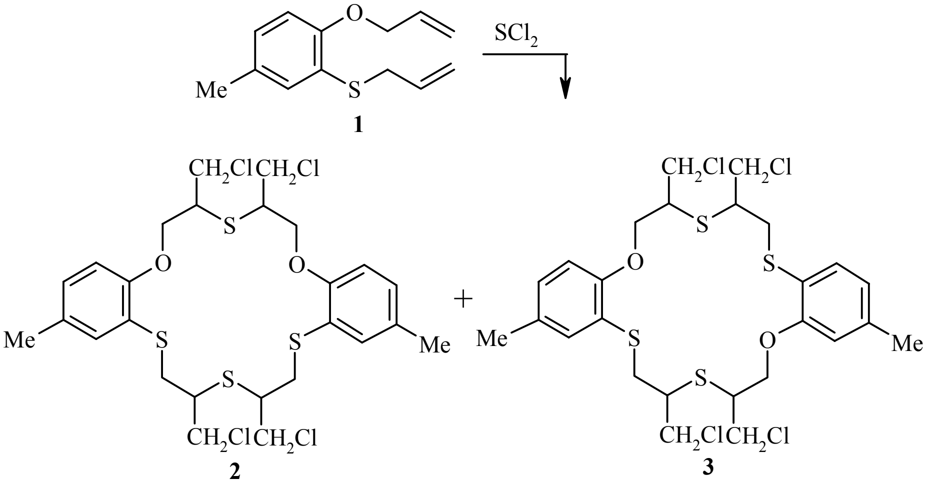
The conformational control method can be used in cases where the existence of several conformations, only one of which is active, is possible for the initial reagents under the reaction conditions [10]. If the concentration of the active component is low, cyclization can be conducted with high concentrations of the initial reagents and in some cases even without a solvent.

Since the reaction of the dihalogen derivatives and dithiols presents wide possibilities for varying the size of the macrocycle and the number of heteroatoms in it and also for realizing stereoselective and stereocontrolled synthesis, dihalogen derivatives already containing sulfur atoms in the carbon chain were used for the synthesis of the thiacrowns. The most accessible of this type of compound are the β,β-dichloro sulfides, formed as a result of the addition of SCl_2 to olefins with various structures [11]. The reaction of SCl_2 with olefins and other organic compounds can be used successfully for the synthesis of various heterocyclic compounds [11, 12].

The reaction of sulfur dichloride with the diallyl ethers of glycols and mercaptophenols, with the allyl ethers of phenols and allyl aryl sulfides, and with cycloolefins has been used for the production of sulfur-containing macrocyclic oxathia- and thiacrowns by the reaction of sulfur dichloride with unsaturated compounds. In the last two cases the dichloro sulfides were brought into reaction with dithiols and glycols, resulting in the formation of the macrocycles.

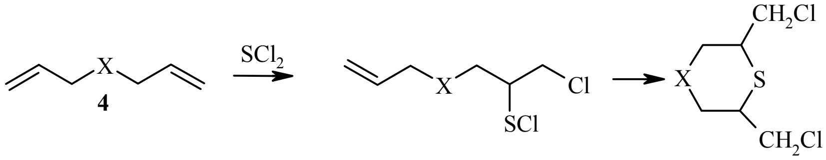
As an example of the first approach it is possible to cite the reaction of 1-allyloxy-2-allylthio-4-methylbenzene (**1**) with sulfur dichloride in dichloromethane [13]. This reaction resulted in the formation of a mixture of two macrocyclic compounds **2** and **3** with an overall yield of 35% and with different arrangements of the S and O atoms in the macrocycle. They could not be separated by chromatographic methods.



The formation of the two isomeric oxathiacrowns **2** and **3** can be represented as resulting from the reaction between the intermediate product from addition of sulfur dichloride at the double bond (sulfenyl chloride) and the initial thioether **1** by a path involving an "allyloxy group" with an "allyloxy group" or an "allyloxy group" with an "allylthio group." Small amounts of substituted benzodithiin and benzoxathiin were formed as side products in this reaction.

For the reactions of sulfur dichloride with the diallyl ethers of diethylene glycol and ethylene glycol the initial stage is anti-Markovnikov addition at the double bond with the formation of monosulfenyl chloride. The reaction can then proceed in various directions:

a) Intramolecular cyclization



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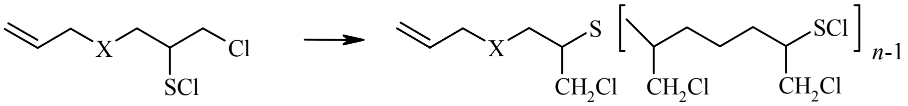
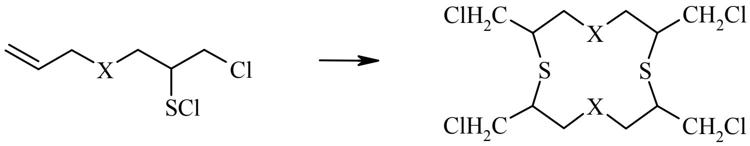
X = O(CH$_2$CH$_2$)$_n$O, n = 1, 2

