Allyl Esters and Allyl Epoxy Esters from Crambe Oil

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ABSTRACT

Room temperature transesterification of crambe oil with allyl alcohol gave allyl esters previously prepared by hydrolysis of the oil and reesterification of the mixed acids at elevated temperatures. Treating the esters with m-chloroperbenzoic acid in the presence of sodium bicarbonate resulted in the selective epoxidation of ethylenic bonds and suppression of side reactions. Bifunctional allyl epoxy esters produced in 88% overall yield by this method contain 5.08% oxirane oxygen and an unsaturation equivalent to 91% allyl group; they are prospective monomers for various types of polymerization.

INTRODUCTION

The U.S. Food and Drug Administration has cleared more than 20 allyl esters as additives for perfumes and foods (1). Data published by Jenner and coworkers indicate that the higher esters are less toxic than the lower ones (2,3). Allyl esters of long chain acids have many prospective uses. If their acid moieties possess a double bond, the esters can be further converted to allyl epoxy esters, which are versatile in polymerizations. Seed oil from *Crambe abyssinica* Hochst, ex R.E. Fries, containing ca. 60% erucic and 20% oleic acids as glyceride esters (4), is a suitable starting material.

The route to allyl esters described here is much simpler than one reported earlier (5). The modified epoxidation procedure is an improvement that allows selective derivatization without ring opening.

EXPERIMENTAL PROCEDURES

Materials

Crambe oil (IV, 95; MW, 1016 calculated on the basis of saponification equivalent) was available from previous work and m-chloroperbenzoic acid (85% pure), was supplied by Aldrich.

Transesterification

A fresh solution prepared by bubbling dry hydrogen chloride into 100 g allyl alcohol until it weighed 110 g was introduced into a 500 ml flask containing 100 g crambe oil. The flask was stoppered, and the contents were shaken at room temperature for 2 days. The resulting allyl esters were diluted with 800 ml ethyl ether, washed with water (eight 500 ml portions), dried over magnesium sulfate, filtered, and recovered by removal of the solvent. The product weighed 108 g (100%).

Epoxidation

A 1 liter flask with a magnetic stirring bar was charged with 20 g allyl esters of mixed acids (IV, 148; MW, 366), 15 g sodium bicarbonate, and 250 ml benzene. Stirring was started, and the temperature was kept below 25 C by cooling as required during addition of a solution of 26 g (10% in excess on the basis of 2.28 double bond/ester) m-chloroperbenzoic acid in 300 ml benzene. Stirring was continued for 1.5 hr at room temperature to allow completion of the epoxidation. The reaction mixture was filtered. The filtrate was treated with 10% sodium sulfite in a separatory funnel until a test with starch-iodide paper was negative. The organic layer was washed with 5% sodium bicarbonate and water. Removal of benzene by lyophilization afforded allyl epoxy esters weighing 18.4 g (88%).

RESULTS AND DISCUSSION

Allyl Esters

Previously, crambe acid allyl esters (5,6) were prepared by splitting the seed oil at elevated temperature and reesterifying the mixed acids under conditions in which water was removed azeotropically. Room temperature transesterification is advantageous, provided there is no addition of hydrogen chloride to the double bonds and provided that transesterification proceeds at a reasonable speed.

Thin layer chromatography (Silica Gel G, benzene) shows that the amounts of alcohol affected the rate of reaction. The conversion of glycerides to allyl esters in 1 hr was roughly 20-40%. Quantitation by temperature-programmed gas liquid chromatography (GLC, 4 C/min, 250-390 C, OV-1 column, 20% sample in toluene as solvent) of the reaction mixture containing 2000 mole % allyl alcohol revealed that the conversion was essentially complete after 1 day; 2 days were required for similar conversion in the mixture containing 500 mol % allyl alcohol. The composition of the resulting allyl esters, as determined by isothermal (180 C) GLC, is listed in Table I.

These data show that the transesterification is feasible and convenient.

Allyl Epoxy Esters

Allyl epoxy esters are not easily derived from epoxy glyceride oils because the highly strained oxirane ring tends to open in the presence of acid or base catalysts used in hydrolyzing or transesterifying the oils. Warson et al. (8) synthesized allyl epoxy ester by Darzens Condensation of acetone and allyl chloroacetate, but the yield was low (45%) and the purity poor (65.2%).

In general, the epoxidation of isolated internal double bonds occurs easily in 2-4 hr as compared with 28 hr under the same conditions for terminally unsaturated compounds (9). This generalization was borne out by the present work,

TABLE I

Isothermal (180 C) Gas Liquid Chromatography of Crambe Acid Allyl Esters

5% Ap. L.		5% R-446	
Component	Area, %	Component	Area, %
14:0	0.05	14:0	0.06
16:1	0.41		
16:0	1.84	16:0	1.86
18:3	6.60	16:1	0.22
18:2	8.39	Unknown[a]	0.18
18:1	17.07	18:0	0.61
18:0	0.72	18:1	15.91
20:0	0.03	18:2	7.81
20:1	1.81	18:3	6.15
20:0	0.34	20:0	0.93
22:1	62.30	20:1	3.28
22:0	0.45	20:2	0.06
		Unknown[b]	0.72
		22:0	1.78
		22:1	59.65
		24:0	0.39
		24:1	0.39

[a] ECL (7):17.76.
[b] ECL: 21.75.

but the process was only successful after modification to suppress side reactions.

The infrared spectrum of the product (thin film) showed strong allylic bands at 10.05 and 10.75 μm without hydroxy absorption. On the other hand, NMR (90 MHz, $CDCl_3$) showed unresolved mutiplet centered at $\delta 3.2$ for $C\underline{H}$-OH in the fatty chain and GLC (6ft x 1/8 in. 3% OV-1 glass column, 200-250 C at 2 C/min) gave an additional peak (retention times:30-34 min) amounting to 12.87% for the product from epoxidation in the absence of sodium bicarbonate. Obviously, the partial cleavage of oxirane ring by m-chlorobenzoic acid, which is more strongly acidic than the corresponding peracid, generated during epoxidation did not occur because of the presence of the added sodium bicarbonate which neutralized the generated acid in situ.

Analyses of the product gave the oxirane oxygen as 5.08% and iodine value as 58.5. The MW of allyl epoxy esters, based on the MW of allyl esters (366) and the number of double bond/molecule (2.18 calculated from GLC composition in Table I), is estimated to be 385 [366 + (16) (2.18 - 1) $\cong$ 385]. Assuming that epoxidation took place only at the double bond of fatty chain (1.18), the calculated iodine value for the remaining unsaturation due to the allyl group of allyl epoxy esters is:

$$\frac{147.7}{2.18} \times \frac{366}{385} = 64.4$$

where 147.7 is the observed iodine value of the allyl esters. The observed iodine value of the mixed allyl epoxy esters, 58.5, indicates that more than 1.18 double bond/molecule were epoxidized and that an average of ca. 0.91 double bond/molecule remains ($\frac{58.5}{64.4} = 0.91$). In other words the data suggest that ca. 9% of the allyl groups were epoxidized or that the epoxidation took place preferentially at the internal double bonds.

Because of the difference in reactivities of ethylenic epoxy and allyl groups, these esters are versatile in polymerizations, including free-radical-initiated polymerization of the allyl with the epoxy intact (10), curing of the epoxy with the allyl intact (11), and polymerization-curing of both groups to give a high polymer (12). When used in powder coating (13) and light curable (14,15) formulation, allyl epoxy esters will require no solvent and less energy, respectively.

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