

states in a patent³ that the sole product is an acid melting at 160°, but we obtained a complicated mixture of substances from which only one acid, m. p. 228°, was isolated. It is easily separated as the sparingly soluble sodium salt, but the yield is only 10% of the theoretical amount. The acid group was found to be in the β -position, for the substance on oxidation yielded first an anthraquinone keto acid and then β -anthraquinonecarboxylic acid, which was identified as the methyl ester, m. p. 168°, by comparison with an authentic sample. The acid is thus of no interest in connection with the present study of *peri* condensations. The properties of the acid and its derivatives may be recorded briefly.

β -(2-Anthroyl)-propionic acid: long, yellow needles, m. p. 228°. *Anal.* Calcd. for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.29; H, 4.88.

The methyl ester formed pale yellow blades, m. p. 148°. *Anal.* Calcd. for $C_{19}H_{16}O_3$: C, 78.05; H, 5.52. Found: C, 77.90; H, 5.51.

β -(2-Anthraquinonyl)-propionic acid: yellow needles, m. p. 207°. *Anal.* Calcd. for $C_{18}H_{12}O_5$: C, 70.11; H, 3.92. Found: C, 69.58; H, 3.95.

γ -(2-Anthryl)-butyric acid: greenish-yellow plates, m. p. 197°. *Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.11. Found: C, 81.56; H, 6.08.

Summary

When β -(3-acenaphthoyl)-propionic acid (I) is heated in molten sodium aluminum chloride, a rather remarkable intramolecular condensation takes place. A seven-membered ring is closed across the *peri* positions of acenaphthene with the formation of *peri*-succinoylacenaphthene (VII). The reaction is far from being a general one, for none of the other keto acids investigated gave similar results.

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SOME NEW ESTERS OF ALPHA-HEXABROMOSTEARIC ACID¹

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Introduction.—The solid α -hexabromostearic acid, $C_{17}H_{29}Br_6COOH$, (often called α -linolenic acid hexabromide), in contrast to its parent acid, the unsaturated linolenic acid, $C_{17}H_{29}COOH$, which forms only liquid esters, has the property of forming solid salts and esters.² As pure linolenic acid is obtained by the debromination of the solid α -hexabromostearic acid, it seems possible that the solid esters of the latter acid might also be debrominated to yield linolenic acid or its esters. As a related phase of this prob-

¹ Based upon a thesis by Kenneth E. Stanfield submitted to the Department of Chemistry, and the Committee on Graduate Work of the University of Wyoming, in partial fulfillment of the requirement for the Degree of Master of Arts (1931).

² (a) Erdmann and Bedford, *Ber.*, **42**, 1330 (1909); (b) Samuel Coffey, *J. Chem. Soc.*, 119, 1412 (1921); (c) Imperial and West, *Philippine J. Sci.*, **31**, 441 (1926); (d) Almoradie and West, *ibid.*, **33**, 257 (1927); (e) Vincente and West, *ibid.*, **36**, 73 (1928).

lem thirteen new esters of α -hexabromostearic acid have been prepared and their melting points determined.

Experimental

The solid α -hexabromostearic acid used in this investigation was prepared by brominating the free acids of linseed oil according to the method of Erdmann and Bedford,^{2a} with the modifications suggested by Eibner and Muggenthaler.³ The slightly yellow hexabromide so obtained was recrystallized two or three times from boiling benzene and dried in a vacuum desiccator over concentrated sulfuric acid. The melting point of the flour-like product was 179.5–180.5°. This hexabromide, often known as the alpha form to distinguish it from the liquid beta form,^{2a,b} was then esterified with various alcohols in the presence of sulfuric acid (0.5 cc./50 cc. of alcohol) according to a procedure suggested by Vincente and West.^{2e} The alcohols were commercial products of the highest purity obtainable and were used without further purification. The yield of the ester obtained compared to the theoretical yield based upon the weight of the α -hexabromostearic acid used was from 30 to 84%.

