MACROHETEROCYCLES.

32.* HOMOLYTIC DEHYDRODIMERIZATION OF CROWN ETHERS

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The corresponding bis(crown ethers), as well as phenyl- and hydroxy-substituted crown ethers, were obtained by homolytic dehydrodimerization of 12-crown-4, 15-crown-5, and 18-crown-6 in benzene or water.

Binuclear crown ethers frequently display unusual complexing properties; this is evidently due to the cooperative effect of two polyether rings joined by a short aliphatic chain [2, 3].

The simplest approach to the synthesis of binuclear crown ethers with a C-C link is their homolytic dehydrodimerization [4]. We have studied the dehydropolymerization of 12-crown-4 (I), 15-crown-5 (II), and 18-crown-6 (III) in benzene in the presence of tert-butyl peroxide, the decomposition of which was initiated photochemically and in water in the presence of hydrogen peroxide and divalent iron sulfate.



I, IV, VII, X n=1; II, V, VIII, XI, XIII, XV n=2; III, VI, IX, XII, XIV, XVI n=3

The yields of dimerization products IV-VI in the first case were 53-63% and were substantially higher as compared with the 15% yield obtained when the reaction was carried out with hydrogen peroxide. In addition to the expected dimerization products, we also isolated from the reaction mixtures phenyl- and hydroxy-substituted crown ethers VII-XVI, the formation of which is possible as a result of recombination of the corresponding radicals. The yields of the mono- (VII-IX, XIII, XIV) and disubstituted crown ethers (X-XII, XV, XVI) relative to the dimeric compounds decrease with an increase in the size of the polyether ring. One cannot exclude the possibility that this is due to different conformational rigidities of binuclear crown ethers IV-VI, which evidently should increase with a decrease in the ring size.

All of the compounds obtained are colorless oily substances. Compound IV undergoes slow crystallization during prolonged standing. The compositions and structures of the compounds obtained were confirmed by the results of elemental analysis and PMR and mass-spectroscopic data. Their properties and spectral characteristics are described in Table 1.

In the PMR spectra of binuclear crown ethers IV-VI the signals of all of the protons appear in the form of a singlet at 3.56-3.58 ppm.

*See [1] for Communication 31.

A. V. Bogat'skii Physicochemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1179-1182, September, 1987. Original article submitted March 31, 1986. TABLE 1. Characteristics of the Synthesized Compounds

