1,2-Cycloaddition of Haloalkenes to Conjugated Fatty Esters[1]

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Abstract

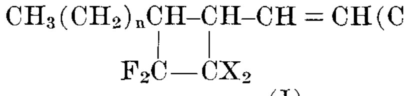
We have studied the reaction of 1,1-dichloro-2,2-difluoro-, chlorotrifluoro-, and tetrafluoroethylenes and also hexafluoropropylene with *cis, trans* and *trans,trans* isomers of conjugated methyl octadecadienoate. Reactions gave 50–82% yields of cycloaddition products. The preponderance of products with a cyclobutane structure and a double bond α,β to the cyclobutane ring was shown by IR and NMR spectra.

Reactions were carried out in diluent with hydroquinone inhibitor at autogenous pressure and a temperature of 200C for 5 hr. The distilled adducts are colorless liquids with viscosities ranging from 11 to 19 centistokes at 100F. These products and their hydrogenated derivatives exhibit low pour points (down to −76F) and may be useful as low-temperature plasticizers or lubricant additives.

Introduction

In a previous publication (4) we described the preparation of C_{20} cyclic monocarboxylic acid by the reaction of ethylene and conjugated soybean and octadecadienoic acids. The cyclic acids are 1,4-disubstituted cyclohexenes. Other publications (1,2,6,7) have covered the 1,2-cycloaddition of fluoro- and chlorofluoroalkenes to conjugated dienes. These investigations showed that a four-membered ring is formed in preference to a six-membered ring when fluorinated alkenes add to conjugated dienes. With few exceptions the conjugated dienes had a terminal methylene group, a short carbon chain, or both.

Because of the apparent activating influence of the gem-fluorine group on the double bond of fluoroalkenes, the reactions of fluoroalkenes and conjugated fatty esters were studied. This paper describes the reaction of haloalkenes and conjugated methyl octadecadienoate, a long carbon-chain internal diene. The yield of cycloaddition products was 50–82%, based on original conjugated diene content. Elemental analysis and iodine value (IV) gave evidence of cycloaddition products. A 1,2-cycloaddition product similar to the generalized structure (I) was shown to be the primary product by IR and NMR spectra. The other possible type of cycloaddition product (II) contains the 1,4-disubstituted cyclohexene structure.

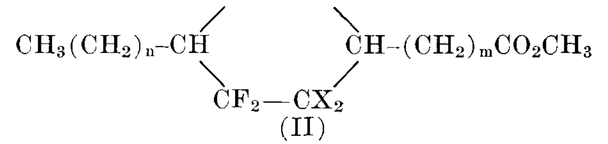


$$\begin{array}{l} CH_3(CH_2)_nCH\text{–}CH\text{–}CH=CH(CH_2)_mCO_2CH_3 \\ \qquad\quad\; | \quad\;\; | \\ \qquad\; F_2C\text{—}CX_2 \end{array}$$

(I)

$n + m = 12$

$X = Cl, F, \text{or } CF_3$



(II)

$n + m = 12$

$X = Cl, F \text{ or } CF_3$

No appreciable amount of 1,4-cycloaddition product was found in the 1,1-dichloro-2,2-difluoroethylene and in the chlorotrifluoro-ethylene adducts. There is evidence of some 1,4-cycloaddition of tetrafluoroethylene and hexafluoropropylene.

Experimental Section

Starting Materials

Haloalkenes. 1,1-Dichloro-2,2-difluoroethylene (DDE), chlorotrifluoroethylene (CTE), tetrafluoroethylene (TFE), and hexafluoropropylene (HFP) were obtained as compressed gases from Peninsular Chemical Research Inc., Gainesville, Fla. (10).

CAUTION. Fluorinated alkenes and their cycloaddition products, which contain the fluorinated alkenes in trace amounts, present a toxicity hazard (7) and should be handled only in well-ventilated areas. Exclusion of oxygen from the reaction system is generally desirable, especially with tetrafluoroethylene.

t,t-9,11-Octadecadienoic Acid. Pure *t,t*-9,11-octadecadienoic acid was prepared by the method of Schneider et al. (8).

