with ozone at 0C, and the product reduced by stirring with Lindlar catalyst (0.5 g) under an atmosphere of hydrogen at 0C. Methanol (600 ml) was added and the acetals were formed as above. The methanol was removed and the resulting oil distilled.

The total wt of volatile material collected, bp 40–95C/20 mm, was 20.91 g (81% of a crude mixture of malonaldehyde and caproaldehyde methyl acetals).

The volatile material was heated for 3 hr on a steam bath with propylene glycol (50 ml) and H_2SO_4 (0.2 ml). After the cooled solution was diluted with ether, it was washed with saturated sodium bicarbonate solution, and then ether was removed. The resulting oil (16.57 g) was distilled.

Fraction 1, bp 37–40C/0.1 mm, 0.787 g; fraction 2, bp 41–45C/0.1 mm, 1.94 g; fraction 3, bp 48–49C/0.1 mm, 9.44 g. Fraction 2 contained 50% malonaldehyde dipropylene glycol acetal and fraction 3, 90% by GLC analysis. The total yield was 40%.

The residue from the initial distillation was dissolved in 10% sodium methoxide in methanol (200 ml), and the solution was refluxed for 3 hr. The cooled solution was diluted with ether and washed well with water. After drying, the ether was removed and the resulting oil was distilled to give methyl azelaaldehydate dimethyl acetal (115–120C/0.3 mm, 11.97 g, 54%).

Ozonolysis of Methyl Linoleate. Methyl linoleate (50 g) was ozonized in methanol (350 ml) as described, and the product reduced with hydrogen and Lindlar catalyst (1 g). The methyl acetals were prepared as before and distilled in a 2-in. Vigreaux column to give fraction 1, bp <50C/0.2 mm, 39.23 g (a mixture of 60% malonaldehyde tetramethyl acetal and 40% caproaldehyde dimethyl acetal) and fraction 2, bp 115–120C/0.2 mm, 42.01 g (a 91% yield of crude methyl azelaaldehydate dimethyl acetal).

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Vinyl Esters of Some Aldehydic Acid Acetals[1]

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Abstract

Vinylation of azelaaldehydic and brassylaldehydic acid cyclic acetals from ethylene glycol gave excellent yields of the vinyl esters. Under conditions of the vinyl exchange reaction used, acyclic acetals from monohydric alcohols cleaved to give enol-ethers as major, inseparable impurities. Radical-initiated polymerization of the pure vinyl esters of the aldehydic-acid cyclic acetals resulted in crosslinking when initiation was by either peroxide or azobis(isobutyronitrile).

Introduction

ALDEHYDIC ESTERS, readily obtained by ozonolysis of unsaturated fatty acid esters, are versatile compounds that undergo a wide variety of reactions (8–10). For example, selective alcoholyses may be carried out on the dimethyl acetal of methyl azelaaldehydate to obtain various ester-acetal derivatives of azelaaldehydic acid in good yield (12). We have described the evaluation of certain of these ester-acetal derivatives as external plasticizers for poly(vinyl chloride) (PVC) (11). Possible internal plasticizers for PVC are the vinyl esters of aldehydic acid acetals. This paper describes the preparation and preliminary studies on the polymerization of the vinyl esters of azelaaldehydic and brassylaldehydic acid acetals.

Experimental

Gas-Liquid Chromatographic Analyses. Gas-liquid chromatographic (GLC) analyses of the vinyl esters were carried out on an F&M model 500 programmed temp gas chromatography unit equipped with a ¼ in. x 4 ft copper column packed with 20% butanediol succinate on 60–80 mesh Chromosorb W. The runs were made isothermally at 185C with a flow rate of 50 cc/min.

All other GLC analyses were carried out in a ¼ in. x 4 ft stainless-steel column packed with 20% silicone rubber on 60–80 Chromosorb P. The column was programmed at a rate of 7.9°/min from 100–275C with a flow rate of 50 cc/min.

Aldehyde Esters. Methyl azelaaldehydate and methyl brassylaldehydate were obtained by ozonization in methanol of soybean methyl esters and methyl erucate, respectively, followed by reductive decomposition of the ozonolysis products either by zinc and acetic acid or by catalytic hydrogenation (2,8,9). The aldehyde esters were purified by forming the sodium bisulfite adducts, regenerating the aldehyde ester with 10% NaOH, then fractionally distilling (7). Based on the aldehyde content of the crude aldehyde esters, 75–80% recoveries of pure products were obtained by this purification procedure.

