One recrystallization from aqueous alcohol gave 34 g. (76% yield) of material, m.p. 109.5–110°.

N-(β-Diethylaminoethyl) β-(2-Pyridyl)-propionamide (Procedure E).—In a flask fitted with a twelve-inch helix-packed column there was placed methyl β-(2-pyridyl)-propionate (33.0 g., 0.20 mole) and β-diethylaminoethylamine (23.2 g., 0.20 mole). The mixture was heated so that only methanol would distil from the top of the column. During a five-hour period the temperature of the mixture slowly rose to 205°, at which time the reaction mixture was cooled and taken up in benzene (200 cc.). The benzene solution was washed with 50 cc. of 25% potassium carbonate solution and then dried over anhydrous potassium carbonate. The benzene was removed under vacuum and the residue was distilled through a 10-inch column with wire-screen packing and heated jacket to give 34 g. (68% yield) of product boiling at 150° (0.06 mm.).

N,N-Diethyl β-(2-Pyridyl)-propionamide Methiodide.—A mixture of N,N-diethyl β-(2-pyridyl)-propionamide (15.0 g., 0.073 mole) and methyl iodide (5.0 cc., 11.4 g., 0.08 mole) in benzene (100 cc.) was refluxed for one hour. An oil separated and soon crystallized. After two recrystallizations from acetone (300 cc.) the material melted at 107.5–108.5° and weighed 7.0 g. (28% yield).

N,N-Diethyl β-(2-Piperidyl)-propionamide.—A solution of N,N-diethyl β-(2-pyridyl)-propionamide (25 g., 0.12 mole) in glacial acetic acid (120 cc.) was reduced with hydrogen on a Parr shaker in the presence of 1.0 g. of Adams platinum oxide catalyst. The theoretical amount of hydrogen was taken up in about 2.5 hours. After removal of the catalyst the acetic acid was evaporated under vacuum with a bath temperature of *not over 50°*. The residue was taken up in benzene (500 cc.) and the benzene solution was washed with 240 cc. of 25% potassium carbonate solution. The carbonate wash was cross-extracted with 200 cc. of benzene and the combined benzene solutions were dried over anhydrous potassium carbonate. The benzene was removed under vacuum and the residue was distilled to give 15.5 g. (60% yield) of colorless material boiling at 104–106° (0.3 mm.).

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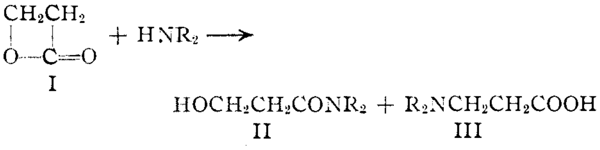
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. XI. Reactions with Ammonia and Amines

BY T. L. GRESHAM, J. E. JANSEN, F. W. SHAVER, R. A. BANKERT AND F. T. FIEDOREK

β-Propiolactone reacts with ammonia and primary and secondary amines to form the corresponding hydracrylamides and β-alanines and under certain conditions will give predominantly one or the other. Tertiary amines react with β-propiolactone to form the β-propiobetaine compounds.

β-Propiolactone[1] (I) reacts with ammonia and most primary and secondary amines to give both the amides (II) and the amino acids (III) and in some cases under favorable conditions will give predominantly one or the other. It would seem that the reactions between I and amines involve two different and competing reactions which open the oxetane ring on different sides of the oxygen. The two competing reactions have been found to vary with the amine, the solvent and the order of addition.



R = H, alkyl, aryl or heterocyclic radical

No direct correlation was found between the formation of amino acids from the primary and secondary amines and the basic strength of the amines.[2] Dimethylamine added to an ethereal solution of I gives mostly amino acid, but diethylamine under the same conditions gives largely the amide. In acetonitrile solution ammonia, dimethyl-, ethyl- and dodecylamines give chiefly the amino acids; methyl-, diethyl- and propylamines under similar conditions give the amides with little or no isolable amino acids. In general the aromatic and cyclohexylamines give amino acids more consistently than the alkylamines but the reaction is slower and with some amines takes place only when heated. Alkylamines which have a high hydration constant[3,4] give mostly the amide even in acetonitrile and those having low hydration constants give amino acids.

