2. It has been found that appreciable quantities of ether as well as ethylene are formed from alcohol and that at 275° and 300° the amount of alcohol decomposed attains a maximum corresponding to about 65% conversion, whereas at 350° the reaction goes to complete dehydration to form ethylene. The maximum yield of ether obtained was 60% at 250°. Ether decomposes readily from 275° up.

3. The results are shown to be explicable on the grounds that the dehydration of alcohol to yield ether is reversible, equilibrium corresponding to about 65% conversion, and that decomposition of alcohol occurs in steps. While the direct dehydration to yield ethylene is a possible mechanism, it is not necessary to assume it in order to account for the results.

4. Water vapor and ethylene diminish somewhat the efficiency of the catalyst toward alcohol dehydration.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY AT THE UNIVERSITY OF WISCONSIN]

DEAMINIZATION OF ESTERS OF ALANINE AND OF AMINO-ISOBUTYRIC ACID

BY A. L. BARKER[1] WITH GLENN S. SKINNER

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It has been shown by one of us[2] that *cis trans* isomerism gives rise to very different products in the deaminization of esters of amino acids derived from cyclopentane, the most striking difference being the non-formation of the ether of a free hydroxy acid in the case of the *cis* compound. The silver salt[3] of this hydroxy acid by treatment with methyl iodide gives in part the same ether acid as that obtained in the nitrite decomposition. This reaction of a silver salt[4] to give an ether instead of an ester has been observed to take place in the case of the salt of the hydroxy acid corresponding to isocampholactone. Likewise the silver salts of lactic and malic acids[5] give ether acids as well as esters. The esters of the corresponding amino acids should be expected to give ethers and this has been found to be true in the case of alanine.

The deaminization of esters of α-amino-*iso*butyric acid has not been previously studied and no quantitative data are given with regard to the esters of alanine. Curtius and Koch[6] have decomposed the hydrochloride

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[1] Abstract of a thesis presented by A. L. Barker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Wisconsin.

[2] Skinner, THIS JOURNAL, **45**, 1498 (1923).

[3] Noyes and Skinner, *ibid.*, **39**, 2692 (1917).

[4] Noyes and Taveau, *Am. Chem. J.*, **35**, 381 (1906).

[5] Purdie and Lander, *J. Chem. Soc.*, 73, 296 (1898).

[6] Curtius and Koch, *J. prakt Chem.*, [2] **38**, 472 (1888).

of the ethyl ester of alanine in an attempt to prepare the diazopropionic ester. Curtius and Lang[7] obtained from the hydrochloride of the methyl ester of alanine a product which they regarded as the impure diazo compound. Curtius and Müller[8] repeated the decomposition of the methyl and ethyl esters, and claim to have obtained from the mixture of decomposition products by repeated treatment with barium hydroxide and steam distillation a very small amount of fairly pure methyl and ethyl diazopropionates. They found that the ethyl ester gave both the α-chloro- and α-hydroxy-propionic esters.

In this investigation the amino acids were converted into the hydrochlorides of the respective esters; the ester hydrochlorides were then treated in aqueous solution with slightly more than the calculated amount of sodium nitrite solution. When the decomposition was complete, the solution was extracted with ether. The acid constituents were removed from the ether solution by extraction with sodium bicarbonate solution; the latter was then extracted with ether to remove neutral substances in solution, acidified, and again extracted with ether. Thus ether solutions of both neutral and acid constituents were obtained. After removal of the ether, the solutions, if large enough in amount, were subjected to fractionation in a vacuum. The percentage of the ether acids in the acid fractions was determined by the Zeisel method for the estimation of methoxy groups.

Table I

Comparative Yields of Decomposition Products

		Acid portion					Ester portion				
Total Ester hydrochloride Prepared for Study		Total	Unsat. acid	Hydroxy acid	Ether acid	Nitrogenous residue	Total	Unsat. ester	Hydroxy ester	Chloro ester	Nitrogenous residue
	G.	G.	G.	G.	G.	G.	G.	G.	G.	G.	G.
Methyl α-amino-*iso*butyrate....	87.5	0.2	+	+	0.07	0	26.8	19.1	+	0	3.4
Ethyl α-amino-*iso*butyrate....	50	0.1	+	..	0.03	0	17.0	14.4	1.0	0	1.6
Methyl ester of alanine........	475	16.8	+	+	+	+	95.6	4.1	15.2	17.3	59.0
Ethyl ester of alanine........	150	1.0	+	+	0.7	+	54.9	1.5	20.5	6.8	26.1

Our results indicate that both esters of alanine yield a mixture of unsaturated, chloro- and hydroxy-esters, as well as a neutral nitrogenous residue; in the acid portion were found the corresponding acids, in addition

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[7] Curtius and Lang, (a) *J. prakt. Chem.*, [2] **44**, 559 (1891); (b) Curtius, *Ber.*, **23**, 3037 (1890).

