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VI. Ketone Ethylenehydrazones*

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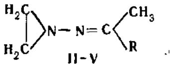
The reaction of N-aminoethylenimine with aliphatic ketones leading to the formation of their ethylenehydrazones has been studied.

Continuing our investigations [2, 3] on the reactivity of N-aminoethyleimine (I), especially its reaction with aliphatic aldehydes, we have also performed the condensation of I with alkyl methyl ketones CH_3COR.

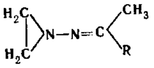
Equimolecular amounts of I and an appropriate ketone react in ethereal solution on heating in 2-3 hr. In view of the poor accessibility of N-aminoethylenimine, the investigation was carried out with small amounts of I (0.5-1.0 g) and therefore the reaction product was separated in a PGK-3 preparative chromatograph.

The individual substances isolated had the physical constants given in Table 1, and the elementary compositions corresponded to the formula


II-V

II $R = CH_3$; III $R = C_2H_5$; IV $R = n\text{-}C_3H_7$, V $R = n\text{-}C_4H_9$

Table 1



Compound	R	n_D^{20}	d_4^{20}	Bp, °C	MR_D		Found, %			Calculated, %			Yield, %
					found	calculated	C	H	N	C	H	N	
II	CH_3	1,4485	0,9531	98—99	30,21	29,53	60,67	10,39	28,71	61,24	10,20	28,56	75
III	C_2H_5	1,4505	0,9037	128	34,40	34,17	63,93	10,55	25,13	64,25	10,85	24,98	70
IV	n-C_3H_7	1,4515	0,8539	154	39,14	38,61	64,60	11,01	22,54	66,64	11,20	22,16	64
V	n-C_4H_9	1,4536	0,8436	176	43,52	43,18	68,23	11,48	20,14	68,50	11,50	20,03	55

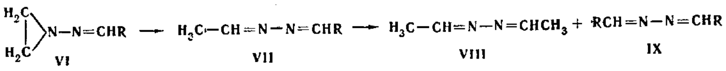
The compounds obtained consisted of colorless mobile liquids with a characteristic ketonic odor. They are readily soluble in ethanol, chloroform, and ether.

Their purity was determined additionally by means of a "Tsvet-1" chromatograph. In all cases the chromatograms contained a single component characteristic for the given substance.

The relationship between the specific retention volumes on the phase E-301 and the boiling points of compounds II-V is linear (see Fig. 1).

The structure of II-V was shown by their IR spectra. The characteristic frequencies in the IR spectra of the hydrazones obtained are given in Table 2.

We have shown previously that the hydrazones obtained by the reaction of I with aliphatic and aromatic aldehydes readily isomerize into the corresponding azines:



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*For Part V, see [1].

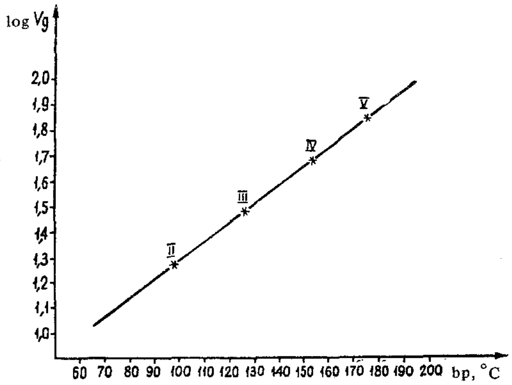
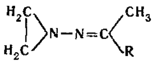


Fig. 1. Relationship between the specific retention volumes and the boiling points.

It appeared of interest to determine whether such as isomerization was characteristic of the products of the reaction of I with aliphatic ketones.

Table 2. Frequencies of the Characteristic Vibrations in the IR Spectra of Hydrazones of the Type of



Compound	R	Frequency, cm^{-1}		
		$\nu_{C=N}$	$\nu_{C-H}\,N\left\langle\begin{matrix}CH_2\\ \vert\\ CH_2\end{matrix}\right.$	$\nu_s N\left\langle\begin{matrix}CH_2\\ \vert\\ CH_2\end{matrix}\right.$
II	CH_3	1655	3005 3085	1230
III	C_2H_5	1650	3000 3085	1230
IV	n-C_3H_7	1645	3005 3080	1230
V	n-C_4H_9	1650	3005 3080	1230

It was found that the presence of two alkyl radicals in compounds II-V (as compared with one in compounds of type VI) hindered their isomerization by the scheme given. The corresponding mixed azines of the type of VII were formed only on prolonged heating or on storage for 3-4 months. The occurrence of isomerization was established by analytical separation in a gas-liquid chromatograph by the procedure that we have described previously [2].

EXPERIMENTAL

With stirring and cooling to 0-5°C, 0.46 g (0.01 mole) of acetone was added to a solution of 0.58 g (0.01 mole) of N-aminoethylenimine in 10 ml of ether. The reaction mixture was kept at room temperature for 3 hr and was dried over sodium sulfate. The analysis of the reaction products was carried out on a "Tsvet-1" chromatograph (flame ionization detector, stationary phase 25% of E-301 or 10% of PEG-1200 on Chromosorb W, or 10% of polyethylenimine M-1200 on Celite-545, T_{therm} 80°C, T_{evap} 120°C, carrier gas helium, V 46.8 cm^3/min).

The isolation of acetone ethylenehydrazone was performed on a PLK-3 preparative chromatograph using an automatic fraction collector. Conditions of isolation: stationary phase E-301, 25% on modified INZ-600 (0.5-0.25 mm fraction), column length 8 m, diameter 18 mm, flame ionization detector in balance with the traps, carrier gas nitrogen, V = 600 cm^3/min, T_{therm} 80°C, T_{evap} 120°C.

The methods of preparing and subsequently isolating compounds III-V were similar to those described above.

REFERENCES

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2. S. A. Hiller, A. V. Eremeev, M. Yu. Lidak, and V. A. Pestunovich, KhGS [Chemistry of Heterocyclic Compounds], 4, 815, 1968.

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