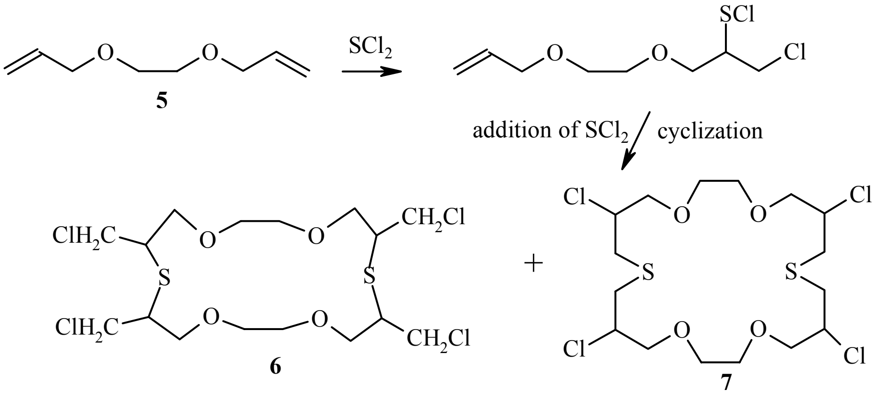
b) The formation of compounds with linear structures



c) Bimolecular cyclization



In path (c) macrocycles containing a larger number of units than during bimolecular cyclization may also be formed. Reaction according to path (a) is most likely in the region of low concentrations of the initial diallyl ether (<0.01 M). Path (b) is realized at temperatures of about 0°C and with substrate concentrations of about 0.1 M. The most favorable conditions for path (c) involve a substrate concentration of 0.5-1.0 M and a reaction temperature between -30 and -50°C (solvent methylene chloride) [14]. In the reaction of ethylene glycol diallyl ether (4,7-dioxa-1,9-decadiene) (**5**) with sulfur dichloride (concentration of the ether 1 M, temperature -60°C) a chromatographically uniform substance was obtained in the form of a highly viscous oil that did not crystallize. The presence of proton signals corresponding to the CH_2S, CHS, CH_2Cl, and CH_2O fragments in the ^{1}H NMR spectrum at 3.37-3.58 ppm indicates the possible formation of a mixture of compounds **6** and **7**, corresponding to initial Markovnikov and anti-Markovnikov addition of sulfur dichloride at the double bond with the formation of intermediate sulfenyl chlorides and their subsequent intramolecular cyclization:



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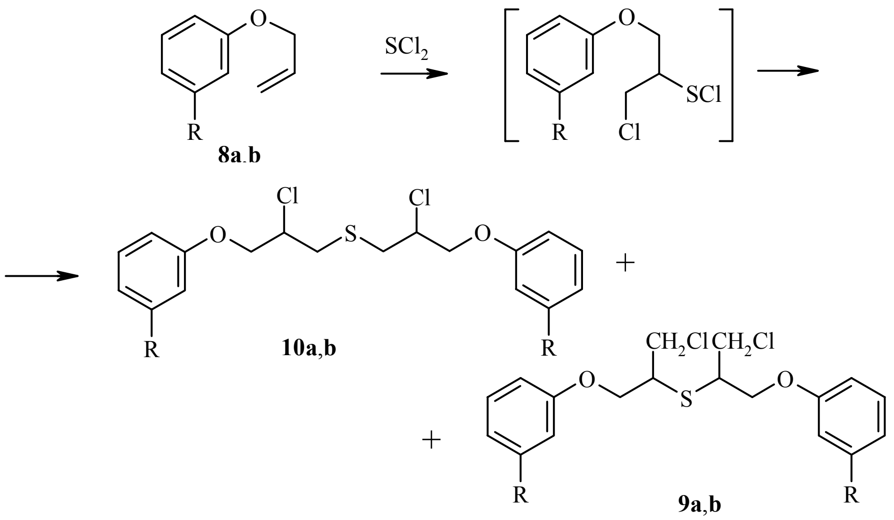
6

7

Analogous results, i.e., the formation of a mixture of macrocyclization products with low yields (5-10%), were obtained during the reactions of diethylene glycol diallyl ether (4,7,10-trioxadecane-1,12-diene), 4,7-dithiadecane-1,9-diene, and 7-oxa-4,10-dithiatridecane-1,12-diene with sulfur dichloride.

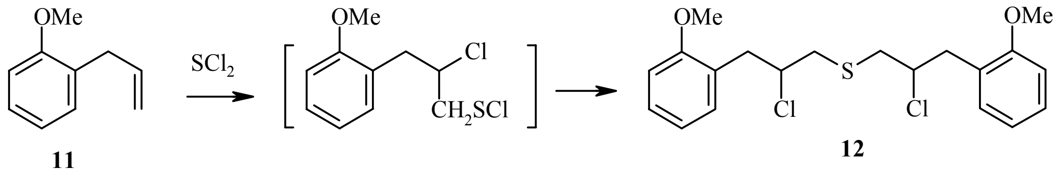
In reaction with sulfur dichloride, depending on the conditions, allyl aryl ethers form not only dichloro sulfides but also chlorine-substituted benzoxaathiins [15-17]. There is little information on the reactions of allyl aryl sulfides with sulfur dichloride [12, 18]. In the reaction of sulfur dichloride with the allyl derivatives **8a**,**b** with a sulfur dichloride–allyl ether ratio of 1:2 the β,β-dichlorosulfides **9a**,**b** were formed as the main products, the total yield of which amounted to 85-88% [19]:



a R = H; **b** R = Me

The structure of the dichloro sulfides indicates initial anti-Markovnikov addition of the sulfur dichloride at the allyl group of the initial ether with the formation of an unstable sulfenyl chloride, the reaction of which with the initial ether leads to the final compound. Up to 10% of the dichloro sulfides **10a**,**b**, i.e., the products from Markovnikov addition of sulfur dichloride to the allyl ethers, is formed as well as the dichloro sulfides **9a**,**b**; cyclic compounds were not found here in the reaction products. According to data in [18], the products from Markovnikov addition were not formed in the reaction of allyl ethers substituted in the aromatic ring with sulfur dichloride in a ratio of 1:2.