Alkali-Conjugated Linoleic Acid. Alkali-conjugated linoleic acid and alkali-conjugated safflower fatty acids were prepared by the method of Danzig et al. (3). Infrared spectra showed that the diene conjugation present was in the *cis,trans* configuration.

Methyl Esters of Conjugated Acids. Methyl esters of *t,t*-9,11-octadecadienoic, alkali-conjugated linoleic, and alkali-conjugated safflower fatty acids were made with absolute methanol and concentrated H_2SO_4 catalyst. Esters were purified by distillation under high vacuum.

Elaidinized Methyl Linoleate. Elaidinized methyl linoleate was obtained from the Pacific Vegetable Oil Corporation, San Francisco, Calif. GLC analysis of distilled esters showed 21.2% *trans,trans* and 8.1% *cis,trans* conjugated diene, 48.2% nonconjugated diene, 13% oleate, 2.7% stearate, and 6.4% palmitate.

Safflower Methyl Esters. Safflower oil was transesterified with absolute methyl alcohol containing hydrogen chloride. Esters were purified by flash distillation under high vacuum. Infrared spectra of the esters showed that they contained a total of <2% *cis,trans* and *trans,trans* conjugated diene.

Reaction Procedure

Cycloaddition Reactions. The cycloaddition reactions were run in stainless steel, high-pressure vessels. Each vessel was packed in solid carbon dioxide and flushed with nitrogen before reactants were added. Liquid haloalkenes, with the exception of TFE, were collected with a vacuum-jacketed condenser, cooled by an isopropyl alcohol-solid carbon dioxide mixture. TFE was added directly to the reactor from a cylinder. An inert solvent, 2,2,4-trimethyl pentane (isooctane), served as a diluent to diminish the possibility of violent decomposition (7). Hydroquinone was used to inhibit polymerization. Autoclaves were heated behind a steel barricade and, after cooling, were vented to the outside. The calculated yields of cycloaddition products were based on conjugated diene content of starting materials and composition of distilled products as determined by GLC analysis.

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Addition of Chlorotrifluoroethylene to Alkali-Conjugated Methyl Linoleate. A 1-liter, stainless steel Magne-Dash vessel was charged with 90 g (0.224 mole diene) of conjugated methyl linoleate, 400 ml of isooctane, 0.9 g of hydroquinone, and 40 g (0.343 mole) of CTE. The autoclave was swept with nitrogen, sealed, and heated to 200C for 5 hr. Maximum autogenous pressure was 225 psi. After cooling, the autoclave was slowly vented. The contents were transferred to a beaker and warmed on a steam bath in a well-ventilated hood to expel unreacted CTE. The solvent was removed in a rotary vacuum evaporator. Flash distillation of crude product (116.8 g) gave 1.9 g, bp 85–146C/0.25–0.36 mm; 103.8 g, bp 146–162/0.35–0.6 mm; 72.7% adduct; and 4.4 g of residue. Calculated yield of cycloaddition product was 82%.

The main distillate fraction was added to a warm solution of 330 g of urea in 600 ml of methanol and was allowed to stand at room temperature. The precipitate containing the urea-complexing fraction was filtered with suction and washed with a saturated methanol solution of urea. The urea complex was decomposed by mixing with 200 ml of water and by heating on a steam bath. After cooling, the mixture was extracted six times with 50-ml portions of ethyl ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. The recovered urea-complexing fraction (5.9 g) contained 5% adduct.

The filtrate from the urea separation was mixed with about 700 ml of water and heated on a steam bath. Most of the nonurea-complexing product settled out and was drawn off with 100 ml of chloroform. The aqueous layer was extracted six times with 50 ml of ethyl ether. The combined solvent extracts were washed with water and dried over anhydrous sodium sulfate. The recovered nonurea-complexing product (94.4 g) contained 75% cycloaddition product. Fractional distillation of the nonurea-complexing fraction gave 62.4 g of purified cycloaddition product with a purity greater than 99%, based on GLC analyses. This standard procedure was followed in the preparation of other cycloaddition products shown in Table I. The HFP cycloaddition products could not be purified beyond 54% by the urea-complexing method. Subsequent distillation increased the purity to 60%.

