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Part II

Halogenation[1]

N. O. V. SONNTAG, Research and Development Division, National Dairy Products Corp., Glenview, Illinois

Abstract

Within the past twenty years, while much of the research and development appeal in the halogenation of fats and fatty derivatives has been associated with the evolution of new and useful derivatives such as arthritis cures and artificial rubber plasticizers, the principal utility of the halogenated fats still continues to be in the production of other materials through halogenated fats as reactive intermediates. Consider, too, the utility of halogenated fats reflected by the fact that considerable quantities of iodochloro fats are discarded down the sinks of our analytical laboratories after the Wijs or other iodine value (I.V.) determinations. Aside from the valuable utility of halogenation as an analytical tool, whatever the use of halogenated fatty materials may be, i.e., for new and useful halogenated products per se, or for use as intermediates for the production of other materials, halogenation is capturing an ever-increasing share of the effort being directed to the modification of the chemical and physical nature of fats. While the standard and well-known methods of utilizing fatty acid chlorides as reactive intermediates continue to flourish, the newer aspects of fat halogenation, as demonstrated by the development of fluorinated derivatives, and in the utilization of chlorination followed by dehydrochlorination for the production of more highly-unsaturated fat molecules, illustrate a few directions in which progress is being made.

Introduction

IN ANY COLLECTION of papers on the subject of Chemical Modification of Fatty Derivatives, the subject of Halogenation obviously does not warrant the attention that topics such as Hydrogenation, Epoxidation, Ozonolysis or even Vinyl Monomers do. Halogenated fatty derivatives, as such, are not produced or sold in large volume commercial quantities today. In fact, they are just beginning to attract attention in the research laboratory and in the province of the applications research man. It is in the area of *reactive*

intermediates that halogenated fatty derivatives deserve attention. A considerable amount of modified fat and fatty derivatives does not contain halogen, but owes its very existence to the fact that it was created through halogenated reactive intermediates. Generally speaking, these final products are unique, and in most cases cannot be prepared in any other way than through the use of such intermediates. This, then, is today's field of importance for halogenated fats. Only the future will reveal the relative importance of halogenated fats and derivatives for use as such. While our subject becomes, of necessity, somewhat projected, long-range and exploratory, its dual nature confers upon it a broad degree of heterogeneous interest. The synthetic organic chemist, the chemical engineer, the analytical chemist, the member of the development department, the "applications" researcher, and also the representative of executive management of the fatty chemical company will find here something upon which to ponder. The latter, in fact, may already be wrestling with the problem of deciding upon the worth and value of budgeting research dollars upon halogenated fats.

Discussion

Analytical Aspects of Halogenation

While a lengthy discussion of the I.V. has no place in a seminar on chemical modification of fat, on the other hand, no comprehensive treatment of the halogenation of fat and fatty derivatives could possibly omit some consideration of it. It is therefore appropriate and pertinent that we begin our treatment of Fat Halogenation by launching a deadly assault upon the misuse of that fundamental bastion of analytical fatty acid chemistry—the I.V.

When A. V. Hubl (1), J. J. A. Wijs (2), and J. Hanus (3) pioneered in the development of an analytical determination of unsaturation in long-chain

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[1] Presented at the AOCS meeting in New Orleans, La., 1962.

TABLE I

Response of Representative Fatty 2-Enoic Acids to Various Iodine Value Determinations[a]

Fatty acid	Method[b]				Theoretical
	Wijs	Hanus	Kaufmann	Woburn	
2-Nonenoic	135(640; 40)	119(500; 46)	160(150; 48)	161(1800; 66)	162.8
2-Tetradecenoic	....	....	112.6(300; 48)	....	112.4
2-Heptadecenoic	....	44(150; 45)	95.8(150; 45)	....	94.8
2-Nonadecenoic	26.1(570; 42)	71(500; 44)	83.2(190; 72)	....	85.7

