tiated by AIBN with vinyl 8-(1,3-dioxolan-2-yl)octanoate also gave a soluble polymer.

The crosslinking might have been the result of trace amt of divinyl ester. Since elaborate precautions were taken to eliminate any diesters, a more likely explanation may be that a tertiary hydrogen is present in an α-position to an ether group. This hydrogen, doubly labilized by the two oxygen atoms of the acetal, is known to be susceptible to free radical attack. For example, acetals add to maleic anhydride and α,β-unsaturated esters under free radical conditions (13). Also, acetals are unusually susceptible to atmospheric oxygen, forming hydroperoxides (5). Accordingly, a free radical, formed by a chain transfer reaction at the site of the α-hydrogen (Fig. 4), could enter the usual radical reactions and give crosslinking either by coupling two polymer chains or by branching in a growing chain.

Although vinyl esters of aldehydic acid acetals polymerize readily, they also tend to undergo simultaneous crosslinking. Accordingly, these esters may not copolymerize readily with other vinyl monomers to give a soluble product.

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Reaction of Dichlorocarbene with Fats and Oils[1]

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Abstract

Dichlorocarbene was generated in the presence of lard, olive, safflower, tung and menhaden oil. When solutions of fats or oils in ethyl trichloroacetate were mixed with sodium methoxide in *n*-heptane at 2C, unsaturated components were transformed in high conversion to dichlorocyclopropane derivatives; fats were converted to methyl-and-ethyl esters (90%) or appeared as glycerides (10%). The proportion of dichlorocyclopropane rings was the same in the glycerides as in the ester products. The reactivity of safflower oil required metered addition of reactants at 25–55C.

Properties were measured on dichlorocyclopropanoid fatty esters freed from glycerides but containing saturated esters. Chlorine content ranged from 12–33%. Compatibility with silicone oils was substantially improved. Viscosities and densities increased with chlorine content. Viscosity indices were 135,150,49,67 and 79 for products from lard, olive, safflower, tung and menhaden oil.

Dichlorocarbene could be generated without alcoholysis of glycerides by decomposition of sodium trichloroacetate. This gave dichlorocyclopropanes from safflower oil unsaturates in 50% conversion, but failed with lard.

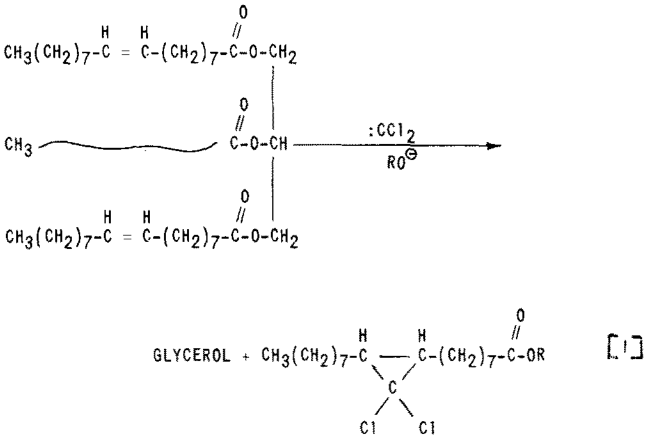
Analyses were performed by TLC, argentation and GLC.

Introduction

THE ADDITION of dichlorocarbene to the double bonds of *cis*-9-octadecene and of methyl oleate, elaidate and linoleate was described in a preceding paper (1). The present paper, on the other hand, deals with the addition of dichlorocarbene to unsaturated fats and oils, utilized as the glycerides themselves. These were lard, olive, safflower, tung and menhaden oils. The first two of these materials have oleic as major unsaturate, and the last three have linoleic, eleostearic and a number of polyunsaturated acids, respectively. The starting fats and oils, as methyl esters, were analyzed by a combination of argentative TLC and GLC. These analyses, together with iodine number and saponification number of the starting materials are given in Table I.

