Hydrogen-Economic Synthesis of Gasoline-like Hydrocarbons by Catalytic Hydrodecarboxylation of the Biomass-derived Angelica Lactone Dimer

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The biomass-derived platform molecule levulinic acid is converted into the angelica lactone dimer (ALD) in high overall yield using simple inorganic catalysts. Hydrodecarboxylation of ALD using a Pd/γ-Al$_2$O$_3$ catalyst under moderate hydrogen gas pressure at high temperatures generates branched C$_8$–C$_9$ hydrocarbons in nearly quantitative yield by consuming as little as a single equivalent of external hydrogen. These molecules are high-octane "drop-in" equivalents of isoalkanes used in commercial gasoline. Catalytic hydrodecarboxylation is presented as a highly effective means to reduce hydrogen demand in biomass-to-biofuel conversion technologies.

Currently, a great deal of effort is being directed towards the conversion of biomass into molecules suitable for automotive fuel use. Indeed, a general search of the term "biofuel" in the Chemical Abstracts database locates >17000 journal references, of which >3100 have "biofuel" in the title. Although there are a variety of naturally derived compounds that could, in principle, serve as fuels, hydrocarbon "drop-ins" are the most attractive commercially, as they integrate directly into the existing transportation infrastructure. Refinement of the biofuel literature search to return only hits that include "hydrocarbons" or "alkanes" narrows the field to approximately 1250 papers, the majority of which describe approaches to straight-chain, saturated C$_{10}$–C$_{22}$ molecules that comprise diesel-range fuels. These are generally produced by condensation reactions of biomass-derived carbonyl compounds followed by hydrodeoxygenation of the products. There are, on the other hand, far fewer examples of biomass processing methods that specifically target the branched, lighter-weight hydrocarbons used in motor gasoline. Those references that also include the term "gasoline" generally fall into the following categories: i) the catalytic hydrocracking of vegetable or algal oils;[1] ii) fast

pyrolysis of biomass and subsequent upgrading of the crude bio-oil;[2] iii) biomass gasification followed by Fischer–Tropsch or methanol-to-gasoline synthesis;[3] iv) oligomerization of biomass-derived olefins by using methods deployed in the petroleum industry;[4] v) microbial approaches to isoprenoids.[5] Plainly missing from this list are chemocatalytic methods related to those used to convert biomass into diesel-type hydrocarbons. The question arises as to why these are not also used to produce gasoline. The answer lies in the nature of the condensation reactions available to such processes, virtually all of which involve biogenic ketones and simple carbohydrate derivatives, such as furans. This gives access to products with more than six carbon atoms, for which a C−C coupling step is essential to achieve the required volatility range for motor and jet fuels. In most cases, however, the carbonyl compounds involved have no branching, and the processes themselves (aldol and related) lead to little, if any, branching in the products.

The quest for renewable gasoline thus becomes an issue of either sourcing a feedstock that already has branching or developing chemistry that leads to branched products. One ingenious approach to the former involves the complete saturation of lignin to give mixtures of branched cycloalkanes, which is also attractive from the standpoint of embracing the complexity of biomass, rather than fighting it.[6] Our own efforts in this area have focused on the introduction of branching into carbohydrate derivatives, the route to which started with levulinic acid (LA, **1**). LA is a green platform molecule of unrivaled potential that is efficiently produced in a two-stage operation from raw, cellulosic biomass, typically agricultural, forestry, or municipal waste.[7] Compound **1** can be dehydrated in high yield to angelica lactone (**2**), which is formed as a mixture of double-bond isomers (α isomer shown, Scheme 1). Branching is introduced by the dimerization of **2**, which proceeds in nearly quantitative yield using simple inorganic catalysts to give the angelica lactone dimer (ALD, **3**). We recently reported the hydrodeoxygenation of **3** under mild conditions to give a mixture of branched C$_7$–C$_{10}$ alkanes, the major product of which was 3-ethyl-4-methylheptane (**4**), constituting a novel approach to "cellulosic gasoline".[8] Related work has adapted Ni-based catalysts to the reduction of **3** as well as a trimer of **2**, but the result was a poorly defined mixture of C$_6$–C$_{17}$ products.[9]

Whereas the conversion of **3** into **4** unlocked access to a hitherto undescribed class of branched, renewable hydrocarbons, the process used a total of 9 equivalents of hydrogen, 6 equivalents of which were used to retain only two of the

