[Contribution from the Northern Regional Research Laboratory[1]]

Reactions of Tertiary Butyl Hypochlorite with Vegetable Oils and their Derivatives. IV.[2] Conversion of Alkyl Oleates and Methyl Linoleate to Derivatives of Ketostearic Acids[3]

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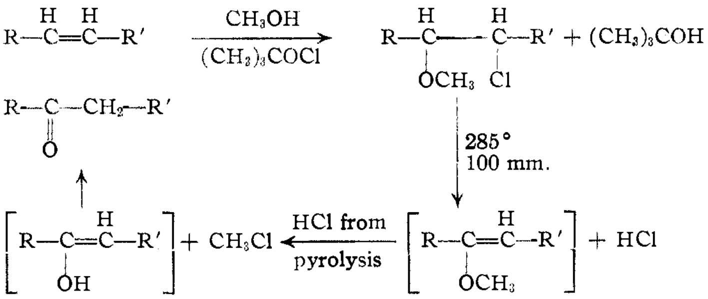
Alkyl alkoxychlorostearates have been prepared by the reaction of an alkyl oleate with *t*-butyl hypochlorite in presence of an alcohol. These compounds are decomposed by heat with the formation of alkyl 9-(10)-ketostearate. 9-(10)-Ketostearic acid was obtained by saponification of the alkyl ketostearate. Methyl dimethoxydichlorostearate has been prepared by the same reaction. It yields a methyl diketostearate on pyrolysis.

Price and Griffith[4] have described the preparation of methyl methoxychlorostearate by chlorination of methyl oleate in methanol solution. We have found that this compound, and other alkoxy chlorostearates, may be obtained from the reaction of methyl oleate with *t*-butyl hypochlorite in the presence of the corresponding alcohol. This method offers the advantages of rapidity and of minimizing the formation of dichlorostearate. It has been applied to lower olefinic compounds by Harford[5] and by Hennion and co-workers.[6]

During attempts to purify methyl methoxychlorostearate by distillation, the sensitivity of this compound to heat was observed. A solid product was obtained which was identified as a mixture of methyl 9- and 10-ketostearates. A study of the reaction conditions showed that this conversion could be accomplished in 70% yield by pyrolysis of methyl methoxychlorostearate at 285–290° and a pressure of 100 mm. The corresponding mixture of 9- and 10-ketostearic acids was readily obtained by saponification of the ester.

Although detailed study of the reaction mechanism was beyond the scope of this investigation, the apparent course of the reaction is indicated by the following scheme, in which R and R′ represent the remaining parts of the methyl oleate molecule

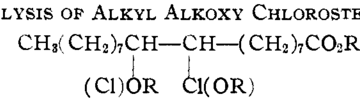


Reverse addition to the double bond leads to the formation of the other isomer of methyl ketostearate. The product obtained consisted of approximately 40% of 9-ketostearate and 60% of 10-ketostearate.

The formation of ketostearates from several other alkyl alkoxy chlorostearates was also studied. The results are given in Table I.

Table I

Pyrolysis of Alkyl Alkoxy Chlorostearates



$$\underset{(\mathrm{Cl})\mathrm{OR}}{CH_3(CH_2)_7CH}—\underset{\mathrm{Cl(OR)}}{CH}—(CH_2)_7CO_2R'$$

R	R′	I. V.	Calcd.	Cl, % found	Cor.[a]	Yield ketoester,[a] %
CH_3	CH_3	0.0	9.78	9.45	9.45	70
CH_3[b]	CH_3[b]	8.0	9.78	9.87	10.9	40
n-C_3H_7	CH_3	21.2	9.08	8.07	10.7	54
i-C_3H_7	CH_3	2.2	9.08	11.6	11.9	55
n-C_4H_9	CH_3	23.7	8.76	7.52	10.4	61
n-C_5H_{11}	CH_3	44.9	8.48	5.27	11.1	37
CH_3	CH_3	7.3	7.70	...	...	38

[a] Shows value for product having zero iodine value. [b] Derivative from methyl elaidate.

The extent of reaction between alkyl oleate and alcohol, as indicated by the iodine number of the product, was substantially less for the higher normal aliphatic alcohols studied. Side reactions also occurred to a greater extent with the higher alcohols and with methyl elaidate. This is shown by the halogen analyses which gave high results after correction for the iodine numbers of the products. Probable products of these side reactions are polychlorinated alkyl oleate[7] and chlorinated alcohols. The latter are relatively high-boiling compounds and would not have been removed under the mild conditions used in working up the products. The low yield of ketoester from the methyl methoxychlorostearate prepared from methyl elaidate, as compared to that from methyl oleate, may be attributed to the *trans* arrangement of hydrogen and chlorine in the elaidate derivative. Barton[8] has pointed out that *cis* elimination occurs in olefin-forming thermal decompositions which are homogeneous and unimolecular.

