Selective synthesis of 2-ethoxyalkanes through ethoxylation of 1-alkenes with bioethanol over zeolite beta catalyst in liquid phase continuous process

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Electronic supplementary information

Identification of the separated products was done by gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph (HP-5MS capillary column, 30 m, 0.25 mm ID, 0.25 µm film thickness) coupled to an Agilent 5973 MSD mass spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance 300 MHz and Bruker AMX 400 MHz instrument. Chemical shifts (δ, ppm) are referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signals (^{13}C).
In the on line GC and GC-MS analysis of the reaction product of the mixture of ethanol and 1-hexene, two peaks were obtained with intensity ratio 20:1 (compound *1* and *2*, respectively). The fragmentation of products in MS and the chemical shift values in ^{1}H and ^{13}C NMR are given below.

GC-MS, 70eV, (fragment, relative intensity, mode of fragmentation) - m/z: Compound 1:- 130 (M^+, <1%); 129 ($[M-H]^+$<0.5); 115 ($[M-CH_3]^+$, 8, α C - C); 101 ($[M-C_2H_5]^+$, 1, C-O); 85 ($[M-OC_2H_5]^+$, 3, C-O); 73 ($[M-C_4H_9]^+$, 100, α C-C); 45 ($[CH_3-CH=OH^+]$, 63, rearrangement); 29 ($[C_2H_5]^+$, 10, C-O).

Compound 2:- 130 (M^+, <0.5%); 129 ($[M-H]^+$, <0.5); 101 ($[M-C_2H_5]^+$, 75, α C-C & C-O); 87 ($[M-C_3H_7]^+$, 3, α C-C); 59 ($[CH_3-CH_2-CH=OH^+]$, 100, rearrangement); 43 ($[C_3H_7]^+$, 63, α C-C); 29 ($[C_2H_5]^+$, 20, α C-C and C-O).

NMR chemical shift values: Compound 1:- δ_H (ppm) (300* MHz; $CDCl_3$; Me_4Si*):- 3.51 - 3.56 (m, 1H), 3.35 – 3.43 (m, 2H), 1.3 - 1.5 (m, 6H), 1.2-1.33 (t, 3H), 1.11-1.2 (d, 3H), 0.90 (t, 3H).

δ_C (ppm)(*300 MHz; $CDCl_3$, Me_4Si*):- 75.23, 63.54, 36.50, 27.88, 22.86, 19.76, 15.65, 14.07.

^{13}C NMR suggested the presence of eight different types of carbon atoms, among which two were showing chemical shift similar to carbon atoms bonded to oxygen, confirming an ether was formed. The molecular ion peak of compounds 1 and 2 in the mass spectra were observed at m/z 130, in agreement with ethoxy hexane molecule. A fragment with m/z 73 was observed in the mass spectra of compound 1, which corresponds to the rupture of α C-C linkage in 2-ethoxy hexane, suggesting that the product obtained was 2-ethoxy hexane, which was also supported by the chemical shift values observed in ^{1}H and ^{13}C NMR. The presence of a fragment with m/z 87 in the mass spectrum of compound 2 suggested the minor product to be 3-ethoxy hexane.

Further information supporting the identification was provided by ^{13}C DEPT (Distortionless Enhancement by Polarization Transfer) NMR spectra of compound 1 (Fig. 1). Signals corresponding to all eight C-atoms in ethoxy hexane were observed in the spectra, confirming that no quaternary C-atom is present in the ether. Of the two carbon atoms showing chemical shift similar to carbon atom linked to oxygen, one belongs to a $-CH_2$ group and the other either a $–CH$ or a $–CH_3$ group. In the case of ethers, a $-CH_3$ group linked to oxygen is possible only in methyl ethers, suggesting the second carbon linked to oxygen belong to a -CH group. The presence of a –CH group rules out the possibility of 1-ethoxy alkane, affirming the conclusion on the formation of 2-ethoxy alkane as the majority product.

