CXC.—*Some Fatty Acid Derivatives.*

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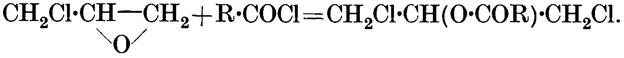
This paper describes the use of the silver salts of the fatty acids (which are obtainable by a convenient procedure described in the experimental part) for the preparation of derivatives such as the glycerides, acid anhydrides, and esters by double decomposition with appropriate halogen compounds. Certain mixed triglycerides have been prepared by treating β-acyl dichlorohydrins with such silver salts :

$$RCO\cdot O\cdot CH(CH_2Cl)_2 \xrightarrow{2R'CO_2Ag} RCO\cdot O\cdot CH(CH_2\cdot O\cdot COR')_2.$$

β-Acyl dichlorohydrins can be prepared by the action of acyl chlorides not only on α-dichlorohydrin, but also on epichlorohydrin : *i.e.*, acyl chlorides add on to epichlorohydrin in the same sense that hydrogen chloride does, the chlorine assuming the α-position :



$$CH_2Cl\cdot \underset{\diagdown O \diagup}{CH-CH_2} + R\cdot COCl = CH_2Cl\cdot CH(O\cdot COR)\cdot CH_2Cl.$$

This has been shown to be the case for propionyl, butyryl, and stearyl chlorides.

The silver salts of the fatty acids react very easily with acyl chlorides, yielding acid anhydrides, and readily with alkyl halides, yielding esters. In a homologous series of esters of palmitic acid and in a similar series of esters of stearic acid, the melting point falls from the methyl ester to a minimum in the butyl ester.

Heintz (*Ann. Phys.*, 1852, **87**, 21, 267; 1854, **92**) concluded that the fatty acids derived from the saponification of spermaceti comprised stearic acid. The present author has isolated cetyl stearate from spermaceti by fractional crystallisation.

EXPERIMENTAL.

Silver Salts of Fatty Acids.—Silver salts of both higher and lower fatty acids were obtained as fine, white powders, which suffered no discoloration when kept for 3 years in the light, by the following procedure : To a 2—4% alcoholic solution of the acid were added, in either order, 1 equiv. of aqueous ammonia (*d ca.* 0·9) and 1 equiv. of silver nitrate (dissolved in twice its weight of water; or dissolved in its own weight of water, and the warm solution diluted with alcohol). After 2—3 hours, the precipitate was filtered off, dried on a porous plate, powdered, and, if desired, dried at 50° for several hours. In the case of the higher fatty acids, the silver salt was precipitated in a more easily filterable form at about 50° than at room temperature. The yields were almost theoretical. Silver stearate, palmitate, laurate, myristate, hexoate, butyrate, propionate, acetate, and oleate prepared by this procedure were shown to be pure by determining their silver content. The stearic acid used melted at 69·5°, and the palmitic acid at 62·5°.

From the higher fatty acids, silver salts were also obtained as white powders, stable in the light, by a modification of Krafft's method (*Ber.*, 1888, **21**, 2266); the precipitates, however, were contaminated with a small amount (usually about 1%) of the free fatty acid, which could be removed by washing with alcohol or extraction with ether : Silver nitrate (1 equiv.) dissolved in a little water was treated with sufficient aqueous ammonia to re-dissolve the precipitate formed. The solution was added to an alcoholic solution of the fatty acid, precipitation completed by the addition of water, and the readily-filterable silver salt washed with alcohol and dried on a porous plate.

The solubility of silver palmitate and stearate in water at 20°, determined colorimetrically (Whitby, *Z. anorg. Chem.*, 1910, **67**, 68), was 0·00123 g. and 0·00065 g., respectively, per litre. These two salts therefore fall in line with the silver salts of the lower acids, the solubilities of which change from member to member in a comparatively regular manner (Lieben, *Monatsh.*, 1884, **15**, 404). Silver palmitate and stearate being less soluble than silver chloride, sodium chloride does not precipitate silver chloride from a solution of silver palmitate or stearate, held up by the minimum quantity of ammonia. Silver palmitate, being more soluble than silver stearate, requires less ammonia to cause it to dissolve in alcohol, and, conversely, it requires more water to precipitate it from ammoniacal alcoholic solution.

