Research Article

An Improved Protocol for the Aldehyde Olefination Reaction Using (bmim) (NTf₂) as Reaction Medium

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Received 18 June 2012; Accepted 21 September 2012

Academic Editor: João Paulo Leal

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[Ru(COD)Cl₂]/CuCl₂·2H₂O/LiCl catalytic system works efficiently in ionic liquid media for aldehyde olefination reaction. It offers good yield and selectivity with the added advantage of 5 times recyclability for [Ru(COD)Cl₂]/CuCl₂·2H₂O/LiCl catalytic system. We also successfully reduced the reaction time from 12 hours to 9 hours for the aldehyde olefination reaction.

1. Introduction

Carbonyl olefination reaction is one of the convenient and universal methods for the preparation of alkenes (C=C) [1, 2]. Although Wittig reaction [2–5] as well as its modified versions like Horner-Wadsworth-Emmons reaction [6–8], Kocienski-Julia reaction [8], and Peterson reaction [9–11] offers its effective and alternative method [6–14] to produce highly reactive carbanion these above-discussed reactions suffer from atom economy [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 [Ru(COD)Cl₂]/CuCl₂·2H₂O/LiCl catalytic system was reported as an efficient combination for aldehyde olefination via decarbonylation addition pathway [15]. This catalytic system was found active for various substrates in terms of yield and selectivity but it suffers from long reaction time and recyclability of catalyst.

Ionic liquids are well documented as 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 [Ru(COD)Cl₂]/CuCl₂·2H₂O/LiCl catalytic system for aldehyde olefination reaction via decarbonylation addition pathway.

2. Experimental Procedure

All the chemicals were purchased from Sigma Aldrich and SD fine chemicals. All the solvents were dried according to the standard procedure and 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 300 WB spectrometer with an advance console at 300 and 75 MHz for ¹H and ¹³C NMR, respectively.

2.1. Typical Experimental Procedure. The reaction tube was charged with [Ru(COD)Cl₂] (0.01 mmol), CuCl₂·2H₂O (0.03 mmol), and LiCl (2 equivalent) along with *p*-anisaldehyde (0.2 mmol) and 1-decyne (0.8 mmol) in ionic liquid (1 mmol) or dry toluene (1 mL). Further, the reaction tube was sealed under argon and the resulting reaction mixture was heated for 9 hours at 120°C. Later, the reaction mixture was allowed to cool up to room temperature. Isolation of corresponding reaction product was isolated according to the solvent system as described below.

While using toluene as a solvent, the reaction mixture was first filter 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 pure reaction product.

SCHEME 1

SCHEME 2

TABLE 1: Aldehyde olefination reaction in different solvent systems.

Entry	Ionic liquid (1 mmol)	Yield (%) ^a	<i>E/Z</i> ^b
1	(bmim)(Cl)	70	3 : 1
2	(bmim)(PF ₆)	75	5 : 1
3	(bmim)(NTf ₂)	88	10 : 1
4	Toluene	73	6 : 1

^aYield was calculated after column chromatography.^bAll *E/Z* ratios were calculated by ¹HNMR.

In case of Ionic liquids as a reaction medium, the reaction product was extracted with ether (5 × 2 mL) and the combined ether extract was evaporated in vacuo. Later the residue was further purified by column chromatography (Petroleum ether : Ether = 100 : 1) to isolate the pure reaction product.

3. Results and Discussion

We selected one model reaction between *p*-anisaldehyde and 1-decyne using [Ru(COD)Cl₂]/CuCl₂·2H₂O/LiCl catalytic system with three different types of ionic liquid (1 mmol), that is, [bmim] [Cl], [bmim] [PF₆], and [bmim] [NTf₂]. Among these three ionic liquids, [bmim] [NTf₂] mediated olefination of *p*-anisaldehyde offers a good yield (88%) and selectivity (*E/Z* 10 : 1) (Scheme 1, Table 1).