[a] P. Savary, Bull. soc. chim. France, *1950*, 624.
[b] Figures in parentheses: (% excess reagent; time in hr).

aliphatic compounds by halogen addition at the close of the nineteenth century, little did they realize to what extent their methods would be applied in the 1960's. Today there are over two dozen useful modifications of the I.V. determination which have been thoroughly evaluated on a variety of unsaturated compounds (4). The pioneering developers of the I.V. determination, for the most part, applied their techniques to the analysis of naturally-occurring, non-conjugated, non-hindered, long-chain aliphatic compounds with "isolated" double bonds (unsaturated functional groups separated by at least two carbon atoms). They were careful to point out the limitations of the respective methods, as they were known to exist at the time, and were particularly precise about the conditions under which the determinations were to be carried out. When one considers the fact that the room temperature addition of bromine to oleic acid is accompanied by about 8–10% of anomalous substitution resulting in the evolution of hydrogen bromide and the formation of bromo derivatives halogenated in other than the 9- and 10-positions of the stearic acid skeleton (5), one realizes the necessity for strict adherance to precisely defined reaction conditions in the analysis. Moreover, the increasing number of chemically-modified fatty acid derivatives which are attracting research attention, and in some cases, actually being produced, demands further evaluation of the I.V. determination in order to define the scope and applicability of the analysis for these products. Fatty chemical derivatives with epoxy, hydroxy, amino, amido, and nitrilo groups, and those which contain triple-bond unsaturation, extensive branching in the aliphatic chain, or cyclic groups, such as the six-membered ring found in "dimerized linoleic acid," or the heterocyclic ring in fatty imidazolines, for example, do respond to the I.V. determination as readily as does oleic acid. It is now fairly generally realized that the greatest care must be exercised in interpreting I.V. determinations carried out on selectively hydrogenated vegetable oils or fatty acids. Whenever unsaturated fatty structures are isomerized, positionally or geometrically, changes in the mode and ease of halogen addition to the isomerized products are quite apt to occur. A brief review of the "ground rules" for the scope of the I.V. determination in unsaturated fatty acids is presented in order to fix firmly in mind the nature and extent of certain of its limitations. The data in Table I demonstrate that 2-enoic fatty acids do not

respond to the usual I.V. determinations, and that modifications of the techniques such as those of Woburn (6) or Kaufmann (7) are required for these "protected" double bond compounds. In Table II are data which indicate that the double bond must be at least three methylene groups removed from the carboxyl group for absorption of halogen to be approximately theoretical. Table III summarizes some generally appreciated data indicating that conjugated dienoic or trienoic fatty acid chains respond to the extent of $\frac{1}{2}$ or $\frac{2}{3}$, respectively, of the total number of bonds present. Brevity in this portion of our presentation prevents a more detailed survey of the limitations of fatty acids containing branched chains, triple-bond unsaturation and other structural features.

Briefly, then, we wish to point out positively that the I.V. determination of unsaturation can be applied with reasonable assurance to unsaturated fatty materials, particularly chemically-modified fatty acid derivatives, only if some detailed knowledge of the structural configuration of the derivative is already known.

