Diels-Alder Adducts From Safflower Oil Fatty Acids: I. Maleic Anhydride as Dienophile

G.S.R. SASTRY, B.G.K. MURTHY and J.S. AGGARWAL, Regional Research Laboratory, Hyderabad, India

Abstract

The Diels-Alder reaction between alkali conjugated and elaidinized safflower oil fatty acids and maleic anhydride was studied under various experimental conditions. The principal product which was obtained in 51–55% yields was a mixture of the adduct of maleic anhydride and maleic acid in 40:60 proportions. The isolation and properties of this mixed adducts from the reaction mixture and their conversion to trimethyl, tributyl and triallyl esters are described. The trimethyl ester was also obtained in good yield from the methyl esters of the fatty acids and dimethyl maleate.

Introduction

Maleic anhydride has been extensively studied as a dienophile in the Diels-Alder reaction with a variety of diene compounds including fatty materials (1–6). Teeter et al. (7,8) prepared maleic anhydride adducts from conjugated and elaidinized soybean and safflower oil fatty acids and from safflower oil directly by reaction with dialkyl maleate in the presence of sulfur dioxide (9). Products of very indefinite structures were obtained in the last case. Some alkyl esters of these adducts and their epoxides were evaluated (10) as plasticizers.

The present work forms part of a comprehensive program for the development of economical processes for the preparation of Diels-Alder products using safflower oil as raw material. For the alkali isomerization of safflower oil fatty acids, ethanol (95–97%) has been found superior to ethylene glycol (11). Further, powdered sulfur catalyst as an elaidinization agent produced a higher yield of *trans-trans* dienoic acids than iodine or selenium catalysts used by other workers (7,8,12).

Experimental Procedures and Results

Materials and Methods

Safflower oil had linoleic acid content of 70% (13). Maleic anhydride, dimethyl maleate, methanol, hydroquinone and sulfur powder were pure grade materials. Allyl alcohol, butanol, ethanol and acetic acid were of commercial grade and were distilled before use. Silica gel (70–325 mesh, Merck) was used for column chromatography.

Thin layer chromatography (TLC) on Silica Gel C (A.S. Works, India) plates was used to monitor fractions obtained by column chromatography. The plates were developed with petroleum ether-ethyl ether (50:50 v/v). The spots were visualized by charring after spraying with 50% chromic acid.

IR spectra (liquid films) were obtained with a Perkin-Elmer (Model 221) spectrophotometer. PMR spectra were taken with Varian 60 MC instrument on 10% CCl_4 solutions and the band positions were recorded as parts per million using TMS as external standard.

Molecular weight determinations of the adducts were made by the cryoscopic method using dioxane or cyclohexane as solvents. Other analytical determinations including iodine, acid and saponification values were carried out by standard AOCS procedures.

Conjugated Safflower Oil Fatty Acids

Safflower oil (200 g) in ethanol (95–97%; 450 ml) containing commercial NaOH (90%, 66 g) was heated in a 1 liter stainless steel autoclave at 210–215 C (pressure 45–50 kg/cm^2) for 6 hr and the fatty acids were isolated by extraction with ethyl ether after acidification with 18 N dilute H_2SO_4. The fatty acids contained 62% of diene conjugation (calculated as the cis,trans isomer).

Preparation of Diels-Alder Adducts

The general procedure for conducting the Diels-Alder reaction consisted of heating in an R.B. flask a definite weight of conjugated acids or their methyl esters with or without solvent, maleic anhydride or dimethyl maleate (1.2 or 2 moles/mole of linoleic acid content) and sulfur powder (0.03% to 0.05% or fatty acids) and hydroquinone (0.2% to 0.3% of the combined weights of fatty acids and dienophile) at 110–130 C for 1–3 hr in an atmosphere of nitrogen. The effect of trichloroacetic acid (14) on the reaction was studied in two experiments. At the end of the reaction period, the solvent, if added, was distilled off and the residue washed with water and freed of moisture by heating at 110–130 C under reduced pressure (20 mm).

