Reaction of Tertiary Butyl Hypochlorite With Vegetable Oils and Their Derivatives. II. Methyl Oleate[1]

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ALTHOUGH several investigators (2, 7, 11, 12) have described reactions of ethyl hypochlorite, the literature gives little information on the type of product to be expected from the reaction of *t*-butyl hypochlorite and olefinic compounds in the absence of a reactive solvent. Harford (9) has claimed the production of vinyl type halides; for example, 1-chloro-2-methylpropene-1 from isobutene and 2-methyl-3-chlorobutene-2 from trimethylethylene. On the other hand, Kenner (10) has reported a 65% yield of the allylic halide 3-chlorocyclohexene-1 from the reaction of cyclohexene and *t*-butyl hypochlorite under Ziegler's (20) conditions for effecting halogenation with positive halogen compounds. Hanby and Ryden (8) have described the preparation of the *t*-butyl ether of styrene chlorohydrin by the reaction at 25°C. of *t*-butyl hypochlorite and styrene in the presence of water.

In a previous paper (18) the reaction of *t*-butyl hypochlorite with soybean oil was described. It was noted that when soybean oil was chlorinated with an equivalent amount of *t*-butyl hypochlorite, from 50% to 75% of the halogen present could be eliminated thermally, but that the remaining halogen was resistant to removal by heat.

It was of interest therefore to examine the reaction of *t*-butyl hypochlorite with the methyl esters of the pure component fat acids of soybean oil. This paper reports the results of the study involving methyl oleate in which the conditions for reaction and the nature of the products were investigated.

Discussion

In the absence of catalysts the reaction between equimolecular amounts of methyl oleate and *t*-butyl hypochlorite proceeds slowly at room temperature, requiring 2 to 3 weeks for completion. The reaction is strongly accelerated by heat, ultraviolet light, and catalytic amounts of methyl α-eleostearate. Oxygen inhibits the reaction strongly.

The catalyzed reactions are strongly exothermic. Peak temperatures as high as 126° C. were reached when the reactants were mixed at 25°. In the subsequent discussion the reaction product after removal of by-product *t*-butyl alcohol will be called chlorinated methyl oleate.

To obtain information about the type of products formed, chlorinated methyl oleate was treated with alcoholic silver nitrate, both at room and at reflux temperatures. It was found that considerable halogen was removed at room temperature, that a further amount was removed at reflux temperature, and that a residue of halogen remained which was inert to refluxing alcoholic silver nitrate. By varying the time of contact and the excess of silver nitrate employed, procedures were developed for the removal of the maximum amount of halogen at room and reflux temperatures. Application of these procedures, which are empirical in nature and should not be expected to give more than roughly quantitative data, will be referred to as classification of halogen.

The data for classification of halogen in chlorinated methyl oleate prepared under a variety of conditions are summarized in Table I. These data indicate a correlation between the peak temperature reached during reaction and the proportion of chlorine reactive to hot and cold alcoholic silver nitrate. Thus, as the peak temperature increases, the amount of halogen reactive to hot silver nitrate increases, but that reactive to cold silver nitrate decreases. The amount of inert halogen remains essentially constant.

A series of chlorinations in the presence of solvents was also conducted. The results are given in Table II. When the solvent was *t*-butyl alcohol or carbon tetrachloride, reactions run at room temperature were strongly inhibited. The products, however, contained much greater amounts of halogen inert to alcoholic silver nitrate. When the reactions were catalyzed, the distribution of halogen was essentially the same as that found when solvents were absent. Chloroform did not significantly inhibit the reaction at room temperature. The amount of inert halogen was increased in both the catalyzed and uncatalyzed reactions. Peak temperatures were low in all catalyzed reactions owing to the increased volume resulting from the presence of the solvent.

Dehydrochlorination of chlorinated methyl oleate at 200°C. and 5 mm. pressure eliminated from 62% to 100% of that part of the halogen which originally could be removed by alcoholic silver nitrate at room temperature. Simultaneously, diene conjugation was produced in an amount approximately equivalent to the halogen eliminated. The remaining halogen consisted principally of types reactive and inert to hot silver nitrate. The proportions of these types of halogen, expressed as fractions of the total halogen in the original sample, were of the same order of magnitude as in the sample before dehydrochlorination.

