

Preparation of the Vinyl Ester of the Diels-Alder Adduct of Petroselinic Acid and Hexachlorocyclopentadiene

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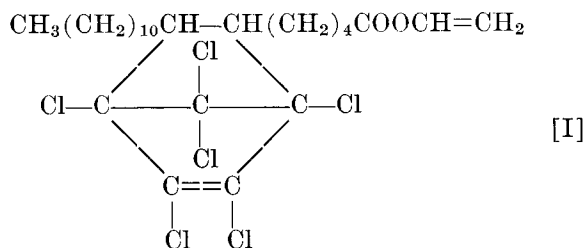
Abstract

Vinyl 5-(1,4,5,6,7,7-hexachloro-3-undecylbicyclo [2.2.1]-5-hepten-2-yl)-pentanoate [I] was prepared by the vinylation of the Diels-Alder adduct of *cis*-6-octadecenoic (petroselinic) acid and hexachlorocyclopentadiene (HCCPD). The HCCPD adduct of methyl petroselinate was also prepared, and distilled.

Introduction

IN THE SEARCH for new oilseed crops in the New Crops Program of the United States Department of Agriculture one of the families of plants selected for study was the *Umbelliferae* (carrots, fennel, parsley, etc.). The seed oils of these plants contain 30–75% petroselinic (*cis*-6-octadecenoic) acid, an isomer of oleic acid found with very few exceptions only in this family of plants.

Any unique use of these seed oils would probably depend on their content of petroselinic acid. Consequently the research on the oils from these plants has been concentrated on the chemistry of petroselinic acid and various derivatives of the acid. One suggested possible use of petroselinic acid is the vinyl ester of the Diels-Alder adduct of the acid with hexachlorocyclopentadiene, vinyl 5-(1,4,5,6,7,7-hexachloro-3-undecylbicyclo [2.2.1]-5-hepten-2-yl)-pentanoate [I], for copolymerization with polyvinyl chloride as an internal plasticizer. This paper describes a procedure for making the vinyl ester of this adduct.



Materials and Methods

The petroselinic acid was isolated from parsley seed oil by the procedure of Fore, Bickford and Holmes (1) and was above 96% in purity. Methyl petroselinate was prepared from petroselinic acid and absolute methanol in the presence of 3% concentrated sulfuric acid catalyst. The hexachlorocyclopentadiene (HCCPD) was used as received from the Hooker Chemical Corporation. The vinyl acetate was purchased from the Eastman Kodak Company and distilled just before use. The activated alumina was that obtained from Alcoa (Grade F-20, mesh 80–200).

Preparation of Petroselinic Acid Adduct of HCCPD

One hundred fifty grams (0.53 mole) of petroselinic acid and 295 g (1.08 moles) of HCCPD were heated in a boiling flask equipped with a condenser in an oil

bath for 28 hr at 134C. The mixture in the flask was kept covered with a nitrogen blanket. The excess HCCPD was distilled off by heating the flask to 130C in an oil bath under ca. 150 μ pressure.

Two hundred sixty-four grams of the dark-colored crude Diels-Alder adduct was dissolved in 900 ml of absolute methanol by stirring. This methanol solution was then added to a large beaker containing 1200 g of urea dissolved in 4 liters of hot methanol (if a precipitate formed the beaker was reheated on a steam bath until solution was effected). The solution was allowed to stand at room temperature overnight. The urea complexed crystals were filtered by gravity and pressed dry without washing. The filtrate was heated to a clear solution, then stored at -5C overnight. The resulting crystals were filtered out as before. The two crops of crystals were combined and treated with hydrochloric acid and water. The precipitated oil was extracted with ethyl ether, the ether solution washed to neutrality with water and dried with Na_2SO_4 . The ether was removed in a rotating evaporator under aspirator vacuum at less than 80C to yield 43 g of material which GLC showed to be mostly petroselinic acid. The methanol was removed from the filtrate in a rotating vacuum evaporator. The residue was treated with hydrochloric acid and water. The precipitated oil was recovered as above, to yield 212.4 g. This was a 72% yield based on the petroselinic acid used. The acid adduct contained 1.4% of petroselinic acid as determined by GLC of the methyl ester using a known weight of methyl palmitate as an internal standard. The acid adduct melted at -15 to -11C and had an IR spectrum as shown in B of Figure 1; n_D^{25} 1.5145 (curve A of Figure 1 is the IR spectrum of HCCPD, for comparison).