Synthetic Aspects of Fat Halogenation

Halogenated fats or fatty derivatives are generally prepared by *addition* to carbon-carbon unsaturated functional groups or by *substitution* of the hydrogen atoms of methylene groups, by substitution of hydroxyl groups, or by substitution of the hydroxyl component of carboxyl groups. The common free halogens, namely, chlorine, bromine, and iodine, add to unsaturated double or triple bonds; hydrogen halide may also be added. Substitution of the hydrogen atom of a methylene group of an aliphatic chain occurs with the common free halogens, and may be directed specifically to the 2-position, or may be made "random" in the sense that monohalogenation of other positions more remote from the carboxyl group may be carried out. Polychlorination, where no more than one chlorine atom may be attached to the site of a single carbon atom, may also be achieved. Except in the case of acetic acid, which is unique, rarely do two halogen atoms enter fatty molecules by substitution at the site of a single carbon atom of the chain. Fluorinated derivatives are prepared by unique techniques and occasionally, by the replacement of other halogen atoms already introduced by substitution.
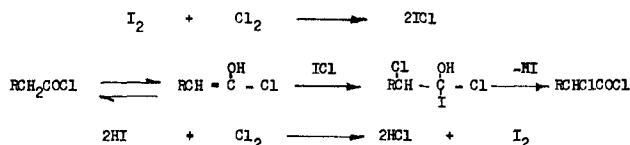
Two kinds of "ionic" substitution of hydrogen by halogen are recognized in which specificity for 2-position replacement is exhibited: iodine-catalyzed and phosphorus-catalyzed. Fatty acid halides, anhydrides and certain esters chlorinate and brominate at the 2-position of the chain in the presence of iodine. The reaction is apparently unaffected by light. The fatty acid, however, displays very little reactivity under the same conditions that the acid halide, anhydride or ester readily respond to. This is generally attributed to the fact that the derivatives are more capable of enolization, which permits addition to the double bond followed by dehydrohalogenation in the case of the derivatives, but not, generally, in the case of the

TABLE II

Response of Representative Monoethenoid Fatty Acids to I.V. Determinations[a]
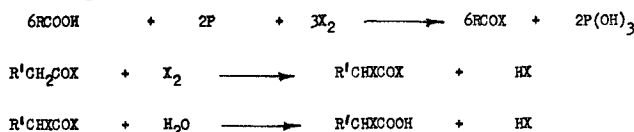
Fatty acid	Iodine value			
	Hubl (4 hr)	Wijs (0.5 hr)	Hanus (0.5 hr)	Calc'd
CH₃CH=CHCOOH	17.4	10.3	4.3	295.0
CH₃(CH₂)₁₂CH=CHCOOH	6.6	20.4	1.9	99.8
CH₃(CH₂)₁₄CH=CHCOOH	8.7	18.0	3.0	89.7
CH₃(CH₂)₁₃CH=CHCH₂COOH	16.27	......	......	89.7
CH₃(CH₂)₁₂CH=CH(CH₂)₂COOH	26.96	......	......	89.7
CH₃(CH₂)₇CH=CH(CH₂)₇COOH	89.7	89.7	89.7	89.7
CH₂=CH(CH₂)₈COOH	135.1	137.3	......	137.8

[a] G. Ponzio and C. Gastaldi, Gazz. chim. ital., *42*, II, 92 (1912); A. Eckert and O. Halla, *Monatsh.*, 1815 (1913).
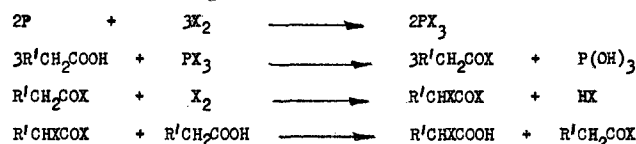
fatty acids. Iodine presumably functions as a catalyst through formation of a mixed halogen which regenerates iodine during the process of halogenation. This may be illustrated in the chlorination of a typical acid chloride:

$$I_2 + Cl_2 \longrightarrow 2ICl$$

$$RCH_2COCl \longrightarrow RCH = \overset{OH}{\underset{}{C}} - Cl \xrightarrow{ICl} R\overset{Cl}{\underset{I}{CH}} - \overset{OH}{\underset{}{C}} - Cl \xrightarrow{-HI} RCHClCOCl$$

$$2HI + Cl_2 \longrightarrow 2HCl + I_2$$

The phosphorus-catalyzed halogenation, typified by the Hell-Volhard-Zelinsky bromination (8) is even more specific for 2-position halogenation than is the iodine-catalyzed procedure when applied for bromination, chlorination or iodination (fluorination is apparently not possible by this method). In the Hell-Volhard-Zelinsky bromination a 2-bromofatty acid is formed, free of bromo isomers, by addition of liquid bromine to a fatty acid in the presence of red phosphorus. Early interpretations of this halogenation inferred that one mole of phosphorus was required for each three moles of fatty acid halogenated, and that the 2-haloacid halide intermediate required hydrolysis to generate the 2-haloacid:

