

A Modified Protocol for the Aldehyde Olefination Reaction using Ionic liquid as Reaction Medium

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[Ru(COD)Cl₂]_n /CuCl₂.2H₂O/LiCl catalytic system was found highly active in ionic liquid medium for aldehyde olefination reaction in term of yield and selectivity. Aromatic aldehydes with more electron-donating groups on the phenyl ring gave higher yield than those with electron withdrawing groups. Reduced reaction time as well as 5 times recycling of catalytic system reflects the importance of this modified process.

Keywords: [Ru (COD) Cl₂]_n /CuCl₂.2H₂O/LiCl, Ionic liquid, Aldehyde olefination.

1. INTRODUCTION

Carbonyl olefination reaction is one of the convenient and efficient method for the preparation of alkenes (C=C) [1]. Although, various other organic transformations like Wittig reaction [2-5], Horner-Wadsworth-Emmons reaction [6-8], Kocienski-Julia reaction [8] and Peterson reaction [9-11] offers effective and alternative method [1, 6-14] to produce highly reactive carbanion but these above mentioned reactions suffer from atom economy, long reaction time, etc. [15]. Transition-metal-catalyzed decarbonylation reaction of aldehydes is an attractive

subject that has been studied for decades [1-14]. However, very limited research has focused on decarbonylative addition reactions. Recently, $[\text{Ru}(\text{COD})\text{Cl}_2]_n / \text{CuCl}_2 \cdot 2\text{H}_2\text{O} / \text{LiCl}$ catalytic system was reported as an efficient combination for aldehyde olefination *via* decarbonylation addition pathway [15]. Although this catalytic system was found active for various substrates in term of yield and selectivity, it also suffers from various drawbacks like longer reaction time, costly starting materials, recyclability of catalyst etc.

Ionic liquids are well documented as a solvent for different type of transition metal catalyzed organic transformations with the added advantage of catalyst recyclability [16-20]. Here, we are reporting first time ionic liquid mediated $[\text{Ru}(\text{COD})\text{Cl}_2]_n / \text{CuCl}_2 \cdot 2\text{H}_2\text{O} / \text{LiCl}$ catalytic system for aldehyde olefination reaction *via* decarbonylation addition pathway.

2. EXPERIMENTAL

All the chemicals were purchased from Sigma Aldrich and SD fine chemicals. All the solvents were dried according to the standard procedure as well as all the reactions were performed under argon in a sealed tube. The work-up and purification procedures were carried out with reagent-grade solvents. NMR spectra were recorded on standard Bruker 300WB spectrometer with an advance console at 300 and 75 MHz for ^1H and ^{13}C NMR respectively.

Typical Experimental Procedure

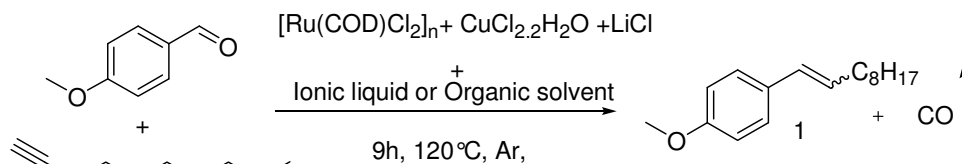
The reaction tube was charged with $[\text{Ru}(\text{COD})\text{Cl}_2]_n$ (0.01 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.03 mmol) and LiCl (2 equivalent) along with *p*-anisaldehyde (0.2 mmol), 1-decyne (0.8 mmol) in ionic liquid (1 mmol) or dry organic solvents (1 cm³). Afterwards, the reaction tube was sealed under argon and the resulting reaction mixture was allowed to be heated for 9 hours at 120°C. Next, the reaction mixture was allowed to be cooled and corresponding reaction product was isolated according to the solvent system as per described below.

While using *organic solvents (THF, DCM, Toluene and Acetonitrile)*, the reaction mixture was first filtered through silica plug with dichloromethane and then the organic solvent was evaporated *in vacuo*. The residue was further purified by column chromatography (Petroleum ether: Ether = 100:1) to recover the pure reaction product.