8,7 CielliaOs 54 8,9 CzolliaOis 54 9,0 CzolliaOis 54 7,9 CielliaOis 54 7,9 CielliaOis 66 8,5 CielliaOis 63 7,9 CielliaOis 63 7,7 CzelliaOis 63 7,6 CzelliaOis 63 7,6 CzelliaOis 63 7,6 CzelliaOis 63 8,8 CiolliaOis 61 8,8 CiolliaOis 60 8,8 CiolliaOis 61 8,5 CiolliaOis 50 8,2 CiolliaOis 51
8,7 3,9 3,0 3,0 3,5 7,7 7,7 7,9 8,8 8,8 8,8 8,2 8,2 8,2
89 55,0 89 55,1 89 55,1 89 55,1 80 54,9 95 66,4 95 66,4 104 65,3 165 73,3 165 73,3 160 70,9 180 70,9 180 69,5 107 51,6 107 51,6 115 47,9
$ \begin{array}{c} 526 & (0,1) & (77 & (0,5) & (19 & (3,1) & (33 & (2,5) & (31) \\ 775), 87 & (6,3) & 78 & (4,6) & 73 & (10,1), 59 & (4,0) & 45 \\ 7252 & (0,6) & 195 & (1,8) & 165 & (1,4) & 133 & (1,9) & 121 \\ (1,10), 89 & (1,1) & 83 & (5,1) & 133 & (5,2) & 121 \\ (11,0), 89 & (10,1) & 73 & (8,7) & 83 & (7,2) & 58 & (9,6) & 45 \\ (11,0), 89 & (10,1) & 73 & (8,7) & 83 & (7,2) & 58 & (5,2) & 45 \\ (11,0), 89 & (10,1) & 73 & (8,7) & 83 & (7,2) & 58 & (5,2) & 45 \\ (11,0) & 89 & (10,1) & 73 & (8,7) & 83 & (7,2) & 58 & (5,0) & 45 \\ (11,0) & 89 & (10,1) & 73 & (8,7) & 83 & (7,2) & 58 & (5,0) & 45 \\ (11,0) & 89 & (10,1) & 73 & (8,7) & 83 & (7,2) & 58 & (5,0) & 45 \\ (12,5) & 104 & (4,2) & 89 & (7,7) & 73 & (4,8) & 58 & (5,0) & 45 \\ (4,2) & 133 & (2,6) & 89 & (4,7) & 73 & (4,8) & 58 & (5,0) & 45 \\ (5,4) & 177 & (2,3) & 133 & (2,5) & 133 & (2,6) & 45 \\ (6,7) & 133 & (2,6) & 83 & (4,4) & 83 & (6,6) & 73 & (5,9) & 45 \\ (6,7) & 133 & (2,6) & 83 & (4,4) & 83 & (6,6) & 73 & (2,6) & 45 \\ (6,7) & 133 & (2,6) & 83 & (4,4) & 83 & (6,6) & 73 & (2,6) & 45 \\ (6,7) & 133 & (2,6) & 83 & (4,4) & 83 & (6,6) & 73 & (2,9) & 117 \\ (6,7) & 133 & (2,6) & 89 & (12,6) & 73 & (2,9) & 117 \\ (6,7) & 133 & (2,6) & 87 & (12,0) & 73 & (2,9) & 117 \\ (5,25) & 89 & (12,0) & 87 & (12,0) & 73 & (2,0) & 13 \\ (2,4) & 89 & (12,0) & 87 & (12,0) & 73 & (2,9) & 117 \\ (2,5) & 89 & (12,0) & 87 & (10,0) & 58 & (9,9) & 45 \\ (2,4) & 89 & (12,0) & 87 & (12,0) & 73 & (2,9) & 117 \\ (2,5) & 133 & (2,6) & 117 & (0,6) & 133 & (2,9) & 117 \\ (2,5) & 133 & (2,6) & 117 & (0,6) & 133 & (2,9) & 117 \\ (2,6) & 130 & 130 & 87 & (0,4) & 177 & (0,6) & 133 & (2,9) & 117 \\ (2,5) & 234 & (0,4) & 177 & (0,6) & 150 & (0,5) & 133 & 12 \\ (2,4) & 89 & (12,0) & 177 & (0,6) & 150 & (0,5) & 133 & 12 \\ (2,6) & 120 & 0,6) & 127 & (0,6) & 150 & (0,5) & 133 & 12 \\ (2,6) & 120 & 120 & 120 & 120 & 120 & 120 & 120 \\ (2,6) & 234 & (0,4) & 177 & (0,6) & 150 & (0,5) & 133 & 12 \\ (2,6) & 120 & 12$
