Diels-Alder Adducts From Safflower Fatty Acids: III. Acrylic and Related Acid Dienophiles

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ABSTRACT

The Diels-Alder adducts from alkali conjugated and elaidinized safflower fatty acids with acrylic, methacrylic, crotonic and cinnamic acids and their esters as dienophiles were obtained in 40-64% yields. Low yields of 16-18% were obtained when 10-undecenoic acid and its ester were used. Most of the adducts could be estimated quantitatively in the reaction products by column chromatography or gas liquid chromatography (GLC). For the estimation of the adducts from crotonic and 10-undecenoic acids a combination of column chromatography and GLC techniques was employed. Partitioning between hexane and 90% methanol, partial esterification with alkali washing, and splitting and fractional distillation under reduced pressure were methods used to obtain the adducts in 90-95% purity.

INTRODUCTION

Acrylic acid has been studied as a dienophile in the Diels-Alder reaction with some conjugated fatty materials (1-5). Except for the work of Teeter et al. (6) and Kaufman et al. (5) on the use of ethyl crotonate, no work of similar nature has been undertaken with acrylic acid, methacrylic acid(2-methyl acrylic acid), crotonic acid (3-methyl acrylic acid), and cinnamic acid(3-phenyl acrylic acid) as dienophiles. However Teeter et al. (1) could not isolate any Diels-Alder adduct from the reaction products of *t,t*-9,11-octadecadienoic and crotonic or cinnamic acids. The work carried out with the above dienophiles and their esters in the Diels-Alder reaction with alkali conjugated safflower fatty acids is summarized in this paper. For comparison, 10-undecenoic acid with a double bond far remote from the carboxyl group was also studied as a dienophile.

EXPERIMENTAL PROCEDURES AND RESULTS

Materials

Safflower oil (linoleic acid, 70%) and acrylic acid, methyl acrylate, methacrylic acid, methyl methacrylate, crotonic acid, ethyl crotonate, cinnamic acid, methyl cinnamate, 10-undecenoic acid and methyl 10-undecenoate, methanol, hydroquinone and sulfur powder of C.P. grade were used. Commercial grade butanol, ethanol and acetic acid were distilled before use. Silica gel (100-200 mesh, A.S. Works, India) was used for column chromatography. Hexane was freed of aromatics by treatment with sulfuric acid and subsequent washing with water and distillation.

Analytical Techniques

The reaction products from acid dienophiles were column chromatographed on silica gel (20 g) and eluted successively with hexane-ethyl ether 90:10, 60:40, and ethyl acetate to determine the unreacted fatty acids, Diels-Alder adducts and polymers, respectively. Except for ethyl cerotonate and methyl 10-undecenoate, the unreacted fatty esters, adduct esters and polymers were eluted from the reaction products with hexane, hexane-ethyl ether 80:20, and ethyl acetate, respectively. The crotonate and undecenoate were separately estimated by gas liquid chromatography (GLC) (7). Their percentages in the reaction products were calculated by correcting the GLC results for the polymers determined by column chromatography. The procedures for thin layer chromatography (TLC), GLC, IR and proton magnetic resonance (PMR) spectra and determination of other characteristics of the adducts such as molecular weights, iodine, acid and saponification values have already been reported (8).

Preparation of Diels-Alder Adducts

Except for methyl acrylate, methyl methacrylate and ethyl crotonate, the general procedure for the Diels-Alder reaction consisted of heating in a round-bottom flask a definite weight of the conjugated safflower fatty acids (9) or their methyl esters with or without solvent, dienophile (1.2 or 2 moles per mole linoleic acid content), sulfur powder (0.03-0.05% of fatty acids) and hydroquinone (0.2-0.3% of the combined weights of fatty acids and dienophile) at 110-130 C for 1-3 hr in an atmosphere of nitrogen, the temperature might then be raised up to 210 C for a specified period. With low boiling dienophiles the reaction was carried out in an autoclave under an initial nitrogen pressure of about 5 kg/cm^2. At the end of the reaction period the solvent (if added) was distilled off, and the unreacted dienophile from the reaction product was either removed under reduced pressure or by washing with water and freeing the residue of moisture. The details of the various experiments and the analysis of the reaction products are given in Table I.

