[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE REGULARITIES IN THE MELTING POINTS OF SOME CRYSTALLINE DERIVATIVES OF VARIOUS ALIPHATIC ALCOHOLS[1]

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Introduction

The fact that certain regularities exist in the melting points of various homologous series of aliphatic organic compounds is well known. As early as 1877 Baeyer[3] pointed out a definite alternation in the melting points of the saturated dibasic acids. Tsakalotos[4] and Forcrand[5] investigated the hydrocarbons of the methane series, while Biach[6] and Timmermans[7] made rather exhaustive investigations of many different series, the latter concluding that the alternation in melting points between the odd and even members of homologous series is a general phenomenon and attempting an explanation on the basis of the symmetry and spatial structure of the molecule. Tammann,[8] Cuy,[9] Pauly[10] and Garner and his co-workers[11] have studied the same general phenomenon of the fatty acids somewhat at length. This brief summation is by no means exhaustive, but it illustrates the type of work done. Throughout very little is said of the melting points of the alcohols themselves. Such alternation as may be seen from an examination of the melting points is much smaller than that of the hydrocarbons and fatty acids for example, and it was thought consequently that the alternate high and low melting points might be much more pronounced in a series of derivatives of the alcohols from one to ten carbon atoms. Such regularities have been found in a series of ketones, homologs of acetophenone,[12] in which the alkyl varies from C_{10} to C_{17}. Accordingly, the 3,5-dinitrobenzoates of the normal

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[1] Presented at the Columbus Meeting of the American Chemical Society, May, 1929.

[2] From a section of the Ph. D. dissertation of G. B. Malone, 1929.

[3] Baeyer, *Ber.*, **10**, 1286 (1877).

[4] Tsakalotos, *Compt. rend.*, **143**, 1235 (1907).

[5] Forcrand, *ibid.*, **172**, 31 (1921).

[6] Biach, *Z. physik. Chem.*, **50**, 43 (1905).

[7] Timmermans, (a) *Bull. soc. chim. Belg.*, **25**, 300 (1912); (b) *ibid.*, **27**, 334 (1914); (c) *ibid.*, **28**, 392 (1919); (d) *ibid.*, **30**, 62 (1921); (e) *ibid.*, **30**, 89 (1921).

[8] Tammann, *Z. anorg. allgem. Chem.*, **109**, 221 (1920).

[9] Cuy, *ibid.*, **115**, 273 (1921).

[10] Pauly, *ibid.*, **119**, 271 (1922).

[11] (a) Garner and Randall, *J. Chem. Soc.*, **125**, 881 (1924); (b) Garner and Ryder, *ibid.*, **127**, 720 (1925); (c) Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926); (d) Garner and Rushbrooke, *ibid.*, 1351 (1927).

[12] Majima, Nagaoka and Yamada, *Ber.*, **55**, 215 (1922).

alcohols from methyl to decyl were prepared because there have been more of these particular derivatives reported for these alcohols than any of the standard ones. Later this series was supplemented with an *iso* (homologs of *iso*butyl, *iso*-amyl, etc.) and a secondary (hydroxyl on carbon atom number two) series.

Discussion of Results

The accompanying figure shows the melting points of the three above-mentioned series of esters plotted against number of carbon atoms. The *iso* series extends to octyl and the secondary series to nonyl. In the normal series the alternating effect may be seen all the way through (with the esters of an even number of carbon atoms in the aliphatic portion high and those of odd carbon atoms low). With the lower members the effect is not so pronounced, in view of the low percentage of the molecular weight due to the alkyl part of the ester. The *iso* series shows the same type of curve except for a slightly greater tendency toward convergence and that the general swing of the curve has not reached a minimum

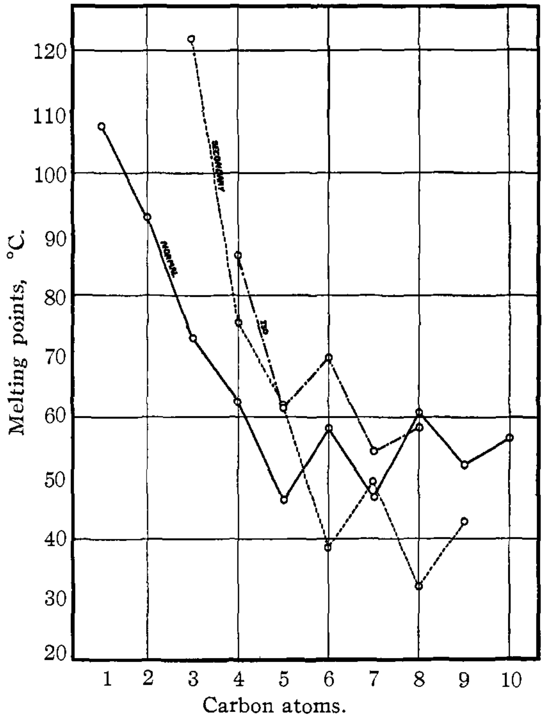
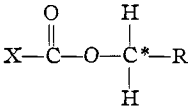


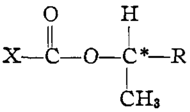
Fig. 1.—Melting points of alkyl esters of 3,5-dinitrobenzoic acid.

and started back up again, which would probably be the case could the curve be extended.