Acetal Esters. Aldehyde esters were converted to dimethyl acetals in 90–95% yields by using 2,2-dimethoxypropane as a water scavenger (8). Conversion of the dimethyl acetal of methyl azelaaldehydate to dibutyl, distearyl and ethylene glycol acetals, and of the dimethyl acetal of methyl brassylaldehydate to the ethylene glycol acetal, was carried out by selective alcoholyses in the presence of potassium acid sulfate as reported (12).

8-(1,3-Dioxolan-2-yl)octanoic Acid. The hydrolysis of methyl azelaaldehydate ethylene glycol acetal to the azelaaldehydic acid ethylene glycol acetal [8-(1,3-dioxolan-2-yl)octanoic acid] is described in detail as a representative example. Methyl 8-(1,3-dioxolan-2-yl) octanoate (87.3 g, 0.379 mole) was added to 400 ml

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[1] Presented at the AOCS Meeting, Toronto, October 1962.

[2] A laboratory of the No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I
Acetals of Aldehydic Acids

Acid	Yield, %	Mp, °C	n_D^{30}	Carbon, %		Hydrogen, %		Neut. equiv.	
				Calc.	Found	Calc.	Found	Calc.	Found
8(1,3-Dioxolan-2-yl)octanoic	95	59.5–60.5	....	61.07	61.02	9.33	9.37	216.5	216.3
9,9-Dimethoxynonanoic	92	....	1.4414	60.52	60.27	10.16	10.03	218.3	217.9
9,9-Dibutoxynonanoic	91	....	....	67.50	67.14	11.40	10.95	302.0	294.0
9,9-Dioctadecanoxynonanoic	93	53–54	....	77.73	76.83	13.05	13.08	695.2	690.0
12(1,3-Dioxolan-2-yl)dodecanoic	95	77–78	....	66.12	66.20	10.32	10.48	272.3	271.1

3 *N* methanolic KOH. The reaction mixture was refluxed for 2 hr with small amt of water added periodically (total, 100 ml). The reaction mixture was cooled in an ice-salt bath to 0–5C and neutralized with 6 *N* hydrochloric acid with methyl orange as an indicator. The organic acid was extracted with methylene chloride, the methylene chloride solution was dried, and the methylene chloride was stripped off under water aspirator pressure. Crude yield of acid was 77.7 g with mp 58.5–60.0C. Crystallization from acetone gave white crystals, mp 59.5–60.5C. Analytical data for this acid and the others prepared are given in Table I.

Mercuric Sulfate Catalyst. Vinyl esters were prepared by vinyl exchange with vinyl acetate catalyzed by mercuric sulfate (1,3,6). The catalyst was made by dissolving 3.2 g of mercuric acetate in 100 ml commercial vinyl acetate, cooling the solution to 0–5C, and adding 0.8 g of 100 % sulfuric acid with vigorous stirring. The active catalyst solution was a light green and contained a small amt of flocculent precipitate.

Vinyl 8-(1,3-dioxolan-2-yl)octanoate. 8-(1,3-Dioxolan-2-yl)octanoic acid (50.0 g, 0.23 mole) and 0.1 g copper resinate stabilizer were dissolved in 100 ml vinyl acetate at room temp. The mercuric sulfate catalyst solution (100 ml) was added slowly with stirring; the temp was kept below 31C. The reaction flask was wrapped with aluminum foil to exclude light, and the reaction mixture was allowed to stand for 72 hr under a nitrogen atmosphere with occasional stirring. At the end of the reaction period, 5.0 g of sodium acetate were added to quench the catalyst. After stirring for 15 min, the reaction mixture was filtered through a Büchner funnel that contained a small amt of Celite. The filtrate volume was reduced one-half by evaporation under reduced pressure, in a 20C water bath, and the solution was then passed through a 9:1 alumina-Darco column (1 x 6 in.) to remove residual free acid. The column was washed with an equal volume of petroleum ether. The petroleum ether and remaining vinyl acetate were removed by evaporation at 20C under reduced pressure. The residue (56.4 g, 100% yield) had an acid value of less than 1. The crude vinyl ester was purified by low-temp fractional crystallization.