Hydrogenated Chlorotrifluoroethylene Cycloadduct of Alkali-Conjugated Methyl Linoleate. The crude cycloadduct was prepared from CTE and alkali-conjugated methyl linoleate by the standard procedure. The 1-liter, stainless steel Magne-Dash autoclave was charged with the crude cycloadduct (128 g, 69.6% adduct), 1.3 g of palladium-on-carbon catalyst, and 700 ml of absolute methanol. After the autoclave was flushed and pressurized with hydrogen to 100 psi, the hydrogenation was conducted at room temperature for 4.25 hr. During this period the hydrogen pressure was maintained between 75 and 100 psi. Catalyst was removed by filtration, and methanol was stripped off. The recovered hydrogenated product showed 65.4% cycloadduct and IV 2.8.

The crude hydrogenated product (127 g) was purified by urea-complexing method and fractional distillation. The purified product (51.1 g) had IV 0.0 and >99% cycloadduct. This standard procedure was used in the hydrogenation of other cycloaddition products listed in Table II.

Discussion

The cycloaddition reaction of haloalkenes and conjugated methyl octadecadienoate was conducted under various conditions of time, temperature, and concentration of reactants. In general, the reaction was carried out with 10–20% excess of haloalkene, in an inert solvent containing polymerization inhibitor, at autogenous pressure and at a temperature of 200C for about 5 hr.

Under these conditions DDE, CTE, TFE, and HFP added readily to the *cis,trans* and *trans,trans* isomers of conjugated methyl octadecadienoate to give 50–82% yields of cycloadducts, based on conjugated diene. The cycloadducts of the *cis,trans* and *trans,trans* isomers with the same haloalkene were shown to be identical by comparison of their gas chromatograms and IR and NMR spectra. The order of reactivity of the haloalkenes was TFE > CTE > DDE > HFP. The reactions of CTE and DDE and nonconjugated safflower methyl esters containing 1.4% conjugated diene were studied under the optimum conditions for conjugated esters. With CTE no reaction occurred, and with DDE the yield of addition product was 8.2%, based on total linoleate content. This formation of cycloadduct from nonconjugated diene was unexpected since, under the same conditions, no apparent reaction occurred between methyl oleate and haloalkenes. Possibly some conjugation of the safflower methyl esters took place and resulted in the formation of cycloaddition products.

The use of more than a 20% excess of haloalkenes did not improve the yield of cycloadduct but did increase the amount of nondistillable residue, which consisted predominantly of haloalkene polymers and contained 0–10% cycloadducts. Distillation of crude cycloaddition products was discontinued at the first sight of discoloration in the distillate, and the pot contents were considered residue. Thus the actual

TABLE I

Preparation of Haloalkene Cycloaddition Product of Conjugated Methyl Octadecadienoate
(Reaction conditions: 200C, 5 hr, 1% hydroquinone inhibitor, and isooctane solvent)

Run	Methyl octadecadienoate conjugated diene (mole)		Haloalkene (mole)	Yield Calcd. (%)
1[a]	Me *t,t*-9-11-octadecadienoate	(0.016)	DDE[b] (0.017)	15.9
2	Me *t,t*-9-11-octadecadienoate	(0.012)	DDE (0.075)	50.0
3[c]	Elaidinized Me linoleate	(0.101)	DDE (0.526)	76.5
4[d]	Alkali-conjugated Me safflowerate	(0.084)	DDE (0.158)	56.1
5	Alkali-conjugated Me linoleate	(0.273)	DDE (0.340)	60.2
6	Me *t,t*-9,11-octadecadienoate	(0.032)	CTE (0.068)	51.0
7	Elaidinized Me linoleate	(0.049)	CTE (0.171)	74.6
8	Alkali-conjugated Me safflowerate	(0.128)	CTE (0.171)	69.7
9	Alkali-conjugated Me linoleate	(0.224)	CTE (0.343)	82.0
10	Alkali-conjugated Me safflowerate	(0.482)	TFE (0.450)	79.5
11	Alkali-conjugated Me safflowerate	(0.301)	TFE (2.120)	71.4
12	Alkali-conjugated Me Safflowerate	(0.482)	HFP (0.508)	71.4

[a] Five hours at 175C.

