$$\left(A - \frac{B}{0.69 \pm 0.05}\right)\frac{1}{D} = \frac{C}{D} = M \quad (3)$$

$$N = (0.88 \pm 0.06)M + (0.03 \pm 0.04) \quad (4)$$

Dehalogenations with sodium iodide were carried out on other stilbene dihalides which were available. The directions for debrominations were followed with heating for various lengths of time. The results are summarized in Table III.

Solutions in 95% ethanol made up from 10 ml. of 1.09×10^{-3} *M cis*-stilbene, 10 ml. of 5.39×10^{-4} *M* iodine, and 50 ml. of 0.10 *M* sodium iodide were boiled for 22 hr. After dilution to 100 ml. and removal of triiodide ion by sodium sulfite the absorption spectrum showed a maximum of 2% isomerization to *trans*-stilbene.

Dehalogenation by Zinc or Copper.—A 4.0×10^{-3}-g. sample (1.18×10^{-5} mole) was weighed and dissolved in 50 ml. of 95% ethanol in a flask of low actinic red borosilicate glass. Excess (0.01 g.) powdered zinc or copper bronze was added and the mixture was boiled under reflux. The solution was filtered and the filtrate was diluted to 100 ml. total volume. The spectrometric analyses of the reaction mixtures are summarized in Table IV.

Solutions of 10 ml. of 1.09×10^{-3} *M cis*-stilbene, 0.005 g. of copper or zinc metal, and 0.005 g. of copper(II) bromide or zinc bromide with 40 ml. of 95% ethanol were boiled under reflux for 22 hr. The solutions were diluted to 100 ml. Analysis showed 5% isomerization with zinc bromide and 10% isomerization with copper(II) bromide.

A 0.20-g. sample of *dl*-dibromide in 50 ml. of 95% ethanol containing 0.20 g. of zinc bromide was boiled for 0.5 hr. With copper(II) bromide a similar reaction mixture was boiled 22 hr. The dibromide which was isolated by dilution with water in each case was essentially pure *dl*-dibromide based on infrared analysis. With 0.20 g. each of copper(II) bromide and copper metal the product was a mixture of *dl*-dibromide and *trans*-stilbene. No *meso*-dibromide could be detected by infrared analysis. Similar experiments carried out at room temperature with mixtures of bromine and excess copper bronze for 14 days gave products which were *meso*-dibromide contaminated in several experiments with *trans* stilbene. No *dl*-dibromide could be detected by infrared analysis.

Absorption Spectra.—Ultraviolet spectra were measured in 1.00-cm. silica cells on a Cary Model 11 recording spectrophotometer. Analyses of stilbene mixtures were based on the following molar absorptivities: at 295 mμ, *trans* 2.70×10^4, *cis* 0.78×10^4; at 307 mμ, *trans* 2.61×10^4, *cis* 0.47×10^4; at 320 mμ, *trans* 1.63×10^4, *cis* 0.17×10^4.

Infrared spectra were measured in carbon disulfide solutions in 1.0-mm. potassium bromide cells. Mineral oil mulls were also used. Measurements were made on the following Perkin–Elmer spectrometers: Model 21 with a sodium chloride prism, NaCl Model 137B Infracord, and KBr Model 137 Infracord. The predominant, useful absorption bands are summarized in Table II.

Other Methods of Analysis of Stilbene Dibromides.—Since *meso*-dibromide is quite insoluble a gravimetric analysis was possible, but in such a determination the amount of *dl*-dibromide could not be checked quantitatively. Melting points of mixtures of *meso*- and *dl*-dibromides were of little value. The *meso* isomer was essentially insoluble in the liquid *dl* isomer so that there was little effect on the m.p. with relatively large amounts of *dl* present. Solutions of *meso*- and *dl*-dibromides in carbon tetrachloride showed only very small differences (0.0003 at 10^{-3} *M*) in refractive index. Such differences could be accentuated by the use of a Zeiss Laboratory Interferometer with an all-glass, 10-cm. cell. The liquid in the constant temperature bath of the instrument had to have approximately the same index of refraction as the solvent used in the cell so that the interference fringes would be properly aligned. The best bath liquid tried for carbon tetrachloride ($n^{15}D$ 1.46305) as a solvent was a mixture ($n^{15}D$ 1.46301) of 40% alkane fraction, b.p. 135–144°, and 60% mixed xylenes. Although this was a possible method of analysis for dilute solutions of the dibromides, the use of the interferometer was not pursued further in the present investigation.