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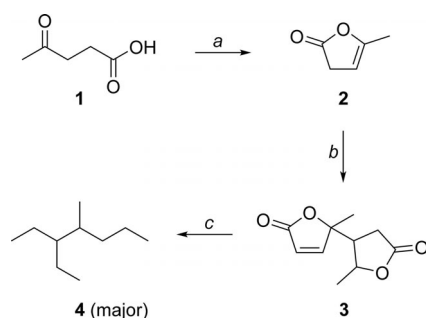
Scheme 1. Hydrodeoxygenation of the angelica lactone dimer. Reagents and conditions: a) K10, 165 °C, 50 torr (10 torr = 1.3 kPa), 92%; b) K₂CO₃, 70 °C, 94%; c) Ir-ReOₓ/SiO₂, 54 bar H₂, 220 °C, 7 h.[8]

carbon atoms in product **4**. Although green routes to H₂ are under development, most notably through the electrolysis of water using photovoltaic-supplied electricity,[10] the most economic source of hydrogen remains petroleum-derived hydrocarbons or coal through the water–gas shift reaction. Given that hydrogen demand can impose significant limitations on the commercial relevance of any biomass-to-hydrocarbons technology, we recognized the potential appeal of reducing this burden on the economics of the process.

One approach to lowering the oxidation state of carboxylic acid derivatives dramatically is thermal decarboxylation, in which oxygen is carried away in the form of CO₂. Hydrothermal decarboxylation has, for example, been practiced on fatty acids using no external hydrogen.[11] The process involves the use of a typical hydrogenation catalyst in H₂O at temperatures in excess of 300 °C, and works well with saturated acids to give *n*-alkanes with high selectivity. With unsaturated acids, lower mass balances are observed as an apparent result of oligomer formation. In our hands, submitting **3** to such conditions gave mainly polymeric products.

An alternative approach is to perform hydrodecarboxylation (HDC), which includes a hydrogen atmosphere to saturate any olefinic bonds present in the feed or that arise in the course of the decarboxylation process.[12] The reaction also succeeds with fatty acid esters.[13] Although generally applied to unsaturated fatty acids, HDC was seen as particularly suitable for **3**, which not only starts with a C=C bond but can also generate two more on opening of the lactone rings. Another attractive aspect of HDC is that oxygen is removed without the generation of water, which can leach metals from catalysts and necessitates drying of the product.

We undertook the HDC of **3** under solvent-free conditions using a relatively low starting pressure of H₂ in an attempt to avoid hydrodeoxygenation (HDO) reactions. The expected product was 3,4-dimethylhexane (**10**) (Scheme 2), a molecule with a measured antiknock index of 79, which is an average of its motor octane number (MON) and research octane number (RON).[14] Lactone ring opening is catalyzed by Lewis acids, particularly γ-Al₂O₃,[15] and a control reaction with H₂ over Pd/C at 300 °C in the absence of a Lewis acid led to partially reduced intermediates but no hydrocarbons. We first considered whether a simple, mechanical mixture of Pd/C and γ-Al₂O₃

would suffice, and found that indeed some alkane products were observed using this system, although overall conversion was low (Table 1, entry 2). In HDO-type reactions, the most effective catalysts are bifunctional, and as both oxophilic character and hydrogen-transfer ability are also essential in the HDC process, we prepared a palladium catalyst with γ-Al₂O₃ as the support material. The use of this catalyst resulted in a significant increase in hydrocarbon yield, although the expected C₈ product **10** was accompanied by two C₉ alkanes, **13** and **14**. As shown in Scheme 2, the main product **10** is the result of a reaction cascade involving first the reduction of the double bond in **3** followed by a Lewis acid promoted ring opening. Stereo-electronic requirements suggest that the proton at the 5-position of intermediate **5** is better situated to participate in β elimination than the ring protons at the 3-position, although in either case the double bond would be hydrogenated to give **7**. Some degree of double-bond transposition is also likely under the conditions. Intermediate **7** is a branch point at the junction of two slower steps. A second ring opening, again from the orbitally better-aligned carbon atom (C9), can occur, followed by hydrogenation of the double bond and finally twofold decarboxylation to give **10**. Alternatively, HDO of the ester function followed by decarboxylation of **12** leads to 3-ethyl-4-methylhexane (**13**). This process is slow because the initial pressure of H₂ in the reactor was kept lower (10–20 bar; 10 bar = 1.0 MPa), than that used for the targeted HDO of **3**,[8] which was conducted at an initial H₂ pressure of >50 bar. An alternative HDO–decarboxylation process including a cyclization reaction also led to the observation of 1-ethyl-2-methylcyclohexane (**14**), which was favored at the expense of **13** at higher temperatures and lower H₂ pressures. An attempt to run the reaction at a lower temperature (Table 1, entry 5) led to incomplete conversion, and the use of a Brønsted acidic zeolite support (Table 1, entry 8) triggered extensive isomerization and C−C bond cracking. The optimal results were seen at 350 °C under low initial hydrogen pressure, either with or without presaturation of **3**, under which 99% of the hydrocarbon product could be accounted for.