Low-Temperature Fractional Crystallization. In Friedrich's (4) crystallization apparatus, vinyl 8-(1,3-dioxolan-2-yl)octanoate (1.7 g of 96.0% purity) was dissolved in 40 ml of pentene-hexane, and the solution cooled to −30C. The crystals were filtered and recrystallized from 30 ml of the solvent. A third crystallization gave 1.2 g (74%) of 100% pure vinyl ester as determined by GLC.

Vinyl 12-(1,3-dioxolan-2-yl)dodecanoate (27.0 g of 93.1% purity) was recrystallized from a 7% solution of 20:1 pentane-hexane/acetone at −20C to give 18.9 g (75.3%) of 99.4% product. Recrystallization from dry pentane-hexane at 0C gave 10.6 g (56%) of 100% pure vinyl ester as determined by GLC.

Analytical data for the vinyl esters are given in Table II. Unless stabilized with copper resinate, the vinyl esters polymerized when stored in clear bottles at room temp.

Vinyl 9,9-dimethoxynonanoate. Vinylation of 9,9-dimethoxynonanoic acid by the described procedure resulted in a mixture of two compounds. GLC analysis indicated that ca. 78% of the vinyl ester was in a form suspected to be a cracked acetal (12) and ca. 22% in the form of the desired dimethyl acetal. We were unable to obtain a pure product by fractional crystallization.

The following sequence of reactions was carried out to prove the presence of the cracked acetal (an enol-ether). The crude mixture of vinyl esters was hydrogenated to the ethyl esters by hydrogenation over 10% palladium on charcoal at room temp and 20–30 psig. The ethyl esters were fractionally distilled, and a fraction rich in the suspected enol-ether compound (91.7% purity by GLC) was isolated. This fraction was allowed to stand in methanol for 1 hr at room temp in the presence of potassium acid sulfate (12). The reaction product was isolated and identified as ethyl 9,9-dimethoxynonanoate (90.7% purity) by GLC.

Bulk Polymerization. Vinyl 8-(1,3-dioxolan-2-yl) octanoate (2.0 g, 0.008 mole) and benzoyl peroxide (0.01 g) were sealed in an evacuated glass tube. The sealed tube was placed in an oil bath at 72C and allowed to stand for 6 hr. The tube was then removed from the bath, cooled and broken open. The reaction product was a clear, colorless gel that was insoluble in organic solvents and that melted only near the ignition temp.

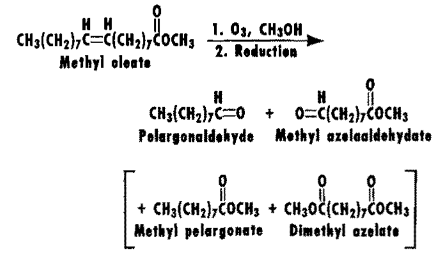
Vinyl 12-(1,3-dioxolan-2-yl)dodecanoate (2.5 g, 0.008 mole) and benzoyl peroxide (0.03 g) were also sealed in an evacuated glass tube. After the tube was heated in an oil bath at 80–85C for 6 hr, it was removed, cooled and broken open. The product inside was a clear rubbery gel that was insoluble and did not melt until near the ignition temp.

Crude vinyl 9,9-dimethoxynonanoate (20 g, 0.008

TABLE II
Vinyl Esters of Aldehydic Acid Acetals

Vinyl ester	Yield, %	BP/P (°C/mm Hg)	n_D^{30}	Carbon, %		Hydrogen, %		Density	M_R	
				Calc.	Found	Calc.	Found		Calc.	Found
8(1,3-Dioxolan-2-yl)octanoate	87	$\frac{110–110.5}{0.17}$	1.4515	64.43	64.40	9.15	9.18	1.009	64.51	65.20
9,9-Dimethoxynonanoate[a]	96	$\frac{96.5–97.5}{0.11}$	....	63.90	62.34	9.90	9.14	....	....	....
9,9-Dibutoxynonanoate[a]	91	$\frac{92–106}{0.07}$	....	69.5	68.28	11.1	10.10	....	....	....
12(1,3-Dioxolan-2-yl)dodecanoate	97	$\frac{141–143}{0.08}$	....	68.50	68.19	10.00	10.23	....	....	....

