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Renewable Chemicals

Hydrodeoxygenation of the Angelica Lactone Dimer, a Cellulose-Based Feedstock: Simple, High-Yield Synthesis of Branched C_7–C_{10} Gasoline-like Hydrocarbons**

Mark Mascal, Saikat Dutta, and Inaki Gandarias*

***Abstract:** Dehydration of biomass-derived levulinic acid under solid acid catalysis and treatment of the resulting angelica lactone with catalytic K_2CO_3 produces the angelica lactone dimer in excellent yield. This dimer serves as a novel feedstock for hydrodeoxygenation, which proceeds under relatively mild conditions with a combination of oxophilic metal and noble metal catalysts to yield branched C_7–C_{10} hydrocarbons in the gasoline volatility range. Considering that levulinic acid is available in >80% conversion from raw biomass, a field-to-tank yield of drop-in, cellulosic gasoline of >60% is possible.*

In the race to produce biomass-derived, hydrocarbon-based, drop-in automotive fuels, most effort has focused on the condensation chemistry of carbohydrate derivatives, which can provide molecules with extended carbon chains (> C_6) for deoxygenation to alkanes with hydrogen and a catalyst. Examples abound. One of the earliest efforts in this area was the aqueous phase reforming (APR) process,[1] in which sugars and hydrogen reacted to give hydrocarbons, based on work originally described by Huber, Cortright, and Dumesic in 2004–2005.[2,3] Since then, related approaches have been reported by the research groups of Dumesic,[4,5] Corma,[6–8] and others,[9–13] which have been summarized in recent reviews.[14–17] In many cases, the electrophile is a furfural, either 5-(hydroxymethyl)furfural (HMF) or furfural itself.[18] These processes have inherent drawbacks in the poor availability of HMF on an industrial scale,[19] and the lower relative abundance of C_5 sugars in biomass compared to C_6, respectively. In other instances, polyols, biogenic ketones, γ-valerolactone, or related molecules are used as feedstocks. In all cases, however, the products are linear alkanes or long-chain alkanes with single branches, and are generally described by the authors as renewable substitutes or additives for diesel or jet fuel. In no study that we are aware of have branched alkanes suitable for drop-in use as gasoline been produced by any of these methods.

Motor gasoline is a mixture of C_4 to C_{12} *n*-alkanes and isoalkanes along with varying proportions of cycloalkanes, arenes, and oxygenates. An important characteristic of gasoline is its antiknock index, which is estimated by measuring the octane rating of the fuel. Straight-chain alkanes generally have octane numbers inferior to branched alkanes. For example, the Research Octane Numbers (RONs) of hexane and its isomer 3-methylpentane are 25 and 75, respectively.[20] Further branching gives even higher RONs. Regular unleaded gasoline is generally 87 octane in the US, with premium grades up to 93. A higher octane rating allows for a higher compression ratio, which translates to more power and better performance of the engine. In this study, we demonstrate a high-yielding, three-step preparation of gasoline-like, branched C_7–C_{10} hydrocarbons using biomass-derived levulinic acid as the sole organic starting material.

Levulinic acid (LA, **1**) is one of the most recognizable products in the modern concept of the biorefinery. LA is on the U.S. National Renewable Energy Laboratory top-twelve list of value-added chemicals from biomass,[21] as well as Bozell's newer top-ten list of chemical opportunities from biorefinery carbohydrates.[22] While a number of routes have been described over the years for the production of LA from biomass, the most efficient to date are the "Biofine Process," a two-stage, high-pressure, high-temperature procedure for which yields of **1** between 70 and 80% have been reported,[23] and the hydrolysis of biomass-derived 5-(chloromethyl)furfural, which gives **1** in >80% overall yield.[24]

It is well known that **1** can undergo intramolecular dehydration to give α-angelica lactone (AL, **2**; Scheme 1),[25] although the reaction has attracted relatively little interest in the renewables field, being largely eclipsed by the reduction and subsequent cyclization of **1** to γ-valerolactone.[26] The reaction, as described, has generally involved the slow distillation of **2** from a mixture of **1** and a strong acid catalyst. The reaction gives AL in good yields, but also results in a polymeric residue in the distillation pot, which would present problems for recycling the acid on scale up. We proposed that the use of a heterogeneous acid catalyst in this reaction would facilitate product separation and catalyst recycling. This was ultimately accomplished by using montmorillonite clay (K10), which gave >90% yields of isolated **2** without the formation of polymeric materials or noticeable deactivation of the catalyst over three consecutive cycles. In a typical preparation, a mixture of LA and K10 (10 wt%) was distilled using a fractionating column under controlled vacuum (50 mmHg), resulting in a two-phase mixture of water and product, which could simply be separated.

