HYDROGENATION OF 2,4-HEXADIENOIC ACID METHYL ESTER

P. Kluson, P. Kukula, E. Kyslingerova and L. Cerveny
Department of Organic Technology, Institute of Chemical Technology - Prague
166 28 Prague 6, Technická 5, Czech Republic

Received June 30, 1995
Accepted June 25, 1996

Abstract
Hydrogenation of 2,4-hexadienoic acid methyl ester on supported metal catalysts (Pd/C, Pt/C, Rh/C and Ru/C) has been investigated. Methyl esters of 2-hexenoic and 3-hexenoic acids were formed and further hydrogenated to the methyl ester of hexanoic acid. Palladium was found to be the most active and selective catalyst for this reaction owing to the formation of intermediates.

Keywords: Leaf alcohols, hexenols, selective hydrogenation, sorbic acid

INTRODUCTION

n-Hexen-1-ols (leaf alcohols) are important components of fruity and vegetable fragrances and flavors occurring in a number of various plants [1-3]. 2,4-Hexadienoic acid, its esters and salts can be used as initial compounds for their alternative preparation by either catalytic or chemical reductions [2]. Perfume industry utilizes them directly or may use them for esterification of various carboxylic acids.

In this paper we report on the catalytic hydrogenation of methyl 2,4-hexadienoate. The reaction leads to esters of 2-hexenoic and 3-hexenoic acids and methyl hexanoate. The monoolefinic esters prepared are suitable intermediates for the preparation of the desired n-hexen-1-ols. In this study we were seeking to evaluate the activity and selectivity of various supported noble metal catalysts for this reaction.
EXPERIMENTAL

Catalysts

All catalysts were group VIII metals supported on active carbon: 5% ruthenium, 97 and 19A types supplied by Johnson & Matthey; 5% rhodium and 5% platinum prepared at ICT-Prague; 2.8% palladium supplied by Chemopetrol, Litvinov. The catalysts were in a form of fine powders.

Chemicals

Methanol, p.a., Lachema, Brno, was used as a solvent. Methyl ester of 2,4-hexadienoic acid was prepared by esterification of sorbic acid (2,4-hexadienoic acid) with methanol at ICT-Prague [2]. Hydrogen and nitrogen, grade A, were from Linde-Technoplyn, Prague.

Kinetic measurements and analysis

Kinetic measurements were carried out in a semi-batch isothermal stirred reactor connected to gasometric burettes in the kinetic regime. Scheme of the apparatus used is given elsewhere [4]. Experiments were conducted in 15 mL of a solvent (methanol) with an initial substrate volume of 0.1-0.3 mL and 0.02-0.7 g of catalyst. The experiments were performed in the liquid phase at atmospheric pressure of hydrogen and at 303 K. Ruthenium catalysts were activated in a furnace in hydrogen (50 mL/min) at 373 K for 100 min. Other catalysts were activated for 15 min in flowing hydrogen in the reactor under conditions of hydrogenation.

Samples of the reaction mixture were taken at regular time intervals and analyzed on a gas chromatograph (H&P 5890 SERIES II Plus) using a FID detector with a capillary column HP-20M (15m/0.530mm/0.32 μm) T=373-463 K and P(N₂)=0.14x10⁵ Pa, split 1:25.

RESULTS AND DISCUSSION

Besides hydrogenation of the double bond in position 4 (Fig. 1), concurrent hydrogen addition to the double bonds in positions 2 and 4 in 2,4-hexadienoic acid also occurred. Electrons of the methyl ester of 3-hexenoic acid formed are