$$6RCOOH + 2P + 3X_2 \longrightarrow 6RCOX + 2P(OH)_3$$

$$R'CH_2COX + X_2 \longrightarrow R'CHXCOX + HX$$

$$R'CHXCOX + H_2O \longrightarrow R'CHXCOOH + HX$$

It soon became apparent that the 2-halofatty acid could be formed from less than equivalent molar quantities of phosphorøus (9), and that the overall reaction involved a "halogen carrier" as an intermediate. Today we interpret this halogenation in the true light of its dual character: halogen reacts with phosphorus first to form a catalytic amount of phosphorus trihalide, which creates, almost immediately, a small amount of acid halide. The acid halide halogenates rapidly in the 2-position through enol addition. The resulting 2-halo acid halide transfers its 2-halogen atom to a fatty acid molecule by disproportionate interchange:

$$2P + 3X_2 \longrightarrow 2PX_3$$

$$3R'CH_2COOH + PX_3 \longrightarrow 3R'CH_2COX + P(OH)_3$$

$$R'CH_2COX + X_2 \longrightarrow R'CHXCOX + HX$$

$$R'CHXCOX + R'CH_2COOH \longrightarrow R'CHXCOOH + R'CH_2COX$$

The resulting acid halide molecule is then available for a repetition of the bromination carrier process. The disproportionate interchange is Mother Nature's way of "sharing-the-wealth," since the 2-haloacid halide, which contains two heavy and bulky halogen atoms, exists in an environment of non-halogenated fatty acid molecules, at least, at the beginning of the reaction. While it is still not entirely clear why one-half of the total halogen is transferred exclusively from the 2-position of the 2-halo fatty acid halide to the 2-position of the fatty acid, nevertheless, the resulting acid halide is capable of almost immediate rebromination and re-enters the cycle repeatedly until free fatty acid is almost entirely halogenated. It is usually common practice to quench the final crude reaction product in water in order to hydrolyze the residual amounts of acid halide remaining. Much synthetic use has been made of this procedure, and a host of 2-halofatty acids have been prepared in the laboratory by means of it. Generally, when the phosphorus-catalyzed method, or even the iodine-catalyzed method, of "directed halogenation" is applied to

TABLE III
Response of Representative Conjugated Fatty Acids to I.V. Determinations

Fatty acid	Method			
	Standard Wijs	Woburn [a]	Modified pyridinium sulfate dibromide	Theoretical
α-Eleostearic	....	....	273.8 [b]	273.7
β-Eleostearic	183.0 [c]	273.7 [d] 273.8 [e]	272.8 [b]	273.7
9,11-Octadecadienoic	91.2 [c]	183.3 [f] 182.6 [g]	....	181.0

[a] J. D. von Mikusch and C. Frazier, Ind. Eng. Chem., Anal. Ed., *13*, 782 (1941).
[b] R. W. Planck, F. W. Pack and L. O. Goldblatt, JAOCS *30*, 417 (1953).
[c] J. D. von Mikusch and C. Frazier, Ins. Eng. Chem., Anal. Ed., *15*, 109 (1943).
[d] Temp, 20C; time, 1 hr; excess reagent 500–600%.
[e] Temp, 0C; time, 3 hr; excess reagent 600–2000%.
[f] Temp, 20C; time, 1 hr; excess reagent, 400–500%.
[g] Temp, 0C; time, 3 hr; excess reagent 400–500%.

esters the 2-position is halogenated, but, the reaction tends to be difficult to stop at this stage and proceeds further to afford polyhalogenated products.

