A Facile Aldol Reaction in Bronsted Acid Ionic Liquid

LIU Bao-you, YANG Hui-long, DONG Jian-fang, HAN Ju, WEI Fu-xiang
(College of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China)

Abstract: α, β-unsaturated ketones were prepared efficiently via Aldol condensation reaction of unmodified ketones and aromatic aldehydes in Bronsted acid ionic liquid (BAIL) BMImHSO$_4$. The novel method had advantages of high yield and selectivity, mild reaction conditions, ease of product isolation and recycle of ionic liquid.

Key words: Bronsted acid ionic liquid (BAIL); catalyst; aldol reaction; α, β-unsaturated ketones
CLC number: TQ622.6 Document code: A Article ID: 0529-6579 (2007) Sl-0278-03

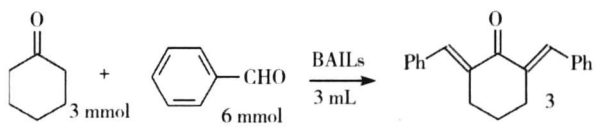
The aldol reaction is considered to be one of the most important carbon-carbon bond forming reactions and the product α, β-unsaturated carbonyl compounds are widely used as intermediates in pharmaceutical and flavor chemicals[1]. However, the corrosive and expensive catalyst (such as a strong acid, base or RuCl$_3$[2]), the rigid reaction conditions, low efficiency and use of poisonous molecular solvents in traditional aldol reaction of ketone and aldehyde were also left to be improved in order to establish an industrial competitive process. In recent years, ionic liquids have been effectively used in many organic reactions as potential green alternative solvents. In fact some pioneers have reported aldol reaction in ionic liquids. For example, Zhang[3] reported the aldol reaction of TMSCl modified aldehyde with ketones in BMImBF$_4$. Albel[4] explored the supported choline hydroxide ionic liquid as heterogeneous catalyst in aldol condensation with high conversion and low selectivity. Herein, we reported our preliminary results on the efficient and practical aldol reaction of unmodified ketones and aldehydes to afford α, β-unsaturated ketones in Bronsted acid ionic liquid (BAIL). The BAILs used were 1-methylimidazolium tetrafluoroborate acid (HMImBF$_4$), 1-butyl-3-methylimidazolium dihydrogen phosphate (BMImH$_2$PO$_4$), 1-ethylimidazolium trifluoroacetic acid (HEImTA) and 1-butyl-3-methylimidazolium hydrogen sulphate (BMImHSO$_4$). All the ionic liquids were prepared according to the literature[5].

1 Experimental

Preparation of 3-benzylidene-2-butanone (3d) in BMImHSO$_4$ and recycled procedure

BMImHSO$_4$ (3 g), butanone—2 (0.22 g, 3 mmol), benzylaldehyde (0.32 g, 3 mmol) were added successively to a 25 mL round-bottomed flask under stirring, then the reaction was kept for 4 h at r.t. till GC/MS detection indicated the completion. The object product could be vacuum distilled or extracted by ethyl acetate (10 mL×2) from the mixture, 0.39 g, yield 81%, purity>99%, m.p. 37~39 ℃. The left ionic liquid could be reused in the next run without any further disposal, and similar yield and selectivity could be obtained.

2 Results and discussion



We initiated our study to speculate suitable BAILs as reaction media by using benzaldehyde and cyclohexanone as substrates, the same reaction catalyzed by a common base such as NaOH or Na$_2$CO$_3$ in a neutral

①收稿日期: 2007-01-10
基金项目: 国家自然科学基金资助项目 (P061103); 河北省科技攻关计划资助项目 (04213036); 石家庄市科技局招标课题 (05907371A—7); 河北科技大学博士科研启动基金资助项目 (QD200518); 河北省环境工程重点学科经费资助项目
作者简介: 刘宝友 (1973年生), 男, 博士, 副教授, 硕士生导师; 通讯联系人: 魏福祥; E-mail: wfxss@sohu.com

ionic liquid 1—butyl—2, 3—dimethylimidazolium hexafluorophosphate (BDMImPF6) was also explored in order to compare (Tab. 1) the efficiency.

