DIAZA CROWN ETHERS BASED ON sym-TRIAZINE DERIVATIVES

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The reaction of 2-dialkylamino-4,6-dichloro-1,3,5-triazines with the disodium derivatives of di- and triethyleneglycols, has given four new diaza crown ethers. The structures of the compounds synthesized have been established by IR and PMR spectroscopy and elementary analysis.

Among sym-triazine derivatives, compounds are known which possess various biological activities [1-3]. Furthermore, polyoxapolyaza crown ethers [4] and polyoxamonoaza crown ethers [5], each containing a sym-triazine fragment, have recently been described. The compounds are capable of forming complexes with salts of the alkali metals and can be used as catalysts of interphase transfer [4, 5].

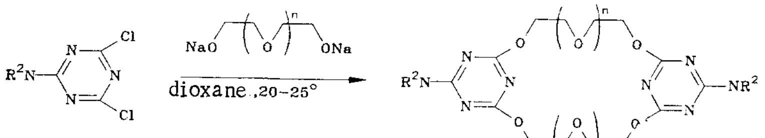
In order to find new aza crown ethers based on sym-triazine derivatives, in the present work we have synthesized bis(2-dialkylamino-1,3,5-triazino)-1,11-diaza-20-crown-8s (III, V) and bis(2-dialkylamino-1,3,5-triazino)-1,14-diaza-26-crown-10s (IV, VI). The diaza crown ethers (III-VI), in the form of white crystalline substances, were produced by the reaction of the dichlorotriazines (I) and (II) with the disodium derivatives of di- and triethyleneglycols in anhydrous dioxane solution at room temperature under high-dilution condition.

The compounds (III-VI) that we synthesized, like known polyoxapolyaza crown ethers [4], crystallize well from acetonitrile and ethanol, the dimethylamino-substituted diaza crown ethers (III, IV) having higher melting points than the diethylamino-substituted diaza crown ethers (V, VI). The melting points, spectral characteristics, results of elementary analysis, and yields of the substances obtained are given in Table 1.

The IR spectra of the diaza crown ethers (III-VI) show strong absorption bands of the C—O—C bond in the 1125-1135 cm^{-1} region. Thanks to the high symmetry of the molecules of the diaza crown ethers synthesized, their PMR spectra are easily interpreted. The protons of the methylene groups of the oligoethyleneglycol bridges in the α positions to the triazine rings give a signal in the form of a triplet at 4.48-4.58 ppm, the protons of the β-methylene groups a triplet at 3.82-3.92 ppm, and the protons of the γ-methyl groups of compound (IV) a singlet at 3.68 ppm. The signals of the γ-methylene protons in compound (VI) coincide with the signals of the protons of the methylene groups of the diethylamino substituents and give a complex multiplet at 3.67 ppm.

EXPERIMENTAL

The melting points of the compounds obtained were determined on a Kofler block. The course of the reactions was monitored by the TLC method on plates with a nonfixed layer of LSL 50/40 μ silical gel with a luminescent indicator in the ethyl acetate—chloroform—ethanol (6:3:1) system. The individuality of the diaza crown ethers obtained was checked on plates with a nonfixed layer of anhydrous Al_2O_3 in the diethyl ether—chloroform (2:3) system. The substances were revealed on the plates in ultraviolet light and in iodine vapor. IR spectra were recorded in KBr tablets on a UR-20 spectrometer, and PMR spectra were taken on a Jeol



I,II

III R=CH_3, n=1; IV R=CH_3, n=2;
V R=C_2H_5, n=1; VI R=C_2H_5, n=2

III–VI

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TABLE 1. Characteristics of the Diaza Crown Ethers (III-VI)