The Diels-Alder adducts from acrylic, methacrylic and cinnamic acids were isolated in about 90% purity when partitioned between hexane and 90% methanol. The adduct concentrated in methanol layer. The methanol was removed and the residue was dissolved in mixture of hexane and ethyl ether 1:1 and kept at -10 to -15 C overnight when most of the polymerized matter separated. When crotonic acid was used as dienophile, by this process the yield was only half of that present in the reaction product. Even urea adduct separation in methanol solution was not very successful. The crotonic acid reaction product was refluxed for 2 hr with twice its weight of methanol and concentrated sulfuric acid (2%) as catalyst and the solvent was distilled off. The partially esterified product was dissolved in ethyl ether, washed with water and then with caustic soda solution (2%). The adduct formed the sodium soap and dissolved in the aqueous alkaline layer. It was separated from the ether solution, acidified and the adduct isolated in almost theoretical amount. Further purification of the adduct was effected by column chromatography using silica gel and 10% and 40% v/v ethyl ether in hexane, respectively, as elution solvent. The yield was less with 10-undecenoic acid dienophile (Table I, Experiment 38). The adduct was directly isolated by the above column chromatographic procedure. The IR spectra of all the adducts gave peaks at 1710 cm^{-1} and 720 cm^{-1} showing the presence of carboxyl and cyclohexene groups.

The adducts of acrylic and methacrylic acids were converted to their dimethyl aid dibutyl esters by refluxing for 8 hr with five times their weights of the respective alcohols in the presence of *p*-toluenesulfonic acid (2%). The excess alcohols were removed, the products dissolved in ethyl ether, washed with caustic soda solution (1%) and water, and dried over anhydrous sodium sulphate. The ether solutions were passed through activated charcoal

TABLE I

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

		Reaction conditions[c,d,e]		Analysis by column chromatography		
Sl. no.	Dienophile[b]	Temperature, C	Time, hr	Fatty acid-alkyl esters, %	Diels-Alder adduct, %	Polymer, %
1	2	3	4	5	6	7
1	A (1.2)	150-160	4.0	40.1	47.9	12.0
				40.6	47.4	12.0[f]
2	A (1.2)	200-210	5.0	42.6	46.2	11.2
				43.0	45.8	11.2[f]
3	A (2.0)	150-160	4.0	37.8	53.0	9.2
				36.4	54.4	9.2[f]
4	A (2.0)	150-160	3.0[g]	36.2	55.2	8.6
5	A (2.0)	150-160	3.0[h]	46.1	44.5	9.4
6	A (1.2)	110-130	6.0[i]	44.6	49.2	6.2
				43.1	50.7	6.2[f]
7	A (2.0)	110-130	6.0[i]	34.4	57.2	8.4
				34.0	57.6	8.4[f]
8	A (2.0)	110-130	4.0[i]	35.6	58.2	6.2
9	A (1.2)	200-210	2.0[j,k]	40.5	51.2	8.3
				41.7	50.0	8.3[f]
10	B (1.2)	200-210	2.0[k]	33.6	60.2	6.2
				35.1	58.7	6.2[f]
11	B (1.2)	200-210	2.0[j,k]	40.2	50.6	9.2
				38.9	51.9	9.2[f]
12	C (1.2)	160-170	4.0	44.5	50.0	5.5
13	C (1.2)	200-210	2.5	35.0	59.2	5.8
14	C (2.0)	200-210	2.5	34.6	59.4	6.0
15	C (1.2)	200-210	3.0[g]	34.8	58.2	7.0
16	C (1.2)	110-130	4.0[i]	42.4	49.8	7.8
17	D (1.2)	200-210	2.0[k]	39.8	53.4	6.8
				40.4	52.8	6.8[f]
18	D (2.0)	200-210	2.5[k]	34.4	58.6	6.8
				34.8	58.4	6.8[f]
19	D (1.2)	200-210	2.0[j,k]	51.6	40.4	8.0
				50.2	41.8	8.0[f]
20	E (1.2)	160-170	4.0	61.3	31.8	6.9
21	E (1.2)	210-220	4.0	48.3	43.2	8.6
22	E (1.2)	110-130	4.0[i]	77.1	19.7	3.2
23	E (1.2)	210-220	6.0	35.4	56.6	8.0
24	E (2.0)	210-220	6.0	33.4	56.0	10.6
25	F (1.2)	210-220	3.0[k]	66.0	22.8	11.2[l]
26	F (1.2)	210-220	6.0[k]	58.0	29.8	12.2[l]
27	F (2.0)	210-220	3.0[k]	60.2	27.4	12.4[l]
28	F (2.0)	210-220	6.0[k]	47.8	38.6	13.6[l]
29	F (2.0)	210-220	8.0[k]	45.6	39.6	14.8[l]
30	G (1.2)	160-170	3.0	68.2	26.8	5.0
31	G (1.2)	210-220	3.0	38.0	51.3	10.7
32	G (1.2)	210-220	6.0	36.0	54.5	10.5
33	G (2.0)	210-220	6.0	36.0	57.2	6.8
34	H (1.2)	210-220	3.0	36.7	56.7	6.6
				36.4	57.0	6.6[f]
35	H (1.2)	210-220	6.0	29.0	63.8	7.2
				29.2	63.6	7.2[f]
36	I (1.2)	160-170	3.0	88.0	7.4	4.2
37	I (1.2)	210-220	3.0	75.2	15.6	9.2
38	I (1.2)	210-220	6.0	72.2	18.2	9.6
39	I (3.0)	210-220	6.0	75.2	16.8	8.0
40	J (1.2)	210-220	3.0	80.0	14.4	5.6[l]
41	J (1.2)	210-220	6.0	76.2	15.8	8.0[l]

