Diels-Alder Adducts From Safflower Oil Fatty Acids: II. Styrene as Dienophile

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Abstract

Methyl esters of alkali-isomerized safflower oil fatty acids after elaidinization with sulfur were treated with styrene in the presence of hydroquinone, with or without solvents. A combination of column chromatography and gas liquid chromatography techniques was employed for the estimation of the methyl esters of unreacted fatty acids, Diels-Alder adduct and polymers in the reaction products. Maximum yield of the Diels-Alder adduct (26.6%) was obtained when the elaidinized methyl esters of the fatty acids were treated with 1.5 moles of styrene per mole of linoleic acid in safflower oil fatty acids at 200–210 C for 6 hr. The methyl ester of the adduct was isolated in about 90% purity from the reaction product by vacuum distillation followed by solvent fractionation. The butyl ester of the adduct and the epoxy derivative of the methyl ester adduct were prepared and characterized.

Introduction

The Diels-Alder reaction between styrene and sorbic acid has been studied extensively (1–4). Styrenation of drying oils to modify their properties has been carried out under various conditions by many workers (5). Brunner and Tucker (6) and Armitage and Kut (7) showed the presence of Diels-Alder adducts in the addition copolymer products of styrene and eleostearic acids. Crofts (8) isolated small quantities of Diels-Alder adduct from the reaction product of methyl 9,11-linoleate and styrene at 140 C.

Since styrene is comparatively cheap and produced in commercial quantities, its use as a dienophile in the Diels-Alder reaction with conjugated safflower oil fatty acids has been investigated.

Experimental Procedures

Materials

Safflower oil had a linoleic acid content of 70%. Commercial styrene was distilled in the presence of sulfur under reduced pressure (bp 38–39 C/18–20 mm Hg). Hexane was freed of aromatics by treatment with sulfuric acid, subsequent washing with water and distillation. Methanol, acetic acid, hydroquinone and sulfur powder were chemically pure grade materials.

Analytical Techniques

To estimate separately the methyl esters of unreacted fatty acids, Diels-Alder adduct and polymers in the reaction products, a method based on a combination of column and gas liquid chromatographic (GLC) techniques was employed.

Preliminary analysis of the reaction product was effected by thin layer chromatography (TLC) on Silica Gel C (A.S. Works, India) with hexane-ethyl ether (95:5 v/v). Spraying with 50% chromic acid followed by charring showed three spots; the two nearer the solvent front were very close to each other. Column chromatography of the reaction product on silica gel (70–325 mesh, Merck) with hexane-ethyl ether (95:5 v/v) separated material corresponding to these two spots. It was shown to be a mixture of methyl esters of unreacted fatty acids and Diels-Alder adduct by saponification value, IR and GLC. Further elution of the column with ethyl acetate gave the material corresponding to the last spot at the base line on TLC. This material appeared to be a styrene-ester copolymer by IR spectrum. The methyl esters of unreacted fatty acids and Diels-Alder adduct were separately estimated by GLC in an F and M model 1609 instrument using a coiled stainless steel column (2 ft × $^3/_{16}$ in. i.d.) packed with 5% silicone SE 30 in Chromosorb W (60–80 mesh). The column temperature was programmed from 230–280 C at 7.5 C/min (Fig. 1). The percentages of these two components in the reaction products were determined by correcting the GLC results for the polymers determined by column chromatography.

The other analytical techniques have been described earlier (9).

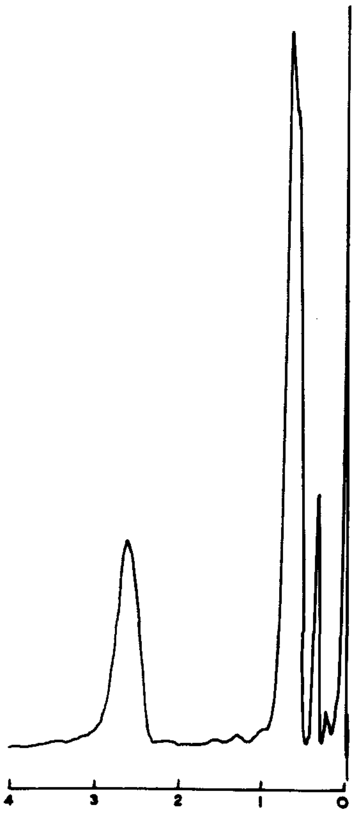

FIG. 1. Typical gas chromatogram of the reaction product after removal of polymers by column chromatography. The peak eluting at approximately 2.3–3.0 1 in. represents the Diels-Alder adduct. Those eluting before 1.0 1 in. are fatty acid methyl esters.