Preparation and Distillation of the HCCPD Adduct of Methyl Petroselinate

Thirty-five grams (0.119 mole) of methyl petroselinate and 65 g (0.238 mole) of HCCPD were heated as described above. The mixture was distilled at ca 150 μ to give 3 fractions: (1) 40.9 g excess HCCPD, 60–140C; (2) 12.7 g unreacted methyl petroselinate, 145–202C; and (3) 44.2 g (65% yield) methyl ester adduct, 235–236C. The IR spectrum of fraction 3 was very similar to that shown in E of Figure 1 for the ethyl ester; n_D^{25} 1.5072.

Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{Cl}_6\text{O}_2$: C, 50.64; H, 6.38; Cl, 37.37.

Found: C, 50.58; H, 6.51; Cl, 37.38.

Vinylation of the HCCPD Adduct of Petroselinic Acid

One hundred ninety-one grams (0.344 mole) of acid adduct was treated with vinyl acetate in the presence of HgSO_4 catalyst by the procedure of Lewis and Hedrick (2). The excess vinyl acetate was removed below 40C with water aspirator vacuum, then with pump vacuum. The crude vinyl ester was transferred to a 2 liter separatory funnel with 1 liter of a 1:1 mixture of diethyl ether and

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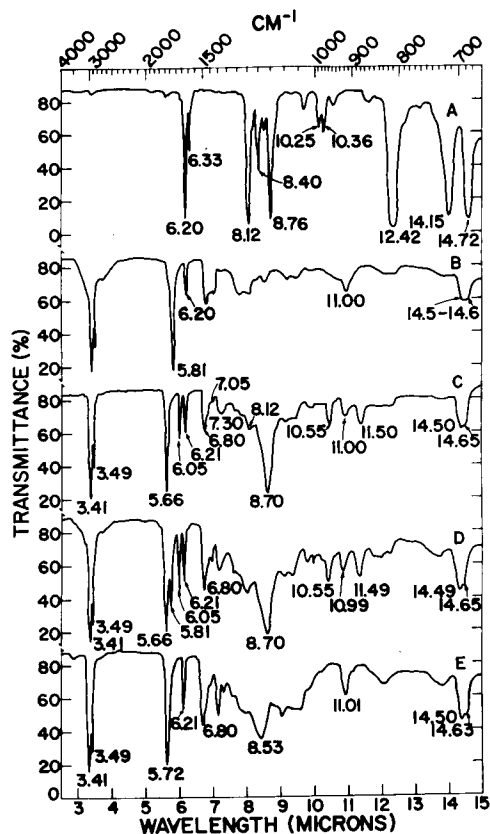


FIG. 1. Infrared spectra: *A*, hexachlorocyclopentadiene (HCCPD); *B*, petroselinic acid adduct of HCCPD; *C*, pure vinyl ester of *B*; *D*, crude vinyl ester of *B*; *E*, ethyl ester of *B*. (The spectra were obtained for liquid films using a Perkin-Elmer Infrared Spectrophotometer, Model 21, with NaCl optics).

petroleum ether (bp 30–60C). The ether layer was washed with 200 ml of 0.5% H_2SO_4 , then with 200 ml of distilled water. These washings were discarded. The ether solution was extracted 3 times with 200 ml of 0.5 N KOH containing 25% absolute ethanol and then with water to neutrality. The ether solution was treated with Na_2SO_4 and carbon black, then filtered through diatomaceous earth in a Buchner funnel under vacuum. The solvent was removed below 40C with water aspirator vacuum, then with pump vacuum. The weight of [I] obtained was 170 g, which is an 85% yield based on the acid adduct and 61% yield based on the petroselinic acid. This sample had the IR spectrum shown in C of Figure 1 and in the UV showed λ max 198 $m\mu$, a 24.5; n_D^{25} 1.5082.

Anal. Calcd for $C_{25}H_{36}Cl_6O_2$: C, 51.7; H, 6.24; Cl, 36.6; M.W. 581.

Found: C, 51.3; H, 6.27; Cl, 36.0; M.W. 542.