A New Method for the Synthesis of Amino Acids. Synthesis of Amino Acids and Their Derivatives through 2,4-Disubstituted 2-Imidazolin-5-ones[1]

AKHLAQ R. KIDWAI AND GANAPATHIPLACKAL M. DEVASIA

Department of Chemistry, Aligarh Muslim University, Aligarh, India

Received April 27, 1962

Unsaturated 2,4-disubstituted 2-imidazolin-5-ones were prepared in good yields by the condensation of aldehydes with a mixture of glycine ester and an imidic acid ester as well as with a mixture of their hydrochlorides. They were hydrogenated to saturated 2-imidazolin-5-ones which were hydrolyzed to acylamino acid amides, acylamino acids, and amino acids under different conditions.

One of the best methods of preparing α-amino acids (especially aromatic) is the reduction and hydrolysis of unsaturated 2,4-disubstituted 5-oxazolones (azlactones) (IV, —O— instead of —NH—).[2] Unsaturated 2,4-disubstituted 2-imidazolin-5-ones (IV) which are the nitrogen analogs of the oxazolones have not been used so far in the synthesis of amino acids. The present work describes (a) two improved methods of synthesis of the unsaturated 2-imidazolin-5-ones (IV); (b) their hydrogenation to the saturated 2-imidazolin-5-ones (V); and (c) hydrolysis of the latter into acyl amino acid amides (VI), acyl amino acids (VII), and amino acids (VIII).

(a) Synthesis of Unsaturated 2,4-Disubstituted 2-Imidazolin-5-ones (IV).—The known methods of preparing the unsaturated 2,4-disubstituted 2-imidazolin-5 ones (IV) are not of much practical importance.[3,4]

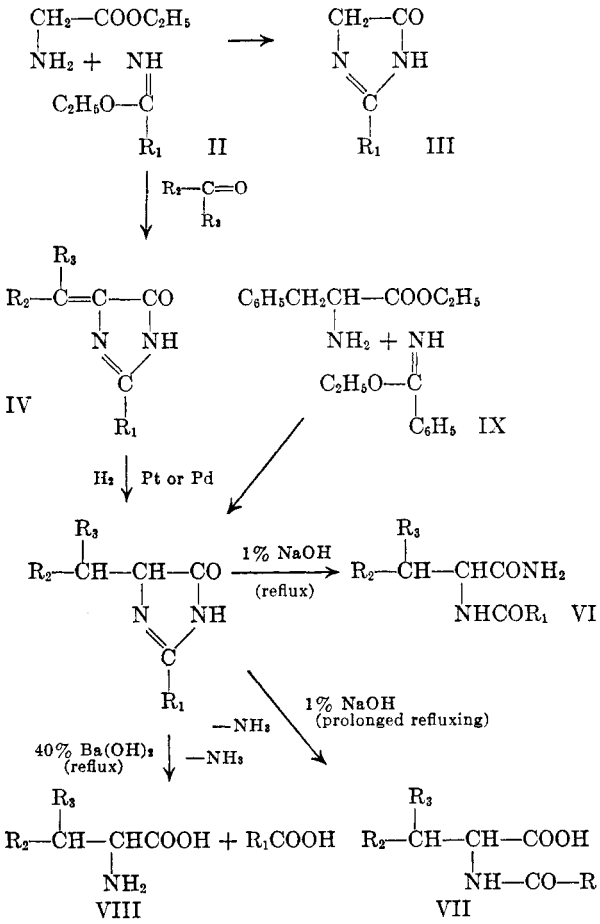
(1) From the Ph.D. thesis of G. M. Devasia, 1961. This work was supported by the Scientific Research Committee, U.P., and the Aligarh Muslim University.

(2) H. E. Carter, "Organic Reactions" Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1947, pp. 198–239.