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[*] Prof. M. Mascal, Dr. S. Dutta, Dr. I. Gandarias
Department of Chemistry, University of California Davis
1 Shields Avenue, Davis, CA 95616 (USA)
E-mail: mjmascal@ucdavis.edu

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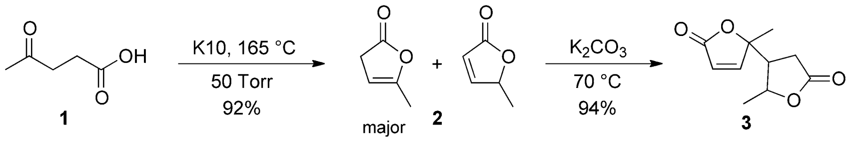


Scheme 1.

It is also known that **2** can dimerize, although again, the reaction is largely obscure. The angelica lactone dimer (ALD, **3**) was first described in 1914,[27] but not structurally characterized until 1954.[28] The dimerization reaction is a base-catalyzed conjugate addition between the double bond isomers of **2**, which exist in equilibrium under the reaction conditions. Catalysts have included hydroxide or alkoxide salts,[29] active metals,[29] tertiary amines,[30] and organometallic compounds,[31] and we also tried these methods, but with mixed results. The most attractive procedure from an applied standpoint made use of anhydrous K_2CO_3 as the base in a solid-state reaction, but the reported yield was only 10.8%.[28] In our hands, optimization of this reaction by conducting it in a melt eventually resulted in a 94% yield of **3**.

We saw **3** as a potentially valuable renewable feedstock for hydrodeoxygenation (HDO),[32] due to its C_{10} carbon count and branched character which, as described above, would make it an ideal precursor to cellulosic gasoline. Traditional hydrotreating catalysts such as sulfided NiMo and CoMo are commonly used for the reduction of esters to hydrocarbons, but we were deterred by the gradual deactivation of these catalysts by sulfur leaching.[33] We were attracted to a copper-zinc mixed oxide catalyst on alumina (Cu-ZnO/Al_2O_3) that has been used to hydrogenate esters to the corresponding alcohols in nearly quantitative yield under relatively mild conditions (230 °C).[34] Since γ-Al_2O_3 is known to dehydrate alcohols under similar conditions,[35] we speculated that a combination of these two catalysts could achieve a one-pot conversion of **3** into hydrocarbons. In a typical reaction, **3** and the catalysts (10 wt% Cu-ZnO/Al_2O_3 + 20 wt% γ-Al_2O_3) were loaded into a pressure vessel and the system was pressurized with hydrogen to about 50 bar and heated with stirring at 300 °C for three hours. Analysis of the reaction mixture showed a 41% yield of C_7–C_{10} hydrocarbons alongside a considerable quantity of alcohol and ether products. Since the dehydration of the intermediate alcohols was apparently not efficient enough, we replaced the γ-Al_2O_3 with phosphotungstic acid ($H_3W_{12}O_{40}P$) loaded on mesoporous silica (MCM-41), which is known to dehydrate aliphatic alcohols under even milder conditions than γ-Al_2O_3.[36] When a combination of Cu-ZnO/Al_2O_3 and HPW/MCM-41 was employed, the total yield of hydrocarbons improved to 68%.

The hydrogenation of carbohydrate derivatives in general tends to favor noble metal catalysts, and recently it was reported that such catalysts modified with an oxophilic metal such as Re show higher catalytic activity in C–O bond hydrogenolysis.[37] In particular, an Ir-ReO_x/SiO_2 catalyst described by Tomishige and co-workers has demonstrated great promise in the reduction of glycitols to alkanes under mild conditions, along with good reusability.[38] Interestingly, we have found that Ir-ReO_x/SiO_2 is also highly active in the HDO of lactones.

