Supporting Materials for

Renewable High-Density Spiro-fuel from Lignocellulose-Derived Cyclic Ketones

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1 Materials

Cyclohexanone (99.5%), cyclopentanone (99.5%) were obtained from Tianjin Guangfu Fine Chemical Research Institute. Titanium tetrachloride, Zn powder, anhydrous magnesium sulfate, sodium carbonate, sodium bicarbonate, sodium chloride, diethylene glycol, n-Pentane, methanol, tetrahydrofuran, ether, dichloromethane were purchased from Tianjin Yuanli Chemical Co., China. Potassium tert-butoxide (99%), hydrazine hydrate (80%), Tin tetrachloride (99.9%), were obtained from Beijing Bailingwei Technology Co., China. Acetonitrile was supplied by Shanghai Aladdin Biochemical Technology Co., China. All chemicals were used without further purification.

2 Experiment

2.1 Reductive coupling of cyclic ketones

To a gray suspension of Zn powder (26 g, 0.4 mol) and ethyl ether (300 mL) was added TiCl$_4$ (11 mL, 0.1 mol) under nitrogen atmosphere. After stirring for 10 min, cyclohexanone (9.814 g, 0.1 mol) or cyclopentanone (8.412 g, 0.1 mol) was added dropwise. Then the reaction mixture was stirred under reflux and nitrogen atmosphere for 15 h. The reaction mixture was quenched with 400 mL of 10 wt% Na$_2$CO$_3$ aqueous solution followed by 100 mL ether. The suspension was filtered, and the filtrate was twice extracted with 100 mL ether. The extracts were washed with saturated NaCl, dried over anhydrous MgSO$_4$, and finally purified by recrystallization from ether.

2.2 Pinacol rearrangement

Bicyclopentyl-1,1'-diol (7.828 g, 39.5 mmol) or bicyclohexyl-1,1'-diol (6.715 g, 39.5 mmol) was dissolved in 200 mL of CH$_2$Cl$_2$, stirred with 10 g anhydrous magnesium sulfate at room temperature under nitrogen for 2 h, treated with 5 mL SnCl$_4$ in an ice bath and stirred for 10 min. Then 100 mL CH$_2$Cl$_2$ and 100 mL saturated aqueous NaHCO$_3$ was added and stirred for 10 min. After filter, the organic layer was separated, and the trace organics in aqueous layer was extracted with CH$_2$Cl$_2$, then The organics was washed with brine, dried over anhydrous MgSO$_4$, and concentrated.
2.3 Wolff-Kishner-Huang reduction of spiro ketones

A mixture of spiro[5, 6]dodecan-7-one (6.098 g, 31.08 mmol) or spiro[4, 5]decan-6-one (4.724 g, 31.08 mmol), 80% hydrazine hydrate (30 mL) in diethylene glycol (100 mL) was refluxed for 1.5 h. Then the excess hydrazine hydrate was distilled off. After cooling to room temperature, t-BuOK (10 g) was added and heated at 190-200°C for another 3 h. The reaction mixture was extracted with pentane (100 mL×3), and the extracts was distillated to obtain the spirocycloalkane.

3 Analytical method

The products were determined qualitatively using an Agilent 6890/5975 gas chromatography-mass spectrometry (GC-MS) equipped with HP-5 capillary column (30 m × 0.5 mm) and 13C and 1H NMR spectra were collected using Bruker Avance 400M or Bruker Avance 500M Spectrometers spectrometer. The concentration of each compounds was analyzed by a gas chromatography (Agilent-7820A) equipped with an FID detector and a capillary column HP-1 capillary column (30 m × 0.53 mm). Fourier transform infrared (FTIR) spectra of the samples were recorded using a Bruker Vertex 70 IR spectrometer (4 cm⁻¹) in potassium bromide media.

4 Conversion and selectivity calculation

The conversion and selectivity were calculated as follows:

conversion (wt%) = \( \frac{m(\text{reactant converted})}{m(\text{original reactant})} \times 100\% \)

selectivity (wt%) = \( \frac{m(\text{product produced})}{m(\text{reactant converted})} \times 100\% \)

\[ \text{yield (wt%)} = \text{conversion} \times \text{selectivity} \]

Take the following reaction as example:
conversion of cyclohexanone (wt%) = \frac{m(\text{cyclohexanone converted})}{m(\text{original cyclohexanone})} \times 100\

selectivity of bicyclohexyl - 1,1'-diol (wt%) = \frac{m(\text{bicyclohexyl - 1,1'-diol})}{m(\text{cyclohexanone converted})} \times 100\

selectivity of cyclohexanol (wt%) = \frac{m(\text{cyclohexanol})}{m(\text{cyclohexanone converted})} \times 100

5 Yield of by-products

Cyclohexanol and cyclopentanol by-products are produced with 21.5% and 23.9% yield in reductive coupling of cyclohexanone and cyclopentanone, respectively. 1,1'-bicyclohexene and 1,1'-bicyclopentene by-products are produced with 20.6% and 5.6% yield in pinacol rearrangement of bicyclohexyl-1,1'-diol and bicyclopentyl-1,1'-diol. In Wolff-Kishner-Huang reduction of spiro[5, 6]dodecan-7-one and spiro[4, 5]decan-6-one produces by-products with yield of 16.6% and 9.9%, respectively.