(3) K. Hofmann, "The Chemistry of Heterocyclic Compounds," Vol. VI, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 93–97.

(4) H. Lehr, S. Karlan, and M. W. Goldberg, *J. Am. Chem. Soc.* **75**, 3640 (1959).

Finger and Zeh[5] and Kjaer[6] obtained them (IV) by condensing glycine ester (I) with an imidic acid ester (II), isolating the product (III) formed and condensing the latter with aromatic aldehydes. Lehr and co-workers[4] prepared IV by refluxing ketones with a mixture of I and II.



We have observed that aldehydes (aromatic aldehydes and isobutyraldehyde) condense easily even at room temperature with a mixture of glycine ester (I) and an imidic acid ester (II) to give good yields of the unsaturated 2-imidazolin-5-ones (IV) (method A). Best yields were obtained when the aldehyde, the glycine ester, and the imidic acid ester were taken in the proportion of 1:1.2:1.15. We have also observed that IV could be prepared by condensing aromatic aldehydes with a mixture of the hydrochlorides of I and II in presence of sodium bicarbonate (method B). Thus the preconversion of the ester hydrochlorides to the free esters can be avoided. Best yields of IV were obtained when the aldehyde and the hydrochlorides of I and II were used in the proportion of 1:1.5:1.2. Table I shows the unsaturated 2-imidazolin-5-ones prepared by these two methods and also two unsaturated 2-imidazolin-5-ones (last two in the table) prepared according to Lehr and co-workers.[4] The stability of the unsaturated 2-imidazolin-5-ones decreases in the order $C_6H_5 > C_6H_5–CH_2 > CH_3$ for the substituent R_1 in position 2. The conjugation of the double bonds with the benzene nucleus may be responsible for the increased stability when $R_1 = C_6H_5$.

(b) **Hydrogenation of Unsaturated 2,4-Disubstituted 2-Imidazolin-5-ones.**—Hydrogenation of exocyclic double bond of the unsaturated 2-imidazolin-5-ones (IV) (using palladium oxide and sodium amalgam as catalysts) has been reported only in two cases.[7,8] In both the cases yields were not reported.

The unsaturated oxazolones undergo reduction and hydrolysis to amino acids (and their derivatives) on treatment with hydriodic acid and red phosphorus in the presence of acetic anhydride or glacial acetic acid.[2] However, similar treatment of the unsaturated 2-imidazolin-5-ones by us failed to give amino acids or their derivatives.

We studied the selective hydrogenation of the exocyclic double bond unsaturated 2-imidazolin-5-ones using platinum oxide, palladium oxide, and palladium on carbon, strontium carbonate, or barium sulfate as catalysts. Ethanol, acetic acid, and ethyl acetate were used as solvents. Platinum oxide or palladium on strontium carbonate in ethyl acetate provided the best conditions for the reduction of IV to the saturated 2-imidazolin-5-ones (V). Table I gives the list of the saturated 2-imidazolin-5-ones prepared in this manner.

The structure of the hydrogenation products was confirmed by an unambiguous synthesis of one of them, namely 2-phenyl-4-benzyl-2-imidazolin-5-one (V. $R_1 = R_2 = C_6H_5$; $R_3 = H$), by the condensation of benzimidic acid ester (IX) with phenylalanine ester (X).[9]

All the above saturated 2-imidazolin-5-ones except (V. $R_1 = R_2 = C_6H_5$; $R_3 = H$) are reported here for the first time. The saturated compounds are less stable than the corresponding unsaturated ones. It is probable that the disappearance of cross conjugation on hydrogenation is responsible for this lower stability of the saturated 2-imidazolin-5-ones.

(c) **Hydrolysis of Saturated 2,4-Disubstituted 2-Imidazolin-5-ones.**—Alanine has been detected among the products of hydrolysis of 2-phenyl-4-methyl-2-imidazolin-5-one.[10] However, amino acids and their derivatives have not so far been prepared by the hydrolysis of the saturated 2-imidazolin-5-ones.

We have observed that hydrolysis of the saturated 2-imidazolin-5-ones (V) with dilute sodium

(5) (a) H. Finger, *J. prakt. Chem.*, **76**, 93 (1907); (b) H. Finger and W. Zeh, *ibid.*, **82**, 50 (1910).

