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Synthesis of Bio-Based Methylcyclopentadiene from 2,5-Hexanedione: A Sustainable Route to High Energy Density Jet Fuels

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ABSTRACT

The sustainable, bio-based, platform chemical, 2,5-hexanedione [HD (**1**)], was efficiently converted to methylcyclopentadiene [MCPD (**4**)] through a three-step process consisting of intramolecular aldol condensation, catalytic chemoselective hydrogenation, and dehydration. Base-catalyzed aldol condensation of **1** resulted in the formation of 3-methyl-2-cyclopenten-1-one [MCO (**2**)], which was then converted to 3-methyl-2-cyclopenten-1-ol [MCP (**3**)] by chemoselective reduction with a ternary Ru catalyst system [$RuCl_2(PPh_3)_3/NH_2(CH_2)_2NH_2/KOH$]. The hydrogenation proceeded with 96% chemoselectivity. **3** was then dehydrated over $AlPO_4/MgSO_4$ at 70 °C under reduced pressure to yield **4**, which can undergo an ambient temperature [4+2]-Diels-Alder cyclization to generate dimethyldicyclopentadiene (DMDCPD), a commodity chemical useful for the preparation of high-performance fuels and polymers. Through this approach, advanced jet fuels and materials can be conveniently produced from sustainable cellulosic feedstocks.

INTRODUCTION

Over the last several decades, remarkable progress has been made on the development of alternative transportation fuels from biomass sources.[1-3] This research has been driven by the need to reduce CO_2 emissions and help mitigate the impacts of global warming and ocean acidification.[4] Although ground vehicles, including cars and light trucks, can be easily powered by renewable electricity or hydrogen, the immense power requirements of commercial and military jet aircraft are currently dependent on hydrocarbon fuels. Petroleum-derived jet fuels are composed of *n*-paraffins, isoparaffins, cycloalkanes, and aromatic compounds. These complex mixtures contain up to 25% aromatic compounds, [5,6] which have low gravimetric heats of combustion and can increase particulate emissions. To address these issues, a significant amount of research has been focused on the production of a diverse portfolio of full-performance bio-based jet fuels with reduced aromatic content. For example, hydrotreatment of lipid/fatty acid feedstocks or Fischer-Tropsch upgrading of bio-based synthesis gas can readily generate synthetic paraffinic kerosenes (SPKs),[7-13] which are currently approved for use in commercial aircraft at blend ratios of up to 50% with traditional jet fuel.[14,15] Most SPKs are composed of C9 – C15 acyclic *n*-paraffinic and isoparaffinic hydrocarbons, with no aromatic compounds, and low sulfur content.[16] The lack of aromatics results in higher gravimetric net heats of combustion (NHOCs), ~43.7 – 44.0 MJ/kg,[17] compared to conventional jet fuel (≥ 42.8 MJ/kg), but these fuels are limited by their lower densities and volumetric NHOCs. In addition, these mixtures of acyclic alkanes do not adequately swell nitrile rubber engine seals, and without engine system modifications, may cause elastomer seals to shrink and malfunction.[18,19] In contrast, recent studies have shown that 30% cycloalkane blends have the same swelling capability as low (8%) aromatic fuel blends.[20-23] Cycloalkanes also have higher densities due to their constrained geometries, and significantly higher volumetric NHOCs than SPKs and traditional jet fuels.[17]

Due to growing interest in the development of high-performance bio-based jet fuels that can out-perform conventional jet fuels, while reducing net CO_2 emissions, a number of new technologies for the conversion of biomass feedstocks to sustainable cycloalkane fuels have been explored.[24-36] These studies have even extended to high-density, bicyclic compounds with applications as missile fuels. For example, our group demonstrated the conversion of the acyclic terpenoid linalool to dimethyltetrahydrodicyclopentadiene (RJ-4) in 2011.[37] RJ-4 has a gravimetric and volumetric NHOC of 42.21 MJ/kg and 39.04 MJ/L (up to 17.7% higher than Jet-A)[17], respectively, with a density of 0.925 g/mL. Zero-aromatic, high-performance jet fuel surrogates prepared from RJ-4 and various SPKs have recently been studied with RJ-4 concentrations as high as 50%.[17] Due to its high density, pure RJ-4 has applications as a high energy density fuel for cruise missile propulsion, [38-40] while its low volatility and high flashpoint are well suited for ramjet engines.[41] More recently, researchers have shown that RJ-4 can be efficiently converted to 1,3-dimethyladamantane, a thermally stable jet fuel of interest for high speed applications.[42]