The alcohol used in conjunction with *t*-butyl hypochlorite to form the alkoxychloro derivative is subject to oxidation by the hypochlorite.[9] Hydrogen chloride is a product of this oxidation

$$RCH_2OH + (CH_3)_3COCl \longrightarrow RCHO + HCl + (CH_3)_3COH$$

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Report of a study in which certain phases were carried on under the Research and Marketing Act of 1946. Article not copyrighted.

(2) For the previous paper in this series see *J. Am. Oil Chem. Soc.*, **27**, 102 (1950).

(3) A portion of this paper is based upon the thesis submitted by Lyle C. Woods in partial fulfillment of the requirements for the Degree of Master of Science in the Graduate Division of Bradley University, June, 1950. This paper was presented at the 118th Meeting of the American Chemical Society, Chicago, September 3–8, 1950, and at the American Oil Chemists' Society Meeting, San Francisco, California, September 26–28, 1950.

(4) Price and Griffith, U. S. Patent 2,392,100 (1946).

(5) Harford, U. S. Patent 2,207,983 (1940).

(6) Irwin and Hennion, This Journal, **63**, 858 (1941); Emling, Vogt and Hennion, *ibid.*, **63**, 1624 (1941).

(7) Teeter and Jackson, *J. Am. Oil Chem. Soc.*, **26**, 535 (1949).

(8) Barton, *J. Chem. Soc.*, 2174 (1949).

(9) Clark, *Chemical News*, **143**, 265 (1931).

Occasionally transesterification or esterification occurs as a result of catalysis by the hydrogen chloride. Thus when *n*-propyl oleate or oleic acid was treated with methanol and *t*-butyl hypochlorite, methyl methoxychlorostearate was formed as shown by isolation of methyl ketostearate after subsequent pyrolysis.

Methyl linoleate was converted by *t*-butyl hypochlorite and methanol to a product which appeared to be principally methyl dimethoxydichlorostearate. This product could not be obtained pure. Thermal decomposition resulted in a product which contained a maximum of 2.12% of carbonyl oxygen, corresponding to 21.7% of methyl diketostearate. A methyl diketostearate, m.p. 65°, was isolated from the reaction product by fractional crystallization.

Experimental

Reagents.—*t*-Butyl hypochlorite was prepared by a previously described method.[10] Methyl oleate was prepared from red oil by the method of Wheeler and Riemenschneider[11] I.V. 85.3; calcd. 85.5. Methyl linoleate was prepared by debromination of tetrabromostearic acid in methanol rather than ethanol solution as described by McCutcheon[12]; I.V. 170.3; calcd. 172.3. *n*-Propyl and isoöctyl oleates were prepared by direct esterification of oleic acid (obtained by saponification of methyl oleate) with a 20- to 30-mole excess of the alcohol in the presence of 1% of *p*-toluenesulfonic acid as a catalyst.

n-**Propyl Oleate.**—Neutral oil; $n^{27}\text{D}$ 1.4488; I.V. 77.03. Calcd. I.V. 78.21.

Isoöctyl Oleate.—Neutral oil; $n^{27}\text{D}$ 1.4538; IV., 60.4. Calcd. I.V., 64.33.

These esters were used without further purification.

Methyl Elaidate.—A mixture of 19.3 g. of oleic acid and a solution of 1 g. of sodium nitrite in 4 ml. of water was warmed to 60° in a steam-bath with stirring. A solution of 5 ml. of concentrated nitric acid in 5 ml. of water was added during a period of 15 minutes. The mixture was allowed to stand for one hour, cooled and extracted with ether. The ether solution was washed free of mineral acid, dried over sodium sulfate, and cooled to −27°. The crystals obtained were recrystallized from ether. The yield was 10.3 g. (53.5%) of colorless plates, m.p. 43–44°. Ten grams of this product was esterified by the procedure described above. The product was a colorless oil; $n^{25}\text{D}$ 1.4494. It was used without further purification.

Methyl Methoxychlorostearate.—Dissolved oxygen was removed from 59.4 g. (0.2 mole) of methyl oleate by passing a current of carbon dioxide below the surface for 1 hour. The inert atmosphere was maintained while 225 g. (7 moles) of methanol was added. This was followed by the addition, with constant stirring, of 25.0 g. (0.23 mole) of *t*-butyl hypochlorite which was added at a rate whereby the temperature of the reaction mixture did not exceed 55°. The reaction mixture was then allowed to stand for 2 hours. Excess methanol and by-product *t*-butanol were removed by evaporation under reduced pressure at temperatures below 100°. The residual oil (72 g., 99%, $n^{30}\text{D}$ 1.4545) was nearly pure methyl methoxychlorostearate. It could not be purified by distillation because of decomposition.

Anal. Calcd. for $C_{20}H_{39}O_3Cl$: Cl, 9.78; OCH_3, 17.08; I.V., 0. Found: Cl, 9.45; OCH_3, 16.2; I.V., 0.

Other alkyl alkoxychlorostearates were made by the same procedure using the appropriate alcohol and alkyl oleate. Analyses of the products are given in Table I.

