secured by the reduction of tropinone, one of these isomers when converted to the tropic or mandelic acid ester had no mydriatic properties, whereas the tropic and mandelic acid esters of the other had strong mydriatic effects. Use of the physical properties and methods of formation of these isomers was shown to be unreliable as a method of predicting their probable physiological effects.

The author wishes to express his gratitude to the Cincinnati Board of Health, in whose laboratory he was given the opportunity to determine the physiological effects of these alkaloids.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE RELATIVE STABILITY OF HALOGEN SUBSTITUTED ALIPHATIC ACIDS IN WATER SOLUTION.

II. THE PROPIONIC ACID AND BUTYRIC ACID SERIES.

BY G. S. SIMPSON.

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In a recent paper from this laboratory[1] the relative stability of halogen substituted acetic acids as determined by the hydrolysis of their sodium salts was discussed. This article describes the result of a similar investigation of the stability of several halogen substituted acids in the propionic and butyric acid series.

Preparation of Materials.

The ethyl esters of α-bromobutyric acid and α-bromoisobutyric acid, which were in stock, were readily purified by distillation. All other acids or esters were prepared as described below.

α-Chloropropionic ester was made from lactic acid by the method of Loven.[2] Dried calcium lactate was allowed to react with phosphorous pentachloride and the α-chloropropionyl chloride obtained was added to absolute alcohol to form the ester. After purification the product boiled at 145–147°.

α-Bromopropionyl bromide was made by adding bromine to dry propionic acid in the presence of red phosphorus according to Zelinsky's[3] method. This was added to absolute alcohol to form α-bromopropionic ester which, after purification, boiled at 157–159°.

β-Iodopropionic acid was prepared by heating iodine and yellow phosphorus with an aqueous solution of glyceric acid, obtained by the oxidation of glycerine with fuming nitric acid and purification by means of its calcium salt. This method of purification of glyceric acid, suggested by

[1] Drushel and Simpson, THIS JOURNAL, **39**, 2453 (1917).

[2] *J. prakt. Chem.*, [2] **29**, 367 (1884).

[3] *Ber.*, **20**, 2026 (1887).

Drushel,[1] gives a crystalline product which is much more convenient to isolate and wash than the gelatinous lead salt. The iodopropionic acid was obtained as pearly white plates by recrystallization from hot water.

β-Bromopropionic acid was formed by adding an aqueous solution of β-iodopropionic acid to bromine and subsequent heating according to Richter.[2] The free iodine formed was filtered off and all excess of halogen was removed by pressing the product on a porous plate. It was purified by recrystallizing from petroleum ether giving pearly plates melting at 62°.

β-Chloropropionic acid has been made by different methods by several investigators but in each case a different melting point was recorded. DeBarr[3] and Richter[4] prepared it by the replacement of iodine of β-iodopropionic acid in aqueous solution with chlorine. The product was then distilled several times over mercury or silver. Such a procedure might easily give adipic acid according to this equation:

$$2ClCH_2 - CH_2COOH + 2Ag \longrightarrow (CH_2\text{-}CH_2COOH)_2 + 2AgCl$$

The acid prepared in this manner melted at 58–61° while all the other procedures gave products melting at 35.5° to 41°. As De Barr gave no analysis of his product it is difficult to determine the true value of his method. Since β-iodopropionic acid was the only material available at this time for the preparation of β-chloropropionic acid, the method described by Drushel[5] for preparing esters of β-chloropropionic acid was used. Fifty g. of β-iodopropionic acid were dissolved in 100 g. of chloroform. This solution, which was well cooled, was treated with chlorine in the dark until no more iodine trichloride separated out. This precipitate was filtered on asbestos and the filtrate was placed in a vacuum desiccator over caustic soda. After distilling off the chloroform the remainder of free halogen was removed by pressing the product on a porous plate. On recrystallization from petroleum ether 20 g. of white pearly crystals melting at 39° were obtained. This product thus melted well within the limits given by several investigators. On analysis the following figures were obtained:

Subst., 0.2160, 0.2320; AgCl, 0.2902, 0.3084.
Calc. for $C_3H_5O_2Cl$: Cl, 32.70. Found: 32.90, 33.25.

An attempt was made to prepare β-chloropropionitrile by the selective action of potassium cyanide on β-chloro-α-bromoethane, synthesized by the method of James,[6] but large amounts of vinyl chloride were produced due to the alkalinity of potassium cyanide.