The Ir-ReO_x/SiO_2 catalyst was prepared[38] and reactions were carried out in batch mode as described above for the Cu-ZnO/Al_2O_3 system, except that a range of temperatures between 200 and 300 °C were studied. The results for the deoxygenation of **3** are shown in Table 1. Starting at the same temperature as used for Cu-ZnO/Al_2O_3, an improved yield of 72% hydrocarbons was observed on using the Ir-ReO_x/SiO_2 catalyst. A considerable degree of C–C bond cleavage was seen, as was the case with the copper-zinc catalyst, which prompted us to attempt the hydrogenation at lower temperatures. As shown in Table 1, reduction of the reaction temperature first to 240 and then to 220 °C increased the selectivity for the C_{10} product, that is, the product which would result if no C–C bond cleavage occurred, while increasing the overall hydrocarbon yield up to 88%. Decreasing the reaction time (not shown) or the reaction temperature (200 °C) was found to lower the yield of hydrocarbons.

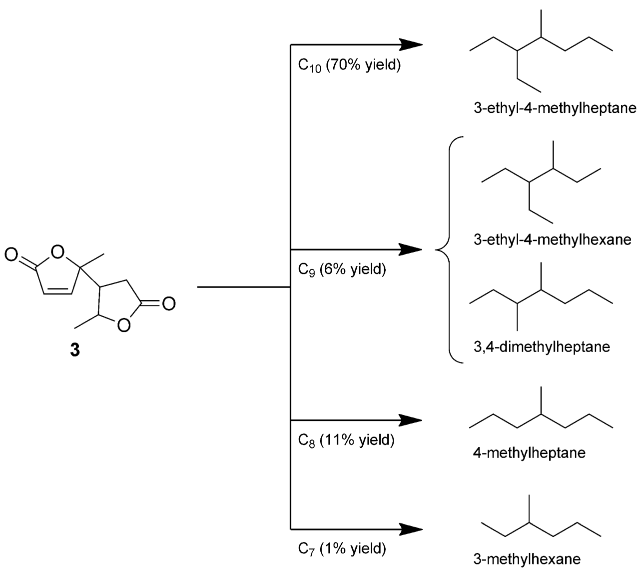
Table 1: Conversion of the angelica lactone dimer (**3**) and hydrocarbon yield with different catalyst systems.

Catalyst	*T* [°C]	*t* [h]	Conv. [%]	Hydrocarbon yield [%][a]				
				C_7	C_8	C_9	C_{10}	total
Cu-ZnO/Al_2O_3 + γ-Al_2O_3	300	3	100	3	12	5	21	41
Cu-ZnO/Al_2O_3 + HPW/MCM-41[b]	300	3	100	4	15	35	14	68
Ir-ReO_x/SiO_2	300	3	100	4	16	19	33	72
Ir-ReO_x/SiO_2	240	6	100	1	13	10	60	84
Ir-ReO_x/SiO_2	220	7	100	1	11	6	70	88
Ir-ReO_x/SiO_2	200	7	100	0	6	1	3	10
Pt-ReO_x/C	240	6	100	2	8	18	60	88
Pt-ReO_x/C	220	7	100	2	4	7	13	26
Pt-WO_x/Al_2O_3	240	6	100	1	7	1	10	19

[a] Molar %C yields as determined by GC-MS integration against *n*-alkane standards. [b] 20 wt% 12-phosphotungstic acid (HPW) loaded on mesoporous silica (MCM-41).

In light of the strong performance of the Ir-ReO_x/SiO_2 catalyst, we elected to try two other catalysts consisting of an oxophilic metal–noble metal combination, namely Pt-ReO_x/C[39] and Pt-WO_x/Al_2O_3.[40] Pt-ReO_x/C also gave a high yield of hydrocarbons at 240 °C, although the yield decreased significantly at 220 °C. With the Pt-WO_x/Al_2O_3 catalyst, however, the hydrocarbon yield was notably lower at the same temperature at which the M-ReO_x catalysts performed well (240 °C).

