Technical

Long Chain N-Alkyl Monoaza Crown Ethers

P.-L. KUO, M. MIKI, I. IKEDA and **M. OKAHARA,** Department of Applied Chemistry,
Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka, Japan 565

ABSTRACT

Homogeneous polyoxyethylated long chain alkylamines with 5 to 7 oxyethylene units were prepared by the reaction between oligoethylene glycol monochlorides and alkylamines. They were converted to the corresponding long chain N-alkyl monoaza crown ethers by treatment with *p*-toluene-sulfonyl chlorides in the presence of alkali metal hydroxides in dioxane. The physical and spectral properties of these new derivatives of alkylamines were investigated in detail.

INTRODUCTION

Some crown compounds with long chain alkyl substituents and their complexes with metal salts have recently attracted special interest as new types of surfactants and their surface active properties have been reported (1-3).

N-Alkyl monoaza crown ethers, which are new derivatives of alkylamines, also are expected to have surface active properties if the alkyl substituent is long enough. They may be useful as new surfactants with complexing ability with metal salts, phase-transfer catalysts and selective ion carriers, for example.

In a previous paper (4), we reported a simple synthetic method for preparing N-alkyl monoaza crown ethers with a short alkyl group from N,N-di(polyoxyethylene)alkylamines by treatment with *p*-toluenesulfonyl chloride in the presence of alkali metal hydroxide in polar aprotic solvents.

For the purpose of obtaining a new surface active crown ether, the synthesis of long chain N-alkyl monoaza crown ethers was undertaken and their physical and spectral properties were investigated. Homogeneous polyoxyethylated long chain alkylamines also were investigated.

EXPERIMENTAL PROCEDURE

Materials

Alkylamines, alkyl bromides, monoethanolamine, diethanolamine and ethylene chlorohydrin of analytical reagent grade were obtained from a commercial source. Their purity was checked by gas liquid chromatography (GLC) and they were purified by distillation when necessary.

Ethylene oxide was purified by passing it through 35% NaOH aqueous solution and dried over NaOH and soda lime prior to the reaction.

Oligoethylene Glycol Monochlorides (5)

Ethylene oxide was introduced to ethylene chlorohydrin (167 g, 2.05 mol) including 1.2% of BF_3 etherate as catalyst at 80 C. After 152 g of weight increase was attained, the reaction was stopped and the product was purged with nitrogen gas to remove unreacted ethylene oxide. Triethylene glycol monochloride (1a, 47 g, bp 98-99 C/0.5 mm Hg) and tetraethylene glycol monochloride (1b, 45 g, bp 130-131 C/0.5 mm Hg) were respectively separated from the polydisperse adduct by fractional distillation under reduced pressure.

N-(2-Hydroxyethyl)alkylamine

A solution of octyl bromide (57.9 g, 0.3 mol) dissolved in 100 ml of butanol was added to a butanol solution of monoethanolamine (73.2 g/100 ml) dropwise for a period of 1 hr at 100 C. After heating the mixture for 4 hr, butanol was evaporated off and the residue was extracted with ether. N-(2-Hydroxyethyl)octylamine 39.2 g (yield 75.5%, bp 85-87 C/0.09 mm Hg) was obtained by distillation of ether extract.

By the same procedure, N-(2-hydroxyethyl)-hexyl-, decyl- and dodecylamine were obtained in 72-80% yields.

N,N-Di(polyoxyethylene)alkylamines

N-(2-Hydroxyethyl)-N-(tetraoxyethylene)alkylamines. In a 100-ml round-bottomed flask, N-(2-hydroxyethyl)octylamine (2.7 g, 0.015 mol), 1b(3.2 g, 0.015 mol) and powdered sodium carbonate (2.5 g) were placed and the mixture was heated at 120 C with stirring. After 6 hr of reaction, it was diluted with alcohol, filtered and the solvent was removed from the filtrate. By distilling the residue at the reduced pressure using a Kugelrohr apparatus, 3.6 g of pure compound (2b, 68.7%) was obtained. Using similar procedure, hexyl (2a), decyl (2c) and dodecyl (2d) derivatives also were obtained (Table I).