When *n*-propyl oleate or oleic acid was treated with methanol and *t*-butyl hypochlorite, transesterification in the first case, and esterification in the second, occurred. This was shown by the fact that in both cases methyl ketostearate was obtained on subsequent pyrolysis.

Alkyl Ketostearates.—The alkyl alkoxychlorostearate was heated with constant stirring for 4 hours at 285–290° and 100 mm. pressure. The extent of conversion to ketostearate was estimated by determination of carbonyl oxygen.[13] Results are given in Table I.

Methyl 9-(10)ketostearate was isolated from the reaction product from methyl methoxychlorostearate by fractional crystallization from acetone at −10°. Recovery was 75%; colorless crystals, m.p. 42–43°; $E^{1\%}_{1\text{cm.}}$ in ethanol solution, 0.836 at 2840 Å. (determined with a Beckman spectrophotometer).

Anal. Calcd. for $C_{19}H_{36}O_3$: OCH_3, 9.96; sapn. equiv. 312.5. Found: OCH_3, 10.50; sapn. equiv. 309.7.

9-(10)**Ketostearic Acid** was obtained by saponification of methyl ketostearate. It was recrystallized first from acetone and then from methanol at −10°; colorless crystals, m.p. 71.5–72.0°. This melting point corresponds to that of a mixture of 40% of 9-ketostearic acid and 60% of 10-ketostearic acid.[14] The product was compared with a mixture of 9- and 10-ketostearic acids obtained by hydration of stearolic acid.[12] In ethanol solution, the ultraviolet absorption coefficients ($E^{1\%}_{1\text{cm.}}$) were 1.14 at 2800 Å. for the product from methyl methoxychlorostearate and 0.98 at 2810 Å. for the product from stearolic acid.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.37; H, 11.47; neut. equiv., 298.4. Found: C, 72.2; H, 11.60; neut. equiv., 297, 304.

n-**Propyl Ketostearate.**—This ester was obtained by direct esterification; colorless crystals, m.p. 33–34°; $E^{1\%}_{1\text{cm.}}$ in ethanol, 0.925 at 2800 Å.

Anal. Calcd. for $C_{21}H_{40}O_3$; C, 74.07; H, 11.84. Found: C, 74.2; H, 11.70.

Isoöctyl Ketostearate was obtained by direct esterification; colorless crystals, m.p. 35–36°.

Anal. Calcd. for $C_{26}H_{50}O_3$: C, 76.04; H, 12.27. Found: C, 76.1; H, 12.22.

Methyl Dimethoxydichlorostearate.—Dissolved oxygen was removed from 25.9 g. (0.088 mole) of methyl linoleate by passing a stream of nitrogen below the surface for 2 hours. While the inert atmosphere was maintained, 282 g. (8.8 moles) of methanol was added. This was followed by the addition, with constant stirring, of 21.1 g. (0.194 mole) of *t*-butyl hypochlorite at a rate whereby the temperature of the reaction mixture did not exceed 30°. The reaction mixture was then allowed to stand 1 hour. Unreacted methanol and *t*-butyl hypochlorite, and by-product *t*-butanol, were removed *in vacuo* in a current of nitrogen. The product (36.4 g., 96.7%) was a pale yellow oil; $n^{30}\text{D}$ 1.4636.

Anal. Calcd. for $C_{21}H_{40}O_4Cl_2$: OCH_3, 21.78; Cl, 16.6; I.V., 0. Found: OCH_3, 19.93; Cl, 15.40; I.V., 0.8.

Methyl Diketostearate.—Five grams of methyl dimethoxydichlorostearate was heated for 2 hours at 285–290° and 100 mm. pressure. The product was an oil which solidified at 0° and contained 21.9% of methyl diketostearate.

Anal. Found: carbonyl oxygen, 2.14; OCH_3, 10.86; Cl, 0.79.

This product was dissolved in 4–5 volumes of acetone and crystallized by cooling to −20°. The crystals obtained were recrystallized three times from acetone. Darco G-60 was used in the first recrystallization for decolorizing. Colorless, lustrous plates were obtained; m.p. 65–65.5°; $E^{1\%}_{1\text{cm.}}$ in ethanol, 2.07 at 2795 Å.

Anal. Calcd. for $C_{19}H_{34}O_4$: C, 69.9; H, 10.50; OCH_3, 9.51; carbonyl oxygen, 9.80. Found: C, 70.0; H, 10.45; OCH_3, 9.53; carbonyl oxygen, 9.67.

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[10] Teeter, Bachmann, Bell and Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949).

[11] Wheeler and Riemenschneider, *Oil & Soap*, **16**, 207 (1939).

[12] McCutcheon, *Org. Syntheses*, **22**, 77 (1942).

[13] Knight and Swern, *J. Am. Oil Chem. Soc.*, **26**, 366 (1949).

[14] Robinson and Robinson, *J. Chem. Soc.*, 2204 (1926),