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Production of cellulosic gasoline *via* levulinic ester self-condensation†

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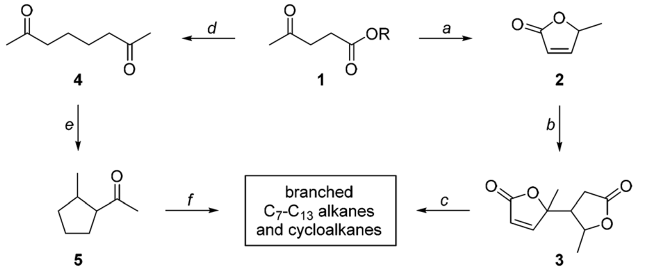
Most biomass to biofuel processes are limited to the production of linear or minimally branched hydrocarbons. Motor gasoline, however, consists of highly branched linear and/or cyclic alkanes. This work describes the optimization of the levulinic ester self-condensation reaction and the efficient conversion of its products, which are highly branched cyclopentadienes, into a mixture of substituted cyclopentanes with high octane ratings and excellent density and flow properties.

Introduction

The production of bio-based fuels by the condensation of biogenic aldehydes or ketones with carbohydrate-derived platform molecules, often furfurals, followed by hydrodeoxygenation generally leads to C_{9+} products. The application of this approach has given rise to dozens of papers describing routes to diesel-type fuels, which consist mainly of linear alkanes in the C_{10}–C_{20} range.[1–3] The paraffinic fraction of motor gasoline, on the other hand, is comprised of hydrocarbons up to about C_{12}, a key characteristic of which is the extent of branching in the carbon chains. In general, the more highly branched the molecule, the higher the performance of the fuel, as measured by the antiknock index, expressed in terms of research octane number or "RON". Thus, while 2,2,4-trimethylpentane (RON = 100) performs well in spark-ignition engines, its singly branched isomer 3-ethylhexane has RON = 34, while the unbranched *n*-octane has RON = −20.

To date, few reports of cellulosic biomass-derived alkanes sufficiently branched to serve as biogasoline or even mid-performance gasoline blendstocks have surfaced. Those that do emerge generally involve the cracking, pyrolysis, or gasification of biomass or its derivatives in combination with catalytic upgrading or reforming methods commonly employed in the petroleum industry, *i.e.* essentially using biomass as a feed for refinery practices. Recently, we have shown that the intrinsic branching in the angelica lactone dimer **3** made it possible to produce branched C_7–C_{10} hydrocarbons with RON values between 70 and 80.[4,5] Compound **3** can be derived in high yield from levulinic acid **1** (R═H), a platform molecule of unrivaled potential which can be generated directly from raw, cellulosic biomass.[6] We have also reported the synthesis of branched cycloalkanes *via* ketone intermediate **5**, the product of an intramolecular aldol condensation of 2,7-octanedione **4**, a Kolbe dimer of levulinic acid (Scheme 1).[7]

In yet another approach to levulinic acid oligomerization, we recently introduced cyclopentadiene- and cyclopentane-based diesters **6** and **7** in the context of novel, renewable monomers with branched, carbocyclic cores of interest for the preparation of low surface energy materials.[8] Although **6** had been previously synthesized by base-induced self-condensation of ethyl levulinate, yields were very low and the structure was found to have been misassigned. Below, we describe the optimization of the dimerization reaction that leads to **6**, as well as the conversion of a mixture of cyclic condensates of levulinic ester into C_8–C_{13} branched hydrocarbons that, like those in Scheme 1, are characteristic of motor gasoline.



Scheme 1 Reagents and conditions: *a.* K10 montmorillonite, 165 °C, 92%; *b.* K_2CO_3, 70 °C, 94%; *c.* H_2, Ir-ReOx/SiO_2, 220 °C, 88%; *d.* $-e^-$, KOH/MeOH, Pt–Pt, undivided cell, 65%; *e.* PTSA, H_2, Pd/C, hexane, 80 °C; *f.* H_2, Pd/C, $Al(OTf)_3$, 220 °C, 85% over two steps.

