Synthesis of orthoaminocarbonitrile tetrahydronaphthalenes catalyzed by butyl-3-methylimidazolium hexafluorophosphate ionic liquid base catalyst

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ABSTRACT
In this research, the treatment of cyclohexanone, malononitrile, and aromatic aldehydes was carried out for the successful synthesis of orthoaminocarbonitrile tetrahydronaphthalenes by using butyl-3-methylimidazolium hexafluorophosphate as a base catalyst. In this protocol, the target products were obtained in high to excellent yields between 85% and 95% and short reaction times between 10 and 20 min under mild conditions. All products were identified by the melting points, FT-IR, and \(^1\)H NMR techniques.

GRAPHICAL ABSTRACT

ARTICLE HISTORY
Received 31 July 2022

KEYWORDS
Catalyst; cyclohexanone; ionic liquid; synthesis; tetrahydronaphthalenes

Introduction

Multicomponent reactions (MCRs) are essential synthetic methods in organic chemistry, medicinal chemistry, drug discovery programs, combinational chemistry, natural
product synthesis, agro chemistry, and polymer chemistry. MCRs develop when three or more raw materials react to produce a product with more atoms replaced by new ones.

Among the naturally occurring bioactive chemicals, the heterocyclic skeletons exist rather abundantly. The heterocyclic compounds account for over half of all known organic substances. These amazing organic molecules are important structural components of a broad range of medicinal molecules, vitamins, and bioactive substances including antiviral, antimalarial, anti-tumor, anti-depressant, anti-HIV, and other drugs. The important chemical compounds produced from benzaldehyde, cyclic ketones, and malononitrile are diverse derivatives of bicyclic orthoaminocarbonitrile.

Orthoaminocarbonitriles are also important intermediates for the preparation of various heterocyclic compounds and have two chiral centers exhibiting optical activity. Several bioactive molecules contain tetrahydronaphthalene nuclei, effectively preparing anti-depressants and anti-cancer agents.

Several compounds and ionic liquids are applied as reagents and catalysts such as; N-butylypyridinium tetrafluoroborate (BPy)BF₄, triethylammonium acetate (TEAA), imidazole, borax, [Co(TPPASO₃H)]Cl, ortho-benzene disulfonimide (OBS) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]). All of the synthetic substances regarding the aforementioned processes have benefits, but they also have some disadvantages for example; extended reaction times, limited yields, and substantial reaction work-up.

Salt in a liquid condition is known as an ionic liquid. The essential advantages of ionic liquids include non-volatility. Furthermore, applications of ionic liquids as solvents or catalysts in multicomponent reactions are very important because they have low vapor pressure and are biodegradable and they have a broad array of applications. They are strong solvents that can also serve as electrolytes due to their low vapor pressure, salts that are liquid at near-ambient temperatures are essential for electric battery applications.

Recently, it was reported a chemical reaction for the synthesis of orthoaminocarbonitrile tetrahydronaphthalenes under mild conditions. Also, Zhang et al. in 2015 synthesized D-glucopyranosyl bromide.

In this research, the authors attempt to examine the performance of butyl-3-methyl imidazolium hexafluorophosphate as a homogeneous catalyst in multicomponent reactions with high efficiency and short reaction times. The reaction of cyclohexanone with malononitrile followed by the addition of aromatic aldehydes and malononitrile yielded one-pot ortho aminocarbonitrile tetrahydronaphthalenes under mild conditions.

**Results and discussion**

This research describes the multicomponent treatment of cyclohexanone, malononitrile, and aromatic aldehydes in a process to yield orthoaminocarbonitrile tetrahydronaphthalenes with excellent efficiency and short reaction times. This reaction was carried out in
the presence of butyl-3-methylimidazolium hexafluorophosphate as an effective homogeneous catalyst (Scheme 1).

