



Hydrogenated intramolecular cyclization of diphenylmethane derivatives for synthesizing high-density biofuel



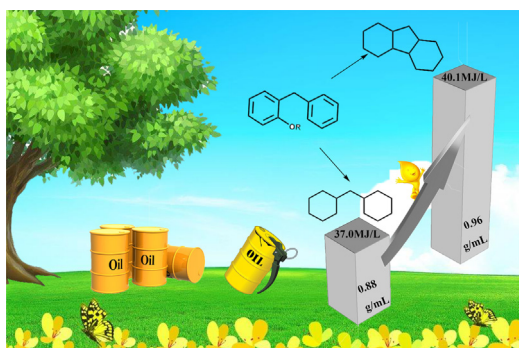
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HIGHLIGHTS

- Unexpected cyclization of diphenylmethane derivatives with hydrogenation catalyst.
- Selectivity of perhydrofluorene as high as 96.0%.
- Competitive pathways of hydrodeoxygenation and cyclization are illustrated.
- Perhydrofluorene has the highest density among the biofuels reported.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-cyclic hydrocarbons from biomass are sustainable alternative for jet fuel. Here we report an unexpected hydrogenated intramolecular cyclization of diphenylmethane derivatives synthesized by alkylation of bio-derived compounds. With the presence of commonly used zeolite-Pd/C dual catalyst, conventional hydrodeoxygenation (HDO) occurs to produce dicyclohexylmethane. However, when only hydrogenation catalysts like Pd/C or Ni is used, novel intramolecular cyclization takes place to produce perhydrofluorene with the selectivity as high as 96.0%. The two pathways were illustrated by step-by-step controlled reactions in detail and a mechanism was proposed to explain the reason for perhydrofluorene formation. Moreover, this intramolecular cyclization is versatile for diphenylmethane with $-\text{OCH}_3$ or $-\text{OH}$ group at any position. The synthesized perhydrofluorene shows density of 0.96 g/mL, much higher than any biofuels reported and even higher than the widely used high-density fuel JP-10 derived from petroleum. It is believed that this biofuel can be excellent additive to improve the density of other jet fuels.

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1. Introduction

Catalytic conversion of inedible and renewable biomass to high quality biofuels (like jet fuel and diesel) and chemicals has attracted a lot of attention as response to the concerns to

sustainable development of energy sources and environmental protection (Arias et al., 2015; Corma et al., 2011; Kasakov et al., 2015; Li et al., 2015; Wang and Rinaldi, 2013). Specifically, many endeavors have been devoted to synthesizing jet fuel range hydrocarbons from biomass such as terpenes, cellulose and lignin (Deng et al., 2016; Harvey et al., 2014, 2015; Meylemans et al., 2011; Zhang et al., 2016; Zhao and Lercher, 2012). Generally, the fuels obtained from biomass can be divided into three categories

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according to their molecular structure and density. One is straight and branched chain alkanes with relatively low density (~ 0.78 g/mL) (Harvey and Quintana, 2010). The second is monocyclic branched chain alkanes with density at about 0.83 g/mL (Deng et al., 2016; Yang et al., 2015; Zhang et al., 2016). The third is bicyclic and polycyclic hydrocarbons with density ranging from 0.87 g/mL to 0.94 g/mL (Chen et al., 2016a, 2016 b; Harvey et al., 2010; Jung et al., 2016; Meylemans et al., 2012, 2013; Nie et al., 2014; Sheng et al., 2015, 2016; Zhao et al., 2012; Zou et al., 2012). High-density fuel is much desirable because it can extend the flight range of volume-limited aircraft due to its high density and high volumetric heat value (Chung et al., 1999; E et al., 2015; Pan et al., 2015; Wang et al., 2011; Wang et al., 2012), therefore in such case the polycyclic biofuels are very promising. Specifically, the terpene-derived biofuel has density comparable to the widely used petroleum-derived high-density fuel, namely JP-10 (with density of 0.93 g/mL) (Harvey et al., 2010; Harrison and Harvey, 2017; Meylemans et al., 2013).

The C–C coupling reactions like aldol condensation, oligomerization, Diels–Alder addition, and alkylation of bio-derived compounds are widely used to synthesize polycyclic hydrocarbons (Arias-Ugarte et al., 2015; Corma et al., 2007; Deng et al., 2015a, 2015 b; Nie et al., 2014). The synthesized molecules usually contain oxygen atoms and unsaturated C=C bonds, so a hydrogenation/hydrodeoxygenation (HDO) reaction has to be conducted to get hydrocarbon biofuels. Recently, we reported biofuel with density (0.93 g/mL) and low-temperature properties (freezing point of -40 °C) surpassing the state-of-art of biofuel reported (Nie et al., 2017). This biofuel was synthesized by alkylation reaction of phenols and benzyl ether, followed with hydrogenation treatment. Phenols, such as phenol, anisole, and guaiacol etc. are main chemicals produced by fast pyrolysis and HDO of lignocellulosic biomass (Kang et al., 2013; Pandey and Kim, 2011; Xinghua et al., 2014), whereas benzyl ether can be produced from pyrolysis of α -O-4 moieties in lignin (Zakzeski et al., 2010). In the alkylation reaction, hydroxy or methoxyl substituted diphenylmethane was produced with selectivity over 85.1%. Generally, the alkylated product is expected to be converted to dicyclohexylmethane by HDO. Unexpectedly, lots of perhydrofluorene is produced, which suggests the intramolecular cyclization occurs in the reaction. It is worth noting that the density of dicyclohexylmethane is only 0.88 g/mL while perhydrofluorene has density ranging from 0.95 g/mL to 1.01 g/mL (Fischer and Weiss, 1986; Serijan and Wise, 1951), and the commercial perhydrofluorene is typically a mixture of isomers. This indicates that the cyclization reaction is very desirable for the synthesis of high-density biofuel by producing additional five-membered ring in the molecule. However, it is still ambiguous how this intramolecular cyclization takes place. In this work, we illuminated the pathway for the formation of perhydrofluorene via series controlled reactions. 2-benzylphenol was chosen as the model reactant because it is the simplest alkylated product and can be synthesized easily according to our recent work (Nie et al., 2017). Then we realized the intramolecular cyclization on diphenylmethane derivatives to perhydrofluorene with almost 100% selectivity. Finally, we showed the potential of perhydrofluorene as additive to increase the density of jet fuels.