[8] Curtius and Müller, *Ber.*, **37**, 1269 (1904).

to a small amount of ether acid and a considerable quantity of high-boiling nitrogenous residue. The two esters of α-amino-*iso*butyric acid yield as the chief product the unsaturated ester, together with some hydroxy ester and a very small amount of ether acid. The final residue contained nitrogen but no chlorine was present in any of the fractions.

The results of the decomposition of the four esters are summarized in Table I.

The percentage by moles of the ether acid formed from the four esters was as follows: Methyl α-amino-*iso*butyrate 0.67%; ethyl α-amino-*iso*butyrate 0.077%; methyl α-aminopropionate 3.0%; ethyl α-aminopropionate 0.6%.

Experimental Part

α-Amino-*iso*butyric Acid.—This acid was prepared by the method of Zelinsky and Stadnikoff[9] as modified by Noyes.[10] The yield was usually from 48 to 51% of that calculated. In some preparations the first product obtained was contaminated with chlorides and had to be recrystallized from water. The melting point of the compound is not given in the literature. Our product in a sealed capillary tube melted at 333–334° (corr.). A sample of pure imported α-amino-*iso*butyric acid melted at 335° (corr.) under similar conditions.

Hydrochloride of Ethyl α-Amino-*iso*butyrate.—This compound is not described in the literature. It was prepared by the method of E. Fischer[11] for the preparation of similar compounds. The crystalline product was kept for several days in a vacuum desiccator over solid sodium hydroxide in order to remove the excess of hydrochloric acid. From 25 g. of the amino acid was obtained from 25 to 28 g. of the dry ester hydrochloride, corresponding to a 70% yield. The melting point of the pure crystals was 155–157° (corr.).

Analyses. Subs., 0.4922, 0.5854: AgCl, 0.4241, 0.5026. Calc. for $C_6H_{14}O_2NCl$: Cl, 21.16. Found: 21.31, 21.24.

DECOMPOSITION.—A solution of 25 g. of the ester hydrochloride in 50 cc. of water was mixed at 0° with a solution of 11.3 g. (1.1 equivalents) of sodium nitrite. A slow evolution of nitrogen took place and was accelerated by the dropwise addition of hydrochloric acid. A total of 0.5 cc. of the concentrated acid was added in the course of ten hours. After the mixture had stood for 24 hours at room temperature, a greenish-yellow oil floated on the surface. This was extracted with ether. The ethereal solution was extracted four times with 25cc. portions of saturated sodium bicarbonate solution to remove the acid constituents. The bicarbonate solution was then extracted several times with ether. The original ether extract, containing the neutral substances, was dried over anhydrous sodium sulfate and examined as described below. The bicarbonate solution was acidified with hydrochloric acid and again extracted with ether. This latter extract, containing the acid substances, was also dried over sodium sulfate and studied as described below.

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[9] Zelinsky and Stadnikoff, *Ber.*, **39,** 1726 (1906).

[10] Noyes, "Organic Chemistry for the Laboratory," Chemical Publishing Co., 3rd ed., **1916,** p. 234.

[11] Fischer, *Ber.*, **34,** 443 (1901).

Examination of the Decomposition Products.—On removal of the ether from the neutral extract, 11.8 g. of a faintly colored, mobile liquid with an ethereal odor was obtained. A similar decomposition yielded 10.5 g. of material. The combined material was then fractionated under 30mm. pressure, using the distilling flask and column described by Noyes and Skinner.[12] Three fractions were obtained: Fraction I, 35–40°, 4.7 g.; Fraction II, 40–50°, 9.7 g.; Fraction III, 50–60°, 1.0 g.; residual gum, 1.6 g. A similar neutral extract from another decomposition was distilled under atmospheric pressure, the greater portion going over between 115° and 130°. Polymerization took place, a thick sirupy mass, which became gummy as it cooled, being left in the flask. It is evident that the polymer is also formed when the distillation is carried out in a vacuum.

Fractions I, II and III had ethereal odors, decolorized permanganate, and contained no nitrogen and no chlorine. They were kept in sealed tubes for six months. The first two fractions gradually polymerized, changing first to a gum and finally to a hard, glassy solid. The tendency of these fractions to polymerize is in accord with the properties of ethyl α-methylacrylate. The identity was confirmed by the analysis of the Fraction I polymer.

