(1H, s, CH), 9.38 ppm (1H, s, CH). Found, %: C 38.5; H 2.4; N 22.4. $C_{10}H_7N_5O_3S_2$. Calculated, %: C 38.8; H 2.3; N 22.6.

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POLYFUNCTIONAL MACROHETEROCYCLES.

2.* SYNTHESIS OF CROWN COMPOUNDS THAT INCLUDE DIMETHYL ASPARTATE FRAGMENTS

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The reaction of 1-[1,2-bis(carbomethoxy)ethyl]aziridine with ethane-1,2-dithiol leads to 1,8-bis[1,2-bis(carbomethoxy)ethylamino]-3,6-dithiaoctane. Condensation with phthalic and terephthalic acid dichloride gives 9,10-benzo-8,11-dioxo-7,12-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,12-diazacyclotetradec-9-ene and 9,12-benzo-8,13-dioxo-7,14-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,14-diazacyclohexadeca-9,12-diene, respectively, while condensation with formaldehyde gives 7,9,18,20-tetrakis[1,2-bis(carbomethoxy)ethyl]-1,4,12,15-tetrathia-7,9,18.29-tetraazacyclodocosane. The corresponding disulfone is formed in the oxidation of 9,10-benzo-8,11-dioxo-7,12-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,12-diazacyclotetradec-9-ene with 30% hydrogen peroxide.

Crown compounds that contain exocyclic functional groups are widely used in the synthesis of polymers and their "immobilization" on solid supports, as well as in obtaining new types of macroheterocycles [2]. The effect of functional groups of crown compounds on complexing with metal ions and the stabilities of the resulting complexes has also been investigated [2].

We have previously synthesized sulfur-containing macrocyclic diamides and obtained their complexes with the copper(II) ion [3-7], which can be used as models for the investigation of copper-containing proteins ("blue proteins") [8, 9].

Continuing our study of the properties of model compounds of metalloproteins we have synthesized sulfur-containing macroheterocycles III-VI, which include dimethyl aspartate fragments.

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*See [1] for Communication 1.

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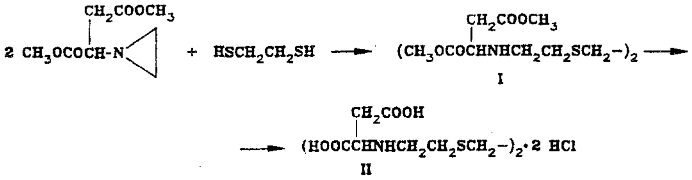
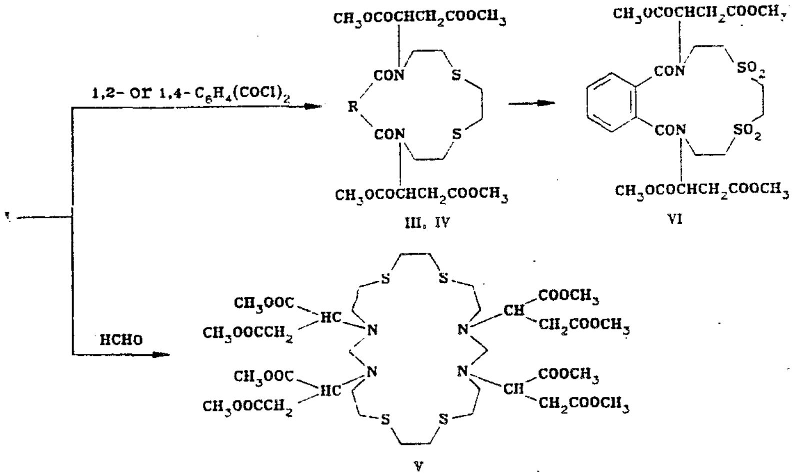
The most suitable methods for obtaining nitrogen- and sulfur-containing crown compounds in high yields are acylation of heterochain α,ω-diamines with dicarboxylic acid dichlorides and condensation of them with formaldehyde [3, 4, 10]. Diamine I was obtained in 86% yield from 1-[1,2-bis(carbomethoxy)ethyl]aziridine and ethane-1,2-dithiol. The acidic hydrolysis of diamine I with a solution of concentrated HCl in acetic acid at 90°C leads to 1,8-bis[1,2-bis(carboxy)ethylamino]-3,6-dithiaoctane dihydrochloride (II) in 70% yield.



The cyclization of diamine I with phthalic and terephthalic acid dichlorides in dry benzene under high-dilution conditions leads to macroheterocycles III and IV in ~60% yields.



III R=1,2-C_6H_4; IV R=1,4-C_6H_4

The condensation of diamine I with formaldehyde in methanol under high-dilution conditions gives the 22-membered crown compound V in 65% yield.

The oxidation of crown compound III with a solution of 30% hydrogen peroxide in acetic acid at 90°C gives 9,10-benzo-1,1,4,4,8,11-hexaoxo-7,12-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,12-diazacyclotetradec-9-ene (VI) in 60% yield.

Compounds I-VI are colorless crystalline substances or viscous oils that are soluble in benzene, chloroform, methanol, DMF, and DMSO.

Absorption bands of ester and amino groups at 1735 and 3330 cm^{-1}, respectively, are present in the IR spectrum of diamine I. An intense absorption band of a carboxy group (1730 cm^{-1}) and a number of absorption bands at 2400-3030 cm^{-1} are observed in the spectrum of dihydrochloride II. The spectra of crown compounds III-VI contain frequencies of vibrations of an ester group at 1730-1735 cm^{-1}, while the spectra of macrocycles III, IV, and VI contain a band of an amido group (1640 cm^{-1}). The sulfo group of VI gives absorption bands at 1110, 1140, and 1300 cm^{-1}.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were obtained with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ were recorded with a Tesla BS-487C spectrometer (80 MHz).