The choice of solvent is important in determining where the lactone ring opens. With water as the solvent ammonia and I give mostly hydracrylamide and in acetonitrile the same reactants give excellent yields of β-alanine. With few exceptions water was the best solvent for amide formation and acetonitrile the best for amino acid.

In some cases the order of addition determines whether the product will be largely the amide or amino acid. When dimethylamine is added to I in ether the major product is the amino acid; however, if I is added to an ethereal solution of dimethylamine the major product is the amide. Simultaneous addition of I and dimethylamine to ether gives essentially an equal mixture (44 and 47%) of amide and amino acid, the net result indicating in this case that the rates of formation of the amide and amino acid are nearly the same.

There is evidence that the reactions of I with the different amines are nearly quantitative, but it is difficult to separate quantitatively the amide from the amino acid. This is in contrast to some of the other reactions of I where it was found[5] that the main reaction was accompanied by polyester formation. When an amino acid, obtained from an aliphatic amine, is the major component, it is usually a solid material and can be filtered from the soluble amide. If an amide is the major component it can be separated from the amino acid by distillation but even here some of the amino acid sublimes or distills over with the amide. The amino acids from the aromatic amines can be separated from the concomitant amides by basic extraction and al-

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[1] Gresham, Jansen and Shaver, THIS JOURNAL, **70**, 998 (1948).

[2] Choh-Hao Li and T. D. Stewart, *ibid.*, **59**, 2596 (1937).

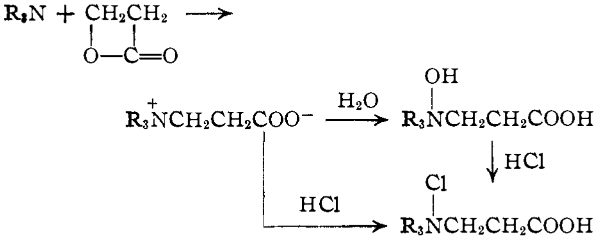
[3] Moore and Winmill, *J. Chem. Soc.*, **91**, 1373, 1379 (1907).

[4] Moore and Winmill, *ibid.*, **101**, 1635 (1912).

[5] Gresham, Jansen, Shaver, Gregory and Beears, THIS JOURNAL, **70**, 1004 (1948).

though the two isolated products may be relatively pure a quantitative separation is difficult.

The tertiary amines react with I in non-aqueous solvents to form the betaines. The betaines have salt-like properties and are quite hygroscopic. This latter property is probably associated with the tendency of these compounds to form the hydrate. In aqueous solution the hydrate is formed directly from the tertiary amine and I.



The identities of the reaction products were established by their chemical characteristics and analyses, and confirmed by potentiometric titration curves. The amides, except those formed from the hydrazines, followed a neutral or pure water titration curve. The amino acids and betaines showed breaks in both the acidic and basic titrations as would be predicted for such compounds. Some of the hydracrylamides were further checked by comparison of melting point and mixture melting point with hydracrylamides made by aminolysis of ethyl hydracrylate. A few of the compounds were too hygroscopic for satisfactory analyses and it was necessary to make non-hygroscopic derivatives.

Work is in progress on the mechanism of the reactions between amines and β-propiolactone which should explain some of the anomalous results obtained.

Experimental

Materials.—The amines used in these experiments were Eastman Kodak Co. White Label grade or of comparable purity. The acetonitrile was the commercial grade of Niacet Chemicals Division.

The amides, amino acids and betaines were made according to the general procedures which show the method of conducting the reactions and isolating the products. These procedures are indicated by the capital letters A, B, C, D, E, F. The small letters in the parentheses denote the order of addition and exceptions to the general procedures and are listed in the footnotes to Table Ia.