(6) A. Kjaer, *Acta Chem. Scand.*, **7**, 1030 (1953).

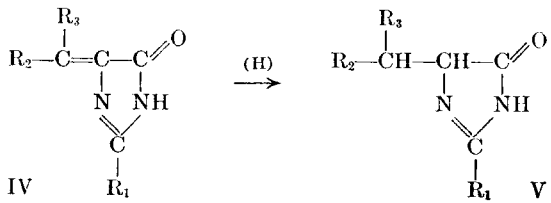
(7) A. Kjaer, *ibid.*, **7**, 900 (1953).

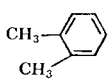
(8) M. Brenner, J. P. Zimmermann, J. Wehrmuller, P. Quitt, A. Hartmann, W. Schneider, and U. Beglinger, *Helv. Chim. Acta*, **40**, 1497 (1957).

(9) Compare the synthesis of 2-phenyl-4-methyl-2-imidazolin-5-one in ref. 6.

(10) J. W. Cornforth and H. T. Huang, *J. Chem. Soc.*, 731 (1948).

TABLE I



R_1	R_2	R_3	Method of synthesis	Solvent; m.p., °C.	Yield, %	Calcd.	Found		Catalyst[a]	Solvent; m.p., °C.	Yield, %	Calcd.	Found	
						C	H	N				C	H	N
C_6H_5	C_6H_5	H	A	Benzene; 272–273	76	77.40	4.87	11.28	X	Benzene–petroleum ether; 168–169	84	76.78	5.64	11.19
			B	Benzene; 272–273	70		77.77	4.84	11.21				76.83	5.48	11.68
C_6H_5	p-OHC_6H_4	H	A	Ethanol; 291–292	86	72.71	4.58	10.60	X		87			
			B		57		72.97	4.80	10.48					
C_6H_5	p-$CH_3OC_6H_4$	H	A	Amyl acetate; 289–290	85	73.36	5.07	10.07	Y	Benzene–petroleum ether; 160–161	82	72.84	5.75	9.99
			B		79		73.15	5.08	10.17				72.72	5.44	9.67
C_6H_5		H	A	Ethyl benzoate; 258–259	88	70.11	5.23	9.09						
			B		79		69.82	5.46	9.00					
C_6H_5	CH_2CHCH_3 | C_6H_5	H	A	Benzene; 181–182	56	72.87	6.59	13.03						
							73.32	6.53	12.79					
$C_6H_5CH_2$	C_6H_5	H	A	Benzene; 177–178	46	77.84	5.38	10.68	Y	Crude; 114–124	60			
						77.84	5.50	10.57						
$C_6H_5CH_2$	p-$CH_3OC_6H_4$	H	A	Benzene; 186–187	49[b]	73.95	5.52	9.58	Y	Crude; 134–135	65			
						74.23	5.75	9.65						
CH_3	C_6H_5	H	A	Benzene; 177.5–178.5	15	70.95	5.41	15.05						
						71.01	5.41	14.94						
			B		28									
CH_3	p-$CH_3OC_6H_4$	H	A	Benzene; 201–202	57[b]	66.65	5.59	12.96						
						66.74	5.66	12.84						
C_6H_5	CH_3CH_2	CH_3	A	Dioxane; 174.5–175.5	50[b]	72.87	6.59	13.08	Y	Benzene–petroleum ether; 142–144	72	72.19	7.46	12.95
						72.84	6.44	13.12				72.73	7.59	12.80
C_6H_5	CH_3	CH_3	A	Dioxane; 192–192.5	64	71.98	6.04	13.99	Y	Benzene–petroleum ether; 161–163	75	71.26	6.98	13.85
						72.40	6.08	13.60				71.55	6.95	14.01

[a] X, platinum oxide; Y, palladium on strontium carbonate. [b] Compounds reported for the first time.

