SYNTHESIS OF CARBAMOYL DERIVATIVES OF AZACROWN ETHERS

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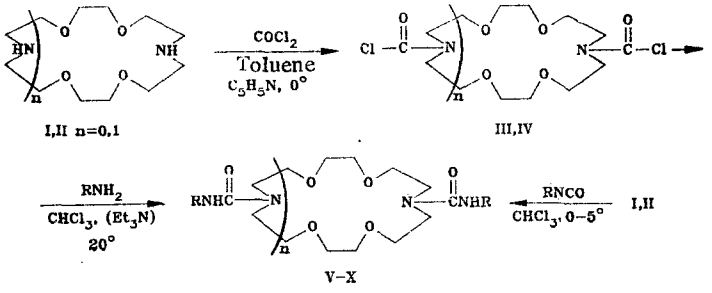
Steric hindrance to the formation of aminals from azacrown ethers makes it possible to obtain N-methoxymethyl derivatives, which are universal reagents for the functionalization of azacrown ethers by aminomethylation reactions, in high yields [1]. We assumed that a similar steric hindrance should also be observed in the case of formation of ureas from azacrown ethers. Taking the sterically hindered diisopropylamine as a model compound, it was shown that the latter does not react with diisopropylcarbamoyl chloride (48 h at 80°C and 6 months at 20°C). Accordingly, we succeeded in obtaining in high yields from crown ethers I, II, the N-chlorocarbonyl derivatives III and IV, which readily form ureas V-X when reacted with amines. These compounds were identical with product of an alternate synthesis from ethers I, II and alkyl isocyanates.



Thus, carbamoyl chlorides III and IV are also effective reagents for the functionalization of azacrown ethers. Compound III (n = 0), yield 78%, mp 41°C (from pentane); IV (n = 1): yield 69%, mp 87-88°C (from hexane); V (n = 0, R = Me): yield 90%, mp 75-76°C (from ether); VI (n = 0, R = $PhCH_2$): yield 90%, oil; VII [n = 0, R = (R)-Ph(Me)CH]: yield 87%, oil, $[\alpha]^{20}_D$ = −12.8° (c 7.1 $CHCl_3$); VIII (n = 1, R = Me): yield 88%, mp 155-156°C (from acetonitrile); IX (n = 1, R = $PhCH_2$): yield 94%, mp 107-108°C (from benzene); X [n = 1, R = (R)-Ph(Me)CH]; yield 89%, mp 126-127°C (from a mixture of ethanol and ether, 1:5), $[\alpha]^{20}_D$ = −9.5° (c 2.1 $CHCl_3$).

The structure of the reaction products was confirmed by IR, PMR, mass spectra, and elemental analysis.

The PMR spectra (400 MHz) of compounds IV and of the analogous model acyl and nitroso derivatives indicate an isomerism due to an inhibited amide rotation: Two singlet signals correspond to the OCH_2CH_2O fragments in the syn-isomer, and AA'BB' type spectrum corresponds to these fragments in the anti-isomer.

LITERATURE CITED

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