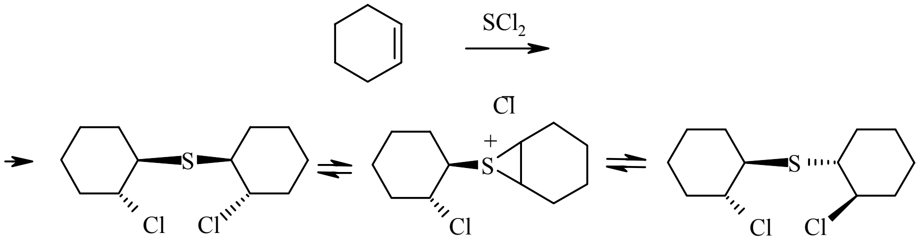
For 2-allyl-1-methoxybenzene (**11**) the reaction with sulfur dichloride takes place with almost 100% selectivity; the only product 2,6-dichloro-1,7-di(2-methoxyphenyl)-4-thiaheptane (**12**) is formed as a result of initial Markovnikov addition of the sulfur dichloride to the allyl group:



In contrast to allyl aryl ethers the reaction of allyl phenyl sulfide with sulfur dichloride is less well-defined. With the sulfur dichloride and allyl phenyl sulfide in a ratio of 1:2 a complex mixture of compounds, containing the initial allyl phenyl sulfide, the products from its chlorination at the allyl group and benzene ring, and compounds similar in structure to the dichloro sulfides produced in the reaction of sulfur dichloride with allyl phenyl ethers, is formed [19].

It is known that the complexing ability of oxygen- and sulfur-containing macrocyclic ligands increases in the presence of electron-donating fragments such as aliphatic and alicyclic groups in their molecules [20]. It therefore seemed to us expedient to develop suitable synthetic approaches to thiacrowns with mono- and bicyclic fragments at the periphery of the molecule. By the reaction of sulfur dichloride with cycloolefins as the first stage of such a process it was possible to obtain dichloro sulfides with high yields and selectivity.

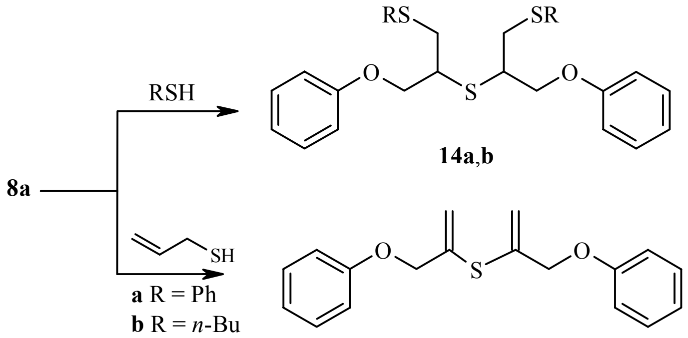
Study of the addition of sulfur dichloride to cyclohexene, cycloheptene, and cyclooctene showed that the main process in each case was the formation of di(β-chlorocycloalkyl) sulfides, the yields of which amounted to 80-95% [21, 22]. The addition of sulfur dichloride to cyclohexene takes place in such a way that two diastereomeric *trans*-di(chlorocycloalkyl) sulfides **13a**,**b** are formed in a ratio of 10:1. One of them rearranges to the other up to a ratio of 1:1 in the mixture [22]:



13a **13b**

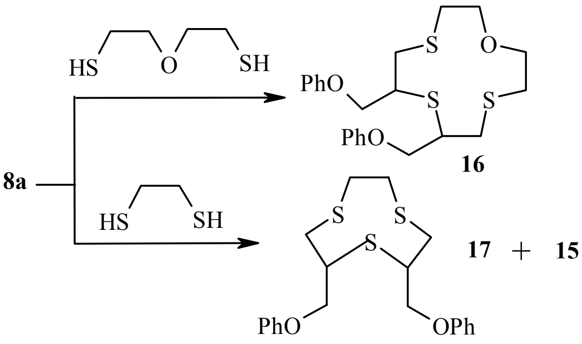
The reaction of sulfur dichloride with cyclopentene and cyclooctene takes place similarly. They also form a mixture of two diastereomeric di(chlorocycloalkyl) sulfides **19** with preferred *trans* orientation of the substituents in each alicycle and approximately equal contents of the *dl* and *meso* forms [23]. On account of difficulties of isolation of the individual diastereomers in the pure form a 1:1 mixture of the diastereomeric di(chlorocycloalkyl) sulfides was subsequently used to produce the podands and the macrocyclic compounds.