TABLE II

R_3—CH—CH—CO—NH_2 (VI); R_3—CH—CH—COOH (VII); R_3—CH—CH—COOH (VIII)

R_1	R_2	R_3	Solvent; m.p., °C.	Yield, %	Calcd. / Found C	Calcd. / Found H	Calcd. / Found N
C_6H_5	C_6H_5	H	$CHCl_3$; 197.5–198	27	71.62; 71.20;	6.01; 6.10;	10.44; 10.67
$C_6H_5CH_2$	C_6H_5	H	Dil. ethanol; 189–190	29	72.32; 72.02;	6.43; 6.54;	9.92; 10.15
C_6H_5	CH_3CH_2	CH_3	Dil. ethanol; 216–216.5	68[a]	66.64; 66.91;	7.74; 7.77;	11.96; 11.94
C_6H_5	CH_3	CH_3	Dil. ethanol; 219–219.5	47[a]	65.43; 65.68;	7.32; 7.29;	12.72; 12.10
C_6H_5	p-HOC_6H_4	H	Acetic acid; 190.5–191.5	19	67.36; 67.71;	5.30; 5.43;	4.91; 5.75
C_6H_5	p-$CH_3OC_6H_4$	H	Gl. acetic acid–ether; 176.5–177.5	48	68.21; 68.37;	5.73; 5.73;	4.68; 5.14
$C_6H_5CH_2$	p-$CH_3OC_6H_4$	H	Gl. acetic acid–ether; 154–155	70[a]	68.99; 69.25;	6.11; 6.23;	4.47; 4.80

R_1	R_2	M.p., °C.	Yield, %	Calcd. / Found C	Calcd. / Found H	Calcd. / Found N
C_6H_5	C_6H_5	278	68	65.44; 65.53;	6.71; 6.56;	8.48; 8.84
$C_6H_5CH_2$	C_6H_5			71.36; 71.68;	5.61; 5.60;	5.20; 5.61
C_6H_5	CH_3CH_2	305	32	51.26; 51.38;	9.46; 9.25;	11.96; 12.05
C_6H_5	CH_3	275	59	61.52; 61.53;	6.71; 6.49;	7.18; 7.08
C_6H_5	p-HOC_6H_4			72.06; 72.39;	6.05; 6.26;	4.94; 4.97

[a] Compounds reported for the first time.

hydroxide solution gives first acylamino acid amides (VI) and then acylamino acids (VII). Hydrolysis of V with strong barium hydroxide solution gives directly the amino acids (VIII). Table II shows the amino acids and their derivatives prepared in this manner.

The preparation of acylamino acid amides by this method is easier than the known methods for obtaining these compounds.[11–13] The availability of acylamino acids, which are largely used for the resolution of amino acids is an added advantage of this method.

The synthesis of amino acids and their derivatives *via* 2-imidazolin-5-one formation has certain definite advantages. (1) Both aldehydes and ketones form the 2-imidazolin-5-ones in high yields by a one-step process and under very mild conditions. (2) The starting materials for 2-imidazolin-5-one synthesis are easily available. (3) The hydrolysis of the 2-imidazolin-5-ones gives directly amino acids and their derivatives under suitable conditions.

Experimental[14]

Starting Materials.—Glycine ethyl ester hydrochloride was prepared by refluxing for 2.5 hr. 1 mole of glycine with about ten times its weight of absolute ethanol in which 3 moles of dry hydrogen chloride gas had been absorbed.[15] The solution was seeded to induce crystallization and the flask was cooled in the refrigerator overnight. The product was filtered off, washed with ice-cold absolute ethanol, and dried. The white crystals, m.p. 144–145°, weighed 111.7 g. (80%) . From the mother liquor and washings a second crop of 16.7 g. (12%) of the product was obtained.

Acetimidic and benzimidic acid, ethyl ester hydrochlorides were prepared (from acetonitrile and benzonitrile, respectively) in 91 and 95% yields according to the directions of Dox.[16] The powdered imidic acid ester hydrochlorides were kept under dry ether overnight, filtered off, washed with ether, and dried in a vacuum desiccator over solid potassium hydroxide and phosphorus pentoxide. Phenylacetimidic acid ethyl ester hydrochloride was prepared in 82% yield by absorbing 1.1 moles of dry hydrogen chloride gas in a 1:1 mole mixture of benzylcyanide and absolute ethanol dissolved in an equal weight of dry ether at 0°.[17] The reaction mixture was cooled in the refrigerator for 2 days and seeded. The product which separated was slightly colored but it became perfectly white on keeping under fresh ether. More product was obtained from the mother liquor on keeping refrigerated.