[b] DDE, 1,1-dichloro-2,2-difluoroethylene; CTE, chlorotrifluoroethylene; TFE, tetrafluoroethylene; HFP, hexafluoropropylene.

[c] No solvent.

[d] No inhibitor.

TABLE II
Properties of Cycloaddition Products of Conjugated Methyl Octadecadienoate

Halo-alkene	F, %		Cl, %		IV		n^{30}_D	d^{30}_4	Viscosity, cs/sec		Pour point F	Boiling point, C	
	Calcd.	Found	Calcd.	Found	Calcd.	Found			100F	210F			mm
DDE[a]	8.87	8.89	16.58	16.51	59.2	53.7	1.4603	1.0737	15.11	3.24	−85	165–180	0.16–0.2
DDE[b]	8.81	8.97	16.51	16.62	0.0	4.5	1.4550	1.0642	18.46	3.60	−76	155–190	0.15–0.25
CTE	13.87	14.08	8.63	8.93	61.8	57.5	1.4456	1.0506	11.51	2.66	−85	146–176	0.05–0.08
CTE[b]	13.8	12.8	8.59	8.26	0.0	0.0	1.4398	1.0454	13.85	3.08	−88	158–162	0.05–0.15
TFE	19.26	20.27	....	....	64.4	55.0	1.4320	1.0276	9.37	2.46	−79	128–132	0.05–0.07
TFE[b]	19.16	19.38	....	....	0.0	0.9	1.4248	1.0247	10.88	2.70	−79	149–152	0.07
HFP[b]	25.52	25.14	....	....	0.0	0.4	1.4188	1.0785	12.14	2.75	−83	147	0.09

[a] See abbreviation key in Table I.
[b] Hydrogenated cycloaddition product.

yield of cycloaddition products was usually higher than reported in this paper. At temperatures below 200C, reactions conducted with DDE, CTE, and HFP gave yields of less than 40%. At 250C all reactions gave a small increase in yield, but with the fluorochloroalkenes the residue was increased up to 100% over the 200C reaction. With the perfluoroalkenes no increase in residue was found at 250C.

When the cycloadducts were hydrogenated at room temperatures with 5% palladium-on-carbon catalyst, with and without absolute methanol as a solvent and at pressures ranging from 19–500 psi, there was no noticeable hydrogenolysis. The perfluoro cycloaddition products are more stable to hydrogenolysis than the chlorofluoro products. During hydrogenation of purified DDE cycloadduct at 200C and 200 psi with palladium-on-carbon catalyst, the sample decomposed so much that the stainless steel liner of the autoclave was etched. The crude cycloaddition products can be hydrogenated before separation of the purified product. The order of the stability of the haloalkene cycloaddition products to hydrogenolysis was TFE > HFP > CFE > DDE.

Table II summarizes the elemental analysis, IV determinations, and physical properties of the cycloaddition products. The products were purified by distillation and urea-inclusion methods. The fluorine was determined by the method of Trutrovsky (9). In general, the F analyses were less reliable than the Cl, C, and H analyses. The HFP cycloaddition product was not isolated in purity greater than 60%. The urea-inclusion method, suitable for the separation of all the residual straight-chain esters, also removed 77% of one of the isomers of the HFP cycloadduct, as shown by GLC. These results were unexpected since the HFP adduct had the bulkiest pendant group.

As expected, the densities of the cycloadducts were greater than one. For the hydrogenated cycloadducts the densities were slightly less, and the viscosities were greater than those of the unsaturated counterparts. Kinematic viscosities were determined in Ostwald-Cannon-Fenske pipets. The pour points were determined by the method of Friedrich et al. (5) and ranged from −76 to −88F.

