SYNTHESIS OF PERHYDRO-1,5-DIOXA-3-AZEPINE DERIVATIVES

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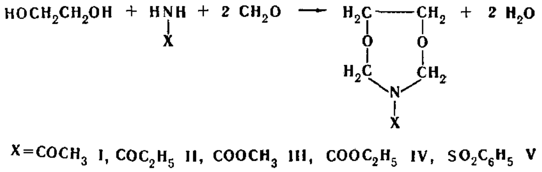
N-Acyl-, N-alkoxycarbonyl-, and N-benzenesulfonylperhydro-1,5-dioxa-3-azepine derivatives were obtained in 9-20% yields by condensation of ethylene glycol with unsubstituted amides, urethanes, and formaldehyde in refluxing xylene in the presence of a catalyst (concentrated HCl).

3-Acetyl- (I), 3-propionyl- (II), 3-carbomethoxy- (III), 3-carbethoxy- (IV), and 3-benzenesulfonylperhydro-1,5-dioxa-3-azepines (V), formed via the scheme



were obtained by condensation of ethylene glycol with unsubstituted amides, urethanes, and formaldehyde.

The reaction was carried out in refluxing xylene in the presence of concentrated HCl (catalyst) with azeotropic distillation of the water formed during the reaction.

EXPERIMENTAL

3-Acetylperhydro-1,5-dioxa-3-azepine (I). Acetamide [59.07 g (1 mole)], 62.07 g (1 mole) of ethylene glycol, and 66 g (2.2 mole) of paraformaldehyde were mixed with 400 ml of xylene. The reaction was completed in 30 min in the presence of 0.01 mole of concentrated hydrochloric acid with vigorous stirring and refluxing of the solvent; the end of the reaction was determined from the cessation of water production. The reaction mixture separated into layers on cooling. It was then neutralized with triethylamine, the upper layer was separated, and the lower layer was washed with 400 ml of xylene. The xylene solutions were combined and fractionated.

II and III were similarly obtained.

TABLE 1. Characteristics of the Compounds Obtained

Compound	Bp (3 mm)	Mp	d_4^{20}	n_D^{20}	Empirical formula	Found				Calculated				Yield, %
						C, %	H, %	N, %	MR_D	C, %	H, %	N, %	MR_D	
I	94—96	—	1,1987	1,4780	$C_6H_{11}NO_3$	49,3	7,8	9,8	34,28	49,7	7,6	9,7	34,61	14
II	102—104	37—39	—	—	$C_7H_{13}NO_3$	52,9	7,8	8,9	—	52,8	8,2	8,8	—	12
III	91,5—92,5	—	1,2450	1,4633	$C_6H_{11}NO_4$	44,9	6,6	8,3	35,67	44,7	6,9	8,7	36,07	15
IV	94,5—95,5	—	1,1702	1,4576	$C_7H_{13}NO_4$	48,3	7,3	7,4	40,81	48,0	7,5	8,0	40,69	19
V	—	82,5—83,5	—	—	$C_{10}H_{13}NO_4S$	49,5	5,6	5,9	—	49,4	5,4	5,8	—	9

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The reaction mixture did not separate into layers during the synthesis of IV, and the solution was fractionated after neutralization of the HCl and filtration.

In the synthesis of V the solvent was removed by vacuum distillation after neutralization of the mixture, and the solid residue was extracted with hot petroleum ether (bp 70-90°), from which V crystallized on cooling.

The compounds obtained (Table 1) are colorless liquids or white, crystalline powders which are soluble in most organic solvents and, except for V, in water. Their structures were confirmed by their IR spectra. The IR spectrum of I contains bands at 1660 cm^{-1} (C=O) and 1125 cm^{-1} (C–O–C); III has bands at 1710 cm^{-1} (C=O) and 1130 cm^{-1} (C–O–C); V has bands at 1346 and 1182 cm^{-1} (S=O) and at 1138 cm^{-1} (C–O–C). Bands which correspond to N–H and O–H groups are not present in the IR spectra. The IR spectra of the solids (in KBr pellets) and of the liquids (in a film between KBr plates) were recorded with a UR-10 spectrometer.