in ultrachromatograms and in checking the purity of these compounds.

4. An inexpensive and rapid method for viewing fluorescent materials in solution and chromatograms has been given.

ADRIAN, MICHIGAN RECEIVED NOVEMBER 14, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

# Anhydrides of the Normal Aliphatic Saturated Monobasic Acids

BY JAMES M. WALLACE, JR., AND J. E. COPENHAVER

The alternation of the melting points of the acids of the acetic acid series is well known. It seemed of interest to make a comparison of the melting point pattern of these acids with that of the corresponding anhydrides. All but three of the anhydrides have been described but the data are from different sources and do not agree among themselves. Holde[1] and co-workers have prepared the most complete series, consisting of the even carbon acids and anhydrides from caprylic through stearic. In order to obtain consistent values, we have prepared all the anhydrides from heptylic to stearic, including the three not previously known, by the same method and have taken their melting points under the same conditions. These values, along with those obtained by previous workers, are given in Table I. The acids from capric to stearic were generously furnished from the extremely pure preparations of Meyer and Reid.[2] Heptylic, caprylic and pelargonic acids were obtained from the Eastman Kodak Company. The melting points of the complete series of the anhydrides, along with those of the corresponding acids are plotted in Fig. 1.

TABLE I

MELTING POINTS OF THE ANHYDRIDES, °C.

| Anhydrides | This research | Prior values |
|---|---|---|
| Heptylic | −10.8 | −12.4[a] |
| Caprylic | + 0.9 ± 0.1 | −1.0[b] |
| Pelargonic | 14.8 | 16[c] |
| Capric | 24.7 ± .2 | 23.9[b] |
| Undecylic | 36.7 | 35[d] |
| Lauric | 42.1 ± .1 | 41,[c] 41.8,[b] 44[e] |
| Tridecylic | 49.9 ± .2 | ... |
| Myristic | 53.5 ± .1 | 51,[c] 53.4[b] |
| Pentadecylic | 60.6 | ... |
| Palmitic | 63.9 ± .1 | 63–64,[b] 63,[f] 63.5–64[g] |
| Margaric | 67.6 | ... |
| Stearic | 70.7 | 71–71.5,[b] 70.5,[f] 71.5–72,[g] 70–71[h] |

[a] Deffet, *Bull. soc. chim. Belg.*, **40**, 385–402 (1931). [b] Holde and Gentner, ref. 1. [c] Kraft and Rosing, *Ber.*, **33**, 3577 (1900). [d] Backer and van der Baan, *Rec. trav. chim.*, **56**, 1161–1174 (1937). [e] Mannick and Nadelmann, *Ber.*, **63**, 796 (1930). [f] Whitby, *J. Chem. Soc.*, **128**, 1462 (1926). [g] Rankov, *Ann. univ. Sofia, II, Faculté phys.-math.*, Livre 2, **33**, 221–227 (in German 228–229) (1937). [h] Autenrieth and Thomae, *Ber.*, **57B**, 423–437 (1924).

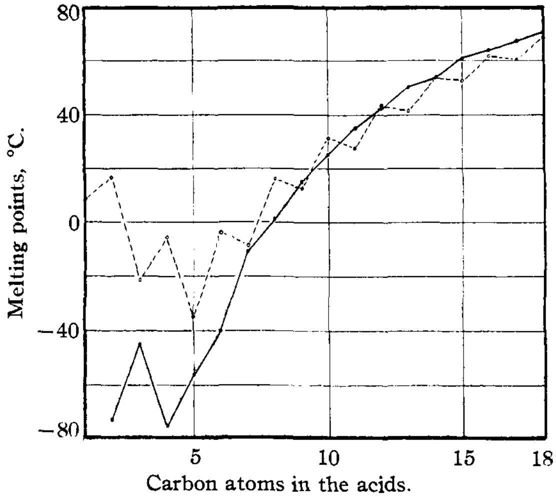

Fig. 1.—Melting points of the acids and anhydrides: acids ---; anhydrides —.

In general the method of Holde and Tacke was used. The acids were refluxed for six to eight hours in a flask, with ground-in condenser, with three equivalents of acetic anhydride. The acetic acid and excess acetic anhydride were distilled off under vacuum and the resulting anhydrides purified by vacuum distillation or by recrystallization from a suitable solvent. The anhydrides from heptylic through pelargonic were distilled under vacuum and capric through stearic were recrystallized three or four times from either diethyl or petroleum ether by cooling in an ice–salt-bath or with dry-ice. The yields ranged from 50 to 80%.