In view of the fact that the reactions of the dichloro sulfides with mono- and binucleophiles can have identical stereochemical results the investigation of the macrocyclization of the dichloro sulfides was preceded by the production of the podands by the reaction of dichloroarylalkyl sulfides and di(chlorocycloalkyl) sulfides with alcohols and thiols [19, 24]. In each case the reaction of the dichloro sulfide **8a** with butanethiol and thiophenol leads to the corresponding trisulfides **14a**,**b** with yields of up to 65%. The reaction with allyl hydrosulfide under analogous conditions leads to the elimination of HCl and the formation of the substituted divinyl sulfide **15** [19]. The reaction of the dichloro sulfide **8a** with di(2-mercaptoethyl) ether leads to the formation of the macrocyclic compound 6,8-diphenoxymethyl-1-oxa-4,7,10-trithiacyclododecane (**16**) with a 31% yield. The reaction of the same dichloro sulfide with 1,2-ethanedithiol gives a very small yield (5%) of 2,9-diphenoxymethyl-1,4,7-trithiacyclononane (**17**) containing the divinyl sulfide **15** as impurity:



14a,**b**

15

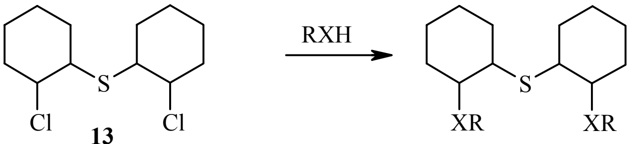


8a

16

17 + **15**

The methoxylation of bis(2-chlorocyclohexyl) sulfide (**13**) gives a 5:4 mixture of the two stereoisomers **18a** with the *trans* configuration of the methoxy groups in both cyclohexane rings. The reaction of the same dichloro sulfide with thiophenol and butanethiol also leads in each case to a 1:1 mixture of two stereoisomers **18b**,**c** with the *trans* arrangement of the substituents [24]:



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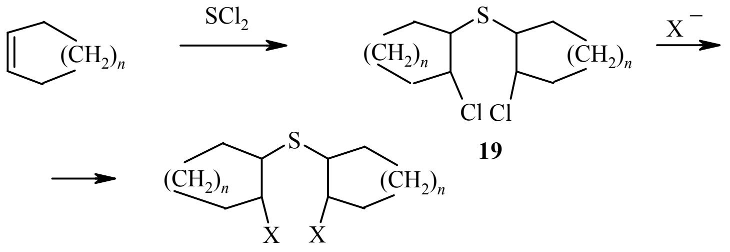
18a–c

18 a R = Me, X = O; **b** R = *n*-Bu, X = S; **c** R = Ph, X = S

In each case the reaction of dichloroheptyl and cyclooctyl sulfides **19** with sodium methoxide and thiophenolate gives a mixture of two diastereomeric dimethoxy- and diphenylthio-substituted dicycloalkyl sulfides **20** in a ratio of ~1:1, as in the case of cyclohexane derivatives [23]:



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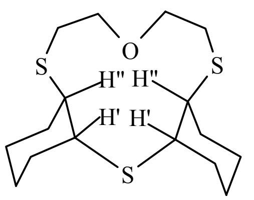
20a–d

20 a X = MeO, **b** X = PhS; *n* = 3; **c** X = MeO, **d** X = PhS; *n* = 4

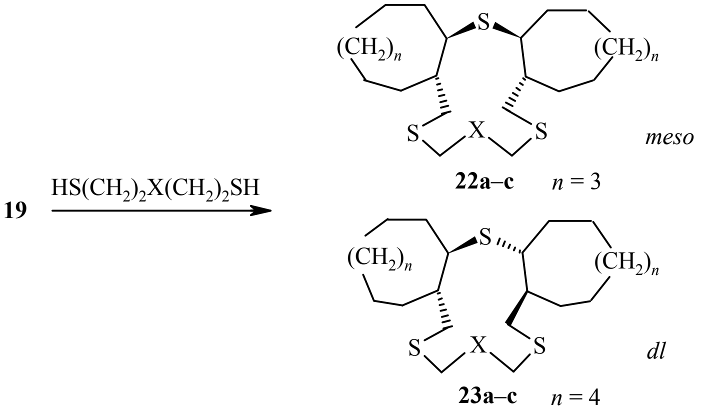
The reaction of di(chlorocycloalkyl) sulfides with dithiols and glycols with different numbers of sulfur and oxygen atoms in the chain led to the formation of the respective macrocycles having various structures – from 9- to 18-membered. For example, the reaction of the sulfide **13** with di(mercaptoethyl) ether leads to a mixture of the two diastereomeric *trans*-5,6-*trans*-8,9-bicyclohexano-1-oxa-4,7,10-trithiacyclododecanes (**21**) with a 35% yield. The values of the vicinal constants (4 and 3 Hz) for the H' and H" in the macrocycle indicates conclusively the presence of the *trans*-diaxial conformation in both cyclohexane fragments [22]:



21

The formation of a macrocycle with such geometry is the first example of the inclusion of two consecutive transoid S–C–C–S fragments in the relatively small 12-membered ring.