Generation and Reaction Course

For addition to double bonds, dichlorocarbene was generated *in situ* by the action of sodium methoxide on ethyl trichloroacetate (2). Consequently, during the formation of the dichlorocyclopropane derivatives, the glycerides were predominantly converted by alkoxide to simple esters:



[1]

R = Me and Et

In general the reaction with dichlorocarbene was performed by adding a solution of a fat or oil in excess ethyl trichloroacetate to a vigorously stirred suspension of sodium methoxide in *n*-heptane at 2C. After

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[1] Presented at the AOCS Meeting, Minneapolis, 1963.
[2] A laboratory of the E. Utiliz. Res. & Dev. Div., ARS, USDA.

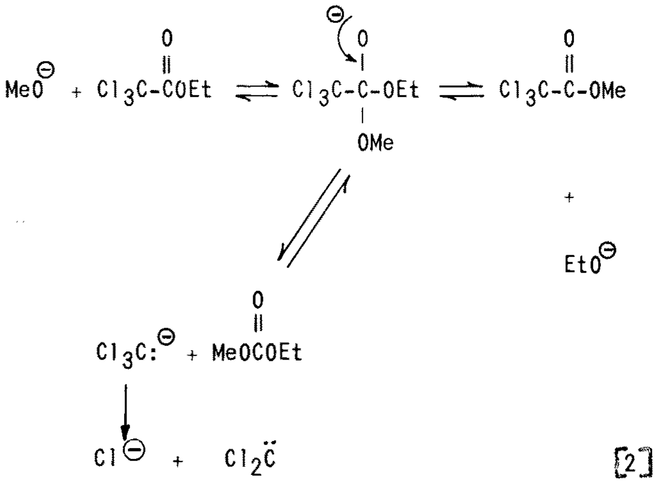
a short exothermic reaction and total stirring of 3–8 hr, the reaction mixture was separated by chromatography on Florisil into simple ester and glyceride fractions, whose wt and iodine numbers were determined. From these (Table II) conversion of glyceride to ester was found to range from 84–100% and conversion of available double bonds to dichlorocyclopropane derivatives from 85–95%.

Addition of dichlorocarbene to safflower oil was so violently exothermic that special conditions were necessary: By metered addition of the safflower oil-ethyl trichloroacetate solution, the temp was brought to and held at ca. 55C during the period of exothermic reaction. The vigor of the reaction with safflower oil may stem from the special reactivity of its pentadiene unit.

Both the ester and glyceride fractions of each product had IR absorption peaks at 805 and 780 cm^{-1}, attributable to the two chlorine atoms of dichlorocyclopropane rings. Double-bond peaks at 1650 and 3010 cm^{-1} in the starting materials were missing in the products. The spectrum of the ester product from olive oil, shown in Figure 1, closely resembled that of the dichlorocyclopropane from methyl oleate (1).

Methyl-Ethyl Esters

The alcohol moieties of the monohydric ester products were freed by saponification and determined by GLC. Results showed that a mixture of methyl and ethyl esters was formed from each oil, as reported in Table III. The mixture seems to be due to the method used for carbene generation:



[2]

According to this scheme, the orthoester intermediate is in equilibrium with ethoxide as well as methoxide ion, both of which apparently play an active part in the alcoholysis of the glycerides. The high proportion of ethyl ester formed from the fats was unexpected in view of the insignificance of alcoholysis as a side reaction of methyl fatty esters (1). It may be due to a greater ease of alcoholysis of glycerides compared to monohydric esters.

Although mixed esters were avoidable by pairing the alkyl groups in the alkyl trichloroacetate and the alkoxide ion, lower yields were obtained using methyl trichloroacetate with sodium methoxide or ethyl trichloroacetate with sodium ethoxide.

Decomposition of Sodium Trichloroacetate

To preserve the glyceride structure during the preparation of dichlorocyclopropanes, sodium trichloroacetate was decomposed to the carbene by refluxing a dimethoxyethane solution of the salt and lard or safflower oil. In either substrate the glyceride structure remained intact. The unsaturates of the safflower oil were converted ca. 50% to dichlorocyclopropanes, but those of lard underwent virtually no addition.