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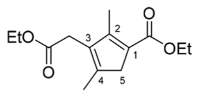

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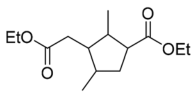

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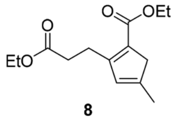

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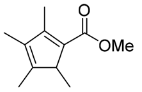

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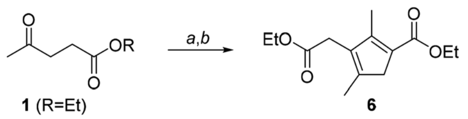
Results and discussion

The sodium ethoxide catalyzed aldol condensation of ethyl levulinate **1** (R=Et) was first reported by Duden and Freydag as early as 1903,[9] and revisited by Shimizu in 1950.[10] The structure of the dimer was (wrongly) assigned as the 2-(2-carboxyethyl)-4-methylcyclopenta-1,3-diene-1-carboxylic acid system **8**, and the yield of the product was <10%, due mainly to the competing hydrolysis of the starting material to sodium levulinate in the course of the condensation reaction. We repeated the procedure and determined that the correct structure was in fact the 3-(carboxymethyl)-2,4-dimethylcyclopenta-1,3-diene-1-carboxylic acid system **6**, the hydrogenation of which proceeded smoothly to cyclopentane **7**.[8] Considering the potential usefulness of **6** and **7** as renewable platforms for materials and biofuel production, we undertook to examine the chemistry in greater detail and optimize the condensation reaction to a standard of preparative usefulness.

The rationale for assigning structure **8** to the self-condensation of ethyl levulinate was reasonable, even if it ultimately led to the wrong conclusion. Duden and Freydag considered both structures **6** and **8**, but inclined toward the latter based on the notion that the kinetic product (enolization to the methyl group) should dominate the condensation chemistry.[9] With the benefit of modern analytical techniques, we quickly ascertained that the NMR data supported structure **6**. In particular, ^{13}C-NMR using a DEPT (Distortionless Enhancement by Polarization Transfer) pulse sequence showed peaks for four methyl and four methylene groups, rather than the three methyl and five methylene groups that would be expected for **8**. Computational modeling of the NMR shielding tensors of **6** using the gauge-independent atomic orbital (GIAO) *ab initio* method gave a satisfactory agreement for all shifts apart from the ^{13}C peak for the carbon at the 4-position. Thus, while the absolute average deviation from the experimental shifts for all carbons apart from C4 was 0.95 ± 0.72 ppm, the calculated value for C4 was 8.1 ppm downfield of its observed shift. The computation of shielding tensors for alternative conformers led to only minor variations in the data. This anomaly led us into the literature to determine whether (1) there was a potential issue with our structural assignment, or (2) the applied method systematically overestimates ^{13}C shifts in related systems. A search of the Reaxys database turned up a single example of a 1-carboxy-4-methyl-substituted cyclopentadiene with reported ^{13}C NMR data, *i.e.* 2,3,4,5-tetramethylcyclopenta-1,3-diene-1-carboxylic acid **9**.[11] Interestingly, the modeled ^{13}C NMR shifts show an absolute average deviation from the reported values of only 1.08 ± 0.56 ppm with the exception of C4, the calculated shift for which was 9.0 ppm too far downfield. We therefore unequivocally assign structure **6** to the base-induced self-condensation product of ethyl levulinate, and conclude the anomalous shift value for C4 in the computational model is the result of a limitation in the method.