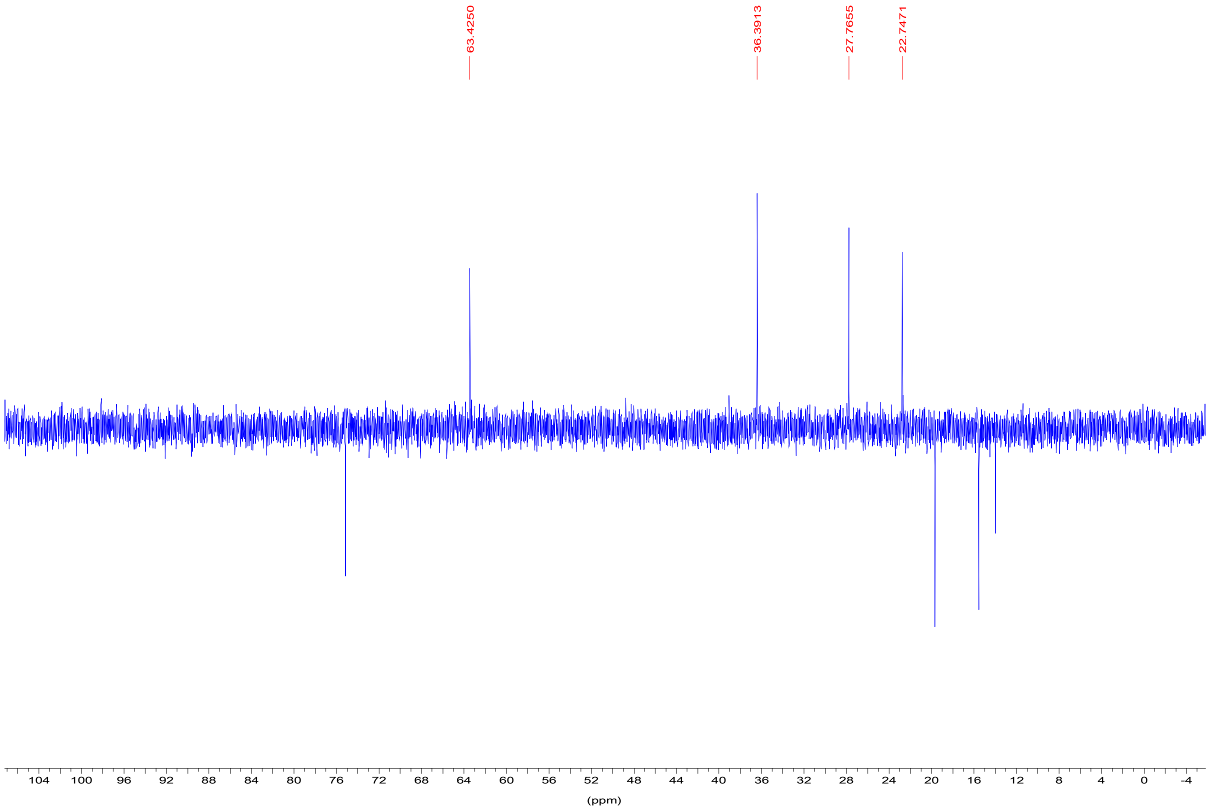

Figure 1: ^{13}C DEPT NMR spectrum of Compound 1 (2-ethoxy hexane)

The product identification was validated by the analysis of products from EtOH/1-octene and EtOH/1-decene conversions. Fragments with m/z 73 and 87, characteristic for 2-ethoxy and 3-ethoxy alkanes respectively among the various ethoxy alkane isomers, were observed in the mass spectra of the products in both the reactions and hence confirming our conclusion that the products obtained are 2-ethoxy alkanes and 3-ethoxy alkanes.

Identification of products of ethanol- 1-octene reaction:- Compounds 3&4 in 18:1 molar ratio
GC-MS, 70eV, (fragment, relative intensity, mode of fragmentation) - m/z: Compound 3**:-** 158 (M^+, <1%); 157 ($[M\text{-}H]^+$<0.5); 143 ($[M\text{-}CH_3]^+$, 4, α C - C); 129 ($[M\text{-}C_2H_5]^+$, <0.5, C-O); 113 ($[M\text{-}OC_2H_5]^+$, <0.5, C-O); 73 ($[M\text{-}C_6H_{13}]$, 100, α C-C); 45 ($[CH_3\text{-}CH{=}OH^+]$, 47, rearrangement); 29 ($[C_2H_5]^+$, 8, C-O).
Compound 4:- 158 (M^+, <0.5%); 157 ($[M\text{-}H]^+$, <0.5); 129 ($[M\text{-}C_2H_5]^+$, 56, α C-C & C-O); 87 ($[M\text{-}C_5H_{11}]^+$, 100, α C-C); 59 ($[CH_3\text{-}CH_2\text{-}CH{=}OH^+]$, 73, rearrangement); 45 ($[C_2H_5O]^+$, 3, C-O); 29 ($[C_2H_5]^+$, 17, α C-C and C-O).

According to the fragmentation pattern, compounds 3 & 4 could be identified as 2-ethoxy and 3-ethoxy octane respectively.

Identification of products of ethanol- 1-decene reaction:- Compounds 5&6 in 17:1 molar ratio
GC-MS, 70eV, (fragment, relative intensity, mode of fragmentation) - m/z: Compound 5**:-** 186 (M^+, <1%); 185 ($[M\text{-}H]^+$<0.5); 171 ($[M\text{-}CH_3]^+$, 3, α C - C); 157 ($[M\text{-}C_2H_5]^+$, <0.5, C-O); 73 ($[M\text{-}C_8H_{17}]$, 100, α C-C); 45 ($[CH_3\text{-}CH{=}OH^+]$, 39, rearrangement); 29 ($[C_2H_5]^+$, 7, C-O).
Compound 6:- 186 (M^+, <0.5%); 185 ($[M\text{-}H]^+$, <0.5); 157 ($[M\text{-}C_2H_5]^+$, 39, α C-C & C-O); 87 ($[M\text{-}C_7H_{15}]^+$, 100, α C-C); 59 ($[CH_3\text{-}CH_2\text{-}CH{=}OH^+]$, 56, rearrangement); 45 ($[C_2H_5O]^+$, 2, C-O); 29 ($[C_2H_5]^+$, 15, α C-C and C-O).

The fragmentation patterns of compounds 5 & 6 suggest them to be 2-ethoxy and 3-ethoxy decane respectively.

Information obtained from GC-MS and NMR of all the three experiments discussed above confirms that the major product of the reaction is a mixture of 2-ethoxy and 3-ethoxy alkane, of which 2-ethoxy alkane is predominantly formed.