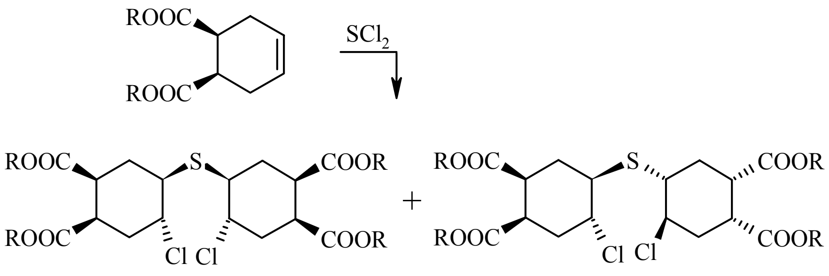
A 12-membered macrocycle with four sulfur atoms in the ring and with the same configuration was produced in the reaction of the sulfide **13** with di(mercaptoethyl) sulfide. The analogous reactions of dichlorocycloheptyl and dichlorocyclooctyl sulfides **19** with glycols and dithiols led in each case to the formation of a mixture of two stereoisomeric 12- and 15-membered macrocycles in the *dl* and *meso* forms **22** and **23** [23], for example:



22, 23 a X = O; **b** X = S, **c** X = $O(CH_2)_2O(CH_2)_2$

In the ^{13}C NMR spectra of all the obtained macrocycles the signals of the carbon atoms are doublets in which the intensity ratios (~1:1) correspond to those for the initial dichloro sulfides. This gives reason to conclude that a mixture of two stereoisomers is formed in each case, as was established during the production of macrocycles from the sulfide **13**. In all cases the high-dilution method was used for the production of the macrocycles, since the use of a template (cesium carbonate) did not make it possible to increase the yield of the macroligand substantially and even led to a decrease (compared with the high-dilution method) from 40 to 28% for the thiacrown **22a** [23].

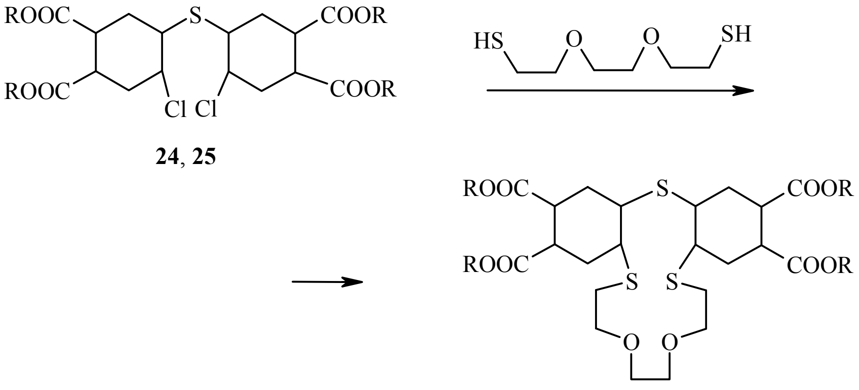
In order to produce macrocyclic ligands where the complexing ability can be increased by the presence of functional groups at the periphery of the molecule we used as starting compounds derivatives of cyclohexene containing the ester groups CO_2Me and CO_2Et and also their synthetic precursor *cis*-4-cyclohexene-1,2-dicarboxylic anhydride [26]. The reaction of substituted cyclohexenes with sulfur dichloride leads in each case to a complex mixture of di(chlorocyclohexyl) sulfides. Preliminary examination of the possible stereoisomeric composition of the products of this reaction using data on the stereochemistry of 1,2,4,5-substituted cyclohexanes [27] and the results of the addition of sulfur dichloride to unsubstituted cyclohexene [22] predicted the formation of six isomers, four of which according to the ^{13}C NMR data were obtained. From these data it was possible to conclude that the *dl* and *meso* forms of the dichloro sulfides **24** and **25** are formed preferentially in each case:



24a,**b** **25a**,**b**

a R = Me, **b** R = Et

Reaction of the dichloro sulfides **24** and **25** with 1,8-dimercapto-3,6-dioxaoctane by the high-dilution method led to the formation of the corresponding macrocycle **26a**,**b** as a mixture of four stereoisomers (according to ^{13}C NMR spectroscopy); the spectral data corresponded to the structure and agreed with the calculated chemical shifts [26]:

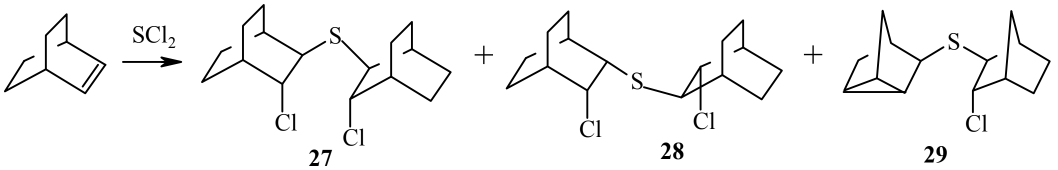


24, **25**

26a,**b**

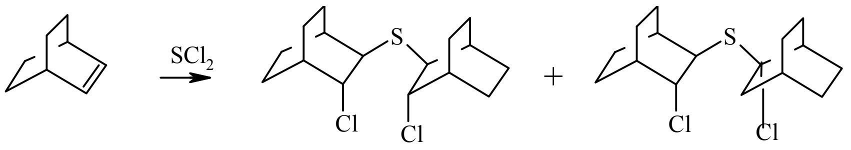
a R = Me, **b** R = Et

An important feature for selective bonding of the metal cation is the conformation of the macrocycle, which is affected by the presence of functional groups or alicyclic fragments with different conformational mobility. Macroligands with the bicyclic bicycloheptene and bicyclooctane fragments were synthesized in order to obtain macrocycles with various conformational mobility. Macrocycles attached to such structural units must possess greater conformity mobility than the cyclohexane, cycloheptane, and cyclooctane derivatives by virtue of the conformational features of the bridging systems. During the addition of sulfur dichloride to bicycloheptene a complex mixture of substances was formed. The main components were the diastereomeric dichloro sulfides **27** and **28** in a ratio of 3:2 with the chlorine atom in the *endo* position and the sulfur atoms in the *exo* positions in relation to the bicycloheptane fragment, and also the nortricyclene derivative **29** [28]:



