Solidification Point Curves of Binary Acid Mixtures. VI. Tetratriacontanoic-Hexatriacontanoic Acids[1]

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IN earlier communications (5) there have been presented the solidification point diagrams of "even" fatty acids from eight to 34 carbon atoms. Their value as analytical tools has been demonstrated in several reported instances (1, 3, 6) by the characterization of the saturated fatty acids of certain naturally occurring waxes and glyceride oils. We here report the extension of the series by an additional pair, the C_{34}-C_{36} acids.

The lower acids of the series either had been prepared by conventional methods from readily available materials (Neo Fats) or had been isolated from natural products. Since the objective in this case of necessity required the preparation of one of the higher members of the series, a method permitting the addition of more than a few carbon atoms at a time to a lower member was a desideratum. The synthesis used by Spielman and Schneider (7) for the preparation of 10-methyl stearic acid as modified by Schuette and Roth (5d) for the preparation of tetratriacontanoic acid appeared to be the most suitable in spite of low yields and other inherent difficulties.

Behenic acid, which is readily prepared from the erucic acid of rape seed oil, provides a convenient point of departure for the synthesis of its higher homologues. The chief criticism of such a course, however, stems from the fact that it does not lead to good yields when such long-chain compounds are involved. Although further modifications in technique were introduced in the procedure as previously described (5d), the changes did not produce the sought-for higher yields. The substitution of cadmium chloride for the very hygroscopic zinc chloride in the coupling of behenyl metal halide with ω-carbethoxynonoyl chloride was a decided improvement. Behenyl bromide, used in preparing the Grignard compound, was found to be superior to the iodide with respect to ease of starting the reaction and to its completeness. A Gilman color test (2a) of the Grignard solution indicated an 87% yield of behenyl magnesium bromide. However, the overall yield to the ketoester was only about 30%. It appears, then, that the low yield is due primarily to the failure of the ω-carbethoxynonoyl chloride to couple properly.[3] Acceptable quantities of the desired ketoester were obtained by conducting the reaction in dry benzene at reflex temperature for two hours. From this point to the saturated normal acid a series of reactions involving reduction of the ketone, replacement of the resulting hydroxy group by iodine, and substitution of the iodine by hydrogen with zinc in acetic acid gave excellent yields.

Conversion of dotriacontanoic acid to hexatriacontanoic acid was effected through the use of the malonic ester synthesis in two stages. An improvement in one step in the procedure was the hydrogenolysis of ethyl dotriacontanoate and ethyl tetratriacontanate to the corresponding alcohols in practically quantitative yields at 200°C. and 400 atmospheres pressure rather than at 250°C. and 250 atmospheres.

The transition point data of tetratriacontanoic and hexatriacontanoic acids are given in Table I.

TABLE I

Transition Point Data

Acid	Solidification Point Observed °C.	Resolidification Point[1] Reported[2] °C.	Melting Point	
			Observed °C.	Reported[2] °C.
Tetratriacontanoic............	97.70	97.8	......	......
Hexatriacontanoic............	99.65	99.7	99.8	99.9

[1] The resolidification point is that temperature at which the *partly* molten specimen in the capillary tube commences to resolidify when the temperature is lowered very slowly. It is a close approximation of the true solidification point.

[2] Francis, F., and Piper, S. H., J. Am. Chem. Soc., *61*, 577 (1939).

The solidification point curve for the C_{34}-C_{36} acids was prepared as before described for the lower members of the series. In order to conserve material 0.4 gram of the tetratriacontanoic acid was weighed into the solidification point tube and small increments of the hexatriacontanoic acid were carefully added after each determination of the solidification point. The data used in the construction of the curve (Fig. 1) are given in Table II.

TABLE II

Solidification Points of Binary Mixtures of Tetratriacontanoic and Hexatriacontanoic Acids

Composition C_{34} acid mole per cent	Composition C_{36} acid mole per cent	Solidification Point °C. (corr.)
100.00	0.00	97.70
90.32	9.68	95.22
85.38	14.62	94.24
80.71	19.29	93.91
78.88	21.12	93.80
76.00	24.00	93.72
70.99	29.01	93.66
65.41	34.59	93.81
57.19	42.81	94.13
50.24	49.76	94.17
44.79	55.21	94.26
41.46	58.54	94.44
32.05	67.95	95.37
23.05	76.95	96.94
13.17	86.83	98.00
0.00	100.00	99.65

Experimental Procedure

Docosanol-l. Ethyl behenate (200 g.) was subjected to high-pressure hydrogenolysis over 10 g. of copper-chromium oxide catalyst. Upon recrystallizing the product from ethanol there were obtained 170 g. of docosanol, m.p. 70-70.4°.

Docosyl Bromide. Dry hydrogen bromide, prepared by combustion of bromine vapor in hydrogen (4), was passed for four hours into a molten, 160-gram portion of docosanol-l contained in a 500-cc. distilling flask. The docosyl bromide was recovered by extraction with petroleum ether but only after considerable difficulty with emulsion formation to which the sul-

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[3] R. G. Jones (J. Am. Chem. Soc., 69, 1947, 2350) has recently reported good yields of long-chain keto esters by coupling ω-carbethoxyacyl chlorides with octadecyl zinc chloride and using an excess of this Grignard compound.

furic acid treatment for the removal of unreacted docosanol was a contributive factor. A 90-gram yield of the bromide was obtained after distillation, b.p. 218-220°C. at 0.2 mm.