Dehydrochlorination at 280°C. and 30 mm. pressure removed all halogen reactive to cold silver nitrate and from 25% to 95.3% of that reactive to hot silver nitrate. The amount of diene conjugation produced did not exceed that formed by dehydrochlorination at the lower temperature. The amount of inert halogen expressed as a fraction of the total halogen in the original sample was somewhat smaller after dehydrochlorination than it was before. In the spectrophotometric determination of conjugation no absorption similar to that of crotonic esters was observed. The data obtained are given in Tables III and IV.

These observations concerning classification of halogen and dehydrochlorination led to the conclusion that chlorinated methyl oleate consists mainly of a

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TABLE I

Chlorination of Methyl Oleate With *t*-Butyl Hypochlorite

Experiment No.	Conditions	Base temperature °C.	Peak temperature °C.	Cl %	Fraction of total Cl removed by $AgNO_3$–EtOH		
					Cold %	Hot [1] %	Inert %
1	Dark	−10	......[2]	1.14[3]	64.0	15.8	20.2
2	Dark	25	......[2]	10.51[4]	53.0	26.1	20.9
6	Dark; 0.5% methyl α-eleostearate	25	115	8.99	51.7	28.6	19.7
5	Ultra-violet radiation	25	126	9.33	49.5	30.5	20.0
3	Dark	100	131	8.20	46.6	34.8	18.6
4	Dark	130	178	7.79	41.8	33.4	24.8

[1] Total removed hot less that removed cold. [2] Reactions at constant temperature. [3] After 23 days. [4] After 17 days.

mixture of a) an allylic chloride; b) a secondary chloride in which the halogen atom is not adjacent to either the double bond or the carbomethoxy group; c) a saturated dichloride; and d) unreacted methyl oleate.

The validity of this conclusion would be strengthened if it could be shown that fatty derivatives of the types specified actually possess the properties they were assumed to have in postulating the composition of chlorinated methyl oleate. This problem was attacked through the study of model compounds. No fatty material appeared suitable for the preparation of an allylic halide by an unequivocal method; however, the reactivity of allylic halogen towards cold alcoholic silver nitrate is so well established as to leave little doubt that chlorinated methyl oleate contains such halogen. Model compounds containing the other types of halogen were readily prepared and, as described subsequently, their properties were found to be those expected.

The postulated composition of chlorinated methyl oleate was further substantiated by comparing the observed iodine value with that calculated from the apparent composition by weight of the mixture expressed in terms of the suggested components. Excellent agreement was obtained except in Experiment 11 as shown by the data in Table V. This agreement seems to preclude the presence of significant amounts of vinyl halides and methyl *t*-butoxychlorostearate in methyl oleate chlorinated in the absence of solvents.

In Experiment 11 chlorination was obtained at 25°C. in the presence of a third substance (chloroform) which might be expected to participate in a free-radical reaction and yet did not inhibit reaction, as shown by the percentage of chlorine in the product. These conditions are quite similar to those employed by Hanley and Ryden (8). It therefore seems reasonable to attribute the discrepancy between calculated and observed iodine values found in Experiment 11 to the presence of methyl *t*-butoxy chlorostearate.

Behavior of Model Compounds. Several model substances were studied to determine their behavior towards alcoholic silver nitrate and thermal dehydrochlorination. These included methyl 9,10-dichlorostearate, ethyl stearate chlorinated with *t*-butyl hypochlorite, and the chlorides obtained from methyl 12-hydroxystearate and methyl ricinoleate by replacement of the hydroxyl group with chlorine. The data obtained are given in Table VI.

With the exception of the chloride from methyl ricinoleate these compounds behaved generally in the expected manner. The amount of halogen removed by hot silver nitrate from the chlorides from ethyl stearate and methyl 12-hydroxystearate was lower than anticipated, but it was found that an increase in the excess of silver nitrate used in the analysis resulted in removal of 96% of the halogen in the chloride from methyl 12-hydroxystearate. This result was obtained because the sample contains substantially more non-allylic halogen than does chlorinated methyl oleate for which the halogen classification procedure was developed.