TABLE I

Composition of Starting Fats and Oils

Fat or oil (Major unsaturate)	Total saturates,[a] %	Unsaturates,[b] %		Iodine no.	Sapon. no.
Lard (oleic)	41.6	16:1	2.0	62.4	192.8
		18:1	46.4		
		18:2	10.0		
			58.4		
Olive (oleic)	6.2	18:1	84.3	83.7	187.9
		18:2	7.9		
			92.2		
Safflower (linoleic)	11.7	18:1	16.2	136.3	189.6
		18:2	71.6		
			87.8		
Tung (eleostearic)	3.3	18:1	9.2	175.0	191.5
		18:2	6.5		
		18:3 conj.	80.3		
			96.0		
Menhaden (polyunsaturated)	29.6	16:1	8.1	174.9	186.2
		18:1	16.9		
		18:2	1.8		
		18:3	1.9		
		20:4	3.4		
		20:5	19.4		
		22:5	3.3		
		22:6	12.3		
			67.1		

[a] By totalling individual saturated components.
[b] Chain-length: number of double bonds.

Although generation of dichlorocarbene from phenyl (trichloromethyl) mercury (3) may offer a route to dichlorocyclopropanes in which the glyceride linkages are retained, this reagent was not applied in the present work.

Properties of Dichlorocyclopropanoid Fatty Esters

Selected properties were measured on dichlorocyclopropane derivatives of fatty esters freed chromatographically from glycerides but still containing saturated esters derived from the original oils and minor amt of unsaturated fatty acids esters. These are reported in Table III. Previous work with methyl oleate had shown that dichlorocyclopropane rings confer compatibility with silicone fluids to fatty esters originally entirely incompatible. Table III shows that

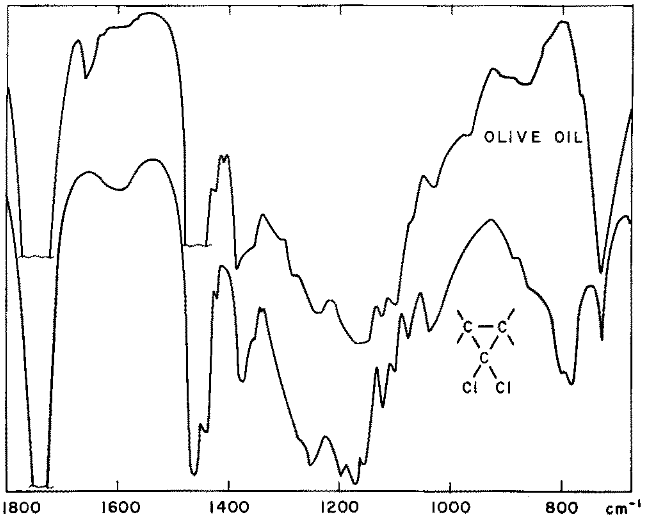


FIG. 1. Section of IR spectra of olive oil and of the corresponding dichlorocyclopropane fatty acid ester product.

TABLE II

Reaction of Dichlorocarbene with Fats and Oils

Fat or oil	Surviving unsaturation			Conversion	
	In esters[a]		In glycerides	Glycerides to esters	Unsatn. to cyclo-propanes
	By I. no.	By GLC	In I. no.		
	%	%	%	%	%
Lard	10.36	16:1 0 18:1 7.5 18:2 0	11.10	91	85
Olive	3.89	18:1 <2 18:2 0	5.46	84	95
Safflower	3.65	18:1 <1 18:2 0	0	100	95
Tung	11.91	18:1 <1 18:2 0 18:3 0	9.08	97	90
Menhaden	3.44	16:1 <1 18:1 <2 18:3 to 22:6 0	3.08	90	95

[a] The difference between unsaturation found by iodine number and by GLC seems to be due to polyunsaturates only partially converted to cyclopropanes, which were not detected by GLC under the conditions used.

increasing content of chlorine or of dichlorocyclopropane rings leads in general to increased compatibility with Silicone Fluid SF-96(50). The product from tung oil (with a content of 32% chlorine) had the greatest compatibility, being soluble to the extent of 55%. Another factor enters in, however, i.e. the non-cyclic fatty esters, saturated or unsaturated, surviving in the ester product. A high content of such non-cyclic esters accounts for the reversal evident in passing to menhaden. In spite of 33% chlorine, this product, owing to a 32% content of non-cyclic fatty esters, was compatible to only 16% with the silicone oil.