1,8-Bis[1,2-bis(carbomethoxy)ethylamino]-3,6-dithiaoctane (I). A mixture of 11.2 g (60 mmoles) of 1[1,2-bis(carbomethoxy)ethyl]aziridine and 2.8 g (30 mmoles) of ethane-1,2-dithiol in 250 ml of methanol was removed by distillation, the residue was dissolved in chloroform, and petroleum ether was added in the cold to give 1.20 g (86%) of an oil. PMR spectrum: 2.74 (m, CH_2N, CH_2S), 3.71 ppm (s, OCH_3). Found, %: C 45.7; H 7.1; N 5.4; S 13.2. $C_{18}H_{32}N_2O_8S_2$. Calculated, %: C 46.1; H 6.8; N 5.9; S 13.6.

1,8-Bis]1,2-bis(carboxy)ethylamino]-3,6-dithiaoctane Dihydrochloride (II). A mixture of 3.0 g of diamine I and 10 ml of concentrated HCl in 50 ml of acetic acid was heated for 2 h at 90°C, after which the solvent was removed by distillation at reduced pressure, and the residue was dissolved in methanol and precipitated with ether to give 2.0 g (70%) of a viscous oil. Found, %: C 14.0; S 12.6. $C_{14}H_{24}N_2O_8S_2\cdot 2HCl$. Calculated, %: Cl 14.6; S 13.2.

9,10-Benzo-8,11-dioxo-7,12-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,12-diazacyclotetradec-9-ene (III). A solution of 2.8 g (6.0 mmoles) of diamine I in 350 ml of dry benzene and a solution of 1.2 g (6.0 mmole) of phthalic acid dichloride in 350 ml of dry benzene were added simultaneously in the course of 5 h with vigorous stirring at 20°C to 1 liter of dry benzene containing 1.2 g (12 mmoles) of triethylamine, after which the resulting precipitate was removed by filtration, and the solvent was removed by distillation at reduced pressure. The residue was purified by chromatography on aluminum oxide by elution with benzene–methanol (5:1). The solvent was removed by distillation, and the residue was dissolved in chloroform and precipitated with petroleum ether in the cold to give 2.0 g (57%) of an oil. PMR spectrum: 2.85 (m CH_2), 3.75 (s, OCH_3), 7.45 ppm (m, C_6H_4. Found, %: C 51.6; H 5.2; N 4.3; S 10.5; M 580 (cryoscopically in benzene). $C_{26}H_{34}N_2O_{10}S_2$. Calculated, %: C 52.1; H 5.6; N 4.6; S 10.9; M 598.

9,12-Benzo-8,13-dioxo-7,14-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,14-diazacyclohexadeca-9,12-diene (IV). This compound was obtained from 2.8 g (6.0 mmoles) of diamine I and 1.2 g (6.0 mmoles) of terephthalic acid dichloride by a method similar to that used to prepare III. Workup gave 2.1 g (60%) of a product with mp 67-69°C. PMR spectrum: 2.80 (m, CH_2), 3.70 (s, CH_3O), 7.60 ppm (m, C_6H_4). Found, %: C 51.7; H 5.3; N 4.2; S 10.6; M 575. $C_{26}H_{34}N_2O_{10}S_2$. Calculated, %: C 52.1; H 5.6; N 4.6; S 10.9; M 598.

7,9,18,20-Tetrakis[1,2-bis(carbomethoxy)ethyl]-1,4,12,15-tetrathia-7,9,18,20-tetraazacyclodocosane (V). A solution of 2.8 g (6.0 mmoles) of diamine I in 350 ml of methanol and a solution of 2.4 ml of a 40% solution of formaldehyde in 350 ml of methanol were added simultaneously to 800 ml of methanol at 60°C in the course of 6 h. At the end of the reaction bulk of the methanol was removed in vacuo, and the residue was filtered and diluted with ether in the cold. The resulting colorless oil was separated and dried in vacuo. The yield was 1.9 g (65%). PMR spectrum: 2.55 (s, CH_2CO), 2.69 (m, CH_2S), 3.27 (m, CH_2N), 3.52 (s, CH_3O), 4.01 ppm (s, CHCO). Found, %: C 47.1; H 6.3; N 5.4; S 13.1. $C_{38}H_{64}N_4O_{16}S_4$. Calculated, %: C 47.5; H 6.6; N 5.8; S 13.3.

9,10-Benzo-1,1,4,4,8,11-hexaoxo-7,12-bis[1,2-bis(carbomethoxy)ethyl]-1,4-dithia-7,12-diazacyclotetradec-9-ene (VI). A solution of 1.0 g of sulfide III and 3.3 ml of 30% H_2O_2 in 10 ml of acetic acid was heated for 2 h at 90°C, after which it was cooled and poured over ice, and the aqueous mixture was extracted with chloroform. The solvent was evaporated in vacuo, and the residue was washed with methanol and dried to give 0.66 g (60%) of a product with mp 150-152°C. Found, %: C 46.8; H 4.8; N 4.0; S 9.5. $C_{26}H_{34}N_2O_{14}S_2$. Calculated, %: C 47.1; H 5.1; N 4.2; S 9.8.

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