

Reaction of Dichlorocarbene with Fats and Oils¹

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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

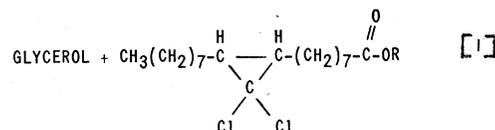
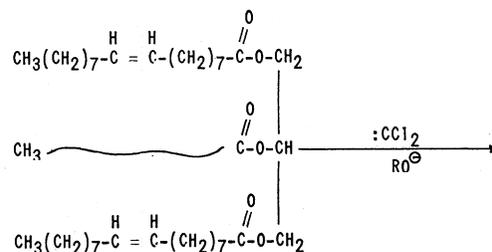
THE ADDITION of dichlorocarbene to the double bonds of *cis*-9-octadecene and of methyl oleate, elaidate and linoleate was described in a preceding paper (1).

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:



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

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 cyclopropanes
	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 lubrica-

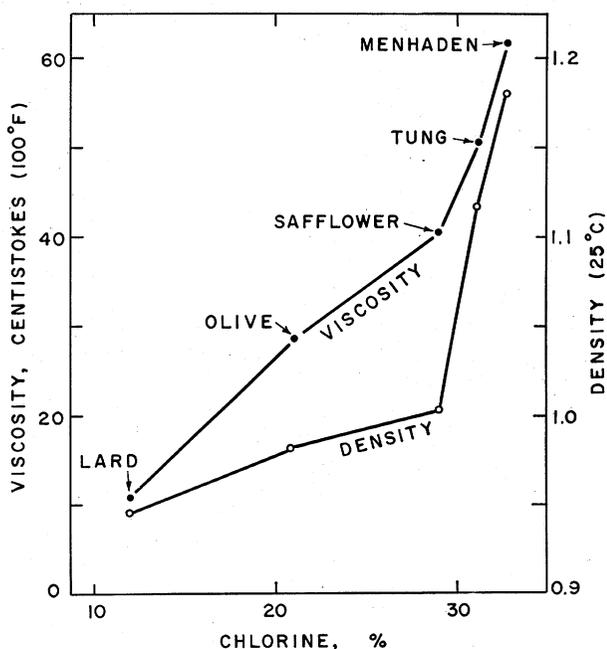


Fig. 2. Viscosity and density of dichlorocyclopropanoid mixed ester products as functions of chlorine content.

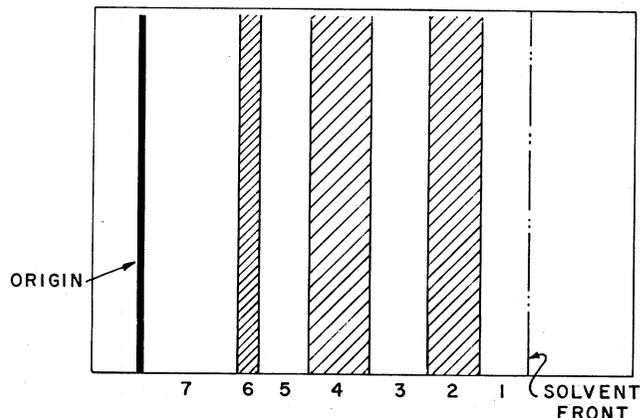


Fig. 3. Argentative TLC for segregation of methyl esters of lard acids according to degree of unsaturation: band 2 < 4 < 6.

tion. Viscosity indices were highest for the products from lard and olive oil.

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 1/4 in. O.D. and a balancing column 2 ft x 1/4 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

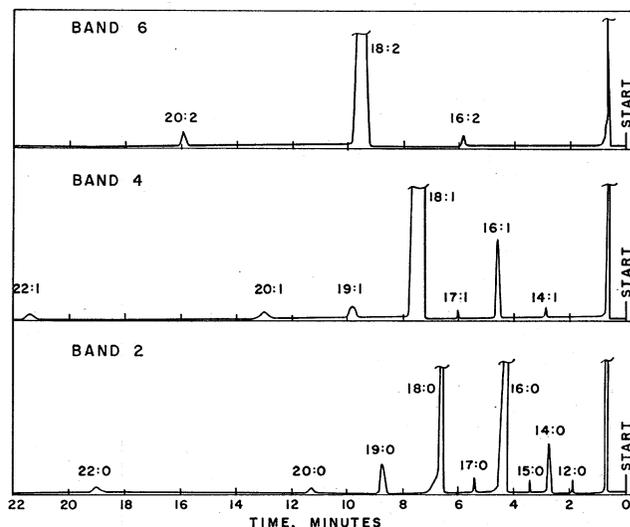


Fig. 4. GLC analysis of saturated, mono- and diunsaturated thin-layer bands of methyl esters of lard acids.

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 impeller. 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.

ACKNOWLEDGMENTS

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