

# Diol Diricinoleates From Dihaloalkanes<sup>1</sup>

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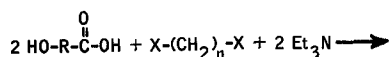
## Abstract

A series of alkanediol diricinoleates was prepared by heating ricinoleic acid with triethylamine and dibromo- or dichloroalkanes containing 2 to 10 carbon atoms. As expected, the dibromides react more rapidly than the dichlorides. This method of esterification avoids the side reaction of estolide formation which occurs when ricinoleates are prepared by direct esterification or transesterification. The products are high molecular weight diols which should be useful in the preparation of polyurethanes.

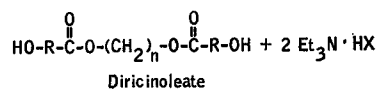
## Introduction

In the course of work on the preparation of urethane elastomers from castor oil derivatives, it seemed probable that elastomers with improved properties could be obtained by the use of higher molecular weight, dihydroxy derivatives. Castor oil is largely a triglyceride of ricinoleic acid (12-hydroxy-9-octadecenoic acid). The hydroxyl group at the 12 position makes ricinoleate derivatives particularly useful in polyurethane formation. Diols, such as the mono-ricinoleates of ethylene and propylene glycols are available, but derivatives of higher molecular weight were desired such as the diricinoleate esters of dihydroxy compounds.

These diricinoleates can be prepared by the standard techniques of direct esterification of ricinoleic acid or transesterification of ricinoleate esters. However, in these cases appreciable amounts of by-products such as monoricinoleates and estolides may be formed. An esterification procedure that is particularly well suited for the preparation of diricinoleates is that of Mills et al. (1,2). As applied to the preparation of diricinoleates this involves the reaction of the triethylamine salt of ricinoleic acid with a dihaloalkane to form a diricinoleate plus triethylammonium halide.



Ricinoleic acid



Diricinoleate



Estolide formation by self-condensation of ricinoleic acid is avoided since alcoholic hydroxyl groups are not involved in this reaction.

## Experimental Procedures

### Materials

Crude ricinoleic acid (OH No. 163, Acid No. 176) was prepared by saponification of castor oil. Pure ricinoleic acid (OH No. 186.7, Acid No. 185) was prepared by saponification of fractionally distilled methyl ricinoleate.

The dihaloalkanes were used as received from Eastman Kodak Co. Triethylamine was purified by distillation from sodium hydroxide.

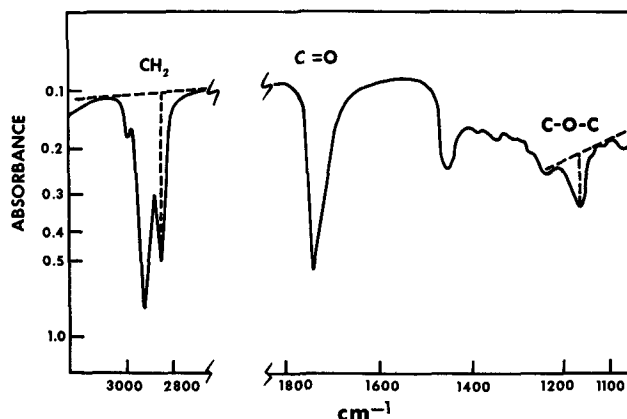


FIG. 1. Infrared spectrum of thin film of 1,4-butanediol diricinoleate.

### Diricinoleate Preparation (0.1–0.2 mole scale)

A mixture of 1.1 mole ricinoleic acid and 1.1 mole triethylamine per 1.0 mole of a dihaloalkane was heated under reflux to a pot temperature of 150 C as rapidly as possible (20–60 min with dibromoalkanes, 120–240 min with most dichloroalkanes), and then held at 150 C for 1 to 3 hr. The reaction mixture was cooled, taken up in ether and washed free of triethylamine hydrohalide and excess triethylamine with 5% HCl and water.

In most cases, unreacted ricinoleic acid was then extracted with 5% sodium hydroxide and the product diricinoleate obtained by removal of solvent. The unreacted ricinoleic acid was recovered by acidification and ether extraction of the sodium hydroxide extract.

In a few cases, unreacted ricinoleic acid was removed by passing a tetrahydrofuran solution of the product through a column of Dowex 1 ion exchange resin in the OH<sup>-</sup> form. The ricinoleic acid was then eluted with a solution of 14 ml conc. HCl/100 ml tetrahydrofuran solution.

### Measurement of Ricinoleate Concentration

About 1 ml samples were withdrawn from the reaction mixtures at intervals, taken up in ether, washed with 5% HCl and water, and evaporated to dryness.

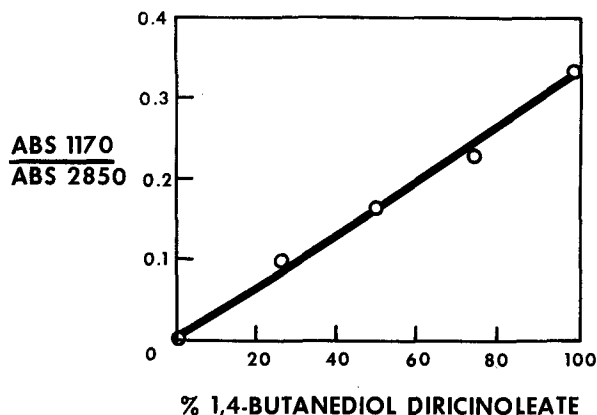


FIG. 2. Ratios of absorbance at 1170 cm<sup>-1</sup> to absorbance at 2850 cm<sup>-1</sup> for mixtures of 1,4-butanediol diricinoleate with ricinoleic acid.

