Reactions of Conjugated Fatty Acids. VI. Selenium Catalysis, a Method for Preparing Diels-Alder Adducts from Cis,trans-Octadecadienoic Acid[1]

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IN PREVIOUS PAPERS we have described the preparation of Diels-Alder adducts from a variety of dienophiles and pure *trans,trans*-octadecadienoic acid (5) or from conjugated soybean fatty acids in which the contained conjugated linoleic acid had been isomerized to the *trans,trans* configuration (1). In the latter paper the potential utility of esters and epoxidized esters of certain of these adducts as plasticizers and stabilizers of polyvinyl chloride was pointed out.

Among domestic vegetable oils, soybean oil and, because of its linoleic acid content, safflower oil are of particular interest as raw materials for preparing Diels-Alder adducts. Alkali conjugation of these oils yields conjugated fatty acids in which the contained conjugated linoleic acid is in the *cis,trans* configuration (2). The preparation of adducts would be simpler and more economical if these alkali-conjugated fatty acids could be used directly without separate isomerization of the contained conjugated linoleic acid to the *trans,trans* configuration as previously reported.

In the analytical determination of the "pandiene" number Von Mikusch (6) employed iodine as a catalyst to induce isomerization of *cis,trans* to *trans,trans* conjugated fatty acids during simultaneous addition of maleic anhydride. Since iodine did not appear to give satisfactory results in the presence of certain dienophiles, the use of selenium was investigated.

Discussion

It was found that adducts were formed readily by heating alkali-conjugated fatty acids or their esters with appropriate dienophiles (Table I) in the presence of a small amount of selenium (1.5–2 g. per mole of contained conjugated fatty acid or about 0.5–0.7% by weight). Dienophiles tested included esters of maleic acid, acrylic acid and its esters, acrolein, and acrylonitrile. Yields of crude adducts ranged from 64–82%, based on the conjugation present in the alkali-conjugated fatty acids.

Nearly all of the selenium present separated out of the reaction products when they were allowed to stand, and it could then be removed by filtration. However traces of reduced selenium compounds remained in the adducts. These traces were most readily detected by heating the adduct to about 300°C. and noting the odor of hydrogen selenide. Ordinary vacuum distillation was not effective in removing this residual selenium. Codistillation of product and selenium-containing compounds appeared to take place so that distilled fractions had an objectionable odor of hydrogen selenide. This odor could be removed by several methods, such as stirring the distillate with mercury, colloidal silver, or mercuric chloride solution, passing it through charcoal columns, or washing it with lead acetate solution. However material so treated usually redeveloped objectionable odor on heating.

Surprisingly, distillation of the adducts in a centrifugal molecular still was found to yield distillate free of selenium as judged by failure upon heating to cause development of odor. Several passages of the main fractions through the still were generally required to yield products apparently free of selenium. Foreruns contained some selenium, but most condensed as a gray deposit in the cold trap of the still.

Pure adducts obtained by this selenium isomerization technique gave theoretical analyses and, on the basis of physical properties and infrared spectra, they appeared to be identical with those obtained from *trans,trans* conjugated linoleic acid. Because of the difficulty of removing selenium, yields of purified adducts were lower than desired. Selenium isomerization is however an effective method for preparing adducts directly from *cis-trans* conjugated fatty acids. If a cheap and efficient means of removing selenium can be found, this method should have considerable potential for large-scale preparation of adducts.

Epoxidation of adduct esters is complicated by the reactivity of the oxirane ring, which is readily opened by acidic materials present during epoxidation to give products low in content of oxirane oxygen. For this reason we originally used perbenzoic acid for epoxidation (1). We have found that epoxidation can be accomplished without excessive opening of the oxirane ring by using peracetic acid (4) (Table II) or by using hydrogen peroxide and acetic acid with an ion-exchange resin as catalyst (3).

