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Sustainable production of biofuel precursors by aldol condensation with biomass-derived 5-methylfurfural

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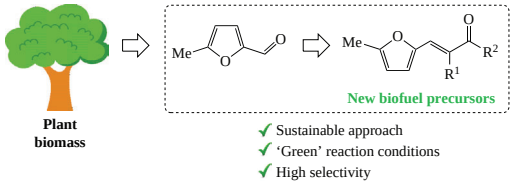
Renewable 5-methylfurfural was subjected to a 'green' base-catalyzed aldol condensation with a variety of ketones to afford the corresponding furan-containing α,β-unsaturated carbonyl compounds with high yields and selectivities. The products obtained can serve as precursors for the long-chained fuel-grade liquid bio-alkanes.



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The utilization of renewable energy sources for industrial applications has gained great attention in recent years.[1–5] Conversion of plant biomass to furanic platform chemicals provides great opportunities to replace the fossil-based products with renewables in accordance with the principles of 'green' chemistry.[6–12] When renewable resources are used as the feedstock, the production cycle becomes carbon-neutral because does not lead to an increase in carbon content into the environment. Although the full integration of renewable resources is most acute in non-oil-producing countries, the Russian Federation has colossal reserves of plant biomass, therefore, the availability of technologies for its efficient processing should help to diversify the existing industrial structure in accordance with the modern trends of the world industrial development.

Efficient replacement of oil-based liquid fuels by renewable alternatives requires full compatibility of biofuels with existing combustion engines. One of the general methods for the synthesis of biofuels from plant resources is the conversion of common hexose carbohydrates into C_6 furanic intermediates such as 5-methylfurfural (MF), 5-(hydroxymethyl)furfural (HMF) or its derivatives followed by catalytic hydrodeoxygenation.[13–15] Bio-based alkanes are the promising candidates for biofuels due to their high chemical and energetic similarity to traditional alkane-based gasoline, diesel and jet fuels.[16,17] Aldol condensation of furfurals with highly accessible ketones leading to biofuel precursors (enones or dienones, depending on molar ratio of the reactants) followed by transition-metal catalyzed full hydrodeoxygenation is the well-known approach used for the synthesis of long-chained alkanes.[18,19] However, the production of alkanes from HMF has some disadvantages associated with the presence of a highly reactive hydroxy group in the products, which should require harsh reaction conditions of the following reduction, thus causing its low selectivity.[20] Additionally, chemical instability and high polarity of HMF complicate its efficient preparation and utilization.[21,22] MF is a renewable compound that may be produced from bio-based furfural, HMF, or directly from carbohydrates.[23–25] In our previous work,[26] MF was efficiently used as an alternative to HMF for the synthesis of biofuel 2,5-dimethylfuran and some long-chain alkane precursors.

In this work, we further studied the synthetic utility of MF in the aldol condensation reaction with ketones for the synthesis of new long-chained (C_9–C_{22}) alkane precursors (Figure 1). For this, two reaction systems based on 8-diazabicyclo[5.4.0]undec-7-ene (DBU) or sodium hydroxide were investigated for the synthesis of ten known and new furanic biofuel precursors. First, optimization of the reaction conditions was performed. Both solvent-free and conventional solvent systems were tested for mono- or di-aldol condensation of MF with acetone or methyl isobutyl ketone according to previously reported methods[27,28] (Table 1). The solvent-free process with DBU as a base was moderately effective (entries 1–7). When DBU (0.1 equiv.) was used with a 10-fold excess of methyl isobutyl ketone at room temperature, no conversion of MF has occurred (entry 1). The maximum yield of product **2** using DBU as a base was 58% at 100 °C (entry 5). Further increasing in the base concentration and reaction temperature resulted in a drop in the yield of **2** due to side oligomerization processes. Sodium hydroxide showed higher efficacy in the aldol condensation. An almost quantitative yield of product **2** was reached using 0.1 M solution of sodium hydroxide in methanol/water mixture with 2 equiv. of methyl isobutyl ketone at room temperature (entry 9).

The reaction of MF with acetone using NaOH as a base was also investigated. Maximum yield of mono-aldol product **1** (92%) was obtained in the presence of 10 equiv. of acetone

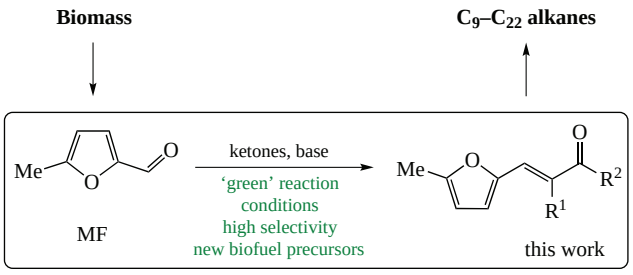

Figure 1 Aldol condensation of MF with ketones leading to long-chained alkane precursors described in this work.