The silver salts of the higher fatty acids swell, disperse, and, on cooling, yield gels in various organic liquids, *e.g.*, aromatic hydrocarbons, on heating (compare Whitby, *Science*, 1921, **53**, 580). Silver oleate yields gels more readily than does silver palmitate or stearate. Thus it gives a gel in benzene, whereas silver stearate requires the higher-boiling xylene to yield a firm gel; in toluene, it gives only a weak gel, and in benzene it merely swells. Silver oleate gives a weak gel in amyl alcohol. In *n*-propyl alcohol, it swells and disperses, but on cooling separates as flocks, not as a gel. Gelation in organic liquids can be obtained at a lower point in the fatty acid series in the case of the silver than in the case of the alkali salts. Thus, silver hexoate dissolves in hot xylene and on cooling the sol will set to a weak gel, whereas potassium and sodium hexoates remain undispersed in boiling xylene.

β-*Acyl Dichlorohydrins.*

The α-dichlorohydrin used was prepared by the action of fuming hydrochloric acid on epichlorohydrin.

β-*Butyryl Dichlorohydrin.*—(a) A mixture of 29·58 g. of α-dichlorohydrin and 23·72 g. of butyryl chloride was, after the initial reaction had subsided, warmed at 50° to complete the reaction, moisture being excluded (loss, 7·95 g. Calc., 7·82 g.). Distillation yielded a product, b. p. 223·5°, having a fruity odour, $n_D^{20^\circ}$ 1·4540, $d_{20^\circ}^{20^\circ}$ 1·1796, saponification number 843 (Calc. for $C_7H_{12}O_2Cl_2$, 845·5). (*b*) A mixture of 23·05 g. of epichlorohydrin and 29·05 g. of butyryl chloride (*ca.* 10% excess) was heated under reflux for 8 hours at 75°, the entry of moisture being prevented. The twice-distilled product had b. p. 223·5°, $n_D^{20^\circ}$ 1·4540, $d_{20^\circ}^{20^\circ}$ 1·1792, saponification number 841·5. Truchot (*Compt. rend.*, 1865, **61**, 1170) gives b. p. 226°/738 mm. and $d_4^{11^\circ}$ 1·194.

β-*Propionyl dichlorohydrin* was prepared in similar ways to those mentioned above, except that in (*b*) the mixture of epichlorohydrin and propionyl chloride was heated in a sealed tube at 135° for 3 hours. The methods gave identical products, b. p. 208°, $d_{20^\circ}^{20^\circ}$ 1·2222.

β-*Palmityl Dichlorohydrin.*—Reaction between 13·79 g. (*ca.* 20% excess) of α-dichlorohydrin and 22·15 g. of palmityl chloride was completed by heating the mixture for 1 hour in a boiling water-bath (loss, 2·93 g. Calc., 2·94). The product, which set solid on cooling, crystallised from alcohol in white crystals, m. p. 34·4°, $n_D^{50^\circ}$ 1·4527 [Found : saponification number, 456·7; Cl, 19·2 (by saponification), 19·1 (by Carius). $C_{19}H_{36}O_2Cl_2$ requires Cl, 19·3%; saponification number, 458·7]. Palmitic acid isolated after saponification, 68·97 (calc., 69·76%).

β-*Stearyl Dichlorohydrin.*—(a) This was prepared from α-dichlorohydrin and stearyl chloride in the manner described for the preparation of β-palmityl dichlorohydrin. It had m. p. 39·5° and $n_D^{50^\circ}$ 1·4528 (Found : saponification number, 424·1; Cl, 17·8. $C_{21}H_{40}O_2Cl_2$ requires Cl, 17·85%; saponification number, 426·0). Stearic acid isolated after saponification, 72·18 (calc., 71·91%). (b) 20·8 G. of stearyl chloride were heated with 6·8 g. of epichlorohydrin in a sealed tube at 130° for 3½ hours. The product, on recrystallisation from alcohol, readily yielded pure β-stearyl dichlorohydrin. It contained a small amount of material of low melting point and very slight solubility in alcohol, the nature of which was not investigated. $n_D^{50^\circ}$, 1·4530. Saponification number, 423.

Mixed Triglycerides.