The stability of the DDE, CTE, and TFE cycloaddition products to alcoholic potassium hydroxide was studied. The cycloaddition products were refluxed with 50% excess (based on five reactive sites) of 0.5 *N* solution of KOH in ethanol. Halogen removed was 66% chlorine and 18% fluorine for the DDE cycloadduct, 4.3% chlorine and 7.3% fluorine for the CTE cycloadduct, and 6.1% fluorine for the TFE cycloadduct. No dehalogenation of the hydrogenated CTE, TFE, and HFP cycloadducts was found. For the hydrogenated DDE cycloadduct about 2% of the halogen was removed. The more stable hydrogenated cycloaddition products may have potential use as low-temperature plasticizers or lubricant additives.

Gas chromatograms of the unsaturated cycloadducts (Fig. 1) were obtained at 190C and helium flow of 35 ml/min. A gas chromatogram of alkali-conjugated safflower methyl esters is included for comparison. GLC analyses were made with a Pye-Argon chromatograph, equipped with a radium-D detector, and a 4-ft × ¼-in. O.D. glass column, packed with 14% EGSS-X on Gas-Chrom P, 100–120 mesh (organosilicon polyester packing from Applied Science Laboratories Inc., State College, Pa.). Peak-area measurements were made from an electronically integrated curve. The TFE and HFP cycloadducts could not be completely separated from the isomers of conjugated methyl octadecadienoate. For this reason, samples of hydrogenated TFE and HFP cycloadducts were submitted to GLC analysis.

Optimum resolution of the conjugated methyl esters were obtained at 175C and helium flow of 35 ml/min. Under these conditions cycloadducts were separated from straight-chain methyl esters, but the DDE and CTE cycloadducts had broad peaks. GLC analyses could best be made with programmed-temperature operation. The gas chromatograms of the HFP cycloadduct show the straight-chain impurities which could not be removed. Gas chromatograms of the hydrogenated cycloadducts appear in Fig. 2. The resolution

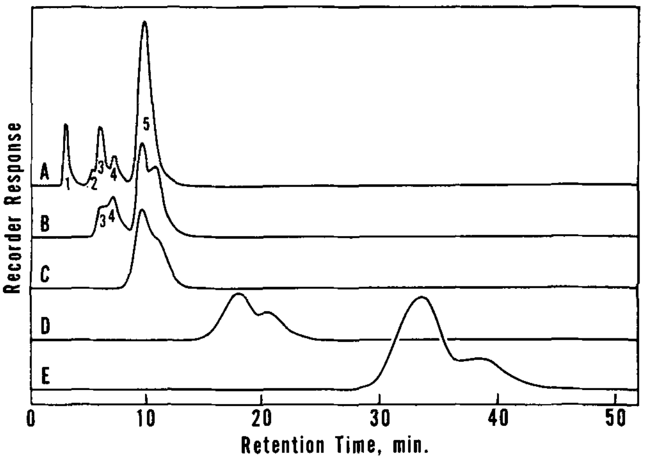

FIG. 1. Gas chromatograms of methyl ester of alkali-conjugated safflower acids, A, and of cycloaddition products of conjugated methyl octadecadienoate and hexafluoroethylene, B; tetrafluoroethylene, C; chlorotrifluoroethylene, D; and dichlorodifluoroethylene, E. Peaks: 1, methyl palmitate; 2, methyl stearate; 3, methyl oleate; 4, methyl linoleate; and 5, *c,t* conjugated methyl octadecadienoate.

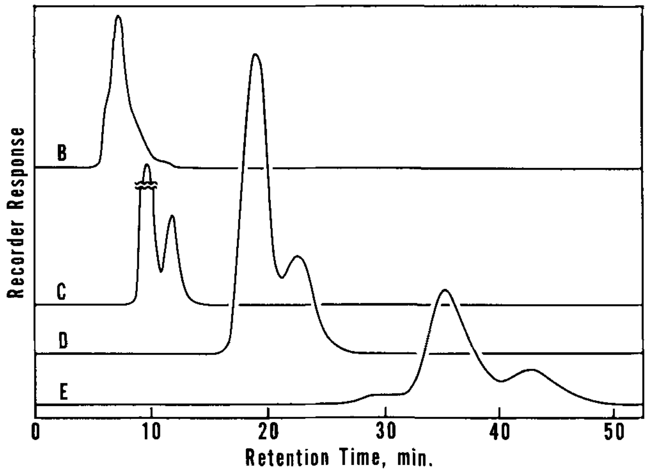

FIG. 2. Gas chromatograms of hydrogenated cycloaddition products of conjugated methyl octadecadienoate: B, hexafluoropropylene; C, tetrafluoroethylene; D, chlorotrifluoroethylene; and E, dichlorodifluoroethylene.

