Tetrahedron Letters Vol. 21, pp 313 - 314
0040-4039/80/0115-0313$02.00/0

MACROHETEROCYCLES-I. THE SYNTHESIS AND TAUTOMERIC TRANSFORMATIONS OF CROWN ETHERS CONTAINING THIOUREA MOIETY

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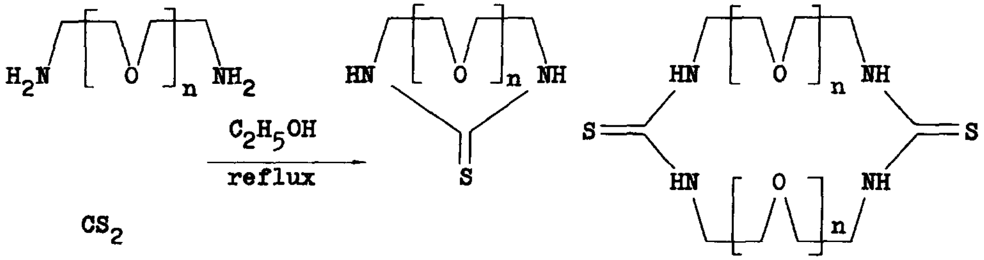
As an extension of our studies on polyfunctional macroheterocycles[1,2] we wish to report the synthesis of new crown ethers, containing thiourea moiety.

Cyclic polyoxyethylenethioureas 1-4 have been prepared by simultaneous dropwise addition to the 700 ml ethanol solutions of CS_2 (0.05 mol) and corresponding polyoxyethylenediamine (0.05 mol) in 150 ml ethanol at room temperature under a nitrogen atmosphere during 4-5 hours. The resulting mixture was refluxed for 6 hours and then acidified with concentrated hydrochloric acid (1 ml) and refluxing was continued until hydrogen sulfide ceased to evolve (~13 hours). The products were isolated and purified by column chromatography (kiselgel, chloroform-methanol as eluent).



1 n = 1
2 n = 2

3 n = 1
4 n = 2

The IR spectra of 1-4 (KBr disks) show no bands for C=N and SH bonds indicating their thione structure. Solutions of 1-4 (tetrachloroethane) exhibit bands of C=N (1615-1660 cm^{-1}) and SH (2455±5 and 2500 cm^{-1}). The intensity of these bands slowly increases in time and at heating. The intensity of C=N band sharply increases after acidifying by hydrogen chloride while the decrease of the intensity of band at 1540-1570 cm^{-1} took place which might be assigned to N-C=S vibrations. Such spectra changes indicate the existence of thione-thiol tautomerism of 1-4.

The UV spectra of 1-4 (water solutions) are typical for thione form of thioureas[3]. The only band at 255-260 nm was observed in dichloromethane. This band might be considered the structural feature of thiol form as the similar band is to be observed in spectra of cyclic isothioureas[4].

Yields and Physical Properties of Polyoxyethylenethioureas

Compound	Yield %	mp ^0C	NMR spectra (60MHz) ppm in DMSO-d_6	IR spectra cm^{-1}, KBr	UV spectra λ_{max} nm ($lg\varepsilon$)	Mass spectra M^+
1	41	216	8.00 (2H,s,NH), 3.80 (8H,s,CH_2-O; CH_2-N)	3190 (NH), 1575 (N-C=S), 1140 (C-O-C)	208.5(4.09), 246 (4.09)	146
2	27	141	8.07 (2H,s,NH), 3.73 (12H,s,CH_2-O; CH_2-N)	3320, 3280 (NH), 1560 (N-C=S), 1125 (C-O-C)	209 (4.08), 240 (4.07)	190
3	18	233	7.60 (4H,s,NH), 3.68 (16H,s,CH_2-O; CH_2-N)	3310, 3210 (NH), 1570 (N-C=S), 1095 (C-O-C)	209 (4.40), 238 (4.33)	292
4	8	223	7.73 (4H,s,NH), 3.73 (24H,s,CH_2-O; CH_2-N)	3370,3340,3300(NH), 1550 (N-C=S), 1090 (C-O-C)	209 (4.37) 238 (4.31)	380

The signals of NH (7.93 ppm) and SH (2.22 ppm) were observed in the NMR spectrum of 2 in $CDCl_3$. Calculated content of thiol form makes up 16±2%. The NMR spectra of 1,3,4 in $CDCl_3$ were not obtained because of low solubility. The NMR spectra of 1-4 in DMSO-d_6 show no signals of SH and the intensity of peaks of NH group corresponds to thione form.

Thus, polyoxyethylenethioureas in solid state as well as in polar solvents exist as thione form while in aprotonic nonpolar solvents thione-thiol tautomerism is observed.

Molecular models show the possibility of syn-anti isomerization of thiol forms of 2-4 by the same way as in the case of cyclic imidates and thioimidates[5]. Further investigations on this problem are in progress.

References

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(Received in UK 16 October 1979)