Addition of Chlorine to Unsaturated Fatty Acids and Esters[1]

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THE ADDITION of halogens to the unsaturated fatty acids or their derivatives is one of the important and frequently employed reactions in fatty acid chemistry. Such reactions not only offer many synthetic possibilities but also form the basis of several analytical procedures. While bromine and iodine have been used widely in this application, the use of either chlorine or fluorine has received little attention.

Addition of chlorine to such compounds has been reported by Piotrowski (2), who obtained from elaidic acid a 9,10-dichlorostearic acid melting at 32°C., and Van Atta *et al.* (4), who chlorinated both oleic and linoleic acids. The latter group used less than the theoretical amount of chlorine and obtained mixtures of the chlorinated acids and the starting compounds. Teeter and Jackson (3) used Van Atta's procedure to add chlorine to methyl oleate, obtaining methyl 9,10-dichlorostearate of estimated 91–92% purity which melted at 5–7°C. These workers also isolated a saturated dichloro ester from a mixture which resulted when *t*-butyl hypochlorite acted upon methyl oleate, which may have been methyl 9,10-dichlorostearate. Bouquet and Paquot (1) reported obtaining 9,10-dichlorostearoyl chloride from the action of sulfuryl chloride on oleic acid, and the corresponding acid by saponification and acidification. In nearly all such reports there was a lack of purity of the product obtained, or failure to describe the physical properties when pure compounds were produced.

Experimental

Chlorination of Methyl Oleate. A solution of 50 g. of methyl oleate[3] in 150 ml. of chloroform in a 500-ml., 3-necked flask was immersed in acetone in a Dewar flask and cooled to —20°C. by addition of "dry ice." Chlorine gas was introduced into the stirred solution through a sintered glass disperser at such a rate that the reaction temperature remained at —20°C. ± 2 while the bath temperature was maintained at —35°C. After 25 min. a sudden drop in temperature occurred, which was thought to indicate the completion of the addition reaction. The flow of chlorine was stopped immediately, and the mixture was stirred for 1 hr. at —20°C., or below.

Excess chlorine was then removed from the solution by reducing the pressure to about 25 mm. and allowing a small stream of nitrogen to sweep the flask. The reaction mixture was kept dark during the entire reaction and during removal of chlorine to decrease the tendency toward substitution. After removal of chloroform under reduced pressure a residue of 62 g. of colorless oil (100% yield) remained. This material had the following properties: N_D^{25} 1.4649, m.p. 5.5–7.5°C., chlorine: found 19.15%, theory for methyl dichlorostearate 19.30%. A cooled hexane solution yielded white crystals which melted at 10–11°C.; the refractive index and chlorine content however remained essentially unchanged.

Oleic acid chlorinated in the same way also produced approximately quantitative yields of the expected products. Solvents other than chloroform were also satisfactory media for chlorination; carbon tetrachloride and an equal-volume mixture of chloroform and glacial acetic acid were used with no apparent difference in the rate of reaction or quality of product.

The temperature of chlorination was found to be critical. In a trial chlorination of methyl oleate at 0 to —5°C., using an ice-salt bath, a noticeable quantity of HCl was evolved. At —10°C. ± 2 there seemed to be no HCl formation. Various reaction temperatures below —10°C. were tried with no apparent differences in the rate of chlorine absorption and only minute differences in the product (Table I).

TABLE I

Properties of Products Obtained from Chlorination of Methyl Oleate at Various Temperatures (50 g. methyl oleate in 150 cc. chloroform).

Expt.	Temp.	Wt.	Iodine No.	N_D^{25}	M.P.	Chlorine[a]	Yield
	°C.	*g.*			*°C.*	%	%
1	0 to —5	59	1.3	1.4659	......	....	95
2	—10 ±2	62	0	1.4648	7–8	18.87	100
3	—20 ±2	62	0	1.4639	5.5–7.5	19.15	100
4	—30 ±2	61	0	1.4653	6.5–8.5	19.20	98
5	—40 ±2	62.5	0	1.4647	6.5–8.5	18.98	101

[a] Theory: 19.30%.

Distillation of Methyl Dichlorostearate. A 50-g. sample of impure methyl dichlorostearate (mother liquors from several recrystallizations) was distilled from a Claisen flask through a 12-in. section of Vigreux-type indented column at reduced pressure (*ca.* 1 mm.). A capillary introduced nitrogen to the bottom of the pot to prevent excessive bumping. Three fractions were obtained (Table II).

TABLE II

Fractions Obtained on Distillation of Crude Methyl Dichlorostearate

Fraction	Boiling Range °C.	mm. of Hg.	Weight grams	N_D^{25}
1	135–192	1.0–0.9	4	1.4554
2	192–202	0.9	5	1.4621
3	190–200	0.6	23	1.4641
Residue			18	1.471

Fraction 3 was a light yellow liquid with a melting range of 3–6°C. and a chlorine content of 17.7%. No decomposition was noticed during distillation.

