

Letter

Catalytic synthesis of a novel tertiary ether, 3-methoxy-3-methyl heptane, from 1-butene

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Abstract

1-Butene was selectively dimerised with a high yield to 2-ethyl-1-hexene using a zirconocene/MAO catalyst. 2-Ethyl-1-hexene was further etherified with methanol to a novel tertiary ether compound, 3-methoxy-3-methyl heptane. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tertiary ethers, such as methyl *tert*-butyl ether (MTBE, 2-methoxy-2-methyl propane) and *tert*-amyl methyl ether (TAME, 2-methoxy-2-methyl butane), are commonly used as gasoline components to improve the combustion and to reduce exhaust emissions [1]. Also, some larger ether compounds have been studied [2]. Tertiary ethers are produced from tertiary alkenes and alcohol usually with strong cation exchange resins as catalysts under mild process condi-

tions. This paper presents a totally new large tertiary ether, a tertiary octyl methyl ether, 3-methoxy-3-methyl heptane, a molecule whose existence and synthesis to the best of our knowledge has not been reported earlier.

The synthesis is carried out in two steps. In the first step, 1-butene is selectively dimerised to 2-ethyl-1-hexene. In the second step, reacting with methanol under the conditions typically applied for the synthesis of tertiary ethers, this alkene produces the new ether compound, 3-methoxy-3-methyl heptane.

2. Olefin synthesis

The tertiary alkene, 2-ethyl-1-hexene, was conveniently synthesised from 1-butene according to Eq. 1 using a zirconocene-alumoxane

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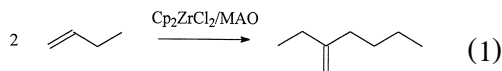
E-mail addresses: reetta.karinen@hut.fi (R.S. Karinen), krause@polte.hut.fi (A.O.I. Krause), esa.tikkanen@joensuu.fi (E.Y.O. Tikkanen), tuula.pakkanen@joensuu.fi (T.T. Pakkanen).

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catalyst. Use of a low Al/Zr ratio in polymerisation of α -olefins has been found to produce dimers instead of polymers [3,4].



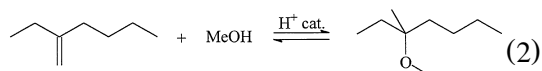
2-Ethyl-1-hexene was prepared in an autoclave (150 cm³) equipped with a magnetic stirrer. Cp₂ZrCl₂ (26.7 mg, 0.091 mmol), MAO (10% solution in toluene) (Al/Zr = 15) and toluene (10 ml) were added into the autoclave in a glovebox. The reactor was then charged with 1-butene (9.2 g, 0.164 mol) using standard vacuum manifold techniques. Finally, the reactor was pressurized with nitrogen gas to ca. 5 bar in order keep 1-butene in the liquid phase. The temperature of the reaction solution was raised to 60°C. After 24 h, the progress of the reaction was monitored taking a sample from the reactor into a vial closed with a septum. The catalyst was destroyed with a small amount of water containing a few drops of HCl. The organic phase was separated and analysed with a gas chromatograph equipped with a flame ionisation detector and a capillary column.

The product analysis showed that the metallocene catalyst system produced 2-ethyl-1-hexene with a high selectivity (85.5%). The conversion after 24 h was ca. 95%. Some higher oligomers (C₁₂, C₁₆, C₂₀, C₂₄) were also produced. After destruction of the catalyst, 2-ethyl-1-hexene was separated from the reaction solution with a fractional distillation. The formation of 2-ethyl-1-hexene was confirmed with a GC/MS analysis and ¹³C NMR.⁴

3. Ether synthesis

The attained 2-ethyl-1-hexene was further etherified with methanol according to Eq. 2.

