ETHYLENEIMINE CHEMISTRY

VII. SYNTHESIS AND PROPERTIES OF 2-ALKYL-SUBSTITUTED 1,3-DIAZABICYCLO[3.1.0]HEXANES

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

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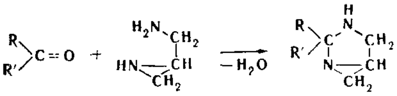
The previously unknown 2-alkyl-substituted 1,3-diazabicyclo[3.1.0]hexanes are formed as the major products in the reactions of C-aminomethylethyleneimine with aldehydes and ketones. Their structures were proved by IR and PMR spectroscopy.

Continuing our study of the reactions of ethyleneimine and its derivatives with aliphatic aldehydes and ketones [1], we have synthesized 2-alkyl-substituted 1,3-diazabicyclo[3.1.0]hexanes (III), which are representatives of a new heterocyclic system consisting of condensed three-membered and five-membered rings having a nitrogen atom in common.



I

IIIa-e

III a $R=R'=CH_3$; b $R=CH_3$, $R'=H$; в $R=C_2H_5$, $R'=H$; d $R=C_2H_5$, $R'=CH_3$; e $R=R'=H$

We found that the corresponding III derivatives are formed in almost quantitative yield by the reaction of C-aminomethylethyleneimine (I) with a group of aliphatic aldehydes and ketones in the absence of catalysts at room temperature. Analysis of the reaction mixture by means of gas-liquid chromatography indicates the presence of only two components – III and water. Preparative isolation of III was accomplished by vacuum distillation of the reaction mixture after it was dried over calcium hydride.

Derivatives III are colorless, mobile ($R' = H$, $R = CH_3$) or rather viscous ($R = C_2H_5$, $R' = CH_3$) liquids with the characteristic odor of higher aliphatic amines. The physicochemical constants of III are presented in Table 1.

The structures of the compounds were proved by means of their IR (Table 2) and PMR spectra (Table 3).

TABLE 1

Comp.	R	R′	bp (mm)	d_4^{20}	n_D^{20}	Found				Calculated			
						C, %	H, %	N, %	MR	C, %	H, %	N, %	MR
IIIa	CH_3	CH_3	34—35 (5)	0,9586	1,4729	63,72	10,49	24,61	31,92	64,25	10,70	25,05	32,81
IIIb	CH_3	H	39 (2)	0,9742	1,4824	61,13	9,59	28,54	27,96	61,86	9,25	28,86	28,37
IIIc	C_2H_5	H	54—55 (9)	0,9637	1,4760	63,42	11,01	26,01	32,02	64,25	10,70	25,05	32,81
IIId	CH_3	C_2H_5	37—38 (5)	0,9261	1,4754	65,15	10,96	22,15	37,90	65,70	11,10	22,20	38,81
IIIe	H	H	60—61 (20)	0,9974	1,4800	57,26	9,18	33,06	23,10	57,13	9,52	33,33	23,92

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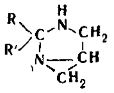
TABLE 2. Characteristic Frequencies of III



III a	III b	III c	III d	III e	Assignment
3275	3265	3260	3260	3080	ν_{NH}
3050	3053	3054	3053	3060	$\nu\,\mathrm{CH_2{>}N}$ (ring $\mathrm{CH_2}$–$\mathrm{CH_2}$)
3021	3021	3025	3025	3028	The same
1462	1473	1472	1483	1465	Scissors vibrations of imide ring $\mathrm{CH_2}$ groups
1381	1392	1388	1390	1373	ν of the imide ring
1221	1219	1210	1210	1220	$\delta_s\,\mathrm{CH_2{>}N}$ (ring $\mathrm{CH_2}$–$\mathrm{CH_2}$)
983	986	980	984	980	Pendulum vibrations of imide ring $\mathrm{CH_2}$ groups
850	858	833	860	860	$\delta_{as}\,\mathrm{CH_2{>}N}$ (ring $\mathrm{CH_2}$–$\mathrm{CH_2}$)