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TABLE I  
Diol Diricinoleates

Dihalide	Ricinoleic acid	Yield diester %	Acid recovered %	OH No. theory/found	I <sub>2</sub> No. theory/found	Halogen %	C % theory/found	H % theory/found
1,2-Dichloroethane	Crude	52	94					
1,3-Dibromopropane	Crude	80 <sup>a</sup>	80					
1,4-Dibromobutane	Pure	83	95	173/176	77.9/77.5	Nil	73.8/73.5	11.5/11.4
1,4-Dichlorobutane	Crude	77	97	150/151	80.8/80.3	0.9		
1,5-Dibromopentane	Pure	81	92	169/171	76.3/76.6	0.2	74.1/73.7	11.5/11.4
1,5-Dibromopentane	Crude	83 <sup>a</sup>	82			Nil		
1,10-Dibromodecane	Pure	86 <sup>b</sup>	94	153/152	69.1/69.4	0.04	75.1/75.0	11.8/11.7
1,10-Dibromodecane (recrystallized)	Pure	.... <sup>c</sup>	....	153/153	69.1/68.9	Nil	75.1/75.4	11.8/11.9
1,4-Dichloro-2-butene	Crude	39	77			Nil		

<sup>a</sup> Unreacted ricinoleic acid removed on ion exchange resin.

<sup>b</sup> Mp 27-31 C.

<sup>c</sup> Mp 44.0-44.5 C.

In these samples, unreacted ricinoleic acid was determined by titration, and ricinoleate concentration was estimated from the infrared absorption of the ester groups. A portion of the infrared spectrum of a thin film of 1,4-butanediol diricinoleate is shown in Figure 1.

Ester formation could be followed qualitatively by the shift in position of the carbonyl peak, but a more quantitative estimate of ricinoleate concentration was made by measuring the ratio of the C-O-C ester absorbance at about 1170 cm<sup>-1</sup> to the CH<sub>2</sub> absorbance at 2850 cm<sup>-1</sup>. It was shown (Fig. 2) that this ratio of absorbances was proportional to the concentration of a diricinoleate in a mixture of this diricinoleate with ricinoleic acid. This procedure was not useful with ricinoleate ester concentrations less than about 25% since the ester absorbance in this range could not be measured accurately.

### Results and Discussion

The increase in ricinoleate concentration with time of heating for the reactions of 1,4-dibromobutane and 1,4-dichlorobutane with triethylammonium ricinoleate is shown in Figure 3. Ricinoleate concentrations, determined by infrared, agree well with those deter-

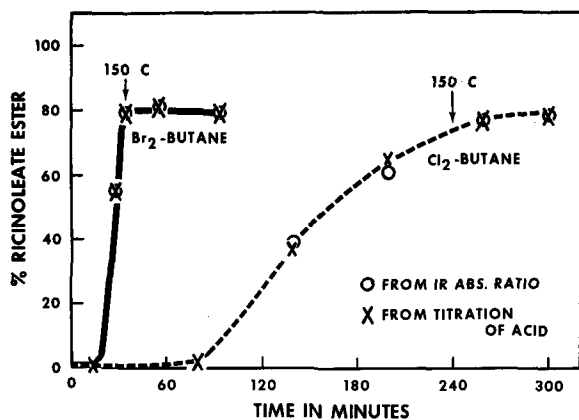


FIG. 3. Ricinoleate ester conc. vs. time of heating for reactions of 1,4-dibromobutane and 1,4-dichlorobutane with triethylammonium ricinoleate.

mined by titration of unreacted ricinoleic acid. The much more rapid reaction of the dibromide can be seen. The time at which the temperature of the reaction mixtures rose to 150 C is indicated. The temperature does not rise to this point until most of the low boiling triethylamine has been converted to the hydrohalide.

A series of diricinoleates was prepared, as indicated in Table I, from pure and crude ricinoleic acid and  $\alpha,\omega$ -dihaloalkanes containing 2 to 10 carbon atoms. The yields ranged from 77% to 86% when using the C<sub>3</sub> to C<sub>10</sub> dihaloalkanes. Because of its low boiling point, 1,2-dichloroethane reacted very slowly (8 hr to 150 C) and yielded only 52% diricinoleate. The allylic compound, 1,4-dichloro-2-butene, reacted rapidly (50 min to 150 C) but gave only a low yield of the desired diricinoleate. Over 92% of the ricinoleic acid was recovered when sodium hydroxide extraction was used during workup of product from dihaloalkanes.

Purity of the diricinoleates was determined by the functional group and elemental analyses listed in Table I. In every case, the values found agree well with the theoretical values for hydroxyl number, iodine number and carbon and hydrogen content. Low halogen contents indicate the absence of significant amounts of partly reacted dihalides. Iodine numbers within 0.5% of theoretical values indicate the absence of dehydrohalogenated products. Nitrogen contents were less than 0.03% indicating the absence of quaternary ammonium halides.

Diricinoleates of the lower molecular weight diols are oily liquids. However, that of 1,10-decanediol is a solid, melting at 44 C, which may be readily crystallized from petroleum ether.

These diricinoleates, as isolated directly from their reaction mixtures, appear to be sufficiently pure for use as urethane elastomer intermediates and their utility as such is being investigated.

### REFERENCES

- Mills, R. H., M. W. Farrar and O. J. Weinkauff, Chem. Ind., 2144 (1962).
- Mills, R. H., and O. J. Weinkauff (Monsanto Co.), U.S. Patent 3,148,200 (Sept. 8, 1964).

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