Reactions of *t*-Butyl Hypochlorite with Vegetable Oils and their Derivatives. VI. Dechlorination of Methyl Alkoxychlorostearates with Alkali[1]

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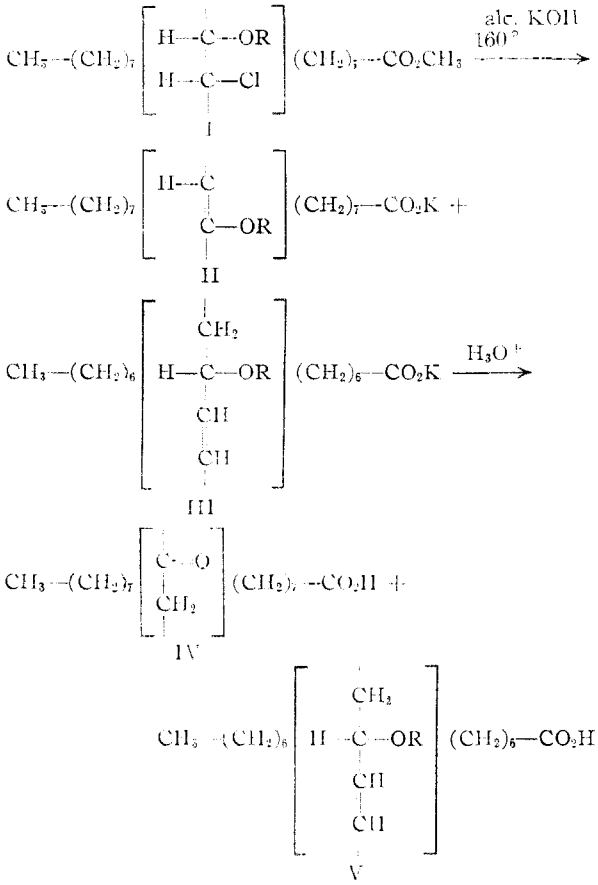
Previous work at this Laboratory[2] has shown that pyrolysis of methyl 9(10)-alkoxychlorostearates (I) produces methyl 9(10)-ketostearate, from which 9(10)-ketostearic acid (IV) is obtained by saponification. This acid may also be obtained by dechlorination of methyl alkoxychlorostearates with alcoholic potassium hydroxide followed by acidification to decompose soaps and to hydrolyze the intermediate vinyl ether (II).



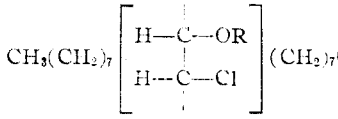
These reactions were applied to a series of methyl alkoxychlorostearates in which R was varied from methyl through *n*-amyl and to methyl methoxychlorostearates derived from elaidic acid and from a commercial grade of oleic acid. The results obtained are shown in Table I. When R was a group larger than methyl, and particularly when R was the branched-chain isopropyl group, yields of 9(10)-ketostearic acid were substantially smaller than when R was methyl. In these reactions, dechlorination to (III) appeared to be the predominant reaction.

Methyl methoxychlorostearate derived from methyl elaidate was dechlorinated to the same extent as was the corresponding derivative from methyl oleate. The low yield of 9(10)-ketostearic acid in this reaction may be attributed to the stereochemical relationship between the two methyl methoxychlorostearates.

The oily residue remaining after isolation of 9(10)-ketostearic acid from dechlorinated methyl methoxychlorostearate was degraded by hydroxylation of the double bonds and cleavage with periodic acid. The scission products were found to retain a substantial proportion of the methoxyl groups present in the original residue. This indicates the presence of the expected by-product, methoxyoctadecenoic acid (V).

Table I

Dechlorination of Methyl Alkoxychlorostearates with Alcoholic Potassium Hydroxide



R	Chlorine removed, %	Yield of ketostearic acid,[a] %	R	Chlorine removed, %	Yield of ketostearic acid,[a] %
CH_3	90	61	*n*-C_3H_7	87	38
CH_3[b]	90	38	*i*-C_3H_7	73	14
CH_3[c]	98	68	*n*-C_4H_9	88	47
C_2H_5	90	31	*n*-C_5H_{11}	85	31

[a] Calcd. from carbonyl analysis. [b] Derivative from ethyl elaidate. [c] Derivative from commercial 93% methyl oleate.

Experimental

The methyl alkoxychlorostearates were prepared as described by Teeter, *et al.*[2] Methyl ethoxychlorostearate, a compound not reported previously, was an oil. It could not be further purified because of decomposition on heating.