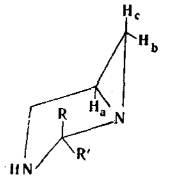
TABLE 3. Chemical Shifts in the PMR Spectra of 30% Solutions of III in CCl_4

Comp.	Chemical shifts, , ppm					
	H_c	H_B	H_a	NCH_2	NH	N(RR')N
IIIa	9,0	8,8	7,85	7,07	7,73	8,91; 8,86
IIIb	9,0	8,8	7,85	7,15	7,8	CH_3: 9,01 ; 8,89* H: 6,23
IIIc	9,0	8,7	7,85	7,15	7,57	CH_3CH_2: 9,01 ; H 6,43
IIId	9,0	8,7	7,9	7,12	7,94	CH_3: 8,94

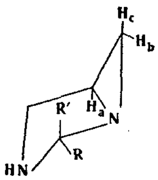
*In the endo and exo isomers, respectively.

The PMR spectra of the compounds indicate that they have structure III. They contain the proton signals of the heteroring at 7.8-9.0 ppm, which are characteristic for C-substituted aziridines. The resonance of the N-methylene protons (τ = 7.1 ppm) is extremely characteristic for imidazolidine derivatives [2].

An analysis of the PMR spectra makes it possible to conclude that III, which have bicyclic structures, have, like 1-azobicyclo[3.1.0]hexane derivatives [3], sufficient conformational rigidity. The spectrum of 2,2-dimethyl-1,3-diazabicyclo[3.1.0]hexane at room temperature contains separate signals for the protons of the endo (8.91 ppm) and exo (8.86 ppm) methyl groups. Consequently, one might expect that the products of condensation with aldehydes or unsymmetrical ketones may be a mixture of the endo and exo isomers.



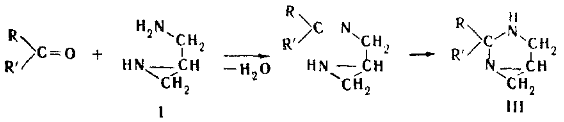
endo



exo

In fact, the PMR spectrum of IIIb contains two types of methyl protons (9.01 ppm and 8.89 ppm), despite the fact that the purity of the compound was proved chromatographically. This means that IIIb is a mixture (1 : 3) of endo and exo isomers.

The mechanism of the cyclization is apparently as follows. An azomethine derivative forms initially and then, as a result of addition to the active C=N bond of the imino group, is converted to III.



EXPERIMENTAL

The IR spectra were obtained with an IKS-14 spectrograph, while the PMR spectra were obtained with a YaMR-5535 TsLA spectrometer (40 MHz). The chromatograms were obtained with a Tsvet-1 gas-liquid chromatograph. The chromatography conditions were as follows: the stationary phase was PÉG-1500 (20%) and KOH (0.1%) on Zeolite-545, the column length was 2 m, the detector was a flow meter, the column temperature was 150°, the vaporizer temperature was 190°, I = 150 mA, and the gas carrier was helium with a flow rate of 5.1 liter/h.

2-Alkyl-Substituted 1,3-Diazabicyclo[3.1.0]hexane. A solution of 0.05 mole of the appropriate carbonyl compound was added to a solution of 0.05 mole of I in 50 ml of absolute alcohol. The reaction proceeds exothermically, and the reaction mixture was therefore cooled with water. The course of the reaction was monitored by means of gas-liquid chromatography. When the reaction was complete, the mixture was dried over calcium hydride, filtered, and vacuum distilled. The purity of the fraction selected was analyzed with a gas-liquid chromatograph.

LITERATURE CITED

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2. E. N. Randall, C. H. Joder, and J. J. Zuckermann, Inorg. Chem., 6, 744 (1967).
3. A. L. Logothetis, J. Am. Chem. Soc., 87, 749 (1965).