Analyses. Subs., 0.2730: CO_2, 0.6234; H_2O, 0.2180. Calc. for $C_6H_{10}O_2$: C, 63.04; H, 8.77. Found: C, 62.21; H, 8.87.

Fraction III did not polymerize after a year and decolorized permanganate slowly. It was shown to be ethyl α-hydroxy-*iso*butyrate as follows. A small portion was hydrolyzed with sodium hydroxide, acidified, and extracted with ether. The product obtained from the ether solution melted at 74–76° (corr.).

Morkownikoff[13] gives 79° as the melting point of freshly sublimed α-hydroxy *iso*butyric acid. A sample of our acid was titrated for the neutralization equivalent.

Analysis. Subs., 0.0774: 13.5 cc. of 0.0564 *N* NaOH. Calc. for $(CH_3)_2COH$-COOH, 13.2 cc.

A sample of the hydroxy acid made by treating the free amino acid with nitrous acid melted at 75–78° (corr.).

The corresponding higher-boiling fraction from another decomposition, which melted at 38–40° (5–6 mm.), showed no signs of polymerization. The saponification equivalent was determined.

Analyses. Subs., 0.2350, 0.2010: 16.85, 14.78 cc. of 0.1 *N* NaOH. Calc. for saponification eq.: 132. Found: 139, 136.

This indicates that the higher boiling fraction consists largely of the hydroxy ester.

From the ethereal extract of the acid constituents was obtained 0.1 g. of a light yellow, odorless liquid, which dissolved slightly in water giving a solution which was acid to litmus and which decolorized permanganate instantly. The material from two decompositions served for the determination of the neutralization equivalent and the Zeisel number.

Analyses. Subs., 0.0516, 0.1075: 6.0, 12.4 cc. of 0.05 *N* NaOH. Calc. for CH_2CCH_3COOH: 11.86, 24.71 cc.

Subs., 0.0840: AgI, 0.0210. Calcd. for $C_6H_{12}O$: $-OC_2H_5$, 34.09. Found: 4.8.

It was evident that it consisted largely of free methyl acrylic acid, formed by the hydrolysis of the ester during the decomposition, together with a small amount of the ether acid.

Hydrochloride of Methyl α-Amino-*iso*butyrate.—This compound has been made

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[12] Ref. 3, p. 2718.

[13] Morkownikoff, *Ann.*, **146**, 341 (1868).

by Franchimont and Friedmann[14] by the usual method of esterification with hydrogen chloride. After the product was filtered it was washed with small quantities of alcohol and ether. It was then kept in a vacuum desiccator over solid sodium hydroxide to remove the excess of hydrogen chloride. The substance thus obtained melted at 180–181° (corr.) without decomposition, whereas Franchimont and Friedmann state that the substance decomposes without melting at 183°.

Analyses. Subs., 0.3700, 0.3448: AgCl, 0.3510, 0.3242. Calc. for $C_5H_{12}O_2NCl$: Cl, 23.13. Found: 23.47, 23.26.

DECOMPOSITION.—The decomposition was carried out as described for the ethyl ester. A total of 87.5 g. of the ester hydrochloride was decomposed. There was obtained less than 0.2 g. of material which dissolved the sodium bicarbonate solution. The acid portion was nearly colorless, soluble in water, acid to litmus, and it decolorized permanganate. It gave a light yellow color with ferric chloride. A Zeisel determination was made on a sample from two runs.

Analysis. Subs., 0.1310: AgI, 0.1780. Calc. for $C_5H_{10}O_3$: $-OCH_3$, 26.28. Found: 17.94.

On the basis of this analysis the product contained 68% of the ether acid, methoxy-*iso*butyric acid. The qualitative tests showed the presence of the unsaturated and hydroxy acids.

The neutral portions from the three runs amounted, respectively, to 4.3, 3.5 and 19.0 g. The first portion yielded on distillation 3.3 g. of material with a boiling range of 105–125°, and a residue, evidently a polymer, of 0.7 g. The 19.0-g. portion was fractionated.

Fraction	Temperature °C.	Pressure Mm.	Yield G.
I	20–22	25–30	13.0
II	40–42	24–26	1.3
III	75–80	17–18	1.0
IV (residue)	...	...	2.0

Fraction I was redistilled and boiled at 25–29° (35–38 mm.). It decolorized permanganate and had a strong ethereal odor. The saponification equivalent indicated that it was methyl α-methylacrylate.

Analyses. Subs., 0.1959, 0.1827: 19.45, 18.41 cc. of 0.1 *N* NaOH. Calc. for C_3H_5-$COOCH_3$: saponification eq., 100. Found: 100.7, 99.2.

