[Contribution from the Department of Chemistry, the University of
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THE PRODUCTS FORMED FROM THE REACTIONS OF 1,2-DIAMINES AND DIBASIC ACIDS

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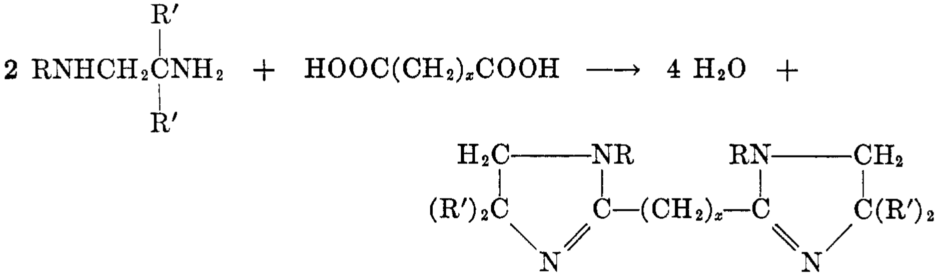
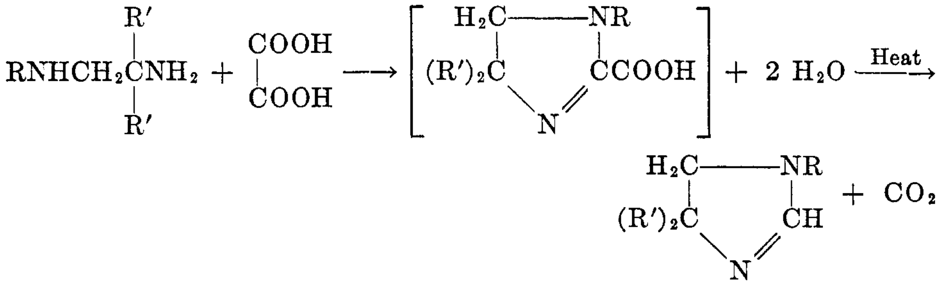
It has been shown previously (1, 2, 3, 4) that when 1,2-diamines are heated with carboxylic acids under conditions to remove water, imidazolines (or their complexes) may be produced in satisfactory yields. These reactions were especially satisfactory when there was one secondary- and one primary-amino group in the diamine.

In view of the above, it seemed reasonable to anticipate that dibasic acids should react under similar conditions with two molar equivalents of typical 1,2-diamines to produce *bis*-imidazolines (I) in accordance with the equation below. It is assumed that the mechanism is similar to that previously suggested for monobasic acids.



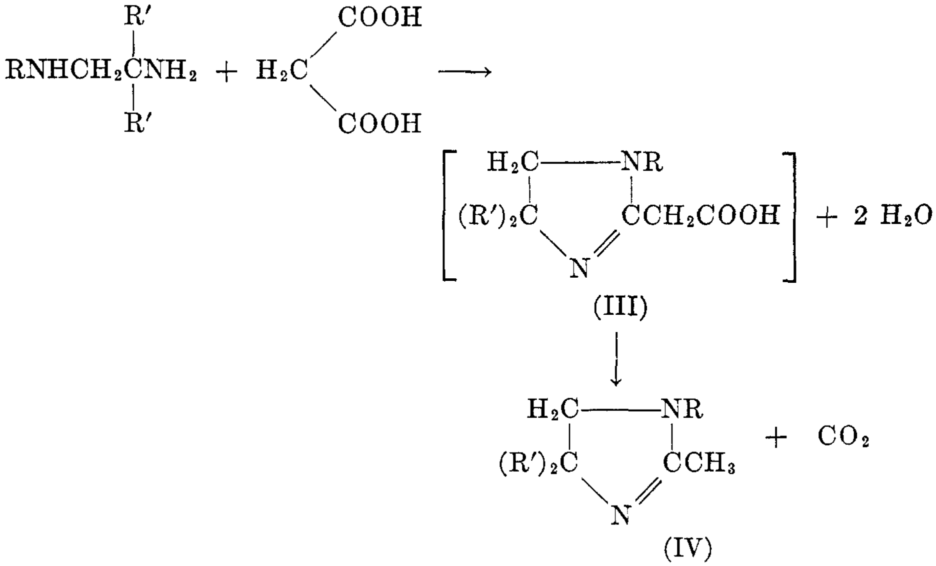
I

With the expected exceptions of oxalic and malonic acids, other dibasic acids have been found to behave as indicated above. When oxalic acid was allowed to react with a diamine, an imidazoline (II) was produced in low yield and was the same compound which one obtains with formic acid and the same diamine. Thus, in the general case, oxalic acid appears to behave as follows:



II

Similarly, malonic acid with a typical diamine may proceed as indicated:



It is not possible to state with certainty whether the postulated imidazolinylacetic acid (III) formed as indicated, or the malonic acid first lost carbon dioxide to form acetic acid which in turn formed the imidazoline (IV). In any event, the effect was the same as if acetic acid had interacted with the diamine.

EXPERIMENTAL

N-(2-Aminoisobutyl)isopropylamine and oxalic acid. A mixture of 26 g. (0.2 mole) of N-(2-aminoisobutyl)isopropylamine and 25.2 g. (0.2 mole) of oxalic acid dihydrate was prepared. A little 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 returned constantly to the reaction mixture. The temperature was increased to 100° at which temperature 6.5 g. of water collected. The temperature was then increased during a 3-hour period to 190°, thus removing 4.5 g. of water. Heating one more hour at 190° gave no more water. The product was transferred to a modified Claisen flask and the benzene was removed *in vacuo*. A mixture of solid and liquid remained. Ether was added and the insoluble solid was removed. Upon distillation, the ether extract boiled from 55–85° at 25 mm. and weighed 16.2 g. Upon redistillation, an 8.0-g. fraction was obtained, boiling from 55–80° at 25 mm.; this was mainly the original diamine. A second fraction weighing 6.0 g. boiled at 80–83° at 25 mm. This fraction was redistilled and a middle cut taken for analysis (1-isopropyl-4,4-dimethyl-2-imidazoline).

