60%, α-pinene; 9%, dipentene; 8%, cadinene; 6%, di-, tri- and higher terpenaceous compounds; 4%, elemol-like sesquiterpene alcohol; 4%, phellandral (probably); 3%, sesquiterpene alcohol with an azulene nucleus; 2%, guajene-like sesquiterpene; 2%, terpene ketone or aldehyde; 2%, β-pinene and small amounts of an easily oxidizable terpene.

The significance of these compounds in relation to the formation of rubber in the plant has been discussed.

PASADENA, CALIFORNIA RECEIVED JULY 24, 1944

[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

The Chlorination of Certain Long Chain Esters

BY HERBERT H. GUEST AND CHARLES M. GODDARD, JR.[1]

Normal aliphatic acids with more than seven carbon atoms undergo almost exclusively alpha bromination when treated according to Hell–Vollhard–Zelinsky.[2] Upon chlorination of such acids by the same procedure, we have found that a much larger amount of by-products, particularly products of disubstitution, is formed. As the acids decompose readily upon distillation, the methyl esters were investigated as possibly being more suitable starting material.

Methyl caprylate, laurate, myristate and stearate were treated with chlorine in the presence of various catalysts. Chlorination took place readily and fractional distillation of the products was effected without decomposition. It was possible to obtain a fraction from which unaltered and dichloro ester were removed but this fraction was not resolvable into isomers by further distillation. Isomers were present, however, because derivatives prepared from this highly purified fraction differ from those prepared in a similar manner from authentic α-chloro or α-bromo esters.

Experimental

Chlorination of Methyl Laurate.—The ester used as starting material was obtained from commercial acid which had been fractionally distilled on a large scale. After esterification, very careful distillation through a Stedman[3] fractionation column further purified it to the desired degree. It had the characteristics: b. p. (8 mm.) 136–139°; saponification equivalent 214; calcd. for $C_{13}H_{26}O_2$: 214.

It was found that the methyl esters were preferable, not only on account of their lower boiling point, but also because they reacted more readily with chlorine than the other alkyl esters.

Twenty-five experiments were conducted in which the average amount of ester used was 200 g. The time of chlorination ranged between one-half and seventeen hours. The temperature also was varied between 7 and 130°, the optimum being 30°. As catalysts, sulfur, phosphorus chlorides, and chloroacetyl chloride were used. In every case it was found that there was unaltered ester, ranging from 13 to 54%; the amount of dichloro ester correspondingly varying from 40 to 8%.

Experiments 1 to 12 were carried out in a dark hood, and 13 to 24 with illumination from 120-watt electric light bulb.

In Experiment 5, the cold reaction mixture (7°) held enough unreacted chlorine in solution to cause such rapid evolution of gases upon warming to room temperature that more than half the ester was lost from the reaction flask.

Experiment 6 showed the effect of washing out the dissolved chlorine before it could react completely. There was only 3.7% chlorine in the portion washed with ice-water as compared to 8.4% chlorine in the remainder which had been allowed to reach room temperature.

In Experiment 19 the flask was coated with wax, to determine whether glass acted as a catalyst. The result was negative.

In Experiments 22, 23 and 24, the cold ester containing dissolved chlorine was dropped slowly through a glass tower loosely packed with glass wool which was kept at 70°. It was hoped that the shortened time of reaction allowed the dissolved chlorine would prevent the formation of polychloro ester.

Data on Purified Fractions of Monochloro Esters

	B. p., °C.	Mm.	n_D	Analyses, % Cl Found	Calcd.
$C_7H_{14}ClCOOCH_3$	100	4	1.4435	18.9	18.4
$C_{11}H_{22}ClCOOCH_3$	158–164	7	1.4505	14.2	14.3
$C_{13}H_{26}ClCOOCH_3$	167–174	6	1.4531	12.5	12.9

Chlorination of Methyl Myristate using Phosphorus Pentachloride as Catalyst.—Methyl myristate (412 g.) to which 20 g. of phosphorus pentachloride was added, was treated with dry chlorine for one hour when increase in weight was 40 g. After standing at room temperature for thirty-six hours a further quantity of chlorine was added until final weight had increased by 82 g.; temperature was held between 25 and 32°. Distillation at 3 mm. gave the following fractions.