On a product-weighted basis, the conversion of **3** into the product mixture in Table 1, entry 7 would involve the consumption of 3.4 moles of hydrogen per mole of **3** (0.76 × 3 + 0.23 × 5). Given, however, that the conversion of cellulose into levulinic acid coproduces 1 equivalent of formic acid, it may be taken into account that 2 moles of formic acid as an H₂ carrier can be subtracted from this value[16] to give a total hydrogen burden of only 1.4 moles per mole of **3** to produce 1 mole of hydrocarbon.[17] Overall, the hydrocarbon products in Scheme 2 are four low-process intensity steps removed from raw biomass. In general terms, the maximum mass yield of saturated hydrocarbon from 1 kg cellulose is 532 g, which can be represented by its quantitative hydrogenation into *n*-hexane, which requires 7 molar equivalents of H₂. Note that *n*-hexane has a RON of 25 and is, therefore, of no value for gasoline use and too volatile for diesel fuel use. The process represented in Table 1, entry 7, on the other hand, would give a maximum theoretical return of 357 g of branched, high-octane hydrocarbons while formally consuming 1.4 molar equivalents of H₂.

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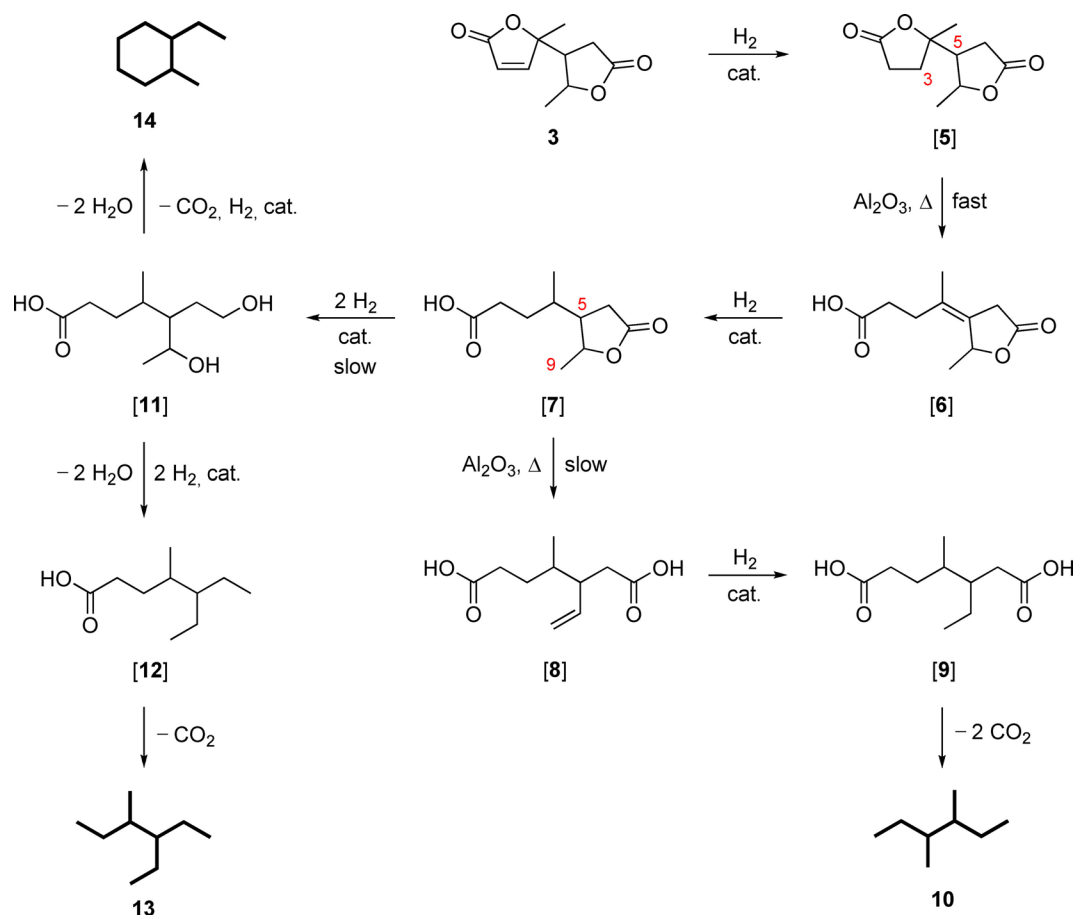
Scheme 2. Chemistry involved in the conversion of ALD **3** into branched hydrocarbons **10**, **13**, and **14**. Compound numbers in brackets represent intermediates; observed products are bolded.