Anal. Calcd. for $C_{21}H_{41}O_2Cl$: Cl, 9.42; OC_2H_5 (including OCH_3 calcd. as OC_2H_5), 23.9. Found: Cl, 10.23; OC_2H_5, 20.8.

Each was dechlorinated in accordance with the following general procedure. The results are shown in Table I.

Dechlorination.—The methyl alkoxychlorostearate (1 mole) and a solution of 2.2 moles of potassium hydroxide in 1100 g. of methanol were placed in an autoclave equipped with an efficient stirrer. The mixture was heated and stirred at 150–160° for 1.5 hours, cooled, and transferred to a distillation apparatus. After most of the methanol had been removed, water was added, the *p*H was adjusted to 7.5 by addition of concentrated hydrochloric acid,[3] and distillation was continued until all methanol was eliminated. The mixture was then acidified with hydrochloric acid and boiled to ensure decomposition of soaps and hydrolysis of the intermediate vinyl ether. The aqueous layer was discarded, and the product was washed with hot distilled water until the washings were free of mineral acid. The washed product set to a greasy solid on standing. The amount of 9(10)-ketostearic acid in this product was determined by analysis for carbonyl groups.[4] Approximately 85% of the ketostearic acid present could be recovered as a purified product, m.p. 68–70°, neut. equiv. 305 (calcd. 298) by recrystallization of the crude material at −15° from petroleum ether (b.p. below 60°).

Degradation.—The oily residue remaining after isolation of 9(10)-ketostearic acid from dechlorinated methyl methoxychlorostearate was found to contain 20% of 9(10)-ketostearic acid which could not be removed by crystallization and to have iodine value 43.5, neut. equiv. 300 and methoxyl 8.8%. This residue (15 g.) was hydroxylated by the method

(1) Presented at 121st National Meeting of the American Chemical Society in Milwaukee, Wisconsin, March 30–April 3, 1952.

(2) H. M. Teeter, L. E. Gast, D. Raleigh and L. C. Woods, This Journal, **73**, 2302 (1951).

(3) The mixture must be kept alkaline during removal of methanol to avoid partial re-esterification of the product.

(4) H. B. Knight and D. Swern, *J. Am. Oil Chemists' Soc.*, **26**, 366 (1949).

of Nunn and Smedley-Maclean.[5] The product was separated into a fraction insoluble in petroleum ether (6.3 g.; neut. equiv. 307; iodine value 5.3; OCH_3 7.74%; OH 6.2%) and a fraction soluble in petroleum ether (7.0 g.; neut. equiv. 285; iodine value 7.7; OCH_3 5.95%). The latter fraction contained most of the 9(10)-ketostearic acid present in the original residue. The fraction insoluble in petroleum ether (5.5 g.) was cleaved with periodic acid, and the products were oxidized to carboxylic acids by the method of King.[6] The carboxylic acids were separated into a fraction insoluble in petroleum ether (0.6 g.; neut. equiv. 160; OCH_3 5.5%) and a fraction soluble in petroleum ether (2.1 g.; neut. equiv. 219; OCH_3 5.6%).

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(5) L. Nunn and I. Smedley-Maclean, *Biochem. J.*, **32**, 1974 (1938).
(6) G. King, *J. Chem. Soc.*, 1826 (1938).
(7) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

The Preparation and Stabilities of Some β-Dialkylaminopropionamides

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Morsch[2] has described the preparation of N,N-diethyl-β-diethylaminopropionamide from diethylamine and methyl acrylate. Except for this case, no β-dialkylaminopropionamides appear to have been reported. We have prepared several compounds of this type, wherein the amide groups are unsubstituted, by the addition of secondary aliphatic amines to acrylamide.

$$R_2NH + CH_2{=}CHCONH_2 \longrightarrow R_2NCH_2CH_2CONH_2$$

Dimethylamine, dipropylamine, dibutylamine and morpholine were used. This reaction is analogous to that of ammonia or amines with acrylic esters[2] and with acrylonitrile.[3] The reactions proceed readily in alcohol solution at room temperature, giving good yields of the products.

