CLEAVAGE REACTIONS OF THE AZIRIDINE RING

III. Reaction of N-Arylethylenimines with Three-Membered Heterocycles*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 4, pp. 475-476, 1970

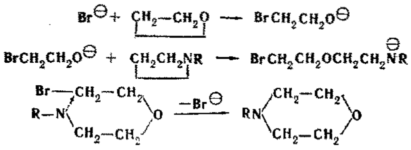
N-Arylethylenimines react with ethylene oxide in the presence of tetraethylammonium bromide with the formation of N-arylmorpholines. In a number of cases, N,N'-diarylpiperazines were isolated as by-products. Ethylene sulfide does not react with N-arylethylenimines.

It is known that three-membered heterocyclic compounds – ethylene oxide, ethylene sulfide, and N-substituted ethylenimines – are capable of dimerizing to form dioxane [2], dithiane, and N,N'-disubstituted piperazines [4, 5], respectively.

We assumed that in the presence of tetraethylammonium bromide (TEAB), which causes the opening of an oxide ring [6] and the dimerization of N-phenylethylenimine [1], the reaction of N-arylethylenimines with ethylene oxide (sulfide) would lead to the formation of N-arylmorpholines (triamorpholines).

In actual fact, when N-arylethylenimines were heated with ethylene oxide at 150°C the expected compounds were isolated in high yields. To confirm their structure, analogous substances were obtained by the dehydration of bis(β-hydroxyethyl)arylamines with concentrated sulfuric acid [7]. The constants of the compounds synthesized by the two methods and their IR spectra were identical.

The following scheme of the reaction is proposed:



In order to suppress the possible dimerization of the ethylenimines, an excess of ethylene oxide was used. However, in the case of N-o-tolyl- and N-o-methoxyphenylethylenimines the corresponding piperazines were obtained with a yield of about 30%. It might be assumed that the mospholines are obtained through a stage of the formation of piperazines with their subsequent reaction with ethylene oxide. However, N,N'-diphenylpiperazine does not react with ethylene oxide even at 200°C.

The reaction of N-phenylethylenimine with ethylene sulfide in the presence of TEAB did not lead to the expected thiamorpholine because of the polymerization of the ethylene sulfide.

EXPERIMENTAL

The N-arylethylenimines were obtained by the dehydrochlorination of N-(β-chloroethyl)arylamine hydrochlorides by analogy with the dehydrobromination of their hydrobromides [8]. The β-chloroethylamine hydrochlorides (Table 1) were synthesized in a similar manner to β-chloroethylaniline hydrochloride [9] by treating the corresponding β-hydroxyethylarylamines with phosphorus oxychloride [10].

N-o-Methoxyphenylethylenimine: Bp 77-80°C (5 mm); n_D^{20} 1.5625. Found %: C 72.20; 72.33; H 7.36, 7.37; N 9.59, 9.63; mol. wt. 150; 148. $C_9H_{11}NO$. Calculated %: C 72.48; H 7.31; N 9.39; mol. wt. 149.

N-p-Methoxyphenylethylenimine: Bp 88-90°C (4 mm); n_D^{20} 1.5540. Found %: C 72.40, 72.57; H 7.41, 7.35; N 9.37, 9.43; mol. wt. 147; 148. $C_9H_{11}NO$. Calculated %: C 72.48; H 7.37; N 9.39; mol. wt. 149.

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*For part II, see [1].

Table 1. $RC_6H_4NHCH_2CH_2Cl \cdot HCl$

R	Mp, °C	Empirical formula	Equiv.	
			found	calculated
H	154—155[9]	$C_8H_{10}ClN \cdot HCl$	193,5; 183	182
o-CH_3	166—168	$C_9H_{12}ClN \cdot HCl$	205; 206	206
p-CH_3	161—163	$C_9H_{12}ClN \cdot HCl$	204; 205	206
o-CH_3O	163—164	$C_9H_{12}ClNO \cdot HCl$	221; 220	221
p-CH_3O	150—151	$C_9H_{12}ClNO \cdot HCl$	220; 219	221

Table 2. N-arylmorpholines

Aryl	Bp, °C (pressure, mm)	Mp, °C	Empirical formula	Found				Calculated				Yield, %
				C, %	H, %	N, %	*M*	C, %	H, %	N, %	Mol. wt.	
C_6H_5	96—98(2)	53[7]	$C_{10}H_{13}NO$	73,45 73,53	8,13 8,20	8,70 8,58	163 162	73,62	7,97	8,58	163	94
o-$CH_3C_6H_4$	102—104(4)[a]	—	$C_{11}H_{15}NO$	74,47 74,52	8,38 8,51	7,55 7,20	179 180	74,50	8,47	7,89	177	65
p-$CH_3C_6H_4$	108—110(4)	42	$C_{11}H_{15}NO$	74,25 74,37	8,33 8,46	7,70 7,67	176 180	74,50	8,47	7,89	177	85
o-$CH_3OC_6H_4$	114—116(2)[b]	—	$C_{11}H_{15}NO_2$	68,30 68,59	7,75 7,62	7,04 6,90	196 192	68,40	7,77	7,25	193	70
p-$CH_3OC_6H_4$	125—126(2)	67	$C_{11}H_{15}NO_2$	68,35 68,41	7,72 7,68	7,11 7,22	196 195	68,40	7,77	7,25	193	90

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[a] n_D^{20} 1.5435. [b] n_D^{20} 1.5560.

Reaction of N-arylethylenimines with ethylene oxide. A mixture of 0.02 mole of a N-arylethylenimine, 0.08 mole of ethylene oxide, and 0.01 g of TEAB was heated in a tube at 140-150°C for 40-50 hr. After the elimination of the excess of ethylene oxide, the reaction products were fractionated in vacuum. The constants of the N-arylmorpholines are given in Table 2.

In the cases of N-o-tolylethylenimine and N-o-methoxyphenylethylenimine, N,N'-ditolyl- and N,N'-dimethoxyphenylpiperazines were isolated as by-products with yields of 25-30%.

N,N'-Di-o-tolylpiperazine: mp 170-171°C (from acetone). Found %: C 81.06, 81.37; H 8.29, 8.29; N 10.20, 10.39. $C_{18}H_{22}N_2$. Calculated %: C 81.20; H 8.27; N 10.52.

N,N'-Di-o-methoxyphenylpiperazine: mp 173-174°C (from acetone). Found %: C 73.04, 73.00; H 7.55, 7.40; N 9.75, 9.83. $C_{18}H_{22}N_2O_2$. Calculated %: C 72.48; H 7.39; N 9.39.

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23 December 1968