[Contribution from the Department of Chemistry, the University of New Mexico]

A STUDY OF THE REACTION PRODUCTS OF 1,2-DIAMINES WITH ALDEHYDES

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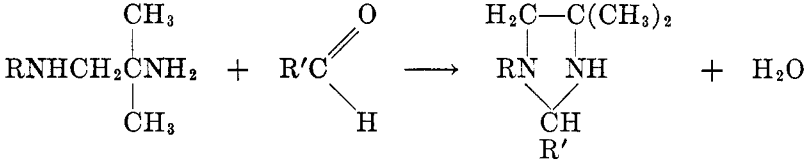
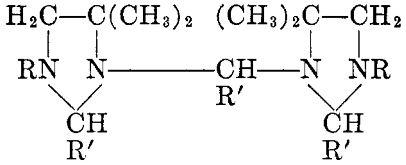
In view of the successful removal of water by heating 1,2-diamines with carboxylic acids to produce imidazolines (1), it seemed reasonable to anticipate that one might be able to split water from aldehydes or ketones and 1, 2-diamines to produce imidazolidines. This expectation was fulfilled in the case of aldehydes which react to give compounds of type I.



I

In the study reported here, R was isopropyl or phenyl and R′ was either hydrogen, methyl, *n*-propyl, phenyl or *α*-furyl. The experience thus gained would suggest that any 1,2-diamine and any aldehyde of the types indicated above would behave similarly. The literature reveals comparable results by other workers (2, 3, 4).

Previous experience with comparable compounds indicated that *bis*-methylene compounds of type II might be prepared by interacting 3 molar-equivalents of the aldehyde with 2 molar-equivalents of the diamine. All attempts to do so resulted in failure.



II

The compounds of type I were colorless liquids or solids soluble in common organic solvents. When R (Formula I) was phenyl, they titrated potentiometrically as monoacid bases. When R was alkyl, the neutral equivalents were between the values for mono- and di-acid bases.

It seemed desirable to try to prepare derivatives of these compounds in order to have a more complete proof of their structures. All attempts to prepare the hydrochlorides or benzoyl derivatives by the usual procedures resulted in ring opening. While these results are in keeping with those of Rameau (5) they do not contribute greatly to the elucidation of the structures.

About the only reasonable alternative series of compounds which might have been formed would be the corresponding Schiff bases. Lob (6) has shown that imidazolidines are stable toward 10% sodium hydroxide or sodium ethoxide while Schiff bases are reduced by sodium and alcohol to form the corresponding amines. When the compound which is believed to be 1-phenyl-4,4-dimethylimidazolidine was treated with sodium and alcohol, it was recovered unchanged thus showing that a Schiff base was not involved.

Finally, two of the compounds in this series were carefully purified and their molar refractivities were observed. The observed values checked quite well with those calculated.

Bergmann and others (7) have shown recently that cyclohexanone will react with a 1,2-diamine to produce the corresponding imidazolidine. In the present work, several attempts were made to substitute ketones for aldehydes in these reactions, but in all instances only the starting materials were recovered.

EXPERIMENTAL

One example will suffice to illustrate the method of preparation of the compounds listed in Table I.

1-Phenyl-2-(2'-furyl)-4,4-dimethylimidazolidine (III). A mixture was prepared containing 82 g. (0.5 mole) of N-(2-aminoisobutyl)aniline and 48 g. (0.5 mole) of furfural. A small quantity of benzene was added and the mixture was heated under conditions to distill the benzene-water azeotropic mixture through a 4' packed-column. The column was fitted with a decanter stillhead so that the benzene was returned constantly to the reaction mixture. The temperature was increased slowly to a maximum of 110°. This five-hour period of heating caused the removal of 9 g. of water. The product was distilled at 151–159° at 4 mm. Upon redistillation, practically all the material distilled at 157–159° at 4 mm. Yield, 84.5 g. or 70%.

Anal. Calc'd for (III) $C_{15}H_{18}N_2O_4$: C, 74.35; H, 7.90; N, 11.57; Neut. equiv., 242.1.
Found: C, 74.16; H, 7.47; N, 11.69; Neut. equiv., 236.6.