Since the crude reaction product obtained in experiments 1–9 (Table I) yielded four spots on TLC, column chromatographic separation of the components was attempted. Twenty grams of silica gel was made into a slurry with petroleum ether, poured into a column (50 × 2 cm) and settled. The crude product (100–150 mg) was applied on top of the column and eluted successively with petroleum ether-ethyl ether (70:30), ethyl ether and ethyl acetate. Solvent change was made when no more material was eluted by the previous solvent. TLC of the petroleum ether-ethyl ether fraction gave one spot having the highest R_f and similar to that of the fatty acids, while the ethyl ether fraction yielded two spots, their R_f lying between the origin and the fatty acid spot. The ethyl acetate fraction remained at the origin and was presumed to be highly polymerized material.

The two components in the ethyl ether fraction were fractionated again by column chromatography. On a silica gel column (30 g) prepared as described above, 100 mg were applied and eluted with petroleum ether-ethyl ether (30:70). When no more substance was eluted, the column was eluted again with ethyl ether. The petroleum ether-ethyl ether fraction yielded 40 mg and gave one spot on TLC. It was identified as the maleic anhydride adduct by IR and PMR. IR spectrum showed bands due to anhydride (1820 and 1760 cm^{-1}), carboxyl (1710 cm^{-1}) and

TABLE I
Reaction Conditions for Adduct Formation From Alkali-Conjugated Safflower Oil Fatty Acids[a] and Analyses of the Products

Experiment No.	Dienophile,[b] g	Solvent, 200 ml	Reaction conditions[c] Temperature C	Reaction conditions[c] Time, hr	Analysis by column chromatography Fatty acids, %	Analysis by column chromatography Diels-Alder adduct, %	Analysis by column chromatography Polymerised matter, %
1	A[d](30)	Xylene	110–145	5	35.8	51.3	12.9
2	A(30)	Benzene[e]	80– 85	4	68.5	27.2	4.3
3	A(30)	Xylene[e]	110–145	3.5	32.5	53.3	14.2
4	A(30)	Acetic acid	110–120	5	31.9	55.1	13.0
					32.8	54.2	13.0
5	A(30)	....	110–170	6[f]	33.6	53.5	12.9
					34.3	52.8	12.9
6	A(30)	....	110–170	5[g]	34.8	54.2	12.8
7	A(30)	....	110–170	5	52.4	33.6	14.0
8	A(49)				53.0	33.0	14.0
		Acetic acid	110–120	5	31.8	54.0	14.2
9	A(49)	....	110–170	5[g]	33.4	53.4	13.2
10	B(41)	....	110–180	6[f]	34.8	53.4	11.8
11	B(41)	....	110–240	5[f]	33.0	54.8	12.2
					34.2	53.6	12.2

[a] One hundred grams containing 62% conjugated linoleic acid used in experiment 1–9 and their methyl esters in experiment 10 and 11.
[b] Based on 1.2 or 2 moles/mole linoleic acid in safflower oil fatty acids.
[c] Sulfur (0.03 to 0.05 g) added except in experiment 7; hydroquinone (0.3 to 0.4 g) used in each experiment; nitrogen atmosphere.
[d] A, maleic anhydride; B, dimethyl maleate.
[e] Trichloroacetic acid (50 g) added.
[f] First elaidinization and then adduct formation.
[g] Elaidinization and adduct formation in situ.

cyclohexene (720 cm^{-1}) group. The PMR spectrum was characterized by its proton counts and chemical shifts as follows: COOH (1H, 11.12 ppm), cyclohexene vinyl hydrogens (2H, 5.76 ppm), CH_2 protons adjacent to carbonyl and protons in C adjacent to carbonyls and allylic to cyclohexene double bond (6H, 2.1–3.1 ppm), the remaining CH_2 (22H, 1–2 ppm) and terminal CH_3 (3H, 0.6–1 ppm). It had a molecular weight of 373 (calc. 378) and iodine value 65.5 (calc. 67.1). The ethyl ether fraction, on evaporation of the solvent, yielded 60 mg and gave a single spot on TLC. IR spectrum showed peaks due to carboxyl and cyclohexene groups while the peaks due to anhydride group (1820 and 1760 cm^{-1}) were absent. It had a molecular weight of 390 (calc. 396) and I.V. 62.4 (calc. 64.1). From this and from other evidence described later, this was found to be the hydrolysis product of the maleic anhydride adduct, the corresponding tricarboxylic acid.