Methyl 9,10-dichlorostearate was found to be almost completely inert to either cold or hot silver nitrate and to dehydrochlorination at 200°C. About 25% of its halogen was however eliminated at 280°, thus accounting for the decrease in inert halogen observed when chlorinated methyl oleate was dehydrochlorinated at 280°.

The chloride from methyl ricinoleate showed several peculiarities in behavior. Thus, this chloride was found to have 24.6% of its halogen in a form reactive to cold silver nitrate. This phenomenon is undoubtedly an example of the well-known fact that long-chain secondary alcohols form mixtures during reactions involving replacement of the hydroxyl group. Replacement of the 12-hydroxyl group in methyl ricinoleate might thus be expected to lead to a mixture of at least the 13-, 12-, and 11-chloro derivatives, of which the latter would be an allylic chloride.

TABLE II

Chlorination of Methyl Oleate With *t*-Butyl Hypochlorite in the Presence of Solvents

Experiment No.	Solvent	Conditions	Peak temperature °C.	Cl %	Fraction of total Cl removed by $AgNO_3$–EtOH		
					Cold %	Hot [1] %	Inert %
7	*t*-BuOH	Dark[2]	......[3]	1.62	19.7	29.1	51.2
8	*t*-BuOH	Ultra-violet radiation[4]	62.5	9.18	54.2	25.6	19.2
9	CCl_4	Dark[2]	......[5]	0.47	3.4	12.2	84.4
10	CCl_4	Ultra-violet radiation[4]	73.0	10.09	48.4	31.9	19.7
11	$CHCl_3$	Dark[2]	......[6]	8.38	8.9	14.7	76.4
12	$CHCl_3$	Ultra-violet radiation[4]	63.0	8.30	38.8	19.6	41.6

[1] Total removed hot less that removed cold. [2] 15 ml. solvent per g. oil. [3] Reaction at constant temp. (25°) for 22 days. [4] 9 mol. solvent per mol. of oil. [5] Reaction at constant temp. (25°) for 24 days. [6] Reaction at constant temp. (25°) for 16 days.

TABLE III

Dechlorination of Chlorinated Methyl Oleate at 200°C. and 5-mm. Pressure

Experiment No.[1]	Cl original %	Cl after dechlorination %	Fraction of original Cl removed %	Fraction of original Cl equivalent to conjugation[2] %	Conjugation			Fraction of original Cl removed by $AgNO_3$–EtOH		
					Diene %	Triene %	Tetraene %	Cold %	Hot[3] %	Inert %
2	10.51	6.25	40.6	38.4	31.6	0.97	0.04	11.9	30.6	16.9
6	8.99	4.86	46.0	48.8	28.7	1.18	0.07	3.2	30.8	20.0
5	9.33	5.65	39.5	38.1	27.8	0.84	0.04	7.6	34.0	18.9
3	8.20	5.87	28.4	32.2	21.4	0.26	0.02	14.0	37.1	20.5
4	7.79	5.99	24.4	24.7	15.8	0.18	0.02	15.9	35.6	23.1
12	8.30	5.61	32.4	33.2	21.8	0.55	0.02	3.0	19.8	44.8
8	9.18	4.07	55.7	49.2	32.0	2.72	0.10	0.7	28.6	15.0

[1] See Tables I and II. [2] See text for calculation. [3] Total removed hot less that removed cold.

Most unexpectedly, it was found that the chloride from methyl ricinoleate lost comparatively little of its halogen during dechlorination either at 200° or 280°C. Instead, the allylic-type halogen was converted into forms relatively stable even at 280°. This change occurred during heating at 200° but did not appear to proceed further during heating at 280°. These observations clearly indicate the occurrence of some type of thermally induced rearrangement or isomerization. No data is available which might indicate more definitely the nature of these stable halogen derivatives. Apparently some change of this type also occurred during dehydrochlorination of chlorinated methyl oleate at 200° since it may be noted from Tables I, II, and III that all but one of the dehydrochlorinated samples contained somewhat more halogen reactive to hot silver nitrate than did the original sample. Further indication of structural changes was noted during a molecular distillation discussed subsequently.