TABLE I

Reaction Conditions for Adduct Formation From the Methyl Esters of Alkali-Conjugated Safflower Oil Fatty Acids[a] Using Styrene as Dienophile and Analyses of the Products

Experiment No.	Dienophile[b] g	Yield[c] g	Reaction conditions[d]		Analyses of reaction products as esters		
			Temperature, C	Time, hr	Fatty acids, %	Diels-Alder adduct, %	Polymerized matter, %
1	25.0	109.1	160–170	4	75.7	12.7	11.6
2	25.0	121.8	200–210	4	56.6	17.8	25.6
3	31.0	128.2	200–210	4	51.2	18.0	30.8
4	37.0	132.6	200–210	4	48.0	22.2	29.8
5	50.0	142.9	200–210	4	35.9	17.7	46.4
6	37.0	100.5	Ca. 120	4[e]	98.2	1.8	0
7	37.0	133.9	200–210	4[f]	48.4	14.3	37.3
8	37.0	134.6	200–210	6	44.8	26.6	28.6
9	37.0	133.9	200–210	6[g]	49.5	18.0	32.5
10	37.0	133.8	200–210	4[h]	42.9	21.3	35.8
11	37.0	135.4	250	1[h]	46.3	15.3	38.4
12	37.0	134.3	240	1[i]	57.0	8.5	34.5

[a] For each experiment, 100 g containing 62% methyl ester of conjugated linoleic acid were used.

[b] Based on 1, 1.25, 1.5 or 2 moles/mole of methyl linoleate.

[c] The yields of the reaction products were taken after removal of solvents, unreacted styrene and in the case of No. 6, polystyrene.

[d] Hydroquinone (0.3 to 0.4 g) and sulfur (0.03–0.05 g) added in all experiments, except the latter omitted from No. 7. The nitrogen was atmosphere.

[e] Acetic acid added (200 ml).

[f] Elaidinization of methyl esters of conjugated safflower oil fatty acids with sulfur not carried out.

[g] Sulfur and hydroquinone mixed with the methyl esters and heated to 150 C; styrene added during 30 min and temperature raised to 200–210 C.

[h] Same as No. 4, except heating carried out under initial nitrogen pressure of 5 kg/cm^2.

[i] Benzene (200 ml), styrene and hydroquinone added to elaidinized safflower oil methyl ester and heated to 240 C in an autoclave.

Preparative Methods

Preparation of Diels-Alder Adduct. The general procedure of conducting the Diels-Alder reaction consisted in the elaidinization of methyl esters of conjugated safflower oil fatty acids (100 g, 62% conjugation) with sulfur powder (0.03–0.05% of esters) at 110–130 C for 2 hr in a nitrogen atmosphere (10) after which hydroquinone (0.2% to 0.3% of the combined weights of esters and dienophile) were introduced and the temperature raised to 150 C. Styrene (1–2 moles per mole of linoleic acid present in safflower oil fatty acids) was then added below the surface of the fatty acid esters during the course of 30 min and the reaction was carried out at the desired temperature and time. When the process was carried out under pressure, styrene and hydroquinone were introduced into an autoclave containing elaidinized esters at about 100 C. An initial pressure of about 5 kg/cm^2 was obtained using nitrogen and the reaction mixture was heated at the required temperature and duration. In one experiment carried out in acetic acid solution, styrene was added at the refluxing temperature (118–120 C) of the solvent.

After the reaction, the unreacted styrene and solvent, if any, were removed under low pressure at about 100 C. Any polystyrene, if formed, was removed from the reaction product by precipitation with hexane. Only in Experiment 6 (Table I) was a precipitate of polystyrene formed when the hexane was added.

For large scale preparation of the Diels-Alder adduct in about 90% purity, the reaction product (200 g) obtained by the procedure outlined in Experiment 8 was distilled at about 1 mm Hg. A fraction boiling up to 150 C consisted of the methyl esters of unreacted fatty acids and minor amounts of the adduct. The residue was dissolved in twice its volume of hexane; then methanol, equivalent to five times the volume of hexane, was added with thorough mixing. The material was kept overnight at about 5 C. The viscous mass which separated was found to have a molecular weight of 850. The Diels-Alder adduct was isolated from the clear solution by distilling off the solvents. It had a molecular weight of 385 (calculated 398), saponification value of 146 (calculated 141). This adduct (5 g) was further purified by passing it through a column of silica gel (200–300 mesh, Merck) using hexane-ethyl ether (95:5 v/v) as eluant. The first 100 ml of the solution was discarded. The material (4.5 g) eluted thereafter gave only a single peak in GLC. The adduct obtained after removal of the solvents had a molecular weight of