6 Measurements of fuel properties

The density was measured by Mettler Toledo DE40 density meter according to ASTM D4052. Freezing point was measured according to ASTM D2386, and kinematic viscosity was determined using capillary viscometer according to ASTM D445. The net heat of combustion was measured by the IKA-C6000 isoperibol Package 2/10 Calorimeter according to ASTM D240-02. Differential scanning calorimetry (DSC) was performed on a NETZSCH-DSC 200 F3 Maia differential scanning calorimeter using hermetically sealed aluminum pans with a nitrogen flow of 50 mL/min. High purity indium was used to calibrate the calorimeter. Sample sizes were between 5-10 mg and the samples were ramped from -100 °C to 50 °C, down to -100 °C and then back to 50 °C, all at 10 °C /min.
Scheme S1. Reaction pathway of reductive coupling

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\text{Scheme S1. Reaction pathway of reductive coupling}
\]

\[
\begin{align*}
\text{C}_n\text{O} + \text{TiCl}_4 \xrightarrow{\text{Zn}} & \begin{array}{c}
\text{vicinal dialkoxydes intermediate} \\
\text{n=1 bicyclopentyl-1,1'-diol} \quad \text{n=2 bicyclohexyl-1,1'-diol}
\end{array} \\
\hline
\end{align*}
\]

Scheme S2. Side reaction of reductive coupling

\[
\text{Scheme S2. Side reaction of reductive coupling}
\]

\[
\begin{align*}
\text{O} \quad \xrightarrow{\text{reduction}} \quad \text{OH} \\
\text{n=1, 2}
\end{align*}
\]

Scheme S3. Reaction pathway of pinacol rearrangement

\[
\text{Scheme S3. Reaction pathway of pinacol rearrangement}
\]

\[
\begin{align*}
\text{C}_n\text{OH} + \text{C}_n\text{OH} \xrightarrow{\text{H}^+} & \begin{array}{c}
\text{C}_n\text{OH} + \text{C}_n\text{OH} \\
\text{n=1, 2}
\end{array} \\
\hline
\end{align*}
\]

Scheme S4. Side reaction of pinacol rearrangement

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\]

\[
\begin{align*}
\text{C}_n\text{OH} + \text{C}_n\text{OH} \xrightarrow{\text{H}^+} & \begin{array}{c}
\text{n=1 bicyclopentyl-1,1'-diol} \quad \text{n=1 1,1'-bicyclopentene} \\
\text{n=2 bicyclohexyl-1,1'-diol} \quad \text{n=2 1,1'-bicyclohexene}
\end{array} \\
\hline
\end{align*}
\]
Figure S1. $^1$H (a) and $^{13}$C (b) NMR spectra of pinacols.

\[ \text{bicyclohexyl-1,1'-diol} \]

$^1$H NMR $\delta$ (500 MHz, CDCl$_3$) $\delta$ 1.84 (2H, s), 1.72-1.62 (6H, m), 1.61-1.50 (8H, m), 1.38-1.27 (4H, m), 1.14-1.02 (2H, m)

$^{13}$C NMR $\delta$C (500MHz, CDCl$_3$) $\delta$ 75.90, 30.93, 26.12, 22.01.
bicyclopentyl-1,1'-diol

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$) $\delta$ 1.98 (2H, brs), 1.97, 1.90-1.55 (16H, m)

$^{13}$C NMR $\delta_C$ (400 MHz, CDCl$_3$) $\delta$ 87.13, 36.40, 24.83.
Figure S2. Mass spectra of pinacols.

Spectrum of bicyclohexyl-1,1'-diol synthesized in this work.

Prob is 87.7 % with NIST# 156581.
Name: 1,1'-Bicyclohexyl-1,1'-diol
MW: 198 CAS#: 2888-11-1 NIST#: 156581
The molecular ion peak m/z 170.1 isn’t detected because the structure is unstable under the electronic flow bombardment. The m/z 152.1 and m/z 134.1 can generate by losing one or two –OH. Prob is 88.4 % with NIST# 154712.

Name: 1,1'-Bicyclopentyl-1,1'-diol
MW: 170  CAS#: 5181-75-9  NIST#: 154712
Figure S3. Mass spectra of by-products in reductive coupling.

Spectrum of cyclohexanol synthesized in this work.

![Spectrum of cyclohexanol synthesized in this work.](image)

Standard spectrum of cyclohexanol in NIST.

![Standard spectrum of cyclohexanol in NIST.](image)

Prob is 84.3 % with NIST# 291439.
Name: Cyclohexanol
MW: 100 CAS#: 108-93-0 NIST#: 291439
Spectrum of cyclopentanol synthesized in this work.