is slightly better for the hydrogenated products than for their unsaturated counterparts. Retention times for hydrogenated DDE, CTE, and TFE adducts are slightly longer than those for the corresponding unsaturated adducts. Retention time of the hydrogenated HFP cycloadduct was slightly shorter than that of the unsaturated HFP cycloadduct.

Fig. 3 depicts the NMR spectra of cycloaddition products at 60 megacycles (MC) per sec on a Varian A-60 spectrometer with tetramethylsilane (TMS) as an internal standard. Spectra of the perfluorocycloadducts were of deuterochloroform solutions. All other spectra were of carbon tetrachloride solutions. A spectrum of the ethylene adduct of methyl t,t-9,11-octadecadienoate, a 1,4-cycloaddition product, is included for comparison. The 1,4-cycloaddition products have a sharp signal at 4.5τ. Comparison of spectra established that the greatest chemical shift from TMS (internal standard) was at 4.36τ. The vinyl absorption of the perhaloethylene adducts shifted downfield slightly owing to the nearness of halogens, and the numerous peaks indicate many spin splitting interactions. The complexity of vinyl absorption in the new adducts provides overwhelming evidence for the formation of 1,2-cycloaddition products, but the formation of some 1,4-cycloaddition products is not ruled out.

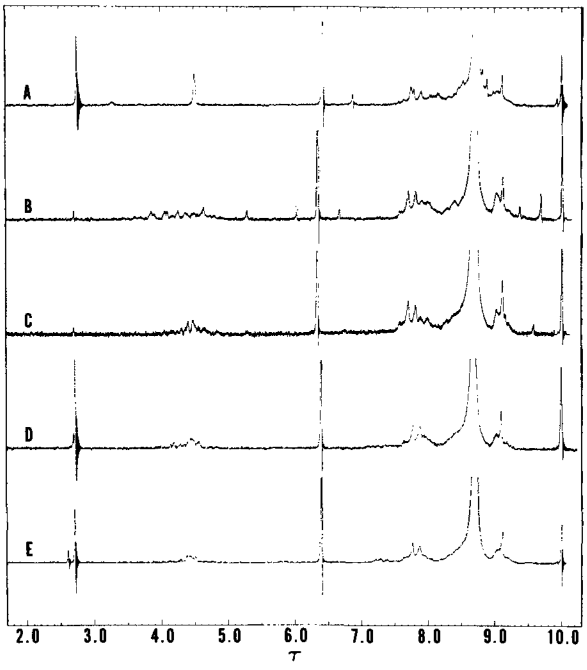

FIG. 3. NMR spectra of cycloaddition products of conjugated methyl octadecadienoate: A, ethylene; B, hexafluoropropylene; C, tetrafluoroethylene; D, chlorotrifluoroethylene; and E, dichlorodifluoroethylene.

