[Contribution from the Research Laboratory of Armour and Company]

2-Alkylbenzimidazoles as Derivatives for the Identification of Aliphatic Acids

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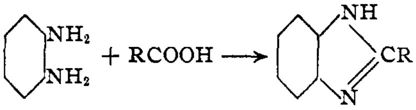
In the course of work involving the identification of normal fatty acids the need of a complete series of satisfactory derivatives became apparent. Of the various derivatives described in the literature for the characterization of organic acids the 2-alkylbenzimidazoles of Seka and Müller[1] appeared most promising.

These 2-alkylbenzimidazoles were prepared by heating a mixture of the acid and *o*-phenylenediamine. The resulting compounds were comparatively high melting and the melting point range of the series was continuous and broad.



The series of 2-*n*-alkylbenzimidazoles through the *n*-heptadecyl derivative has now been completed. The procedure of Seka and Müller has been improved in that the time required for the preparation of a derivative has been greatly reduced and the compounds obtained by the present method have been found to possess higher melting points than those reported by Seka and Müller.

Experimental Part

Procedure.—A mixture of 1 to 3 g. of acid and a molecular equivalent of *o*-phenylenediamine was heated at the boiling temperature for thirty minutes. The mixture was then dissolved in hot alcohol and the unreacted acid neutralized by the addition of potassium hydroxide solution until just alkaline to phenolphthalein. In the case of capric and higher acids the 2-alkylbenzimidazole crystallized when this alcohol solution was cooled. In the case of pelargonic and lower acids ether was added to the alcohol solution and this ether solution then washed with successive portions of water. The 2-alkylbenzimidazole was obtained by evaporation of the ether. The products were purified by recrystallization from alcohol, dilute alcohol or water with the addition of decolorizing carbon.

Table I

Constants for 2-*n*-Alkylbenzimidazoles

n-Alkyl	M. p. (corr.),[i] °C.	Mixed m. p. with[j] next higher homolog (corr.), °C.	Analyses,[k] % N Calcd.	Analyses,[k] % N Found
Hydrogen[a,n]	172.0–173.0	130–132	23.73	23.81
Methyl-[b,m,n]	177.0–177.5	157–158	21.21	21.42
Ethyl-[c,m,n]	174.5	155–156	19.18	19.03[o]
n-Propyl-[d,l,m]	157.0–157.5	141–143	17.50	17.76
n-Butyl-[e,m]	155.0–155.5	152–153		
n-Pentyl-[c,l,m]	163.0–163.5	138–143	14.89	14.88[p]
n-Hexyl-[c,m]	137.5–138.0	132–135	13.86	14.04
n-Heptyl-[c,l]	144.5–145.0	136–137	12.96	12.97
n-Octyl-[c]	139.5–140.5	128–131	12.17	12.11[q]
n-Nonyl-[c,l]	127.0–127.5	117–120	11.47	11.80
n-Decyl-[c]	114.0–114.5	106–107	10.85	11.06
n-Undecyl[f,l]	107.5	107–108	10.29	10.27[r]
n-Dodecyl-[c]	109.0–109.5	105–106	9.79	10.05
n-Tridecyl-[c]	105.0–105.5	100–102	9.33	9.47
n-Tetradecyl-[g]	98.5– 99.5	97– 98	8.91	9.46[s]
n-Pentadecyl-[c,l]	96.5– 97.0	94– 96	8.53	8.62
n-Hexadecyl-[c]	93.5– 94.5	93– 94	8.18	8.52
n-Heptadecyl-[h,l]	93.5– 94.5		7.86	8.08[t]

[a] The acid was Baker c. p. 90% grade. [b] The acid was Baker c. p. glacial acetic acid. [c] The acid was Eastman best grade. [d] The acid was obtained by fractionation of Merck technical grade (98–100%). [e] The acid was synthesized from *n*-butyl bromide by means of the Grignard reagent and carbon dioxide; b. p. 185.0–185.6°. [f] The acid was obtained from coconut oil by fractionation of esters and subsequent recrystallization of the acid from acetone; m. p. 44.0–45.0°. [g] The acid was synthesized from Eastman myristic acid by the usual method: acid ⟶ ester ⟶ alcohol ⟶ iodide ⟶ nitrile ⟶ acid. Recrystallized from acetone; m. p. 52.5–53.5°. [h] The acid was obtained by fractionation of hydrogenated ethyl oleate followed by recrystallization of the acid from acetone; m. p. 70.0–71.0°. [i] M. p. thermometer standardized against known substances. [j] M. p. of a 50% mixture with next higher homolog. [k] Analyses by Dr. Ing. A. Schoeller, Berlin–Schmargendorf, Tolzerstrasse 19, except the analysis of *n*-tetradecylbenzimidazole which was by Dr. Kurt Eder, University of Illinois, Urbana, Illinois. [l] Previously prepared by Seka and Müller.[1] [m] See Weidenhagen, *Ber.*, **69**, 2263 (1936). [n] See Phillips, *J. Chem. Soc.*, 2393 (1928). [o] Calcd.: C, 73.93; H, 6.90. Found: C, 74.06; H, 6.90. [p] Calcd.: C, 76.54; H, 8.57. Found: C, 76.71; H, 8.71. [q] Calcd.: C, 78.19; H, 9.63. Found: C, 78.43; H, 9.68. [r] Calcd.: C, 79.34; H, 10.37. Found: C, 79.54; H, 10.41. [s] Calcd.: C, 80.18; H, 10.90. Found: C, 80.13; H, 10.52. [t] Calcd.: C, 80.82; H, 11.31. Found: C, 80.67; H, 11.19.