GLC analyses showed that the precipitates from the solubility studies were mainly fatty esters having no dichlorocyclopropane rings. Thus removal of non-cyclic esters by centrifugation or filtration would lead to greater compatibility with the silicone fluid.

Viscosities and viscosity indices are reported for the ester products as a gauge to the possible application of these products or products related to them in lubrication. Viscosity indices were highest for the products from lard and olive oil.

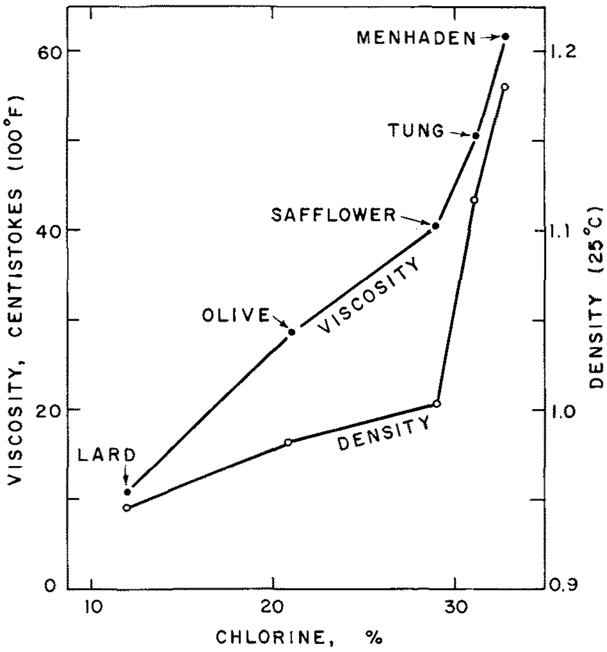


Fig. 2. Viscosity and density of dichlorocyclopropanoid mixed ester products as functions of chlorine content.

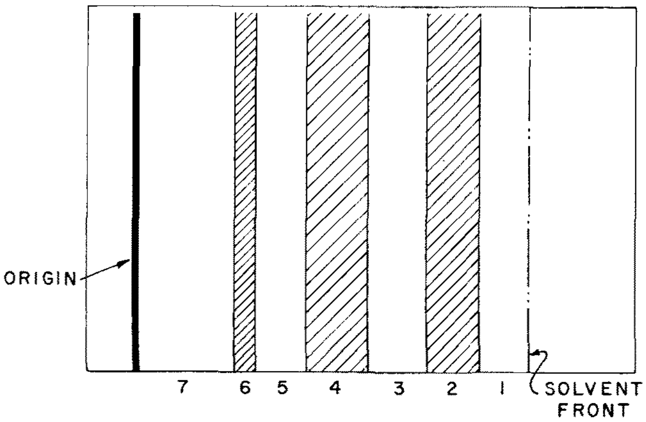


Fig. 3. Argentative TLC for segregation of methyl esters of lard acids according to degree of unsaturation: band 2 < 4 < 6.

Figure 2 shows the increase of viscosity and density with chlorine content. These increases are not linear but are affected to some extent by the detailed composition of the starting fat or oil.

Experimental

Analysis of Fats and Oils. Commercial fats and oils were converted to methyl esters by refluxing one hr with 0.3N NaOMe in excess methanol (4). The esters were quantitatively analyzed by GLC (F & M Model 500 control panel, Model 1720 dual-column oven, 24-volt W-2 thermal conductivity detector). A column 8 ft long x ¼ in. O.D. and a balancing column 2 ft x ¼ in. were packed with 10 wt % diethylene glycol succinate on 60–80 mesh Chromosorb W. Peaks in the GLC were qualitatively identified by comparison of plots of log retention volume vs. carbon number with log plots of data from ester fractions segregated according to unsaturation by argentative TLC. For the segregation, TLC plates were coated with an 0.5-mm layer of Silica gel G–silver nitrate (80–20) applied as an aqueous slurry.