Further purification of this sample by column chromatography on silica gel did not significantly change the above analyses or properties, except for the UV absorption, which gave λ max 198 $m\mu$, a 27.0. The material did not crystallize when cooled to –60C, but set to a firm glass. A melting range of –30 to –27C was obtained by inserting a thermometer into a small test tube containing [I], chilling the sample and then suspending the thermometer. The melting range was taken as the temperature at which the test tube began to fall to that at which it dropped free of the thermometer.

Removal of Acids with Alumina

Fifty grams of alumina was packed by gravity into a 19 mm diam column filled with diethyl ether.

A 10.2 g sample of crude vinyl ester containing 36% acid adduct was eluted with 200 ml of ether. Ninety-five per cent (6.2 g) of the theoretical amount of vinyl ester was recovered. The IR spectrum of the eluted vinyl ester was the same as that shown in Figure 1, *C*.

Results and Discussion

A substantial amount of work has been done on the Diels-Alder reaction with HCCPD, and the reactions with a variety of dienophiles are cited as references in a review by Ungnade and McBee (3). It has been shown that neither HCCPD nor the adduct absorbs bromine (4). We therefore found it convenient to follow the reaction of petroselinic acid with HCCPD by the decrease in Wijs iodine value (I.V.) (5). Petroselinic acid alone has an I.V. of 89.9. The mixture of petroselinic acid and HCCPD (1 mole:2 moles) had an I.V. of 29.8 before heating. After 20 hr at 134C the I.V. dropped to 10.1. Continued heating to 28 hr lowered the I.V. to 7.0, indicating a yield of 75 to 80% of the adduct. Previously unpublished results obtained in this laboratory on the reaction of HCCPD with oleic acid showed that heating over 28 hr did not appreciably lower the I.V.

An attempt to remove the unreacted petroselinic acid from the impure acid adduct by distillation under reduced pressure was unsuccessful. The petroselinic acid could be distilled off but the residue charred. The urea complexing method suggested by Swern et al. (6), was then tried for removing the unreacted petroselinic acid. The method was awkward because of the large volume of methanol but proved to be effective. It was found that the unreacted petroselinic acid could be reduced to about 1% using the procedure described in the above method.

As another approach to [I], the HCCPD adduct of methyl petroselinate was prepared and successfully distilled. This approach, however, required the 2 additional reactions of esterification of petroselinic acid and the saponification of the methyl petroselinate adduct to recover the acid adduct. Adelman showed that the vinylation will proceed only through the acid and not with an ester (7).

Infrared analysis was extremely useful as a means of following the preparation of the acid adduct and its vinyl ester. HCCPD gives 2 bands in the double bond stretching region (6.20 μ and 6.33 μ) and 3 bands in the C-Cl stretching region (12.42 μ , 14.15 μ , 14.72 μ), Figure 1, *A*. The acid adduct has absorptions at 5.81 μ , 6.20 μ , 11.00 μ , and 14.5–14.6 μ , Figure 1, *B*. The vinyl ester was characterized by absorptions at 5.66 μ , 6.05 μ , 8.70 μ , 10.55 μ , and 11.50 μ , Figure 1, *C*.

Since the conversion of the acid adduct to vinyl ester comes to an equilibrium without going to completion, a problem was encountered in eliminating the unreacted acid adduct from the vinyl ester of the adduct. The IR spectrum of the impure vinyl ester adduct (Fig. 1 *D*) clearly shows the presence of unreacted acid by the acid carbonyl absorption at 5.81 μ . Titration of a sample showed 30.4% acid to be present calculated as the acid adduct. The unreacted acid adduct was successfully removed by alcoholic alkaline washings as described in the procedure. This mixture of solvents was found to be necessary because of emulsion problems and because earlier runs had shown the alkaline salts of the acid adduct to be difficultly soluble in the aqueous alkaline extracts.

An attempt to remove the acid adduct by dissolving the impure vinyl ester in absolute ethanol and eluting through a Dowex 1 column in the OH form resulted in alcoholysis of the vinyl ester to the ethyl ester, as shown by IR (Fig. 1 *E*). The vinyl peaks at 6.05, 10.55 and 11.50 μ and the carboxyl peak at 5.81 μ have been completely eliminated, and the ester peak has been shifted from 5.66 μ to 5.72 μ . These changes were interpreted as indicating that the acid had been removed, but that the vinyl ester had been completely converted to the ethyl ester.