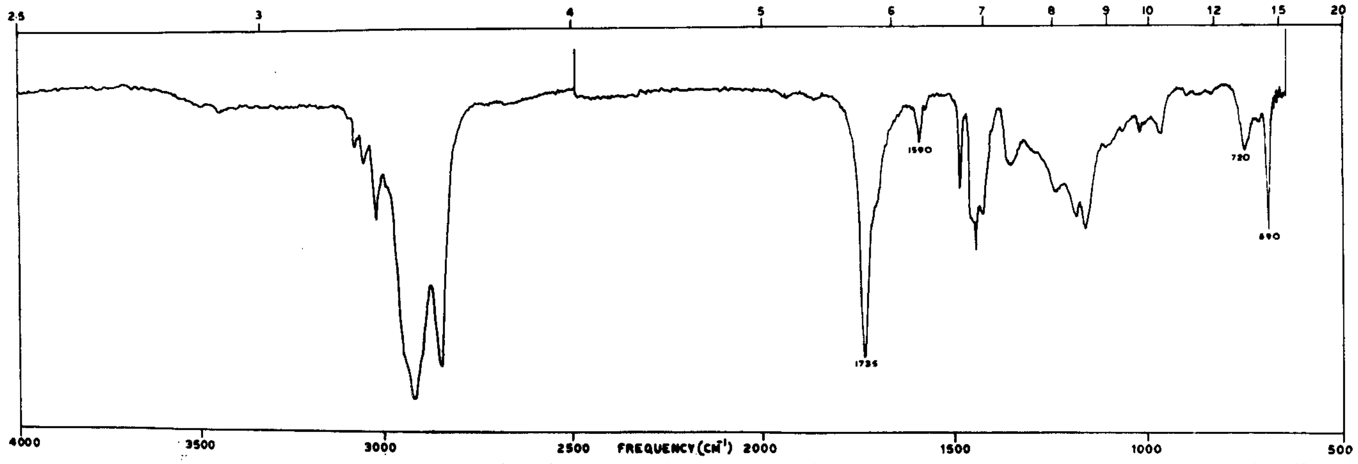

FIG. 2. IR spectrum of Diels-Alder adduct (neat) isolated from the reaction product of styrene and methyl esters of safflower oil fatty acids showing bands corresponding to cyclohexene (720 cm^{-1}), phenyl (690 and 1590 cm^{-1}) and ester (1735 cm^{-1}) groups.

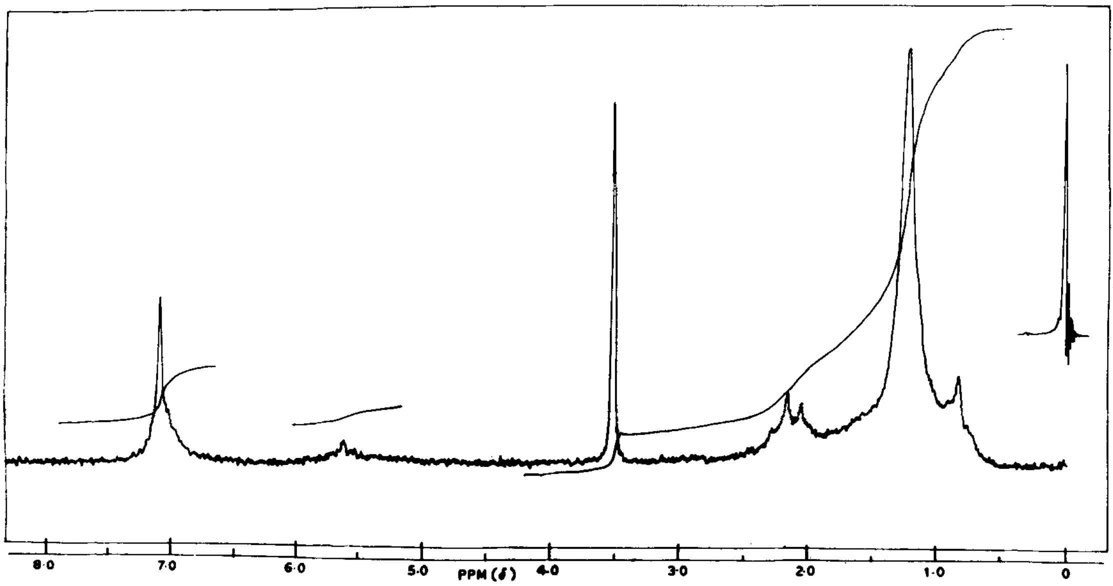

FIG. 3. PMR spectrum of the Diels-Alder adduct isolated from the reaction product of styrene and methyl esters of safflower oil fatty acids taken in CCl_4.