The "free-radical" substitution of hydrogen by halogen in aliphatic chains appears to be much less specific and directed than does the catalyzed "ionic" substitution. These halogenations may be classified with respect to the source of the halogen free radicals, thus: from free halogens by irradiation, from sulfuryl chloride with peroxides (10), from N-halosuccinimides with peroxides (11), from carbon tetrachloride by irradiation (12) etc. Considerable research effort has already been expended on halogenation using free halogens in order to achieve optimum reaction conditions for the controlled and directed mono-, and polyhalogenation of aliphatic chains. The variables studied include selection of specific halogenation catalysts, intensity, wavelength, and duration of irradiation, and reaction temperature.

Table IV includes some representative data on the uncatalyzed photochlorination of lower-homolog acids, nitriles, acid chlorides and esters with irradiation of 3100–4100 A. It serves to illustrate the complexity of the halogenation. While the reaction conditions for this study afforded a maximum of monochlorination, the specificity was shown to be directed to the β-position preferentially but certainly not exclusively. Acetic acid and acetyl chloride behaved uniquely, and methyl esters, in general, exhibited more randomness than other derivatives in the chlorination. Polychlorination of fatty acids appears to be attained more easily when the photochlorination is catalyzed by iron (13). One can expect renewed and further extensions of this type of halogenation research in the near future.

TABLE IV
Monochlorinated Derivatives from Uncatalyzed Photochlorination of Acids Nitriles, Acid Chlorides and Esters [a]

Reactant	Total Mono-chlorination, %	Products			
		% 2-Chloro	% 3-Chloro	% 4-Chloro	% 5-Chloro
CH₃COOH	2	100	....	....	....
CH₃CN	None	....	....	....	....
CH₃COCl	2	100	....	....	....
CH₃CH₂COOH	....	30	70	....	....
CH₃CH₂CN	86	25	75	....	....
CH₃CH₂COOCH₃	91	34	66	....	....
CH₃(CH₂)₂COOH	86	5	64	31	....
CH₃(CH₂)₂CN	89	....	69	31	....
CH₃(CH₂)₂COOCH₃	90	....	69.5	30.5	....
(CH₃)₃CCOOH	95	....	100	....	....
CH₃(CH₂)₃CN	90	....	75	25	....
(CH₃)₂CHCH₂COOH	86	26	69	5	....
(CH₃)₂CHCH₂COCl	....	32	60	8	....
(CH₃)₂CHCH₂COOCH₃	100	49	49	2	....
CH₃(CH₂)₃COOCH₃	91	....	70	29	....
CH₃(CH₂)₄COOCH₃	93	....	77	....	23

[a] A. Bruylants, M. Tits and R. Dauby, Bull. Soc. Chim. Belges, *58*, 310 (1949); A. Bruylants, M. Tits, C. Dieu and R. Gauthier, *Ibid.*, *61*, 366 (1952).

TABLE V
Characteristics of "Ionic" and "Free-Radical" Substitution of Hydrogen by Halogen in Acids and Acid Chlorides

Type	Catalyst	Relative speed	Position preferentially attacked	Proposed mechanism	Effect of inhibitors
"Ionic"	I₂ P	RCOCl> RCOOH	α	Enol addition, loss of HCl	None
"Free Radical"	Light	RCOOH> RCOCl	β and γ	Chain free radical	Stops reaction

In order to summarize the basic differences between "ionic" and "free-radical" substitution of hydrogen by halogen, we have collected in Table V the pertinent comparative data.