[a] 100 Grams containing 62% conjugated linoleic acid or their alkyl esters for each experiment.

[b] Moles per mole of linoleic acid. A, acrylic acid; B, methyl acrylate; C, methacrylic acid; D, methyl methacrylate; E, crotonic acid; F, ethyl crotonate; G, cinnamic acid; H, methyl cinnamate; I, 10-undecenoic acid; J, methyl 10-undecenoate.

[c] Sulfur (0.03-0.05 g) added.

[d] Hydroquinone (0.3-0.4 g) used in each experiment.

[e] Nitrogen atmosphere.

[f] Gas liquid chromatography data.

[g] Elaidinization and adduct formation in situ.

[h] Sulfur not added.

[i] Acetic acid (100 ml) added.

[j] Benzene (100 ml) added.

[k] Heating carried out under initial nitrogen pressure of 5 kg/cm^2.

[l] Analysis by combining column chromatographic and gas liquid chromatography data.

TABLE II

Characteristics of Diels-Alder Adducts[a]

Sl. no.	Adduct from acid dienophile and derivatives	Molecular wt	Acid value	Saponification value	Iodine value	Oxirane oxygen, %
I	Acrylic acid	349 (352)	320 (318.4)	---	71.3 (72.1)	---
A	Dimethyl ester	376 (380)	---	287.4 (292.6)	65.6 (66.8)	---
B	Dibutyl ester	458 (464)	---	237.1 (241.8)	65.6 (54.7)	---
C	Epoxidized dimethyl ester	---	---	---	2.6	3.4 (4.3)
II	Methacrylic acid	363 (366)	307.2 (306.5)	---	69.7 (69.4)	---
A	Dimethyl ester	394 (394)	---	287.2 (284.8)	64.3 (63.6)	---
B	Dibutyl ester	474 (478)	---	238.2 (234.7)	55.0 (53.1)	---
C	Epoxidized dimethyl ester	---	---	---	5.4	3.0 (3.9)
III	Crotonic acid	364 (366)	307.0 (306.5)	---	69.8 (69.4)	---
A	Dimethyl ester	392 (394)	---	282.0 (282.2)	64.2 (64.5)	---
B	Diethyl ester	418 (422)	---	262.0 (265.9)	60.4 (60.2)	---
C	Epoxidized dimethyl ester	---	---	---	7.5	3.1 (3.9)
IV	Cinnamic acid	424 (422)	259.4 (265.9)	---	---	---
A	Dimethyl ester	454 (450)	---	244.0 (249.3)	---	---
B	Epoxidized dimethyl ester	---	---	---	---	2.8 (3.4)
V	10-Undecenoic acid	462 (464)	240.0 (241.8)	---	56.0 (54.7)	---
A	Dimethyl ester	484 (492)	---	228.0 (228.0)	52.4 (51.9)	---

[a] Figures in parentheses are calculated values.

columns and the dialkyl ester adducts were recovered after removal of the solvents. The dimethyl esters of crotonic and cinnamic acid adducts were similarly prepared. The dimethyl ester adducts (100 g) were epoxidized in benzene (20 g), with acetic acid (8 g), hydrogen-bonded amberlite resin (5 g) and hydrogen peroxide (30-32%, 37-40 g), and the mixture was heated at 70-75 C for 6 hr. The product was dissolved in ethyl ether and the solution filtered. The clear filtrate was washed with water and the solvent removed under reduced pressure to obtain the epoxidized material. The various characteristics of the acid Diels-Alder adducts, their alkyl esters and epoxidized derivatives are given in Table II.

