The order of the conversion reaction of ether (IIc) was determined at initial concentrations of 0.1, 0.5, and 1.0 mole/liter of the starting compound at 50°C according to Eq. (2). The values of $\omega_{0.1}$ and $\omega_{0.2}$ were determined graphically by means of the slope of the tangent lines drawn through the first points of the curves of the dependence of the concentration from the time.

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DIRECTED SYNTHESIS OF MACROCYCLIC PHENYLENE SULFIDES

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A method has been developed for the directed synthesis of macrocyclic phenylene sulfides with 4-8 phenylene sulfide fragments, by condensation of dihaloaromatic compounds of various types with sodium sulfide or dithiophenate. A combination of this method with high dilution techniques has afforded pure macrocycles in high yields, and the macrocycle with six phenylene sulfide fragments in yields as high as 73%.

Macrocyclic phenylene sulfides (MPS), first detected by mass spectrometry [1] in the low-molecular-weight products of the polycondensation of 1,4-dichlorobenzene with Na_2S, have so far received little attention. Cyclic tetra- and penta-1,4-phenylene sulfides were then isolated in the pure state [2]. These compounds are of interest as selective complexing agents and polymerizable monomers for the synthesis of polyphenylene sulfides. From the low-molecular-weight fraction from the polycondensation of 1,4-dichlorobenzene with Na_2S, we isolated pure, crystalline hexa-, hepta-, and octa-1,4-MPS [3, 4], the main component of the macrocyclic fraction being the cyclic hexamer. The cyclic trimer, cyclo-(tris-1,3-phenyl sulfide), has been obtained from the polycondensation products of 1,3-dihalobenzene and Na_2S [5, 6]. The structures of these compounds were confirmed by spectral methods and x-ray diffraction analysis. The MPS have also been obtained by the thermal degradation of linear poly-1,4-phenylene sulfide under high vacuum [7].

It is noteworthy that in all instances 1,4-disubstituted MPS are formed as multicomponent mixtures of oligo-homologs with from four to eight phenylene sulfide untis in the ring, which complicates their isolation in the pure state. The overall yield of the macrocyclic fraction in the polycondensation of 1,4-dichlorobenzene with Na_2S does not exceed 3% [1].

The present investigation was aimed at developing selective methods for the synthesis of MPS. The starting materials used for this purpose were the polynuclear α,ω-dihalodiaryl

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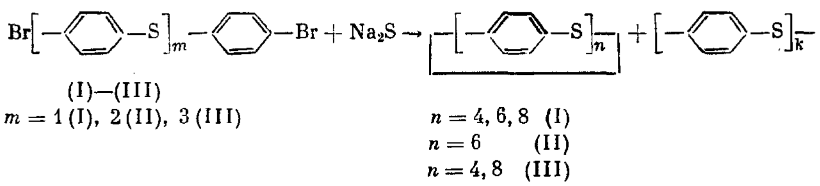
TABLE 1. Effects of the Structure of the Dihalodiaryl Sulfide and Concentrations of Reactants on the Yields and Ratios of MPS

Dihalide	Concentration of reactants, mole/liter	Yield, %				
		polymer	macrocyclic fraction	pure macrocycles		
				$n=4$	$n=6$	$n=8$
(I)	1,0	78	2,1	0,4	1,2	0,2
(II)	1,0	54	4,7	–	4,2	–
(III)	1,0	67	0,9	0,4	–	0,3
(I)	0,1	31	38,0	10,0	12,0	5,0
(II)	0,1	4	78,0	–	73,0	–
(III)	0,1	29	29,0	17,0	–	7,0

TABLE 2. Effects of the Structure of the Dihalodiaryl Sulfide on the Yields and Ratios of MPS in the Reaction of Sodium 4,4'-Diphenyl Sulfide Dithiolate

Dihalide	Concentration of reactants, mole/liter	Yield, %					
		polymer	macrolytic fraction	pure macrocycles			
				$n=4$	$n=5$	$n=6$	$n=8$
(I)	0,1	17	19	12	–	–	4
(II)	0,1	23	22	–	18	–	–
(III)	0,1	37	15	–	–	11	–

