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Preparation of C_9-aldehyde *via* aldol condensation reactions in ionic liquid media

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C_9-aldehyde has been prepared *via* aldol condensation reactions in ionic liquid media; catalyst investigation showed enhanced product selectivity for the desired aldehyde in ionic liquid media than in conventional solvent systems.

The aldolization[1] of ‘oxo’ aldehydes is a large volume process and important for the production of plasticizers. This reaction[2] utilizes *n*-butyraldehyde as a carbon building block and is carried out with a world production capacity of more than 2.3 × 10^6 t a^{-1}. After the self-aldol condensation reaction of *n*-butyraldehyde, followed by hydrogenation, the resulting product 2-ethylhexanol is used for the production of dioctyl phthalate plasticizer. Alternatively, propanal can be used as a carbon building block and be converted *via* two consecutive aldol condensation reactions (Fig. 1) to generate 2,4-dimethylhept-2-enal. The unsaturated aldehyde can be hydrogenated and further used as a precursor for the preparation of phthalate ester.

The first step involves the self-aldol condensation of propanal to form 2-methylpent-2-enal (Aldol I). Followed by the selective hydrogenation of the condensation product the resulting complex 2-methylpentanal is further reacted with propanal in a cross-aldol condensation reaction (Aldol II). The hydrogenation of the resulting aldehyde gives the alcohol 2,4-dimethylheptanol, which is a potential feed for the production of phthalate ester.

Next to solventless reaction systems,[3] many aldol condensation reactions are carried out in the liquid-phase using aqueous base-catalysis (*e.g.* NaOH or basic ion exchanged resins). Although water is clearly preferred as a solvent, other criteria like recyclability, waste water contamination, and selectivity of the aldol reaction have to be considered when choosing the most appropriate solvent. Therefore we investigated ionic liquid phases as a potential solvent medium for aldol condensation reactions.

Ionic liquids[4] are currently investigated for a variety of different applications, *e.g.* solvent media for homogeneous catalysis,[5] extraction processes,[6] membrane technology,[7] oligomerization and polymerization catalysis.[8] These ionic systems are salts that have melting points at or below ambient temperatures and can be utilized for a wide variety of applications. The liquid phases exhibit very low vapor pressure, tunable polarity, and high thermal stability. Depending on the application the ionic fragments can be designed to accommodate catalysis or separation in the most efficient way. Fig. 2 shows imidazolium based ionic liquids containing tetrafluoroborate and hexafluorophosphate anions, which have been investigated in our study.

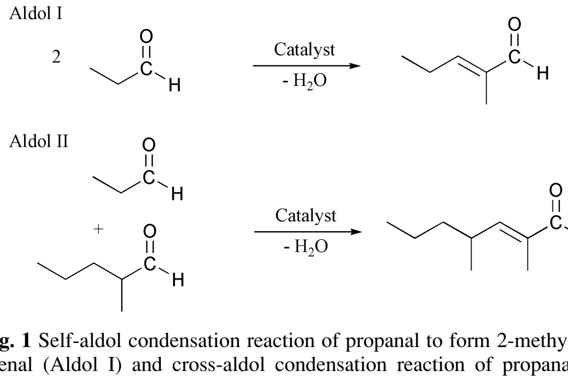


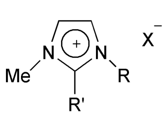
Fig. 1 Self-aldol condensation reaction of propanal to form 2-methylpent-2-enal (Aldol I) and cross-aldol condensation reaction of propanal and 2-methylpentanal to form 2,4-dimethylhept-2-enal (Aldol II).

For the catalyst preparation† the ionic liquid phases were treated with a concentrated solution of sodium hydroxide. The resulting mixtures were investigated in parallel with the aqueous solution‡ of the base. The hydroxyl concentration of the aqueous solution and the ionic liquid phases were adjusted to 1 molar, which corresponds to a conventional concentration for an aldol catalyst system (4 wt% NaOH).