[1] *Am. J. Sci.*, **39**, 113 (1915).
[2] *Zeit. Chem.*, **1868**, 461.
[3] *Am. Chem. J.*, **22**, 336 (1899).
[4] *Loc. cit.*
[5] *Am. J. Sci.*, **34**, 69 (1912).
[6] *J. prakt. Chem.*, [2] **26**, 380 (1882).

The α,α-dibromopropionic acid was made by Drushel's[1] modification of the method of Phillipi and Tollens.[2] Dry propionic acid was heated in a sealed tube with bromine and the tube opened to allow the escape of hydrobromic acid. An equal amount of bromine was again added and the heating continued. The product was freed from hydrobromic acid and free halogen by pressing on a porous plate and then was recrystallized from a small amount of water. The material melted at 61°.

The preparation of α,β-dibromopropionic acid required the use of allyl alcohol which was made by Koehler's[3] method. By allowing allyl alcohol and bromine to stand in two crystallizing dishes several days under a bell jar β,γ-dibromohydrine was formed as described by Munder and Tollen.[4] This product was steam-distilled and then oxidized to α,β-dibromopropionic acid by means of fuming nitric acid. The material after recrystallizing from water melted at 63°.

α,β-Dichloropropionic acid was similarly made from allyl alcohol by Tollen's[5] method. The β,γ-dichlorohydrine formed by passing chlorine into a cooled flask containing allyl alcohol was distilled in a vacuum and then oxidized by fuming nitric acid to α,β-dichloropropionic acid. It was purified by washing and recrystallizing from hot water, giving a product melting at 49°.

α-Chlorobutyric acid was obtained by the method of Freer.[6] Ethyl malonic ester was formed by the action of ethyl iodide on sodiomalonic ester. This was chlorinated by Gutzeit's[7] method. The chloroethyl malonic ester was converted to potassium ethyl chloromalonate by an alcoholic solution of potassium hydroxide and from this the free acid was obtained by means of dilute sulfuric acid. On distilling ethyl chloromalonic acid in a vacuum (15 mm.) at 101°, carbon dioxide was split off and α-chlorobutyric acid passed over, as described by Freer.[8]

β-Chlorobutyric acid was made by saturating an ethereal solution of crotonic acid with hydrochloric acid gas according to De Barr.[8] After removing the ether β-chlorobutyric acid was distilled in a vacuum (22 mm.) at 116°. The crotonic acid was made by the method of Komnenos,[9] by heating malonic acid, acetic acid and paraldehyde together on a steam bath. It was separated from methyl glutaric acid, formed at the same time by removing the portion distilling over between 170–210°. This was puri-

[1] *Loc. cit.*
[2] *Ann.*, **171**, 315 (1874).
[3] *Bull. soc. chim.*, [4] **13**, 1103 (1913).
[4] *Ann.*, **167**, 224 (1873).
[5] *Ibid.*, **156**, 247 (1869).
[6] *Ibid.*, **319**, 357 (1904).
[7] *Ibid.*, **209**, 232 (1881).
[8] *Loc. cit.*
[9] *Ann.*, **218**, 145 (1883).

fied by repeated distillation and recrystallized from hot ligroin giving a product melting at 71–72°.

When the esters were available, the sodium salts of halogen substituted aliphatic acids were obtained by treatment with a strong solution of caustic soda as previously described.[1] By this method sodium α-bromoisobutyrate separated out at once since it is quite insoluble in alcohol. In all other cases concentration of the solutions in a vacuum and subsequent isolation of the sodium salts was found necessary.

In cases where the free halogen substituted aliphatic acids were available they were simply neutralized by a calculated amount of 0.1 N solution of caustic soda free from sodium carbonate. These solutions were then hydrolyzed as described below.

Hydrolysis of Sodium Salts.

The sodium salts of the above halogenated fatty acids were hydrolyzed in 0.1 N solutions using 15 cc. portions sealed in glass tubes as previously described.[1] In all cases, with the exception of sodium α-bromoisobutyrate, which was found to be very unstable, the temperature of hydrolysis was 70°. The values of K are based upon the silver nitrate necessary to precipitate the halide liberated at various time intervals by the usual titration formula for a monomolecular reaction.

$$K = 2.3/t_n \, [\log_{10}(T\infty - T_0) - \log_{10}(T\infty - T_n)].$$

Senter[2] has previously discussed the hydrolysis of sodium α-bromopropionate at 52.4° but has given no temperature coefficient. This work has been repeated to compare its stability with the stability of other salts at the same temperature. These experiments confirm his statement that the methyl group substituted in the α-position renders the compound less stable than the homologous sodium bromoacetate.