After activation of the plates at 105C for 2 hr, the fat methyl esters were applied in 50-mg streaks under a nitrogen atmosphere. Ascending development was carried out with solvent systems ranging

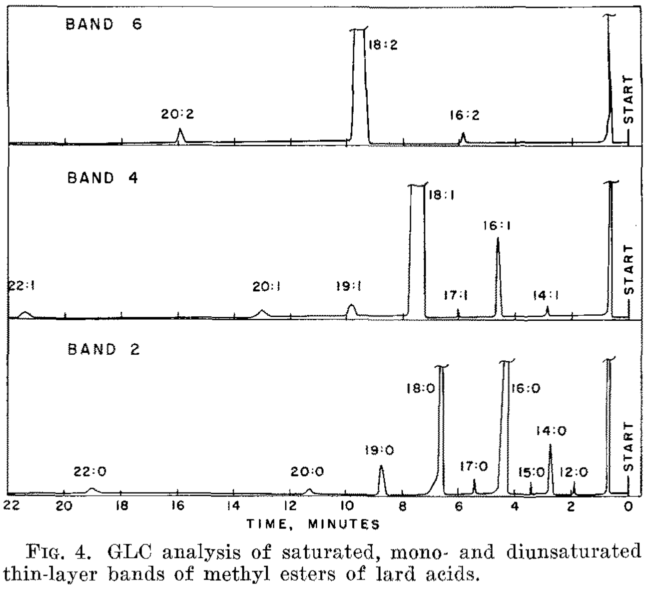


Fig. 4. GLC analysis of saturated, mono- and diunsaturated thin-layer bands of methyl esters of lard acids.

TABLE III

Properties of Mixed Esters of Dichlorocyclopropanoid Fatty Acids[a]

Source	Cl, %	Methyl:ethyl ester ratio	d_4^{25}	Viscosity, cts.		Viscosity index	Color, Gardner	Non-cyclic fatty esters, %	Compatibility with silicone SF-96(50), %
				100F	210F				
Lard	12.1	41:59	0.9547	9.08	2.58	134.8	10–11	49.1	10
Olive	20.9	45:55	1.0413	16.7	3.93	150.2	9–10	7.7	28
Safflower	28.7	35:65	1.1020	21.0	3.90	49.4	2–3	12.2	41
Tung	31.8	47:53	1.1575	43.2	5.65	67.1	11–12	4.1	55
Menhaden	32.8	22:78	1.1788	62.0	6.64	78.7	14–15	31.9	16

[a] Containing non-cyclic esters derived from saturates and minor amt of residual unsaturates.

from hexane-benzene 25:75 to benzene, according to the amt of unsaturation in the fat under study.

The methyl esters of lard (Fig. 3) were separated into three thin-layer bands. After detection by spraying with water, the bands were scraped from the plate and the esters extracted with ether. As shown in Figure 4, band 2 extract, when analyzed by GLC, represented only a homologous series of saturated fatty esters; band 4 contained the monounsaturated, and band 6 the diunsaturated esters.

Log plots of the GLC of these segregated fractions assured accurate peak assignments in the quantitative chromatogram of total fat methyl esters. In all the fats and oils, trace components appeared in the GLC of segregated fractions that had been obscured in the total chromatograms.

Preparation of Mixed Dichlorocyclopropanes. The general procedure for reaction of dichlorocarbene with the present fats and oils was a modification of that used earlier (1), and is typified by the reaction with lard.