Attempted Isolation of Components of Chlorinated Methyl Oleate. Experiments were directed toward the isolation of the components of the mixture. For isolation of the saturated methyl dichlorostearate a sample of chlorinated methyl oleate prepared in chloroform solution was selected because such preparations were known to contain the higher percentages of halogen inert to refluxing alcoholic silver nitrate. By dehydrochlorination at 280° C., distillation, and low temperature crystallization a material having the properties of methyl dichlorostearate was isolated. The melting point of this compound was identical with and did not depress the melting point of methyl 9,10-dichlorostearate. However, because closely related long-chain fatty acid derivatives frequently form eutectic mixtures separable only with extreme difficulty and because shift of the double bond is known to occur (1, 3, 14, 18) during various types of substitution of long-chain fatty acid derivatives, it cannot be concluded that the isolated compound is necessarily the 9,10 derivative.

Because of the low decomposition temperature of the non-allylic monochloride, molecular distillation was employed in an attempt to isolate this material from chlorinated methyl oleate which had been dehydrochlorinated below 200° C. Data are given in Table VII. This distillation separated the unchlorinated material from that containing chlorine, but separation of monochlorinated material from dichlorinated material was unsatisfactory. It appears that volatility in the molecular still was influenced more by introduction of one atom of chlorine into the previously unchlorinated methyl oleate than by introduction of the second chlorine atom into the monochlorinated material.

The fraction volatile at 76°-79° C. and the nonvolatile fraction contained more halogen reactive to hot silver nitrate and less inert halogen than would be expected from the composition of the original dehydrochlorinated ester. This appears to indicate that an isomerization or other undesired reaction occurred during the distillation, a surprising result in view of the low temperatures involved.

Mechanism of the Reaction. The reaction of *t*-butyl hypochlorite with methyl oleate to produce allylic halide is apparently a chain reaction which may proceed according to the following equations:

$$(CH_3)_3COCl \longrightarrow Cl\cdot + (CH_3)_3CO\cdot \quad \ldots\ldots\ldots \quad (I)$$

$$R{-}CH{=}CH - CH_2 - R^1 + (CH_3)_3CO\cdot \longrightarrow$$
$$R{-}CH{=}CH - \underset{\bullet}{C}H - R^1 + (CH_3)_3COH \quad \ldots\ldots \quad (II)$$

$$R{-}CH{=}CH - \dot{C}H - R^1 + (CH_3)_3COCl \longrightarrow$$
$$R{-}CH{=}CH - CHCl - R^1 + (CH_3)_3CO\cdot \quad \ldots\ldots \quad (III)$$

Attack of the *t*-butoxy radical at a methylene group not adjacent to the double bond should occur to a lesser extent with formation of a non-allylic secondary halide. In either case termination of the chain

TABLE IV

Dehydrochlorination of Chlorinated Methyl Oleate at 280°C. and 30-mm. Pressure

Experiment No.[1]	Cl original %	Cl after dechlorination %	Fraction of original Cl removed %	Fraction of original Cl equivalent to conjugation[2] %	Conjugation			Fraction of original Cl removed by $AgNO_3$–EtOH		
					Diene %	Triene %	Tetraene %	Cold %	Hot[3] %	Inert %
2	10.51	3.41	67.5	35.5	28.4	1.26	0.01	0.0	1.68	15.7
5	9.33	3.63	61.1	39.5	26.9	1.86	0.04	0.2	22.9	16.0
8	9.18	1.24	86.5	42.0	29.6	1.20	0.03	0.0	1.2	12.3

[1] See Tables I and II. [2] See text for calculation. [3] Total removed hot less that removed cold.

would result from any of several reactions of the *t*-butoxy radical such as decomposition (13), combination with a fat acid radical, or recombination with a chlorine atom.