To develop a route to RJ-4 from lignocellulosic feedstocks, it was of interest to explore 2,5-hexanedione [HD (**1**)] as a platform chemical for the synthesis of methylcyclopentadiene [MCPD (**4**), Scheme 1]. Fructose can be readily converted to 5-hydroxymethylfurfural (HMF) through isomerization and acid-catalyzed dehydration, followed by selective hydrogenolysis, to generate 2,5-dimethylfuran (DMF).[43] Alternatively, Mascal has demonstrated the efficient conversion of cellulose to 5-(chloromethyl)furfural (CMF) followed by a two-stage acetalization/hydrogenation reaction to generate DMF.[44,45] Hydrolysis of DMF then yields **1** (Scheme 1), which can be readily converted to 3-methyl-2-cyclopenten-1-one [MCO (**2**)] by a base-catalyzed intramolecular aldol condensation.[46,47] More recently, Zhang demonstrated the conversion of CMF to **1** via a one-pot hydrodechlorination/hydrogenolysis/hydrolysis step. **2** was then produced via cyclization with an MgO catalyst at 453 K.[48] **2** can be converted to 3-methyl-2-cyclopenten-1-ol [MCP (**3**)] via chemoselective hydrogenation of the carbonyl group. Although the Luche reduction ($NaBH_4/CeCl_3•7H_2O$) is chemoselective and has previously been used for the conversion of **2** to **3**,[49] it requires a stoichiometric amount of $NaBH_4$, which limits the sustainability of this approach for the production of high-performance jet fuels. In contrast, Ru-based Noyori catalysts[50] exhibit high selectivity for the hydrogenation of carbonyl groups in the presence of alkenes and in some cases are capable of promoting TONs > 1,000,000, using cheap and readily available hydrogen gas as the reagent.

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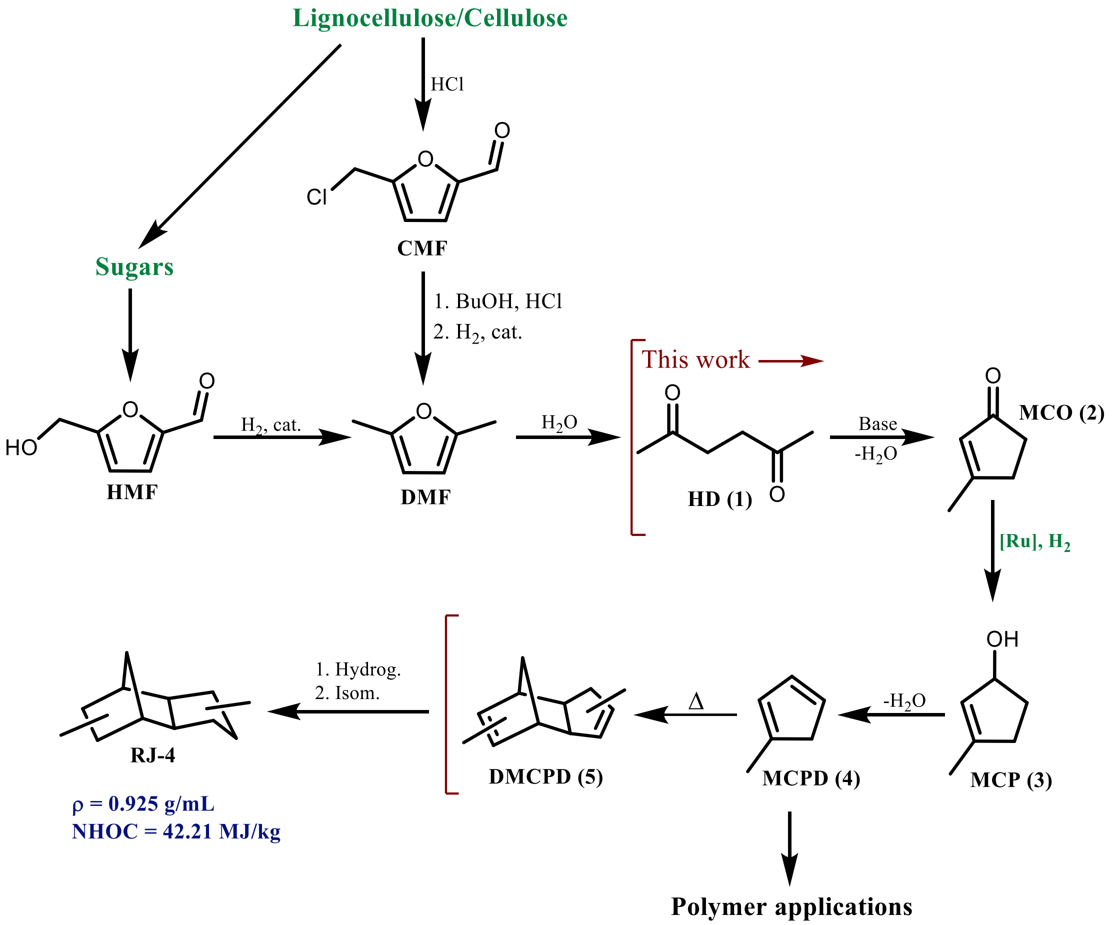
Leveraging the potential of 1 as a readily available bio-based substrate, this work describes the synthesis of sustainable methylcyclopentadiene (**4**) and dimethyldicyclopentadiene [DMDCPD (**5**)] via a three-step process consisting of aldol condensation, catalytic chemoselective hydrogenation, and dehydration. Through this approach, we demonstrate the ability to generate both a valuable chemical precursor and high-performance jet fuel blendstock from ubiquitous biomass feedstocks.