N,N-Dimethyl-β-alanine. Procedure A(d).—Gaseous dimethylamine (50 g., 1.1 moles) was bubbled into a stirred solution of 72 g. (1 mole) of I in 300 ml. of ether, over a

TABLE Ia

HYDRACRYLAMIDES (II) AND β-ALANINES (III)

Procedure: (c), lactone is added to amine; (d), amine added to lactone; (e), simultaneous addition of lactone and amine to ether; (j), lactone added to amine at 145–155°; (k), amine added to the lactone all at one time; (m), reaction run at 83°

Amine	Procedure	Solvent[a]	Yield, %[b] Amide	Amino acid	Ref.[o] number
Ammonia	B(c)	Water	90	. .	1
	A(d)	*t*-BuOH	. .	79	2
	A(d)	MeCN	. .	97	
Methyl	B(c)	Water	91	. .	3
	B(d)	Ether	74	. .	
	B(c)	Ether	78	. .	
	B(d)	MeCN	90	. .	
Dimethyl	B(c)	Water	79	13	
	A(d)	Ether	. .	84	4
	B(c)	Ether	95	. .	5
	AB(e)	Ether	44	47	
	A(c)	MeCN	. .	87	
Ethyl	B(c)	Water	97	. .	6
	B(d)	Ether	76	. .	
	A(d)	MeCN	. .	87	7
Diethyl	B(c)	Water	80	. .	8
	B(d)	Ether	71		
				4[f]	9
	B(d)	MeCN	70	. .	
Propyl	B(c)	Water	86	. .	10
	B(c)	Ether	76	. .	
	B(c)	MeCN	72	. .	
Dipropyl	A(d)	MeCN	62[g]		11
				25[h]	12
	B(c)	Water	68[g]	24[h]	
Butyl	B(d)	Water	98	. .	13
Dodecyl	A(d)	MeCN	. .	61	14
Ethanol	A(d)	MeCN	. .	66	15
Diethanol	A(d)	MeCN	. .	56	16
	A(c)	EtOH	. .	65	
Hydrazine hydrate	A(d)	MeCN	36	. .	17
Cyclohexyl	A(d)	MeCN	. .	95	18
	A(c)	MeCN	. .	98	
	A(d)	Ether		40[f]	
			16[i]		19
Dicyclohexyl	D(j)	None	. .	74	20
Aniline	C(k)	Ether	52		21
				17	22
	C(k)	MeCN	27	35	
	C(c)	Water	. .	93[l]	
Diphenyl	D(j)	None	. .	70	23
α-Naphthyl	C(k)	Ether	17		24
				61	25
β-Naphthyl	C(k)	Ether	40		26
				55[l]	27
Phenyl hydrazine	A(k)	Ether	63	. .	28
Piperidine	B(d)	MeCN	. .	79	29
Morpholine	A(d)	MeCN	. .	92	30
Benzyl	C(c)	Water	51		31
				36	32
	C(c)	Ether	44	11.1[f]	
	A(d)	MeCN		94	
Dibenzyl	A(d)	MeCN	. .	67[f]	33
	C(m)	MeCN	7[n]		34
				78[f]	
Methyl-aniline	C(m)	MeCN		76[f]	35
			6[n]		36
o-Chloro-aniline	A(m)	MeCN	. .	95	37
o-Nitro-phenyl	A(m)	MeCN	. .	92	38

[a] Reactions run between 0 and 30° unless otherwise noted. [b] The yield represents isolated material, blank space indicates that no material was isolated and identified although some was probably present. [f] Isolated as hydrochloride. [g] The amide and amino acid distill together and it was difficult to completely separate the two products. [h] This represents minimum yield; some of the amino acid was dissolved in the amide portion. [i] Amide extracted from amino acid salt with chloroform. [l] Isolated as the sulfate. [n] Isolated as the phenyl urethan. [o] The reference number refers to the corresponding product in Table Ib.