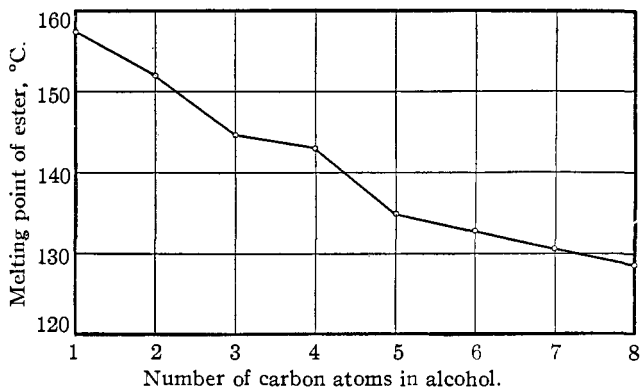


Fig. 1.—Graph of the melting points of the α -hexabromostearic acid esters against the number of carbon atoms in the primary alcohol.

The esters were further purified to give constant melting points by successive recrystallizations. Ethyl alcohol was found to be the most satisfactory solvent although glacial acetic acid and ethyl acetate were also used. After the esters had been dried in a vacuum desiccator over concentrated sulfuric acid for twenty-four hours the melting points were determined.

The constant melting products obtained in two different preparations of the same ester were proved to be identical by showing that a mixed sample of the two products had the same melting point as each of the individual samples. These melting points were found to remain constant when the esters had been allowed to stand in a desiccator for a period of three months.

The esters were confirmed by comparing their actual bromine content with the calculated value. These values were expressed as the number of moles of bromine and the per cent. of bromine in the esters. According to a modified method of Fisher⁴ a mixture

³ Eibner and Muggenthaler, *Farben.-Ztg.*, **131**, 641 (1912).

⁴ Fisher, "Laboratory Manual of Organic Chemistry," 2d ed., John Wiley and Sons, Inc., New York, 1924, p. 317.

of a known weight of the ester and powdered sodium peroxide, potassium nitrate and sugar ($C_{12}H_{22}O_{11}$) was fused in a Parr sulfur bomb. The cold melt was then disintegrated in hot water, acidified with nitric acid, and the bromine precipitated as insoluble silver bromide by the addition of an excess of standard silver nitrate solution. The excess silver nitrate was determined by back titration with a standard solution of potassium thiocyanate according to the Volhard method. An analysis for the bromine in α -hexabromostearic acid gave the following results.

	No. moles bromine	Bromine, %
Determined	3.01	63.49
Calculated	3.00	63.28

With the exception of the esters of the tertiary alcohols these esters were generally soluble in the following hot solvents: acetone, glacial acetic acid, benzene, toluene, chloroform, carbon tetrachloride, carbon disulfide, methyl alcohol, methyl acetate, ethyl ether, ethyl alcohol, ethyl acetate, propyl alcohol, butyl alcohol, amyl alcohol and amyl acetate. The esters of the tertiary alcohols were soluble in hot glacial acetic acid and the acetone but only slightly soluble in the other solvents. All of the esters were insoluble in petroleum ether and water.

When the melting points of the esters are graphed against the number of carbon atoms in the alcohol, a general decrease in the melting point is noted with the increase in the number of carbon atoms. This is especially evident when the esters are classified according to whether they are derived from primary, secondary, or tertiary alcohols.

TABLE I
ESTERS OF HEXABROMOSTEARIC ACID

The temperatures were not corrected because but 1.2 cm. of the mercury thread of the thermometer extended above the surface of the liquid in the Thiele tube. The liquid was circulated by a current of air.