Table 1. Optimization of the ALD-to-hydrocarbon reaction.

Entry	Catalyst[a]	T [°C]	Pressure [bar]	$t^{[b]}$ [h]	**10** [%]	**13** [%]	**14** [%]	Total [%][c]
1	Pd/C	300	16	3	mixture of intermediates			
2	Pd/C + γ-Al$_2$O$_3$	300	20	3	2	2	10	14
3	Pd/γ-Al$_2$O$_3$[d]	300	20	5 (1)	42	15	18	75
4	Pd/γ-Al$_2$O$_3$	300	20	5 (1)	40	13	13	66
5	Pd/γ-Al$_2$O$_3$	280	10	5 (1)	mixture of intermediates			
6	Pd/γ-Al$_2$O$_3$	350	10	3 (1)	68	3	28	99
7	Pd/γ-Al$_2$O$_3$	350	10	3	76	0	23	99
8	Pd/zeolite Y	300	20	3	C—C bond cleavage			

[a] Catalyst loading: 10–20 wt%. [b] The number in parentheses indicates presaturation time. [c] Percentage of theoretical yield. [d] Prepared 5% *w/w* Pd/γ-Al$_2$O$_3$ catalyst; for entries 4–7, the equivalent Strem Escat 1241 catalyst was employed.

As noted above, the measured octane rating of compound **10** is 79.[14] This agrees well with the calculated value of 78 obtained using the group contribution model of Dahmen and Marquardt.[18] The same method yields predicted RON values of 70 for **13** and 78 for **14**, which renders them useful blendstocks for motor gasoline. If the Table 1, entry 7 mixture were combined with 10% *v/v* ethanol (blending RON = 129)[19] as an oxygenate, the weighted RON value would be 84. Blend this mixture with an additional 10% of a high-octane aromatic, such as renewable 2,5-dimethylfuran[20] (RON = 119),[21] and the

87–90 octane grade of commercial gasoline is easily attainable, fully sourced from renewables.

In conclusion, catalytic hydrodecarboxylation is a reaction that has been little explored for the purpose of deoxygenating cellulosic biofuel candidates. We developed a method by which the biomass-derived angelica lactone dimer (**3**) can be converted into a mixture of branched hydrocarbons using the bifunctional noble-metal–Lewis-acid Pd/γ-Al$_2$O$_3$ catalyst under conditions that minimize competing hydrodeoxygenation (relatively low H$_2$ pressure and high temperature). A valuable