Sodium α-chloropropionate is found to be more stable than sodium α-bromopropionate, but it is less stable than sodium chloroacetate which was discussed in the previous paper.[3]

The hydrolysis of sodium β-chloropropionate, sodium β-bromopropionate, and sodium β-iodopropionate, which have not been studied before, produce hydracrylic acid under the conditions of these experiments. It was found that these salts are much more unstable than the isomeric α-halogen substituted compounds. Of the three, β-chloropropionic acid is the most stable, while little difference exists between the stability of β-bromopropionic acid and β-iodopropionic acid. This shows that the position of the halogen has a greater effect on the stability of the acid than does the identity of the halogen. In the latter two salts it will be noted

[1] Drushel and Simpson, *Loc. cit.*

[2] *Trans. Chem. Soc.*, **95**, 1827 (1909).

[3] THIS JOURNAL, **39**, 2453 (1917).

from Table I, D, E, that the reaction was about one-third complete before the solution reached the temperature of reaction. The great difference in the titrations with sodium hydroxide and silver nitrate is in accord with the recent work of Johannsen[1] on the formation of β-lactones.

TABLE I.—VELOCITIES OF HYDROLYSIS OF SODIUM α-CHLOROPROPIONATE, SODIUM α-BROMOPROPIONATE, SODIUM β-BROMOPROPIONATE, SODIUM β-IODOPROPIONATE, SODIUM β-CHLOROPROPIONATE AND SODIUM α,α-DIBROMOPROPIONATE IN 0.1 *N* SOLUTION AT 70°.

t (min.).	Cc. 0.1 *N* NaOH.	Cc. 0.1 *N* $AgNO_3$.	10^5K.
A. Sodium α-Chloropropionate.			
0	0.10	0.10	...
180	2.45	2.98	126.0
360	3.50	3.95	89.1
780	6.48	6.90	85.5
1620	9.93	10.43	82.5
2250	11.23	11.70	78.5
3480	12.53	13.05	74.3
4800	13.12	13.42	62.5
∞	13.88	14.10	...
B. Sodium α-Bromopropionate.			
0	1.22	1.30	..
15	3.60	3.77	1410
30	5.05	5.43	1270
60	7.60	7.85	1170
90	9.10	9.20	1040
120	9.65	10.03	945
180	11.03	11.33	835
240	11.50	11.65	682
∞	13.98	14.15	...
C. Sodium β-Chloropropionate.			
0	0.30	0.50	...
30	2.60	3.15	651
60	3.95	4.90	581
90	5.10	6.30	545
120	5.90	7.30	505
180	7.35	8.75	442
300	9.00	10.40	353
480	10.40	11.85	295
∞	15.30	15.50	...
D. Sodium β-Bromopropionate.			
0	4.15	4.60	..
5	6.15	6.60	4670
10	7.20	7.85	4060
20	8.55	9.45	3490
30	9.77	10.33	2980
40	10.40	10.95	2690
65	11.40	11.95	2240
120	12.57	12.88	1620
∞	14.10	14.30	..
E. Sodium β-Iodopropionate.			
0	4.13	4.55	..
5	6.12	6.55	4530
10	7.15	7.78	4040
20	8.87	9.42	3470
30	9.80	10.30	3010
40	10.35	10.97	2720
65	11.48	12.00	2240
120	12.65	12.93	1650
∞	14.10	14.30	..
F. Sodium α,α-Dibromopropionate.			
0	0.80	0.80	...
60	6.45	6.75	426
150	11.35	12.00	368
240	14.35	14.90	326
420	17.85	18.45	264
630	20.15	21.00	229
1080	23.00	23.58	196
1860	25.50	25.90	165
∞	27.15	27.18	...

The hydrolysis of sodium α,α-dibromopropionate, in which both halogen atoms are removed, is of the same nature as sodium dichloroacetate that has been discussed in a previous paper.[2] It shows that the introduction of a second halogen into the α-position renders the compound much more stable.

In the hydrolysis of the sodium salts of α,β-dichloropropionic acid and

[1] *Ber.*, **48**, 1262 (1915); *Chem. Zentr.*, II, 557 (1916).

[2] Drushel and Simpson, *Loc. cit.*

α,β-dibromopropionic acid under the conditions of experiment only the β-halogen was replaced producing α-halogen substituted hydracrylic acid. In both cases it was found that the presence of the halogen in the α-position, which was not removed, greatly increased the stability of the salt.