In the case of *Ionic liquid as a reaction medium*, the reaction product was extracted with ether ($5 \times 2 \text{ cm}^3$) and the combined ether extract was evaporated *in vacuo*. The residue was further purified by column chromatography (Petroleum ether: Ether = 100:1) to isolate the pure reaction product.

3. RESULTS AND DISCUSSION

In order to compare the catalytic activity of $[\text{Ru}(\text{COD})\text{Cl}_2]_n / \text{CuCl}_2 \cdot 2\text{H}_2\text{O} / \text{LiCl}$ catalytic system in ionic liquids (1 mmol) with conventional solvents, olefination between *p*-ani-saldehyde and 1-decyne was carried at 120°C for 9 hours under argon atmosphere. The results are shown in Table 1 and Scheme 1. $[\text{bmim}][\text{NTf}_2]$ mediated olefination of *p*-anisaldehyde offers a good yield (88%) and selectivity (*E/Z* 10:1) (Scheme 1, Table 1). Except toluene, olefination reaction was found less active (yield 61-67, *E/Z* = 3:1-4:1) with dichloromethane (DCM), tetra-hydrofuran (THF) and acetonitrile solvent system (Scheme 1, Table 1, entry 5-7).



Scheme 1.

Table: 1 Aldehyde olefination reaction in different solvent systems.

Entry	Ionic Liquid [1 mmol]	Yield [%] ^a	<i>E/Z</i> ^b
1.	$[\text{bmim}][\text{Cl}]$	70	3:1
2.	$[\text{bmim}][\text{PF}_6]$	75	5:1
3.	$[\text{bmim}][\text{NTf}_2]$	88	10:1
4.	Toluene	73	6:1
5.	DCM	61	3:1
6.	THF	65	3:1
7.	Acetonitrile	67	4:1

a – Yield was calculated after column chromatography.

b – all *E/Z* ratio was calculated by $^1\text{HNMR}$

The quantity of Ru (II) catalyst along with its additives was further optimized. Ru(II) catalyst (0.01 mmol) with 0.03 mmol hydrated CuCl_2 and 2 equivalent of LiCl in $[\text{bmim}][\text{NTf}_2]$ offered the olefination reaction product **1** in good yield (85%) and selectivity (E/Z ratio 10:1), while in toluene, the above optimized quantity of $[\text{Ru}(\text{COD})\text{Cl}_2]_n/\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{LiCl}$ catalytic system (Ru (II) catalyst 0.01 mmol, 0.3 mmol of hydrated CuCl_2 and 2 equivalent LiCl) gave corresponding olefinated product **1** with lower yield (52%) and decreased selectivity (E/Z ratio 2:1) (Fig. 1).

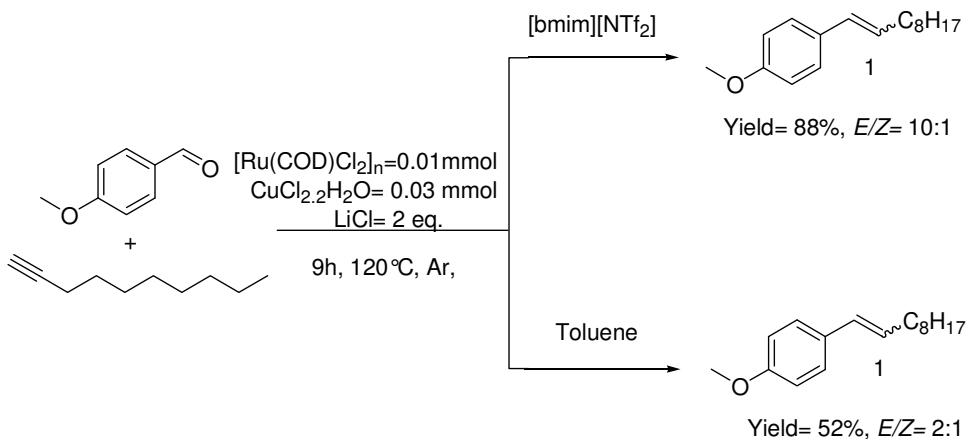
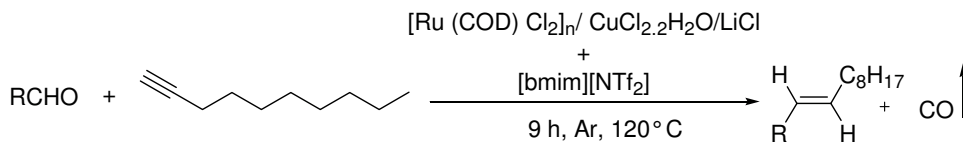