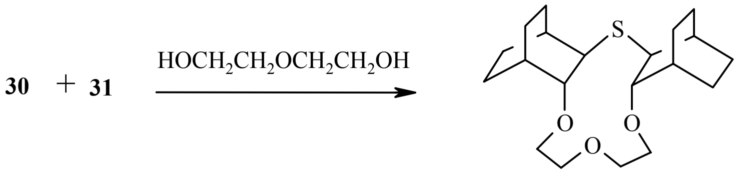
27 **28** **29**

The addition of sulfur dichloride to bicyclo[2.2.2]octene takes place more selectively and without rearrangement of the framework and leads to the formation of a mixture of the two *trans*,*trans*-bis(3-chlorobicyclo[2.2.2]oct-2-yl) sulfides (**30**) and (**31**) in a ratio of 3:2 with an overall yield of 75% [28]:



30 **31**

The reaction of the mixture of the dichloro sulfides **30** and **31** with diethylene glycol by the high-dilution method leads to the formation, according to ^{13}C NMR data, of only one stereoisomer of 5,6,8,9-dibicyclo[2.2.2]octano-1,4,10-trioxa-7-thiacyclododecane (**32**):



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The synthesized oxathia- and thiacrown compounds were used to investigate the extraction of the ions of various metals. It is known that the extraction of metal ions with macrocyclic ligands is a very convenient method of studying their complexing ability, and makes it possible to determine the degree and selectivity of interaction of the metal cation with the macrocycle. Study of the extraction equilibria is always promising also from the standpoint of the separation of mixtures and the concentration of substances, including radionucleides.

Some of the oxathia- and thiacrown compounds and podands described above and also macrocyclic compounds obtained in [29] were investigated as complexing agents for the extraction of strontium, lead, palladium, silver, and radium cations.

Most of the publications on the extraction of metal ions by macrocyclic compounds refer to extraction from picrate solutions [30], and there are somewhat fewer papers in which nitrate ions are used as anion [30]. In our case picrate and nitrate solutions were mainly used for ease of comparison with data for previously described macrocyclic compounds in other aqueous media.

According to Pearson's concept [31], oxygen-containing crown ethers belong to the so-called hard ligands, the thiacrowns are soft ligands, and azacrowns occupy an intermediate position. It is more difficult to classify mixed macrocyclic compounds containing different heteroatoms. The extracted metal cations and counter-ions can also be classified according to these same principles. Of the metals that we investigated the strontium and radium cations and also the nitrate anion are considered hard, the picrate anion and silver and palladium cations are soft, and calcium ions occupy an intermediate position.

Tables 1-3 give the distribution coefficients of Sr(II), Pb(II), Ag(I), Pd(II), and Ra(II) during their extraction from nitrate and picrate solutions with various macrocyclic compounds and podands. The ionic radii of some of the elements were close: 1.8 E for Sr(II), 1.19 E for Pb(II), and 1.15 for Ag(I) [32]; in the Sr(II) and Pb(II) ions the charge coincides.

If the extraction process is treated according to Pearson's concept, during extraction with soft thiacrowns the Ag > Pd > Pb > Sr series applies both for the soft picrate anion and for the hard nitrate anion. In the case of extraction by crown ethers both from picrate solutions and from nitrate solutions the order of selectivity is almost reversed: Pb ~ Sr > Ag > Pb. The following facts that are of interest from the complexing standpoint should be noted: The oxathiacrown and thia crown compounds with a 12-membered ring exhibit high affinity toward Pb(II) and Ag(I) ions in contrast to their oxygen analogs. This can be explained on the assumption that the size of the cavity in the macrocycle increases in the transition from the sulfur-containing compound to its oxygen analog, but there are as yet no data to confirm this. Earlier we established that during the extraction of silver by the macroligand **20** the extracted complex has the composition AgL_2Pi, i.e., a sandwich structure, for which agreement between the sizes of the metal ion and the macrocycle cavity is by no means essential, is formed [33].

The fact that not only the principle of dimensional correspondence must be taken into account during the extraction of thiacrown compounds is also demonstrated by the fact that the extractants **38** and **39** are acyclic sulfides while the distribution coefficients are comparable with those for the 12-membered thiacrowns. The 18-membered thiacrown compounds give lower distribution coefficients than the thiacrowns with a 12-membered ring. One of the reasons for this effect may be the formation of twist structures in these macrocycles and the resultant deterioration of the complexation with metal ions.