Our first investigation (Table 1) focused on the evaluation of the self-aldol condensation reaction of propanal to form 2-methylpent-2-enal (Aldol I). The reaction progresses through an aldol intermediate and produces the unsaturated aldehyde under the applied reaction conditions. We investigated two types of ionic liquid phases consisting of [bmim] and [bdmim] cations with tetrafluoroborate and hexafluorophosphate anions. Most of the reactions reached quantitative conversion of the propanal after a reaction time of 3 h. The highest product selectivity (82%) was found for the ionic liquid [bdmim][PF_6], which is identical to the selectivity obtained for our aqueous base case study. Although the conversion values of the other ionic liquid phases were comparable to water, their product selectivities were reduced. In most of these reactions a large amount of higher boiling aldehydes were produced. Due to the increased solubility of the formed C_6-aldehydes in the ionic liquids higher boiling side-products are formed *via* cross-aldol condensation reactions. In contrast, if the reaction is carried out in an aqueous solution the resulting C_6-aldehydes have only a limited solubility and therefore side-reactions are limited.

Similar to our results for the Aldol I investigation the catalyst evaluation of Aldol II reactions showed comparable conversion values for the basic ionic liquids and the aqueous sodium hydroxide system. However, the selectivity towards the condensation products were significantly increased for the sodium hydroxide containing ionic liquid phases. In our investigation of basic [bmim][BF_4] (entry 7) the selectivity towards the desired 2,4-dimethylhept-2-enal was 20% higher than in the sodium hydroxide–water system. This increased selectivity is attributed to the higher solubility of the starting material 2-methylpentanal in the ionic liquid phase.

In the cross-aldol condensation reaction (Aldol II) it is very important that both substrates have high enough solubility in the



R = ethyl, R' = H:	[emim]
R = butyl, R' = H:	[bmim]
R = hexyl, R' = H:	[hmim]
R = octyl, R' = H:	[omim]
R = butyl, R' = methyl:	[bdmim]

X = BF_4; PF_6

Fig. 2 Imidazolium based ionic liquid phases.

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Table 1 Aldol condensation reaction carried out in sodium hydroxide containing ionic liquid media

Entry[a]	Reaction Media[b]	Reaction Type[c]	Temperature/ °C	Conversion[d]/ wt%	Selectivity[e] $C_6^=$/wt%	Selectivity[f] C_6/wt%	Selectivity[g] $C_9^=$/wt%	Selectivity[h] $>C_9$/wt%	Comments
1	[bmim][BF_4]	Aldol I	80	99	64	2	—	33	
2	[bmim][PF_6]	Aldol I	80	99	74	1	—	25	
3	[bdmim][BF_4]	Aldol I	80	99	68	1	—	31	
4	[bdmim][PF_6]	Aldol I	80	100	82	1	—	17	
5	H_2O	Aldol I	80	100	82	0	—	18	Base case
6	[emim][BF_4]	Aldol II	90	100	4	6	69	21	
7	[bmin][BF_4]	Aldol II	95	100	3	3	80	14	
8	[bmim][BF_4]	Aldol II	96	99	10	9	62	19	1st recycle
9	[bmim][BF_4]	Aldol II	99	100	8	12	48	32	2nd recycle
10	[bmim][BF_4]	Aldol II	97	99	6	7	26	61	3rd recycle
11	[hmim][BF_4]	Aldol II	90	100	12	15	57	16	
12	[omim][BF_4]	Aldol II	90	100	10	19	60	21	
13	[bmim][PF_6]	Aldol II	96	99	13	13	59	15	
14	[bdmim][BF_4]	Aldol II	95	96	15	9	54	21	
15	[bdmim][PF_6]	Aldol II	95	99	11	20	45	24	
16	H_2O	Aldol II	90	100	36	0	59	5	Base case

[a] Reaction time of 3 h. [b] Ionic liquid media: [emim] 1-ethyl-3-methylimidazolium, [bmim] 1-butyl-3-methylimidazolium, [hmim] 1-hexyl-3-methylimidazolium, [omim] 1-methyl-3-octylimidazolium, [bdmim] 1-butyl-2,3-dimethylimidazolium. [c] Aldol I - self-aldol condensation reaction of propanal, Aldol II - cross-aldol condensation reaction of propanal and 2-methylpentanal. [d] Conversions of propanal. [e] $C_6^=$ — 2-methylpent-2-enal. [f] C_6 — 3-hydroxy-2-methylpentanal and other C_6-derivatives. [g] $C_9^=$ — 2,4-dimethylhept-2-enal. [h] $>C_9$ — higher boiling aldehydes and oligomers.

