

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

PARA-HALOGEN-PHENACYL ESTERS OF THE NORMAL FATTY ACIDS

BY CARRIE GUTMAN MOSES AND E. EMMET REID

RECEIVED FEBRUARY 10, 1932

PUBLISHED MAY 7, 1932

A number of these esters were prepared by Judefind and Reid¹ and others by Hann, Reid and Jamieson.² It has seemed desirable to fill the gaps in the series both for the sake of completeness and to study the relations of the melting points of the various derivatives to each other.

It is well known that the melting points of the normal hydrocarbons and of their simple derivatives show alternations as we go from one member to the next in a series. It has recently been found by Malone and Reid³ that the melting points of the 3,5-dinitrobenzoates of the normal alcohols show the same phenomenon. It was of interest to see whether this would also be found to be true with these derivatives of the acids.

In order to have strictly comparable data, all of the derivatives have been fully prepared whether they had been made previously or not. On recrystallization most of the esters appear as brilliant white plate-like

TABLE I

MELTING POINTS OF THE *p*-HALOGEN-PHENACYL ESTERS OF THE NORMAL FATTY ACIDS

	Chloro, °C.		Bromo, °C.		Iodo, °C.	
Formic	128.0		135.2		163.0	
Acetic	72.4	67.2 ^a	86.0	85.0 ^a	117.0	114.0 ^a
Propionic	98.2		63.4	59.0 ^a	98.0	94.9 ^a
Butyric	55.0		63.0	63.2 ^a	81.5	81.4 ^a
Valeric	97.8		75.0	63.6 ^a	81.0	78.6 ^a
Caproic	62.0		72.0	71.6 ^a	84.0	81.5 ^a
Heptoic	65.0		72.0		78.8	
Caprylic	63.0		67.4	65.5 ^a	79.2	77.0 ^a
Pelargonic	59.0		68.5		77.0	
Capric	61.6		67.0	66.0 ^a	82.0	80.0 ^a
Undecylic	60.2		68.2		81.8	
Lauric	70.0	70.0 ^b	76.0	76.0 ^b	85.8	
Tridecylic	67.0		75.0		88.5	
Myristic	76.0	76.0 ^b	81.0	81.0 ^b	89.8	
Pentadecylic	74.0		77.2		93.0	
Palmitic	82.0	82.0 ^b	86.0	81.5 ^a	86.0 ^b	90.0 ^a
Margaric	78.8		82.6	78.2 ^a	92.0	88.8 ^a
Stearic	86.0	86.0 ^b	90.0	78.5 ^a	90.0 ^b	90.5 ^a

^a Judefind and Reid, *THIS JOURNAL*, **42**, 1043 (1920).

^b Hann, Reid and Jamieson, *ibid.*, **52**, 818 (1930).

¹ Judefind and Reid, *THIS JOURNAL*, **42**, 1043 (1920).

² Hann, Reid and Jamieson, *ibid.*, **52**, 818 (1930).

³ Malone and Reid, *ibid.*, **51**, 3424 (1929).

crystals. The acetic esters are tinged with yellow which becomes more pronounced with exposure to the light. The formic esters suffer this change more quickly and melt with decomposition.

The melting points are given in Table I and are plotted in the figure.

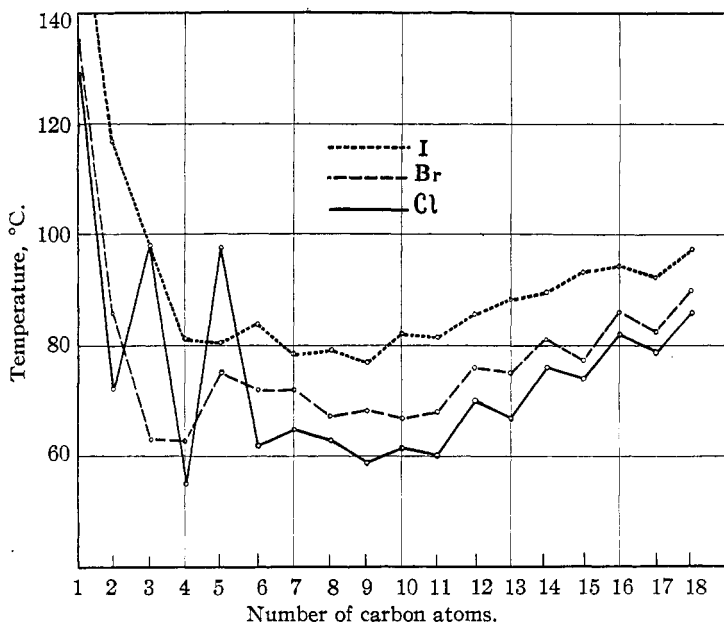


Fig. 1.

The chloro series shows well-defined alternations, the swings being very wide for the first six compounds. At the eighth compound there is a reversal of the alternation, the odd-numbered compounds melting higher up to that point and after it the even. In the bromo series this reversal takes place at the eleventh member. In the iodo series there is a well-defined alternation from five to twelve and again from fifteen to eighteen but in the reversed sense. In this series the butyric and valeric esters melt at nearly the same point while in the bromo series this is true of the propionic and butyric.

It seemed of interest to compare the melting points of the *p*-bromophenacyl derivatives from mixtures of palmitic and stearic acids with that of the margaric acid derivative. The results are given in Table II.

The derivative from 2:1 mixture does not change its melting point on recrystallization. That of 1:2 derivative approximates that of the margaric acid derivative, 82.6°, but is not sharp and is raised on recrystallization. The appearance of the derivative from the mixture is very different from one of the pure acids.

TABLE II

MELTING POINTS OF *p*-BROMOPHENACYL ESTERS OF PALMITIC AND STEARIC ACIDS AND THEIR MIXTURES

Palmitic	Stearic	Crude, °C.	Recryst., °C.
1	0		86.0
0	1		90.0
1	1	79.0	80.4
1	2	82.5	83.8
2	1	80.6	80.6

Experimental

The methods used were substantially those already described in the papers quoted. The one uniformly giving best results was found to be the neutralization of a weighed amount of the acid with slightly less than the theoretical amount of sodium alcoholate, heating (the higher acids) until all was in solution, testing for acidity with slightly moistened litmus paper (the solution must be slightly acid) and, if necessary, adding a minute quantity of the acid itself or, in case of the higher acids, hydrochloric acid. The alcoholate was made by adding three grams of sodium to one liter of 95% alcohol. An amount of the reagent calculated for the quantity of base used was then introduced and the whole refluxed for an hour. With the lower acids a small quantity of water was required but the esters of the higher acids precipitated from the alcoholic solution on cooling under the tap.

The precipitate was filtered rapidly with suction, well washed with cold alcohol, dilute alcohol and water and then dried between filter paper for at least twenty-four hours, after which the melting point was taken and the compound recrystallized. This procedure was repeated until a constant melting point was obtained. The melting points were determined in a Thiele tube filled with mineral oil, using a thermometer corrected by the Bureau of Standards.

Summary

The para chloro, bromo and iodophenacyl esters of the normal acids from acetic to stearic have been prepared and their melting points compared.

Alternation in the melting points appears in all these series.

BALTIMORE, MARYLAND