The crude hydrochlorides of the glycine ester and the imidic acid esters were converted into the free esters by cooling their saturated aqueous solutions in presence of ether and adding a little excess of ice-cold sodium hydroxide solution (40%).[18] After saturating the aqueous layer with potassium

(11) E. Mohr and F. Stroschein, *Ber.*, **42**, 2521 (1909).
(12) E. Erlenmeyer and J. Kunlin, *Ann.*, **307**, 146 (1899).
(13) J. Max, *ibid.*, **369**, 276 (1909).
(14) Melting points are uncorrected. Analyses were performed by Mr. Alfred Bernhardt, Mikroanalytisches Laboratorium, in Max-planck-Institut fur Kohlenforschung, Mulheim (Ruhr), W. Germany.
(15) *Cf.* C. Harries and M. Weiss, *Ann.*, **327**, 355 (1903).
(16) A. W. Dox, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., January, 1946, pp. 5–7.
(17) *Cf.* A. J. Hill and I. Rabinowitz, *J. Am. Chem. Soc.*, **48**, 732 (1926).
(18) *Cf.* (a) E. Fischer, *Sitzungsber. Akad. Wiss. Berlin*, **48**, 1062 (1900); (b) E. Fischer, *Ber.*, **34**, 433 (1901); (c) ref. 4.

carbonate the ether layer was collected and the aqueous layer was extracted twice more with ether. The combined ether extracts were dried over anhydrous potassium carbonate and filtered, and the ether was evaporated under reduced pressure. Glycine ester was obtained in 87% yield while the imidic acid esters were obtained in about 95% yields. The glycine ester and the imidic acid esters were used for condensation without further purification.

Synthesis of Unsaturated 2,4-Disubstituted 2-Imidazolin-5-ones (V). Method A.—The imidic acid ethyl ester (0.054 mole), glycine ethyl ester (0.056 mole), dry benzene (15 ml.), and the aldehyde (0.048 mole) were quickly mixed and kept closed in a flask at room temperature with occasional shaking. The mixture gradually became yellow and finally red. After about 30 min. the 2-imidazolin-5-ones separated as yellow crystals, when the shaking was stopped. After about 20 hr. the mixture completely solidified into a yellow mass with a red tinge. The product which became more red (because of atmospheric oxidation of the unchanged monosubstituted 2-imidazolin-5-one to glyoxaline red[5a,6]) on opening the flask, was broken and washed with hot ethanol and crystallized.

The reaction was also carried out by heating the reaction mixture on a water bath at 70° for 1 hr. when almost the same yield of the product was obtained.

Method B.—The crude imidic acid ethyl ester hydrochloride (0.054 mole), crude glycine ethyl ester hydrochloride (0.072 mole), and sodium bicarbonate (0.14 mole) were mixed in a dry mortar and transferred quickly into a 250-ml. round-bottomed flask with long neck. To this mixture dry benzene (20 ml.) and the aldehyde (0.048 mole) were added and the flask was heated at once at 72° with constant shaking in a preheated water bath. There was separation of esters with vigorous evolution of carbon dioxide. Within 10 min. of heating the 2-imidazolin-5-one began to separate as yellow crystals. Shaking was stopped and the flask was kept vertically clamped in the water bath for another 50 min. The mixture solidified into an yellow mass which gradually turned slightly red. The solid mass which became more red on cooling was broken and washed with hot ethanol, water, and again with ethanol, and crystallized.

Hydrogenation of Unsaturated 2,4-Disubstituted 2-Imidazolin-5-ones.—Adams' platinum oxide and palladium-on-strontium carbonate (prepared from 1 g. of palladium chloride and 50 g. of strontium carbonate) were used as catalysts. A 50-mg. sample of Adams' platinum oxide or 6 g. of palladium on strontium carbonate were used for 5 g. of the unsaturated 2-imidazolin-5-one.