The formation of a saturated dichloride may be explained by direct addition of chlorine atoms to the double bond or by the following reactions:

$$\mathrm{R{-}CH{=}CH - CH_2 - R^1 + Cl\cdot \longrightarrow R{-}CH{=}CH - \underset{\bullet}{C}H - R^1 + HCl} \quad . \; . \; . \; . \; . \; . \; . \quad \mathrm{(IV)}$$

$$\mathrm{(CH_3)_3COCl + HCl \longrightarrow (CH_3)_3COH + Cl_2} \quad . \; . \; . \quad \mathrm{(V)}$$

$$\mathrm{R{-}CH{-}CH - CH_2 - R^1 + Cl_2 \longrightarrow RCHClCHClCH_2R^1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \mathrm{(VI)}$$

Reaction (IV) would be expected to occur to a lesser extent than reaction (II) since the heat evolved in combination of a hydrogen and a chlorine atom is about 22 kcal. per mole (16) whereas Skell (15) estimates that 106.5 kcal. per mole are liberated in combination of the *t*-butoxy radical and a hydrogen atom. The fat acid radical produced in reaction (IV) could then participate in reaction (III). Comastri (4) has indicated the possibility of reaction (V).

TABLE V

Composition by Weight and Iodine Value of Chlorinated Methyl Oleate

Experiment No.[1]	Allylic monochloride %	Non-allylic monochloride %	Saturated dichloride %	Unreacted oleate %	Iodine Value	
					Obs.	Calc'd
2	50.6	25.1	12.4	11.9	64.0	67.0
6	42.2	23.5	10.1	24.2	69.7	70.0
5	41.5	26.1	10.7	21.7	69.0	70.0
3	34.4	26.4	8.9	30.3	70.4	71.2
4	29.0	23.8	11.0	36.2	71.9	70.3
11	5.5	9.9	34.7	49.9	44.5	53.5

[1] See Tables I and II.

Experimental

Starting Materials. Methyl oleate was prepared from methyl esters of red oil by the procedure of Swern, Knight, and Findley (17). It had an iodine value of 84.0 (calculated 85.5). *t*-Butyl hypochlorite was prepared by a previously described method (18).

Methyl 9,10-dichlorostearate was prepared by chlorination of methyl oleate according to the procedure used by Van Atta, Houston, and Dietrich (19) to obtain 9,10-dichlorostearic acid. The product contained 17.8% chlorine (calculated 19.3) and had an iodine value of 7.65 (calculated 0.0). These data indicate that the product contained 91-92% of methyl 9,10-dichlorostearate. The melting point was 5°-7°C.

Chlorinated ethyl stearate was prepared from pure ethyl stearate by chlorination with *t*-butyl hypochlorite using ultra-violet light as a catalyst. See discussion of methods of chlorination below.

Chlorination With t-Butyl Hypochlorite. The apparatus was constructed from the male and female components of a $\frac{29}{42}$ standard taper joint. The male component was closed with a cork stopper (Note: Rubber will react violently with *t*-butyl hypochlorite) fitted with a mechanical stirrer passing through a close-fitting glass sleeve, a thermocouple well, a gas-inlet tube, a small funnel, and a vent. The reaction flask was made by closing the end of the female component of the joint. The stirrer and thermocouple well reached the bottom of the reaction flask while the gas-inlet tube was arranged so that it could be inserted or withdrawn as needed to supply inert gas below or above the surface of the reaction mixture. The length of the apparatus obviated the need of a condenser. In those chlorinations where the initial temperature of the methyl oleate was high, a jet of air just below the joint was sufficient to insure condensation.

TABLE VI

Halogen Classification Data for Several Model Compounds

Analysis \ Compound	Chlorinated ethyl stearate	Chloride from methyl ricinoleate (crude)	Chloride from methyl 12-hydroxystearate (crude)	Methyl 9,10-dichlorostearate
Cl, original %	8.56	6.94	5.48	17.79
Classification:[1]				
Removed cold, %	5.5	24.6	0.0	1.9
Removed hot,[2] %	30.0	61.2	78(96)[3]	1.1
Inert, %	64.5	14.2	22(4)[3]	97.0
Cl, after dechlorination at 200°C., %	8.56	6.53	5.48	17.79
Fraction removed, %	0.0	5.9	0.0	0.0
Classification:[1]				
Removed cold, %	......	1.1	0.0	......
Removed hot, %	......	72.0	70.0	......
Inert, %	......	21.0	30.0	......
Cl, after dechlorination at 280°C., %	2.70	6.17	2.95	13.40
Fraction removed, %	68.5	11.2	46.2	24.7
Classification:				
Removed cold, %	......	2.3	......	......
Removed hot,[2] %	......	68.3	......	......
Inert, %	......	18.0	......	......