The hydrolysis of sodium α-chlorobutyrate has not been studied previously. It was found to be more unstable than sodium chloroacetate and sodium α-chloropropionate. This is in accord with the work of Senter[1] on sodium α-bromobutyrate. This shows that the acid becomes more unstable with the increase in size of the group substituted into chloroacetic acid. The work of Senter on the hydrolysis of sodium α-bromobutyrate has been repeated to compare its stability with sodium α-chlorobutyrate and sodium α-bromoisobutyrate at 70°. Sodium α-chlorobutyrate was found to be more stable than the corresponding bromine compound, as is shown in Table II, C, D.

TABLE II.—SODIUM α,β-DICHLOROPROPIONATE, SODIUM α,β-DIBROMOPROPIONATE, SODIUM α-CHLOROBUTYRATE, AND SODIUM α-BROMOBUTYRATE IN 0.1 N SOLUTION AT 70°.

t (min.).	Cc. 0.1 N NaOH.	Cc. 0.1 N $AgNO_3$.	10^5K.	t (min.).	Cc. 0.1 N NaOH.	Cc. 0.1 N $AgNO_3$.	10^5K.
A. Sodium α,β-Dichloropropionate.				B. Sodium α,β-Dibromopropionate.			
0	0.10	0.15	..	0	0.75	1.10	...
720	2.20	2.65	25.0	60	2.10	2.65	190
1440	4.20	4.75	24.9	180	5.75	6.35	250
2880	7.50	7.90	24.6	360	8.60	9.10	226
4320	9.80	10.15	24.5	600	10.90	11.25	203
5760	11.18	11.60	24.0	840	11.70	12.15	176
7200	12.15	12.75	24.1	1380	13.20	13.66	157
9360	13.20	13.73	23.6	2100	14.60	15.03	160
∞	14.90	15.38	..	∞	15.10	15.50	...
C. Sodium α-Chlorobutyrate.				D. Sodium α-Bromobutyrate.			
0	0.20	0.20	...	0	1.35	1.55	..
120	2.10	2.40	134	15	4.70	5.20	2240
240	3.80	4.03	124	30	6.75	7.25	1970
420	5.65	5.90	116	60	9.25	9.88	1720
660	7.60	7.75	108	90	10.55	11.05	1510
1260	10.30	10.50	94	120	11.45	11.83	1380
1980	12.00	12.30	86	165	12.30	12.75	1280
2820	12.75	13.05	72	225	12.60	13.15	1080
∞	14.70	15.00	...	∞	14.10	14.28	..

The hydrolysis of sodium α-bromoisobutyrate was found to proceed very rapidly at room temperature. For this reason it was found necessary to carry out the hydrolysis in flasks at 25° and 35° in a water thermostat. At definite time intervals 15 cc. portions of the solution were drawn off in a pipet, added to ice water and immediately titrated in flasks which were chilled by an ice-salt bath. It will be noted from the tables that the

[1] *Trans. Chem. Soc.*, **95**, 1827 (1909).

values for K are fairly constant at 25° but at 35° decrease rapidly as the reaction proceeds. The values calculated for the hydrolysis at 70° are derived from the results at 35° by means of the temperature coefficient and can only approximate the true figures. It will also be evident that these temperature coefficients decrease rapidly as the reaction progresses.

TABLE III.—VELOCITIES OF HYDROLYSIS OF SODIUM β-CHLOROBUTYRATE IN 0.1 N SOLUTION AT 70°.

t (min.).	Cc. of 0.1 N NaOH.	Cc. of 0.1 N $AgNO_3$.	10^5K.
0	0.60	1.80	..
10	2.70	5.00	3020
20	4.50	7.17	2790
30	5.20	8.30	2490
45	7.15	10.23	2440
60	8.30	11.08	2440
75	9.00	11.90	2180
120	9.90	12.87	1760
∞	10.25	14.40	..

TABLE IV.—VELOCITIES OF HYDROLYSIS OF SODIUM α-BROMOISOBUTYRATE IN 0.1 N SOLUTION AT 25°.

t (min.).	Cc. of 0.1 N NaOH.	Cc. of 0.1 N $AgNO_3$.	10^5K.	Temp. coef. 25–35°.
0	0.95	1.45	...	..
15	1.90	2.50	685	4.75
30	3.00	3.40	662	4.53
60	4.30	5.00	667	4.27
120	6.60	7.30	646	4.03
180	7.95	8.85	633	3.78
270	9.30	9.90	628	3.52
360	10.05	10.50	663	3.12
∞	12.03	12.30	...	..