The synthesis of **6** was initially reproduced exactly as described in the literature (Scheme 2),[9] which involved the reaction of **1** (R=Et) with an equimolar quantity of sodium ethoxide in cold ethanol followed by two days of standing at room temperature. Filtration of the reaction mixture, evaporation of the solvent, and neutralization with aq H_2SO_4 led to the separation of an oil which proved to be mainly a monoester of **6**. The crude product was therefore dissolved in ethanol, a few drops of H_2SO_4 were added, and the mixture was heated at 50 °C overnight prior to analysis. The yield of **6** that we obtained by this method (5%) was consistent with that in the literature.[9,10] As the condensation reaction proceeds, the production of H_2O leads to hydrolysis of the starting ester, and accumulation of the sodium levulinate salt was evident as the reaction gradually thickened to an unstirrable paste. It was therefore proposed that a drying agent be included in the mixture, and to this end Na_2SO_4, CaO, 3 Å molecular sieve, and triethyl orthoformate were evaluated. In all cases, significant improvements in yield were noted. Bases other than sodium ethoxide were also tried, including sodium carbonate, triethylamine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), however no production of **6** was observed in any of these cases. It was found that the reaction time could be reduced from 48 hours to only 5 hours if the temperature was raised to 50 °C, and this also had a positive effect on yield (Table 1). Concentration was determined to be another key parameter, where increasing dilution improved the yield of **6** to a maximum of 40% (Table 1, entry 8). The remaining mass balance of reactions at full conversion was found to be mainly a complex mixture of trimeric products.

The varying degrees to which self-condensates of ethyl levulinate could be reduced was explored. Simple hydrogenation of **6** over Pd/C gave a high yield of **7** (92%), which is formally an annulated adipic ester, as mixture of stereoisomers for which no separation was attempted. We have previously noted the



Scheme 2 Self-condensation of ethyl levulinate. Reagents *a*. NaOEt, Na_2SO_4, EtOH. For conditions, see Table 1; *b*. EtOH, H_2SO_4, 50 °C, overnight.

Table 1 Conversion of **1** (R=Et) to **6** under various conditions[a]

Entry	Volume of EtOH (mL)	*T* (°C)	*t* (h)	Conversion of **1** (%)	Yield of **6** (%)
1	12	50	5	100	22
2	20	50	5	100	28
3	30	50	1.25	88	17
4	30	50	2.5	94	26
5	30	50	5	100	28
6	40	50	5	84	36
7	40	50	7.5	100	33
8	40	70	5	100	40
9	60	50	5	75	38
10	60	50	7.5	87	34
11	60	70	7.5	95	33
12	60	35	24	81	35

[a] Reaction conditions: 5.0 g of ethyl levulinate, 1.5 g of Na_2SO_4, 2.4 g NaOEt in the stated volume of ethanol at the stated temperature. After the stated reaction period, the mixture was neutralized to pH 2, filtered, and subjected to esterification conditions (see ESI).

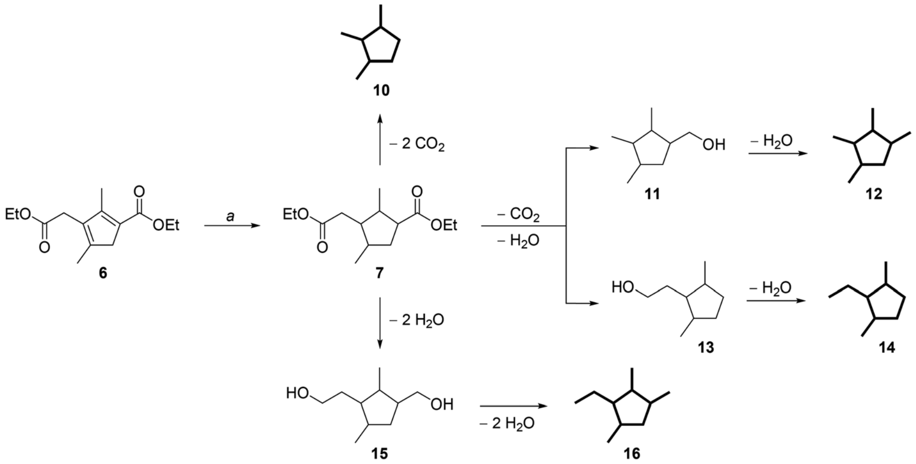
potential application of **7** as a novel monomer.[8] For the purposes of producing a biofuel, the complete deoxygenation of dimer **6** was undertaken. We have established in previous work that the most hydrogen-economic approach to generate hydrocarbons from carboxylic acids is thermal decarboxylation, which in effect removes three C–O bonds at the cost of no external hydrogen.[5] This is typically accomplished by heating at a high temperature in the presence of a hydrogenation catalyst. A test reaction with **6** and Pd/C under 4 MPa H_2 at 320 °C in tetradecane solvent gave a partially reduced mixture including **7** alongside alcohol and ester products, but little hydrocarbon (Table 2, entry 1). Our follow-up approach was to include a Lewis acid, in this case γ-Al_2O_3, to promote the decarboxylation reaction. Adjustment of conditions eventually led to a 94% yield of C_8–C_{10} branched cycloalkanes, quantified by GC-MS against an internal standard (see ESI†).