Prob is 90.7% with NIST# 233847.
Name: Cyclopentanol
MW: 86  CAS#: 96-41-3  NIST#: 233847

Standard spectrum of cyclopentanol in NIST.
Figure S4. $^1$H (a) and $^{13}$C (b) NMR spectra of spiro ketones.

**spiro[5, 6]dodecan-7-one**

**$^1$H NMR** $\delta$H (500 MHz, CDCl$_3$) $\delta$ 2.47 (2H, t), 1.76-1.27 (18H, m),

**$^{13}$C NMR** $\delta$C (500 MHz, CDCl$_3$) $\delta$ 218.17, 50.88, 39.56, 34.91, 33.38, 30.37, 26.62, 25.92, 24.15, 22.00.
spiro[4, 5]decan-6-one

$^1$H NMR $\delta_H$ (500 MHz, CDCl$_3$) $\delta$ 2.38 (2H, t), 2.10-1.99 (2H, m), 1.86-1.76 (2H, m), 1.74-1.67 (4H, m), 1.63-1.52 (4H, m), 1.44-1.33 (2H, m).

$^{13}$C NMR $\delta_C$ (500 MHz, CDCl$_3$) 214.87, 57.08, 40.18, 39.67, 35.68, 27.57, 25.46, 23.14.
Figure S5. Mass spectra of spiro ketones.

Spectrum of spiro[5, 6]dodecan-7-one synthesized in this work.

Standard spectrum of spiro[5, 6]dodecan-7-one in NIST.
Prob is 93.3 % with NIST# 187784.
Name: Spiro[5, 6]dodecan-7-one
MW: 180  CAS#: 4728-90-9  NIST#: 187784
Spectrum of spiro[4, 5]decan-6-one synthesized in this work.

Standard spectrum of spiro[4, 5]decan-6-one in NIST.

Prob is 94.3 % with NIST#190202.
Name: Spiro[4, 5]decan-6-one
MW: 152  CAS#: 13388-94-8  NIST#: 190202
Figure S6. Mass spectra of by-products in pinacol rearrangement.

Spectrum of 1,1'-bicyclohexene synthesized in this work.

The molecular ion peak is 162.
81 is a fragment ion of
Spectrum of 1,1'-bicyclopentene synthesized in this work.

The molecular ion peak is 134.

67 is the fragment ion of
Figure S7. $^1$H (a) and $^{13}$C (b) NMR spectra of spirocycloalkanes.

spiro[5, 6]dodecane

$^1$H NMR $\delta_H$ (500 MHz, CDCl$_3$) $\delta$ 1.53-1.19 (22 H, m)

$^{13}$C NMR $\delta_C$ (400MHz, CDCl$_3$) $\delta$ 39.70, 38.75, 35.36, 30.74, 26.67, 22.72, 22.05.
spiro[4, 5]decane

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$) $\delta$ 1.63-1.25 (18 H, m).

$^{13}$C NMR $\delta_C$ (400 MHz, CDCl$_3$) 42.59, 38.59, 38.44, 26.53, 24.50, 23.83.
Figure S8. Mass spectra of spirocycloalkanes.

Spectrum of spiro[5, 6]dodecane synthesized in this work.

![Mass spectrum of spiro[5, 6]dodecane synthesized in this work.](image)

Standard spectrum of spiro[5, 6]dodecane in NIST.

![Standard spectrum of spiro[5, 6]dodecane in NIST.](image)

Prob is 89.4% with NIST# 6224.
Name: Spiro[5, 6]dodecane
MW: 166  CAS#: 181-15-7  NIST#: 6224
Spectrum of sample spiro[4, 5]decane synthesized in this work.

Standard spectrum of spiro[4, 5]decane in NIST.

Prob is 85.8% with NIST# 39290..
Name: Spiro[4, 5]decane
MW: 138 CAS#: 176-63-6 NIST#: 39290
In Wolff-Kishner-Huang reduction of spiro ketones, by-products should be some bridged compound that we do not know its exact structure (Bulletin of the Chemical Society of Japan, 1969, 42, 1351-1353).
Figure S9. FTIR spectra of spiro[4, 5]decane (A) and spiro[5, 6]dodecane (B)

spiro[4, 5]decane
characteristic peaks: 1448, 2854, 2923 cm\(^{-1}\).
spiro[5, 6]dodecane
characteristic peaks: 1452, 2850, 2922 cm\(^{-1}\)

2923 cm\(^{-1}\) and 2850 cm\(^{-1}\) belongs to the stretching vibration of C-H in -CH\(_2\)-. 1452 cm\(^{-1}\) is the rocking vibration of methyl and methine.
Figure S10. Mass spectra of products synthesized from cycloheptanone.

Spectrum of bicycloheptyl-1,1'-diol synthesized in this work.

Spectrum of spiro[6.7]tetradecan-8-one synthesized in this work.

Spectrum of spiro[6.7]tetradecane synthesized in this work.
Figure. S11 Differential scanning calorimetry (DSC) of spiro[5, 6]dodecane (A) and spiro[4, 5]decane (B).