[1] Fraction of halogen in original sample expressed as %.

[2] Total removed hot less that removed cold.

[3] Figures in parentheses obtained with 4 times usual excess of silver nitrate.

To eliminate the possible introduction of small bits of rubber or other contaminant from rubber hose used to connect the supply of inert gas, a tuft of cotton was inserted in the upper end of the gas-inlet tube. This tube was then fitted with a cork stopper and inserted in the wide end of a drying tube loosely filled with cotton. Connection to the hose was made at the opposite end of the drying tube.

Temperatures were measured with a copper-Constantan thermocouple connected to a recording potentiometer.

Chlorinations were conducted on 5-g. samples of methyl oleate. An equimolecular amount (1.83 g.) of *t*-butyl hypochlorite was used. Since the hypochlorite was poured into the apparatus from a small beaker, it was necessary to determine the average hold-up by the beaker. Allowance was then made for this hold-up.

The procedure followed in a typical chlorination was as follows: The 5-g. sample of methyl oleate was placed in the reaction tube and stirred. The

TABLE VII

Molecular Distillation of Chlorinated Methyl Oleate

Sample	Cl %	Halogen[1] removed by $AgNO_3$–EtOH		
		Cold %	Hot[2] %	Inert %
Chlorinated methyl oleate	10.17	5.56	2.91	1.70
Same, dehydrochlorinated	5.95	1.23	3.24	1.48
Fraction volatile at 50°-55°	1.92	0.08	1.24	0.68
Second fraction volatile at 51°-54°[3]	5.21	0.66	3.72	1.49
Fraction volatile at 76°-79°	13.30	3.00	9.01	4.29
Fraction non-volatile at 76°-79°	16.82	3.94	11.96	4.86

[1] Actual per cent by weight. [2] Total removed hot less that removed cold. [3] See text.

gas-inlet tube was adjusted to admit a gentle stream of carbon dioxide below the surface. Stirring and flushing with carbon dioxide were maintained for 30 minutes to remove oxygen introduced during weighing. At the end of this time the gas-inlet tube was withdrawn from beneath the liquid, but the current of gas was continued in order to provide an inert atmosphere. While stirring was continued, the proper amount of *t*-butyl hypochlorite was added and the reaction mixture was irradiated with ultra-violet light (quartz mercury-vapor lamp without filter). The temperature was then observed to rise first slowly, then quite rapidly, finally reaching a peak of 126.5° C. After the reaction mixture had cooled, by-product *t*-butyl alcohol was removed at reduced pressure (1 mm. or less) by passage of a stream of carbon dioxide. Temperature was maintained at or below room temperature. Evaporation was continued until the weight of the residue was constant.

The reaction was also catalyzed by heat or by the addition of one drop of methyl α-eloastearate. Even in complete absence of light the reaction was strongly exothermic. In the absence of catalysts the reaction proceeded slowly, requiring 2 to 3 weeks for completion. Nevertheless, the uncatalyzed reaction was the most convenient for preparative purposes because no sudden rises in temperature occurred and no special equipment was required. It was sufficient to place the desired amount of methyl oleate in a flask, flush for 30 minutes with carbon dioxide, add the proper amount of hypochlorite, close the flask with a glass stopper, and set the assembly aside in a dark place for several weeks.

Reaction was judged complete when the characteristic odor and color of the hypochlorite had disappeared. Quantities of methyl oleate as large as 50 g. have been chlorinated in this way, and there is no indication against chlorination of even larger amounts if desired. Standing for prolonged periods after chlorination was complete caused some yellowing of the product. Colorless products were obtained by working up the reaction mixture promptly after reaction was complete and by avoiding exposure to temperatures above room temperature. Samples may be preserved indefinitely in a colorless condition by storage at 0° under carbon dioxide.