Although a number of minor modifications of the latter procedure were tried (Table III), epoxidation did not proceed as extensively as with peracetic acid. However epoxidations of 80% and more could be obtained with only minor opening of the oxirane ring, as shown in figures for "hydroxy-acetoxy" in Table III. Highest epoxidation (92.9%) was obtained by epoxidation and re-epoxidation of the product. Best yields of epoxide in a single step (85.6%) were obtained in the presence of a large amount of ion-exchange resin.

Both the adduct esters and their epoxides show promise as plasticizers and stabilizers for polyvinyl chloride (4). Investigations are in progress to evaluate these products more fully for this and other related uses.

Experimental

Preparation of Adducts

Alkali-conjugated safflower fatty acids containing 72–76% of diene conjugation [calculated as the *cis,trans* isomer, $E^{1\%}_{1\,\mathrm{cm.}}$, 950 (2)] were employed. Re-

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TABLE I

Adducts Prepared from Alkali-Conjugated Safflower Fatty Acids

Product	Reactants[a]	n_D^{30}	B. P.	Analysis				Sap. eq.		Iodine value		Yield[i]	
				Theory		Found							
				C	H	C	H	Theory	Found	Theory	Found	Crude[j]	Pure
Acrylic adduct esters			°C.									%	%
Methyl	A	1.4681	115–30/10μ[b]	72.59	10.60	72.43	10.49	190	193	66.7	67.1	73	59[c]
n-Butyl	B	1.4630	150–65/12μ[b]	74.95	11.28	74.95	11.23	232	235	54.4	55.7	78	72[c]
2-Ethylhexyl	B	1.4652	180–200/11μ[b]	77.03	11.88	76.86	11.67	288	286	44.0	44.3	64	49[d]
Maleic adduct esters													
Methyl	A	1.4693	140–65/15μ[b]	68.46	9.60	68.75	9.70	—	—[e]	57.5	55.6	80	52[d]
n-Butyl	A	1.4642	170–80/13μ[b]	72.29	10.70	72.24	10.53	—	—[e]	45.0	44.1	79	56[d]
2-Ethylhexyl	A	1.4659	215/16μ[b]	75.35	11.28	74.55	11.23	—	—[e]	34.5	34.6	82	67[d]
Methyl ester of acrylonitrile adduct	C	1.4754	185–200/0.03 mm.	75.76	10.64	76.03	10.73	—	—	—	—	—	20[f,h]
Methyl ester of acrolein adduct	C	1.4800	172–77/0.03 mm.	75.38	10.93	75.57	10.93	—	—	—	—	—	23[g,h]

[a] See Experimental for key to reactants. [b] Molecular distillation. [c] Purified by two passes through molecular still. [d] Purified by passing twice through molecular still and once through a carbon-alumina column. [e] Maleic adducts do not saponify completely (1). [f] Purified by conventional distillation. [g] Purified by conventional distillation and chromatography on alumina. [h] Large foreruns were taken and discarded to facilitate removal of selenium. [i] Based on conjugation originally present. [j] After first pass through molecular still.

actants for the various products in Table I were as follows:

a) an alkyl ester of conjugated safflower fatty acids and the corresponding alkyl ester of acrylic or maleic acid;

b) conjugated safflower fatty acids and acrylic acid (The crude acrylic adduct, obtained in quantitative yield, was esterified to obtain the products shown in Table II.); and

c) methyl esters of conjugated safflower fatty acids and acrylonitrile or acrolein.

Two general procedures for preparing acrylic and maleic adducts were established. The first procedure should be used when the dienophile is too volatile to permit the desired reaction temperature to be reached. The second procedure is generally applicable to reactions involving maleic esters or other high-boiling dienophiles.