Scheme 1. Synthesis of methylcyclopentadiene (**4**), dimethyldicyclopentadiene (**5**), and RJ-4 from biomass sugars

EXPERIMENTAL SECTION

General. 2,5-hexanedione (≥98%) and tris(triphenylphosphine)ruthenium(II) dichloride (97%), were obtained from Millipore Sigma and used as received. Ethylenediamine was freshly distilled (62 – 65 °C, 100 mmHg) prior to use. ^{1}H NMR spectra were recorded on a Bruker Avance III 500 spectrometer at 25 °C, operating at 500.46 MHz. Proton-decoupled $^{13}C\{^1H\}$ NMR spectra were recorded with the same instrument at 25 °C, operating at 125.86 MHz. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane, and are referenced relative to the NMR solvent ($CDCl_3$), according to the literature values – $\delta(^1H) = 7.26$, $\delta(^{13}C) = 77.23$.

Synthesis of 3-methylcyclopent-2-en-1-one [MCO (2)]. 2,5-Hexanedione (41.76 g, 0.37 mol) was added over 10 min to a stirred solution of KOH (5.25g, 0.094 mol g) in H_2O (250 mL) at reflux. The reaction mixture was refluxed for an additional 30 min, cooled rapidly to 0 ˚C, saturated with sodium chloride (45.0 g), and filtered through Celite. The solution was then extracted with CH_2Cl_2 (3 × 200 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by distillation (50 – 55 °C, 3.6 mmHg) to afford 3-methyl-2-cyclopent-1-one (22.63 g, 64%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 2.56 - 2.55 (m, 2H), 2.40 - 2.39 (m, 2H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.8, 178.8, 130.3, 35.5, 32.8, 19.2. MS for C_6H_8O: 96.06 *m/z*.

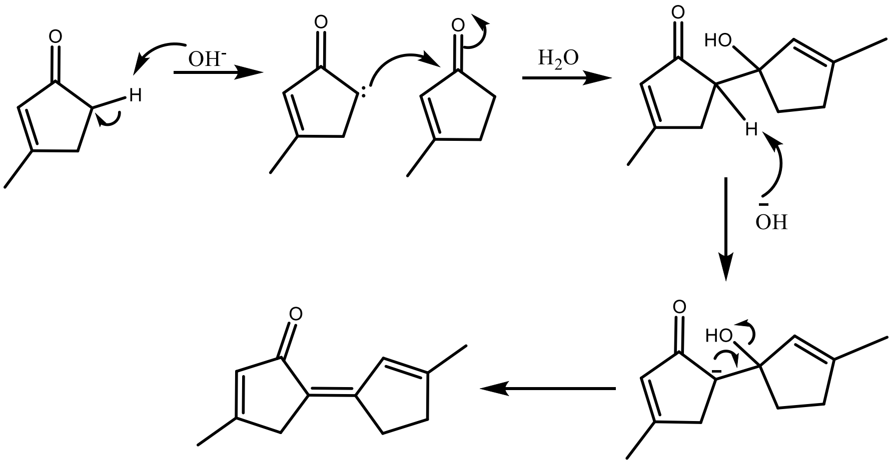
Synthesis of 3-methylcyclopent-2-en-1-ol [MCP (3)] 7.22 mL of a solution containing ethylene diamine (0.1 M, 0.722 mmol) and KOH (0.2 M, 1.44 mmol) in anhydrous 2-propanol were added to a 6:1 (v/v) mixture of anhydrous 2-propanol:benzene (140 mL). The mixture was thoroughly degassed under reduced pressure. $RuCl_2[P(C_6H_5)_3]_3$ (0.693 g, 0.722 mmol) was then added to the solution under flowing N_2. The resultant mixture was sonicated for 90 min to obtain a yellow homogenous solution. A [0.5M] solution of 3-methyl-2-cyclopent-1-one (6.94 g, 72.2 mmol) in 2-propanol was degassed and added to the catalyst solution, which was then transferred to a 600 mL Parr bomb under nitrogen. The bomb was evacuated and refilled with H_2 three times, pressurized to 500 psi, and then vigorously stirred for 3.5 h at ambient temperature. Upon completion, the reaction mixture was filtered through Celite and concentrated under reduced pressure. The crude product was combined with the product from a previous reaction (6.12 g) and purified by fractional distillation (39 – 45 ˚C, 2.4 mmHg) to yield 3-methyl-2-cyclopenten-1-ol (10.01 g, 75%) as a colorless oil. GC analysis showed an MCP purity of 94% with 4% methylcyclopentanol and 2%

starting material (Figure S4). On this basis, the conversion was 98% with 96% chemoselectivity to **3**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (d, 1H, *J* = 1.4 Hz), 4.76 (bs, 1H), 2.27 - 2.15 (m, 1H), 2.144 - 2.139 (m, 1H), 2.137 - 2.131 (m, 1H), 2.05 (bs, 1H), 1.76 (s, 3H). 1.74 - 1.68 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 127.6, 77.9, 35.3, 34.4, 16.8. MS for $C_6H_{10}O$: 98.07, 71.05 *m/z*.