Ester of	Type of alc.	Cc./g. of hexabromide	Yield, %	No. of crystns.	Moles detd.	Bromine		Melting point, °C.
						% detd.	% calcd.	
MeOH ^a	prim.							157-158
EtOH ^a	prim.							151.5-152.5
<i>n</i> -PrOH ^b	prim.	120.0	76					144-146
Iso-PrOH ^b	sec.	120.0	66					141-143
<i>n</i> -BuOH	prim.	39.0	54	8	2.98	58.58	58.92	143.0-143.1
Iso-BuOH ^b	prim.	120.0	56			58.79	58.92	136-138
<i>Tert.</i> -BuOH	tert.	62.5	49	5	3.02	59.24	58.92	162.0-162.5
<i>n</i> -AmOH ^c	prim.	35.7	52	4	3.03	58.67	57.92	135.0-135.2
Et ₂ CHOH	sec.	6.7	59	4	2.97	57.37	57.92	135.8-135.9
Iso-BuCH ₂ OH	prim.	7.1	45	4	2.97	57.41	57.92	135.0-135.1
MePrCHOH	sec.	7.1	64	4	3.02	58.32	57.92	135.7-135.9
Me ₂ EtCOH	tert.	6.3	85	6	3.03	58.54	57.92	159.0-159.5
<i>Sec.</i> -BuCH ₂ OH	sec.	10.0	73	4	2.99	57.58	57.92	133.4-133.8
Hexanol	prim.	7.0	30	6	3.04	57.80	56.96	132.6-132.8
Heptanol	prim.	15.5	38	6	3.01	56.05	56.03	130.6-130.8
Heptanol-4	sec.	6.3	49	4	3.03	56.72	56.03	135.1-135.2
Octanol	prim.	5.0	41	4	3.05	56.06	55.12	128-129
Octanol-2	sec.	6.3	57	4	3.03	55.80	55.12	129.1-129.2
Benzyl alc.	prim.	17.3	81	4	3.00	56.53	56.56	140.4-140.5

^a First prepared by Erdmann and Bedford. ^b First prepared by Vincente and West.

^c First prepared by Vincente and West, but the data given are those obtained by the authors.

In the case of the series of esters of the primary alcohols a zig-zag graph is obtained when adjacent points are joined by straight lines. The esters of the alcohols containing an even number of carbon atoms have melting points which lie above a smooth curve approximating the points, whereas those esters of alcohols containing an odd number of carbons lie below this curve. This type of graph is not unusual, for similar step-like arrangements are observed when the melting points are graphed against the number of carbons in various series of hydrocarbons, acids, aldehydes, amines and esters of mono-basic and dibasic acids.

Several unsuccessful attempts were made to prepare the α -hexabromostearic acid esters of the following alcohols: dimethylpropylcarbinol, diphenylcarbinol, triphenylcarbinol and myricyl alcohol. The crude products obtained in these cases resembled the above esters; however, due to difficulty in extracting them, they could not be obtained in the pure state.

Summary

Thirteen new esters of α -hexabromostearic acid were prepared and their melting points determined. These white, wax-like solids have definite melting points and are generally soluble in hot organic solvents. The esters of the tertiary alcohols seem to deviate considerably from those of the primary and secondary alcohols in that they have abnormally high melting points and are much less soluble in hot organic solvents. The melting points of the esters decrease with the increase in the number of carbons in the alcohol. A graph of the melting points against the number of carbons in the alcohol indicates a step-like arrangement in which the esters of the alcohols having an even number of carbons lie above a smooth curve approximating the points.

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS
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MIXED BENZOINS. IX. MESO CHLORO DERIVATIVES

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The original purpose of this work was to seek a route for the conversion of a mixed benzoïn into its isomer. Four benzoïns were investigated—benzoïn (as check), 4'-methoxybenzoïn¹ (benzanisoïn), 2-chloro-4'-methoxybenzoïn (*o*-chlorobenzanisoïn) and 2-chloro-3',4'-dimethoxybenzoïn (*o*-chlorobenzveratroïn). The first steps were the conversion of the benzoïn into the corresponding benzil, and this in turn into the phenyl α,α -dichlorobenzyl ketone. On the basis of data in the literature, it was believed that the chlorine atoms might be sufficiently firmly attached to withstand catalytic reduction, while the CO group was reduced to CHOH. The chlorine atoms could then be removed. Assuming that the chlorine atoms attached themselves to the carbon atom which originally carried

¹ Nomenclature of Buck and Ide, THIS JOURNAL, 54, 3302 (1932).