2. Experiment

2.1. Catalysts and chemicals

HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$), HY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.4$) purchased from Nankai Catalysts Co., China, were calcinated in air at 580 °C for 3 h before use. Pd/C (5 wt%) was purchased from Shaanxi Rock New Materials Co., Ltd. 2-benzylphenol and 4-benzylphenol were

purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Nickel catalyst (ZV-N411) was purchased from Anshan Zhongli Catalysts Factory. 2-benzylcyclohexan-1-one was purchased from Beijing Yi Nuokai Science and Technology Co., Ltd. 1-benzyl-4-methoxybenzene, 1-benzyl-2-methoxybenzene, 2-benzylcyclohexan-1-ol and 2-benzyl-5-methoxyphenol were synthesized in our lab according to previous work (Nie et al., 2017).

2.2. Hydrogenation

The hydrogenation was performed in a 100 mL autoclave (Easy-Chem E100). 50 mL water (as solvent), 10 mmol substrate and the corresponding catalysts were sealed in the reactor and hydrogenated under hydrogen pressure of 6 MPa and 453 K for 10 h. The products were extracted from water using ethyl acetate for analysis. Qualitative analysis was conducted using an Agilent 6890/5975 GC–MS equipped with HP-5 capillary column (30 m \times 0.5 mm), and the composition was analyzed using ethyl acetate as internal standard on Bruker 456 GC equipped with a flame ionization detector and a capillary column (ZB-5 HT, 60 m \times 0.25 mm \times 0.25 m) with flame ionization detector. ^{13}C and ^1H NMR spectra of synthesized hydrocarbons were collected at 298 K using a Bruker AVANCE III-400 MHz spectrometer equipped with 5 mm PABBO BBI probe head.

3. Result and discussion

3.1. Reaction pathways for hydrodeoxygenation and intramolecular cyclization

The hydrogenation of 2-benzylphenol (**i.e.** 1) catalyzed by mixture of Pd/C and HZSM-5 is shown in Fig. 1. At the beginning, 2-benzylphenol is converted to 2-benzylcyclohexanone (**i.e.** 2), 2-benzylcyclohexanol (**i.e.** 3) and cyclohexyl(phenyl)methanol (**i.e.** 7). Then the concentration of 2 decreases but that of 3 and 7 continues to increase. Finally, the concentration of both 3 and 7 decreases and about 29.1% dicyclohexylmethane (**i.e.** 6) and 68.9% perhydrofluorene (**i.e.** 9) are produced. In this process, trace of (cyclohex-1-en-1-ylmethyl)benzene (**i.e.** 4, Fig. S1 (refer to supplementary material), Mass spectra), (cyclohexylmethyl)benzene (**i.e.** 5, Fig. S2 (refer to supplementary material), Mass spectra) and 2,3,4,4a,9,9a-hexahydro-1H-Fluorene (**i.e.** 8, Fig. S3 (refer to supplementary material), Mass spectra) are detected. According to the time-dependent product distribution, a brief reaction pathway is proposed (Fig. 1). Initially 1 is hydrogenated to 2 by hydrogenation of benzene substituted with $-\text{OH}$ firstly and then pinacol rearrangement. Then 2 is hydrogenated to 3 by hydrogenating the $-\text{C}=\text{O}$ to $-\text{C}-\text{OH}$, and 7 is formed by the transfer of $-\text{OH}$. Both 3 and 7 are converted to 6 and 9 with 4, 5 and 8 as intermediates, where 4 is the dehydration product of 3 and 5 is the partial hydrogenated product of 4. Obviously, 6 is formed by hydrogenation of 5 whereas 9 is derived from hydrogenation of 8. But it is not clear whether 8 is derived from 4 or not.

It is obvious that 6 is the HDO product of 2-benzylphenol and 9 must be formed via an intramolecular cyclization. The co-production of 6 and 9 indicates there is a competition between the HDO and intramolecular cyclization. Generally, acid zeolite like HZSM-5 accelerates the deoxygenation while Pd is responsible for hydrogenation (Wang et al., 2016; Zhao and Lercher, 2012). In order to explore the effect of catalyst on the reaction, the amount of Pd/C and zeolite was changed and the product distribution was analyzed. As presented in Table 1, with the increase of HZSM-5 the yield of 9 decreases whereas that of 6 increases. Interestingly, when only Pd/C is used, 9 with yield of 96.7% is produced (Fig. S4 (refer to supplementary material), a-mass spectra;

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