The reaction product obtained from methyl esters of the fatty acids and dimethyl maleate (Table I, experiments 10 and 11) gave only three spots on TLC. Fractionation of this product on a silicic acid column with petroleum ether-ethyl ether (85:15), petroleum ether-ethyl ether (60:40) and ethyl acetate, successively, yielded the unreacted methyl esters of fatty acids, the trimethyl ester adduct and a polymer fraction, respectively. The IR spectrum of the trimethyl ester adduct showed bands characteristic of ester carbonyl (1735 cm^{-1}) and cyclohexene (720 cm^{-1}). The proton counts and chemical shifts observed in the PMR spectra were $COOCH_3$ (9H, 3.57–3.6 ppm), CH_2 (22H, 1–2 ppm) CH_3 (3H, 0.6–1 ppm) and 6H (2–3.1 ppm) for hydrogens adjacent to carbonyls and allylic to cyclohexene double bond.

The Diels-Alder adduct consisting of maleic anhydride adduct; tricarboxylic acid adduct (40:60) was obtained 90% pure by a solvent fractionation process. The crude product (100 g; Table I, experiment 6) was extracted with 400 ml of boiling petroleum ether. The remaining product (60 g) was dissolved in 200 ml of petroleum ether-ethyl ether (60:40) and cooled to −10 to −15 C for 16 hr when the polymerized material (8 g) separated. Removal of the solvent from the clear filtrate yielded the adduct (50 g). The saponification value of 357 (theoretical value 433) indicated that the complete hydrolysis with alcoholic alkali did not take place.

The trimethyl ester adduct was prepared from the tricarboxylic acid derived from the Diels-Alder adduct isolated as above. The adduct was refluxed with 15% aqueous NaOH for 4 hr and acidified with dilute H_2SO_4. The tricarboxylic acid thus obtained was refluxed for 8 hr with five times its weight of methanol in the presence of 1% *p*-toluene sulfonic acid. The solvent was removed under reduced pressure, the product was dissolved in ethyl ether, washed with 1% NaOH and water and dried over anhydrous Na_2SO_4. The ether solution was passed through a column of activated charcoal and the trimethyl ester adduct was recovered after removal of the solvent under reduced pressure (molecular weight 442, IV 57.5). The trimethyl ester adduct was also obtained from the reaction products of experiment 10, by removal of the fraction distilling at 170 C (1 mm) and by passing a petroleum ether solution of the residue through activated charcoal as described previously.

Tributyl and Triallyl Esters of Maleic Anhydride Adduct

The tricarboxylic acid adduct, obtained by aqueous alkaline hydrolysis of the anhydride adduct was refluxed in nitrogen atmosphere with excess of the respective alcohols and *p*-toluene sulfonic acid (1%) for 10 hr. Copper bronze powder was used as a polymerization inhibitor in esterification with allyl alcohol (7). After isolation of the esters, their ether solutions were passed through a column packed with activated charcoal and the solvent removed. The tributyl and triallyl esters had molecular weights of 559, 510, and IV 45.9 and 190, respectively. Their IR spectra showed peaks at 1735 cm^{-1}. In addition, peaks at 920 and 985 cm^{-1} for the allyl group were present in the triallyl ester.

Discussion

A comparison of the yields of the adducts obtained in experiment 6 and 7 reveals that the addition of the dienophile is facilitated if the dienoic system is in the *trans,trans* form. This was effected in situ without prior transformation of the alkali conjugated fatty acids to the *trans,trans* configuration, thereby making the method simpler and more economical.

Since the recovered fatty acids were found to contain only less than 3% of conjugated dienoic acids, it is reasonable to conclude that the dienoic acids were converted quantitatively to adducts and polymers. The yield of the adducts was not influenced by the solvent medium in which the reaction was carried out. However, with low boiling solvents, the yield was considerably reduced, and addition of an equimolar quantity of trichloroacetic acid shortened the time required for adduct formation. The mixture of the anhydride and acid adducts obtained in experiments 1–9 is probably due to partial hydrolysis of the anhydride adduct during the isolation procedure.

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