The experiments were carried out in a batch reactor of 80 cm³ at 60–90°C and 8 bar with the commercial cation exchange resin, Amberlyst 35 (Rohm & Haas) as the catalyst. The molar ratio of methanol to the alkene was 1:1 mol/mol and iso-octane and toluene were used as a diluent. The products were analysed with a gas chromatograph equipped with a flame ionisation detector a capillary column.



In addition to the reactants and the diluent, five new peaks were detected in the gas chromatograms of the products. The peaks were identified with GC/MS. In addition to the reactant, four tertiary alkene isomers were found: 3-methyl-(Z)-2-heptene, 3-methyl-(E)-2-heptene, 3-methyl-(Z)-3-heptene, and 3-methyl-(E)-3-heptene, all of which can be formed from 2-ethyl-1-hexene via the isomerisation of the double bond from the α -position to the β -position. All of these alkenes have the tertiary carbon atom, which means that all the isomers should react with methanol in the etherification reaction under mild conditions, as observed for various C₅ alkenes [5], and yield the same ether. Indeed, only one ether compound 3-methoxy-3-methyl heptane was detected in the product. After distillation from the product mixture, the structure of the ether was confirmed with IR and ¹³C NMR⁵ analyses.

The influence of temperature on conversions of equilibrium limited etherification was studied in temperature range 60–90°C. The maximum conversion of 2-ethyl-1-hexene to the ether were 18%, 23% and 27% at the temperatures of 90°C, 80°C and 70°C, respectively. However, the total conversions of 2-ethyl-1-hexene at these tem-

⁴ ¹³C NMR (62.9 MHz, CDCl₃): δ 12.98 (CH₃), δ 14.30 (CH₃), δ 22.80 (CH₂), δ 29.10 (CH₂), δ 30.37 (CH₂), δ 36.31 (CH₂), δ 107.40 (=CH₂), δ 152.00 (=C) ppm.

⁵ ¹³C NMR (50.289 MHz, CDCl₃, δ_c = 77.0): δ 7.8 (CH₃), δ 14.0 (CH₃), δ 22.1 (CH₃), δ 23.2 (CH₂), δ 25.6 (CH₂), δ 29.6 (CH₂), δ 36.6 (CH₂), δ 48.6 (O–CH₃), δ 76.6 (C) ppm.

peratures after 24 h were 98%, most of which resulted from the isomerisation. At 60°C, the maximum conversion was not reached within 24 h due to the lower reaction rate at lower temperature. However, due to exothermic nature of etherification reaction, the maximum conversion to the ether at 60°C will be higher than those observed at higher temperatures.

It is known that the reactivity of alkenes in the etherification is dependent on the location of the double bond: when the double bond is near the end of carbon chain in the α -position, the reaction is faster than with the compounds where the double bond is in the β -position [5]. Of the above-mentioned isomers, 2-ethyl-1-hexene is the only one in which the double bond is located in the α -position, and thus the etherification of 2-ethyl-1-hexene is expected to be faster than etherification of other observed alkene isomers, which are β -alkenes. Accordingly, also the isomerisation of 2-ethyl-1-hexene is a rapid reaction, and thus a major part of the reactive reactant for the etherification is consumed quite fast, both in etherification and isomerisation reactions. In thermodynamic equilibrium between these alkenes, 2-ethyl-1-hexene is consumed almost completely to the other isomers.

Etherification of 2-ethyl-1-hexene with other alcohols, i.e., ethanol, propanols, butanols, pro-

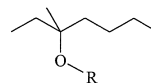


Fig. 1. Structure of the novel ethers. R represents alkyl group originating from alcohol, i.e., methyl, ethyl, etc.

duces homologous ether compounds, 3-alkoxy-3-methyl heptanes, where alkoxy group originates from the alcohol used. The structure of these ethers is shown in Fig. 1. In our experiments, we have already verified the formation of methyl and ethyl ethers. Analogously to the formation of other ethers with the similar structure [6], the formation of ethers from larger alcohols and 2-ethyl-1-hexene is possible.

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