Table 1 Optimization of the reaction conditions for mono-aldol condensation.[a]

Entry	Base (equiv.)	Ketone (equiv.)	Solvent	*T*/ °C	Product (yield, %)[b]
1	DBU (0.1)	MeC(O)Bu^i (10)	–	~24	**2** (0)
2	DBU (0.5)	MeC(O)Bu^i (10)	–	~24	**2** (20)
3	DBU (0.1)	MeC(O)Bu^i (10)	–	80	**2** (36)
4	DBU (0.5)	MeC(O)Bu^i (10)	–	80	**2** (52)
5	DBU (0.5)	MeC(O)Bu^i (10)	–	100	**2** (58)
6	DBU (0.5)	MeC(O)Bu^i (10)	–	120	**2** (54)
7	DBU (1.0)	MeC(O)Bu^i (10)	–	100	**2** (42)
8	NaOH (0.25)	MeC(O)Bu^i (1)	MeOH/H_2O 1 : 1	~24	**2** (90)
9	NaOH (0.25)	MeC(O)Bu^i (2)	MeOH/H_2O 1 : 1	~24	**2** (98)
10	NaOH (0.25)	acetone (3)	MeOH/H_2O 1 : 1	~24	**1**+**7** (63+36)
11	NaOH (0.25)	acetone (5)	MeOH/H_2O 1 : 1	~24	**1**+**7** (72+27)
12	NaOH (0.25)	acetone (10)	MeOH/H_2O 1 : 1	~24	**1**+**7** (92+7)
13	NaOH (0.25)	acetone (0.5)	MeOH/H_2O 1 : 1	~24	**7** (91)[c]

[a]Conditions: MF (1 mmol), solvent (2 ml). [b]NMR yield. [c]Isolated yield.

(see Table 1, entry 12). When 2-fold excess of MF was used in the reaction with acetone in water/methanol mixture, compound **7** with two enone moieties was obtained in 91% isolated yield (entry 13).

An evaluation of the synthetic potential of MF in the NaOH-catalyzed aldol condensation with some other highly accessible ketones was then performed (Figure 2). As a result, most of the compounds **1**–**10** were prepared with high yields and selectivities. Compound **5** formed from MF and heptan-3-one also contained a ~10% admixture of the second regioisomer. All products except for compound **6** were isolated without chromatographic separation by extraction or filtration from the reaction mixture.

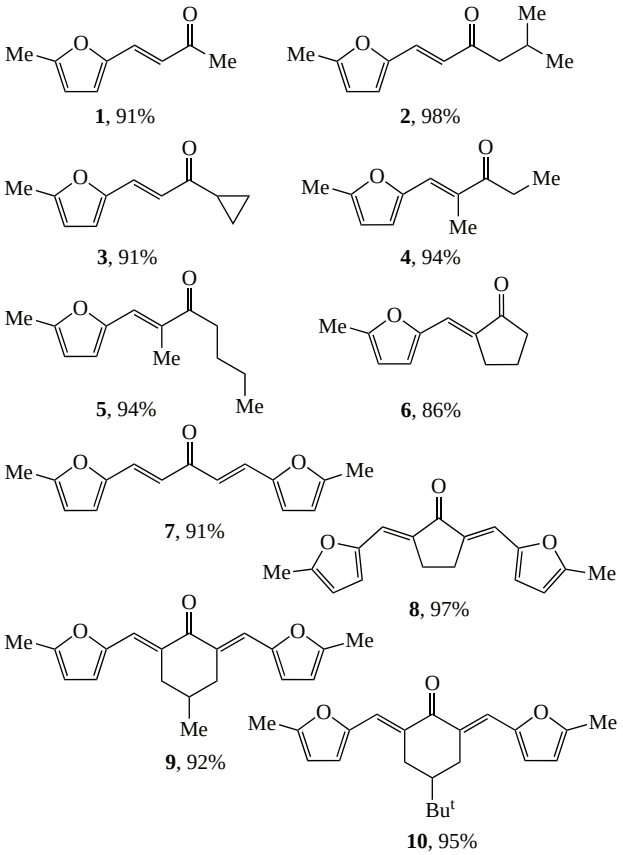

Figure 2 Scope of aldol condensation of MF with cyclic and acyclic ketones. *Reagents and conditions*: MF (1 mmol), ketone (0.5 mmol for **7**–**10**, or 2 mmol for **2**, **3**, or 10 mmol for **1**, **4**–**6**), NaOH (0.25 mmol), MeOH/H_2O (1 : 1, 2 ml), 24 °C, 12 h.

The reaction of MF with 10 equiv. of cyclopentanone proceeded with good selectivity to afford mono-aldol product **6** which was isolated in 86% yield after purification by column chromatography on silica gel. A significant amount of di-aldol condensation product **8** was detected after the reaction of MF with a smaller amount of cyclopentanone. Di-aldol products **7**–**10** were obtained using 2 mol of MF per 1 mol of ketone and were isolated with high yields simply by filtration from the reaction mixture followed by washing with water (for compounds **7**, **8**, **10**) or by extraction from the reaction mixture (for compound **9**).

The structures and *E*-configurations of all synthesized compounds were confirmed by NMR spectroscopy through comparison with the recently reported spectral data (see Online Supplementary Materials for details). As follows from the literature, base-catalyzed aldol condensation of aromatic aldehydes with ketones affords α,β-unsaturated products with predominant *E*-stereoselectivity.[29,30] Products **1**–**10** are lipophilic water-immiscible substances soluble in main polar and non-polar organic solvents. Di-aldol products **7**, **8**, **10** are solids with intensive colours from yellow to red-yellow.

To summarize, the base-catalyzed aldol condensation of MF with various commercially assessable ketones was studied. In most cases, high regio- and stereoselectivity was achieved in mono- and di-aldol condensation reaction of MF with both cyclic and acyclic ketones. These results demonstrate the high applicability of MF for the synthesis of long-chained alkane precursors towards gasoline, diesel and jet biofuels.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.037.

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