N,N-Di(trioxyethylene)alkylamines (2e, 2f, 2g, 2h). Octylamine (1.94 g, 0.015 mol), 1a (5.05 g, 0.03 mol) and sodium carbonate (3.3 g) were reacted by a similar manner as that already described. The crude product obtained was distilled to give pure N,N-di(trioxyethylene)alkylamine (2f, 4.25 g, 72%). When hexyl-, decyl- and dodecylamine were used, the title compounds with corresponding alkyl group were obtained (Table I).

N-(Trioxyethylene)-N-(tetraoxyethylene)alkylamines (2i, 2j, 2k). Compound 1a (25.3 g, 0.15 mol) was reacted with excess octylamine (58.5 g, 0.45 mol) in the presence of 13 g of sodium carbonate in a similar manner, and N-(trioxyethylene)octylamine (26.3 g, 66.9%, bp 123-125 C/ 0.06 mm Hg) was obtained.

This compound (10.5 g, 0.04 mol) was treated with 2b (8.5 g, 0.04 mol) and sodium carbonate (4.2 g) to give 14.7 g of 2j (85%, bp 230-232 C/0.05 mm Hg).

By a similar procedure, hexyl (2i) and decyl derivative (2k) were also obtained. The results of the synthesis of polyoxyethylated alkylamines are shown in Table I.

Long Chain N-Alkyl Monoaza Crown Ethers

A suspension of powdered NaOH (1.2 g, 0.028 mol) in 100 ml dioxane was placed into a 250-ml 4-necked, round-bottomed flask equipped with a reflux condenser, 2 dropping funnels and a thermometer. A solution of 2b (2.45 g, 0.007 mol) in 20 ml dioxane, and a solution of *p*-toluenesulfonyl chloride (1.33 g, 0.007 mol) in 20 ml dioxane were put into the 2 separate dropping funnels. Both solutions were added dropwise to the NaOH suspension at the same rate for 3 hr at 30 C with vigorous stirring. After the addition was completed, the precipitate was removed and the solvent was evaporated. The residue was distilled by a Kugelrohr apparatus to give N-octyl monoaza 15-crown-5 (3b, 2.1 g, 90.4%) in the pure state.

Other N-alkyl monoaza 15-crowns (3a = C_6H_{13}, 3c = $C_{10}H_{21}$, 3d = $C_{12}H_{25}$) were obtained in the same way. N-Alkyl monoaza 18-crowns (3e, 3f, 3g, 3h) were also prepared analogously using KOH instead of NaOH. For the synthesis of N-alkyl monoaza 21-crowns (3i, 3j, 3k), benzenesulfonyl chloride and KOH were used instead of *p*-toluenesulfonyl chloride and NaOH and the reaction was carried out at 70 C.

The results of synthesis of monoaza crown ethers are tabulated in Table II.

RESULTS AND DISCUSSION

Although the addition reaction of ethylene oxide to alkylamines is a convenient and practical means to get N,N-di(polyoxyethylene)alkylamines, it could not be applied for the preparation of homogeneous compounds with long alkyl chains which were the intermediates for the synthesis of the objective crown ethers, since their separation from the polydisperse adducts was difficult.

Therefore, the homogeneous polyoxyethylated alkylamines (2a-k) were prepared by alkylation of alkylamines with oligoethylene glycol monochlorides (1a,b) and were effectively converted to N-alkyl monoaza crown ethers by a previously described intramolecular cyclization reaction method (4). The overall reaction scheme for the synthesis of N-alkyl monoaza crown ethers (3a-k) is shown in Scheme I.

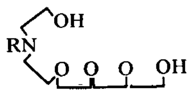
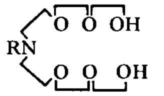
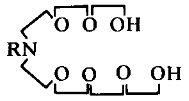
For the synthesis of oligoethylene glycol monochloride (1), monochlorination of oligoethylene glycol was found inadequate because the reaction gave a mixture of dichloride, monochloride (1) and unreacted oligoethylene glycol and the separation of 1 from the mixture was rather difficult.

