[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE]

Identification of Carboxylic Acids as Carboxylates of Benzylamine and Alpha-Phenylethylamine

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Although simple addition compounds are not regarded generally as being suitable derivatives for the identification of organic compounds, those which benzylamine and α-phenylethylamine form with solid carboxylic acids are exceptions. These amines, with dissociation constants of the order of ammonia,[1] unite with both aliphatic and aromatic carboxylic acids to form stable compounds, but, unfortunately, the derivatives of some of the liquid aliphatic acids are difficult to isolate because of their low melting points, their deliquescent nature, and their tendency to supercool when in the liquid state. It is interesting to note, however, that these carboxylates, melting near room temperature, are of sufficient stability to withstand vacuum distillation. Among the solid derivatives prepared, the stability is such that various solvents such as ethyl acetate or absolute alcohol may be used for purification, although the former is to be preferred because of the lower solubility of the carboxylates in it. The compounds thus obtained are white in color, unless a group such as the nitro or amino is present, and they possesss two easily found constants, the melting point and the neutralization equivalent. The latter was determined by the method[2] recommended for the salts of aliphatic amines. All the compounds listed in Tables I and II are new, and of a 1:1 molecular ratio.

TABLE I

BENZYLAMMONIUM CARBOXYLATES

Acid	Formula	Melting point., °C. Obsd.	Melting point., °C. Corr.	Neut. equiv. Calcd.	Neut. equiv. Found	Nitrogen, % Calcd.	Nitrogen, % Found
Formic[a]	$C_8H_{11}O_2N$	94–96	95–97	153.1	155.9	9.15	9.04
Acetic[a]	$C_9H_{13}O_2N$	95.4–96.2	96.3–97.1	167.1	167.6	8.38	8.47
Propionic	$C_{10}H_{15}O_2N$	46.5–47.3	46.7–47.5	181.1	186.5	7.72	7.59
n-Butyric	$C_{11}H_{17}O_2N$	[b]		195.1	194.0	7.18	6.98
n-Caproic	$C_{12}H_{19}O_2N$	51.6–52.6	51.7–52.7	223.2	224.8	6.28	6.19
Chloroacetic	$C_9H_{12}O_2NCl$	118.4–119.4	119.9–120.9	201.6	200.1	6.95	6.91
Trichloroacetic	$C_9H_{10}O_2NCl_3$	118.8–119.8	120.3–121.3	270.5	275.1	5.18	5.33
Phenylacetic	$C_{15}H_{17}O_2N$	120.4–121.0	122.0–122.6	243.1	241.6	5.76	5.90
o-Toluic	$C_{15}H_{17}O_2N$	143.2–144.2	145.4–146.4	243.1	242.0	5.76	5.84
Cinnamic	$C_{16}H_{17}O_2N$	134.0–134.6	135.9–136.3	255.1	254.4	5.49	5.42
Benzoic	$C_{14}H_{15}O_2N$	125.4–126.6	127.2–128.4	229.1	229.8	6.11	5.96
o-Aminobenzoic	$C_{14}H_{16}O_2N_2$	110.8–112.0	112.0–113.2	244.1	241.0	11.48	11.62
m-Aminobenzoic	$C_{14}H_{16}O_2N_2$	134.0–134.6	135.9–136.5	244.1	247.8	11.48	11.57
p-Aminobenzoic	$C_{14}H_{16}O_2N_2$	194.6–195.6	197.6–198.6	244.1	247.8	11.48	11.33
m-Bromobenzoic	$C_{14}H_{14}O_2NBr$	157.6–158.2	160.6–161.2	308.0	304.9	4.55	4.58
o-Chlorobenzoic	$C_{14}H_{14}O_2NCl$	148.4–149.4	150.5–151.5	263.6	262.9	5.31	5.19
m-Chlorobenzoic	$C_{14}H_{14}O_2NCl$	146.8–147.4	149.2–149.8	263.6	265.4	5.31	5.28
p-Chlorobenzoic	$C_{14}H_{14}O_2NCl$	157.4–158.4	160.3–161.3	263.6	262.3	5.31	5.48
o-Hydroxybenzoic	$C_{14}H_{15}O_3N$	93.4–94.6	94.3–95.5	245.1	245.8	5.71	5.54
m-Hydroxybenzoic	$C_{14}H_{15}O_3N$	184.6–186.0	188.2–189.6	245.1	242.7	5.71	5.87
p-Hydroxybenzoic[c]	$C_{14}H_{15}O_3N$	211.4–212.0	216.6–217.2	245.1	235.4	5.71	5.72
o-Methoxybenzoic	$C_{15}H_{17}O_3N$	119.8–120.6	121.5–122.3	259.1	260.0	5.41	5.62
m-Methoxybenzoic	$C_{15}H_{17}O_3N$	111.8–112.8	113.1–114.1	259.1	255.6	5.41	5.46
p-Methoxybenzoic	$C_{15}H_{17}O_3N$	142.6–143.4	144.8–145.6	259.1	260.4	5.41	5.47
o-Nitrobenzoic	$C_{14}H_{14}O_4N_2$	141.4–143.2	143.9–145.7	274.1	277.1	10.22	10.34
m-Nitrobenzoic	$C_{14}H_{14}O_4N_2$	171.4–172.0	174.9–175.5	274.1	269.6	10.22	10.16
p-Nitrobenzoic	$C_{14}H_{14}O_4N_2$	193.0–194.6	197.3–198.9	274.1	272.1	10.22	10.24