TABLE V.—VELOCITIES OF HYDROLYSIS OF SODIUM α-BROMOISOBUTYRATE IN 0.1 N SOLUTION AT 35° AND 70°.

t (min.).	Cc. of 0.1 N NaOH.	Cc. 0.1 N $AgNO_3$.	10^5K at 35°.	K at 70° (calc.).
0	2.20	2.80	..	..
5	3.50	4.30	3380	8.37
10	4.60	5.30	3100	5.87
20	6.30	7.05	2860	4.62
40	8.30	9.00	2750	3.60
60	9.37	10.07	2350	2.45
90	10.50	11.00	2140	1.76
120	11.05	11.57	2020	1.09
∞	12.10	12.43	..	..

Although β-chlorobutyric acid has not been previously studied, β-bromobutyric acid has been hydrolyzed at 38° by Johannsen. At this temperature he found that this acid decomposed to produce β-butyrolactone which he isolated and studied. The hydrolysis of sodium β-chlorobutyrate at 70° clearly indicates the formation of this lactone, by the great

difference in titrations with sodium hydroxide and silver nitrate, but at this temperature this lactone has been partially hydrolyzed to form β-hydroxybutyric acid. The chlorobutyric acid is shown to be less stable than the isomeric α-chlorobutyric acid and the homologous β-chloropropionic acid.

This investigation in addition to showing the relative stability of several halogen substituted aliphatic acids, has furnished considerable evidence on the mechanism of the hydrolysis of their alkali salts.

The intermediate formation of a lactone in the hydrolysis of the β-halogen substituted aliphatic acids recently described by Johannsen[1] has been indicated in these results. We may also expect that an intermediate lactide has been formed similarly in the hydrolysis of α-substituted aliphatic acids under the conditions of these experiments.

New evidence has been found in support of the explanation advanced by Senter[2] to account for the decrease in the rate of reaction during the hydrolysis of sodium phenylchloroacetate. The best example of such a case found in this investigation is that of sodium α-bromoisobutyrate for which the following explanation is offered: In decinormal solutions the salts may be considered completely dissociated so that the hydrolysis takes place between water and the α-bromoisobutyric ion thus:

$$(CH_3)_2\,CBrCOONa \longrightarrow (CH_3)_2CBrCOO^- + Na^+$$

$$(CH_3)_2\,CBrCOO^- + HOH \longrightarrow (CH_3)_2COHCOO^- + H^+ + Br^-$$

As α-bromoisobutyric acid is not so highly dissociated as its sodium salt an equilibrium is formed between the α-bromoisobutyric and hydrogen ions and the undissociated acid:

$$(CH_3)_2CBrCOO^- + H^+ \rightleftharpoons (CH_3)_2CBrCOOH.$$

The undissociated α-bromoisobutyric acid may also be hydrolyzed but Senter[2] has shown that acids react in this manner much slower than the ions. De Barr[3] has shown that high temperatures are required to decompose the free acids, so we should expect that the latter reaction would be negligible at sufficiently low temperatures and then the value of K should be constant. Such a condition has been realized in the hydrolysis of sodium α-bromoisobutyrate at 25°, but at 35° the decreasing values of K indicate the activity of undissociated α-bromoisobutyric acid in the reaction. This experiment also shows that hydrobromic acid formed by the reaction does not act as a negative catalyst in this case, although Senter[4] has been able to measure its influence in the hydrolysis of α-bromopropionic acid, phenylchloroacetic acid, and phenylbromoacetic acid.

[1] *Loc. cit.*

[2] *Trans. Chem. Soc.*, **107**, 908 (1915).

[3] *Am. Chem. J.*, **22**, 336 (1899).

[4] *Trans. Chem. Soc.*, **99**, 1049 (1911); **107**, 908 (1915); **109**, 681 (1916).

Some very interesting speculations are found in applying this theory to the hydrolysis of salts of dihalogen substituted aliphatic acid in which both halogens are replaced. Examples of such salts are sodium α,α-dibromopropionate of this article and sodium dichloroacetate previously discussed.[1] The equations for the hydrolysis of the latter salt according to the above theory would be written thus:

$$CHCl_2COONa \longrightarrow CHCl_2COO^- + Na^+$$
$$CHCl_2COO^- + HOH \longrightarrow CHOCOO^- + 2H^+ + 2Cl^-$$
$$CHOCOO^- + H^+ \rightleftharpoons CHOCOOH$$
$$CHCl_2COO^- + H^+ \rightleftharpoons CHCl_2COOH$$
$$CHCl_2COOH + HOH \longrightarrow CHOCOO^- + 2H^+ + 2Cl^-$$

From this it is evident that the concentration of undissociated dichloroacetic acid is relatively great compared with the concentration of chloroacetic acid during the hydrolysis of sodium chloroacetate due to the greater number of hydrogen ions. This explains the unusually large decrease in the rate of reaction as hydrolysis proceeds.