The substitution of the hydroxyl component of a carboxyl group, as illustrated by the formation of an acid chloride from a fatty acid with phosphorus trichloride, is a well known, but, unfortunately, little understood organic chemical reaction of wide synthetic utility. Table VI summarizes the experimental

TABLE VI
Stearoyl Chloride Formation
Classical Equation: $3C_{17}H_{35}COOH + PCl_3 \longrightarrow 3C_{17}H_{35}COCl + H_3PO_3$

Experimental Facts

1. About 30% more PCl₃ is required than equation demands.
2. From 10–20% of Cl from PCl₃ is evolved as HCl. This originates from lower layer interface, and not at beginning.
3. The lower layer is not phosphorous acid; its density is much higher.
4. At slightly elevated temperatures bright yellow-colored pyrophoric phosphorus-containing deposits are formed.
5. In the presence of oxygen, chlorine enters the aliphatic chain at methyl group.

facts which have been observed in the formation of stearoyl chloride and which are at variance with the classical chemical equation most frequently written to describe this reaction. In Table VII we have assembled what appears to us to be a composite explanation of this complicated reaction in the light of most recent experimental data. It is consistent to suppose, and infrared absorption spectra supports, the notion that the reaction passes through fatty acid anhydride as an intermediate. One should remember that fatty acid chloride is itself the mixed anhydride of a fatty acid and hydrogen chloride. Further research will undoubtedly elucidate the nature and intricacies of this complex halogenation.

The direct fluorination of fatty acids and derivatives by substitution is a field in which much progress can be expected. Despite the fact that fluorine is far too reactive to be applied for the direct halogenation of organic compounds, there are now diluent techniques which can control the violence of direct fluorination and promise to afford a degree of specificity. Furthermore, fluoro derivatives can be prepared by the replacement of halogens, usually chlorine, already introduced into the parent molecule by substitution. The terminally fluoro-substituted acids and their methyl esters from acetic to octadecanoic, including 2-dodecenoic and 2-tridecenoic, have been prepared from 1,1,1,3-tetrachloropropane by a series of halogen

TABLE VII
Stearoyl Chloride Formation

Possible Explanations

1. The reaction is obviously not fourth order; it passes through fatty acid anhydride.
2. HCl is not formed predominantly by
$$RCOOH + RCOCl \longrightarrow (RCO)_2O + HCl,$$
but rather by
$$PCl_3 + 5H_3PO_3 \longrightarrow 3H_4P_2O_5 + 3HCl,$$
also
$$6RCOOH + PCl_3 \longrightarrow 3(RCO)_2O + 3HCl + H_3PO_3.$$
3. Lower layer conforms to pyrophosphorous acid, H₄P₂O₅.
4. There are at least six side reactions.

(a) $RCOOH + RCOCl \longrightarrow (RCO)_2O + HCl$
(b) $PCl_3 + 5H_3PO_3 \longrightarrow 3H_4P_2O_5 + 3HCl$
(c) $(RCO)_2O + HCl \longrightarrow RCOCl + RCOOH$
(d) $CH_3(CH_2)_nCOOH \longrightarrow Cl_2PO(CH_2)_{n+1}COOH$
(e) Complex phosphorus reductions.

exchange and chain lengthening methods (14). Electrolytic fluorination methods (15) have now been devised suitable either for the preparation of perfluoro derivatives, in which all the chain hydrogen atoms are replaced by fluorine atoms, or for monofluoro compounds. The telomerization of tetrafluoroethylene, $F_2C = CF_2$, provides fluoro-containing alcohols with one hydrogen atom remaining on the terminal carbon atom (16):

$$n(F_2C = CF_2) + CH_3OH \longrightarrow$$
$$H(F_2CCF_2)_nCH_2OH \longrightarrow H(F_2CCF_2)_nCOOH$$
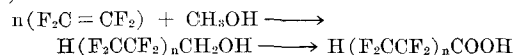
Perfluorocyclohexene, on oxidative cleavage, affords octafluoroadipic acid (17):

$$\xrightarrow{KMnO_4} \quad HOOC(CF_2)_4COOH$$
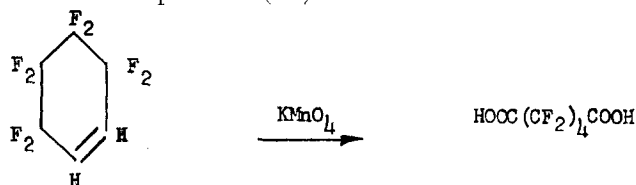
Economic Aspects of Halogenation

Some appreciation of the cost of production of representative halogenated fatty acid derivatives is valuable in projecting commercial chemical development for halogenated fatty products for use as such. The raw materials, the four free halogens, are available today at the large tonnage prices given in Table VIII. Fluorine, while priced at $17.65/lb in 6 lb cylinders, is already available for sale in large quantities at $2.00/lb.