Dichlorocyclopropanes Prepared from Lard. Sodium methoxide, 7 g (0.13 mole), was placed with 14 ml of *n*-heptane in a four-necked, round-bottomed 2–1, flask fitted with a thermometer, by-pass funnel and large-bore condenser protected with a drying tube. Nitrogen was introduced through the addition funnel. The reaction mixture was cooled to 2C by an ice-salt bath and stirred at high speed by a cruciform impellor. A mixture of lard, 10 g (0.011 mole), and ethyl trichloroacetate, 14 g (0.11 mole), was added dropwise in 15 min. After 5 min the ice bath was removed. The temp rose in 15 min to ca. 25C, and the solution turned dark brown. After four hr stirring at room temp, a sample was removed and chromatographed in the form of methyl esters. GLC showed 30% of the 18:1 component still unreacted. An additional 3.5 g (0.06 mole) sodium methoxide, and 7 g (0.05 mole) ethyl trichloroacetate were added to the reaction flask. After a total of eight hr reaction at room temp, GLC showed less than 10% of the 18:1 component unreacted. The reaction mixture was now extracted with ether. The ether solution after water-washing and evaporation yielded 12.1 g of crude product. Argentative TLC indicated only minor amt of unsaturation surviving. In the IR spectrum chlorine bands appeared at 780 and 805 cm^{-1}, and the double bonds peaks at 1650 and 3010 cm^{-1} were absent. The product was dissolved in *n*-hexane, placed on 120 g Florisil, and eluted with *n*-hexane and then with benzene.

GLC and TLC showed that the *n*-hexane fraction (9.1 g) consisted of ethyl and methyl esters of the saturates, some unreacted unsaturated material (7.5% of the 18:1 component; no unreacted 16:1 or 18:2 component), plus the desired dichlorocyclopropane derivatives. The benzene fraction consisted of triglycerides (1.0 g), which after methanolysis gave a GLC analysis similar to the *n*-hexane fraction. By iodine numbers (6.47 and 6.93 compared to 62.44 originally) there survived in the ester and glyceride fractions 10.4 and 11.1% of the original unsaturates respectively. Other chemical and physical properties are shown in Table III.

Dichlorocyclopropanes from Safflower Oil. In a 2–1 four-necked flask equipped as in the lard experiment, was placed 8.19 g (0.15 mole) sodium methoxide and 20 ml *n*-heptane. To this mixture at room temp, 9.0 g (0.011 mole) safflower seed oil dissolved in 16.5 g (0.12 mole) ethyl trichloroacetate was added with stirring at such a rate that the reaction temp rose to and remained at 50–55C. Total time of addition was 20 min. The mixture was then stirred until it reached room temp (40 min), when a small sample was taken and methylated. GLC analysis showed 30–40% of the major component (18:2) unreacted. At two and five hr (timed from start of first addition) 4.05 g (0.07 mole) sodium methoxide and 8.25 ml (0.06 mole) ethyl trichloroacetate were added under conditions similar to the first addition. A sample taken before the last addition showed less than 10% 18:2 unreacted. A sample taken after seven hr showed no unreacted 18:2 component.

The mixture was extracted with ether and the ether solution washed with water and evaporated, yielding 16.3 g of crude product. This material was placed on a Florisil chromatography column (10:1 ratio of Florisil to sample) and eluted with *n*-hexane and benzene. The hexane-eluted material consisted entirely of methyl-ethyl esters, and elution with neat benzene revealed no surviving glycerides.

The first hexane fraction, 0.38 g, comprised mainly the 16:0 and 18:0 components. The second to tenth fractions contained 11.75 g of product rich in dichlorocyclopropanes. Iodine number, 4.98, of the ester product indicated survival of 3.7% of the original unsaturates; GLC showed the survival of less than 1% of the 18:1 component. TLC indicated the absence of triglycerides, and argentative TLC indicated no unsaturation. The IR spectrum had a chlorine peak at 775–800 cm^{-1} and lacked the double bond peaks at 1650 cm^{-1} and 3020 cm^{-1} originally present.

GLC of the alcohol moiety, set free by saponification of a small sample, showed a mixture of methyl and ethyl in ratio 35:65.

Compatibility with Silicone Fluid. To 3-ml samples of silicone fluid SF-96(50) stirred and thermostatted at 28C, small increments of the dichlorocyclopropanoid oils were added. The wt percentage of each oil first causing cloudiness was reported as its compatibility.

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