	Boiling range, °C.	% of total	Chlorine content, %	Sap. equiv.
1	135–150	26	4.7	195
2	150–160	20	9.3	169
3	160–170	24	14.5	132
4	170–185	20	19.6	114
5	Residue	10	23.3	105

Direct Chlorination of Methyl Stearate.—The methyl ester of stearic acid, substantially free from palmitic acid, was prepared and distilled carefully. It was chlorinated at 35° for six and one-half hours until the chlorine content was 10.9%. After washing and drying it was distilled. A fraction b. p. (10 mm.) 203–210° was collected.

Anal. Calcd. for $C_{19}H_{37}O_2Cl$: Cl, 10.7. Found: Cl, 10.6.

Preparation of α-Chlorostearic Acid.—α-Bromostearic acid was converted into α-hydroxystearic acid by heating with potassium hydroxide. By the action of thionyl chloride at 100° for sixteen hours, the hydroxyl group was replaced with chlorine. Distillation at 6 mm. pressure gave an ester with b. p. 190–200.

Anal. Calcd. for $C_{19}H_{38}O_2Cl$: Cl, 10.7; sap. equiv., 167. Found: Cl, 11.8; sap. equiv., 159.

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(1) In active service U. S. N. R.

(2) "Organic Syntheses," Coll. Vol. I, p. 108.

(3) U. S. Patent 2,047,444 (1936), *cf.* L. B. Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).

Action of Alkylolamines.[4]—Fifteen grams of α-chlorostearate (from α-hydroxystearic acid) was heated to refluxing with 20 g. of monoethanolamine until all chlorine had reacted. The reaction mixture was dissolved in water and extracted with ether. Upon removal of ether and recrystallization from methanol, white flake-like crystals were obtained (yield 10 g.), melting at 85°. Calcd. for $C_{22}H_{46}O_3N_2$: N, 7.2. Found: N, 6.9. Mixed with the product obtained from bromostearic acid by similar treatment, there was no lowering of the melting point.

The amide was hydrolyzed with mineral acid and the product was crystallized from alcohol m. p. 220° (dec.). It had the composition of α-(N-β-hydroxyethyl)-aminostearic acid.

Anal. Calcd. for $C_{20}H_{41}O_3N$: C, 70.0; H, 12.0; N, 4.1. Found: C, 69.5; H, 12.6; N, 4.8.

The same reaction carried out on the methyl chlorostearate, made by the direct clorination of methyl stearate, led to the formation of a crystalline solid melting at 94° on repeated recrystallization from methanol. This solid when mixed with that obtained from bromostearic acid, lowered the melting point of the latter and was not identical with the amide described above. It contained only 4.6% N. When chlorinated methyl laurate was treated with ethanolamine, a thick sirup was obtained from which no definite solid would crystallize.

Preparation of Butoxymyristic Acid.—30 g. of α-bromomyristic acid was treated with slight excess of 2 moles of sodium butoxide in excess *n*-butanol. On acidification, an oil, b. p. (4 mm.) 200–208°, was formed.

Anal. Calcd. for $C_{18}H_{36}O_2$: neut. equiv., 300. Found: neut. equiv., 293; iodine value, 4.

The mixed acids obtained from a highly purified fraction of methyl chloromyristate were not identical as shown by distillation and analysis: oil, b. p. (6 mm.) 183–212°.

Anal. Found: neut. equiv., 258; iodine value, 88.

Summary

The chlorination of methyl caprylate, laurate, myristate and stearate by dry chlorine was studied. Various catalysts were used in the unsuccessful endeavor to change the type of reaction, for example to produce α-chloro esters exclusively.