TABLE Ib

HYDRACRYLAMIDES (I) AND β-ALANINES (III)

	Product	M.p. or b.p.,[a] °C. (mm.)	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1	Hydracrylamide	65–66	$C_3H_7NO_2$	40.4	40.5	7.9	7.9	15.7	15.7
2	β-Alanine	204–206 (dec.)	$C_3H_7NO_2$	40.4	40.4	7.9	8.0	15.7	15.8
	β-Alanine hydrochloride	123–124	$C_3H_8ClNO_2$	28.7	28.6	6.4	6.4		(..)[b]
3	N-Methylhydracrylamide	131–135 (3)	$C_4H_9NO_2$	46.6	46.7	8.8	8.7	13.6	13.5
4	N,N-Dimethyl-β-alanine	140–142	$C_5H_{11}NO_2 \cdot 1/2H_2O$	47.6	47.4	9.5	9.6	11.1	10.9
	Hydrochloride	191–192	$C_5H_{12}ClNO_2$	39.1	39.2	7.9	7.8	9.1	9.0
5	N,N-Dimethylhydracrylamide	90–92 (2)	$C_5H_{11}NO_2$	51.3	51.2	9.5	9.4	11.9	11.9
6	N-Ethylhydracrylamide	100–106 (0.1)	$C_5H_{11}NO_2$	51.3	51.3	9.5	9.4	11.9	11.9
7	N-Ethyl-β-alanine	169–170	$C_5H_{11}NO_2$	51.3	51.4	9.5	9.4	11.9	11.8
8	N,N-Diethylhydracrylamide	80–82 (1)	$C_7H_{15}NO_2$	57.9	58.3	10.4	10.2	9.7	10.1
9	N,N-Diethyl-β-alanine hydrochloride	136–138	$C_7H_{16}ClNO_2$	46.3	46.3	8.9	8.9	7.7	7.7[c]
10	N-Propylhydracrylamide	90–91 (0.3)						10.7	10.7
11	N,N-Dipropylhydracrylamide	84–85 (0.45)	$C_9H_{19}NO_2$	62.4	62.5	11.0	10.8	8.1	8.3
12	N,N-Dipropyl-β-alanine	87–88	$C_9H_{19}NO_2$					8.1	8.0
13	N-Butylhydracrylamide	95–97 (0.15)	$C_7H_{15}NO_2$	57.9	57.8	10.4	10.4	9.7	9.5
14	N-Dodecyl-β-alanine	82–84	$C_{15}H_{31}NO_2$	70.0	70.0	12.1	11.8	5.4	5.4
15	N-(2-Hydroxyethyl)-β-alanine	143–145	$C_5H_{11}NO_3$					10.5	10.4
16	N-Di-(2-hydroxyethyl)-β-alanine	109–111	$C_7H_{15}NO_4$					7.9	7.9
17	Hydracrylylhydrazide	103–104	$C_3H_8N_2O_2$					26.9	27.0
	Hydrochloride	143–144	$C_3H_9ClN_2O_2$					19.9	19.8[d]
18	N-Cyclohexyl-β-alanine	170–171	$C_9H_{17}NO_2$	63.1	63.1	10.0	10.2	8.2	8.2
	Hydrochloride	171–172[e]	$C_9H_{18}ClNO_2$	52.0	52.3	8.7	8.6	6.8	6.7[f]
19	N-Cyclohexylhydracrylamide	91–92	$C_9H_{17}NO_2$	63.1	63.0	10.0	9.7	8.2	8.1
20	N,N-Dicyclohexyl-β-alanine	129–130	$C_{15}H_{27}NO_2$	71.1	71.0	10.7	10.6	5.5	5.4
21	N-Phenylhydracrylamide	112–113	$C_9H_{11}NO_2$	65.4	65.4	6.7	6.7	8.5	8.4
22	N-Phenyl-β-alanine	61–62	$C_9H_{11}NO_2$	65.4	65.4	6.7	6.6	8.5	8.3
	Sulfate	174–175							
23	N,N-Diphenyl-β-alanine	112–113	$C_{15}H_{15}NO_2$	74.7	74.2	6.3	6.3	5.8	5.9
24	N-(α-Naphthyl)-hydracrylamide	123–124	$C_{13}H_{13}NO_2$	72.5	72.6	6.1	6.0	6.5	6.4
25	N-(α-Naphthyl)-β-alanine	140–141	$C_{13}H_{13}NO_2$	72.5	72.4	6.1	6.1	6.5	6.4
26	N-(β-Naphthyl)-hydracrylamide	127–128	$C_{13}H_{13}NO_2$	72.5	72.5	6.1	6.1	6.5	6.4
27	N(-β-Naphthyl)-β-alanine sulfate	163–164	$C_{26}H_{28}N_2O_8S$	59.1	59.0	5.3	5.6	5.3	5.3
28	N-Phenylhydracrylyl hydrazide	140–141	$C_9H_{12}N_2O_2$	60.0	59.9	6.7	6.7	15.5	15.6
29	β-(1-Piperidyl)-propionic acid	105–108 (0.5)[g]							
	Hydrochloride	210–211	$C_8H_{16}ClNO_2$	49.6	49.6	8.3	8.2	7.2	7.2[h]
30	β-(1-Morpholinyl)-propionic acid	(..)[i]	$C_7H_{13}NO_3$					8.8	8.7
	Hydrochloride	206–207	$C_7H_{14}NO_3$	43.0	43.2	7.2	7.2	7.2	7.1[j]
31	N-Benzylhydracrylamide	63–64	$C_{10}H_{13}NO_2$	67.0	67.0	7.3	7.3	7.8	7.8
32	N-Benzyl-β-alanine	182–183	$C_{10}H_{13}NO_2$	67.0	66.9	7.3	7.2	7.8	7.8
33	N,N-(Dibenzyl)-β-alanine hydrochloride	203–204	$C_{17}H_{20}ClNO_2$	66.8	66.7	6.6	6.7	4.6	4.5[k]
34	Phenylurethan of N,N-dibenzyl-hydracrylamide	123–124	$C_{24}H_{24}N_2O_3$	74.2	74.2	6.2	6.2	7.2	7.1
35	N-Methyl-N-phenyl-β-alanine hydrochloride	132–133	$C_{10}H_{14}ClNO_2$	55.7	55.7	6.5	6.4	6.5	6.5[l]
36	Phenylurethan of N-methyl-, N-phenyl-β-alanine	142	$C_{17}H_{18}N_2O_3$	68.5	68.5	6.1	6.0	9.5	9.3
37	N-(o-Chlorophenyl)-β-alanine	128–130	$C_9H_{10}ClNO_2$					7.0	7.0
38	N-(o-Nitrophenyl)-β-alanine	142–143	$C_9H_{10}N_2O_4$	51.4	51.5	4.8	4.7	13.3	13.2