β-*Palmitodistearin* (β-*Palmityl αα'-distearyl glyceride.*)—(a) Powdered β-palmityl dichlorohydrin (1 mol.) and silver stearate (2 mols.) were mixed and heated either for 3 hours at 155° or for 5 hours at 135°. An ethereal extract of the product slowly deposited the fat as a pale cream, microcrystalline solid, m. p. 63·5°, and 64·8° after recrystallisation from ether; the crystals from the mother-liquor had the same melting point. $n_D^{70°}$ 1·4467. Mean dispersion $(n_F—n_C)$, 0·00788. Saponification number, 196·2 ($C_{55}H_{106}O_6$ requires 195·2). 1·6269 G. of the mixed silver salts prepared, by the method described earlier, from the mixed fatty acids obtained on saponification gave 0·4595 g. of silver (calc., 0·4593 g.). Freedom of the product from stearic or palmitic acid was shown by the fact that addition of silver nitrate followed by ammonia to an alcoholic solution produced no precipitate. The fat was practically insoluble in cold alcohol.

(*b*) The glyceride was also prepared from β-palmityl dichlorohydrin and silver stearate, reacting in hot phenetole for 2½ hours. The filtrate, on cooling, deposited the fat as rosettes or sheaves of needles, m. p. 64°. After recrystallisation from ether, the product agreed in melting point and saponification number with that described above.

The m. p. of β-palmitodistearin is given as 63° by Kreis and Hafner (*Ber.*, 1903, **36**, 2766) and Bömer and Limprick (*Z. Nahr. Genussm.*, 1913, **25**, 354) and as 67·1° by Amberger and Bromig (*Biochem. Z.*, 1922, **130**, 252).

β-*Stearodipalmitin* (β-*stearyl αα'-dipalmityl glyceride*) was prepared from β-stearyl dichlorohydrin and silver palmitate by method (a). M. p. 63·3° (Amberger and Bromig, *loc. cit.*, give 59·1°). Saponification number, 202·6 ($C_{53}H_{102}O_6$ requires 201·8).

β-*Butyrodipalmitin* (β-*Butyryl αα'-dipalmityl glyceride*).—With the aid of some ether, silver palmitate (2 mols.) and β-butyryl dichlorohydrin (1 mol.) were mixed. The ether was removed by warming on the water-bath, and the mixture heated at 170° for ½ hour with occasional stirring. When cold, the product was extracted with ether, silver chloride filtered off, and the ether removed. The residue was dissolved in alcohol and treated with the quantity of alcoholic potassium hydroxide necessary to neutralise the free acid present. The alcohol was then removed at 40° under reduced pressure, the residue extracted with dry chloroform, the chloroform removed, and the product recrystallised from alcohol. It then had m. p. 43·6°, $n_D^{60°}$ 1·4431, $n_D^{70°}$ 1·4397, $n_D^{80°}$ 1·4359; saponification number, 265·6 ($C_{41}H_{74}O_6$ requires 263·3). 100 G. of absolute alcohol at 20° dissolve 0·55 g. of β-butyrodipalmitin.

β-Palmitodibutyrin (*β-Palmityl αα′-dibutyryl glyceride*).—An intimate mixture of β-palmityl dichlorohydrin (1 mol.) and silver butyrate (2 mols.) was heated at 150° for 40 minutes, being stirred at intervals. The procedure used to isolate β-butyrodipalmitin was then followed. It was necessary to cool the alcoholic solution in ice in order to obtain crystals. These had m. p. 17°, and 18° after recrystallisation from alcohol. $n_D^{20^\circ}$ 1·4530. Saponification number, 388 ($C_{27}H_{50}O_6$ requires 385·1).

Acid Anhydrides.

Propionic Anhydride—Silver propionate (31·8 g.) and propionyl chloride (16·25 g.) developed considerable heat on mixing. No propionyl chloride came over on distillation. The yield of the crude anhydride was 20·0 g. (88%), and on redistillation this gave 80% of pure propionic anhydride, b. p. 165°.