Compound	mp, °C	IR spectrum (COC) cm^{-1}	PMR spectrum, δ ($CDCl_3$), ppm	M·	Found, %			Empirical formula	Calculated, %			Yield, %
					C	H	N		C	H	N	
III	203—206	1135	4,58 (8H, t, α-CH_2O); 3,92 (8H, t, β-CH_2O); 3,16 (12H, s, CH_3—N)	453	47,7	6,4	25,1	$C_{18}H_{28}N_8O_6$	47,8	6,2	24,8	10
IV	182—185	1125	4,51 (8H, t, α-CH_2O); 3,82 (8H, t, β-CH_2O); 3,68 (8H, s, γ-CH_2O); 3,16 (12H, s, CH_3N)	541	48,5	6,7	21,0	$C_{22}H_{36}N_8O_8$	48,9	6,7	20,7	22
V	139—141	1130	4,48 (8H, t, α-CH_2O); 3,83 (8H, t, β-CH_2O); 3,52 (8H, q, CH_2N); 1,14 (12H, t, CH_3C)	508	51,9	6,9	21,7	$C_{22}H_{36}N_8O_6$	52,0	7,1	22,0	20
VI	122—124	1135	4,57 (8H, t, α-CH_2O); 3,84 (8H, t, β-CH_2O); 3,67 (16H, m, γ-CH_2O, CH_2N); 1,20 (12H, t, CH_3C)	596	52,5	7,3	19,0	$C_{26}H_{44}N_8O_8$	52,3	7,4	18,8	8

PS-100 instrument with a working frequency of 100 MHz using TMS as internal standard. The molecular weights were determined by mass spectrometry on a Varian MAT-311 mass spectrometer.

The initial 4,6-dichloro-2-dimethylamino-2,3,5-triazine (I) and 4,6-dichloro-2-diethylamino-1,3,5-triazine (II) were obtained by methods described in the literature [6, 7].

bis(2-Dimethylamino-1,3,5-triazino)-1,11-diaza-20-crown-8 (III). At room temperature, with stirring, a solution of 1.06 g (10 mmole) of diethyleneglycol was gradually added to a suspension of 1.90 g (79 mmole) of sodium hydride in 200 ml of absolute dioxane. After 30 min, a solution of 1.93 g (10 mmole) of the dialkaminodichlorotriazine (I) in 50 ml of anhydrous dioxane was added. The mixture was stirred at the same temperature for 2 h. The solution was filtered, the solvent was evaporated off under reduced pressure, and the residue was treated with benzene. The crystals that deposited were recrystallized from dinitrile. This gave 0.23 g (10%) of compound (III), mp 203-206°C (Table 1).

bis(2-Dimethylamino-1,3,5-triazino)-1,14-diaza-26-crown-10 (IV). The crown ether (IV) was synthesized under similar conditions by the reaction of 200 Mg (83 mmole) of sodium hydride, 300 mg (2 mmole) of triethyleneglycol, and 390 mg (2 mmole) of the triazine (I). The dioxane was driven off, the residue was treated with ethanol, and the crystals that deposited were separated off and recrystallized from the same solvent. This gave 120 mg (22%) of compound (IV). mp 182-185°C (Table 1).

bis(2-Diethylamino-1,3,5-triazino)-1,11-diaza-20-crown-8 (V). The crown ether (V) was synthesized similarly by the interaction of 1.1 g (5 mmole) of the diethylaminotriazine (II), 0.53 g (5 mmole) of diethyleneglycol, and 1.0 g of sodium hydride. After recrystallization of the crude products from ethanol, 250 mg (20%) of compound (V) was obtained. mp 139-141°C (Table 1).

bis(2-Diethylamino-1,3,5-triazino)-1,14-diaza-26-crown-10 (VI) was obtained by the interaction of 200 mg (83 mmole) of sodium hydride, 150 mg (1 mmole) of triethyleneglycol, and 220 mg (1 mmole) of the triazine (II). The residue obtained after the solvent had been driven off was treated with ethyl acetate, and the crystals that deposited were recrystallized from ethyl acetate—ethanol (1:1), giving 23 mg (8%) of the crown ether (VI). mp 122-124°C (Table 1).

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