The melting points were taken, with mechanical stirring in a 200-cc. bulb, fitted with a side arm for the thermometer and melting point tube. Standard Anschütz thermometers were used, so the melting points may be regarded as corrected.

Carbon and hydrogen analyses are given in Table II

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(1) Holde and Smelkus, *Ber.*, **53**, 1889–1897 (1920); Holde and Tacke, *Ber.*, **53**, 1898–1907 (1920); *Chem.-Ztg.*, **45**, 949–950, 954–956 (1921); Holde and Gentner, *Ber.*, **58**, 1418–1424 (1925).

(2) Meyer and Reid, THIS JOURNAL, **55**, 1574–1584 (1933).

for those anhydrides not previously reported in the literature.

TABLE II

| | Carbon, % | | Hydrogen, % | |
|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found |
| Tridecylic | 76.04 | 76.27 | 12.27 | 12.28 |
| Pentadecylic | 77.19 | 77.68 | 12.53 | 12.58 |
| Margaric | 78.55 | 78.31 | 12.79 | 12.60 |

## Discussion

The melting points of the anhydrides alternate in the opposite sense to those of the acids. Up to valeric the swing is wide but from there on it is small, each odd anhydride melting only about 2° above the mean evens. From heptylic to stearic, the average of the melting points of the anhydrides is 1.2° above the average of the acids. Above valeric the alternation is much smaller for the anhydrides than for the acids.

The anhydrides crystallize in leafy plates and are soluble in the usual organic solvents. Limited quantities of the acids, usually one gram or less, prevented the determination of other properties.

This problem was suggested by Dr. E. Emmet Reid, Research Adviser, University of South Carolina, and to him the authors wish to express their appreciation for his valuable help. The melting points of the acids given in Fig. 1 were taken from the same authors.[2]

## Summary

The anhydrides of the normal aliphatic saturated monobasic acids from heptylic to stearic were prepared and their melting points determined. Curves are given for the melting points, through stearic, of the acids and anhydrides. The melting points, above butyric, of the anhydrides form practically a smooth curve, those derived from the odd carbon acids being slightly higher than the even on the mean curve.

COLUMBIA, SOUTH CAROLINA RECEIVED JULY 31, 1940

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY AT ILLINOIS INSTITUTE OF TECHNOLOGY][1]

# Catalytic Dehydrogenation and Condensation of Aliphatic Alcohols

BY V. I. KOMAREWSKY AND J. R. COLEY[2]

In the course of our investigation of complex action catalysts it was found that aromatic hydrocarbons were formed by the simultaneous dehydration and dehydrogenation of normal aliphatic alcohols containing six, seven and eight carbon atoms.[3] It was believed that the dehydration was accomplished by alumina and dehydrogenation–cyclization by chromia.

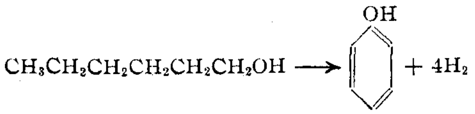
The work of previous investigators[4] indicated, however, that chromia might be a dehydrating as well as dehydrocyclizing catalyst. Therefore, it was of interest to see if chromia alone could carry on a similar complex reaction with alcohols. When the *n*-hexyl, *n*-heptyl, and *n*-octyl alcohols were subjected to the action of various preparations of chromia, complete absence of water in the reaction products indicated that there was no dehydration of the alcohols.

A large percentage of the product obtained was found to be symmetrical ketones formed by the condensation of two molecules of the alcohols charged, according to the equation

$$2RCH_2CH_2OH \longrightarrow RCH_2COCH_2R + CO + 3H_2$$

It seems reasonable that the change takes place through the following steps: (1) dehydrogenation to aldehyde, (2) aldol condensation, (3) removal of carbon monoxide from the aldehyde group of the aldol leaving a secondary alcohol, (4) dehydrogenation to ketone. This mechanism seems to be the most probable since there is no water addition or evolution as in a similar reaction with ethyl alcohol described by Kagan.[5]

At higher temperatures (475–525°) in addition to the ketone formation a direct dehydrocyclization of alcohols took place with the production of small amounts of phenols according to the equation



This result stands out in contrast to the reactions obtained using chromia–alumina catalyst[3] with the same alcohols, and proves that the chro-

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[1] A consolidation of Armour Institute of Technology and Lewis Institute.

[2] Universal Oil Products Company Research Fellow.

[3] Komarewsky, Riesz and Thodos, THIS JOURNAL, **61**, 2525 (1939).

[4] Sabatier, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1923, p. 22.

[5] Kagan, Sobolev and Lyubarskii, *Ber.*, **68**, 1140 (1935).