[a] Since this compound was deliquescent, final drying in a desiccator was necessary. [b] B. p. 109–110° (15 mm.). [c] Compound showed a tendency to decompose below the m. p.

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[1] *K*, for benzylamine, "International Critical Tables," Vol. VI, p. 281, is 2.0×10^{-5}; the value for α-phenylethylamine is not available, but, by analogy with the effect of the substitution of a methyl group in the alpha carbon in other cases, it would be expected to be similar to that of benzylamine.

[2] Buehler, Currier and Lawrence, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 277 (1933).

TABLE II

ALPHA-PHENYLETHYLAMMONIUM CARBOXYLATES

Acid	Formula	Melting point, °C. Obsd.	Melting point, °C. Corr.	Neut. equiv. Calcd.	Neut. equiv. Found	Nitrogen, % Calcd.	Nitrogen, % Found
Formic	$C_9H_{13}O_2N$	97.0–98.0	97.8–98.8	167.1	166.8	8.38	8.52
Acetic	$C_{10}H_{15}O_2N$	91.2–91.6	92.1–92.5	181.1	181.8	7.73	7.75
Propionic	$C_{11}H_{17}O_2N$	[a]		195.1	191.1	7.18	7.23
n-Butyric	$C_{12}H_{19}O_2N$	[b]		209.2	209.1	6.70	6.65
Chloroacetic	$C_{10}H_{14}O_2NCl$	93.6–94.4	94.7–95.5	215.6	209.2	6.50	6.62
Phenylacetic	$C_{16}H_{19}O_2N$	114.0–114.8	115.6–116.4	257.2	259.4	5.45	5.47
o-Toluic	$C_{16}H_{19}O_2N$	111.8–112.2	113.3–113.7	257.2	258.0	5.45	5.37
Cinnamic	$C_{17}H_{19}O_2N$	141.2–141.8	144.5–145.1	269.2	271.4	5.20	5.21
Benzoic	$C_{15}H_{17}O_2N$	138.4–139.0	140.6–141.2	243.1	244.8	5.76	5.72
o-Aminobenzoic	$C_{15}H_{18}O_2N_2$	109.4–110.0	111.0–111.6	258.2	258.4	10.85	10.87
m-Aminobenzoic	$C_{15}H_{18}O_2N_2$	164.6–165.4	168.6–169.4	258.2	258.7	10.85	10.70
p-Aminobenzoic	$C_{15}H_{18}O_2N_2$	180.4–181.2	185.6–186.4	258.2	259.4	10.85	10.82
m-Bromobenzoic	$C_{15}H_{16}O_2NBr$	146.2–147.0	148.9–149.7	322.1	321.7	4.35	4.42
o-Chlorobenzoic	$C_{15}H_{16}O_2NCl$	128.4–129.4	130.9–131.9	277.6	280.4	5.05	4.96
m-Chlorobenzoic	$C_{15}H_{16}O_2NCl$	142.0–142.6	144.7–145.3	277.6	279.7	5.05	5.05
p-Chlorobenzoic	$C_{15}H_{16}O_2NCl$	150.0–151.0	152.2–153.2	277.6	277.5	5.05	5.01
o-Hydroxybenzoic	$C_{15}H_{17}O_3N$	101.0–101.8	102.1–102.9	259.1	260.8	5.41	5.41
m-Hydroxybenzoic	$C_{15}H_{17}O_3N$	135.0–136.2	137.2–138.4	259.1	256.7	5.41	5.51
p-Hydroxybenzoic[c]	$C_{15}H_{17}O_3N$	194.0–194.6	199.3–199.9	259.1	259.4	5.41	5.45
o-Methoxybenzoic	$C_{16}H_{19}O_3N$	155.6–156.0	158.7–159.1	273.2	273.6	5.13	5.16
m-Methoxybenzoic	$C_{16}H_{19}O_3N$.	128.6–129.0	131.4–131.8	273.2	273.9	5.13	5.14