In this research, oligoethylene glycol monochlorides were prepared by the polyoxyethylation of ethylene chlorohydrin in the presence of BF_3 etherate. By controlling the quantity of added ethylene oxide to ethylene chlorohydrin, the objective tri- and tetraethylene glycol monochlorides (1a and 1b) were obtained in moderate yields.

The alkylation of alkylamines with oligoethylene glycol monochlorides was done without solvent in the presence of sodium carbonate. Yields were generally high as shown in Table I, indicating the side reaction affording quaternary

TABLE I

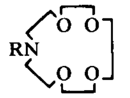
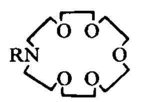
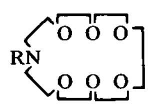
Yields and Physical Properties of Polyoxyethylated Amines

Oxyethylated alkylamine		R	Yield[a] (%)	bp (C/mm Hg)	Refractive index (20 C)	Amine value (calcd)	N% (calcd)
	2a	C_6H_{13}	84	205-210/0.7	1.4640	179.0(174.5)	4.47(4.36)
	2b	C_8H_{17}	69	190-195/0.06	1.4644	162.2(160.7)	4.03(4.09)
	2c	$C_{10}H_{21}$	78	204-207/0.005	1.4653	152.2(148.6)	3.91(3.71)
	2d	$C_{12}H_{25}$	66	—	1.4654	140.9(138.3)	3.57(3.45)
	2e	C_6H_{13}	67	201-205/0.06	1.4659	154.4(153.4)	4.02(3.83)
	2f	C_8H_{17}	72	220-222/0.03	1.4662	146.6(142.7)	3.52(3.56)
	2g	$C_{10}H_{21}$	81	211-213/0.005	1.4665	137.6(133.0)	3.37(3.32)
	2h	$C_{12}H_{25}$	67	—	1.4668	125.9(124.7)	3.15(3.12)
	2i	C_6H_{13}	64	220-222/0.03	1.4663	139.1(137.2)	3.60(3.42)
	2j	C_8H_{17}	57	230-232/0.05	1.4664	129.6(128.4)	3.61(3.20)
	2k	$C_{10}H_{21}$	65	237-239/0.03	1.4668	122.2(120.6)	3.21(3.01)

[a] Based on primary alkylamine.

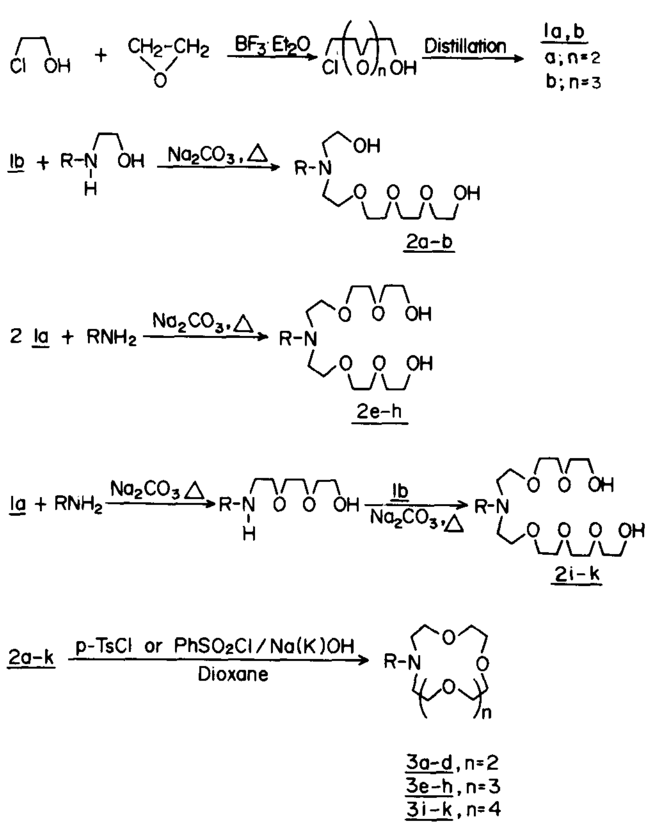
TABLE II

Yields and Physical Properties of N-Alkyl Monoaza Crown Ethers[a]