Synthesis of methylcyclopentadiene [MCPD (4)] and dimethyldicyclopentadiene [DMCPD (5)]. $AlPO_4$, synthesized as previously described,[37,51] (0.894 g, 7.33 mmol) and $MgSO_4$ (1.10 g, 9.17 mmol) were added to **3** (9.00 g, 0.092 mol) in a 50 mL round bottom flask fitted with a small distillation head. The receiving flask was lowered into a dry ice bath and the reaction was placed under reduced pressure (40 mmHg). The reaction was heated to an oil bath temperature of 70 ˚C for 4 h. The organic phase of the distillate (5.07 g) was separated from the aqueous layer, placed in a sealed vial over $NaCO_3$ and allowed to warm to ambient temperature for 24 h. GC-FID analysis revealed a mixture of 7% methylcyclopentadiene, 12% methylcyclopentenols, and 78% dimethyldicyclopentadiene isomers. The residue in the reaction flask was extracted with dichloromethane (30 mL), filtered through Celite, and concentrated under reduced pressure to yield a light orange oil (2.04 g). The oil consisted of 8% unreacted 3-methyl-2-cyclopenten-1-ol, 73% dimethyldicyclopentadiene isomers (DMDCPD), and 9% trimers. The overall yield of MCPD and DMDCPD was 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 (m), 6.25 – 6.15 (m), 6.02 – 5.97 (m), 5.55 (bs), 5.49 - 5.44 (m), 5.15 (bs), 5.11 (bs), 4.88 (bs), 4.79 (bs), 3.02 – 2.55 (m), 2.54-2.04 (m), 1.69 – 1.57 (m), 1.30 – 1.22 (m). ^{13}C NMR of the major isomer (125 MHz, $CDCl_3$) δ 145.7, 140.4, 126.0, 125.5, 57.8, 50.8, 49.7, 46.3, 42.6, 34.5, 17.2, 16.2. MS for $C_{12}H_{16}$: 160.1, 80.1 *m/z*.

RESULTS AND DISCUSSION

The first step in the conversion of **1** to **4** required the intramolecular aldol condensation of **1** to generate **2**. We initially attempted the conversion through a biphasic approach, recently described by Sacia and co-workers, which utilized an aqueous K_3PO_4 solution with a toluene overlay at 180 °C.[47] Although Sacia obtained yields of up to 94%, in our hands we were only able to achieve yields of 25% due to the generation of oligomerization products. This unsatisfactory result was likely due to the much larger (~358-fold) scale used in the current work. The reaction is very time and temperature sensitive, and our inability

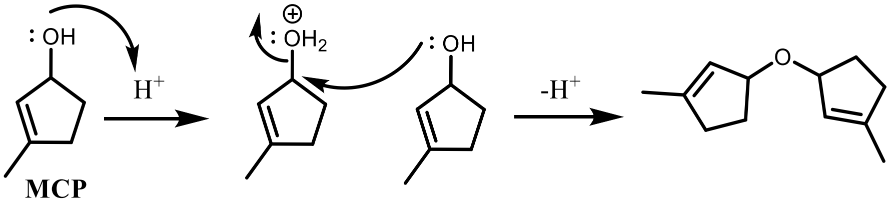


Scheme 2: Formation of dimers during the base-catalyzed self-aldol condensation of **2**.

to rapidly heat and cool our much larger reactor resulted in the generation of heavier reaction products. To overcome this issue, we cyclized **1** under basic aqueous conditions at reflux temperatures.[46] As observed in the biphasic reaction, carefully controlling the reaction time was critical to limiting the formation of dimers and trimers. The reaction was monitored by GC-MS at 10-minute increments and showed >99% conversion to the cyclic enone after 30 min with the formation of 34% dimers. The mass spectra of the dimer peaks were consistent with molecules formed by the self-aldol condensation of **2** followed by dehydration (Scheme 2). After 40 min, dimers and trimers represented 58% of the product distribution. To optimize the yield of **2** we limited the reaction time to 30 min and then immediately cooled the sample in an ice bath to prevent further oligomerization. This allowed for the preparative scale synthesis of MCO in 64% yield, similar to the results obtained by Paterson.[46] Further improvements in the yield are likely achievable through more careful control of the temperature and reaction time through advanced synthetic techniques such as flow chemistry.[52] Alternatively, the dimers and trimers can be converted to C12 and C18 cycloalkane-based fuels by hydrodeoxygenation.[48]