Butyric Anhydride.—(a) From silver butyrate and butyryl chloride in the manner just described, a good yield of butyric anhydride, b. p. 193°, was obtained. (b) Lachowiz's method of preparing acetic and propionic anhydrides (*Ber.*, 1884, **17**, 1218; 1885, **18**, 2920) gave a poorer yield of butyric anhydride than method (a). A mixture of 40 c.c. of butyryl chloride and 600 g. of powdered lead nitrate (dried at 100°) was heated on the water-bath under reflux for 2—3 hours; it was then extracted with dry benzene, and the extract distilled. By several redistillations of the fraction b. p. 165—200°, a 50% yield of butyric anhydride was obtained.

Palmitic Anhydride.—A mixture of 6·40 g. of palmityl chloride and 8·19 g. of silver palmitate was heated and stirred on the water-bath for 10 minutes, and, when cold, was extracted with anhydrous ether. The product, recrystallised from ether, had m. p. 62·6°. Another sample had m. p. 63·0° after recrystallisation from benzene. Saponification number, 226; *M*, cryoscopic in benzene, 402 [$(C_{15}H_{31}\cdot CO)_2O$ requires saponification number 226·8; *M*, 394]. 100 G. of absolute alcohol at 20° dissolve 0·18 g. of palmitic anhydride.

Stearic Anhydride.—This was prepared from stearyl chloride and silver stearate in a similar way to that just described. After recrystallisation from ether, the substance was obtained as large, shining plates, similar in appearance to stearic acid. M. p. 70·5°. Saponification number, 202·5; *M*, cryoscopic in benzene, 540 [$(C_{17}H_{35}\cdot CO)_2O$ requires saponification number, 203·7; *M*, 550·7]. 100 G. of absolute alcohol at 20° dissolve 0·023 g. of stearic anhydride. The solubility in ether was clearly less than that of stearic acid.

The anhydrides of palmitic and stearic acids, although very similar to the corresponding acids in melting point and appearance, are much less soluble and have higher refractive indices. The following measurements were all made with the same instrument.

Refractive indices of some fatty acids and their anhydrides.

Propionic acid : $n_{\mathrm{D}}^{17^\circ}$ 1·3874.	Propionic anhydride : $n_{\mathrm{D}}^{17^\circ}$ 1·4041.
n-Butyric acid : $n_{\mathrm{D}}^{18^\circ}$ 1·3990.	*n*-Butyric anhydride : $n_{\mathrm{D}}^{18^\circ}$ 1·4143.
Palmitic acid : $n_{\mathrm{D}}^{70^\circ}$ 1·4309.	Palmitic anhydride : $n_{\mathrm{D}}^{70^\circ}$ 1·4359.
Stearic acid : $n_{\mathrm{D}}^{80^\circ}$ 1·4300.	Stearic anhydride : $n_{\mathrm{D}}^{80^\circ}$ 1·4362.

Esters of Palmitic and Stearic Acids.

Cetyl Palmitate : Cetyl Stearate.—These were prepared by heating a mixture of the appropriate silver salt (made from a sample of the pure acid) and recrystallised cetyl iodide (m. p. 21·9°) in a boiling water-bath for ½ hour, with stirring at intervals. The reaction mixture was extracted with ether, silver iodide filtered off, and the ethereal solution allowed to deposit crystals. The yields were practically theoretical, and the products, which consisted of lustrous, white plates, were so pure that recrystallisation from ether or glacial acetic acid failed to change the original melting point. Saponification numbers : cetyl palmitate, 117·0 ($C_{15}H_{31}{\cdot}CO_2{\cdot}C_{16}H_{33}$ requires 116·7); cetyl stearate, 111·1 ($C_{17}H_{35}{\cdot}CO_2{\cdot}C_{16}H_{33}$ requires 110·3). Both esters were readily soluble in acetone, carbon disulphide, or chloroform, and were very soluble in benzene. Ethereal solutions were occasionally supersaturated, but crystallisation was immediately induced by touching with ice a point in the vessel.

	Cetyl palmitate.	Cetyl stearate.
Melting point	51·6°	56·6°
$n_{\mathrm{D}}^{60^\circ}$, $n_{\mathrm{D}}^{65^\circ}$	1·4429, 1·4415	—
$n_{\mathrm{D}}^{70^\circ}$	1·4398	1·4410
100 G. of abs. ether dissolve at 22°	21·01 g.	9·08 g.
,, ,, ,, ,, 0°	2·30 g.	0·73 g.
,, ,, alcohol ,, 22°	0·0495 g.	0·0594 g.
,, glacial acetic acid dissolve at 22°	0·0633 g.	0·0388 g.
Turbidity temperature (Valenta test, with 2 c.c. of glacial acetic acid and 2 c.c. of ester)	109°	Turbid to b. p.

