ETHYLENEIMINE CHEMISTRY

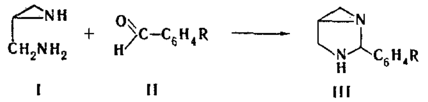
IX.* PREPARATION AND PROPERTIES OF 2-ARYL-SUBSTITUTED 1,3-DIAZABICYCLO[3.1.0]HEXANES

S. A. Giller, M. Yu. Lidak,
A. V. Eremeev, and V. A. Kholodnikov

UDC 547.717'853.5:543.422.4

2-Aryl-1,3-diazabicyclo[3.1.0]hexanes were obtained by the reaction of 2-(aminomethyl)-ethyleneimine with aromatic aldehydes.

In developing our research involving the investigation of the reaction of 2-(aminomethyl)ethyleneimine (I) with the simplest aliphatic aldehydes and ketones, we investigated the reaction of I with a number of aromatic aldehydes (II). The major products of this reaction are 2-aryl-substituted 1,3-diazabicyclo[3.1.0]-hexanes (III-X) (Table 1).



III R=H; IV R=p-NO_2; V R=p-Cl; VI R=m-Cl; VII R=p-Br; VIII R=p-CH_3;
IX R=p-CH_3O; X R=p-$(CH_3)_2N$

The synthesis of III-X was carried out via two methods. The first of them consists in refluxing equimolar amounts of I with the appropriate aldehyde in ethanol, while the second involves the use of azeotropic removal of the water during refluxing of a benzene solution of I and II. The end of the reaction was monitored by gas-liquid chromatography from the disappearance of the starting imine.

The characteristic frequencies of the principal groups in the IR spectra of III-X are presented in Table 2. The stretching vibrations of the N–H bond are characterized by intense absorption at 3230-3312 cm^{-1}. The stretching vibrations of the ethyleneimine ring have absorption at 3010-3070 cm^{-1}. The absorption at 1212-1229 and 825-842 cm^{-1} can be ascribed to the deformation vibrations of the ethyleneimine ring. The assignments of the other frequencies, which correspond to the absorption of other groups in III-X, are given in Table 2.

---

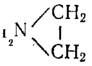
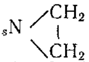
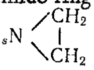
*See [1] for communication VIII.

TABLE 1. 2-Aryl-1,3-diazabicyclo[3.1.0]hexanes (III-X)

Comp.	R	mp, °C, or bp (mm)	Empirical formula	Found, %				Calc., %			
				C	H	N	halogen	C	H	N	halogen
III	H	79—80	$C_{10}H_{12}N_2$	75,1	7,2	17,4		75,0	7,5	17,5	
IV	p-NO_2	118—120	$C_{10}H_{11}N_3O_2$	58,5	5,3	20,5		58,5	5,4	20,5	
V	p-Cl	65—66	$C_{10}H_{11}ClN_2$	61,6	5,3	14,3	18,3	61,7	5,7	14,4	18,2
VI	m-Cl	71—72	$C_{10}H_{11}ClN_2$	61,6	5,7	14,4	18,0	61,7	5,7	14,4	18,2
VII	p-Br	70—71	$C_{10}H_{11}BrN_2$	50,1	4,7	11,7	33,6	50,2	4,6	11,7	33,4
VIII	p-CH_3	63—65	$C_{11}H_{14}N_2$	75,7	8,3	16,1		75,9	8,0	16,1	
IX	p-CH_3O	160 (2)	$C_{11}H_{14}N_2O$	69,8	7,5	14,3		69,5	7,4	14,7	
X	p-$(CH_3)_2N$	58—60	$C_{12}H_{17}N_3$	70,9	8,6	20,7		70,9	8,4	20,7	

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 483-484, April, 1972. Original article submitted May 25, 1971.

TABLE 2. Characteristic Frequencies in the IR Spectra of III-X (cm^{-1})

III	IV	V	VI	VII	VIII	IX	X	Assignment
3312	3247	3290	3269	3275	3230	3275	3235	ν_{NH}
3070	3072	3070	3070	3070	3060	3070	3065	ν_{CH_2} 
3010	2998	3000	3000	3000	3003	3005	3000	
2876	2879	2879	2885	2885	2878	2880	2869	ν_{CH_2}
—	1612	1596	1590	1604	1610	1612	1618	δ_{NH}
1459	1466	1465	1455	1468	1452	1462	1452	δ_{CH_2}
1212	1228	1215	1229	1218	1229	1220	1226	δ_s 
1185	1158	1145	1180	1180	1180	1180	1170	ν imide ring
1092	1091	1091	1090	1096	1090	1095	1090	CH_2 pendulum, imide ring
835	842	840	844	842	825	838	840	δ_{as} 

Preliminary data obtained by means of PMR spectroscopy are evidence for the existence of endo- and exo-isomerism for III-X.

EXPERIMENTAL

The IR spectra of Nujol suspensions were recorded with a UR-20 spectrometer.

2-Aryl-1,3-diazabicyclo[3.1.0]hexanes (III-X). A) A total of 0.1 mole of a solution of the appropriate aromatic aldehyde in 50 ml of absolute alcohol was added with stirring to a solution of 7.2 g (0.1 mole) of 2-(aminomethyl)ethyleneimine in 20 ml of absolute alcohol, and the mixture was refluxed for 2-3 h. It was then cooled, dehydrated with calcium hydride, and filtered. The alcohol was removed by distillation, and the reaction products were vacuum-distilled at 1-2 mm and recrystallized from hexane or ether.

B) A total of 0.1 mole of a solution of the aldehyde in 50 ml of benzene was added to 7.2 g (0.1 mole) of 2-(aminomethyl)ethyleneimine in 50 ml of absolute benzene, and the mixture was refluxed until 0.1 mole of water had distilled. The solvent was removed by evaporation, and the reaction products were isolated as in method A.

LITERATURE CITED

1. S. A. Giller, A. V. Eremeev, M. Yu. Lidak, V. A. Kholodnikov, and V. A. Pestunovich, Khim. Geterotsikl. Soedin., 607 (1971).