TABLE 1. The Distribution Coefficients of Sr(II) and Pb(II) during Extraction with Solutions of the Extractants in Chloroform

Compound	Extractant in $CHCl_3$	Concentration, mol/l	Composition of aqueous phase			
			Sr(II)		Pb(II)	
			0.01 mol/l LiPi*	3 mol/l HNO_3	0.01 mol/l LiPi	3 mol/l HNO_3
33	2,3,5,6-Dicyclohexano-1,4,7-trithia-12-crown-4	$2.2\cdot10^{-3}$	0.05	0.015	5.73	0.26
34	3,5-Diphenoxymethyl-1,4,7-trithia-12-crown-4	$2.2\cdot10^{-3}$	0.015	—	4.50	0.24
35	4,4',5,5'-Tetracarboxyethyl-2,3,5,6-dicyclohexano-1,4,7-trithia-12-crown-4	$2.2\cdot10^{-3}$	0.02	—	66.17	0.40
36	2,3,5,6-Dicyclohexanotetrathia-12-crown-4	$2.2\cdot10^{-3}$	0.05		3.23	0.10
37	2,3,5,6-Dicyclohexano-1-thia-12-crown-4	$2.2\cdot10^{-3}$	0.002	0.002	1.80	0.10
38	Di(2-methoxycyclohexyl) sulfide	$2.2\cdot10^{-3}$	0.04	—	3.70	0.11
39	Di(2-butylthiacyclohexyl) sulfide	$2.2\cdot10^{-3}$	0.02	0.015	2.92	0.24
40	2,3,11,12-Dibenzotetracyclohexano-18-thiacrown-6	$6.0\cdot10^{-3}$	<0.001	0.015	0.08	0.75
41	2,3,11,12-Dibenzotetracyclohexano-1,10-dithiacrown-6	$1.6\cdot10^{-2}$	0.04	0.05	0.15	0.80
42	DB-18-Crown-6	$2.0\cdot10^{-2}$	0.06	—	—	0.07
43	5,6-Benzo-1,10-dithia-18-crown-6	$1.0\cdot10^{-2}$	0.03	—	1.30	—
44	4-Bromo-5,6-benzo-1,10-dithia-18-crown-6	$1.0\cdot10^{-2}$	0.04	0.01	1.37	0.01
45	4-Acetal-5,6-benzo-1,10-dithia-18-crown-6	$1.0\cdot10^{-2}$	0.04	—	1.28	—
46	4-Adamantylbenzo-18-crown-6	$1.0\cdot10^{-2}$	0.03	0.017	1.79	0.023
47	4-Adamantyl-2,3,11,12-dibenzo-18-crown-6	$1.0\cdot10^{-2}$	1.6	—	9.9	—
48	4,4'-Diadamantyl-2,3,11,12-dibenzo-18-crown-6	$1.0\cdot10^{-2}$	0.4	—	3.8	—
49	Bis(2-methoxycyclopentyl) sulfide	$1.0\cdot10^{-2}$	0.04 (0.1)	-(0.02)	4.20	0.15
50	Bis(2-phenylthiocycloheptyl) sulfide	$3.4\cdot10^{-3}$	0.05 (0.13)	-(0.008)	2.80	0.10
51	8,9,11,12-Dicycloheptano-1,4-dioxa-7,10,13-trithiacyclopentadecane	$4.2\cdot10^{-3}$	0.006 (0.009)	0.004 (0.07)	3.50	0.20
52	DB-24-Crown-8	$5.0\cdot10^{-3}$	0.02 (0.14)	(0.08)	—	—

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* LiPi is lithium picrate.

TABLE 2. The Distribution Coefficients of Ag(I) ($c_{\mathrm{Ag(I)}}$ = 10^{-5}) and Palladium-103 (without Support) during Extraction with Solutions of Various Extractants in Chloroform

Compound	Concentration of extractant, mol/l	Composition of aqueous phase			
		0.01 mol/l LiPi	3 mol/l HNO_3	5 mol/l $LiNO_3$	5 mol/l $NaNO_3$
37	$1.0\cdot10^{-2}$	140 (3.2)	10 (1.2)	74	38
38	$6.0\cdot10^{-3}$	—	67	31	—
41	$3.6\cdot10^{-3}$	-(1.6)	27 (1.6)	46	23.5
42	$5.9\cdot10^{-3}$	-0.11 (0.02)	0.034 (0.09)	0.18	0.028
53	$1.0\cdot10^{-2}$	-(0.017)	-(0.022)	—	—

TABLE 3. The Distribution Coefficients (D) of Ra(II) and Pd(II) with Macrocyclic Compounds and Podands

Compound	Extractant, S	c_s, mol/l	Composition of aqueous phase	
			10^{-2} mol/l LiPi	3 mol/l HNO_3
20a	$CHCl_3$, Ra^{2+}	$1.0\cdot10^{-2}$	0.10	0.018
20b	$CHCl_3$, Ra^{2+}	$3.4\cdot10^{-3}$	0.13	0.008
22b	$CHCl_3$, Ra^{2+}	$7.1\cdot10^{-3}$	0/0065	0.067
	$CHCl_3$, Pd^{2+}	$5.0\cdot10^{-3}$	—	1.51
	DCE*, Pd^{2+}	$5.0\cdot10^{-3}$	18.6	16.6
	DCE, Pd^{2+}	$5.0\cdot10^{-3}$	5.00 (1 mol/l $LiClO_4$)	
22a	$CHCl_3$, Ra^{2+}	$4.2\cdot10^{-3}$	0.009	0.070
	DCE, Pd^{2+}	$5.0\cdot10^{-3}$	5.85 (1 mol/l $LiCl)_4$	
22c	$CHCl_3$, Pd^{2+}	$5.0\cdot10^{-3}$	—	2.0
	DCE, Pd^{2+}	$5.0\cdot10^{-3}$	4.8	2.4
51	DB-24-C-8			
	$CHCl_3$, Ra^{2+}	$5.0\cdot10^{-3}$	0.14	0.077
54	18-C-6			
	DCE, Pd^{2+}	$1.0\cdot10^{-2}$	0.068	0.09
53	15-C-5			
	DCE, Pd^{2+}	$1.0\cdot10^{-2}$	0.017	0.22

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* DCE is 1,2-dichloroethane.