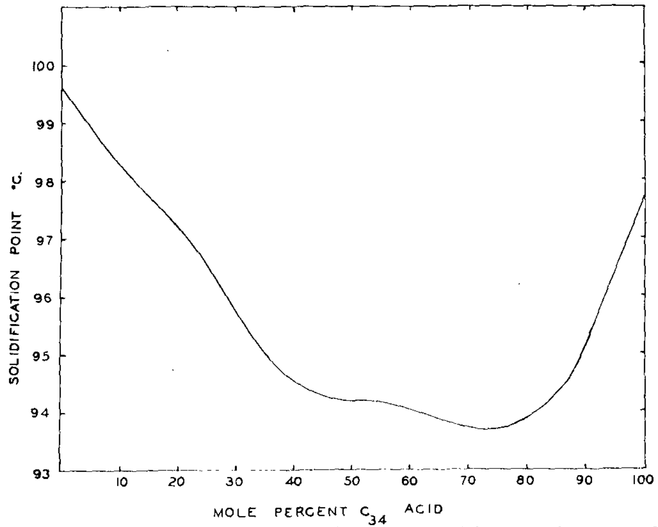

FIG. 1. Solidification point diagram of binary mixtures of tetratriacontanoic and hexatriacontanoic acids.

ω-Carbethoxynonoyl Chloride. A reaction mixture consisting of 90 g. of ethyl hydrogen sebacate (8) and 55 g. of thionyl chloride was heated for four hours at 35° to 50°C. under a reflux condenser protected with a calcium chloride drying tube. The volatile components were removed with an aspirator-type water pump while the temperature of the mixture was kept at 100°C. A yield of 60 g. (b.p. 129°-132°C. at 1 mm.) was obtained upon distillation through a Widmer column.

10-Ketodotriacontanoic Acid. To 1.85 (.077 mole) of magnesium turnings and 10 cc. of anhydrous ethyl ether contained in a thoroughly dried, three-neck flask fitted with a dropping funnel, a condenser, and a mercury-sealed stirrer, there was added, over a three-hour period, a 30-gram (.077 mole) charge of docosyl bromide in 100 cc. of dry ethyl ether while the reaction mixture itself was being vigorously stirred and kept at reflux temperature. When the reaction was complete, as indicated by the disappearance of the magnesium, 0.4 mole (7 g.) of anhydrous cadmium chloride was added. Heating was continued until a sample showed a negative Gilman test (2b). After removal of the ether by distillation and its replacement by 50 cc. of dry benzene .062 mole (15 g.) of ω-carbethoxynonoyl chloride in dry benzene was added, with stirring, to the boiling mixture. After two hours it was cooled, then 10% hydrochloric acid solution was cautiously added, after which the whole was vigorously stirred for 10 minutes. The benzene layer was separated and washed successively with water, 5% sodium bicarbonate solution, and water, whereupon the solution was filtered and the benzene removed by distillation. The residue was saponified with alcoholic potassium hydroxide solution. The potassium soaps were converted to barium soaps by the addition of barium chloride after which they were filtered off, dried, and extracted with benzene. Acidification of the barium soaps with hot 5% hydrochloric acid solution, followed by recrystallization of the liberated acid, resulted in a yield of 24.5 g. of 10-ketodotriacontanoic acid, m.p. 105-106°C.

10-Ketodotriacontanoic to Tetratriacontanoic Acid. The 10-ketotriacontanoic acid was converted to the normal acid and then to tetratriacontanoic acid by the use of procedures described in an earlier communication (5d).

Tetratriacontanoic to Hexatriacontanoic Acid. Five and one-half grams of tetratriacontanol obtained by hydrogenolysis of ethyl tetratriacontanoate, were heated for 5 hours at 135-170°C. with 1.7 g. of iodine and 0.3 g. of red phosphorus. Five grams of tetratriacontanyl iodide were recovered by extraction of the reaction mixture with benzene.

To 30 cc. of *n*-butanol in a 500-cc. round bottom flask equipped with stirrer, condenser, and dropping funnel were added .85 g. (.037 mole) of sodium and 7 cc. (.051 mole) of malonic ester. The tetratriacontanyl iodide (5 g.) was added and the mixture maintained at reflux temperature for 6 hours. Fifteen grams of potassium hydroxide in 300 cc. of ethanol were added and refluxing continued for 4 hours. After cooling, the potassium soaps were removed by filtration and suspended in hydrochloric acid solution. The gelatinous dicarboxylic acid was partially dried in a vacuum oven and then heated in a round bottom flask for 30 hours during which time the temperature was raised from 140° to 170°C. The hexatriacontanoic acid thus obtained was dissolved in hot benzene, decolorized with Norite, and filtered while hot. The solution was diluted to twice its volume with ethanol, containing 15 g. of sodium hydroxide, and heated for 30 minutes. Three grams of barium chloride were added to precipitate the barium soap which after 30 minutes of refluxing was filtered off, dried, and extracted with benzene. The barium soap was suspended in hot hydrochloric acid solution. Recrystallization of the acid from glacial acetic acid yielded 3.7 g. This was recrystallized five times from benzene, using Norite as a decolorizing agent.

Summary

With the synthesis of *n*-hexatriacontanoic acid (sol. pt. 99.65°C.), this time coupling ω-carbethoxynonoyl chloride with cadmium docosyl bromide, rather than with its zinc iodide counterpart (5d), to form *n*-dotriacontanoic acid, from which by malonic-ester synthesis, the chain was lengthened in two stages, the series of solidification point curves of binary mixtures of the homologous acids in question has been increased by one pair. Detailed descriptions of the several steps involved in these syntheses have been given. The curve, although slightly flatter—it is here drawn to a different scale than that previously used (5)—has the same general shape as those previously reported for the homologous fatty acids in this area.

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