$ \begin{array}{c} \begin{array}{c} 1 & 222 & (0.6), & 195 & (1,9), & 165 & (1,4), & 133 & (1,9), & 121 & (2,5), \\ 246 & (0,5) & 177 & (2,2), & 165 & (1,0), & 133 & (5,2), & 121 & (2,6), \\ (11,0), & 89 & (10,1), & 73 & (8,7), & 83 & (7,2), & 58 & (5,2), & 45 & (12,0) \\ (11,5) & 104 & (4,2) & 89 & (7,5), & 83 & (7,2), & 58 & (5,2), & 45 & (12,0) \\ (11,5) & 104 & (4,2) & 89 & (7,5) & 83 & (12,6) & 58 & (5,0), & 45 & (12,0) \\ (12,5) & 104 & (4,2) & 89 & (7,5) & 83 & (12,6) & 58 & (5,0), & 45 & (12,0) \\ (12,2) & 133 & (1,3) & 133 & (2,5) & 197 & (6,0) & 45 & (12,0) \\ (12,2) & 133 & (1,3) & 89 & (4,7) & 73 & (4,8), & 58 & (5,0), & 45 & (12,0) \\ (12,2) & 133 & (12,3) & 133 & (3,2) & 89 & (5,3) & 197 & (4,9), & 181 & (7,4) \\ (6,7) & 177 & (2,3) & 133 & (2,3) & 89 & (5,3) & 197 & (4,9), & 181 & (7,4) \\ (6,7) & 133 & (2,6) & 89 & (4,4) & 83 & (6,6) & 73 & (5,8) & 45 & (11,6) \\ (6,7) & 218 & (0,5) & 177 & (0,5) & 133 & (2,9) & 117 & (2,3) \\ (2,2) & 89 & (12,4) & 87 & (12,0) & 73 & (2,9) & 117 & (2,3) \\ (2,2) & 89 & (12,0) & 87 & (12,0) & 73 & (2,9) & 117 & (1,9) \\ (2,2) & (2,0) & 224 & (0,4) & 177 & (0,5) & 133 & (2,9) & 117 & (1,9) \\ \end{array} \right) ,$
$ \begin{array}{c} (11.0), \ 89, \ (10.1), \ 73, \ (8.7), \ 83, \ (7.2), \ 58, \ (5.2), \ 45, \ (12.0) \\ 340, \ (0,4), \ 253, \ (1,0), \ 177, \ (1,6), \ 165, \ (1,3), \ 133, \ (5.2), \ 121 \\ (1.5), \ 104, \ 253, \ (1,0), \ 197, \ (6,0), \ 181, \ (10,2), \ 180, \ (9,9), \ 165 \\ (4.2), \ 133, \ (1,3), \ 89, \ (4,7), \ 73, \ (4,8), \ 58, \ (5,0), \ 45, \ (12,9) \\ (4.2), \ 133, \ (1,3), \ 89, \ (4,7), \ 73, \ (4,8), \ 58, \ (5,0), \ 45, \ (12,9) \\ (4.2), \ 133, \ (1,3), \ 89, \ (4,7), \ 73, \ (4,8), \ 58, \ (5,0), \ 45, \ (3,8) \\ (4,2), \ 133, \ (1,3), \ 225, \ (4,8), \ 225, \ (5,2), \ 197, \ (7,5), \ 181, \ (6,0), \ 180 \\ (6,7), \ 133, \ (2,6), \ 89, \ (4,4), \ 83, \ (6,6), \ 73, \ (5,9), \ 45, \ (7,4), \ 100 \\ (6,7), \ 133, \ 226, \ (89, \ (4,4), \ 83, \ (6,6), \ 73, \ (5,9), \ 45, \ (7,4), \ 100 \\ (6,7), \ 133, \ 226, \ (89, \ (4,4), \ 83, \ (6,6), \ 73, \ (5,9), \ 45, \ (1,6), \ 107 \\ (2,5), \ 89, \ (12,2), \ 89, \ (12,2), \ 73, \ (12,0), \ 73, \ (2,9), \ 45, \ (1,6), \ 107 \\ (2,4), \ 89, \ (12,2), \ 89, \ (12,1), \ 73, \ (0,6), \ 58, \ (9,9), \ 45, \ (15,7) \\ (2,4), \ 89, \ (12,1), \ 133, \ (2,6), \ 133, \ (2,9), \ 117, \ (2,3), \ 117 \\ (2,4), \ 89, \ (12,1), \ 133, \ (2,6), \ 133, \ (2,9), \ 117 \ (1,9), \ 107 \\ (2,4), \ 89, \ (12,1), \ 177, \ (0,6), \ 133, \ (2,6), \ 133, \ (3,0), \ 117 \ (2,3), \ 115 \\ (2,4), \ 89, \ (12,1), \ 177, \ (0,6), \ 133, \ (2,6), \ 133, \ (3,0), \ 117 \ (1,9), \ 107 \\ (2,4), \ 89, \ (12,1), \ 177, \ (0,6), \ 133, \ (2,6), \ 133, \ (3,0), \ 117 \ (1,9), \ 107 \\ (2,4), \ 89, \ (12,1), \ 177, \ (0,6), \ 133, \ (2,6), \ 133, \ (3,0), \ 115 \ (1,9), \ 117 \\ (1,9), \ 115 \ (1,9), \ 117 \ (1,9), \ 115 \ (1,9), \ 115 \ (1,9), \ 117 \ (1,9), \ 115 \ (1,9), \ 117 \ (1,9), \ 115 \ (1,9), \ 115 \ (1,9), \ 115 \ (1,9), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ 115 \ (1,15), \ $
