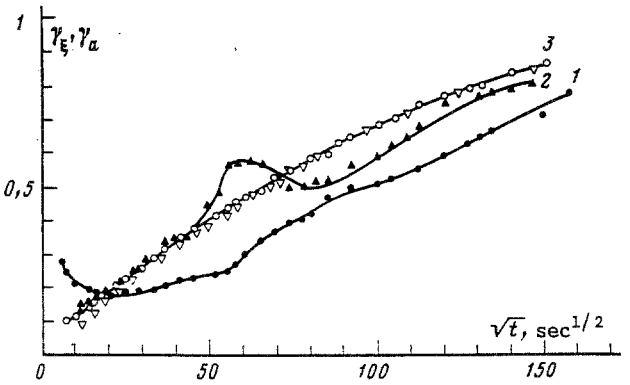

Fig. 2. Kinetic curves for adsorption γ_α (3) and adsorption deformation γ_α for zeolite NaA granulated without binder (1) and with 10% kaolin as binder (2) for the NaA–trans-2-butene system at 30°C.

3. Intracrystalline diffusion was studied for the NaA–trans-2-butene system. The kinetic curves for samples with and without binder have some differences, which have no influence on the equilibrium deformation.

LITERATURE CITED

1. O. K. Krasil'nikova and M. Kocirik, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2424 (1987).
2. O. K. Krasil'nikova and M. Kocirik, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 735 (1988).
3. O. K. Krasil'nikova and M. Kocirik, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4. 740 (1988).
4. V. F. Kononyuk, Chemical Sciences Candidate's Dissertation, Inst. Fiz. Khim. Akad. Nauk SSSR, Moscow (1972).
5. K. G. Krasil'nikov and N. N. Skoblinskaya, Dokl. Akad. Nauk SSSR, 184, No. 1, 151 (1969).
6. T. N. Ivanova, O. K. Krasil'nikova, A. I. Sarakhov, and M. M. Dubinin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 955 (1977).
7. R. Broddak, A. M. Voloshchuk, V. A. Gorlov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 503 (1985).

NEW CROWN ETHER WITH INDOXYL GROUPS

V. A. Popova and I. V. Podgornaya

UDC 542.91:547.898:547.74

The introduction of functional substituents into the benzo rings of dibenzo-18-crown-6 may lead to new complexing agents with useful properties [1]. In the present work, we described the synthesis of a crown ether with indoxyl groups.

The reaction of diaminodibenzo-18-crown-6 (I) with chloroacetic anhydride may give two products depending on the conditions: 4,5'-bis(chloroacetylamino)- (II) and 4,5'-bis-(glycine hydrochloride)dibenzo-18-crown-6 (III). Crown ether (II) is formed at ~ 20°C in dioxane. Product (III) was obtained as a betaine when the reaction was carried out in absolute ethanol at reflux. Upon subsequent cyclization in the presence of water, (III) gives 8,9;17,18-bis-(indoxyl)-18-crown-6 (IV).

Crown ether (II) is a colorless crystalline compound with mp 264-265°C, which is soluble in DMF but insoluble in water, ethanol, and ether. The IR spectra of (II) have characteristic bands for a secondary amide [2] (ν, cm^{-1}): 1652 s, 1628 m (amide(I)), and 1575 m (amide (II)) as well as NH group stretching bands at 3290 m/s, 3170 m, and 3120 m. The presence of chlorine was confirmed by the elemental analysis and the relatively strong IR band for the C–Cl bond at 750 cm^{-1}. Product (II) was also obtained by the reaction of (I) with $ClCH_2COCl$, which confirms

Institute of Chemistry, Urals Branch, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1160-1162, May, 1989. Original article submitted May 12, 1988.