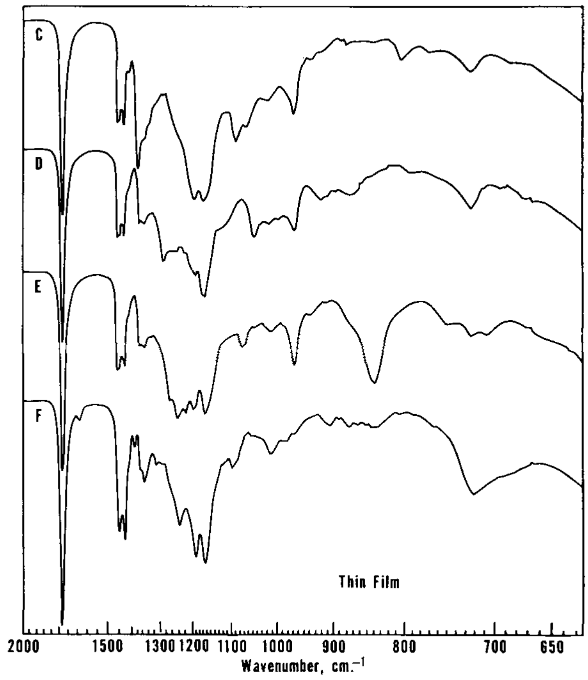

FIG. 4. Infrared spectra of cycloaddition products of conjugated methyl octadecadienoate: C, tetrafluoroethylene; D, chlorotrifluoroethylene; E, dichlorodifluoroethylene; and F, methyl linoleate.

Infrared spectra were determined on a Beckman IR 8 spectrophotometer. Infrared spectra of thin films of the cycloaddition products (Fig. 4) had many major changes over those from methyl linoleate. The C-H

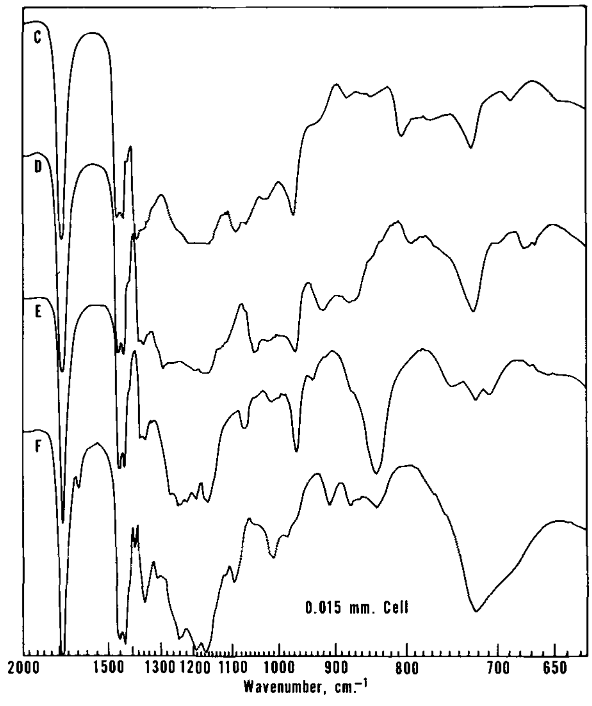

FIG. 5. Infrared spectra of cycloaddition products of conjugated methyl octadecadienoate: C, tetrafluoroethylene; D, chlorotrifluoroethylene; E, dichlorodifluoroethylene; and F, methyl linoleate.

vibrations of CH_3 normally seen in the 1389–1350 cm^{-1} region are substantially changed by the influence of C-F vibrations and an increase in methine (>C-H) vibrations at 1350–1330 cm^{-1}. The characteristic triplet pattern of the C-O stretching vibrations of methyl esters at 1250–1163 cm^{-1} is lost because of interference from the C-F stretching vibrations. The over-all loss of conjugated olefinic absorption and the strong absorption of the *trans* olefinic bond at 971 cm^{-1} give clear support for the cyclobutane structure with an exocyclic double bond predominantly in the *trans* configuration. Infrared spectra of the cycloaddition products with a 0.015-mm cell (Fig. 5) showed C-F vibrations at 1389–1073 and 658–641 cm^{-1}, and C-Cl vibrations at 840–826 and 752–676 cm^{-1}. The skeletal deformation of the cyclobutane structure, complicated by C-F vibrations, C-Cl vibrations, or both, occurs at 935–917 cm^{-1}. The C-H out-of-plane deformation of the cyclohexene structure is at 709–676 cm^{-1}.

Bartlett, Montgomery, and their co-workers (1,6) have reported results that support a two-step, biradical mechanism for the 1,2-cycloaddition of haloalkenes to conjugated dienes. Results in this laboratory with cycloaddition of haloalkenes to conjugated methyl octadecadienoate indicate that a similar mechanism may be involved.

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