

Preparation and Application of 1, 1'-Bis-methyl-3, 3'-methylene-bisimidazolium Dicyanide as a Task-Specific Ionic liquid: An Efficient Catalyst in Benzoin Condensations

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Abstract: A new “task-specific” ionic liquid (TSIL), 1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dicyanide has been prepared and used for the first time as the medium as well as catalyst for the synthesis of α -hydroxy carbonyl group. Application of this ionic liquid in C–C bond formation reaction eliminates the use of the organic solvent, avoids the use of toxic materials, and allows the recovery and re-use of the catalyst.

Keywords: Task-specific ionic liquid, C-C formation, Benzoin Condensation

Introduction

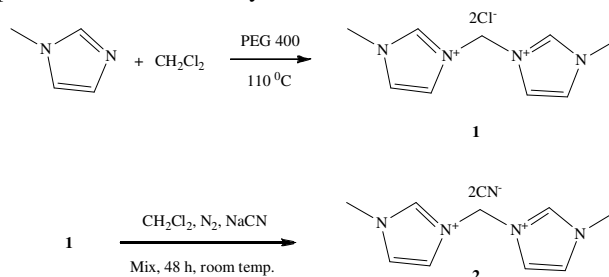
Ionic liquids (ILs) are commonly defined as substances composed only by ions which are liquid at or close to room temperature¹. During the past years a growing number of scientists and engineers have investigated ionic liquids because of their outstanding advantages in several areas. Their unique physical properties and specific chemical behavior make these liquids very interesting for new and innovative applications².

Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications such as replacing them with volatile organic solvents, making new materials, conducting heat effectively, supporting enzyme-catalyzed reactions, hosting a variety of catalysts, purification of gases, homogenous and heterogeneous catalysis, biological reactions media and removal of metal ions³.

Benzoin type α -hydroxy carbonyl group in general is important structural subunit in many biologically active compounds, industrial materials and is also important synthons for stereoselective syntheses of natural products, chiral auxiliaries and ligands⁴. Among the numerous synthetic strategies for introducing this moiety, the benzoin reaction and related additions remain perhaps, the most direct⁵⁻⁹.

Several nucleophilic carbenes derived from heterocyclic compounds including triazolium, thiazole, triazole, imidazole^{10, 11} and benzimidazolium salts are also employed as catalyst in benzoin condensation. Despite these developments, cyanide anion still remains a serious contender for practical synthesis of symmetrical acyloins, as evidenced by recent reports. Indeed, the development of novel cyanide ion catalytic systems has recently been

reported^{12,13}. It became apparent that there was a need for an efficient catalytic system, which would ease handling, and reduce reaction times. Herein, in continuation of our studies on the use of new catalyst for organic transformations^{14,15}, synthesis of a TSIL containing a methylene bridged bisimidazolium cation combined with a cyanide anion is described. Furthermore, this TSIL has been applied as an efficient catalyst and medium for the benzoin condensation.



Scheme 1. Synthesis of methylene bridged bisimidazolium cyanide

Experimental

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. Aldehydes were distilled before use. Yields refer to isolated crude products. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer.

1, 1'-Bis-methyl-3, 3'-methylene-bisimidazolium dichloride (1)

In a sealed tube, 0.03 mol of 1-methylimidazole (2.50 g) and 0.015 mol of dichloromethane (1.27 g, 1 eq.) are dissolved in 3 mL PEG 400 and heated to 110 °C for 12 h. The white precipitate is filtered off and washed twice with 15 mL of THF. The product is obtained as a white hygroscopic powder (Yield: 65%). ¹³CNMR: δ = 36.0 (NCH₃), 64.4 (NCH₂N), 122.8 (NCH), 123.0 (NCH) 137.0 (NCHN).

1, 1'-Bis-methyl-3, 3'-methylene-bisimidazolium dicyanide (2)

Under nitrogen atmosphere the ionic liquid 1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dichloride (3 g) was dissolved in dry CH₂Cl₂ (25 mL) and to this was added NaCN (2 equiv). The mixture was allowed to stir at room temperature for 48 h. The resulting suspension was filtered and the filtrate was subjected to a vacuum to remove volatile material. The residue was dissolved in dichloromethane and again filtered. The filtrate was dried using anhydrous sodium sulfate. Finally, upon concentration under vacuum at 70 °C 1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dicyanide was obtained (Yield: 45%).

