

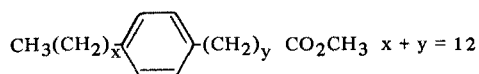
Ethylene Adduct of Conjugated Octadecadienoic Acids: III. Aromatization of C₂₀ Cyclohexene Methyl Esters

ABSTRACT

A procedure is described for the catalytic aromatization of the ethylene adduct of conjugated isomers of methyl octadecadienoate. When the C₂₀ cyclohexene fatty methyl esters were heated at 290-300 C with palladium and 1-octadecene as hydrogen acceptor, C₂₀ aromatic cyclic esters were obtained in 90-95% yield.

INTRODUCTION

In previous publications from this laboratory, we have described the catalytic cyclization and aromatization of *cis,trans*-conjugated methyl octadecadienoate with selenium (1) and the palladium catalyzed aromatization of C₁₈ cyclic fatty acids prepared from linseed oil (2,3). We also have reported the preparation of C₂₀ cyclic monocarboxylic acids by the addition of ethylene to conjugated octadecadienoic and soybean fatty acids (4). This article describes the aromatization of the ethylene adduct of conjugated methyl octadecadienoate. The product is an isomeric mixture of 1,4 disubstituted benzenes represented by formula I:



EXPERIMENTAL PROCEDURES

The isomeric mixture of C₂₀-aromatic cyclic methyl esters was prepared as follows: a 500 ml round-bottomed flask, fitted with reflux condenser, gas delivery tube, and stirrer, was charged with 26 g ethylene adduct of conjugated isomers of methyl octadecadienoate, 3.5 g 5% palladium on carbon and 200 ml 1-octadecene as hydrogen acceptor and solvent. The reaction mixture was heated

¹ARS, USDA.

under a nitrogen atmosphere with constant stirring for 6.5 hr at 290-300 C. After the reaction mixture was cooled and the catalyst removed by filtration, mixed solvents were distilled off under reduced pressure. An ethereal solution of recovered product was treated with decolorizing carbon and alumina.

Gas liquid chromatographic analysis of recovered product showed 90% aromatization. Capillary gas chromatograms were run at 200 C and 55 psi argon on a 200 ft x 0.01 in. inside diameter stainless steel column coated with a 10% chloroform solution of six-ring polyphenyl ether and 0.39% Arquad 2HT-75 in a Barber Coleman model 20 chromatograph with a radium D argon ionization detector. Gas chromatograms also were run at 180 C and helium flow of 35 ml/min on a 6 ft x 1/4 in outside diameter stainless steel column packed with 10% EGSS-X on Gas Chrom P, 100-120 mesh (organosilicon polyester packing, Applied Science Laboratories, State College, Pa.) in a F&M model 5750 gas chromatograph equipped with a hydrogen flame detector. Relative retention times (based upon methyl stearate as 1) of C₂₀ cyclohexene methyl esters and C₂₀ aromatic cyclic methyl esters were 33.7 and 51.9, respectively, run on capillary polyphenyl ether column and 3.4 and 6.8, respectively, run on EGSS-X column. Capillary gas chromatograms showed two large, not completely resolved peaks and three small peaks for the aromatic esters. Cyclohexene esters showed three large, not completely resolved peaks and two small peaks. Gas chromatograms run on EGSS-X column showed one peak for aromatic esters and one peak for the cyclohexene esters.

RESULTS

IR and UV analyses of product showed 95% aromatic isomers with some cyclohexane, cyclohexadiene isomers, and traces of *trans*-isolated double bond.

A portion of the aromatized esters (13.9 g, N_D³⁰ 1.4778) was distilled fractionally (Table I). IR spectra of fractions 1-3 differed only slightly. Fraction 1 contained more

TABLE I

Fractional Distillation of C₂₀ Aromatic Cyclic Esters

Fraction no.	Boiling point C/mm	Wt g	Analysis ^a		N _D ³⁰
			Carbon	Hydrogen	
1	163-165/0.19	1.1	77.91	11.08	1.4774
2	165-170/0.17-0.19	7.2	79.28	11.16	1.4794
3	170-178/0.18-0.19	3.4	78.07	11.07	1.4805
Residue		1.9			1.4697

^aTheory: C, 79.19; H, 10.76. Given in percentage.

trans-isolated double bond than fractions 2 and 3. Fraction 3 contained more cyclohexadiene than fractions 1 and 2.

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