After getting delightful results with [bmim] [NTf₂], we optimised the quantity of Ru (II) catalyst along with CuCl₂ and LiCl. Only 0.01 mmol of Ru (II) catalyst with 0.03 mmol hydrated CuCl₂ and 2 equivalents of LiCl are found sufficient to offer the olefination reaction product **1** in terms of yield (85%) and selectivity (*E/Z* ratio 10 : 1). While in toluene, the above optimised quantity of [Ru(COD)Cl₂]/CuCl₂·2H₂O/LiCl catalytic system, that is, Ru (II) catalyst 0.01 mmol, 0.3 mmol of hydrated CuCl₂, and 2 equivalent LiCl, gives corresponding olefinated product **1** with lower yield (52%) and decreased selectivity (*E/Z* ratio 2 : 1) (Figure 1).

Later, we screened different aromatic aldehydes and alkynes using optimized proportion for [Ru(COD)Cl₂]/

TABLE 2: Decarbonylative addition reaction using different substrates.

Entry	Aldehydes (RCHO)	Isolated yield (%) ^a	<i>E/Z</i> ^b
1		70	6 : 1
2		85	10 : 1
3		65	5.5 : 1
4		75	4 : 1
5		70	7 : 1
6		60	4 : 1
7		95	5 : 1

^aYield was calculated after column chromatography.^bAll *E/Z* ratios were calculated by ¹HNMR.

CuCl₂·2H₂O/LiCl catalytic mixture with 1 mmol of [bmim] [NTf₂], and we observed in our study that aromatic aldehydes with more electron-donating groups give a much better yield with respect to aromatic aldehydes carrying electron withdrawing group (Table 2). In most of the cases, we obtained more than 60% yield with acceptable *E/Z* ratio (Scheme 2, Table 2: Entry 1–7).

To make [Ru(COD)Cl₂] catalytic system more cost-effective for olefination reaction, we extended our work

FIGURE 1: Olefination of *p*-anisaldehyde in different solvent media

SCHEME 3

TABLE 3: Recyclability test for *p*-anisaldehyde olefination reaction.

Recyclability run	Isolated yield (%) ^a	(E/Z) ^b
1	85	10 : 1
2	80	8 : 1
3	78	7.5 : 1
4	71	6.5 : 1
5	72	6.5 : 1

^aYield was calculated after column chromatography.^bAll E/Z ratios were calculated by ¹HNMR.

towards recycling study of this catalytic system. In that context, after completion of the reaction, the product was extracted from the reaction mixture using ether washing. The rest of the catalytic mixture along with ionic liquid was dried for 1 hour under high vacuum. Further, this used catalyst was recycled to the next batch of same olefination reaction. In the same way, we recycled $[\text{Ru}(\text{COD})\text{Cl}_2]/\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{LiCl}$ catalytic system, 5 times and we obtained the corresponding olefinated product **1** with acceptable yield and selectivity (Scheme 3, Table 3).

4. Conclusion

In summary, we extended the application of ionic liquids as a reaction medium for transition-metal-catalysed olefination of aldehydes using decarbonylation pathway. We obtained not only good yield and selectivity for different types of aromatic aldehyde, but we also optimised successfully the quantity of $[\text{Ru}(\text{COD})\text{Cl}_2]/\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{LiCl}$ catalytic system. The most important thing is that we successfully reduced the reaction time from 16 hours to 9 hours and we also

recycled the catalytic system (5 times) along with acceptable yield and selectivity in order to make them nearer to their industrial application.