The chemoselective reduction of **2** was performed under basic conditions using the classic $RuCl_2[P(C_6H_5)_3]_3$-$NH_2(CH_2)_2NH_2$-KOH ternary catalyst system. As previously described by Noyori, the use of two equivalents of ethylene diamine and one equivalent of KOH in combination with the Ru-precatalyst is crucial to enhancing the chemoselectivity.[50,53] A modest catalyst loading (1 mol%) and moderate hydrogen pressure (500 psi) were sufficient to achieve complete conversion of the substrate at ambient temperature, with 96% chemoselectivity to the enol. The presence of the methyl group plays a critical role in enhancing the chemoselectivity. For example, the ruthenium catalyzed hydrogenation of cyclohex-2-en-1-one has been reported to proceed with 70% chemoselectivity, whereas the hydrogenation of 3-methylcyclohex-2-en-1-one proceeded with 99.9% chemoselectivity.[53] As a comparison, the reduction was carried out with $NaBH_4$ and equimolar amounts of $CeCl_3 \bullet 7H_2O$ in anhydrous methanol (see the ESI for experimental details).[49] Under these conditions we achieved >99.9% chemoselectivity to **3** (Figure S12). Despite the higher selectivity obtained through this method, the use of stoichiometric $NaBH_4$ and $CeCl_3 \bullet 7H_2O$ would be impractical for the synthesis of fuels at commercial scale. Moreover, from a green chemistry perspective, this approach would result in the production of an onerous waste stream rich in boron and cerium salts.

Dehydration of secondary alcohols under mild acidic conditions is well known in the literature.[54] During initial work-ups of **3**, dilute HCl solutions were used to extract the product, followed by concentration of the solution under reduced pressure, and at elevated temperatures. Under these conditions, NMR studies confirmed the dehydration of the alcohol. Therefore, in an attempt to develop a sustainable dehydration process, we explored the use of dilute HCl solutions to catalyze the reaction (the results are summarized in Table S1). Temperatures above 60 °C promoted heavier oligomer formation, while lower temperatures resulted in a complicated product distribution due to the formation of ethers (Scheme 3), which were difficult to separate from 5 due to their similar molecular weights and boiling points. Even if the DMCPD isomers could be efficiently separated from the ethers by distillation, small amounts of ethers present in the product mixture would lower the gravimetric net heat of combustion of the finished fuels.



Scheme 3. Ether formation during the dehydration of **3** with 1M HCl at temperatures below 60 °C.

To avoid these issues, we explored the use of a heterogeneous system based on our previous work.[37,51] **3** was dehydrated over $AlPO_4/MgSO_4$ at 70 °C, under reduced pressure (40 mmHg). These reaction conditions were selected to maximize the conversion of **3** to products, while reducing the propensity for dimerization and oligomerization of **4**. The distillate was allowed to phase separate, and the organic phase was warmed to room temperature and maintained at that temperature for 48 h, allowing for Diels-Alder cyclodimerization to generate **5**. Small amounts of residual **4** and unreacted starting material were present in the product mixture (Figure 1). The distillation pot contained primarily **5**, along with a small amount of trimer and residual starting material. The overall yield of product (calculated as the sum of **4** and **5**) from the dehydration reaction was 79%, while higher yields could be obtained by recycling unreacted **3**.

The dimethyldicyclopentadiene fraction consisted of seven resolvable isomers, similar to commercial material.[55] However, the relative amounts of each isomer differed substantially compared to the conventional product distribution. The two most prominent isomers were 3,9-dimethyl-endo-tricyclo[5.2.1.$0^{2,6}$] deca-3,8-diene (**5a**), and 4,9-dimethyl-endo-tricyclo[5.2.1.$0^{2,6}$] deca-3,8-diene (**5b**) (Scheme 4). The identity of these two isomers was confirmed by comparing the retention time and mass spectra of these components to our previous results[37] and a literature report.**[Error! Bookmark not defined.]** The prevalence of isomer **5a** suggests that dehydration of the alcohol to form 1- methylcyclopenta-1,3-diene (**4a**) is followed by isomerization to 2-methylcyclopenta-1,3-diene (**4b**). Diels-Alder cyclodimerization of **4b** yields **5a**, while a cross-cycloaddition between **4a** and **4b** yields **5b**. It is not clear what impact the isomer distribution will have on the final fuel properties of derivative RJ-4 mixtures; this topic will be studied in future work.

The pathway described above resulted in a 38% overall yield for the conversion of **1** to **4/5**. However, other researchers have reported that nearly quantitative yields of **2** can be obtained through the use of a biphasic reaction system[47] or a solid base catalyst.[48] In addition, although we achieved a 75% isolated yield of **3** after the chemoselective hydrogenation step, we obtained a 98% conversion of **2** to **3**. This suggests that a more efficient distillation of **3,** enabled by running the reaction at large scale, would allow for a much higher isolated yield. Finally, the dehydration reaction did not go to completion, and unreacted 3 could be recycled for subsequent conversion to **4**. Therefore, it may be feasible to improve the