Discussion

2-Alkylbenzimidazoles were easily and quickly prepared from small amounts of material. These derivatives crystallized well and possessed sharp melting points. With the lower members of the series the melting point interval between adjacent members was large and there was considerable depression in the melting point of mixtures of adjacent members. The 2-alkylbenzimidazoles of acids above lauric did not serve as a very good means of distinguishing these acids from one

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[1] Seka and Müller, *Monatsh.*, **57**, 95–105 (1931).

another as the melting points of these derivatives lay closely together. In certain cases the compounds contained a colored impurity which was removed only after numerous crystallizations.

These 2-alkylbenzimidazoles form salts with acids (picric, sulfuric, etc.) which might be used in distinguishing the higher members of the series. This possibility has not yet been investigated.

Summary

1. A procedure for the preparation of 2-alkylbenzimidazoles from aliphatic acids and *o*-phenylenediamine has been described.

2. A series of 2-alkylbenzimidazoles has been prepared using normal aliphatic acids containing from one to eighteen carbon atoms.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Liquidus Curve and Surface of the Systems Lithium and Calcium Nitrates and Calcium, Lithium and Potassium Nitrates

BY ALEXANDER LEHRMAN, EDWARD ADLER, JACOB FREIDUS AND MAX NEIMAND

This paper reports an investigation of the liquidus curve and surface of the systems lithium and calcium nitrates and calcium, lithium and potassium nitrates. The work was undertaken in order to be able ultimately to define the liquidus surfaces of the quaternary system composed of the nitrates of lithium, sodium, potassium and calcium. It is hoped that the quaternary system in mind will yield a salt-bath melting below 100°. Such a salt-bath would have distinct advantages.

Of the six binary and four ternary systems that should be known before the quaternary system is investigated, five binary and two ternary are described in the literature.[1]

The completion of the present work leaves uninvestigated only the ternary system lithium, sodium and calcium nitrates (although it seems necessary in the light of the work of Rostkovsky,[1f] of Laybourn and Magdin[1g] and the data presented here, that the ternary system composed of the nitrates of sodium, potassium and calcium as presented by Menzies and Dutt[1b] should be checked).

Experimental

The salts used were prepared from C. P. products by recrystallization followed by drying except the calcium nitrate which was the C. P. salt dissolved, treated with pure lime, filtered, neutralized with nitric acid, evaporated and dried.

Temperature Measurements.—Temperatures were measured with a copper-constantan thermocouple of No. 28 wire in conjunction with a Leeds and Northrup potentiometer indicator, the cold junction being cracked ice. The couple was protected from the molten nitrates by a narrow guard tube made by drawing out Pyrex tubing and sealing at one end. It was standardized by determining the e. m. fs. at the boiling point of water and melting points of U. S. Bureau of Standards tin (231.9°), C. P. cadmium (320.9°), and purified potassium dichromate (397.5°), and plotting the deviations from the standard table of Adams.[2] While the melting point of potassium dichromate is about 10° higher than the upper end of the standard table, it was considered justifiable to extrapolate through this short range.

Method.—Mixtures of the two salts (approximately 20 g.) were made in the 2.5 × 20-cm. Pyrex tubes used in the determinations. The couple in its guard tube was inserted into the salt mixture and held in place by a two-holed stopper. A stirrer made of Pyrex rod passed through a piece of Pyrex tubing in the second hole of the stopper. It was necessary to use Pyrex glassware throughout, as molten lithium nitrate attacks soft glass.

The tube holding the salts was suspended in a small resistance furnace and heated while stirring until the salts were completely molten, care being taken to avoid excessive temperatures. It was then transferred to a double-walled test-tube and held suspended there by an asbestos ring, and constantly stirred.

As the crystallization temperature was approached, crystals formed on the test-tube wall at the surface of the molten salt and were pushed into the liquid by the stirrer. The initial crystallization temperature was seen easily, as clouds of fine crystals suddenly appeared, while above this temperature the crystals when pushed into the melt by the stirrer rapidly dissolved. No supercooling was observed in any of the stirred melts, except in the calcium nitrate region of the ternary system, where it was necessary in some cases to inoculate with very fine crystals in order to prevent the formation of supercooled glasses which when formed did not crystallize on long standing. Crystallization temperature determinations were repeated until they agreed to within 1.0°. The reported values represent at least three determinations.

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[1] (a) Carveth, *J. Phys. Chem.*, **2**, 209 (1898); (b) Menzies and Dutt, THIS JOURNAL, **33**, 1366 (1911); (c) Amadori, *Atti inst. Veneto*, **72**, 451 (1912); (d) Harkins and Clark, THIS JOURNAL, **37**, 1816 (1915); (e) Briscoe and Magdin, *J. Chem. Soc.*, **123**, 1608, 2914 (1923); (f) Rostkovsky, *J. Russ. Phys.-Chem. Soc.*, **42**, 2055 (1930); (g) Laybourn and Magdin, *J. Chem. Soc.*, 2582 (1932), 236 (1933); (h) Laybourn, Magdin and Freeman, *ibid.*, 139 (1934).

[2] "Pyrometric Practice," Bureau of Standards Technological Paper No. 170, p. 309.