As shown in Table 1, a degree of control over the hydrocarbon distribution can be exercised through choice of the reaction temperature and catalyst. A narrow range of products in the given carbon range results under milder conditions, as shown in Scheme 2 for the reaction carried out with the Ir-ReO_x/SiO_2 catalyst at 220 °C. The Pt-ReO_x/C catalyst shows a somewhat lower selectivity towards the C_{10} product in favor of the C_9 isoalkanes. The carbon mass



Scheme 2. Reaction conditions: 2.0 g **3**, 0.30 g Ir-ReO$_x$/SiO$_2$, 54 bar H$_2$, 220 °C, 7 h; total yield 88 %. The hydrocarbons were identified by matching MS fragmentation patterns to NIST database spectra.

Table 2: Reusability of Ir-ReO$_x$/SiO$_2$ catalyst.

Recycle	Conv. [%]	Hydrocarbon yield [%][a]				
		C$_7$	C$_8$	C$_9$	C$_{10}$	total
1	100	1	12	5	67	85
2	100	1	10	5	68	84
3	100	1	9	6	69	85

[a] Reaction conditions: 2.0 g ALD (**3**), 0.30 g Ir-ReO$_x$/SiO$_2$, 54 bar H$_2$, 220 °C, and 7 h. Recovered catalyst was recalcined between experiments.

balances can be satisfied by taking decarbonylation ($C_{10} \rightarrow C_9$ products) and/or ethyl group cleavage ($C_{10} \rightarrow C_8$ and $C_9 \rightarrow C_7$ products) into account.

The stability of the Ir-based catalyst was also tested and the results are shown in Table 2. Recovered catalyst was recycled three times to confirm its robust nature (see the Supporting Information for experimental details). The selectivity was also essentially unchanged.

The key considerations in the quest for economically competitive biofuel production center around issues of 1) yield, 2) feedstock, 3) process economics, and 4) market. Here, we introduce a process that addresses these matters as follows: 1) It operates in up to 76 % overall yield over three steps ($92 \times 0.94 \times 0.88$) from biomass-derived levulinic acid (**1**). Considering that **1** is available in > 80 % conversion from biomass, field-to-tank yields of > 60 % are achievable. 2) It does not involve expensive or impractical feedstocks (e.g. fructose, HMF).[41] 3) It proceeds under relatively mild conditions in the presence of simple (K10, K_2CO_3) and robust (Cu-ZnO/Al_2O_3, Ir-ReO$_x$/SiO$_2$, or Pt-ReO$_x$/C) catalysts. 4) It is the first synthesis of branched hydrocarbons in the commercial gasoline volatility range from biomass, representing a major consumer market.

Central to market considerations is the concept of the "drop-in" product, which is only formally satisfied by a literal equivalent of the commercial product that seamlessly integrates into the prevailing transportation infrastructure. The C_7–C_{10} isoalkanes described here could be blended with C_4–C_6 *n*-alkanes that are available through other processes, such as the hydrogenation of simple sugars,[2,38] to serve as drop-ins for the paraffinic fraction of gasoline. The aromatic fraction could, in turn, be derived from other renewables, such as 2,5-dimethylfuran, which has a high RON (119),[42] or its C_2H_4 cycloaddition-dehydration product *para*-xylene.[43] Other biorefinery products, such as γ-valerolactone and its derivatives,[44] methyl tetrahydrofurans,[45] sugar hydrogenoloysis products,[46] and valeric esters[47] could serve as useful oxygenate additives. Thus, in principle, a basic combination of chemical-catalytic processes has the potential to supply essentially the full component spectrum of motor gasoline entirely from renewable resources.

In summary, we describe here a method whereby a fully practical feedstock (levulinic acid, **1**) is efficiently converted in three steps into the main component fraction of gasoline. We introduce the angelica lactone dimer (**3**) as a novel feedstock for the HDO process, rendered practical here by both the development of a scalable approach to angelica lactone (**2**) itself and the production of **3** in nearly quantitative yield. Finally, we have adapted Cu-ZnO, Pt-ReO$_x$, and Ir-ReO$_x$ catalysts to the HDO of cyclic esters, with branched alkane distribution governed by temperature. This work not only opens up an unprecedented route between raw biomass and branched alkanes, but may also encourage fresh efforts towards the identification of new renewable platform chemicals beyond sugars and simple furans.

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