Fraction II decolorized permanganate, but did not color ferric chloride or contain chlorine or nitrogen. The saponification equivalent was found to be 106, so it contained largely the unsaturated ester. The saponification equivalent of the hydroxy ester is 118.

Fraction III reacted with both permanganate and ferric chloride. It contained a trace of nitrogen but no chlorine. It was suspected of being largely the hydroxy ester. When an attempt was made to saponify it with sodium hydroxide the product was converted into a sticky, resinous mass, evidently a polymer.

The final residue was light brown in color and contained nitrogen. It could not be distilled. It was soluble in alcohol and ether and was precipitated from alcohol by the addition of water.

Alanine.—While inactive alanine has been synthesized by a number of methods, the Zelinsky-Stadnikoff[15] modification of the original Strecker[16]

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[14] Franchimont and Friedmann, *Rec. trav. chim.*, **27**, 197 (1908).

[15] Zelinsky and Stadnikoff, *Ber.*, **41**, 2061 (1908).

[16] Strecker, *Ann.*, **75**, 27 (1850).

synthesis appeared the most promising. It was, therefore, modified for use in preparing the alanine used in this investigation. According to the Zelinsky-Stadnikoff procedure the cold ammonium chloride solution was covered with a layer of ether in which was dissolved the calculated amount of acetaldehyde. The cyanide solution was added and the mixture shaken on a machine for three or four hours. The aqueous and ethereal layers were then separated and worked up independently, the hydrochloride of the amino nitrile being precipitated from the ether solution by means of dry hydrogen chloride. It was found that the conversion of the amino-nitrile into the amino acid was a rather unsatisfactory procedure and hence a method was adopted whereby the ether was omitted from subsequent preparations. The method for handling the aqueous layer was essentially the same as that used by Zelinsky and Stadnikoff.

A solution of 118 g. (2.2 moles) of ammonium chloride was mixed at 0° with 88 g. (2 moles) of freshly distilled acetaldehyde. A cold solution of 98 g. (2 moles) of sodium cyanide was added slowly while the mixture was constantly shaken and cooled. The tightly stoppered bottle containing the solution was allowed to stand first in ice and then at room temperature for 8 to 10 hours. The light yellow solution was then strongly acidified with hydrochloric acid and evaporated over a free flame to about 250 cc. An equal volume of concd. hydrochloric acid was added and the mixture was refluxed for an hour. It was then evaporated to a pasty mass by carefully heating it over a free flame, and was constantly stirred during the latter part of the operation. The mass was finally heated at 118–120° in a large oil-bath for a short time and then allowed to cool, being stirred meanwhile to prevent caking. The pulverized product was extracted with a 10:1 mixture of alcohol and ether to remove the hydrochloride of the amino acid. The gum obtained by the evaporation of the alcohol and ether was dissolved in a little water, the solution heated to 100°, and treated with basic lead carbonate, a small amount at a time, until effervescence ceased. The mixture was thoroughly cooled and filtered, and the filtrate treated with hydrogen sulfide. The filtrate from the lead sulfide was evaporated until crystals began to form and allowed to cool. The crude product was filtered with suction and washed several times with alcohol, which removed most of the color. The alanine is very soluble in water and only slightly so in alcohol. The melting range of the crude product was usually from 240° to 260°. This material was generally contaminated with chlorides, although a few preparations were made containing only a trace of chlorides. The material was purified by dissolving it in the smallest possible quantity of hot water, and filtering into 5 or 6 volumes of 95% alcohol. The product thus obtained was free from chlorides and in a closed capillary tube melted at 264–266° (corr.). Holleman and Antusch[17] give 195° as the melting point of alanine. Zelinsky and Stadnikoff[15] state that the acid after recrystallization from dil. alcohol melts with decomposition at 264–265°. Meyer and Jacobson[18] give the melting point of *dl*-alanine as 285°.

The yield of the crude product was usually from 30 to 50%, as may be seen from Table II.

Runs 3 and 6 were made without the ether layer, and the yields from the water layer were about the same on an average as those from the runs in which ether was used.

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[17] Holleman and Antusch, *Rec. trav. chim.*, **13**, 297 (1894).

[18] Meyer and Jacobson, "Lehrbuch der organischen Chemie," Veit and Co., Leipzig, **1913**, vol. I, Part 2, p. 756.

The hydrolysis of the aminonitrile was attended by considerable loss. For example, the aminonitrile (16.5 g.) from Run 1 on hydrolysis according to the usual method gave only 5.3 g. of alanine, or about 30% of that calculated. The second and third crops of alanine were generally highly contaminated with chlorides and for further purification the treatment with lead carbonate had to be repeated.

