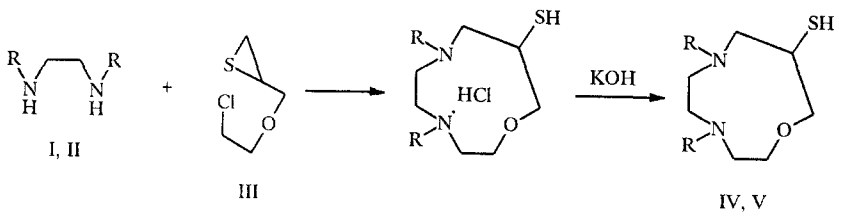
SYNTHESIS OF MERCAPTO-SUBSTITUTED DIAZACROWN ETHERS

A. I. Ismiev, M. A. Allakhverdiev,
V. M. Farzaliev, and A. M. Magerramov

We have developed a method for the synthesis of mercapto-substituted diazacrown ethers IV and V by the reaction of ethylenediamines I and II with 1,2-epithio-4-oxa-6-chlorohexane (III) in methanol with subsequent treatment with alkali:



IV R = Et; V R = CH_2=CH–CH_2

A mixture of 0.05 mole of diamine I or II and 0.05 mole of III in 300 ml of methanol was stirred for 10-12 h at 60°C, after which it was cooled, and a methanol solution of 0.05 mole of KOH was added dropwise. Stirring was continued for another 2 h at 20-25°C, after which the mixture was filtered. The solvent was removed by distillation, and the residue was washed with water and extracted with benzene. The extract was dried with Na_2SO_4, the benzene was removed by distillation, and fractional distillation of the residue in vacuo gave IV and V.

1-Oxa-4,7-diethyl-4,7-diaza-9-cyclodecanethiol (IV). This compound had bp 131°C (2 mm), n_D^{20} 1.5030, and d_4^{20} 1.0064. MR_D found 68.14; MR_D calculated 68.22. IR spectrum (thin layer): 2580 (SH), 1147 cm^{-1} (C—O—C). PMR spectrum (benzene): 1.05 (6H, t, CH_3), 2.45-2.65 (12H, m, NCH_2), 3.15-3.45 ppm (5H, m, OCH_2 and SCH). The yield was 32%.

1-Oxa-4,7-diallyl-4,7-diaza-9-cyclodecanethiol (V). This compound had bp 154°C (2 mm), n_D^{20} 1.5160, and d_4^{20} 1.0098. MR_D found 76.56; MR_D calculated 76.64. IR spectrum (thin layer): 3085 (CH), 2580 (SH), 1648 (C=C), 1150 cm^{-1} (C—O—C). PMR spectrum (benzene): 2.42-2.65 (8H, t, NCH_2), 2.88 (4H, d, NCH_2), 3.15-3.56 (H, m, OCH_2 and SCH), 4.88-4.96 (4H, dd, $=CH_2$), 5.2-5.76 ppm (2H, m, —CH=). The yield was 34%.

The results of elementary analysis of mercapto-containing diazacrown ethers IV and V were in agreement with the calculated values.

Institute of the Chemistry of Additives, Academy of Sciences of the Azerbaidzhan Republic, Baku 370603. M. A. Rasulzade Baku State University, Baku 370073. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 1004, July, 1992. Original article submitted June 25, 1991.

0009-3122/92/2807-0843$12.50