Tab. 1 Aldol reaction of cyclohexanone with benzylaldehyde in different conditions[a]

Entry	Reaction conditions	Temp/℃	Time/h	Conversion /%[a]	Selectivity /%[a]
1	$BMImHSO_4$	20	1	>99[b]	>99
2	$BMImH_2PO_4$	20	1	91	98
3	$HMImBF_4$	60	4	<10	—
4	HEImTA	60	4	<10	—
5	$BDMImPF_6$/NaOH, mmol	20	1	>99	95
6	$BDMImPF_6$/Na_2CO_3, 3mmol	20	2	95	87

a. detected by GC/MS; b. Date from next three runs were 99%, 99%, 99% separately.

Ionic liquid $BMImHSO_4$ was confirmed an effective medium for the reaction, and showed almost the quantitative conversion and highest selectivity compared with $BMImH_2PO_4$, $HMImBF_4$ and HEImTA (Entry 1—4). Under our experiment conditions, side reactions caused by water could be effectively restrained in $BMImHSO_4$ according to GC/MS detection, while in $BDMImPF_6$/NaOH (1 equiv.), several anonymous impurities were detected, although their content was less than 5% by GC/MS (Entry 5). While in $BDMImPF_6/Na_2CO_3$ (equivalent), the reaction of cyclohexanone with benzylaldehyde gave a mixture of α, β-unsaturated ketone and β-hydroxy ketone with the 87% selectivity of 3 (Entry 6). $BMImHSO_4$ can be recycled with 99%, 99%, 99% yields separately in the next 3 runs. The results reflected that $BMImHSO_4$ might be a suitable medium and catalyst in Aldol reactions with the advantage of high conversion and selectivity.

Encouraged by our initial exploration results, then the scope and the limitation of the reactions between different ketones and different aromatic aldehydes were explored in $BMImHSO_4$. The results were listed in Tab. 2, from where can been seen that $BMImHSO_4$ was a good reaction medium for several of the substrates. High conversion and selectivity were always observed at low temperature in very short reaction times. The different substituted groups on the aromatic aldehydes displayed some influence on the reaction results, usually higher conversion and selectivity were obtained when there was a electro withdrawing group other than a electro donating group, we thought the different nucleophilicity might accounted for the observed results. Generally speaking, aromatic methyl ketone is less active than cyclohexanone, therefore, an elevated temperature and prolonged reaction times were needed for a high conversion and yield.

Tab. 2 Aldol reaction of ketones with different aromatic aldehydes in $BMImHSO_4$

Entry	Aldehydes	Ketones	Product	Temp/℃	Time/h	Yield/%	mp (in lit.)/℃
1	p-ClC_6H_4CHO	$(CH_2)_5CO$	3a	r.t.	1	92	145 (145~146)[3]
2	p-$MeOC_6H_4CHO$	$(CH_2)_5CO$	3b	r.t.	4	84	202 (204)[2]
3	p-$NO_2C_6H_4CHO$	$(CH_2)_5CO$	3c	r.t.	1	99	199 (199~200)[3]
4	C_6H_5CHO	$C_2H_5COCH_3$	3d	r.t.	4	81	38 (38~39)[2]
5	p-$NO_2C_6H_4CHO$	$C_2H_5COCH_3$	3e	r.t.	4	94	102(103.5~106)[6]
6	p-$NO_2C_6H_4CHO$	$C_6H_5COCH_3$	3f	50	4	76	165 (165~166)[2]
7	p-$NO_2C_6H_4CHO$	p-$ClC_6H_4COCH_3$	3g	50	4	90	162 (164)[7]
8	p-$NO_2C_6H_4CHO$	p-$MeOC_6H_4COCH_3$	3h	50	4	97	172 (173)[7]
9	p-$NO_2C_6H_4CHO$	p-$NO_2C_6H_4COCH_3$	3i	80	8	72	192 (193~194)[8]
10	p-$MeOC_6H_4CHO$	p-$ClC_6H_4COCH_3$	3j	50	4	94	124 (124~125)[9]

3 Conclusions

In summary, α, β-unsaturated ketones were prepared efficiently via Aldol condensation reaction of unmodified ketones and aromatic aldehydes in Bronsted acid ionic liquid (BAIL) $BMImHSO_4$. The novel method had advantages of high yield and selectivity, mild reaction conditions, ease of product isolation and recycle of ionic liquid.