$ \begin{array}{c} n, & 328 & (0,7), & 225 & (4,8), & 197 & (6,0), & 181 & (10,2), & 180 & (9,9), & 165 & 7 \\ (4,2), & 133 & (1,3), & 89 & (4,7), & 73 & (4,8), & 58 & (5,0), & 45 & (9,8) \\ (5,4), & 177 & (2,3), & 133 & (3,2), & 89 & (5,3), & 73 & (5,6), & 45 & (7,0) \\ (5,4), & 177 & (2,3), & 133 & (3,2), & 89 & (5,3), & 73 & (5,6), & 45 & (7,0) \\ (6,7), & 133 & (2,5), & 89 & (4,4), & 83 & (6,6), & 73 & (5,9), & 181 & (7,4), \\ (6,7), & 133 & (2,6), & 89 & (4,4), & 83 & (6,6), & 73 & (5,9), & 117 & (2,3), \\ (6,7), & 133 & (2,6), & 89 & (4,4), & 83 & (6,6), & 73 & (5,9), & 117 & (2,3), & 107 \\ (6,7), & 133 & (2,6), & 89 & (4,4), & 83 & (6,6), & 133 & (2,9), & 117 & (2,3), & 107 \\ (5,2), & 89 & (12,0), & 87 & (12,0), & 73 & (9,2), & 58 & (13,0), & 45 & (15,1) \\ (2,2), & 89 & (12,0), & 87 & (12,7) & (7,8) & 133 & (2,8), & 117 & (1,9), & 107 \\ (2,2), & 89 & (12,0), & 87 & (12,7) & 73 & (10,0), & 58 & (9,9), & 177 & (15,1) \\ (2,2), & 89 & (12,0), & 87 & (12,7) & 73 & (10,0), & 58 & (9,9), & 117 & (1,9), & 107 \\ (2,2), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (1,9), & 107 \\ (2,2), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (1,9), & 107 \\ (2,4), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (1,9), & 107 \\ (2,4), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (1,9), & 107 \\ (2,4), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (1,9), & 107 \\ (2,4), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (15,9), & 117 \\ (2,4), & 89 & (12,0), & 87 & (12,5), & 73 & (10,0), & 58 & (9,9), & 117 & (15,9), & 115 \\ (2,5), & 89 & (2,0), & 123 & (0,0), & 150 & (0,5), & 133 & (3,0), & 115 \\ (2,6), & 2,6 & (0,0), & 234 & (0,4), & 177 & (0,6), & 150 & (0,5), & 133 & (3,0), & 115 \\ (2,2), & 110 & 110 & 110 & 110 & 110 \\ (2,2), & 110 & 110 & 110 & 110 & 110 \\ (2,2), & 110 & 110 & 110 & 110 & 110 \\ (2,2), & 110 & 110 & 110 & 110 & 110 \\ (2,2), & 120 & 120 & 100 & 110 & 110 \\ (2,2), & 120 & 100 & 110 & 110 & 110 \\ (2,2), & 120 &$
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c}$
s, $\begin{bmatrix} 236 & (00), 238 & (0.5), 177 & (0.5), 133 & (2.0), 43 & (11,0) \\ (2.5), 89 & (124), 87 & (120), 73 & (92), 58 & (130), 117 & (2.3), 107 & 51, 108 \\ (2.5), 89 & (124), 87 & (120), 73 & (92), 58 & (130), 117 & (1.9), 107 \\ (2.4), 89 & (13,0), 87 & (12.5), 73 & (10,0), 58 & (9.9), 45 & (15,7) \\ (2.4), 89 & (13,0), 87 & (12.5), 73 & (10,0), 58 & (9.9), 45 & (15,7) \\ 51 & (2.4), 89 & (13,0), 87 & (12.5), 73 & (10,0), 58 & (9.9), 45 & (15,7) \\ 51 & (2.4), 89 & (13,0), 87 & (12.5), 73 & (10,0), 58 & (9.9), 45 & (15,7) \\ \end{array}$
s, 280 (0,0), 262 (0,6), 177 (0,8), 133 (2,8), 117 (1,9), 107 51,6 (2,4), 89 (13,0), 87 (12,5), 73 (10,0), 58 (9,9), 45 (15,7) s, 252 (0,0), 234 (0,4), 177 (0,6), 150 (0,5), 133 (3,0), 115 47,9