reaction phase. In the aqueous sodium hydroxide system the substrate propanal is fully water-soluble while the other substrate 2-methylpentanal exhibits only limited solubility. Although the reaction is already carried out with a four-fold excess of 2-methylpentanal to compensate for the low solubility, the reaction only reaches a product selectivity of 60%. The major side reaction occurs through the self-condensation of propanal to form 2-methylpent-2-enal with a selectivity of 36%. By carrying out the same reaction under identical conditions in the basic ionic liquid phase [bmim][BF_4] the side reaction was reduced to only 4% and the product selectivity for the desired 2,4-dimethylhept-2-enal increased to 80%. This improvement of the selectivity is attributed to the higher solubility of the substrate 2-methylpentanal in the ionic liquid reaction phase. Further studies on varying the polarity of the ionic liquid phase [bmim][BF_4] revealed that the butyl substituent produced the highest selectivity while hexyl-, octyl-, and ethyl-groups showed slightly decreased values. The polarities of these ionic liquid phases can be further adjusted through structural variations and further improvements of the selectivity could be expected through fine-tuning of the system.

After the conclusion of the reaction the products are conveniently isolated by distillation. The resulting ionic liquid phases were freed from organic sodium salts and reused as solvent media for additional aldol reactions. The formation of organic sodium salts (mostly carboxylic sodium derivatives) is a side-reaction in the aldol condensation process and is apparent in both the ionic liquid and aqueous sodium hydroxide system.

A recycle study of the ionic liquid medium [bmim][BF_4] was carried out for the cross-aldol condensation reaction (entries 7–10). Each of the four runs showed greater than 99% conversion under the reaction conditions applied. Due to the fact that the heavier reaction products were accumulated in the ionic liquid phase the relative product selectivity decreased from 80% to 26%. Therefore, these relative product selectivities need to be evaluated accordingly.

The investigated ionic liquid media offer an interesting alternative to carry out aldol condensation reactions. In light of their enhanced product selectivity and the ease of recycle, these ionic phases could compliment traditional aldol catalyst systems. Further catalyst evaluations and toxicology studies are necessary to fully establish the viability of ionic liquids as a reaction medium for aldol condensation reactions.

Notes and references

† *Aldol I catalyst evaluation:* (a) the ionic liquid (40.0 mmol) was treated with an aqueous solution (1 mL) of sodium hydroxide (8.8 mmol, 0.35 g) and decane (internal standard) (5.6 mmol, 0.7 g). After the resulting mixture was heated to 80 °C, propanal (232.4 mmol, 13.5 g) was added. The reaction mixture was kept under reflux conditions for 3 h; (b) an aqueous solution of sodium hydroxide (1 M) (8.8 mmol, 0.35 g) and decane (internal standard)(5.6 mmol, 0.8 g) was heated to 80 °C. After the addition of propanal (232 mmol, 13.5 g) the reaction mixture was refluxed for an additional 3 h.

Aldol II catalyst evaluation: (a) the ionic liquid (40.0 mmol) was treated with an aqueous solution (1 mL) of sodium hydroxide (8.8 mmol, 0.35 g), 2-methylpentanal (180 mmol, 18.0 g), and nonane (internal standard)(7.8 mmol, 1.0 g). After the resulting mixture was heated to 90 °C, propanal (44.8 mmol, 2.6 g) was added. The reaction mixture was kept under reflux conditions for 3 h; (b) the aldehyde 2-methylpentanal (175 mmol, 17.5 g) and nonane (internal standard)(8.7 mmol, 1.1 g) were added to an aqueous solution of sodium hydroxide (1 M) (8.8 mmol, 0.35 g). The resulting mixture was heated to 90 °C and treated with propanal (44.8 mmol, 2.6 g). The reaction mixture was refluxed for an additional 3 h. Product isolation was carried out *via* distillation under reduced pressure. Conversion and selectivity were determined by GC and GC/MS techniques.

‡ Aldol condensation reactions in aqueous sodium hydroxide solutions can be influenced by phase transfer catalysis (*e.g.* the usage of surfactants like methyltrioctylammonium chloride can accelerate the reaction and change the selectivity).

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