If this hypothesis is correct it explains the stability of α,β-dichloropropionic acid, chloroacetic acid, and iodoacetic acid previously described, toward water at 70°, as their rates of reaction are constant at this temperature. From these experiments it is evident that there is no secondary action due to the hydrolysis of undissociated halogen substituted acid at 70°. This point must be proved by later investigation.

Summary.

From the results of this work the relative stability of the several halogen substituted and propionic and butyric acids is expressed by the following table:

TABLE VI.—RELATIVE STABILITIES.

Propionic Acid Series.	
β-Bromopropionic acid	1.0
β-Iodopropionic acid	1.03
α-Bromopropionic acid	3.31
β-Chloropropionic acid	7.17
α,α-Dibromopropionic acid	10.96
α,β-Dibromopropionic acid	18.68
α-Chloropropionic acid	37.06
α,β-Dichloropropionic acid	186.8
Butyric Acid Series.	
α-Bromoisobutyric acid	1.0
β-Chlorobutyric acid	277.0
α-Bromobutyric acid	374.0
α-Chlorobutyric acid	6171.0

1. Chlorine substituted aliphatic acids are more stable than the analogous bromine or iodine compounds.

[1] Drushel and Simpson, *Loc. cit.*

2. The evidence indicates that some iodine substituted aliphatic acids are more stable than the analogous bromine compounds.

3. α-Halogen substituted acids are more stable than isomeric β-halogen substituted acids.

4. The effect of position on the stability of a halogen substituted acid is greater than the identity of the halogen.

5. The replacement of a hydrogen atom on the carbon atom carrying the halogen by an aliphatic radicle renders the acids less stable.

6. The replacement of a second hydrogen atom on the carbon atom carrying the halogen by an aliphatic radicle greatly decreases the stability of the acid.

7. The larger the aliphatic group substituted the more unstable the acid becomes.

8. The presence of a second halogen in the α-position of the acid (irrespective of the replacement of that second halogen) renders the removal of the first halogen in either the α- or β-positions more difficult.

The writer is indebted to W. A. Drushel for his coöperation in this work.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.

[SEVENTH COMMUNICATION.[1]]

BY LEROY MCMASTER AND LETA WRIGHT.

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This work is a continuation of the preparation and investigation of the properties of neutral ammonium salts of organic acids and their substituted derivatives. The salts described in this paper were prepared by the same general method as was used in the previous investigations, *i. e.*, by passing dry ammonia into solutions of the acids in anhydrous organic solvents. We have thus prepared and studied the ammonium salts of 1,2,3-methylhydroxybenzoic, 1,3,4-methylhydroxybenzoic, 1,4,3-methylhydroxybenzoic, 1,2,4-dihydroxybenzoic, 1,2,5-dihydroxybenzoic, 1,2,4-dinitrobenzoic, *o*-nitrocinnamic, *m*-nitrocinnamic, *p*-nitrocinnamic, α-naphthoic, β-naphthoic, *m*-nitrobenzenesulfonic, *m*-aminobenzenesulfonic (metanilic) 1,2,4-nitrotoluenesulfonic, 1,4-naphthylaminesulfonic (naphthionic), 1,4-naphtholsulfonic, 1,5-naphtholsulfonic, benzilic, oxanilic and phenyl-

[1] For previous papers on this subject see *Am. Chem. J.*, **49**, 84–7 (1913); *Chem. News*, **108**, 136–7 (1913); *Am. Chem. J.*, **49**, 294–301 (1913); *Chem. News*, **108**, 182–3, 193–4 (1913); THIS JOURNAL, **36**, 742–7 (1914); *Chem. News*, **110**, 212–4 (1914); THIS JOURNAL, **36**, 1916–25 (1914); *Chem. News*, **110**, 224–8 (1914); THIS JOURNAL, **37**, 2181–8 (1915); *Chem. News*, **112**, 187–9 (1915); THIS JOURNAL, **38**, 1785–1803 (1916); *Chem. News*, **114**, 217–221, 224–227, 238–239 (1916).