[a] Contaminated by corresponding enol-ether.



$$\underset{\text{Methyl oleate}}{CH_3(CH_2)_7\overset{H}{C}=\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3} \xrightarrow[\text{2. Reduction}]{\text{1. }O_3,\ CH_3OH} \underset{\text{Pelargonaldehyde}}{CH_3(CH_2)_7\overset{H}{C}=O} + \underset{\text{Methyl azelaaldehydate}}{O=\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3}$$

$$\left[+ \underset{\text{Methyl pelargonate}}{CH_3(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3} + \underset{\text{Dimethyl azelate}}{CH_3O\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3}\right]$$

FIG. 1. Products and byproducts formed in the ozonization of methyl oleate.

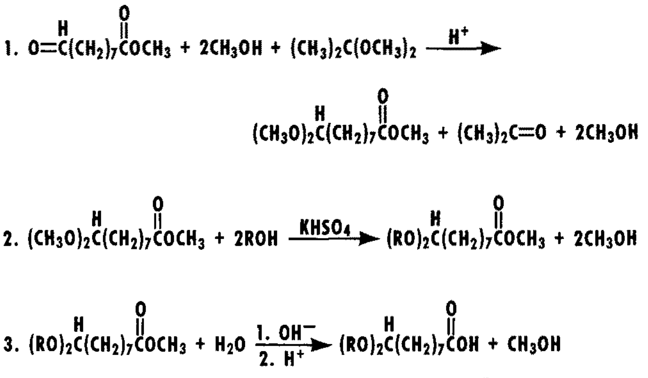
mole) and benzoyl peroxide (0.02 g) were heated for 12 hr at 80C in a sealed tube. This product was a viscous liquid soluble in benzene and having an apparent mol wt of 2,500 as determined by freezing-point depression of benzene. The viscosity number in benzene ($t\text{-}t_0/t_0 \cdot 100/g$) was 7.84.

Solution Polymerization. Vinyl 8-(1,3-dioxolan-2-yl)octanoate (5.0 g, 0.02 mole), 0.1 g of azobis(isobutyronitrile) (AIBN), and 30 ml of pure, dry cyclohexane were heated for 8 hr at 80C in a 3-necked round-bottom flask fitted with a thermometer, a fine capillary inlet for nitrogen and a condenser. The reaction mixture was then poured into 500 ml of methanol, and the solvent was removed under reduced pressure. The residue was a pale, yellow sirup that was soluble in benzene and had a viscosity number of 3.61. Upon standing, the material became more viscous.

Crude vinyl 9,9-dimethoxynonanoate (5.0 g, 0.02 mole), AIBN (0.1 g), and 30 ml of pure, dry cyclohexane were treated as in the preceding paragraph. A pale yellow heterogeneous liquid was isolated. Because of its heterogeneous nature, no further characterization was carried out.

Discussion

Methyl azelaaldehydate and methyl brassylaldehydate are the respective C-9 and C-13 aldehyde esters obtained by ozonolysis of methyl oleate and methyl erucate. These aldehyde esters were prepared in 85–90% yields by ozonization procedures previously reported using methanol as a participating solvent (2,8) (Fig. 1). Methyl azelaaldehydate was also obtained by ozonolysis of soybean methyl esters with the result that methyl myristate and methyl palmitate were present as impurities. Both methyl azelaaldehydate and methyl brassylaldehydate contained the respective dimethyl esters of azelaic and brassylic acids but in varying amt. Relatively small amt of these diesters were present when the ozonolysis products were reductively decomposed with zinc and acetic acid; larger, when catalytic hydrogenation was used (9). The removal of these diesters is essential because only a trace of a divinyl ester causes gelation in vinyl polymerizations.

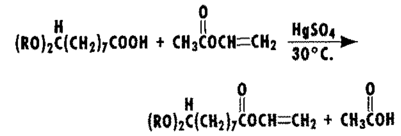


$$\text{1. } O=\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3 + 2CH_3OH + (CH_3)_2C(OCH_3)_2 \xrightarrow{H^+} (CH_3O)_2\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3 + (CH_3)_2C=O + 2CH_3OH$$

$$\text{2. } (CH_3O)_2\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3 + 2ROH \xrightarrow{KHSO_4} (RO)_2\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3 + 2CH_3OH$$

$$\text{3. } (RO)_2\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3 + H_2O \xrightarrow[\text{2. }H^+]{\text{1. }OH^-} (RO)_2\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OH + CH_3OH$$