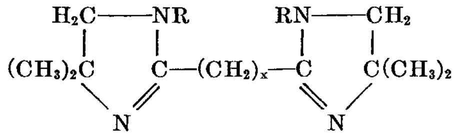
Anal. Calc'd for $C_8H_{16}N_2$: N, 19.98; Neutral equivalent, 140.1.
Found: N, 19.39; Neutral equivalent, 139.8.

N-(2-aminoisobutyl)isopropylamine and malonic acid. To a mixture of 26 g. (0.25 mole) of malonic acid and 65 g. (0.50 mole) of N-(2-aminoisobutyl)isopropylamine was added 150 ml. of benzene. The mixture was heated under the conditions described in the preceding experiment to remove water through a 4′ packed-column. The temperature was maintained at 180–200° for 7 hours. This procedure removed 6.4 g. of water. The temperature was increased to 220° during one hour, but no more water was removed.

Upon distillation at 23 mm., the first fraction boiled from 55–71°. It was mainly the original diamine and weighed 40.2 g. The second fraction boiled from 71–130° at the same pressure and weighed 9.0 g. About 5 g. of tar remained undistilled.

TABLE I

Bis-IMIDAZOLINES OF TYPE



ACID USED	FORMULA	B.P., °C. (MM.)	M.P., °C.	YIELD %	ANALYSES							
					C		H		N		Neut. Equiv.	
					Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
Succinic[a]	$C_{18}H_{34}N_4$	—	115–116	59	70.53	70.39	11.19	11.19	—	—	153.2	157.9
Glutaric[a]	$C_{19}H_{36}N_4$	170–174 (4)	—	33	—	—	—	—	17.48	16.91	160.1	175.3
Adipic[a]	$C_{20}H_{38}N_4$	—	84–85	26	71.76	71.23	11.46	11.30	16.75	16.38	167.1	174.5
Azelaic[a]	$C_{23}H_{44}N_4$	215–220 (4)	—	73	73.33	72.78	11.78	11.72	14.85	14.39	188.2	194.9
Sebacic[a]	$C_{24}H_{46}N_4$	210–215 (2)	—	70	73.77	73.00	11.87	11.65	14.34	13.96	189.2	199.0
Adipic[b]	$C_{26}H_{34}N_4$	235–237 (2)	—	64	—	—	—	—	13.94	13.44	201.2	227.9

[a] Amine used was N-(2-aminoisobutyl)isopropylamine; R = isopropyl. [b] Amine used was N-(2-aminoisobutyl) aniline; R = phenyl.

The 9.0-g. fraction was redistilled at 27 mm. and separated into two main fractions; the first, b.p. 87–90° and the second b.p. 130–132°. The lower-boiling fraction proved by analysis to be 1-isopropyl-2,4,4-trimethyl-2-imidazoline.

Anal. Calc'd for $C_9H_{18}N_2$: N, 18.15; Neutral equivalent, 154.15.
Found: N, 17.93; neutral equivalent, 157.8.

The higher-boiling fraction analyzed correctly for the *acetic acid complex* of *1-isopropyl-2,4,4-trimethyl-2-imidazoline.*

Anal. Calc'd for $C_{13}H_{26}N_2O_4$: N, 10.21. Found: N, 10.70.

Succinic, glutaric, adipic, azelaic, and sebacic acids were each reacted with N-(2-aminoisobutyl)isopropylamine. Also adipic acid was allowed to react with N-(2-aminoisobutyl)-aniline. Since the procedure was about the same for all these examples, only one will be described in detail.

Bis-1,4-(2',2''-diisopropyl-4',4''-tetramethyl)-2',2''-imidazolinylbutane (V). A mixture of 65 g. (0.5 mole) of N-(2-aminoisobutyl)isopropylamine, 36.5 g. (0.25 mole) of adipic acid, and benzene was heated under the conditions described in the preceding experiments to remove water. A total of 11 g. of water was removed by heating at 200–260° for 12 hours. The product distilled at 5 mm. using a modified Claisen flask. After a small forerun, 31 g. of distillate was collected at 175–185°. An undistilled residue of 7 g. remained. Yield of crude product, 40%. It solidified upon standing and was purified by crystallization from petroleum ether (26% yield of purified product). The purified material, m.p. 84–85°, analyzed correctly for (V).

Table I summarizes the data for the examples of this type.

Attempts were made to prepare the *hydrochlorides* of several of the above imidazolines, but in most instances non-crystallizable oils were obtained. In the case of the *bis*-imidazoline produced from N-(2-aminoisobutyl)isopropylamine and succinic acid, a solid hydrochloride was obtained.

Anal. Calc'd for the dihydrochloride: N, 14.77; Cl, 18.72.
Found: N, 14.31; Cl, 18.15.

Since the hydrochlorides were difficult to prepare and since the nitrogen analysis was poor for the product obtained from glutaric acid, the *dipicrate* was prepared from this compound.

Anal. Calc'd for the dipicrate: N, 17.98. Found: N, 18.29.

It is interesting to observe that the neutral equivalents reported are consistently higher than the calculated values. However, they are near enough to suggest that these compounds act as diacid bases.

ACKNOWLEDGMENT

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SUMMARY

1. It has been shown that dibasic acids above malonic react with 1,2-diamines to produce *bis*-imidazolines.

2. Six new compounds of this type have been reported. These compounds behave as diacid bases.

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