[a] Melting points and boiling points uncorrected. [b] Calcd.: Cl, 28.3. Found: Cl, 28.3. [c] Calcd.: Cl, 19.5. Found: Cl. 19.4. [d] Calcd.: Cl, 25.2. Found: Cl, 25.2. [e] Mixture m.p. with base 140–145°. [f] Calcd.: Cl, 17.1. Found: Cl, 17.0. [g] M.p. 82–83° (hygroscopic). [h] Calcd.: Cl, 18.3. Found: Cl, 18.3. [i] Very hygroscopic. [j] Calcd.: Cl. 18.1. Found: Cl, 17.9. [k] Calcd.: Cl, 11.6. Found: Cl, 11.6. [l] Calcd.: Cl, 16.4. Found: Cl, 16.4.

period of two hours, the temperature being maintained at 0°. The solid (104 g., m.p. 136–140°) which had formed was filtered, dried and recrystallized from methanol; yield 98 g. (84%) of N,N-dimethyl-β-alanine, m.p. 142–143°. The amide, if formed, was not recovered.

N,N-Dimethylhydracrylamide. Procedure B(c).—Dimethylamine was bubbled into 300 ml. of ether at 0° until the ether was saturated. One mole (72 g.) of I was added to the stirred solution over a period of two hours while keeping the solution saturated with the amine during the addition to ensure an excess of amine. When the solution reached room temperature the ether was removed and the product distilled. The product distilling at 71–74° (0.17 mm.), 111 g. (95%), was N,N-dimethylhydracrylamide. The residue gave 3.8 g. (3.2%) of N,N-dimethyl-β-alanine, m.p. 141–142°.