The Diels-Alder adducts from the reaction of methyl acrylate, methyl methacrylate, ethyl crotonate and methyl cinnamate and the corresponding alkyl esters of isomerized safflower fatty acids were separated in 90-95% purity from the unreacted fatty esters by fractional distillation under reduced pressure (1 mm Hg). A portion (10 g) of each of these crude adducts was purified by a column packed with silica gel using hexane and ethyl ether-hexane 20:80 successively, when the pure adduct was obtained in the second eluant. The IR of these products showed peaks due to ester (1730 cm^{-1}) and cyclohexene (720 cm^{-1}) groups. Other characteristics were similar to the products obtained by the esterification of the acid adducts with the corresponding alcohols (Table II).

PMR spectra of the purified Diels-Alder adducts from acrylic, methacrylic, crotonic and cinnamic acids gave peaks: 11 to 12, 2H for two carboxyls which disappeared when D_2O exchange was effected; 5.76, 2H for vinyl hydrogens in cyclohexene ring; 1 to 2, 22H for methylenes and 0.6 to 1.0, 3H for terminal methyl in acrylic and cinnamic acid adducts while 6H for methacrylic and crotonic acid products (all chemical shifts are expressed in δ = ppm values). The cinnamic acid adduct gave an additional peak at 7.1, 5H for the phenyl ring.

The Diels-Alder adduct obtained by the reaction of methyl methacrylate and methyl esters of conjugated safflower fatty acids was dehydrogenated by both the methods described by Teeter et al. (1) and Paschke et al. (10) using 10% Pd-C catalyst. The isolated products showed absorption maximum at 273 mμ and a shoulder at 281 mμ for substituted benzene. The PMR spectra of the dehydrogenated products in carbon tetrachloride gave peaks at 7.3 corresponding to aromatic hydrogens, while the singlet at 5.76 due to cyclohexene grouping disappeared.

DISCUSSION

The yields of the Diels-Alder adducts from the reaction products when acrylic, methacrylic, and cinnamic acids and their esters were used, varied between 57-64%. Though crotonic acid gave adduct to the extent of 56%, its ester gave only 40%. The yields of the adducts derived from 10-undecenoic acid and its ester were only 18% as a maximum. Evidently a double bond adjacent to the carboxyl group is required for good yields under our conditions.

The increased hydrocarbon nature of ethyl crotonate and methyl 10-undecenoate may account for these two adducts eluting along with the alkyl esters of unreacted fatty acids in column chromatographic fractions. While methacrylic acid adduct could be separated by partitioning the reaction product between hexane and 90% methanol, the crotonic acid adduct could not be separated although both are structural isomers.

ACKNOWLEDGMENT

This research has been financed in part by grant from USDA under PL-480.

REFERENCES

1. Teeter, H.M., J.L. O'Donnell, W.J. Schneider, L.E. Gast and M.J. Danzig, J. Org. Chem. 22:512 (1957).
2. Danzig, M.J., J.L. O'Donnell, E.W. Bell, J.C. Cowan and H.M. Teeter, JAOCS 34:136 (1957).
3. Teeter, H.M., E.W. Bell, J.L. O'Donnell, M.J. Danzig and J.C. Cowan, Ibid. 35:238 (1958).
4. Teeter, H.M., J.C. Cowan, L.E. Gast, W.J. Yurgen and R.A. Clark, Ibid. 38:117 (1961).
5. Kaufmann, H.P., H. Gruber and H. Bruning, Fette Seifen Anstrichm. 63:633 (1961).
6. Teeter, H.M., C.R. Scholfield and J.C. Cowan, Oil and Soap 23:216 (1946).
7. Balakrishna, R.S., B.G.K. Murthy and J.S. Aggarwal, JAOCS 48:689 (1971).
8. Sastry, G.S.R., B.G.K. Murthy and J.S. Aggarwal, Ibid. 48:686 (1971).
9. Sastry, G.S.R., B.G.K. Murthy and J.S. Aggarwal, Paint Mfr. 40(8):32 (1970).
10. Paschke, R.F., L.E. Peterson and D.H. Wheeler, JAOCS 41:723 (1964).

[Received September 21, 1971]