The various solvents, catalysts, and temperatures were investigated to determine the best conditions for this procedure. The reaction was tested at ambient temperatures (Table 1) and under reflux conditions (Table 2, entry 1) for the first time, but the product yield was low. Then, various catalysts were used in the reaction and the related results are indicated in Table 2. A minimal amount of product was observed in the presence of an acidic catalyst such as; HCl and P-TSA (Table 2, entries 2 and 3). The reaction efficiencies increased using the basic catalysts and ionic liquids such as; BMIM.BF4, BMIM.PF6, Et3N, guanidine, morpholine, and NaOH (Table 2). Among them, the BMIM.PF6 ionic liquid significantly increased the reaction interval and decreased the reaction time.

Also, the reaction was tested in a variety of solvents including ethanol, chloroform, dichloromethane, methanol, and acetonitrile to find the optimal reaction conditions. It was found that the ethanol solvent is the best convenient solvent for this reaction. Thus, the reactions were investigated in ethanol under reflux and room temperature conditions by using an ionic liquid as a catalyst. It was found that the reaction using BMIM.PF6 ionic liquid under reflux conditions has the best results.

**Scheme 1.** Synthesis of orthoaminocarbonitrile tetrahydronaphthalene catalyzed by ionic liquid.

**Table 1.** Study the solvent role for the synthesis of orthoaminocarbonitrile tetrahydronaphthalenea.

| Entry | Solvent     | Temp. (°C) | Time (min) | Yield (%) |
|-------|-------------|------------|------------|-----------|
| 1     | Chloroform  | 25         | 40         | 75        |
| 2     | Dichloromethane | 35      | 45         | 78        |
| 3     | Methanol    | 50         | 35         | 89        |
| 4     | Acetonitrile| 60         | 50         | 75        |
| 5     | Ethanol     | 75         | 15         | 95        |
| 6     | Ethanol     | 80         | 30         | 95        |

*aReaction conditions: cyclohexanone (1 mmol), malononitrile (2 mmol), benzaldehyde (1 mmol), BMIM.PF6 (0.3 mmol).

**Table 2.** Illustrates the catalytic activity of orthoaminocarbonitrile tetrahydronaphthalene synthesisb.

| Entry | Catalyst    | Catalyst amount (mmol) | Time (h) | Yield (%) |
|-------|-------------|------------------------|----------|-----------|
| 1     | None        | 0.1                    | 24       | 10        |
| 2     | P-TSA       | 0.1                    | 24       | 5         |
| 3     | HCl         | 0.1                    | 24       | 7         |
| 4     | NaOH        | 0.1                    | 1.5      | 50        |
| 5     | Et3N        | 0.1                    | 1        | 70        |
| 6     | Pyridine    | 0.1                    | 1        | 65        |
| 7     | Guanidine   | 0.1                    | 0.5      | 80        |
| 8     | Morpholine  | 0.1                    | 1        | 76        |
| 9     | BMIM.BF4    | 0.1                    | 0.5      | 85        |
| 10    | BMIM.PF6    | 0.5                    | 0.5      | 90        |
| 11    | BMIM.PF6    | 0.3                    | 0.5      | 95        |

*bReaction conditions: cyclohexanone (1 mmol), malononitrile (2 mmol), benzaldehyde (1 mmol), solvent (5 mL).*
After optimization of the reaction conditions, the best conditions for the synthesis of orthoaminocarbonitrile tetrahydronaphthalene from cyclohexanone (1 mmol), malononitrile (2 mmol), and benzaldehyde (1 mmol) by using BMIM.BF₄ catalyst in ethanol solvent under reflux conditions at 10–20 min were considered. As a result, orthoaminocarbonitrile tetrahydronaphthalene derivatives were synthesized in 85–95% yields at 10–20 min under reflux conditions (Table 3).

Table 4 shows the results of the comparison of the performance of the BMIM.PF₆ catalyst with the applications of the stated catalysts. The BMIM.PF₆ catalyst outperforms the other used catalysts as can be seen in Table 4, entry 5. The BMIM.PF₆ as a hydrophobic and water-insoluble ionic liquid produced the best results in 95% efficiency at 10 min.