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feature of this solvent-free process is that very little external hydrogen is required owing to the low hydrogen burden of the hydrodecarboxylation reaction and the coproduction of formic acid in the conversion of cellulose into levulinic acid, the precursor to **3**. The product mixture consists of branched C_8–C_9, gasoline-like alkanes with research octane number (RON) values suitable for use in spark-ignition engines, unlocking the potential to sustainably tap into this vast commercial market. This work thus fills a void in the cellulosic biomass-to-biofuels technology space, which is now largely occupied by diesel-type fuels.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1] a) V. Abbasov, T. Mammadova, N. Aliyeva, M. Abbasov, N. Movsumov, A. Joshi, Y. Lvov, E. Abdullayev, *Fuel* **2016**, *181*, 55–63; b) S. D. T. F. Grecco, D. R. de Carvalho, C. H. Zandonai, N. R. C. Fernandes-Machado, L. M. Liao, E. A. Urquieta-Gonzalez, M. D.. C. Rangel, *J. Mol. Catal. A* **2016**, *422*, 89–102; c) C. Zhao, T. Brueck, J. A. Lercher, *Green Chem.* **2013**, *15*, 1720–1739; d) C. V. McNeff, L. C. McNeff, P. G. Greuel, B. Yan, D. T. Nowlan, S. Wyborny, S. J. Rupp, *Biofuels Bioprod. Biorefin.* **2015**, *9*, 258–272; e) R. Zarchin, M. Rabaev, R. Vidruk-Nehemya, M. V. Landau, M. Herskowitz, *Fuel* **2015**, *139*, 684–691.

[2] a) Q. Dang, W. Hu, M. Rover, R. C. Brown, M. M. Wright, *Biofuels Bioprod. Bioref.* **2016**, *10*, 790–803; b) P. Das, M. Dinda, N. Gosai, S. Maiti, *Energy Fuels* **2015**, *29*, 4311–4320; c) D. Howe, T. Westover, D. Carpenter, D. Santosa, R. Emerson, S. Deutch, A. Starace, I. Kutnyakov, C. Lukins, *Energy Fuels* **2015**, *29*, 3188–3197; d) A. de Rezende Pinho, M. B. Bezerra de Almeida, F. Leal Mendes, V. Loureiro Ximenes, *Pure Appl. Chem.* **2014**, *86*, 859–865.

[3] a) S. S. Ail, S. Dasappa, *Renewable Sustainable Energy Rev.* **2016**, *58*, 267–286; b) R. Suárez París, L. Lopez, J. Barrientos, F. Pardo, M. Boutonnet, S. Jaras, *Catalysis* **2015**, *27*, 62–143; c) H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson, S. Gu, *Catal. Sci. Technol.* **2014**, *4*, 2210–2229; d) I. Hannula, V. Arpiainen, *Biomass Conv. Bioref.* **2015**, *5*, 63–74; e) V. L. Dagle, C. Smith, M. Flake, K. O. Albrecht, M. J. Gray, K. K. Ramasamy, R. A. Dagle, *Green Chem.* **2016**, *18*, 1880–1891.

[4] a) J. Xin, D. Yan, O. Ayodele, Z. Zhang, X. Lu, S. Zhang, *Green Chem.* **2015**, *17*, 1065–1070; b) E. C. D. Tan, L. J. Snowden-Swan, M. Talmadge,

A. Dutta, S. Jones, K. K. Ramasamy, M. Gray, R. Dagle, A. Padmaperuma, M. Gerber, *Biofuels Bioprod. Biorefin.* **2017**, *11*, 41–66; c) D. M. Alonso, J. Q. Bond, J. C. Serrano-Ruiz, J. A. Dumesic, *Green Chem.* **2010**, *12*, 992–999; d) X. Hu, X. Wang, C. Song, *Prepr.-Am. Chem. Soc. Div. Energy Fuels* **2012**, *57*, 174–176.

[5] a) S. Cheon, H. M. Kim, M. Gustavsson, S. Y. Lee, *Curr. Opin. Chem. Biol.* **2016**, *35*, 10–21; b) K. W. George, J. Alonso-Gutierrez, J. D. Keasling, T. S. Lee, *Adv. Biochem. Eng. Biotechnol.* **2015**, *148*, 355–389; c) C. Jansson, *Prog. Bot.* **2012**, *73*, 81–93; d) Y. Kung, W. Runguphan, J. D. Keasling, *ACS Synth. Biol.* **2012**, *1*, 498–513.

[6] a) X. Wang, R. Rinaldi, *Catal. Today* **2016**, *269*, 48–55; b) J. Kong, M. He, J. A. Lercher, C. Zhao, *Chem. Commun.* **2015**, *51*, 17580–17583; c) O. Jan, R. Marchand, L. C. A. Anjos, G. V. S. Seufitelli, E. Nikolla, F. L. P. Resende, *Energy Fuels* **2015**, *29*, 1793–1800.