Preparation of α -hydroxy ketones using 1, 1'-bis-methyl-3,3'-methylene-bisimidazolium dicyanide as catalyst

Typical experimental procedure: A mixture of 2 (1.5 mmol) and aromatic aldehyde (1 mmol) was placed in a flask and stirred at oil bath. Progress of the reaction was monitored by TLC, using carbon tetrachloride-ethylacetate (5:1) as eluent. After completion of the reaction ethyl acetate (3×4 mL) and water (10 mL) were added to the reaction mixture with vigorous stirring for 5 min. The mixture was allowed to stand for a further 5 min and the organic phase was decanted. The combined ethyl acetate layers were dried over Na₂SO₄. Evaporation of the solvent *in vacuo* gave the desired product. Further purification was achieved by crystallization in ethanol.

Results and Discussion

First, the benzoin condensation reaction of benzaldehyde was found to proceed efficiently when 1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dicyanide was employed as a catalyst and reaction medium. We then studied the self-condensation of a range of representative substituted benzaldehydes under the best reaction conditions, 1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dicyanide (1.5 mmol), aldehyde (1mmol). These aldehydes gave corresponding substituted benzoin condensation products in 12-82% isolated yields. As shown in Table 1, In the presence of the ionic liquid the self condensation of aromatic aldehydes possessing chloride or a strong electron-accepting group such as CN and NO₂ proceeded to give the corresponding benzoin condensation products in good yields (entries 2-7). As expected, benzoin condensation reaction of aromatic aldehydes possessing a strong electron-donating group such as OH and (Me)₂N proceeded with difficulty and produced product in low yields.

Table 1. Benzoin condensation reactions of various aldehydes catalyzed by 1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dicyanide

Entry	Aldehyde	Product	Time, h	Yield ^{a,b} %	IR Spectra (OH, CO), cm ⁻¹
1			1.15	82	3414, 1680
2			1.15	80	3459, 1665
3			2.15	81 ^c	3465, 1682
4			2.0	74	3383, 1702
5			1.5	82	3407, 1704
6			1.5	80	3424, 1690
7			2.0	73	3419, 1695
8			3.5	12	-
9			-	Trace	-

^a Crude isolated yields. ^b Products were identified by comparison of their physical and spectral data with authentic samples. ^c Determined by GC analysis

It is noticeable to mention that, no toxic cyanide ions were detected in reaction media (AgNO_3 test).

Conclusion

We have demonstrated the synthesis of a new task-specific ionic liquid (1, 1'-bis-methyl-3, 3'-methylene-bisimidazolium dicyanide) and its application has proved to be an effective catalysts as well as reaction medium in benzoin condensation which would reduce reaction times. More importantly, application of this ionic liquid in C-C bond formation reaction there is no formation of any side-products in this process and there is no need for column chromatography for the purification of the products. Thus, we believe the present methodology opening an environmentally benign access route to different types of α -hydroxy ketones.

Acknowledgment

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References

1. Tavares A P M, Rudreguez O and Macedo E, *Biotechnol Bioeng.*, 2008, **101**, 201.
2. Predel T, Schlücker E, Wasserscheid P, Gerhard D and Arlt W, *Chem Eng Technol.*, 2007, **30**, 1475.
3. Keskin S, Kayrak-Talay D, Akman U and Hortacsu O, *J Supercrit Fluids*, 2007, **43**, 150.
4. Coppola G M and Schuster H F, *α -Hydroxy acids in enantioselective synthesis*. Wiley-VCH, Weinheim, Germany, 1997.
5. Iwamoto K I, Hamaya M, Hashimoto N, Kimura H, Suzuki Y and Sato M, *Tetrahedron Lett.*, 2006, **46**, 7175.
6. Enders D and Kallfass U, *Angew Chem Int Ed.*, 2002, **41**, 1743.
7. Hachisu Y, Bode J W and Suzuki K, *J Am Chem Soc.*, 2003, **125**, 8432.
8. Tachibana Y, Kihara N and Takata T, *J Am Chem Soc.*, 2004, **126**, 3438.
9. Linghu X, Bausch C C and Johnson J S, *J Am Chem Soc.*, 2005, **127**, 1833.
10. Enders D, Breuer K, Kallfass U and Balensiefer T, *Synthesis*, 2003, **8**, 1292.
11. Knight R L and Leeper F J, *J Chem Soc Perkin Trans 1*, 1998, **12**, 1891.
12. Bausch C C and Johnson J S, *J Org Chem.*, 2004, **69**, 4283.
13. Demir A S and Reis O, *Tetrahedron*, 2004, **60**, 3803.
14. Kiasat A R and Sayyahi S, *Catal Commun.*, 2010, **11**, 484.
15. Sayyahi S and Saghanezhad J, *Chin Chem Lett.*, 2011, **22**, 300.