A plausible reaction mechanism for the synthesis of tetrahydronaphthalene is shown in Scheme 2. At first, the butyl-3-methylimidazolium hexafluorophosphate as a base catalyst causes the acidic hydrogen separate from malononitrile. Then, the resulting carbanion is attacked by the carbonyl group of cyclohexanone, and the A intermediate is obtained which results in the B intermediate through the loss of a water molecule. The tautomerization of B led to C intermediate. On the other hand, similarly, the treatment of malononitrile with an aromatic aldehyde produces the D intermediate. Finally, the C reacts with D through a Diels–Alder reaction to form an E intermediate via tautomerization resulting in F as a target product.

**Experimental**

All of the chemical ingredients and solvents used in this study were provided by Merck and Aldrich Chemical Companies. The starting materials including cyclohexanone, aromatic aldehyde, and BMIM.PF₆ were purchased from Sigma and the malononitrile and ethanol from Merck Chemical Company. The IR spectra were obtained as KBr pellets on a Perkin Elmer 781 spectrophotometer and on an Impact 400 Nicolet FT-IR spectrophotometer. The ¹H NMR spectra were recorded in DMSO-d₆ solvents on a Broker DRX-400 spectrometer with tetramethylsilane (TMS) as the internal reference. Melting points were obtained with a Yanagimoto micro melting point and uncorrected. Determination of the substrate and reaction monitoring was accomplished by TLC on silica-gel polygram SILG UV 254 plates (from Merck Company).

**General procedure for the synthesis of orthoaminocarbonitrile tetrahydronaphthalenes**

In a 50 mL flask with a circular bottom, cyclohexanone (0.1 mL, 1 mmol) and malononitrile (0.06 g, 1 mmol) in 5 mL of ethanol solvent were mixed to make orthoaminocarbonitrile under reflux conditions. After 10 min, the reaction mixture was mixed with 0.3 mmoles of butyl-3-methylimidazolium hexafluorophosphate ionic liquid (0.06 mL, 0.3 mmol), aromatic aldehyde (1 mmol), and malononitrile (0.06 mg, 1 mmol). Thin layer chromatography (TLC) is used to determine the response of the reaction. When the reaction was completed, then cooled to room temperature, filtered, and rinsed in a mixture of distilled water and ethanol (1:1 ratio). The crude products were recrystallized in ethanol solvent to give the pure products. The
| Compound | R      | Yield (%) | Time (min) | M.p (°C) | TON | TOF (h⁻¹) |
|----------|--------|-----------|------------|----------|-----|-----------|
| 4a       | H      | 95        | 10         | 255-256  | 9.5 | 59.4      |
| 4b       | 2-Cl   | 92        | 15         | 282-284  | 9.2 | 36.8      |
| 4c       | 2-NO₂  | 85        | 20         | 245-247  | 8.5 | 25.7      |
| 4d       | 4-F    | 94        | 20         | 264-266  | 9.4 | 28.4      |
| 4e       | 4-NMe₂ | 91        | 15         | 262-264  | 9.1 | 36.4      |
| 4f       | 4-Me   | 90        | 20         | 235-237  | 9.0 | 27.2      |
| 4g       | 3-Br   | 93        | 15         | 251-254  | 9.3 | 37.2      |
| 4h       | 4-Cl   | 95        | 10         | 247-249  | 9.5 | 59.3      |
| 4i       | 4-OH   | 93        | 20         | 239-240  | 9.3 | 28.1      |
| 4j       | 3,4,5-tri-OMe | 89   | 15         | 233-235  | 8.9 | 35.6      |
| 4k       | 3,4-dimethoxy | 90    | 15         | 288-290  | 9.0 | 36.0      |
| 4l       | 2,4-di-Cl | 94  | 15         | 257-259  | 9.4 | 37.6      |

*a* Reaction conditions: cyclohexanone (1 mmol), malononitrile (2 mmol), benzaldehyde (1 mmol), BMIM.PF₆ (0.1 mmol), ethanol solvent (5 ml), reflux.

*b* Isolated yield.
obtained products were characterized by spectroscopic data such as; FT-IR, $^1$H NMR, and the melting points of known compounds are compared with authentic samples$^{[2,15,21,25,26]}$ the related data are reported in the Supporting Information.