Crown ether		R	Yield[b] (%)	bp (C/mm Hg)	Refractive index (20 C)	Amine value (calcd)	N% (calcd)
	3a	C_6H_{13}	75	150-153/0.01	1.4680	187.3(185.1)	4.70(4.62)
	3b	C_8H_{17}	90	165-168/0.09	1.4680	171.9(169.5)	4.52(4.23)
	3c	$C_{10}H_{21}$	82	203-205/0.10	1.4686	157.1(156.3)	3.82(3.90)
	3d	$C_{12}H_{25}$	67	201-202/0.04	1.4688	146.7(145.0)	3.51(3.61)
	3e	C_6H_{13}	58	170-173/0.01	1.4681	163.3(161.7)	4.10(4.03)
	3f	C_8H_{17}	88	196-197/0.03	1.4682	151.2(149.6)	3.82(3.73)
	3g	$C_{10}H_{21}$	70	205-206/0.03	1.4688	141.4(139.2)	3.52(3.47)
	3h	$C_{12}H_{25}$	94	217-218/0.04	1.4688	132.0(130.2)	3.32(3.25)
	3i	C_6H_{13}	79	202-204/0.03	1.4686	145.3(143.5)	3.97(3.58)
	3j	C_8H_{17}	78	210-212/0.03	1.4686	135.3(133.9)	3.61(3.20)
	3k	$C_{10}H_{21}$	61	220-228/0.06	1.4689	126.8(125.5)	3.50(3.13)

[a] Satisfactory elemental analyses were obtained for all compounds.

[b] Based on oxyethylated alkylamine (2).



SCHEME I

ammonium salts is suppressed considerably.

The homogeneous polyoxyethylated amines (2a-k) were obtained as pale yellow oils and were purified by distillation. They showed only a sole peak in their gas chromatograms and elemental analyses were satisfactory.

The homogeneous polyoxyethylated amines (2a-k) were converted to the corresponding N-alkyl monoaza crown ethers by treating with *p*-toluenesulfonyl or benzenesulfonyl chloride in the presence of an alkali metal hydroxide in dioxane. Sodium hydroxide was used for the synthesis of monoaza 15-crown-5 by considering the effectiveness of the template atom, whereas for the preparation of monoaza 18- and 21-crown ethers, potassium hydroxide was employed. Pure monoaza crown ethers were isolated as hygroscopic liquids from their complexes with alkali metal chlorides or sulfonates by thermolysis under reduced pressure; the purified overall yields from the starting amines were 40-64%.

In the infrared (IR) spectra of monoaza crown ethers absorptions at 3480 and 1060 cm^{-1} resulting from O-H and C-O stretching which were observed in the IR spectra of polyoxyethylated amines (2) were not found. The formation of N-alkyl monoaza crown ethers was characterized mainly by the disappearance of O-H stretching absorption at 3480 cm^{-1} in their IR spectra.

In the nuclear magnetic resonance (NMR) spectra, there was no significant difference between the homogenous polyoxyethylated amines (2) and monoaza crown ethers (3), since the signal of O-H protons of the polyoxyethylated amines overlapped with the signals of methylene protons ($-CH_2-O-$) in most cases.

In the mass spectra, the parent peaks were observed in every monoaza crown ether studied, but were small. The base peaks were m/e 232 for monoaza 15-crown-5, 276 for 18-crown-6 and 320 for 21-crown-7 homologs, respectively, indicating that α-β cleavage of a nitrogen-substituted alkyl moiety occurred most easily analogous to N-alkyl morpholine (6).

N-Alkyl monoaza crown ethers may show the characteristic behavior as novel surfactants. Their surface active properties in the aqueous solution are under investigation.

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[Received February 14, 1980]