Removal of Chlorine from Methyl Dichlorostearate. Treatment of methyl dichlorostearate or dichlorostearic acid with zinc and alcoholic HCl under conditions which removed bromine from tetrabromostearic acid and from dibromostearic acid gave essentially no reaction. After 4 hrs. of refluxing the iodine number was 0.4.

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[3] Prepared by slight modification of the method of Wheeler and Riemenschneider (5); of approximately 98% purity.

In a further attempt to effect dechlorination 40 g. of methyl dichlorostearate and 20 g. of zinc dust were sealed inside a glass tube (after evacuating). The sealed tube was placed inside a 1-in. pipe capped at both ends and heated at 250°C. After heating for approximately 10 min. the sealed tube shattered inside the pipe and was removed after cooling. The organic material was dissolved in benzene and separated from glass and zinc by filtration. The benzene solution was washed with dilute HCl and distilled water and dried. Benzene was removed under reduced pressure, leaving a yellow-brown oil, N_D^{25} 1.4612, iodine number 32.6. A repetition of the treatment produced further change to yield 24 g. of brown oil: N_D^{25} 1.469, iodine number 57.8, and 1.8% chlorine. This material had a neutral equivalent of 710.

Ethyl Tetrachlorostearate. Ethyl linoleate[4] chlorinated at —20°C. by the above procedure produced quantitative yields of ethyl tetrachlorostearate. A portion of the product was saponified and acidified to obtain the corresponding acid. The properties of the various chlorinated compounds prepared are listed in Table III.

Summary

Methyl oleate, oleic acid, and ethyl linoleate were chlorinated with elemental chlorine at temperatures near —20°C. Approximately quantitative yields of the addition products were obtained, with little or no concurrent substitution. The products prepared in this manner had not previously been reported in the pure state. Two new compounds, ethyl tetrachlorostearate and tetrachlorostearic acid, were prepared.

Methyl dichlorostearate was found to distil with no apparent decomposition at 190–200°C. under pressures below 1 mm. Removal of the chlorine atoms required more drastic conditions that removal of bromine atoms from the same positions and was accompanied by complicating side reactions.

TABLE III

Properties of Products of Chlorine Addition

Compound	Melting Range	N_D^{25}	% Chlorine	
			found	theory
	°C.			
Methyl dichlorostearate....	10 – 11	1.4648	19.14	19.30
Dichlorostearic acid.........	35 – 36	1.4722	19.99	20.07
Ethyl tetrachlorostearate.	76.0– 76.4	....	31.31	31.36
Tetrachlorostearic acid....	126.2–126.6	....	33.36	33.42

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[4] Prepared from crystalline tetrabromostearic acid and distilled before use.

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Note on Oils from Seed of Two Wild Species of Arachis[1]

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A FEW PLANTS of *Arachis pusilla* Benth. and *A. villosa* Benth. var. *correntina* Burk. were grown at Experiment, Georgia, by B. B. Higgins from seed obtained from Argentina. Both have the prostrate type of vine, and both produced small pods and seed. *A. villosa* is perennial, *A. pusilla* is an annual.

As the samples were small, a more complete analysis was not possible. However the limited data given in Table I were obtained. The oils from the ground seed were extracted with Skellysolve F, which was later removed from the lipid fractions at low temperature *in vacuo.*

The analyses showed a marked similarity to those generally reported for the peanut, *Arachis hypogaea.* Oil from *A. villosa* resembled that from the Runner type of peanut while *A. pusilla* with the higher linolein and correspondingly lower olein values was somewhat similar to the oil from Spanish nuts.

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TABLE I

Analysis of *Arachis pusilla, A. villosa,* and *A. hypogaea*

Species	Moisture	Total nitrogen, oven dry	Total lipid, oven dry	Characteristics of the oil					
				Iodine No. (Wijs)	Thiocyanogen value	Calculated glycerides			$N_D^{25°}$
						Olein	Linolein	Saturated	
	%	%	%			%	%	%	
A. Pusilla.........................	4.70	5.89	50.40	100.4	69.6	40.4	37.9	21.7	1.4686
A. villosa..........................	4.56	5.14	55.70	94.7	73.1	56.9	26.4	16.7	1.4677
A. hypogaea[a]									
Spanish......................	......	......	52.93	98.9	71.1	46.1	34.2	19.7	....
Runner......................	......	......	53.02	92.2	74.2	62.9	22.0	15.1	....

[a] Fore, Sara P., Morris, Nelle J., Mack, C. H., Freeman, A. F., and Bickford, W. G., J. Am. Oil Chemists' Soc., *30*, 298–301 (1953).

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[1] Paper No. 284, Journal Series, Georgia Experiment Station.