Procedure 1. A Parr[3] medium-pressure hydrogenation vessel is charged with conjugated fatty acids or esters, dienophile in 10% excess based on total fatty acids or esters, and 1.6 g. of each of hydroquinone and selenium per mole of diene present. An equal volume of heptane or benzene is added, and air is flushed from the reactor with nitrogen. The reactor is then filled with nitrogen to a pressure of 30 p.s.i., sealed, and heated with constant stirring to 250° for 45 min. Internal pressures may reach as high as 400 p.s.i. during the reaction. After cooling, the contents of the reactor are removed (*Use hood:* volatile, toxic, reduced selenides are present), filtered to eliminate precipitated selenium, and washed with water. The solvent is removed, and the product is purified by an appropriate method as noted in Table 1.

In this table the yield of pure product refers to the final yield of essentially selenium-free product after purification by the indicated procedure. The "crude" yield represents the amount of product recovered after the first pass of the reaction mixture through a molecular still. Except for the presence of objectionable traces of selenium compounds, these "crude" products are not distinguishable in their ordinary analytical constants from the "pure" products.

TABLE II

Properties of Adducts Epoxidized with Peracetic Acid

Product	Purity[a]	Iodine value	n_D^{30}
Acrylic adduct esters	%		
Methyl	98.0	1.1	1.4669
n-Butyl	95.0	0.8	1.4636
2-Ethylhexyl	94.5	0.2	1.4651
Maleic adduct esters			
Methyl	94.7	2.3	1.4697
n-Butyl	92.0	2.0	1.4642
2-Ethylhexyl	89.4	1.7	1.4675

[a] Based on oxirane-oxygen determination.

TABLE III

Epoxidation of Dimethyl Ester of the Acrylic Acid Adduct with 50% Hydrogen Peroxide[a] and an Ion-Exchange Resin Catalyst

Wt. of resin per double bond	Excess H_2O_2	Time of addition	Temperature[b]	Iodine value	Epoxy oxygen	Hydroxyacetoxy	Epoxidation
g.	*moles*	*min.*	°*C.*		%	%	%
180	0.1[c]	15	60	21.4	2.6	5.1	63.1
—[d]	—	—	—	3.6	3.9	1.7	92.9
180	0.1[c]	30	60	5.9	3.3	10.4	81.5
210	0.1	28	RT-60	8.9	3.3	6.6	80.0
210	0.2	48	RT-60	2.7	3.3	13.5	82.5
456[e]	0.2	31	RT-60	4.7	3.0	6.9	85.6

[a] Hydrogen peroxide was added dropwise to the reaction mixture.

[b] RT indicates addition of peroxide at room temperature followed by heating to temperature stated.

[c] 30% hydrogen peroxide used.

[d] This run represents re-epoxidation under same conditions of product obtained in run described in first line of table.

[e] Di-*n*-propyl ester of adduct used in this run.

This procedure was used for preparation of adducts of methyl esters of conjugated safflower fatty acids with acrylonitrile, acrolein, and methyl acrylate and for the adduct of conjugated safflower fatty acids and acrylic acid. *n*-Butyl and 2-ethylhexyl esters were prepared from the crude acrylic acid adduct by refluxing with three times the equivalent amount of the desired alcohol in the presence of 3% of dry hydrogen chloride as a catalyst. The esters were isolated by conventional means and purified as noted in Table I.

Procedure 2. A three-necked flask, fitted with an efficient stirrer, condenser, and gas inlet tube, is charged with an alkyl ester of conjugated safflower fatty acids, the corresponding alkyl maleate in an amount equivalent to the total fatty ester and 2 g. of selenium mole of diene present. The mixture is heated under a nitrogen atmosphere with constant stirring for 2.5 hrs. at 230°. After cooling the mixture and removing the precipitated selenium by filtration, the product is isolated and purified as indicated in Table I.

Epoxidation Reactions

Epoxidations with peracetic acid (4) were conducted in the laboratories of the Carbide and Carbon Chemicals Corporation by P. S. Starcher. Properties of the products are listed in Table II.

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[3] The name of this company is furnished for information only, and its mention does not constitute an endorsement of this company or its products.