N-Phenylhydracrylamide and N-Phenyl-β-alanine. Procedure C(k).—One mole of I (72 g.) was added to a stirred solution of 93 g. (1 mole) of aniline in 500 ml. of ether. There was some heat of reaction which was controlled at 30° for two hours. While standing overnight the amide crystallized from solution. One mole (40 g.) of sodium hydroxide in 300 ml. of water was shaken with the reaction mixture and the amide removed by filtration. The basic solution was extracted with additional ether, the ether extracts were concentrated and the combined fractions of

TABLE IIa

BETAINES (IV)

Amine	Procedure	Solvent	Yield, %	Ref. number[f]
Trimethyl	E	MeCN[a]	98	1
	E	Water[b]	80[c]	
Dimethylethanol	E	MeCN	93	2
Methyldiethanol	E	MeCN	76	3
Triethanol	E	MeCN	14	4
HMT[d]	E	MeCN	100[e]	5
N-Methylmorpholine	E	Water	52[e]	6
Dimethyldodecyl	F	Ether–MeCN	76	7
Dimethylmyristyl	F	Ether–MeCN	80	8
Dimethylpalmityl	F	Ether–MeCN	82	9
Dimethylstearyl	F	Ether–MeCN	83	10
Pyridine	F	Water	91	11
α-Picoline	F	Water	85[e]	12
Quinoline	F	Water	76[c]	13
Isoquinoline	F	Water	94[e]	14

[a] Gaseous trimethylamine added. [b] Aqueous (25%) trimethylamine used—reaction product converted to the ammonium chloride before isolating. [c] Isolated as hydrochloride. [d] Hexamethylenetetramine. [e] Isolated as the hydrate. [f] The reference number refers to the corresponding product in Table IIb.

TABLE IIb

BETAINES (IV)

	Betaine	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	Methyl β-dimethylaminopropionate-	120.5–121	$C_6H_{13}NO_2$[a]			..	...
	N-(2-Carboxyethyl)-trimethylammonium chloride	200–200.5	$C_6H_{14}ClNO_2$					8.4	8.3[b]
2	Methyl β-(-methyl-N-hydroxyethyl)-aminopropionate-	120.5–121	$C_7H_{15}NO_3$					8.7	8.5
	N-(2-Carboxyethyl)-dimethylhydroxyethyl ammonium chloride	103–104	$C_7H_{16}ClNO_3$					7.1	7.1[c]
3	Methyl β-di(N-hydroxyethyl)-aminopropionate-	124.5–125.5	$C_8H_{17}NO_4$					7.3	7.2
4	Hydroxyethyl-β-di-(N-hydroxyethyl)-aminopropionate-	132–134	$C_9H_{19}NO_5$	48.9	49.0	8.7	8.5	6.3	6.3
5	N-(2-Carboxyethyl)-hexamethylenetetraminium-	Dec.	$C_9H_{16}N_4O_2 \cdot H_2O$[d]					24.3	24.1
	N-(2-Carboxyethyl)-hexamethylenetetraminium chloride	Dec.	$C_9H_{17}ClN_4O_2$					22.5	22.1[e]
6	4-(2-Carboxyethyl)-N-methylmorpholinium-	109–111	$C_8H_{15}NO_3 \cdot H_2O$[d]					7.3	7.3
	4-(2-Carboxyethyl)-N-methylmorpholinium chloride	179–180	$C_8H_{16}ClNO_3$					6.7	6.7[f]
7	Methyl β-(N-methyl-N-dodecyl)-aminopropionate-	137–137.5	$C_{17}H_{35}NO_2$	71.5	71.4	12.4	12.4	4.9	4.9
8	Methyl β-(N-methyl-N-myristyl)-aminopropionate-	132.5–133	$C_{19}H_{39}NO_2$					4.5	4.4
9	Methyl β-(N-methyl-N-palmityl)-aminopropionate-	129–130	$C_{21}H_{43}NO_2$	73.8	73.2	12.7	12.7	4.1	4.1
10	Methyl β-(N-methyl-N-stearyl)-aminopropionate-	129–130.5	$C_{23}H_{47}NO_2$					3.8	3.7
11	1-(2-Carboxyethyl)-pyridinium-	132–134	$C_8H_9NO_2$	63.5	63.1	6.0	6.3[i]		
	1-(2-Carboxyethyl)-pyridinium chloride	151–152	$C_8H_{10}ClNO_2$	51.2	51.0	5.4	5.3		
12	1-(2-Carboxyethyl)-α-picolinium-	127–128	$C_9H_{11}NO_2 \cdot H_2O$[d]	59.0	58.6	7.2	7.2		
	1-(2-Carboxyethyl)-α-picolinium chloride	191–192	$C_9H_{12}ClNO_2$	53.7	53.6	6.0	6.1		
13	1-(2-Carboxyethyl)-quinolinium chloride	241–243	$C_{12}H_{12}ClNO_2$	60.6	60.6	5.1	5.2	5.9	5.2[g]
14	2-(2-Carboxyethyl)-isoquinolinium chloride	211–212	$C_{12}H_{12}ClNO_2$	60.6	60.8	5.1	5.2	5.9	5.3[h]