FIG. 2. Preparation of azelaaldehydic acid acetals from methyl azelaaldehydate.



$$(RO)_2\overset{H}{C}(CH_2)_7COOH + CH_3\overset{O}{\overset{\|}{C}}OCH=CH_2 \xrightarrow[30°C.]{HgSO_4} (RO)_2\overset{H}{C}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH=CH_2 + CH_3\overset{O}{\overset{\|}{C}}OH$$

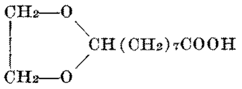
FIG. 3. Vinyl exchange with azelaaldehydic acid acetals.

Purification of the aldehyde esters was accomplished through the sodium bisulfite adducts (7). The methyl and dimethyl esters as well as acetals were removed, and 70–85% yields of essentially pure aldehyde esters were obtained.

The pure methyl azelaaldehydate and brassyaldehydate were converted to their dimethyl acetals in yields of 90–95% (Eq. 1, Fig. 2). Distearyl and ethylene glycol acetals were formed by selective alcoholysis (Eq. 2, Fig. 2) (12). Hydrolysis of the methyl esters in alkaline solution followed by neutralization with acid gave the acid-acetal in ca. 90% yields (Eq. 3, Fig. 2). The dialkyl acetal-acids underwent acid-catalyzed rearrangement to form an enol-ether upon standing at room temp for extended periods of time:

$$(RO)_2CH(CH_2)_7COOH \xrightarrow{H^+} [ROCH=CH(CH_2)_6COOH + ROH] \rightarrow ROCH=CH(CH_2)_6COOR + H_2O$$

For example, 9,9-dimethoxynonanoic acid, the dimethyl acetal of azelaaldehydic acid, rearranged to methyl 9-methoxy-8-nonenoate. The cyclic acetal from ethylene glycol, 8-(1,3-dioxolan-2-yl)octanoic acid, did not undergo this reaction:



The lack of rearrangement illustrates the greater stability of the cyclic acetal to acids.

Vinyl esters were prepared from the acetal-acids by vinyl interchange with vinyl acetate and mercuric acetate/sulfate catalyst (Fig. 3) (1,3,6). Under these strongly acidic conditions, the dialkyl acetals cleaved to give the vinyl ester of the enol-ether as a major impurity:

$$ROCH=CH(CH_2)_6COOCH=CH_2$$

No formation of enol-ethers was encountered with the cyclic acetals, again demonstrating their greater stability. Vinyl esters of the ethylene glycol acetals of azelaaldehydic and brassylaldehydic acids were prepared in 80–85% yields and ca. 95% purity as determined by GLC analysis. Further purification was accomplished by low-temp fractional crystallization to give products having no impurities detectable by GLC analysis.

Free radical polymerizations of the pure vinyl esters both in solution and in bulk were carried out in exploratory tests. The polymers obtained varied from heterogeneous liquids to water-clear, infusible gels as a result of a crosslinking reaction. However, bulk polymerization of crude vinyl 9,9-dimethoxynonanoate gave a soluble polymer. Solution polymerization ini-

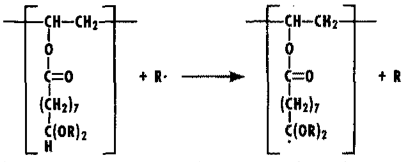


FIG. 4. Hydrogen abstraction resulting in crosslinking of vinyl polymers.

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.

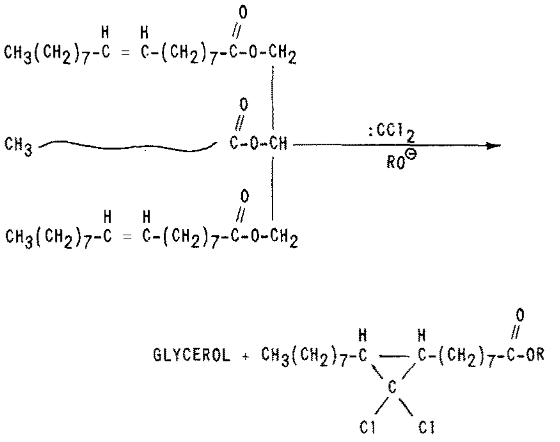
Analyses were performed by TLC, argentation and GLC.

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.