The secondary series offers an interesting variation. Here the esters of odd-numbered carbon atoms melt high and those of even carbon atoms low, just the opposite of the normal and *iso* series. An examination of the structural formulas, representing the aromatic residue by X, would seem to indicate that only the longest carbon chain, namely, that included in R, attached to the "key" carbon atom (designated by a star) affects the melting point. The fact that the *iso*propyl ester has an extremely high melting point is probably due to the presence of two identical units, the methyl group, on the key carbon atom, resulting in a highly symmetrical arrangement.



$X-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C^*}}-R$



$X-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C^*}}-R$

Experimental

3,5-Dinitrobenzoic acid, m. p. 203–205°, was converted into the acid chloride and this treated with about 10% excess of the alcohol, according to the directions given by Mulliken[13] with the following slight variations. In the case of the secondary alcohols the temperature was raised to 85–90° and the time of treatment increased to thirty minutes. The ester was extracted with a mixture of five parts of petroleum ether and

TABLE I

MELTING POINTS OF ALKYL ESTERS OF 3,5-DINITROBENZOIC ACID

Alcohol	M. p. (corr.), °C.	Melting points from literature
Methyl	107.8	107.5;[13] 109;[15] 110–110.5;[14] 112[16]
Ethyl	92.7	90;[17] 91;[18,19] 92–93;[13] 93–94;[14] 94[16,20]
n-Propyl	73.0	73–73.5;[13] 74–75[14]
n-Butyl	62.5	61–63[14]; 64;[13] 61[19]
n-Amyl	46.4	....
n-Hexyl	58.4	60–61[14]
n-Heptyl	46.9	47–48.5[14]
n-Octyl	60.8	61–62[14]
n-Nonyl	52.2	....
n-Decyl	...	56–57[14]
*Iso*butyl	86.5	83–83.5;[12] 87–88[14]
Iso-amyl	...	61–62[14]
*Iso*hexyl	69.8	......
*Iso*heptyl	54.5	......
Iso-octyl	58.3	......
Sec.-propyl	122.1	121–122[14]
Sec.-butyl	75.6	......
Sec.-amyl	62.1	......
Sec.-hexyl	38.6	......
Sec.-heptyl	49.4	......
Sec.-octyl	32.2	......
Sec.-nonyl	42.8	......

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[13] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons Inc., New York, 1914, Vol. I, pp. 166 ff.

[14] Reichstein, *Helv. Chim. Acta.* **9**, 802 (1926).

[15] Curtius, *J. prak. Chem.* [2] **76**, 248 (1907).

[16] Herre, *Ber.* **28**, 595–596 (1895).

[17] Staedel, *Ann.*, **217**, 196 (1883).

[18] Beilstein and Kurbatow, *ibid.*, **202**, 222 (1880).

[19] Brill, THIS JOURNAL, **43**, 1323 (1921).

[20] Hübner, *Ann.*, **222**, 79 (1884).

one part of ethyl ether, in which free acid and acid chloride are only very slightly soluble. The solvent was allowed to evaporate and the residue recrystallized to a constant melting point from 95% ethyl alcohol. Final melting points were taken with Anschütz thermometers graduated in tenths of a degree, for which certificates of the Reichsanstalt were available. These melting points were determined in the ordinary way with finely drawn out tubes of about one mm. diameter. A large glass tube equipped with a rotary stirrer of the paddle wheel type, driven at high speed by a small motor, was employed as a bath. This in turn was encased in a still larger tube whose corresponding dimensions were 1.0–1.5 cm. larger, the intervening air-bath serving to insure more even heating, this being carried out with a micro flame. To the mean of the final melting point range, in no case over 0.4° and in most cases 0.2° or less, were added the proper stem and tabular corrections, the figure to the nearest 0.1° being taken as the true value of the melting point. For brevity, only final corrected melting points are given. Included with these in the accompanying table are melting points obtained from the literature of such of these esters as have been previously reported.

The sources of the various alcohols were as follows. The methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, secondary butyl and *iso*butyl alcohols were cut sharply from good commercial grades on high precision stills, boiling point ranges being 0.2–0.3° and agreeing with accepted values. Normal and secondary octyl alcohols were supplied by the Eastman Kodak Co. and redistilled. The remaining alcohols were synthesized by the Grignard reaction; boiling points of the higher alcohols are:[21] *n*-amyl 137.8_{760}; *n*-hexyl 156.1_{758}; *n*-heptyl 176.0_{755}; *n*-octyl 195.3_{765}; *n*-nonyl 213.5_{758}; *sec.*-amyl 119.3_{760}; *sec.*-hexyl 139.7_{759}; *sec.*-heptyl 158.5_{754}; *sec.*-octyl 180.3_{765}; *sec.*-nonyl 198.2_{760}; *iso*hexyl 151.7_{758}; *iso*heptyl 169.5_{735}; *iso*-octyl 188.0_{767}.

Summary

The 3,5-dinitrobenzoates of twenty saturated aliphatic alcohols have been prepared.

Certain regularities have been observed in their melting points.

BALTIMORE, MARYLAND

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[21] The normal and secondary hexyl, heptyl and nonyl alcohols were synthesized in 200–300 g. quantities by L. M. Ellis, Jr., and R. F. Deese, Jr., and carefully purified for an accurate determination of physical constants to be published by them later. Boiling points given for these alcohols were determined by Ellis.