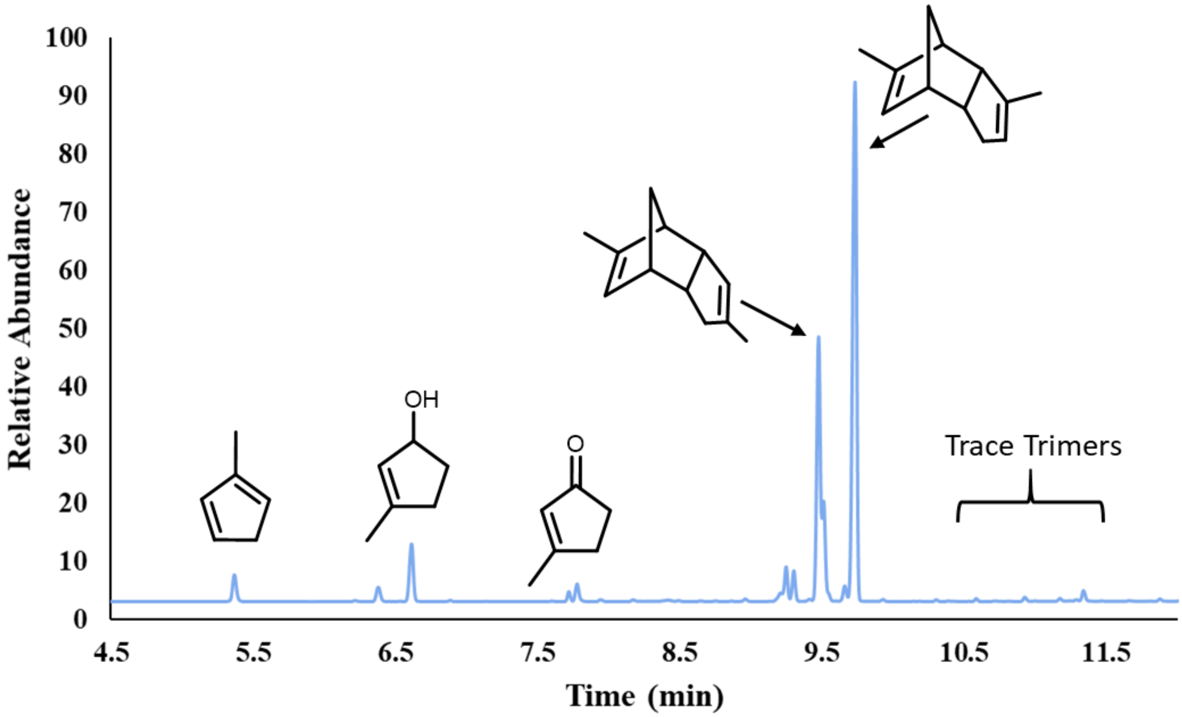
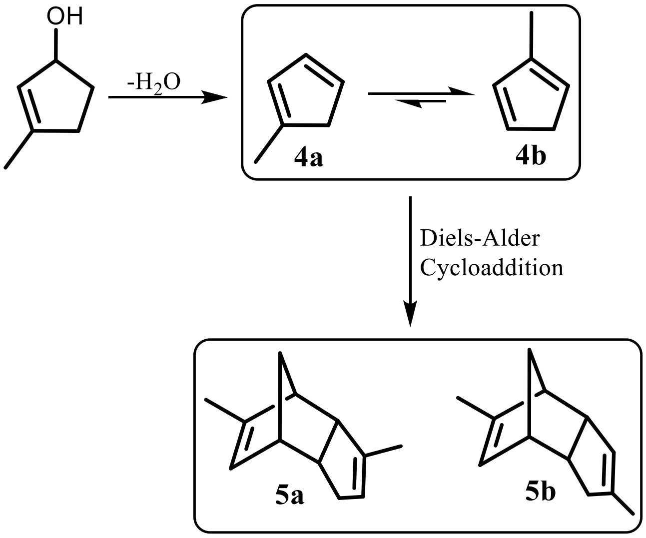


Figure 1. Gas chromatogram of crude dimethyldicyclopentadiene (DMDCPD) synthesized from **1**.



Scheme 4. Dehydration of **3**, followed by Diels-Alder cycloaddition, to generate DMCPD isomers **5a** and **5b**.

yield of **4/5** to greater than 80%. Recent work by Zhang et al.[48] has demonstrated a 71.2% yield of **1** from cellulose. Combining the two approaches at commercial scale may allow for dimethyldicyclopentadiene yields of greater than 55% from cellulose.

CONCLUSIONS

The development of efficient synthetic routes to commodity chemicals conventionally sourced from petroleum is a key pillar of sustainable development. This work has demonstrated that 2,5-hexanedione, a bio-based platform chemical readily generated from lignocellulosic biomass, can be converted to methylcyclopentadiene (MCPD), an important precursor to high performance polymers and fuels. This transformation was accomplished by the utilization of a three-step method combining intramolecular aldol condensation, Ru-catalyzed chemoselective hydrogenation, and dehydration. MCPD can subsequently be converted to tetrahydrodimethyldicyclopentadiene (RJ-4), a high-density fuel that can increase the density and volumetric net heat of combustion of jet fuel blends with acyclic synthetic paraffinic kerosenes. The use of sustainable RJ-4 in jet fuel mixtures may provide an opportunity to reduce particulate emissions and net greenhouse gas emissions from commercial and military aircraft.