References:

[1] MESTRES R. A green look at the aldol reaction[J]. Green Chem., 2004, 6: 583—603.

[2] IRANPOOR N, KAZEMI F. $RuCl_3$ Catalyses Aldol Condensations of Aldehydes and Ketones[J]. Tetrahedron, 1998, 54: 9475—9480.

[3] ZHANG X, FAN X, NIU H, et al. An ionic liquid as a recyclable medium for the green preparation of α, α′-bis (substituted benzylidene) cycloalkanones catalyzed by

FeCl$_3$·6H$_2$O[J]. Green Chem, 2003, 5: 267—269.
[4] ABELLO S, MEDINA F, RODRIGUEZ X, et al. Supported choline hydroxide (ionic liquid) as heterogeneous catalyst for aldol condensation reactions[J]. Chem Commun, 2004, 1096—1097.
[5] XU D Q, LIU B Y, LUO S P, et al. A novel and eco-friendly method for the preparation of ionic liquids[J]. Synthesis, 2003, 17: 2626—2628.
[6] SHEVCHUK M I, VOLYNSKAYA E M, DOMBROVSKII A V. Acylalkylene triphenyl-phosphoranes[J]. Zh Obshch Khim, 1970, 40 (1), 48—57 (Russ). CA 72: 100817b.
[7] CHERVENYUK G I, DOMBROVSKII A V, GRINEV G V. Synthesis of chalcones through the formation of olefins by organophosphorus activated reagents[J]. Zh Obshch Khim, 1968, 38 (2): 225—226 (Russ). CA 69: 26941g.
[8] PETER K, HEINZ G. Chalcones[J]. Chem Ber, 1961, 94: 26—38. CA 55: 10382h.
[9] KOZLOV N S, KOZLOV G N. Action of piperidine on β-arylamino ketones[J]. Zh Obshch Khim, 1962, 32: 2428—31 (Russ). CA 58: 9022c.

Bronsted酸性离子液体催化的 Aldol反应

刘宝友, 杨会龙, 董建芳, 韩 菊, 魏福祥
(河北科技大学环境科学与工程学院, 河北 石家庄 050018)

摘 要: 通过酮和醛的 Aldol反应在 Bronsted酸离子液体 BMImHSO$_4$ 中制备了一系列 α, β—不饱和酮。所建立方法的主要优势有: 高转化率和选择性、温和的反应条件、产物容易分离、离子液体可循环使用。

关键词: Bronsted酸离子液体; 催化剂; Aldol反应; α, β—不饱和酮
中图分类号: TQ 622.6

(上接第 275页)

percent Sn-Ni thin film anode during reaction with lithium[J]. Electrochem Soc, 2005, 152 (3): A560—A565.
[4] XIE J, ZHAO X B, CAO G S. Solvothermal synthesis of nanosized CoSb$_3$ alloy anode for Li-ion batteries[J]. Electrochim Acta, 2005, 50 (9): 1903—1907.
[5] AURBACH D, MARKOVSKY B, NIMBERGER A. Electrochemical Li-insertion processes into carbons produced by milling graphitic powders: The impact of the carbons' surface chemistry[J]. Electrochem Soc, 2002, 149 (2): A152—A161.

锂离子电池负极材料纳米 Ni$_3$Sn$_2$ 的溶剂热合成与电化学性能

秦海英[1], 赵新兵[2], 李洲鹏[1]
(1. 浙江大学 化学与生物工程系, 浙江 杭州 310027;
2. 浙江大学 材料科学与工程系, 浙江 杭州 310027)

摘 要: 采用溶剂热法合成锂离子电池负极材料纳米 Ni$_3$Sn$_2$ 合金粉末并研究了该合金粉末作为新型锂离子二次电池负极材料的电化学性能。合成的合金粉末经过了 XRD和 FESEM的表征, 采用 Li/LiPF6 (EC+DMC) / Ni$_3$Sn$_2$ 模拟电池测定合成的合金粉末的电化学性能。研究表明, 该合金粉末的首次可逆容量为 136 mAh·g^{-1}, 退火后的合金粉末表现出更好的循环稳定性。

关键词: 锂离子电池; 负极; Ni$_3$Sn$_2$; 溶剂热合成; 电化学性能
中图分类号: TG146.1$^+$4