[7] a) "The Biofine Process-Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks": D. J. Hayes, S. W. Fitzpatrick, M. H. B. Hayes, J. R. H. Ross in *Biorefineries-Industrial Processes and Products: Status Quo and Future Directions, Vol. 1* (Eds.: B. Kamm, P. R. Gruber, M. Kamm), Wiley-VCH, Weinheim, **2006**, pp. 144–160; b) B. Girisuta, L. P. B. M. Janssen, H. J. Heeres, *Ind. Eng. Chem. Res.* **2007**, *46*, 1696–1708.

[8] M. Mascal, S. Dutta, I. Gandarias, *Angew. Chem. Int. Ed.* **2014**, *53*, 1854–1857; *Angew. Chem.* **2014**, *126*, 1885–1888.

[9] a) J. Xin, S. Zhang, D. Yan, O. Ayodele, X. Lu, J. Wang, *Green Chem.* **2014**, *16*, 3589–3595; b) O. O. Ayodele, F. A. Dawodu, D. Yan, X. Lu, J. Xin, S. Zhang, *Renewable Energy* **2016**, *86*, 943–948.

[10] a) Z. Yu, F. Li, L. Sun, *Energy Environ. Sci.* **2015**, *8*, 760–775; b) Z. Li, W. Luo, M. Zhang, J. Feng, Z. Zou, *Energy Environ. Sci.* **2013**, *6*, 347–370.

[11] a) J. Fu, X. Lu, P. E. Savage, *ChemSusChem* **2011**, *4*, 481–486; b) J. Fu, C. Yang, J. Wu, J. Zhuang, Z. Hou, X. Lu, *Fuel* **2015**, *139*, 678–683.

[12] Reviews: a) E. Santillan-Jimenez, M. Crocker, *J. Chem. Technol. Biotechnol.* **2012**, *87*, 1041–1050; b) A. Galadima, O. Muraza, *J. Ind. Eng. Chem.* **2015**, *29*, 12–23.

[13] a) J. Han, H. Sun, Y. Ding, H. Lou, X. Zheng, *Green Chem.* **2010**, *12*, 463–467; b) C. Wang, Z. Tian, L. Wang, R. Xu, Q. Liu, W. Qu, H. Ma, B. Wang, *ChemSusChem* **2012**, *5*, 1974–1983.

[14] Knocking Characteristics of Pure Hydrocarbons, STP225-EB, ASTM International, West Conshohocken, PA, 1958, https://doi.org/10.1520/STP225-EB.

[15] a) D. Wang, S. H. Hakim, D. M. Alonso, J. A. Dumesic, *Chem. Commun.* **2013**, *49*, 7040–7042; b) A. B. Kellicutt, R. Salary, O. A. Abdelrahman, J. Q. Bond, *Catal. Sci. Technol.* **2014**, *4*, 2267–2279; c) J. Q. Bond, D. M. Alonso, R. M. West, J. A. Dumesic, *Langmuir* **2010**, *26*, 16291–16298.

[16] M. Grasemann, G. Laurenczy, *Energy Environ. Sci.* **2012**, *5*, 8171–8181.

[17] This assumes a yield of 1 mole of HCO_2H generated per mole of levulinic acid produced from cellulose, and 1 mole of H_2 generated per mole of HCO_2H.

[18] M. Dahmen, W. Marquardt, *Energy Fuels* **2015**, *29*, 5781–5801.

[19] Motor Gasolines Technical Review, Chevron Corporation, **2009**.

[20] S. Dutta, M. Mascal, *ChemSusChem* **2014**, *7*, 3028–3030.

[21] M. T. Barlow, D. J. Smith, D. G. Steward, Eur. pat. EP0082689, **1983**.

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Seeing red: Catalytic hydrodecarboxylation is used to deoxygenate the biomass-derived angelica lactone dimer to provide branched alkanes suitable for use in motor gasoline. The overall process from biomass to "cellulosic gasoline" involves four efficient, low-intensity chemical steps and consumes as little as 1 molar equivalent of external hydrogen.
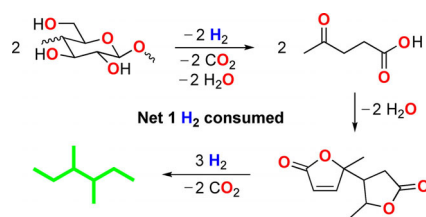
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