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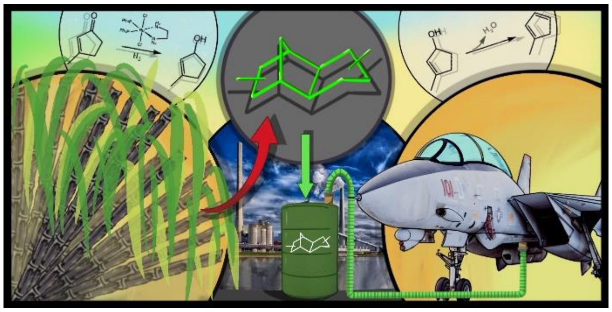
TOC Graphic



Ruthenium is the key: The production of jet fuels from abundant biomass sources is critical for sustainable aviation. This work describes the conversion of 2,5-hexanedione, a bio-based platform chemical readily derived from cellulose, to methylcyclopentadiene, a commodity chemical useful for the preparation of high-performance jet fuel. A key step in the process is the chemoselective hydrogenation of 3-methyl-2-cyclopenten-1-one catalyzed by $RuCl_2(PPh_3)_2(H_2N(CH_2)_2NH_2)$.

REFERENCES

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[1] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098
[2] M. A. Díaz-Pérez, J. C. Serrano-Ruiz, *Molecules* **2020**, *25*, 802.
[3] T. M. H. Dabros, *et al.*; *Prog. Energy Combust. Sci.* **2018**, *68*, 268–309
[4] A. Singhal, P. Prashant, *Biotechnology for Biofuels: A Sustainable Green Energy Solution*, Springer, Singapore, **2020**, p. 1–22
[5] T. M. Lovestead, J. L. Burger, N. Schneider, T. J. Bruno, *Energy Fuels* **2016**, *30*, 10029–10044
[6] M. Bernabei, R. Reda, R. Galiero, G. Bocchinfuso, *J. Chromatogr. A* **2003**, *985*, 197–203
[7] M. C. Vásquez, E. E. Silva and E. F. Castillo, *Biomass Bioenergy* **2017**, *105*, 197–206.
[8] L.Starck, L. Pidol, N. Jeuland, T. Chapus, P. Bogers, J. Bauldreay, *Oil Gas Sci. Technol-Rev. IFP energies nouvelles* **2016**, *71*, 10
[9] H. J. Robota, J. C. Alger, L. Shafer, *Energy Fuels* **2013**, *27*, 985–996
[10] S. Lestari, P. Mäki-Arvela, J. Beltramini, G. Q. M. Lu, D. Y. Murzin, *ChemSusChem* **2009**, *2*, 1109–1119
[11] C. Hamelinck, A. Faaij, H. Denuil and H. Boerrigter, *Energy* **2004**, *29*, 1743–1771
[12] B. H. Davis, *Catal. Today* **2002**, *71*, 249–300
[13] A. D. Klerk, *Green Chem.* **2008**, *10*, 1249
[14] W.-C. Wang, L. Tao, J. Markham, Y. Zhang, E. Tan, L. Batan, E. Warner and M. Biddy, *Review of biojet fuel conversion technologies NREL/TP-5100-66291* **2016**, DOI: 10.2172/1278318
[15] P. Vozka, P. Šimáček, G. Kilaz, *Energy Fuels* **2018**, *32*, 11595–11606
[16] N. Mezher, W. E. Rathbun, H. Wang, F. Ahmad, *Energy Fuels* **2013**, *27*, 3830–3837
[17] J.-D. Woodroffe and B. G. Harvey, *Energy Fuels* **2020**, *34*, 5929–5937
[18] B.E. Anderson, A.J. Beyersdorf, C.H. Hudgins, J.V. Plant, K.L. Thornhill, E.L. Winstead, et al. *Alternative Aviation Fuel Experiment (AAFEX) NASA/TM-2011-217059*, **2011**
[19] E. Corporan, T. Edwards, L. Shafer, M. J. DeWitt, C. Klingshirn, S. Zabarnick, et al., *Energy Fuels*, **2011**, 25, 955-966
[20] J. L. Graham, T. F. Rahmes, M. C. Kay, J.-P. Belières, J. D. Kinder, S. A. Millett, J. Ray, W. L. Vannice, J. A. Trela, *Impact of alternative jet fuel and fuel blends on non-metallic materials used in commercial aircraft fuel systems. Federal Aviation Administration Report DOT/FAA/AEE/2014-10*, **2014**
[21] Y. Liu, C. W. Wilson, *Adv. Mech. Eng*. **2012**, *4*, 127430
[22] M. Romanczyk, *et al. Fuel* **2019**, *238*, 483–492
[23] S. Kosir, J. Heyne, J. Graham, *Fuel* **2020**, *274*, 117832
[24] J. A. Muldoon, B. G. Harvey, *ChemSusChem* **2020**.
[25] K. E. Rosenkoetter, C. R. Kennedy, P. J. Chirik, B. G. Harvey, *Green Chem.* **2019**, *21*, 5616–5623
[26] G. Li, B. Hou, A. Wang, X. Xin, Y. Cong, X. Wang, N. Li, T. Zhang, *Angew. Chem., Int. Ed.* **2019**, *58*, 12154–12158
[27] Q. Deng, G. Nie, L. Pan, J.-J. Zou, X. Zhang, L. Wang, *Green Chem.* **2015**, *17*, 4473–4481
[28] X. Sheng, N. Li, G. Li, W. Wang, J. Yang, Y. Cong, A. Wang, X. Wang, T. Zhang, *Sci. Rep.* **2015**, *5*, 9565
[29] W. Wang, N. Li, G. Li, S. Li, W. Wang, A. Wang, Y. Cong, X. Wang, T. Zhang, *ACS Sustainable Chem. Eng.* **2017**, *5*, 1812–1817
[30] G. Nie, X. Zhang, L. Pan, P. Han, J. Xie, Z. Li, J. Xie, J.-J. Zou, *Chem. Eng. Sci.* **2017**, *173*, 91–97
[31] K. W. Harrison, B. G. Harvey, *Sustainable Energy Fuels* **2017**, *1*, 467–473
[32] B. G. Harvey, W. W. Merriman, T. A. Koontz, *Energy Fuels* **2015**, *29*, 2431–2436
[33] B. G. Harvey, H. A. Meylemans, R. V. Gough, R. L. Quintana, M. D. Garrison, T. J. Bruno, *Phys. Chem. Chem. Phys.* **2014**, *16*, 9448–9457
[34] H. A. Meylemans, L. C. Baldwin, B. G. Harvey, *Energy Fuels* **2013**, *27*, 883–888
[35] H. A. Meylemans, R. L. Quintana, B. G. Harvey, *Fuel* **2012**, *97*, 560–568
[36] B. G. Harvey, M. E. Wright, R.L. Quintana, *Energy Fuels* **2010**, *24*, 267–-273
[37] H. A. Meylemans, R. L. Quintana, B. R. Goldsmith and B. G. Harvey, *ChemSusChem* **2011**, *4*, 465–469
[38] H. S. Chung, C. S. H. Chen, R. A. Kremer, J. R. Boulton, G. W. Burdette, *Energy Fuels* **1999**, *13*, 641–649
[39] G. W. Burdette, *U S Patent 4410749* **1983**
[40] T. Edwards, *J. Propul. Power* **2003**, *19*, 1089–1107
[41] S. Krishnamachary, S. K. Mohan, J. Desingou, S. D. Jena, R. Vivek, T. D. Kumar, V. Ramanujachari *RSC Adv.* **2014**, *4*, 45407–45414