As shown in Scheme 3, diester **6** is first saturated to cyclopentane **7**. The expectation was that **7** would decarboxylate to produce the C_8 product **10**, and this was indeed observed (42%). However, we were not able to fully suppress reduction

Table 2 Conversion of **6** to cycloalkanes

Entry	Catalyst	Atmosphere	*T* (°C)	*t* (h)	Total cycloalkane yield (%)
1	Pd/C	4 MPa H_2	320	5	<5%
2	Pd/Al_2O_3	2 MPa H_2	300	3	34
3	Pd/Al_2O_3	4 MPa H_2	320	5	94

Conditions: 0.80 g of **6**, 0.15 g of catalyst, 10 mL of tetradecane, temperature and time as indicated.



Scheme 3 Conversion of **6** to branched cycloalkanes. Observed products are bolded. Reagents and conditions: *a*. 0.80 g of **6**, 0.15 g of Pd–Al_2O_3, 10 mL of tetradecane, 4 MPa of H_2, 320 °C, 5 h.

of the carbonyl groups, and a mixture of C_9 (assigned as **12** + **14**, 44%) and C_{10} (**16**, 8%) products was also seen. Estimation of the RON of these hydrocarbons using the recently published artificial neural network-based group contribution method of Kubic *et al.*[12] gives values of 101 (**10**), 91 (**12**), 92 (**14**) and 85 (**16**), with a product distribution weighted average of RON = 95, which is higher than standard grades of commercial gasoline.

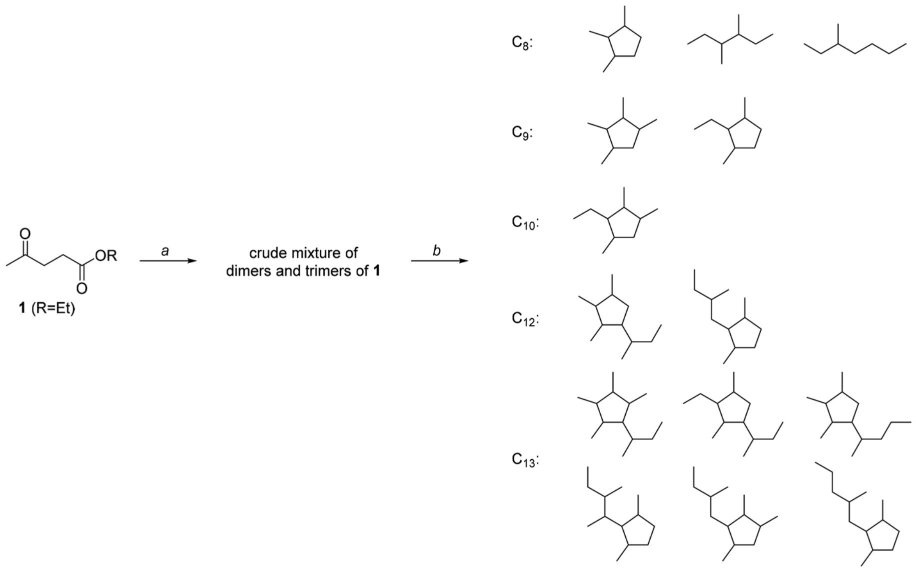
As noted above, the mass balance of the reaction to produce **6** from ethyl levulinate was mainly a mixture of trimeric (C_{15}) products. Rather than esterifying and isolating **6** from this mixture, we submitted the crude condensate to the same decarboxylation–hydrodeoxygenation conditions described above, which yielded a mixture of branched C_8–C_{13} alkanes. The overall process involved heating ethyl levulinate with ethanolic NaOEt in the presence of Na_2SO_4, filtering, and evaporating the solvent to give a crude oil product with a calculated mass recovery of nearly 100%. This material was then treated as shown in Scheme 4 under solvent-free conditions. The reaction was first carried out with 3.50 g of the crude dimer–trimer mixture with careful quantification of the product (see ESI†), leading to isolated hydrocarbon yields in the range of 91–93%.