It is illuminating to present raw material costs for several of the 2-halofatty acids and to use these figures to make predictions concerning the costing of these products, even though large volume potential for these derivatives does not appear to be imminent. The basis for costing, as shown in Table IX, involves an 18¢/lb 90% stearic acid and the employment of the 100%-yield red phosphorus-catalyzed "ionic" substitution of hydrogen by halogen. Costs are calculated both with a credit for byproduct hydrogen halide (at one-half the market value for recovered HX), and for no credit for hydrogen halide. 2-Fluorostearic acid has been costed synthesized by this method despite the fact that fluorine is known not to enter into such directed halogenations.

An obvious conclusion that can be drawn from Table IX is that monoiodinated fatty acids fall into the "fine chemical" category in price, and that any applications for these materials must sustain the high price obviously required. The relatively high value of byproduct hydrogen bromide and hydrogen iodide, furthermore, dictate that for efficient production of the bromo and iodo derivatives recovery of the respective hydrogen halides must be achieved. In the case of the chloro and fluoro derivatives little savings in cost is obtained through recovery of hydrogen halides. The inexpensive monochlorinated stearic acid appears to offer the largest potential as a halogenated fatty intermediate, assuming that the several halogenated products function about equally in replacement reactions. While it is known that the bromo, iodo, and chloro derivatives perform about equally in dehydrohalogenations, it is unfortunately true that the "replacement reactivity" of the halogens varies directly with increasing molecular weight, or, in other words, not necessarily in the order of the cost of the intermediate halogenated derivatives. Whenever the intermediate or final use of the halogenated product permits, the chloro intermediate is obviously preferred.

Applications for Halogenated Fatty Derivatives

The various halogenated fatty derivatives which possess "methylene group-bound halogen" find two principal applications as reactive intermediates. They provide synthetic routes to other more desirable products such as fluoro-, amino-, nitro-, and various sulfur-containing products by direct replacement of the halogen with functional groups difficult to introduce into fats directly. For example: 2-halofatty acids provide α-aminoacids by simple ammonolysis:

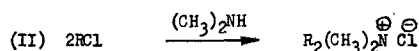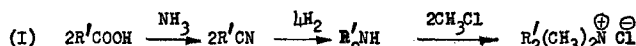$$RCHXCOOH + 2NH_3 \longrightarrow RCHNH_2COOH + NH_4X$$
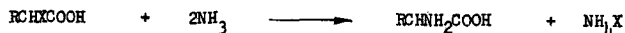
Modified fats more highly unsaturated than many of those found naturally, may be prepared by polychlorination of the long chains of vegetable oil-derived fatty acids followed by dehydrochlorination:

$$R-CH_2-CH_2- \xrightarrow{Cl_2} -CHCl-CH_2- \xrightarrow{-HCl} -CH=CH-$$
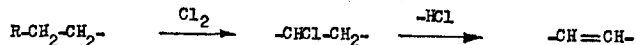
The Japanese (18) have reported the dehydrochlorination and degradation of chloro acids obtained from the chlorination of hydrogenated soybean fatty acids with sodium hydroxide and water at 290C. In France (19) a number of attempts have been made to dehydrochlorinate chlorinated stearic acid or methyl stearate in the liquid phase to polyunsaturated acids or esters by catalysis with metallic salts. Our own Department of Agriculture has directed its attention principally to the vapor phase dehydrochlorination of polychlorinated fatty acids over catalysts such as cobalt phosphate on pumice (20), or to the thermal dehydrochlorination of polychlorinated palmitic and stearic acids, their methyl esters and glycerides at 275–477C (21).