---

[42] B. G. Harvey, K. W. Harrison, M. C. Davis, A. P. Chafin, J. Baca, W. W. Merriman *Energy Fuels* **2016**, *30*, 10171–10178

[43] X. Xiang, J. Cui, G. Ding, H. Zheng, Y. Zhu, Y. Li *ACS Sustainable Chem. & Eng.*, **2016**, *4*, 4506–4510

[44] S. Dutta, M. Mascal, *ChemSusChem* **2014**, *7*, 3028-3030

[45] M. Mascal, E. B. Nikitin, *Angew. Chem. Int. Ed*. **2008**, *120*, 8042–8044

[46] I. Paterson, M. Xuan, S. M. Dalby, *Angew. Chem. Int. Ed*. **2014**, *126*, 7414–7417

[47] E. R. Sacia, M. H. Deaner, Y. L. Louie, A. T. Bell, *Green Chem.* **2015**, *17*, 2393–2397

[48] Y. Liu, G. Li, Y. Hu, A. Wang, F. Lu, J-J. Zou, Y. Cong, N. Li, T. Zhang, *Joule* **2019**, *3*, 1028–1036

[49] J.-L. Luche, L. Rodriguez-Hahn, P. Crabbé, *J. Chem. Soc., Chem. Commun.* **1978**, *14*, 601–602

[50] R. Noyori, T. Ohkuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73

[51] A. W. Wang, Final Report US Department of Energy, Contract No. DE-FC22–94PC93052, **2002**

[52] M. B. Plutschack, B. Pieber, K. Gilmore, P. H. Seeberger, *Chem.* Rev. **2017**, *117*, 11796–11893

[53] T. Ohkuma, H. Ooka, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 10417-10418

[54] N. Akiya, P. E. Savage, *Ind. Eng. Chem. Res.* **2001**, *40*, 1822–1831

[55] M. A. Diez, M. D. Guillen, C. G. Glanco, J. Bermejo, *J. Chromatogr.*, **1990**, *508*, 363-374