*The molecular-ion peak and the 10 most intense ion peaks. *From the sum of the intensities of all of the peaks beginning with mass 45. *The yield of the reaction product when the reaction was carried out in $\rm H_2O$.

In the spectra of monophenyl-substituted crown ethers VII-IX a characteristic spectral feature is a multiplet signal of a PhCH group at 4.47 ppm and a singlet of aromatic protons at 7.13 \pm 0.10 ppm. In the spectra of diphenyl-substituted crown ethers X-XII, which were isolated in the form of mixtures of isomers, a multiplet signal of protons of a PhCH group appears at 4.44 \pm 0.20 ppm, and a signal of aromatic protons shows up in the form of a multiplet at 7.28 \pm 0.10 ppm. A multiplet signal of protons of a CHOH methylidyne group is observed in the spectra of crown ethers XIII-XVI at 4.17 \pm 0.13 ppm, and a broad signal of hydroxy groups is observed at 2.48 \pm 0.18 ppm.

The mass spectra of IV-XII contain molecular-ion peaks with the highest intensity for phenyl-substituted crown ethers VII-XII and with vanishingly low intensity for hydroxy-substituted XIII-XVI. In addition to the indicated peaks, the spectra of all of the investigated crown ethers contain characteristic peaks of ions that are an analytical feature of the polyether ring [5, 6]. These include a homologous series of ions, the mass numbers of which correspond to protonated homologs of the crown ethers (ions A).



Phenyl-substituted analogs of ions A (ions B) are present in the mass spectra of both the mono- and disubstituted crown ethers VII-XII. The formation of ions C, which may serve as an analytical feature of this series of compounds, is characteristic for diphenyl-substituted crown ethers X-XII.

The presence of all three types of indicated ions in the mass spectra of the phenylsubstituted crown ethers constitutes evidence that phenyl substituents in the polyether ring do not affect the realization of "crown-ether" type of fragmentation [5] under electron impact. The formation of ions of the A-C type in the fragmentation of diphenyl-substituted crown ethers X-XII constitutes evidence that these substances are mixtures of isomers with different relative orientations of the phenyl groups.

The transition from phenyl- to diphenyl-substituted crown ethers is accompanied by an increase in the intensities of the peaks of ions B and C with respect to the total ion current. In monophenyl-substituted VII-IX an increase in the ring size leads to an increase in the contribution of ions A to the total ion current (Table 1).

A pecularity of hydroxy-substituted crown ethers XIII-XVI is the ejection of a molecule of water from the molecular ions. Fragmentation with the formation of protonated homologs of crown ethers is also characteristic for these compounds [5].

Thus homolytic reactions are not only a convenient method for obtaining binuclear crown ethers but also are of potential interest as a simple route to mono- and disubstituted crown ethers. It is apparent that the yields of products of this type can be increased substantially by means of an appropriate change in the reaction conditions.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl, were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The mass spectra were obtained with a Varian MAT-112 spectrometer with direct introduction of the samples into the ion source at an ionization energy of 70 eV. Preparative gas—liquid chromatog-raphy (GLC) was accomplished with a Pye-Unicam 204 chromatograph with a flame-ionization detector and a 2.1 m by 8 mm glass column; the liquid phase was SE-30 (5%) on Chromaton N-AW. Analytical GLC was carried out with a Chrom-5 chromatograph with a 3 m by 3 mm column; the liquid phase was SP-2100 (5%) on Chromaton N-Super. Thin-layer chromatography (TLC) was carried out on glass plates with a fixed layer of neutral Al_2O_3 (L 5/40) in a hexane-2-propanol system (20:1).

<u>1,1'-Bis[2,5,8,11-tetraoxacyclododecane](IV), 1,1'-Bis[2,5,8,11,14-pentaoxacyclopenta-</u> <u>decane](V), 1,1'-Bis[2,5,8,11,14,17-hexaoxacyclooctadecane](VI), 1-Phenyl-2,5,8,11-tetra-</u> <u>oxacyclododecane(VII), 1-Phenyl-2,5,8,11,14-pentaoxacyclopentadecane(VIII), 1-Phenyl-2,5,-</u> <u>8,11,14,17-hexaoxacyclooctadecane(IX), Diphenyl-2,5,8,11-tetraoxacyclododecane(X), Diphenyl-</u> <u>2,5,8,11,14-pentaoxacyclopentadecane(XI), and Diphenyl-2,5,8,11,14,17-hexaoxacyclooctadecane</u> <u>(XII)(General Method)</u>. A 160-mmole sample of crown ether I, II, or III was dissolved in 160 ml of benzene, and 8 mmole of tert-butyl peroxide was added. Argon was passed through the solution, and the reaction mixture was irradiated with a mercury lamp (150 W) at 20°C for 48 h. The benzene and excess unchanged crown ether were removed by distillation in vacuo in an inert atmosphere. Column chromatography yielded crown ether IV, V, or VI and a mixture of phenyl-substituted crown ethers. Preparative GLC of the latter gave individual mono-(VII, VIII, or IX) and diphenyl-substituted (X, XI, or XII) crown ethers.