The difficulties in the preparation and use of these polyunsaturated fatty acids are that incomplete removal of chlorine by dehydrochlorination gives a product which is slightly more unstable than desirable and that in some instances the resulting polyunsaturated products do not "dry" as efficiently as naturally polyunsaturated materials do, presumably because of a difference in their geometrical arrangements of double bonds.

The long-chain alkyl halides, particularly the chlorides, are potentially useful in the preparation of quaternary compounds, which find extensive and versatile applications in many areas. Only the prevailing poor economics and the unavailability of the chloride corresponding in composition to the distribution of components found in hydrogenated tallow prevents a utilization of alkyl chloride in the manufacture of dimethyl dihydrogenated tallow ammonium chloride, a large tonnage quaternary finding large uses in household laundry softeners, paints, and bentone greases. This is normally prepared by the overall route (I) from hydrogenated tallow fatty acids, but the single-step quaternization (II) could be utilized:

(I) $2R'COOH \xrightarrow{NH_3} 2R'CN \xrightarrow{4H_2} R'_2NH \xrightarrow{2CH_3Cl} R'_2(CH_3)_2\overset{\oplus}{N} \overset{\ominus}{Cl}$

(II) $2RCl \xrightarrow{(CH_3)_2NH} R_2(CH_3)_2\overset{\oplus}{N} \overset{\ominus}{Cl}$

The fatty acid chlorides (which possess "carbonyl group-bound halogen") have found no direct use as such but provide the synthetic fatty acid chemist with a most valuable means of introducing fatty acyl

TABLE VIII
Bulk Halogen Prices
$/lb, May 1962

Iodine	1.10 crude	2.20 resublimed
Bromine	0.21	
Chlorine	0.043	
Fluorine	2.00 (projected)	(7.65,6 lb cylinders)

TABLE IX
Raw Material Costs for 2-Halo Fatty Acid Production

$$CH_3(CH_2)_{19}COOH + X_2 \xrightarrow{P} CH_3(CH_2)_{15}CHXCOOH + HX$$

Basis: Stearic acid, 90% at 18¢/lb.
100% yields, catalyst use at 2% of F.A., red P at 0.56/lb.
Costs calculated at 100% HX recovery, credited at ½ HX value, also for no HX recovery.

	Halogen costs $/lb May 1962	Hydrohalogen value $/lb	Cost halofatty acid $/lb	
			HX recovery basis	NO HX recovery basis
I	$2.20 (resubl.)	2.92/lb 47% HI	0.527	1.49
Br	0.21	0.48/lb 48% HBr	0.131	0.242
Cl	0.043	0.15	0.172	0.180
F	2.00 ($17.65) projected	0.16	0.427	0.432

groups into a whole host of organic and inorganic materials. Furthermore, in the majority of instances the conditions required to achieve reaction are mild and gentle. Under these conditions the parent fatty acids are usually entirely unreactive. This permits the acylation of such sensitive materials as glucosides, sugars, cellulose, hydroperoxides and a great many other compounds. Halogenated fatty intermediates have thus made possible a number of modified compounds not accessible by any other routes.

While the applications for halogenated derivatives for use as such are romantic and unique, ranging from arthritis cures to artificial rubber specialty plasticizer additives, it is doubtful whether any of the relatively minor present uses are important enough to warrant serious discussion. There is another development area worthy of watchful waiting. Already the polychlorinated fatty derivatives have shown some promise as antirotting, antibacteriocidic, flameproofing or fungicidic textile treating additives. They possess some of the properties that the more expensive chlorinated aromatics do, but lack the inherent stability of these materials. If some way could be discovered to stabilize polychlorinated fatty derivatives, that is, to prevent the slow deterioration which occurs through the evolution of hydrogen chloride, many applications for these products are sure to follow.

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