It was found that a large proportion of polychloro ester was formed even in the presence of a large proportion of unaltered ester.

An attempt was made to find a general method of determining the position in the ester of the substituent chlorine.

GLASTONBURY, CONN. RECEIVED MAY 2, 1944

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[4] Guest, U. S. Patent 2,277,015 (1943).

[CONTRIBUTION FROM THE LABORATORIES OF WALLACE & TIERNAN COMPANY, INC.]

A Carbonyl Reduction by Potassium Hydroxide in Ethanol

BY MARTIN RUBIN

The system ROH–ROM, particularly in the case where M is aluminum, is an efficient reagent, under suitable experimental conditions, for the reduction of carbonyl compounds to the carbinols.[1] Magnesium,[2] tin,[3] zirconium,[3] sodium,[4] zinc and calcium[5] have been used in place of aluminum in this system. Potassium hydroxide in benzyl alcohol has been used to reduce some aldehydes[6] and potassium hydroxide in ethanol under reflux has been utilized for the reduction of substituted benzophenones[7] and at 200–300° for high molecular weight aliphatic ketones.[8] Under these conditions the potassium is predominantly in the form of the alkoxide.[9,10]

In the course of an investigation leading to a synthesis of diethylstilbestrol[11] and various of its functional variants,[12] we had occasion to subject the ketone, anisyl-3-hexanone-4, to the action of potassium hydroxide in ethanol at 200–220°. The major reaction products were the corresponding carbinol and phenol produced by scission of the anisyl ether. The structures of the products were proved by synthesis and the preparation of derived compounds, as described in the experimental section.

Experimental

Melting and boiling points are uncorrected.

***p*-Hydroxyphenyl-3-hexanol-4.**—A mixture of 60 g. of anisyl-3-hexanone-4,[11] 75 g. of potassium hydroxide and 240 cc. of ethanol was heated in a rocking autoclave at 200–220° for six hours. The reaction mixture was poured into 500 cc. of water, the alcohol removed by distillation and the aqueous residue extracted with ether. The ether extracts were washed with 10% potassium hydroxide solution until free of acidic material. The combined alkaline solutions were acidified, extracted with ether and the ether extracts concentrated. On distillation *in vacuo* 30 g. (54%) of colorless, viscous oil, b. p. 145–155° at 1 mm. was obtained. The product crystallized on standing and melted at 82–83° after two recrystallizations from petroleum ether.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.32; H, 9.35.

The diacetate was prepared by refluxing with acetic anhydride for one hour. It was obtained as a colorless oil, b. p. 125–127° at 0.4 mm.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.02; H, 7.89.

The mono benzyl ether was prepared by refluxing equimolar quantities of the phenol and benzyl bromide in ethanol with excess alkali. It was a white solid which melted at 75–76° on recrystallization from dilute ethanol.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.07; H, 8.21.

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[1] A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

[2] Meerwein and Schmidt, *Ann.*, **444**, 221 (1925).

[3] Young, Hartung and Crossley, THIS JOURNAL, **58**, 100 (1936).

[4] Verley, *Bull. soc. chim.*, [4] **37**, 871 (1925).

[5] Meerwein, Bock, Kirschnick, Lenz and Migge, *J. prakt. Chem.*, **147**, 211 (1936).

[6] Palfray, Sabetay and Mastagli, *Compt. rend.*, **203**, 1523 (1936).

[7] Montagne, *Rec. trav. chim.*, **41**, 703 (1922).

[8] Schicht, German Patent 327,510 (1920).

[9] Engel, *Compt. rend.*, **103**, 156 (1886).

[10] Lescoeur, *ibid.*, **121**, 692 (1895).

[11] Rubin, Salmon and Kozlowski, THIS JOURNAL, to be published.

[12] Rubin and Wishinsky, *ibid.*, **66**, 1948 (1944).