The product distribution included the same C_8–C_{10} cyclopentanes seen in Scheme 3 alongside some acyclic homologues, together with cyclic C_{12} and C_{13} products that evidently derive from of ethyl levulinate trimers that have been triply and doubly decarboxylated, respectively. The structures of these products are proposals based on the most likely sites of addition of a third molecule of ethyl levulinate to **6**. In fact, the mixture was complex, including multiple stereoisomers and likely also regioisomers. Despite this complexity, the nearly even distribution of hydrocarbons from C_8 to C_{13} allowed an approximation of the yield to be made based on a weighted average $C_{10.5}H_{21}$ product. The reaction was repeated twice using 15 g of the crude dimer–trimer mixture and the products combined to give an isolated yield of 12.70 g (83%) of hydrocarbons. No solvents were used to aid removal of the product from the reaction vessel, but rather the mixture was immediately distilled and the fractions analyzed by GC-MS to provide an approximate product distribution. A cut of C_{8-10} product was collected below 200 °C, accounting for 47 wt% of the mixture and was contaminated with only trace amounts of higher hydrocarbons. Between 200–240 °C mainly C_{12-13} cycloalkanes were observed, amounting to 48 wt% of the product. The pot residue (bp >240 °C) was mainly C_{13} products contaminated with trace C_{12} cycloalkanes and comprised about 5% of the total mass. The density of the distillate measured at 15 °C was 0.811 g mL^{-1} and its kinematic viscosity at −20 °C was 3.38 mm^2 s^{-1}. Given that the typical density of motor gasoline is 0.74 g mL^{-1},[13] the synthetic fuel mixture has a good balance of properties – satsifactory low temperature viscosity and excellent density.

Finally, we tested the recyclability of Pd/Al_2O_3 catalyst by filtering and reusing it three times without washing or treatment of any kind. The conversion of crude dimer–trimer mixture was at least 95% in all runs.

Conclusions

In conclusion, a Stobbe-like condensation of ethyl levulinate gives a mixture of dimers and trimers in the form of substituted cyclopentadienes. The use of a dehydrating agent during the reaction shuts down a competing hydrolysis of the ester starting material that had previously resulted in the descrip-



Scheme 4 Conversion of the product of the base-induced self-condensation of ethyl levulinate to branched alkanes. Reagents and conditions: *a*. NaOEt, Na_2SO_4, EtOH, 70 °C, 5 h; *b*. 10% Pd–Al_2O_3, 4 MPa H_2, 320 °C, 5 h.

tion of very low product yields. Saturation of the cyclopentadiene is facile, and attempts to decarboxylate the resulting cyclopentanedicarboxylic acid/ester proceeded best under high-temperature hydrogenation conditions, leading to a mixture of decarboxylation and hydrodeoxygenation products. The dimer **6** produced a mixture of branched C_8–C_{10} cyclopentanes with high octane ratings. The raw dimer/trimer mixture likewise delivered C_8–C_{10} plus C_{12} and C_{13} products in high yield with very good fuel properties which, being only four efficient steps removed from raw biomass, may provide a competitive basis for cellulosic gasoline production.

Conflicts of interest

There are no conflicts to declare.

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