References

- [1] O. I. Kolodiazny, *Chemistry and Applications in Organic Synthesis*, Wiley-VCH, New York, NY, USA, 1999.
- [2] R. W. Hoffmann, "Wittig and his accomplishments: still relevant beyond his 100th birthday," *Angewandte Chemie International Edition*, vol. 40, no. 8, pp. 1411–1416, 2001.
- [3] N. J. Lawrence, "The wittig reactions and related methods," in *Preparation of Alkenes: A Practical Approach*, J. M. J. Williams, Ed., pp. 55–64, Oxford University Press, New York, NY, USA, 1996.
- [4] G. Wittig and G. Geissler, "Zur Reaktionsweise des Pentaphenyl-phosphors und einiger Derivate," *Justus Liebigs Annalen der Chemie*, vol. 580, no. 1, pp. 44–57, 1953.
- [5] G. Wittig and U. Schöllkopf, "Über Triphenyl-phosphin-methylene als olefinbildende Reagenzien (I. Mitteil)," *Chemische Berichte*, vol. 87, no. 9, pp. 1318–1330, 1954.
- [6] L. K. Blasdel and A. G. Myers, "Use of lithium hexafluoroisopropoxide as a mild base for Horner-Wadsworth-Emmons olefination of epimerizable aldehydes," *Organic Letters*, vol. 7, no. 19, pp. 4281–4283, 2005.
- [7] A. Lattanzi, L. R. Orelli, P. Barone, A. Massa, P. Iannece, and A. Scettri, "Convenient procedure of Horner-Wadsworth-Emmons olefination for the synthesis of simple and functionalized α,β -unsaturated nitriles," *Tetrahedron Letters*, vol. 44, no. 7, pp. 1333–1337, 2003.
- [8] D. L. Comins and C. G. Ollinger, "Inter- and intramolecular Horner-Wadsworth-Emmons reactions of 5-(diethoxy-phosphoryl)-1-acyl-2-alkyl(aryl)-2,3-dihydro-4-pyridones," *Tetrahedron Letters*, vol. 42, no. 25, pp. 4115–4118, 2001.

- [9] J. Huang, C. Wu, and W. D. Wulff, "Total synthesis of ($\pm$)-phomactin B2 via an intramolecular cyclohexadienone annulation of a chromium carbene complex," *Journal of the American Chemical Society*, vol. 129, no. 44, pp. 13366–13367, 2007.
- [10] D. L. Aubele, S. Wan, and P. E. Floreancig, "Total synthesis of (+)-dactylolide through an efficient sequential peterson olefination and prins cyclization reaction," *Angewandte Chemie International Edition*, vol. 44, no. 22, pp. 3485–3488, 2005.
- [11] T. Takeda, *Modern Carbonyl Olefination: Methods and Applications*, Wiley-VCH, 1st edition, 2004.
- [12] C. Aissa, "Mechanistic manifold and new developments of the Julia–Kocienski reaction," *European Journal of Organic Chemistry*, vol. 12, pp. 1831–1844, 2009.
- [13] C. Calata, J.-M. Catel, E. Pfund, and T. Lequeux, "Scope and limitations of the Julia-Kocienski reaction with fluorinated sulfonylesters," *Tetrahedron*, vol. 65, no. 20, pp. 3967–3973, 2009.
- [14] J. V. Allen, A. P. Green, S. Hardy, N. M. Heron, A. T. L. Lee, and E. J. Thomas, "On the use of the modified Julia olefination for bryostatin synthesis," *Tetrahedron Letters*, vol. 49, no. 44, pp. 6352–6355, 2008.
- [15] X. Guo, J. Wang, and C. J. Li, "An olefination via ruthenium-catalyzed decarbonylative addition of aldehydes to terminal alkynes," *Journal of the American Chemical Society*, vol. 131, no. 42, pp. 15092–15093, 2009.
- [16] K. E. Johnson, "What's an ionic liquid?" *Electrochemical Society Interface*, vol. 16, no. 1, pp. 38–41, 2007.
- [17] N. V. Plechkova and K. R. Seddon, "Applications of ionic liquids in the chemical industry," *Chemical Society Reviews*, vol. 37, no. 1, pp. 123–150, 2008.
- [18] S. Gmouh, H. Yang, and M. Vaultier, "Activation of bismuth(III) derivatives in ionic liquids: novel and recyclable catalytic systems for Friedel-Crafts acylation of aromatic compounds," *Organic Letters*, vol. 5, no. 13, pp. 2219–2222, 2003.
- [19] J. S. Wilkes, "Properties of ionic liquid solvents for catalysis," *Journal of Molecular Catalysis A*, vol. 214, no. 1, pp. 11–17, 2004.
- [20] P. Wasserscheid and W. Keim, "Ionic liquids—new "solutions" for transition metal catalysis," *Angewandte Chemie International Edition*, vol. 39, no. 21, pp. 3772–3789, 2000.