Cetyl Stearate from Spermaceti.—400 G. of a sample of spermaceti (m. p. 42—44°; $n_{\mathrm{D}}^{70^\circ}$ 1·4397; turbidity temperature 77°; saponification number 125·8; iodine absorption 5·89%) were recrystallised from ether nineteen times; 2·2 g. were obtained of a product with a constant melting point of 56·6° and agreeing in saponification number, refractive index, and turbidity temperature with cetyl stearate. On the basis of determinations of the amount and melting point of the material in the mother-liquors from the successive crystallisations, and of determinations of the melting point of artificial mixtures of cetyl palmitate and cetyl stearate, a rough estimate of the amount of cetyl stearate in the sample of spermaceti examined was made as 1·1%. A second sample of spermaceti was also examined. 1200 G. (original m. p. 41—44°) yielded, after ten crystallisations, 1·5 g. of crystals, m. p. 55·5°, having a saponification number of 111·5 (calc., 110·5) and giving cetyl alcohol (m. p. 50° after several recrystallisations from alcohol) and stearic acid (m. p. 65° after three recrystallisations from alcohol) on hydrolysis.

Benzyl Palmitate.—Equivalent quantities of silver palmitate and benzyl chloride were heated, with stirring at intervals, for ½ hour at 145°. The ester was extracted with ether and recrystallised from alcohol. M. p. 36° (compare Shonle and Row, *J. Amer. Chem. Soc.*, 1921, **43**, 361). $n_{\mathrm{D}}^{70^\circ}$ 1·4620. 100 G. of absolute alcohol at 16° dissolve 3·30 g.

Benzyl stearate was prepared similarly to benzyl palmitate. M. p. 44·3° (Shonle and Row, *loc. cit.*, give m. p. 45·8°), $n_{\mathrm{D}}^{70^\circ}$ 1·4627. 100 G. of absolute alcohol at 16° dissolve 0·685 g.

Homologous Series of Esters.—The esters the physical constants of which are recorded in the following table were prepared from the appropriate silver salt and alkyl halide. In the case of methyl stearate, ethyl palmitate, and ethyl stearate a mixture of equivalent amounts of the silver salt and the alkyl iodide was gradually heated in xylene to 100° and maintained at that temperature for about 10 minutes. Silver iodide was filtered off, and washed with hot xylene. The xylene solution was, if necessary, concentrated under reduced pressure, the ester allowed to crystallise, and then recrystallised from alcohol to a constant melting point.

				Saponification number.	
Palmitate.	M. p.	$n_{\mathrm{D}}^{50^\circ}$.	$n_{\mathrm{D}}^{70^\circ}$.	Found.	Calc.
Ethyl	23·5°	1·4278	1·4200	204	197·3
n-Propyl	20·4	1·4290	1·4211	186	188·1
n-Butyl	16·9	1·4312	1·4232	179·5	179·7
n-Amyl	19·4	1·4320	1·4241	171	172
*iso*Amyl	12·5	1·4315	1·4236	175	172
n-Octyl	22·5	1·4358	1·4277	152	152·3
Stearate.					
Methyl	38·8				
Ethyl	33·6	1·4320	1·4238	182	179·5
n-Propyl	30·5	1·4323	1·4242	174	171·9
n-Butyl	27·5	1·4328	1·4250	165·9	164·8
n-Amyl	30	1·4342	1·4266	160	158·3
*iso*Amyl	23	1·4333	1·4260	160	158·3
n-Octyl	31·8	1·4373	1·4300	143	141·5

In the case of the other esters listed, with the exception of the octyl esters, reaction was brought about by heating a mixture of equivalent quantities of the silver salt and the alkyl iodide alone, without xylene, for 1½ hours at 100°. The product was extracted with hot alcohol. In the case of the octyl esters a mixture of the silver salt and octyl bromide was heated for 2½ hours at 130—140°.

Both in the palmitate and in the stearate series the melting point reaches a minimum in the *n*-butyl esters, but the refractive index increases continuously.

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