396 and saponification value of 142.5. The IR spectrum (Fig. 2) showed bands corresponding to cyclohexene (720 cm^{-1}), phenyl (690 and 1590 cm^{-1}) and ester (1735 cm^{-1}) groups. PMR spectrum: 7.1 (s), 5H for phenyl ring; 5.65 (m), 2H for vinyl hydrogens in the cyclohexene ring; 3.5 (s), 3H for $COOCH_3$; 2.0–3.1 (m), 5H:2 adjacent to $COOCH_3$; two allylic to double bond and one adjacent to phenyl ring; 1.0 to 2.0 (m), 24H for methylenes and 0.6–1.0 (t), 3H for terminal methyl (Fig. 3).

The IR spectra of the viscous mass mentioned above and that of the polymer obtained by the column chromatographic techniques were identical, showing the presence of ester group and phenyl group. Similar results were obtained in other experiments.

n-Butyl Ester of the Styrene Adduct. The styrene acid adduct obtained by alkaline hydrolysis of the methyl ester adduct was refluxed in nitrogen atmosphere for 10 hr with an excess of *n*-butyl alcohol using p-toluenesulfonic acid as catalyst. After isolation of the ester, its ether solution was passed through a column packed with decolorizing carbon and the solvent removed. The butyl ester had a molecular weight of 432 (calculated 440) and saponification value of 132.5 (calculated 127.5). Its IR spectrum showed the presence of ester and absence of acid group in addition to the usual peaks of the adduct.

Epoxidation of the Methyl Ester Adduct. To a mixture of the methyl ester of the styrene adduct (100 g), benzene (20 g), and Amberlite resin (IR 120, Rohm and Haas), hydrogen phase (7.2 g), hydrogen peroxide (30–32%, 40 g) was added with stirring at 40–45 C during 30 min. The material was then heated at 70–75 C for 6 hr. The isolated epoxidised product had oxirane oxygen 3.0% (calculated 4.02%).

Discussion

A preliminary experiment was carried out using isomerized safflower oil fatty acids with styrene for the preparation of Diels-Alder adduct. However, no feasible method could be worked out to isolate the acid adduct from the reaction product. Accordingly isomerized methyl esters were used as the diene component in this work. Unreacted fatty acid esters were removed from the reaction product by vacuum distillation and polymers could then be separated from the adduct by fractionation with hexane and methanol.

The methyl esters of unreacted fatty acids and of the Diels-Alder adducts eluted together with all the eluants tried. Their individual amounts were therefore determined by GLC and corrected for the percentage of polymers determined by column chromatography. The results obtained by this analytical technique agreed closely with those obtained by isolation of the components from the reaction products by the fractionation method described above.

The results in Table I (Experiments 1 and 2) show that more of the Diels-Alder adduct was formed when the reaction was carried out at higher temperature than at lower temperature. Further, use of 1.5 moles of styrene per mole of linoleic acid present in safflower oil fatty acids gave a comparatively higher yield of the adduct (Experiment 4). Similar results were obtained when the reaction was carried out under pressure (Experiment 10). The polymeric fractions represented in the last column of the Table were shown by IR to contain both phenyl and ester groups and were presumed to be mainly copolymers. In general, more of polymers than of Diels-Alder adducts were obtained. Crofts (8) got similar results, but obtained a much lower yield (2%) of the Diels-Alder adduct than reported in this work. This was, perhaps, because he carried out the reaction at comparatively lower temperature of 140 C. This observation gains further support from the fact that when the reaction was carried out in acetic acid (bp 118–120 C), less than 2% Diels-Alder adduct (Experiment 6) was formed. Reaction temperatures around 250 C (Experiment 11) do not seem to be conducive to adduct formation, as reversal of the Diels-Alder reaction is known to take place at these temperatures (11). Maximum amount of adduct was formed on carrying out the reaction at 200–210 C for 6 hr and pre-elaidinization of the ester of the isomerized safflower oil fatty acids using sulfur is preferable (Experiments 7–9). Carrying out the reaction in an autoclave in presence of a solvent resulted in a poor yield of the adduct.

The butyl ester of the Diels-Alder adduct could be obtained in a fairly pure state by esterification of the hydrolyzed methyl ester of the adduct, with butyl alcohol.

The polymeric material has been found useful as an additive to alkyd resins.

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