Attempted preparation of hydrochlorides of the imidazolidines. 1-Isopropyl-2,4,4-trimethylimidazolidine was dissolved in anhydrous ether and treated with dry hydrogen chloride gas. A white solid formed which sublimed above 200°.

Anal. Calc'd for N-(2-aminoisobutyl)isopropylamine·2 HCl, $C_7H_{20}Cl_2N_2$: N, 13.64; Cl, 34.97.
Found: N, 13.70; Cl, 35.30.

A similar experiment with 1-isopropyl-2-phenyl-4,4-dimethylimidazolidine gave the same dihydrochloride of N-(2-aminoisobutyl)isopropylamine.

Attempted preparation of benzoyl derivatives of the imidazolidines. 1-Isopropyl-2,4,4-trimethylimidazolidine was treated with benzoyl chloride under the usual conditions for benzoylating an amine. A white solid was isolated which melted at 144°.

Anal. Calc'd for the dibenzoyl derivative of N-(2-aminoisobutyl)isopropylamine, $C_{21}H_{26}N_2O_2$: N, 8.28. Found: N, 8.13.

An experiment similar to the one immediately above was carried out with 1-isopropyl-4,4-dimethylimidazolidine and benzoyl chloride. The product melted at 146–147°.

Anal. Calc'd for the dibenzoyl derivative of N-(2-aminoisobutyl)isopropylamine, $C_{21}H_{26}N_2O_2$: N, 8.28. Found: N, 8.40.

The *dibenzoyl derivative* of N-(2-aminoisobutyl)isopropylamine was prepared. It melted at 146–147°. A mixed melting point with the product above showed no depression.

ACKNOWLEDGMENT

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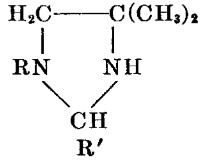
TABLE I

Reaction Products of 1,2-Diamines and Aldehydes



ALDEHYDE USED	FORMULA OF PRODUCT	B.P., °C./MM.	YIELD, %	d_4^{20}	n_D^{20}	MOLECULAR REFRACTION		ANALYSIS							
								C		H		N		NEUT. EQUIV.[c]	
						Calc'd	Ob-served	Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
Acetaldehyde[a]	$C_9H_{20}N_2$	72–75/24	20	0.8498	1.4440	49.12	48.84	69.17	69.01	12.98	12.92	17.95	17.70	156.1	92.6
Butyraldehyde[a]	$C_{11}H_{24}N_2$	93–94/18	60	.8522	1.4479	58.36	57.89	71.63	71.47	13.12	13.01	15.20	14.89	184.2	116.1
Benzaldehyde[a]	$C_{14}H_{22}N_2$	103–105/2	40	.9482	1.5088	—	—	76.99	76.97	10.16	10.03	12.87	12.69	218.1	210.8
Furfural[a]	$C_{12}H_{20}N_2O$	128–130/22	73	.9805	1.4863	—	—	69.23	68.64	9.61	9.53	13.45	13.11	208.1	117.0
Formaldehyde[b]	$C_{11}H_{16}N_2$	m.p. 73°	67	—	—	—	—	74.95	74.93	9.15	9.04	15.90	15.87	176.1	176.8
Acetaldehyde[b]	$C_{12}H_{18}N_2$	124–126/3	71	.9984	1.5510	—	—	75.74	75.74	9.54	9.54	14.72	14.74	190.1	188.4
Butyraldehyde[b]	$C_{14}H_{22}N_2$	134–135/3	71	—	—	—	—	76.58	76.20	10.16	10.27	12.83	12.27	218.1	219.1
Benzaldehyde[b]	$C_{17}H_{20}N_2$	m.p. 95–96°	79	—	—	—	—	80.91	80.95	7.99	7.90	11.10	10.99	252.2	252.9
Furfural[b]	$C_{15}H_{18}N_2O$	157–159/4	70	—	1.5764	—	—	74.35	74.16	7.90	7.47	11.57	11.69	242.1	236.6

[a] Amine used was N-(2-aminoisobutyl)isopropylamine. *R* = Isopropyl. [b] Amine used was N-(2-aminoisobutyl)aniline. R = Phenyl. [c] Calculated as monoacid bases. Potentiometric titrations.

SUMMARY

1. Nine new imidazolidines have been prepared by the interaction of aldehydes and 1,2-diamines. The type reaction seems to be general.

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