p-Methoxybenzoic	$C_{16}H_{19}O_3N$	130.8–131.4	132.8–133.4	273.2	273.5	5.13	5.11
o-Nitrobenzoic	$C_{15}H_{16}O_4N_2$	126.8–127.4	129.5–130.1	288.1	288.5	9.72	9.67
m-Nitrobenzoic	$C_{15}H_{16}O_4N_2$	166.8–167.2	170.7–171.1	288.1	286.8	9.72	9.79
p-Nitrobenzoic	$C_{15}H_{16}O_4N_2$	191.0–192.0	195.8–196.8	288.1	287.0	9.72	9.81

[a] B. p. 120–121° (42 mm.). [b] B. p. 125° (37 mm.). [c] Compound showed a tendency to decompose below the m. p.

Experimental

The benzylamine was the best Eastman grade while the α-phenylethylamine was prepared by the reduction of acetophenone oxime.[3] The fraction of the latter used boiled at 184–187°. Melting points were determined by the method of Mulliken[4] in which a thermometer calibrated by the Bureau of Standards was employed.

To form the carboxylates of the solid acids, 0.01 mole of the acid was dissolved in the smallest possible amount of boiling ethyl acetate, and then a slight excess of the hot solvent was added. Into this hot solution 0.01 mole of the amine was stirred in, after which the resulting solution was poured quickly on a watch glass for crystallization. After the bulk of the crystals had formed, the mother liquor was poured off and the crystals were dried first for a short time in the air and finally between filter paper. For the liquid acids, with the exception of those cited below, equimolecular amounts were mixed, in the absence of any solvent, on a watch glass in which crystallization was induced by gentle tapping at room temperature, or, if necessary, at the lower temperature of an ice-salt mixture. The separation and drying of the crystals were accomplished as before. Final purification in either case was realized by crystallization from ethyl acetate.

Some of the carboxylates in the neighborhood of *n*-butyric acid (see Tables I and II) possess such low melting points that they could not be obtained satisfactorily by crystallization methods. These were prepared by distilling equimolecular amounts of the amine and acid under reduced pressure.

Summary

A series of carboxylates of benzylamine and α-phenylethylamine has been prepared. Those of the solid carboxylic acids are particularly suitable for identification purposes.

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(3) Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York City, 1924, p. 360.

(4) Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley & Sons, Inc., New York City, 1904, p. 218.