Table II

Preparation of Alanine

Run	Moles	Yield amino-nitrile (ether) G.	Yield alanine (water) G.	Per cent. alanine (water)
1	1	16.5	25.0	28.0
2	1	12.0	45.5	51.0
3	1	..	41.2	46.3
4	2	28.0	61.7	35.0
5	2.5	14.0	68.0	30.7
6	2	..	69.0	33.2

Hydrochloride of the Methyl Ester of Alanine.—This compound has been made by Curtius and Lang.[19] The material for use in this investigation was made by the Fischer method, previously described for esters of α-amino-*iso*butyric acid. Twelve runs were made and more than 500 g. of alanine was esterified in this way. The yield was from 66 to 84% of that calculated. One run was made using the Osborne and Jones[20] modification of the Phelps and Hubbard[21] method of esterification. As a result of the distillation with alcohol vapor it was hoped that the removal of the water formed in the reaction would tend to increase the yield, but it amounted to only 70%.

The ester hydrochloride after several days in a vacuum desiccator over solid sodium hydroxide melted between 154° and 158° with a melting interval of not more than 1° or 2° with the material from a given run. A sample after recrystallization from alcohol melted at 158–158.5° (corr.) in an open tube. The first product, without recrystallization, was sufficiently pure for use. It was free from excess of hydrochloric acid.

Analyses. Subs., 0.4469, 0.5256: AgCl, 0.4547, 0.5383. Calc. for $C_4H_{10}NO_2Cl$: Cl, 25.46. Found: 25.18, 25.33.

Decomposition.—The first decompositions were carried out as described for esters of α-amino-*iso*butyric acid. In an attempt to increase the yield of the decomposition products a number of modifications were used. For example, both hydrochloric and sulfuric acids were added in small amounts to hasten the decomposition, but the effect on the yield was slight. A large excess of sodium nitrite did not materially increase the yield. In some of the larger runs, the nitrite solution was introduced beneath the ester solution which was covered with a layer of ether, and the mixture was mechanically stirred during the addition and for several hours afterwards; this procedure did not give any larger yields. Some typical experiments are given in Table III.

Table III

Decomposition Experiments

Ester HCl used, g.	100	100	25	25	25	100	100
Yield, neutral portion, g.	32.0	25.0	4.4	3.6	7.1	26.0	31.7
Yield, acid portion, g.	3.0	2.1	1.0	1.4	1.2	4.6	3.3

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[19] Ref. 7a, p. 560.

[20] Osborne and Jones, *Am. J. Physiol.*, **26,** 212 (1910).

[21] Phelps and Hubbard, *Am. J. Sci.*, [4] **23,** 368 (1907).

Examination of the Decomposition Products.—The neutral portions from the above seven runs were combined and fractionated under diminished pressure.

Fraction	Pressure Mm.	Temperature °C.	Yield G.
I	33	28–32	6.0
II	25	43–46	19.5
III	7	42–44	13.0
IV (residue)	7	...	59.0

Fraction I.—From this fraction was obtained 4.1 g. of a mobile, ethereal liquid which decolorized permanganate instantly and which boiled at 80–81°. Caspary and Tollens[22] give 80.3° (corr.) as the boiling point of methyl acrylate. After seven months our product polymerized to a thick, gummy mass. It was, therefore, methyl acrylate.

Fraction II.—This fraction was free from nitrogen but contained 18.61% of chlorine, According to Curtius and Müller[8] the low-boiling esters obtained in a similar way contained both the chloro- and the hydroxypropionic esters, and the two may be separated by their different solubilities in water. Ten cc. of this fraction was shaken with small portions of water to dissolve the hydroxy ester. There remained insoluble in water 6.4 cc. of material which was dissolved in ether and dried over sodium sulfate. From the ether solution was obtained 5.6 cc. of liquid, three-fourths of which boiled between 127° and 129°. The boiling point of methyl α-chloropropionate is 132.5° as given by Kahlbaum.[23] The chlorine determination indicated that the product contained about 90% of the chloro ester.

Analyses. Subs., 0.1912, 0.1840: AgCl, 0.2003 (Carius), 0.1945 (Stepanow). Calc. for $C_4H_7O_2Cl$: Cl, 28.98. Found: 25.92, 26.15.

With ammonia the ester gave a crystalline derivative, melting point 75–77°. The melting point of α-chloropropionamide is 79°.

The hydroxy ester was recovered from the water layer by extraction with ether. The ester distilled between 138° and 142°. Schreiner[24] gives 144.8° as the boiling point of methyl lactate at 760 mm. The product still contained a trace of chlorine and reduced permanganate slightly. The saponification equivalent was determined.