The macroligands **46** and **47** differ from the widely used DB-18-crown-6 **42** by the introduction of one or two adamantyl residues into the benzene ring. However, this leads to a significant increase in the distribution coefficients and extraction constants of Pb(II) and Sr(II).

It can be concluded from all the foregoing that Pearson's concept explains the selectivity of the extraction of various metal cations by macrocyclic ligands with various structures satisfactorily at a qualitative level. Thiacrown compounds are good complexing agents for "soft" and intermediate metal cations from aqueous media of any composition. Their use has made it possible to develop a fast method for the determination of Pb(II) in transdiffuse liquids [34] and also to isolate palladium-103 from irradiated radium targets.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian VXR-400 spectrometer for 25% solutions of the substances in deuterochloroform with TMS as internal standard. Mass-spectrometric analysis was conducted on a Finnigan MAT112S instrument with electron impact and ionizing energy 80 eV.

4,7-Dioxa-1,9-decadiene (5). To the mixture obtained by dissolving sodium (5.6 g, 0.25 mol) in ethylene glycol (75 ml, 0.79 mol) in an argon atmosphere at 60°C with constant stirring we added allyl bromide (22 ml, 0.25 mol). The reaction mixture was heated at 60°C for 5 h, water was added, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic extracts were washed with sodium chloride solution and with water and dried. The residue was distilled under vacuum. We obtained 5 g (32%) of diallyl ether **5**; bp 65-67°C (20 mm Hg). ^1H NMR spectrum, δ, ppm: 3.5 (4H, m, $–CH_2CH_2–$); 3.8 (4H, m, $–CH_2O–$); 5.3 (4H, m, $=CH_2$); 6.0 (2H, m, =CH–). Mass spectrum (*m/z*) (*I,* %): 141 (1), 127 (1), 113 (1), 101 (5), 85 (3), 73 (17), 57 (22), 45 (13), 41 (100).

6,8,15,17-Tetrachloromethyl-1,4,10-tetraoxa-7,16-dithiacyclooctadecane (6) and 6,10,17,21-Tetrachloro-1,4,12,15-tetraoxa-8,19-dithiacyclodocosane (7). To a solution of the diether **5** (1.5 g, 0.011 mol) in methylene chloride (100 ml) at -40°C we added a solution of sulfur dichloride (1.1 g, 0.012 mol) in methylene chloride (50 ml). The mixture was stirred at -40°C for 2 h and at room temperature for 6 h. At the end of the reaction the mixture was washed with water and dried. After removal of the solvent the residue was chromatographed on silica gel and recrystallized from a 1:1 mixture of pentane and methylene chloride. ^1H NMR spectrum, δ, ppm: 3.37 (m, CHS, CH_2S); 3.40 (m, CHS, CH_2S); 3.47 (m, CHCl, CH_2Cl); 3.58 (m, CH_2O). Found %: C 39.01; H 5.62; S 12.94. $C_{16}H_{28}Cl_4O_4S_2$. Calculated %: C 39.18; H 5.71; Cl 28.98; S 13.06.

5,6,8,9-Dibicyclo[2.2.2]octano-1,4,10-trioxa-7-thiacyclododecane (32). To sodium (0.46 g, 0.02 mol), dissolved in absolute ethanol (350 ml), we added simultaneously over 10 h a mixture of dichloro sulfides **30** and **31** (3.2 g, 0.001 mol) and diethylene glycol (1.06 g, 0.001 mol), both dissolved in ethanol (50 ml). The reaction mixture was stirred at 80°C for 10 h and filtered. The solvent was distilled from the filtrate, and the remaining oil was recrystallized successively from acetone, alcohol, and benzene. We obtained 1.43 g of the oxathiacrown **32** with a yield of 40%; mp 86-86°C. ^{13}C NMR spectrum (deuterochloroform), δ, ppm: $C_{(1)}$ 32.50, $C_{(2)}$ 53.70, $C_{(3)}$ 68.57, $C_{(4)}$ 34.95, $C_{(5)}$ 20.05, $C_{(6)}$ 25.53, $C_{(7)}$ 26.42, $C_{(8)}$ 19.77, $C_{(9)}$ 61.91, $C_{(10)}$ 73.30. Mass spectrum, *m/z* (*I*, %): 352 [M^+] (1), 318 (3), 283 (1), 248 (1), 220 (1), 190 (1), 175 (3), 144 (6), 143 (6), 142 (24), 114 (10), 107 (39), 105 (9), 101 (3), 97 (6), 91 (12), 87 (3), 80 (15), 79 (100), 78 (6), 77 (24), 76 (21), 75 (45), 73 (6), 69 (6), 67 (15), 65 (9), 61 (12), 59 (6), 58 (9). Found %: C 70.42, H 9.27. $C_{20}H_{32}SO_3$. Calculated %: C 68.18, H 9.10.

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