<u>1,1'-Bis[2,5,8,11,14-pentaoxacyclopentadecane]</u> (V), <u>1,1'-Bis[2,5,8,11,14,17-hexaoxacy-clooctadecane]</u> (VI), <u>1-Hydroxy-2,5,8,11,14-pentaoxacyclopentadecane</u> (XIII), <u>1-Hydroxy-2,5,8,11,14-pentaoxacyclopentadecane</u> (XV), and Dihydroxy-2,5,8,11,14-pentaoxacyclopentadecane (XV), and Dihydroxy-2,5,8,11,14,17-hexaoxacyclooctadecane (XVI) (General Method). A 160-mmole sample of crown ether II or III was dissolved in 10 ml of distilled water, one to two drops of concentrated H_2SO_4 were added, and the mixture was cooled to 0°C. An 8-mmole sample of hydrogen peroxide and a solution of 8 mmole of divalent iron sulfate in 10 ml of water were added simultaneously in the course of 20 min with vigorous stirring in an argon atmosphere to the reaction mixture from two dropping funnels while maintaining the temperature at 0°C. Stirring was continued for 1 h. The mixture was then extracted with chloroform (three 50-ml portion), and the extracts were washed with a dilute solution of divalent iron sulfate acidified with H_2SO_4 , and dried with anhydrous magnesium sulfate. The chloroform and excess unchanged crown ether were removed by vacuum distillation in an inert atmosphere. The reaction products were isolated by preparative GLC.

LITERATURE CITED

- 1. N. G. Luk'yanenko and O. T. Mel'nik, Khim. Geterotsikl. Soedin., No. 9, 1173 (1987).
- 2. M. I. Calverley and I. Dale, Chem. Commun., 684 (1981).
- 3. K. Kimura, H. Sakamoto, J. Koscki, and T. Shono, Chem. Lett., No. 8, 1241 (1985).
- 4. M. Kirch and J. M. Lehn, Tetrahedron, <u>40</u>, 4395 (1984).
- 5. Y. C. Lee, A. I. Popov, and S. Allison, Internat. J. Mass Spectrom. Ion Phys., <u>51</u>, 267 (1983).
- A. I. Gren', O. S. Timofeev, N. G. Luk'yanenko, T. I. Kirichenko, and V. V. Limich, in: Summaries of Papers Presented at the 2nd All-Union Conference on the Chemistry of Macrocycles [in Russian], Odessa (1984), p. 71.

NEW METHODS OF SULFONATION IN THE THIOPHENE SERIES*

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Simple preparative methods of sulfonation of thiophene derivatives by complexes of sulfur trioxide with ethers, amides, trialkyl phosphates, and sulfoxides under mild conditions were developed.

Up until now, one of the principal methods for obtaining sulfonic acids of thiophene and its homologs was the sulfonation of thiophenes with a threefold excess of the pyridinesulfur trioxide complex ($Py \cdot SO_3$) at 105-130°C for 8-10 h under pressure in sealed ampuls [1, 2]. This method (Table 1) has a number of substantial drawbacks: low yields and nonhomogeneity of the products obtained, severe conditions (the process is carried out under pressure in sealed ampuls at temperatures above 100°C), excess sulfonating agent (3:1), and the long duration of the process (10-720 h); these drawbacks are due to the low sulfonating activity of the Py.SO₃ complex. A sulfonic acid was obtained in 86% yield in the prolonged reaction of thiophene with the more active (as compared with $Py \cdot SO_3$) $Py \cdot 2SO_3$ complex at 25°C [2]. *The developed methods of synthesis were protected by inventor certificates Nos. 707916 and 914557.

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