Analysis. Subs., 0.1010: 9.41 cc. of 0.1 *N* NaOH. Calc. for $CH_3CHOHCOOCH_3$: saponification eq., 104. Found: 107.

An attempt was made to separate the two esters more completely by dissolving the mixture in a small amount of purified petroleum ether, boiling range 30–50°, and then extracting repeatedly with water. The material from the petroleum ether layer contained 26.05% of chlorine. The hydroxy ester obtained from the water layer still contained 2.85% of chlorine and boiled at 141–142° (742 mm.). The saponification equivalent was found to be 102.7.

The results indicate that Fraction II consisted of approximately 64% of methyl α-chloropropionate and 36% of methyl lactate, with possibly a trace of methyl acrylate. The petroleum ether method of separation is no more efficient than the original method.

Fraction III.—This fraction was free from nitrogen but contained 10.8% of chlorine. It was suspected of being, like Fraction II, a mixture of the chloro and hydroxy esters. A separation was attempted as described under the preceding fraction. From 6.0 g. of material was obtained 1.0 g. of the impure chloroester; b. p., 129–132° (corr.). The impure ester contained 25.47% of chlorine, whereas the formula requires

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[22] Caspary and Tollens, *Ann.*, **167**, 247 (1873).

[23] Kahlbaum, *Ber.*, **12**, 344 (1879).

[24] Schreiner, *Ann.*, **197**, 12 (1879).

28.98%. The product gave a crystalline amide; m. p., 75–78°. On the basis of the chlorine content, this fraction contained approximately 37% of the chloro ester.

Fraction IV.—This consisted of the residue which did not distil at 190° under a pressure of 7 mm.; it weighed 59.0 g. It was a dark colored, viscous liquid, which was free from chlorine but contained nitrogen. The fact that the liquid did not distil under the conditions eliminates the possibility of its being the diazo ester. In view of the tendency of such diazo derivatives to react with unsaturated compounds, it is probable that the acrylic ester formed in the reaction reacted in part with the diazo ester to form a derivative of a pyrazoline dicarboxylic ester.

Analyses. Subs., 0.1550, 0.1138: 16.5 cc. of N (moist) (28°, 742 mm.), 12.3 cc. (30°, 741.9 mm.). Calc. for diazo ester: N, 24.57; calc. for pyrazoline derivative: 14.00. Found: 11.29, 11.33.

This residue was kept in a colorless bottle for seven months during which time a very slight evolution of nitrogen occurred. Duplicate Dumas determinations showed the presence of 11.14 and 10.93% of nitrogen, indicating a negligible loss of this element.

An attempt was made to convert this residue into a crystalline amide by treatment with ammonia. From 3.0 g. was obtained 0.12 g. of a light yellow, crystalline product, which in a closed tube melted at 236–238° (corr.). This substance was soluble in hot water, but it did not decolorize iodine or permanganate solution. It was soluble in strong sulfuric acid without gas evolution; when it was gently warmed with 0.5 *N* sodium hydroxide solution ammonia was evolved. It contained 24.3% of nitrogen. It is probable that the crystalline derivative was the amide of a methyl-cyclopropane-dicarboxylic acid. The ester of this acid could have been formed by the loss of nitrogen from the pyrazoline derivative formed by the union of one molecule each of diazo ester and unsaturated ester.

The filtrate from this crystalline derivative was allowed to evaporate in a warm place. A black, tarry mass was obtained, which evolved gas when warmed. This material contained nitrogen, and was soluble in water and alcohol but not in ether or chloroform. It could not be obtained crystalline.

The results of the examination of the neutral portion would lead one to expect to find among the acid products the following: acrylic acid, lactic acid, α-chloropropionic acid, and certain nitrogenous substances. We were interested particularly in determining whether or not the ether acid was present. The acid portion from 475 g. of the ester hydrochloride, amounting to 16.8 g., was fractionated under 7 mm. pressure yielding 1.0 g. of Fraction I at 30–32°, 2.2 g. of Fraction II at 32–54°, 0.3 g. of Fraction III at 90–95° and 8.0 g. of Fraction IV, residue.

Fraction I was a water-clear, mobile liquid without ethereal odor, and was completely soluble in water. It contained chlorine but no nitrogen, decolorized permanganate instantly and gave a light yellow color with ferric chloride. The Zeisel determination indicated the presence of 57% of the ether acid, α-methoxypropionic acid.

Analysis. Subs., 0.2108: AgI, 0.2736. Calc. for $C_4H_8O_3$: —OCH_3, 29.81. Found: 17.16.

The Zeisel determination on a portion from another similar decomposition corresponded to 63.5% of the ether acid.