Hydrogenations were carried out at room temperature and pressure on 8–10% suspensions of the unsaturated 2-imidazolin-5-ones in ethyl acetate using Tower's semimicro hydrogenation apparatus. One mole of hydrogen was absorbed in 1–5 hr. During the hydrogenation the 2-imidazolin-5-one went into solution. The absorption of hydrogen practically ceased when one molecular proportion of hydrogen was absorbed by the substance. In some cases the product separated from the solvent during hydrogenation. After filtration the solvent was immediately evaporated under reduced pressure at room temperature and the residue washed with ether. Saturated 2-imidazolin-5-ones were crystallized by dissolving in excess benzene and adding an equal volume of petroleum ether.

Synthesis of 2-Phenyl-4-benzyl-2-imidazolin-5-one (V. $R_1 = R_2 = C_6H_5$; $R_3 = H$).—A mixture of phenylalanine ethyl ester (6 ml., 0.033 mole) and benzimidic acid ethyl ester (5 ml. 0.034 mole) was kept closed at room temperature for 15 hr. The mixture completely solidified into a pale yellow mass, which was washed with ether. The product weighed 4.88 g. (59%), m.p. 168–169° (rapid heating). Recrystallization did not raise the melting point. Mixed melting point with V ($R_1 = R_2 = C_6H_5$; $R_3 = H$) (obtained by hydrogenation of the corresponding unsaturated 2-imidazolin-5-one) was not depressed. Infrared spectra of these compounds were also identical.

Anal. Calcd. for $C_{16}H_{14}ON_2$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.79; H, 5.42; H, 11.17.

Hydrolysis of Saturated 2,4-Disubstituted 2-Imidazolin-5-ones.—Crude saturated 2-imidazolin-5-ones were used for the hydrolysis to acylamino acid amides, acylamino acids, and amino acids.

Acyl Amino Acid Amides (VI).—The 2-imidazolin-5-one (1 g.) was refluxed with 1% sodium hydroxide solution (20 ml.). The imidazolone dissolved and within 5 min. IIIa began to separate. After refluxing for another 10 min., the flask was allowed to cool, the amide was filtered, washed with water and ether, and crystallized.

Acyl Amino Acids (VII).—The imidazolin-5-one (3 g.) was refluxed with 1% sodium hydroxide solution (70 ml.) when it was readily dissolved and VI separated within few minutes. On further refluxing with occasional shaking VI disappeared with evolution of ammonia. After a total refluxing period of 2 hr., the reaction mixture was allowed to cool and carbon dioxide passed through it in order to precipitate any unhydrolyzed 2-imidazolin-5-one. A small quantity of solid which separated was removed and the solution shaken twice with 50-ml. portions of ethyl acetate. The aqueous layer was acidified with 2.5 ml. of concentrated hydrochloric acid, when the acyl amino acid precipitated. It was filtered and washed thoroughly with water and ether, and crystallized.

Amino Acids (VIII).—An intimate mixture of the 2-imidazolin-5-one (3 g.) and hydrated barium hydroxide (20 g.) was refluxed with water (50 ml.) in a 500-ml. long-necked flask for 7.5 hr. The flask was shaken often until boiling began and then occasionally. There was copious evolution of ammonia. The reaction mixture was diluted with 300 ml. of water and the barium was precipitated with 30 ml. of dilute sulfuric acid (1:5). The mixture was heated in a water bath at 50–55° for 15 min. with occasional shaking to make the precipitate granular. The barium sulfate was removed by filtration and the filtrate was concentrated under reduced pressure from a water bath at 50–55°, when benzoic acid separated. The benzoic acid was removed by washing thrice with 50-ml. portions of ether. The aqueous layer was again concentrated under reduced pressure to 15 ml. Liquor ammonia (*d.* 0.888) was added until the pH of the solution was about the isoelectric point of the amino acid, when crystals of the amino acid separated. After cooling in the refrigerator overnight it was filtered, washed three times with 3-ml. portions of ice-cold water and three times with 5-ml. portions of ethanol. A second crop of the amino acid was obtained from the mother liquor and water washings on concentration. The amino acids were crystallized from water–ethanol.