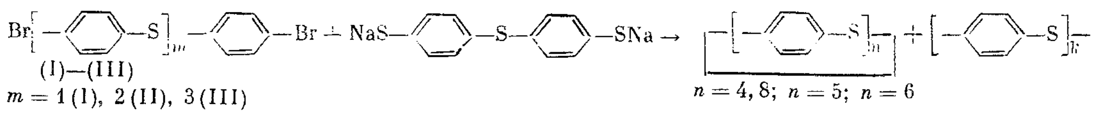
sulfides: 4,4'-dibromodiphenyl sulfide (I), 1,4-bis-(4'-bromophenylthio)benzene (II), and 4,4'-bis-(4"-bromophenylthio)diphenyl sulfide (III).



It will be seen from the above that condensation of (I)-(III) with Na_2S, unlike 1,4-dihalobenzenes, can give only MPS with an even number of phenylene sulfide units, the number of which in the mixture of macrocycles obtained depends on the structure of the starting dihalodiaryl sulfide. For example, while in the case of the binuclear dihalide (I) the mixture contains three macrocycles, condensation of (II) with Na_2S gives the hexameric ring only.

As will be seen from Table 1, on condensation of (II) with Na_2S under conditions similar to those used for the synthesis of linear polyphenylene sulfide at monomer concentrations of 1.0 mole/liter, the yield of the hexameric MPS is the highest, 4.2%, which is slightly higher than the yield of the total macrocyclic fraction in the reaction of 1,4-dichlorobenzene with Na_2S [1]. This is probably due to the ease of closing of the hexameric ring, in which the valence angles C–S–C are close to those in the unstrained diphenyl sulfide molecule, 103.7° [8]. The yields of tetra- and octameric MPS under these conditions are considerably lower than those of the hexamer (Table 1). The use of high dilution techniques (a monomer concentration of 0.1 mole/liter) in the condensation of (II) with Na_2S enabled cyclo-(hexa-1,4-phenylene sulfide) to be obtained in the unusually high yields of up to ~73% (Table 1), the polymer being virtually absent. The yields of the macrocycles with four and eight phenylene sulfide fragments in the condensation of (I) and (III) with Na_2S at high dilutions are also substantially higher, at 5-17%.

Replacement of Na_2S by sodium 4,4'-diphenyl sulfide dithiolate, on reaction with the dihalides (I)-(III) (Table 2) affords another set of macrocycles with an even smaller number of components.



The formation of a hexameric ring in the condensation of (I) with this dithiolate is not possible, since cyclization of three molecules of the starting materials in any combination is not possible, both functional groups being identical (both Br, or both SNa). The resulting macrocycles contain phenylene sulfide units in multiples of four. Examination of the results of the condensation of (I) with the dithiolate and with Na_2S shows that the impossibility of the formation of the hexameric ring does not result in an increase in the yields of the other macrocyclic reaction products.

Unlike the condensation with Na_2S, the use of the dithiolate in the reaction with (II) enables a macrocycle with an uneven number of phenylene sulfide units, namely cyclo-(penta-1,4-phenylene sulfide) to be obtained in the pure state in relatively high yield (18%) (Table 2). It should be pointed out that the yield of the hexameric ring in the condensation of (III) with the dithiolate is significantly lower than when Na_2S reacts with (II) under the same conditions (11 and 73% respectively). This could be due to the lack of symmetry in the intermediate product on ring closure from the four-unit dihalide (III) and the two-unit dithiolate, as opposed to the symmetry of the intermediate in the "doubling" of the three unit molecule (II) with sodium sulfide. This difficult ring closure of the macrocycle is also apparently the reason for the greater yield of linear polymer in the condensation of (III) with the dithiolate.

This method of directed synthesis of specific macrocycles has also been used to obtain some new MPS with 1,3-substituted phenylene fragments. Since condensation of 1,3-dihalobenzene with Na_2S results in the preferential formation of the tricyclic cyclo-(tris-1,3-phenylene sulfide) with only trace amounts of larger macrocycles [5], when the Na_2S is replaced by sodium 1,3-dithiophenate, the trimer cannot be formed as a result of the identical nature of the functional groups at this stage of the condensation. In this case, the principal macrocyclic condensation product is the hitherto unreported cyclo-(tetra-1,3-phenylene sulfide). The yields of this compound when prepared under high dilution conditions was ~14%.