Fraction II was partly soluble in water giving an acid solution. It contained chlorine, decolorized permanganate slowly, and gave a strong yellow color with ferric chloride. These qualitative tests indicate the presence of the unsaturated acid in small amounts, along with the hydroxy and the chloro acids.

Fraction III was partly soluble in water, decolorized permanganate slowly, gave an intensely yellow color with ferric chloride, and contained chlorine. On account of the boiling point it was suspected of being lactic acid, contaminated with the lactid. The crystals of the zinc salt were identical microscopically with crystals of zinc lactate.

The residue, Fraction IV, was dark brown and gummy. It was partly soluble in water and acid to litmus. It reacted very slowly with permanganate and contained no chlorine but gave a positive test for nitrogen and an intense yellow with ferric chloride. The Dumas determination indicated 8.29% of nitrogen.

Hydrochloride of Alanine Ethyl Ester.—This compound has been made by Curtius and Koch.[25] The method previously described was used for the preparation of the compound used in this study. The yield was 95%. The melting point in a closed tube was found to be 70–75° (corr.), whereas Curtius and Koch give 64–68°. Our product was pure, as indicated by the chlorine content.

Analyses. Subs., 0.6186, 0.5050: AgCl, 0.5797, 0.4734. Calc. for $C_5H_{12}NO_2Cl$: Cl, 23.13. Found: 23.18, 23.19.

DECOMPOSITION.—One hundred and fifty g. of the compound described above was decomposed with 1.1 equivalents of sodium nitrite by mixing the two solutions at 0°, allowing the mixture to warm to room temperature and then to stand for 48 hours. After the products as previously described had been separated, there were obtained 1.0 g. of acid portion and 73.0 g. of neutral portion.

Examination of the Decomposition Products.—The neutral portion was fractionated.

Fraction	Pressure Mm.	Temperature °C.	Yield G.
I	...	...	1.5
II	12–15	24–26	0.3
III	7–8	37–42	22.0
IV	7–8	42–44	5.0
V	10–12	60–80	1.1
IV (residue)	...	...	25.0

Fraction I.—This fraction was recovered from the solvent ether by fractionation. It boiled at 99–100° (corr.) in a capillary tube. Caspary and Tollens[26] give 101–102° as the boiling point of ethyl acrylate. Weger[27] gives 98.5° for the same compound. The fraction thickened to a stiff gum after several months, indicating polymerization. This is characteristic of esters of acrylic acid.

Fraction II.—This fraction contained chlorine but no nitrogen; it decolorized permanganate and hence must have contained the unsaturated ester. A Carius determination indicated 11.07% of chlorine, corresponding to 42% of the chloro ester.

Fraction III.—This fraction contained chlorine but no nitrogen and decolorized permanganate very slowly. It was heavier than water and slightly soluble therein. A Carius determination indicated 7.5% of chlorine, corresponding to 29% of chloro-ester. As in the decomposition of the methyl ester, this fraction was suspected of being largely a mixture of the chloro and hydroxy esters. A separation was attempted by means of petroleum ether and water. From the petroleum ether layer was obtained 3.5 g. of a liquid that boiled at 142–146° (742 mm.). Backunts and Otto[28] give 146°, and Brühl[29] gives 146–147° (750 mm.) as the boiling point of ethyl α-chloropropionate. A Carius determination indicated 23.77% of chlorine, corresponding to 90% of the chloro

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[25] Ref. 6, p. 487.

[26] Ref. 22, p. 248.

[27] Weger, *Ann.*, **221,** 80 (1884).

[28] Backunts and Otto, *Ber.*, **9,** 1592 (1876).

[29] Brühl, *Ann.*, **203,** 24 (1880).

ester. This product gave with ammonia a crystalline amide, melting at 75–78°, as in the case of the methyl ester.

From the water layer was obtained 3.0 g. of material which still contained a trace of chlorine and boiled at 140–142°. Schreiner[24] gives 154.5° (corr.) as the boiling point of ethyl lactate at 760 mm. A sample of Pfanstiehl's ethyl lactate after one distillation boiled at 151–152° (741 mm.). The saponification equivalent further confirmed the belief that the product was ethyl lactate.

Analyses. Subs., 0.3060, 0.2000: 52.91, 34.18 cc. of 0.05 *N* NaOH. Calc. for $CH_3CHOHCOOC_2H_5$: saponification eq., 118. Found: 116, 116.4.

Fraction IV.—This fraction contained 1.43% of chlorine and a trace of nitrogen. The saponification equivalent indicated that it was principally the hydroxy ester.