Tables I and II contain data for typical chlorinations under a wide variety of conditions.

Methods of Analysis. Iodine numbers were determined by the standard 30-minute Wijs method. Chlorine content was determined by fusion with sodium peroxide in a Parr bomb, followed by Volhard titration. Conjugation was determined with a Beckman spectrophotometer.

The amount of halogen removed from the samples by alcoholic silver nitrate was determined at room temperature and at reflux temperature. A 0.2000-g. sample of oil was weighed into a 50-ml. Erlenmeyer flask with ground-glass joint. The sample was dissolved in 10 ml. of ethanol, and to this was added 10 ml. of 0.1 *N* solution of silver nitrate in ethanol for reactions at room temperature or 20 ml. of the standard silver nitrate for reactions at reflux. Samples at room temperature were allowed to stand 5 hours, diluted with 50 ml. of water, acidified with 5 ml. of 0.5 *N* nitric acid, and titrated with 0.1 *N* potassium thiocyanate. Samples at reflux were refluxed 10 hours (occasionally a thin silver mirror appears on the flask; this does not alter the result within experimental error), diluted with 100 ml. of water, acidified with 10 ml. of 0.5 *N* nitric acid, and titrated with thiocyanate. Samples may be allowed to stand several hours after completion of reflux and before dilution without altering the results.

Thermal Dehydrochlorination. A sample weighing approximately 1 g. was introduced into a 50-ml. Erlenmeyer flask fitted with a ground-glass joint and a vertical condenser through which connection was made to the vacuum source. To eliminate allylic halogen the flask was evacuated to a pressure of about 5 mm. and immersed in a Wood's metal bath previously heated to 195°-200°C. The flask was kept at this temperature until the contents stopped bubbling, usually about 30 minutes. See Table III.

To eliminate non-allylic halogen the temperature and pressure were raised to 275°-280°C. and 30 mm. These conditions were maintained for one hour or until evolution of hydrogen chloride had ceased. This point was readily recognized both by the disappearance of white fumes over the heated liquid and by the cessation of bubbling. Bubbling was easily distinguished from ebullition of the liquid which usually consisted of occasional, comparatively violent bumping. See Table IV.

Calculations. From the data obtained through classification of halogen with alcoholic silver nitrate the composition by weight of the reaction product and its expected iodine number were calculated on the assumption that the product consisted of a mixture of unreacted methyl oleate, allylic monochloride, non-allylic monochloride, and saturated dichloride. Since experiments with model compounds indicated that the non-allylic monochloride liberates a small amount of halogen with alcoholic silver nitrate, correction should be made in calculating the composition. This was done by the method of successive approximations (5).

The composition was first calculated without making any correction. The resulting percentages were used in conjunction with the halogen classification data (Table VI) for chlorinated ethyl stearate and methyl 9,10-dichlorostearate to calculate first approximate corrections. These were used in calculating the first corrected composition by weight which was again employed to obtain second approximate corrections. This process was continued until the corrections were constant to the desired number of decimal places. In calculating the data given in Table V, it was found that the necessary corrections were quite small. It was therefore unnecessary to proceed beyond calculation of the first corrected composition by weight.

Data given in Tables III and IV for the percentage of original chlorine equivalent to conjugation (P) formed during dehydrochlorination were calculated from the following formula:

$$P = \text{Per cent diene (or triene)} \times \frac{35.45}{294.48 \text{ (or } 292.48)} \times \frac{100}{\text{total per cent Cl.}}$$

In this formula 294.48 and 292.48 are the molecular weights of methyl linoleate and linolenate, respectively. "Total per cent Cl" is the per cent of chlorine in the original sample. The formula allows for the change in weight during dehydrochlorination and also takes account of the fact that chlorine analysis gives directly a percentage by weight whereas conjugation, determined spectroscopically, is expressed as the ratio of the absorption *by* the sample to that *by* a standard.