0568-5230/3805-1055$12.50

Scheme 1

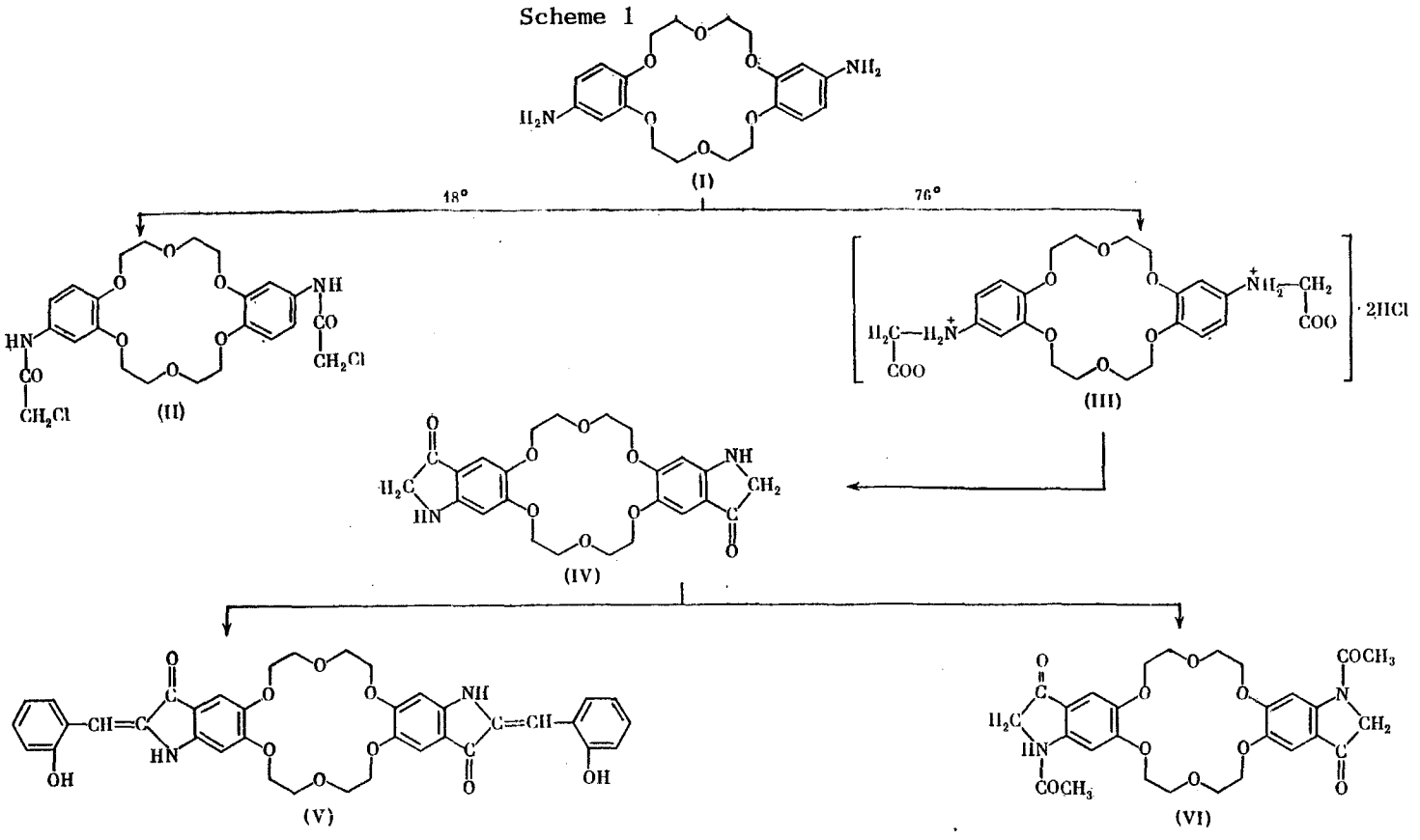

TABLE 1. Characteristics of Compounds Synthesized

Compound	Mp, °C	Solvent		Found, %				Chemical formula	Calculated, %			
		soluble in	insoluble in	C	H	N	Cl		C	H	N	Cl
(II)	264–265	DMF, DMSO	Water, ethanol, ether, benzene, chloroform	53,04	5,31	5,20	12,98	$C_{24}H_{28}N_2O_8Cl_2$	53,04	5,20	5,15	13,05
(III)	125–126	Ethanol, DMF DMSO	Acetone, benzene, dioxane, chloroform	51,23	5,46	5,00	12,42	$C_{24}H_{28}N_2O_8Cl_2 \cdot H_2O$	51,34	5,40	4,99	12,63
(IV)	212–213	DMF	Water, ethanol	59,04	6,01	6,18	–	$C_{22}H_{26}N_2O_8$	59,18	5,89	6,26	–
(V)	218–219	Dioxane, DMF chloroform	Water, ethanol	67,78	5,40	4,37	–	$C_{36}H_{34}N_2O_{10}$	67,24	5,06	4,13	–
(VI)	249–250		Water, ethanol, ether, DMF	60,40	5,62	5,14	–	$C_{28}H_{30}N_2O_{10}$	60,70	5,46	5,05	–

the proposed structure according to Elderfield [3].