The use of an activated alumina column for removing acid also presented a slight problem. Elution of the crude vinyl ester adduct through the alumina column with petroleum ether resulted in a substantial loss of product as well as the unsuccessful removal of acids. Washings with diethyl ether, ac-

tone and ethanol did not remove the product from the column. However, when diethyl ether was used as the initial eluant, the alumina column proved to be the best means of purification.

ACKNOWLEDGMENTS

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REFERENCES

1. Fore, Sara P., R. L. Holmes and W. G. Bickford, *JAOCS* **37**, 490-1 (1960).
2. Lewis, J. B., and G. W. Hedrick, *J. Org. Chem.* **25**, 623 (1960).
3. Ungnade, H. E., and E. T. McBee, *Chem. Reviews* **58**, 250-289 (1958).
4. Fields, E. F., *J. Am. Chem. Soc.* **76**, 2709-10 (1954).
5. AOCs Official Method Cd 1-25.
6. Swern, D., in "Fatty Acids," K. S. Markley, ed., Part III, Interscience Publishers, Inc., New York, 1964, Chap. XX, pp. 2309-58, especially p. 2313.
7. Adelman, R. L., *J. Org. Chem.* **14**, 1057 (1949).

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Reduction of Methyl Oleate Ozonolysis Products to Aldehydes with Activated Zinc

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Abstract

Reduction of methyl oleate ozonolysis products with active zinc in the absence of acid or water gave an 88% yield of methyl azelaaldehyde. Under these neutral conditions, side reactions such as acetalization and aldehyde condensations could be more conveniently avoided than when zinc-acetic acid reduction is used. The activated zinc was prepared by treatment with acetic acid followed by washing to remove the acid.

Introduction

WE HAVE PREVIOUSLY described the ozonolysis of methyl oleate in participating, hydroxylic solvents to give mixtures of alkoxy hydroperoxides, $RC(H)OOH$, and carbonyl compounds, $RC(H)O$ (7).

OR

Reduction of the alkoxy hydroperoxides was accomplished by either zinc and acetic acid or catalytic hydrogenation. The latter procedure gave lower yields unless a poisoned palladium catalyst was used or a mixture of alcohol and carboxylic acid was present during reduction (6,8,9). Following either the chemical or catalytic methods of reduction, carboxylic acids that are present must be removed by elaborate washing with water or aqueous alkali lest the acid catalyze condensation or acetalization of the carbonyl compounds during distillation. We have found that an activated zinc can be used to reduce the ozonolysis products in good yield in an essentially neutral solution.

In examining the literature reporting the use of zinc dust and water for reductive ozonolysis (1,4,5), we found that usually some acid was present and ozonolysis had been performed in a nonparticipating solvent. We could find no comparative data for the

reduction of methoxy hydroperoxides with zinc dust and water. We therefore undertook this reduction but in a participating solvent as well as a comparison of active zinc reduction with that by zinc and acetic acid.

Experimental

Methods of Analysis

A Model 500 F & M temperature programmed chromatograph was used for analyses by gas-liquid chromatography (GLC). Details of both this method and the wet method of analysis have been previously described (9).

Ozonization

The general procedure for ozonization in methanol has been reported earlier (7,8). A standard ozonolysis solution was prepared and stored under nitrogen at 0°C (9); aliquots were withdrawn and weighed as required.

Zinc Activation

Zinc powder or 30-mesh, granular zinc (42 g) was stirred vigorously with glacial acetic acid (100 ml) for 1 hr under a nitrogen atmosphere. Little, if any, hydrogen evolution could be detected. Filtration of the product was carried out so as to minimize air contact. The filter cake was washed quickly 3 or 4 times with 25-50 ml portions of methylene chloride but was left moist with solvent. The final wash indicated a pH of 6 or more with indicator paper. A rubber dam was then used to press the filter cake dry. If stored under nitrogen, the activated zinc could be kept for about 24-48 hr after which the activity became negligible.

Batch Reduction with Activated Zinc

An aliquot of standard ozonolysis solution (147.4 g, corresponding to 39.3 g of pure methyl oleate in

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