We used Morsch's method to prepare several N,N-dialkyl-β-dialkylaminopropionamides

$$2R_2NH + CH_2{=}\overset{R'}{\overset{|}{C}}COOR'' \longrightarrow R_2NCH_2\overset{R'}{\overset{|}{C}}CONR_2 + R''OH$$

II

Dimethylamine was heated with ethyl acrylate to give N,N-dimethyl-β-dimethylaminopropionamide and with methyl methacrylate to give N,N-di-methyl-β-dimethylaminoisobutyramide. Morsch's preparation of N,N-diethyl-β-diethylaminopropionamide from diethylamine and methyl acrylate was repeated. Dibutylamine and methyl acrylate were heated together to give a low yield of N,N-dibutyl-β-dibutylaminopropionamide and much N,N-dibutylacrylamide. This latter compound was apparently formed by decomposition of the aminopropionamide during distillation.

Several interesting observations were made regarding the thermal stabilities of these compounds. Several persons have noted that β-aminopropionic derivatives tend to be rather unstable. For instance, Whitmore and co-workers,[4] Buc, Ford and Wise,[5] and Wiedeman and Montgomery[6] have commented on the instability of β-aminopropionitrile at room temperature. Whitmore and his co-workers also observed that the higher β-dialkylaminopropionitriles are unstable at elevated temperatures. Elderfield and his colleagues[7] state that ethyl β-*p*-anisidinopropionate is not stable and decomposes readily to the amine and ethyl acrylate. McElvain and Stork[8] found that the addition of ammonia to ethyl acrylate, yielding ethyl β-aminopropionate, ethyl β,β′-iminodipropionate and ethyl β,β′,β″-nitrilotripropionate, constitutes a series of reversible reactions.

We found that the N,N-dialkyl-β-dialkylaminopropionamides show a striking gradation in the ease with which they decompose, when heated, to dialkylamines and N,N-dialkylacrylamides

$$R_2NCH_2\overset{R'}{\overset{|}{C}}HCONR_2 \longrightarrow R_2NH + CH_2{=}\overset{R'}{\overset{|}{C}}CONR_2$$

N,N-Dimethyl-β dimethylaminopropionamide (II, R = CH_3, R′ = H) is about 65% decomposed after being refluxed for four hours at 210–215°; no noticeable decomposition occurs at 200°. N,N-Diethyl-β-dibutylaminopropionamide is decomposed to about the same extent upon being heated for 15 minutes at 180–200°. N,N-Dibutyl-β-dibutylaminopropionamide, as has been said, is much less stable; it undergoes much decomposition merely upon being distilled under reduced pressure at 125°.

It will be noted that the stability of these N,N-dialkyl-β-dialkylaminopropionamides decreases with increasing length of carbon chains in the substituent alkyl groups. This increasing instability is not a result only of greater loading upon the amino nitrogen atoms. β-Dibutylaminopropionamide (I, R = C_4H_9) distills undecomposed at 167° while N,N-dibutyl-β-dibutylaminopropionamide (II, R = C_4H_9, R′ = H) is mostly decomposed by distillation at 125°. Clearly, the presence of butyl groups on amide nitrogen atoms has a considerable effect on the stability of the molecule.

Another factor which decreases the stability of these β-aminopropionamides is the presence of an alpha methyl group on the propionamide chain. This is shown by a comparison of N,N-dimethyl-β-dimethylaminopropionamide with N,N-dimethyl-β-dimethylaminoisobutyramide (II, R = R′ = CH_3). The latter compound is the less stable and breaks down to some extent, merely upon distillation, to give dimethylamine; this is shown by the poor yield in which it was obtained, its poor nitrogen analysis, and the persistent odor of dimethylamine over the distilled product.

(1) Research Dept., General Mills, Inc., Minneapolis, Minn.
(2) K. Morsch, *Monatsh.*, **63**, 220 (1933).
(3) U. Hoffmann and B. Jacobi, U. S. Patents 1,992,615 (Feb. 26, 1935) and 2,017,537 (Oct. 15, 1935).
(4) F. C. Whitmore, H. S. Mosher, R. R. Adams, R. B. Taylor, E. C. Chapin, C. Weisel and W. Yanko, THIS JOURNAL, **66**, 725 (1944).
(5) S. R. Buc, T. H. Ford and E. C. Wise, *ibid.*, **67**, 92 (1945).
(6) O. F. Wiedeman and W. H. Montgomery, *ibid.*, **67**, 1994 (1945).
(7) R. C. Elderfield, W. J. Gensler, T. H. Bembry, C. B. Kremer, F. Broady, H. A. Hageman and J. D. Head, *ibid.*, **68**, 1259 (1946).
(8) S. M. McElvain and G. Stork, *ibid.*, **68**, 1049 (1946).