Crown ether (III) is a colorless crystalline compound with mp 125-126°C, which is soluble in absolute ethanol and DMF but insoluble in dioxane, acetone, and chloroform. The IR spectrum shows bands (ν, cm^{-1}) in the 2400-2700 range from the NH_2^+ group at 2649 m and 2140 s and for the carboxy anion at 1640 m and 1615 m. Qualitative analysis for chlorine and elemental analysis of (III) indicated the presence of chlorine but there was no IR band at 750 cm^{-1}. This permits us to represent the structure of the substituent as a betaine dihydrochloride. Ring closure occurs upon the addition of water or aqueous ethanol to (III) giving crown ether (IV) with indoxy groups, mp 212-213°C. Product (IV) gives a dark red color test with $FeCl_3$ and and undergoes reactions, which are usual for ketones and indoxyl, especially condensation [3]. The product of the condensation of (IV) with salicylaldehyde, namely 8,9;17,18-bis(salicylindogenide)-18-crown-6 (V) was isolated as yellow needles. The reaction of (IV) with acetic anhydride gave 8,9;17,18-bis[indoxyl(N-acetyl)]-18-crown-6 (VI) as colorless crystals. The structures and compositions of these compounds were confirmed by elemental analysis and IR spectroscopy.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in vaseline mull and in KBr pellets. 4,5'-Diaminodibenzo-18-crown-6 was obtained according to our previous procedure [4]. Absolute solvents were used. The elemental analysis data, melting points, and solubilities are given in Table 1.

4,5'-Bis(chloroacetylamino)dibenzo-18-crown-6 (II). A sample of 0.7 g (0.4 mmole) $(ClCH_2CO)_2O$ in dioxane was added with stirring to a solution of 0.6 g (0.15 mmole) (I) in dioxane at ~20°C. The crystalline precipitate was separated, washed with dioxane and ethanol, and crystallized from DMF.

A sample of 0.6 g (0.8 mmole) $ClCH_2COCl$ was added with stirring to a suspension of 1.5 g (0.38 mmole) (I) in 20 ml abs. ether. The colorless precipitate was separated, washed with water, and crystallized from DMF.

4,5'-Bis(glycine hydrochloride)dibenzo-18-crown-6 (III). A mixture of 0.6 g (0.15 mmole) (I) and 0.7 g (0.4 mmole) $(ClCH_2CO)_2O$ was dissolved in 10 ml abs. ethanol at 70-76°C. A colorless precipitate formed upon cooling, which was recrystallized from absolute ethanol.

8,9;17,18-Bis(indoxyl)-18-crown-6 (IV) was obtained as colorless crystals from 70% aq. ethanol.

8,9;17,18-Bis(salicylindogenide)-18-crown-6 (V). A sample of 1 g (0.82 mmole) salicylaldehyde was added to 0.5 g (0.112 mmole) (IV) and was heated with stirring until a uniform mass was obtained. Crystallization from 1:1 chloroform–ethanol gave yellow crystalline (V).

8,9;17,18-Bis[indoxyl-(N-acetyl)]-18-crown-6 (VI). A sample of 1 g (0.98 mmole) acetic anhydride was added to a solution of 0.5 g (0.112 mmole) (IV) in DMF at ~20°C. The precipitate was filtered off and washed with DMF and water.

CONCLUSIONS

The reaction of diaminodibenzo-18-crown-6 with monochloroacetic anhydride in dioxane at room temperature gives 4,5'-bis(chloroacetylamino)dibenzo-18-crown-6. The same reaction carried out in ethanol at reflux gives 4,5'-bis(glycine hydrochloride)dibenzo-18-crown-6, which is converted in the presence of water to 8,9;17,18-bis(indoxyl)-18-crown-6.

LITERATURE CITED

1. V. A. Popova, I. V. Podgornaya, V. G. Lundina, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2544 (1987).
2. L. J. Bellamy, The Infrared Spectra of Complex Molecules, 1st ed., Wiley, New York (1954).
3. Heterocyclic Compounds, R. S. Elderfield (ed.), Vol. 3, Wiley, New York (1961).
4. V. A. Popova, I. V. Podgornaya, I. Ya. Postovskii, and N. N. Frolova, Khim.-farm. Zh., No. 6, 66 (1976).