Analysis. Subs., 0.2132: 37.06 cc. of 0.05 *N* NaOH. Calc. for $CH_3CHOHCOOC_2H_5$: saponification eq., 118. Found: 115.

Fraction V.—This fraction was free from chlorine but contained nitrogen. On the basis of the nitrogen content the fraction contained 34% of the diazo ester.

Analysis. Subs., 0.1416: 9.6 cc. of N (moist) (21°, 731 mm.). Calc. for $C_5H_8O_2N_2$: N, 21.87. Found: 7.36.

Fraction VI.—The dark colored residue was free from chlorine but contained 11.7% of nitrogen. It could not be converted into a crystalline amide.

The acid portion was soluble in water and decolorized permanganate. It contained both nitrogen and chlorine. These tests indicate the possible presence of the unsaturated chloro and hydroxy acids, as well as a nitrogenous product from the diazo derivative first formed. The amount of material was too small for fractionation or for extensive study. The Zeisel determination indicated the presence of about 70% of the ether acid, α-ethoxypropionic acid.

Analysis. Subs., 0.2078: AgI, 0.2875. Calc. for $CH_3CHOC_2H_5COOH$: $—OC_2H_5$, 38.13. Found: 26.5.

These observations indicate that the decomposition products of the ethyl ester of alanine include the following: ethyl acrylate, ethyl α-chloropropionate, ethyl lactate, acrylic acid, lactic acid, α-chloropropionic acid, α-ethoxypropionic acid, and certain nitrogenous residues which were not identified.

Summary

1. The esters of α-amino-*iso*butyric acid yield the corresponding unsaturated and hydroxy esters as well as a very small amount of acid material which contains in part the ether acids. The esters of alanine yield the unsaturated, hydroxy, and chloro esters, a high-boiling nitrogenous residue, the unsaturated, hydroxy, and chloro acids, and a small amount of the ether acid. The approximate percentages of these decomposition products have been determined.

2. The experience gained in preparing the above-mentioned amino acids and their ester hydrochlorides in quantity is given. It has been shown that the melting-point determination can be used as a criterion of purity for these compounds provided a sealed tube is used.

3. The results indicate that the introduction of an alkyl group in the case of α-aminopropionic esters diminishes the amount of ether acid formed. The ethyl ester of each acid gives a smaller yield of ether acid

than the methyl ester. The apparent complete absence of chlorine derivatives in the decomposition products of α-amino-*iso*butyric esters is also significant.

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DIPYRIDYLS FROM PYRIDINE

BY C. R. SMITH

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Six isomeric dipyridyls are theoretically possible. At present five of these, α,α, β,β, γ,γ, α,β, and α,γ[1] have been identified. In this paper the preparation and properties of a sixth, β,γ, are described.

This investigation was begun primarily for the purpose of preparing chemical compounds toxic to insects, when used as ingredients of sprays and dusts. It happened that one sample of crude and one of pure γ,γ-dipyridyl, prepared by the usual method of treating pyridine with sodium and then with moistened or laboratory air, similar to the procedures of Anderson,[2] Weidel and Russo[3] and others, were tested for toxicity to certain plant lice. The purified γ,γ-dipyridyl had a negligible toxicity, while the impure sample showed appreciable toxicity. It was surmised that this impure sample contained one or more compounds of high toxicity.

The yield of toxic material in this reaction was very small and it was necessary to make an extended study to find the conditions under which the yield was increased. A method using sodium, pyridine, and air (or oxygen) has been evolved. A high proportion of isomeric dipyridyls other than γ,γ which, up to this time, has been the sole dipyridyl produced directly in this interaction, was obtained. These isomers have been separated and identified as α,α, β,β and a new dipyridyl, β,γ, which is the dipyridyl not previously reported. Anderson[2] prepared the first dipyridyl in 1870 but erroneously considered it to be dipyridine. Weidel and Russo[3] later showed that the substance was γ,γ-dipyridyl. Furthermore, these chemists did not obtain oily bases boiling between 120° and 180°, reported by Anderson in the action of sodium on pyridine, but claimed to have obtained an oil with the composition of dipyridine. Weidel and Russo's "dipyridine" is described as an oil boiling between 286° and 290° (uncorr.), with partial decomposition, easily soluble in water and alcohol. No crystalline salts were prepared. On oxidation with permanganate a small quantity of isonicotinic acid was obtained. "Dipyridine" was unaltered

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[1] Meyer and Meyer, [(a) *J. prakt. Chem.*, **102,** 280 (1921)], prepared the fifth isomer while this study was in progress.

[2] Anderson, *Ann.*, **154,** 270 (1870).

[3] Weidel and Russo, *Monatsh.*, **3,** 851 (1882).