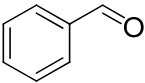
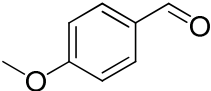
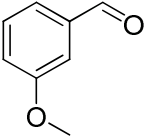
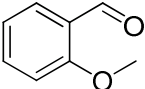
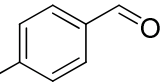
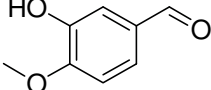
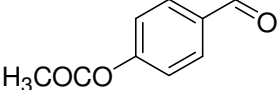
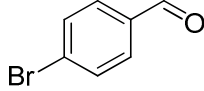
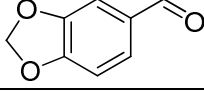
Fig. 1. Olefination of *p*-anisaldehyde in different solvent media.

With optimized reaction condition, different substrates were investigated using this reaction. Aliphatic aldehydes were found inactive to react under the current optimized catalytic system. The aromatic aldehydes with electron-donating groups gave a much better yield than those carrying electron withdrawing groups (Table 2, Entry 1-9). We obtained more than 40% yield with acceptable E/Z ratio in all the cases (Scheme 2, Table 2, Entry 1-9). Introduction of the ester group in the phenyl ring (Table 2, Entry 7) offered lower yield and selectivity.



Scheme 2.

Table 2: Decarbonylative Addition Reaction using different substrates.

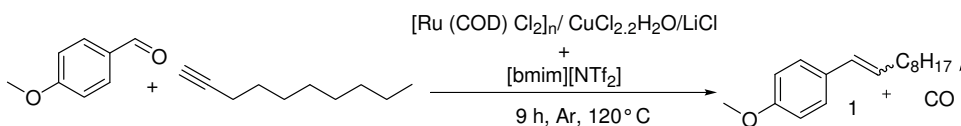
Entry	Aldehydes (RCHO)	Isolated Yield [%] ^a	E/Z ^b
1.		70	6:1
2.		85	10:1
3.		65	5.5:1
4.		75	4:1
5.		70	7:1
6.		71	3:1
7.		45	4:1
8.		60	4:1
9.		95	5:1

a – Yield was calculated after column chromatography.

b – all E/Z ratio was calculated by ¹HNMR

To evaluate the possibility of recycling the ionic liquid mediated catalytic system for the aldehyde olefination reaction, *p*-anisaldehyde and 1-decyne were allowed to react in [bmim][NTf₂] mediated [Ru(COD)Cl₂]_n/CuCl₂·2H₂O/LiCl catalytic system and then the products were extracted with ethyl ether. A second portion of *p*-anisaldehyde and 1-decyne was added in the previously used [bmim][NTf₂] mediated [Ru

(COD)Cl₂]_n/CuCl₂.2H₂O/LiCl catalytic system and the process was repeated up to 5 times as shown in Table 3 (Scheme 3).



Scheme 3.

Table 3 Recyclability test for p-anisaldehyde olefination reaction

Recyclability run	Isolated Yield [%]	Selectivity (E/Z)
1.	85	10:1
2.	80	8:1
3.	78	7.5:1
4.	71	6.5:1
5.	72	6.5:1

a – Yield was calculated after column chromatography.

b – all E/Z ratio was calculated by ¹HNMR

4. CONCLUSION

In summary, a considerable increase in the reaction rate of the aldehyde olefination reaction was observed in [bmim][NTf₂] mediated [Ru (COD)Cl₂]_n/CuCl₂.2H₂O/LiCl catalytic system when compared to other organic solvents (toluene was reported as optimal conventional solvent) with the same catalytic system. In this reaction, significant improvements in yield and selectivity were observed with aromatic aldehydes as substrates. The ionic liquid catalytic system can be recycled after the reaction and reused up to 5 times without considerable reduction in yield and selectivity.

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