[a] Very hygroscopic. [b] Calcd.: Cl, 21.2. Found: Cl, 21.0. [c] Calcd.: Cl, 17.9. Found: Cl, 17.9. [d] Isolated as the hydrated form. [e] Calcd.: Cl, 14.3. Found: Cl, 14.3. [f] Calcd.: Cl, 16.9. Found: Cl, 17.0. [g] Calcd.: Cl, 14.9. Found: Cl, 14.9. [h] Calcd.: Cl, 14.9. Found: Cl, 15.0. [i] Calcd.: Cl, 18.9. Found: Cl, 18.6.

amide were recrystallized from water; yield 86 g. (52%), m.p. 112–113°.

The basic solution was neutralized with 50 g. (0.5 mole) of concentrated sulfuric acid and an oil separated. The oil which failed to crystallize was extracted with ether and the ether was removed. The crystalline sulfate formed when the oil was treated with 100 g. of 25% sulfuric acid. The sulfate was recrystallized from an alcohol–water mixture; yield 32 g. (17%) of N-phenyl-β-alanine sulfate, m.p. 174–175°.

The amino acid was obtained when the sulfate was neutralized with aqueous sodium hydroxide. The oil which separated crystallized on cooling. The solid was filtered and recrystallized from ether by the addition of hexane to give N-phenyl-β-alanine, m.p. 61–62°.

N,N-Diphenyl-β-alanine. Procedure D(j).—Over a period of 15 minutes one mole (72 g.) of I was added with stirring to two moles (338 g.) of diphenylamine at 140°. During the addition the temperature rose to 160° and the reaction mixture was maintained between 140–160° for two hours. The reaction mixture was added to a stirred basic solution (425 ml. of 10% sodium hydroxide solution) and cooled in an ice-bath. The unreacted diphenylamine crystallized and was filtered. The precipitate was washed with water and the combined filtrates were extracted with 5–200-ml. portions of ether. When the basic solution was acidified the amino acid separated as an oil and crystallized on stirring. The solid was filtered and dried to yield 167.5 g. (69.5%) of N,N-diphenyl-β-alanine, m.p. 106–112°, recrystallization from aqueous ethanol solution raised the melting point to 113–114°. It showed no depression in m.p. when mixed with a sample made by the reaction between diphenylamine and ethyl acrylate.

Methyl β-Dimethylaminopropionate Betaine. Procedure E.—Gaseous trimethylamine (0.7 mole) was bubbled into a stirred solution of 36 g. (0.5 mole) of I in 300 cc. of acetonitrile at a temperature of 10–15°. The product precipitated from solution, was filtered and dried; yield 64 g. (98%); m.p. 120.5–121° (the material is very hygroscopic).

The hydrochloride was prepared by treating an alcoholic solution of the betaine with concentrated hydrochloric acid. Crystallization from aqueous alcohol gave N-(2-carboxyethyl)-trimethylammonium chloride, m.p. 200–200.5°.

(Dimethylalkyl)-propiobetaine. Procedure F.—β-Propiolactone (0.2 mole) was added to a stirred solution of the dimethylalkylamine (0.2 mole) in 250 cc. of ether and 75 cc. of acetonitrile, maintaining the temperature at 25–30°. The betaine started to precipitate at once and after standing overnight was filtered, washed with ether and dried. These betaines, when recrystallized from alcohol, form alcoholates which are readily converted to the parent compound when heated under vacuum.

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