EXPERIMENTAL

The NMR spectra were obtained on a Bruker WM-280 spectrometer, IR spectra on a UR-20 spectrophotometer (KBr disks), and mass spectra on a Varian MAT-CH-6 apparatus.

By brominating diphenyl sulfide as described in [9] 4,4'-dibromodiphenyl sulfide (I) was obtained. The 1,4-bis-(4'-bromophenylthio)benzene (II) was prepared by brominating 1,4-bis-(phenylthio)benzene as described in [10]. By brominating 4,4'-bis-(4"-phenylthio)diphenyl sulfide (III) in CCl_4 solution, 4,4'-bis(4"-bromophenylthio)diphenyl sulfide (III) was obtained, yield 36%, mp 187°C. Found: C 52.11; H 2.37; S 17.89; Br 29.21%. $C_{24}H_{16}S_3Br_2$. Calculated: C 51.43; H 2.87; S 17.14; Br 28.57%. M 560 (mass spectrum).

As described previously [11, 12], 4,4'-diphenyl sulfide dithiol and 1,3-phenylenedithiol were obtained by reducing the appropriate disulfonyl chlorides with zinc dust with HCl in dioxane.

Condensation of (I)-(III) with Na_2S. A suspension of 2.4 g (0.01 mole) of $Na_2S \cdot 9H_2O$ in 100 ml of N-methylpyrrolidone was heated under argon with stirring until all the water of crystallization had been removed. An equimolar amount of (I)-(III) was then added, and the mixture refluxed for 16 h. After cooling, the mixture was poured into 500 ml of water, acidified with HCl to pH ~ 5, and the solid which separated was filtered off and dried to constant weight.

The low-molecular-weight macrocyclic fraction was separated from polymeric material by extraction with dichloromethane in a Soxhlet apparatus for 16 h. When extraction was complete, the solvent was removed, and the oily, dark reddish-brown product extracted with ethyl acetate. Recrystallization of the ethyl acetate-insoluble fraction from chloroform gave colorless needles of the cyclic hexamer of 1,4-phenylene sulfide, mp 346°C [3]. The mother liquors were evaporated to remove chloroform, and the solid residue recrystallized from HMPA. On standing for ten days, the latter gave colorless needles of the cyclic octamer of 1,4-phenylene sulfide, mp 305°C [4]. Removal of the solvent from the ethyl acetate-soluble products, followed by successive extraction with ethanol and acetone, gave the cyclic tetra- and penta-

1,4-phenylene sulfide as cubic and acicular crystals, mp 295° and 256°C respectively [2]. The concentrations of the starting materials and the yields of products are given in Table 1.

Condensation of Dibromides (I)-(III) with Sodium 4,4'-Diphenyl Sulfide Dithiolate. A mixture of 2.5 g (0.01 mole) of 4,4'-diphenyl sulfide dithiol and 0.02 mole of NaOH as a 50% aqueous solution in N-methylpyrrolidone was heated with stirring for 4 h. Following removal of the azeotropic mixture, an equimolar amount of the dibromide (I)-(III) was added, and stirring continued at 200°C for 16 h. Isolation of the condensation products, and their separation into their components, was carried out as in the syntheses of (I)-(III) with Na_2S.

Condensation of Sodium Phenylene-1,3-dithiolate with 1,3-Dibromobenzene. The preparation of the dithiol salt and its condensation with 1,3-dibromobenzene were carried out as in the reaction of (I)-(III) with 4,4'-diphenyl sulfide dithiol. The cyclic tetramer of 1,3-phenylene sulfide was isolated as colorless crystals of cubic habit by extraction of the condensation products with acetone, mp 222-224°C, M 432 (mass spectrometry). ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 7.47; 7.33; ^{13}C: 137.78; 134.18; 130.20; 129.31. IR spectrum (ν, cm^{-1}): 780, 1090, 1380, 1470, 1570. Found: C 66.46; H 3.33; S 29.63%. $C_{24}H_{16}S_4$. Calculated: C 66.66; H 3.70; S 29.64%.

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