2-Amino-4-phenyl-4a,5,6,7-tetrahydronaphthalene-1,3,3(4H)-tricarbonitrile (4a); White solid; mp: 255–256 °C, (mp: 255–257 °C) Lit.$^{[2]}$ IR (KBr) $v$: 3417, 3338, 2931, 2865, 2208, 1646, 1599, 1496, 1391, 1275, 1037, 713, 579 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 0.81–0.91 (m, 1H), 1.38–1.52 (m, 2H), 1.62–1.72 (m, 1H), 1.98–2.12 (m, 1H), 2.14–2.25 (m, 1H), 2.72–2.88 (m, 1H), 3.54 (d, $J = 12.0$ Hz, 1H), 5.73 (t, 1H), 7.38 (s, 2H), 7.43 (s, 3H), 7.48–7.62 (m, 2H).

2-Amino-4-(2-nitrophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4H)-tricarbonitrile (4c); Cream solid; mp: 245–247 °C, IR (KBr) $v$: 3444, 3356, 2860, 2215, 1626, 1525, 1443, 1354, 1269, 1045, 726, 507 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 0.98–1.07 (m, 1H),

Table 4. Comparison of the catalytic activity of the BMIM.PF$_6$ as a base catalyst (10 mol %) with other reported catalysts.

| Entry | Catalyst (conditions) | Time (min) | Yield$^a$ (%) | Ref. |
|-------|-----------------------|------------|---------------|------|
| 1     | DDIL (20 mol%, H$_2$O, RT, U.S) | 15         | 86            | [25] |
| 2     | [Bmim-G][Br] (10 mol %, solvent-free, RT) | 360        | 83            | [15] |
| 3     | Morpholine (0.1 mmol, ethanol, RT) | 45         | 95            | [18] |
| 4     | [BPy][BF$_4$] (2 mL, 60 °C) | 300        | 83            | [15] |
| 5     | BMIM.PF$_6$ (0.3 mmol, ethanol, reflux) | 10         | 95            | This work |

$^a$Isolated yield.

Scheme 2. Proposed reaction mechanism for synthesis of orthoaminocarbonitrile tetrahydro-naphthalene.

Table 4. Comparison of the catalytic activity of the BMIM.PF$_6$ as a base catalyst (10 mol %) with other reported catalysts.
1.45–1.52 (m, 2H), 1.69–1.73 (m, 1H), 2.04–2.26 (m, 2H), 2.96–3.08 (m, 1H),
4.03–4.11 (d, J = 12 Hz, 1H), 5.79 (s, 1H), 7.45 (s, 2H), 7.75 (t, 1H), 7.92 (t, 1H),
3.02 (d, J = 8.0 Hz 1H), 8.09 (d, J = 8.0 Hz, 1H).

Conclusions

In this protocol, cyclohexanone, malononitrile, and aromatic aldehydes were treated
一起得到产物。三者反应的产物为对氨基碳酰亚胺四氢萘。丁基-3-
methylimidazoliumhexafluorophosphate ionic liquid 作为催化剂
was employed in this reaction as an effective, convenient, and basic homogeneous
catalyst to yield the products in high to excellent efficiency and minimal reaction
times. In addition to the simplicity of the reaction and workup, the thermal stability
and non-volatility are two advantages of this low vapor pressure ionic liquid as a cata-
lyst. Furthermore, to improve the reaction conditions, an attempt was made to use
ethanol as a green solvent as a novelty in this work.

Full experimental details are included in the IR and 1H NMR spectra. This material
can be found via the “Supplementary Content” section of this article’s webpage.

Disclosure statement

Ionic liquids (ILs) have engrossed comprehensive research concerns as environmentally
safe solvents due to their particular characteristics such as indiscernible vapor pressure,
fast liquid range, non-inflammability, and excellent thermal stability. Ionic liquids have
been extensively applied in reactions as catalysts.

In this study, orthoaminocarbonitrile tetrahydroxaphthalene compounds were synthe-
sized using butyl-3-methylimidazolium hexafluorophosphate as a homogeneous base
catalyst in high efficiency and short reaction time. This reaction was carried out through
a multicomponent reaction between cyclohexanone, malononitrile, and aromatic alde-
hydes under mild conditions.

Funding

The present work was funded by the University of Kashan [159148/91].

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