In considering the data and in making calculations, it is important to distinguish "per cent of chlorine" from "per cent or fraction of original chlorine." The first expression refers to the actual percentage of chlorine in a given sample, as determined analytically. The second expression indicates the ratio (expressed as per cent) of the actual percentage of chlorine in a processed sample to that in the sample before processing.

Isolation of Methyl Dichlorostearate From Chlorinated Methyl Oleate. A sample of methyl oleate chlorinated (room temperature in darkness) in chloroform solution was used. This material contained 8.38% chlorine; 76.4% of this halogen was inert to refluxing alcoholic silver nitrate. A 2.05-g. sample was placed in a 10-ml. alembic flask and distilled at 0.6-0.75-mm. pressure. No capillary or other boiling aid was used, and heat was applied very cautiously in order to secure distillation without ebullition. This procedure was necessary because a stable foam, which filled the distillation flask and ran over into the receiver, was produced by ebullition, bumping, and introduction of gas through a capillary.

A fraction weighing 0.57 g. was collected at a pot temperature of 199°-230° at 0.6-mm. pressure. No further distillate was obtained by increasing the pot temperature to 271°. This fraction contained 14.6% chlorine and had an iodine value of 19.5.

It was crystallized 3 times from methanol at —40° to —50°C., once at a solvent ratio of 10 g. per g., and twice at a solvent ratio of 5 g. per g. It then melted at 5°-7° and contained 19.2% chlorine (calculated 19.3%). The melting point of a mixture of this product and methyl 9,10-dichlorostearate was also 5°-7°.

Preparation of Chlorides From Methyl Ricinoleate and Methyl 12-Hydroxystearate. Methyl ricinoleate and methyl 12-hydroxystearate were converted to chlorides by the method of Darzens (6). The reaction with methyl 12-hydroxystearate, a solid, was conducted in benzene solution to promote mixing. The chloride from methyl ricinoleate contained 6.92% chlorine (calculated 10.71%) and that from methyl 12-hydroxystearate contained 5.48% chlorine (calculated 10.65%). These products were used without further purification. See Table VI.

Molecular Distillation of Methyl Chlorooleate. A 50-g. sample of methyl oleate was chlorinated by mixing with 18.3 g. of *t*-butyl hypochlorite and allowing the mixture to stand in the dark at room temperature for two weeks. *t*-Butyl alcohol was removed from the reaction mixture by evaporation *in vacuo* at room temperature. The alcohol was collected by a series of four traps cooled with Dry Ice and acetone. Recovery of alcohol was 96% of the theoretical. It was dehydrochlorinated to remove allylic halogen by heating for 6 hours at 150°-160°C. and 2 hours at 180°. The pressure was maintained at or below 1 mm. Chlorine analysis and data on the classification of halogen in the sample before and after dehydrochlorination are given in Table VII.

A sample of the dehydrochlorinated ester weighing 43.9 g. was distilled in a falling film molecular still at a pressure of 3-5 microns. The sample was passed through the still twice at 50°-55°C. to obtain a volatile fraction weighing 23.0 g. The non-volatile fraction (19.5 g.) was passed through the still at 100°-103° and found to be almost completely volatile. This volatile fraction (19.4 g.) was therefore again passed twice through the still at 51°-54°. A volatile fraction weighing 8.0 g. was obtained. The non-volatile fraction (10.5 g.) was then passed through the still at 76°-79°, yielding a volatile fraction weighing 8.1 g. and a non-volatile fraction weighing 1.5 g. Chlorine analyses and data on halogen classification for these fractions are also given in Table VII.

Summary

1. The chlorination of methyl oleate with *t*-butyl hypochlorite under varied conditions of reaction has been investigated.

2. Chlorinated methyl oleate obtained by this reaction appears to consist of mixture of an allylic monochloroderivative, a non-allylic monochloroderivative, and a saturated dichloroderivative.

3. Methyl 9,10-dichlorostearate, chlorinated ethyl stearate, and chlorides from methyl ricinoleate and methyl 12-hydroxystearate were prepared, and their behavior towards thermal dehydrochlorination and towards hot and cold alcoholic silver nitrate was studied.

4. A saturated dichloro derivative, possibly methyl 9,10-dichlorostearate, has been isolated from chlorinated methyl oleate.

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