Epoxidation of the dimethyl ester of the acrylic acid adduct with hydrogen peroxide and an ion-exchange resin as catalyst required minor modifications of the published procedure (3). Conditions yielding products representing 80% or more of epoxidation are listed in Table III.

Summary

Adducts of dienophiles and alkali-conjugated safflower fatty acids containing conjugated linoleic acid in the *cis,trans* form were prepared by heating the reactants in the presence of selenium as a catalyst. The products appeared to be identical to those prepared from *trans,trans* conjugated linoleic acid so that isomerization of *cis-trans* to *trans,trans* acids is eliminated as a separate step. Although yields of pure product were lower than desired because of difficulties in removing selenium, yields of crude adducts ranged from 64–82%. The adducts obtained could be epoxidized with hydrogen peroxide and an ion-exchange resin as catalyst in 80–93% yield or with peracetic acid in 89–98% yield.

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The Effect of Gamma Radiation on the Hydrogenation of Cottonseed Oil

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GAMMA RADIATION has been found to affect the rates of certain reactions. This radiation on interacting with atoms of the materials through which it is passing has the ability to eject electrons which may produce ions or free radicals, depending on the substances involved. The ions or free radicals may promote desired reactions or may cause reactions which would not occur otherwise.

Gamma radiation significantly increases the rates of polymerization of ethylene (12, 13) and styrene (3). The common feature of these addition-type of polymerizations is that they all have a free radical mechanism. The reaction between chlorine plus benzene to produce benzene hexachloride also has a free radical mechanism. *Gamma* radiation as well as actinic light vigorously increases the rate of this reaction (10). The radiation presumably forms chlorine atoms from the chlorine molecule.

When the linear-type of polymers are exposed to *gamma* radiation, the properties of the polymers frequently change. In the case of polyethylene (7, 11) the tensile strength and hardness increase and hydrogen gas is released. Apparently some of the hydrogen atoms are knocked off of the polymer chain, and cross-linkage between the chains results. In the case of polymethylmethacrylate however tensile strength decreases rapidly with irradiation (7). Depolymerization and chain cleavage are probably the main reactions. Both cross-linking and depolymerization occur in the polymers, but the dominant reaction depends on the polymer.

Atomic hydrogen is an effective hydrogenation agent for hexadecene-1 and linseed oil even in the absence of a catalyst (4). Some polymerization also occurs, indicating that the atomic hydrogen reacts at the double bond to form a free radical. This radical can react with another hydrogen atom to complete the hydrogenation, or it can react with another radical to form a dimer.

Burton (6) bombarded oleic acid with deuterons. The irradiated material contained 1.7% stearic acid, proving that hydrogenation occurred. In addition, 52.5% of the oleic acid was converted to polymerized acid. Apparently the reactions involved were similar to those with atomic hydrogen. Earlier Sheppard and Burton (16) and Breger and Burton (5) demonstrated that paraffinic compounds were produced by the irradiation of fatty acids with *alpha* particles and deuterons.

The effect of *gamma* radiation from Cobalt 60 was determined for the oxidation reaction between oleic acid or methyl oleate and oxygen (8). Radiation significantly increased the rates of peroxide and carbonyl formation. Long and Proctor (14) utilized high-energy cathode rays to produce monocarbonyl compounds from several vegetable oils. Radiation also decreased the amounts of triene groups. The presence of oxygen did not seem to have any significant effect on the production of monocarbonyls. Antioxidants tended in some cases however to suppress the monocarbonyl formation. The mechanism of the reaction was not determined, but it appears to be a complicated free radical type. Recently Pan, Goldblith, and Proctor (15) studied the effect of ionizing radiation on the *trans*-isomerization of oleic acid and potassium oleate.

No reference was found concerning the effect of *gamma* radiation on the hydrogenation of triglycerides. The results of such an investigation are reported here.

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