

Novel Synthetic Approach to Ionic Liquids: 1-Butyl-3-Methylimidazolium Perchlorate[bmim]ClO₄/1-Butyl-3- Methylimidazolium Hydroxide [bmim]OH

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ABSTRACT: Anion exchange of halide-based ionic liquid precursors with suitable inorganic/organic salts utilizing a mechanochemical/grinding methodology was used to create novel ionic liquids (1-butyl-3-methylimidazolium perchlorate[bmim]ClO₄ and 1-butyl-3-methylimidazolium hydroxide [bmim]OH) in a straightforward and effective metathesis process. The intended ionic liquids were produced in high purity and good yields from the metathesis processes, which were conducted at mild reaction conditions. Effective anion substitution was made possible by the creation and elimination of insoluble by-products, which made the process extremely selective and safe for the environment. Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (¹H, ¹³C NMR and Mass) spectroscopy were used to analyze the produced ionic liquids, confirming effective anion exchange and structural integrity.

KEYWORDS: Ionic liquids, green solvent, grinding, catalysis

I. INTRODUCTION

The goal of the multidisciplinary field of "green chemistry" is to reduce the use of dangerous chemicals and to promote environmentally friendly substitutes for traditional chemical processes and products [1-4]. With a focus on its contribution to the advancement of sustainable chemical synthesis, analytical techniques, and industrial practices, this review offers a thorough examination of the basic ideas, historical evolution, and real-world applications of green chemistry. Green chemistry,

which had its roots in the environmental movement of the 1960s, which was sparked by Rachel Carson's "Silent Spring," was formally formed in the 1990s by Paul Anastas and John C. Warner's 12 principles [5-8]. These guidelines place a strong emphasis on using renewable raw materials, cutting back on dangerous chemicals, preventing waste, and the atomic economy. Green chemistry has a big impact on industries including education, cosmetics, and medicines. It promotes safer, more ecologically friendly analytical techniques in the pharmaceutical sector. Biodegradable products are advantageous to the cosmetics industry, and educational institutions use sustainable laboratory and waste management techniques. Global awareness of green chemistry has increased because to international conferences and scholarly publications, which support sustainability objectives like avoiding waste, maximizing resource usage, and lowering environmental consequences.

Every year, over 20 million tons of solvents are leaked into the environment. About 80% of the total volume of chemicals used in chemical synthesis are solvents. Because solvents are frequently poisonous or combustible, sustainable solvents must be used in place of conventional solvents. Modern sustainable solvents assist catalysts effectively and are easily recovered and repurposed. These include the use of deep eutectic solvents, glycerol, polyethylene glycol, ionic liquids, , supercritical liquid, CO₂ and ionic liquids (ILs) [11-17], a novel family of solvents made entirely of ions, usually organic cations combined with organic or inorganic anions,

have completely transformed the fields of chemistry and materials science. Paul Walden created ethylammonium nitrate, the first room-temperature ionic liquids (RTILs), more than a century ago, which was a major turning point in the investigation of unconventional solvents. One Walden ascribed this ionic compound's exceptionally low melting point (13–14 °C) to the bigger organic cation's lower degree of ion association. Because of their remarkable qualities and revolutionary potential, this groundbreaking discovery generated ongoing interest in the research and development of ILs. With important benefits including minimal volatility, high thermal stability, broad electrochemical windows, and recyclability, ionic liquids are regarded as "designer catalysts" and are therefore environmentally friendly substitutes for volatile organic solvents. They are excellent in biomedicine (drug delivery, antimicrobials), separation procedures, electrochemistry (batteries, supercapacitors, solar cells), and catalysis. High viscosity, production costs, and possible toxicity are obstacles, though, which is why third- and fourth-generation ionic liquids and hybrid materials are being developed for better performance and sustainability.

The capacity of ILs to maintain their liquid state at low temperatures is one of their most distinctive properties; this property makes its special ionic interactions. ILs are ideal for a variety of cutting-edge applications due to their liquid form, which allows them to exhibit several special qualities like low vapor pressure, great heat stability, and adjustable viscosity.

Researchers can create ILs with customized properties to meet certain problems by carefully choosing and combining cations and anions; this adaptability has earned them the moniker "designer solvents." These characteristics are particularly useful in disciplines like chemical synthesis, catalysis, and energy storage that need for accuracy and flexibility.

1-Butyl-3-methylimidazolium salts are among the earliest ionic liquids to be produced and investigated for their potential uses in electrical, thermal, and catalytic processes, as well as biological use. It is generally known that [bmim]salts suspended with Nobel metals such as Pd, Rh, Ir, and Ru have superior catalytic activity and are recyclable [18-22]. They have also been used as a support matrix in enzyme catalysis. It has been observed that the ionic liquid's counter anion is essential to catalytic efficiency. This literature is limited to the use of [bmim] as a catalyst solvent or co-solvent in organic catalytic applications. The

most extensively researched ionic liquids in this class for their organic synthesis applications are all of the [bmim] salts, [bmim]PF₆ [bmim] BF₄.

Researchers in synthetic chemistry are always coming up with new reagents and catalysts to perform chemical reactions. Solvent-free synthetic processes are becoming more and more popular in the synthesis of pharmacologically significant heterocyclic compounds due to their ease of use and low production costs. However, the mechanochemical method has become more well-liked because to its low environmental impact and low cost [23-32]. Its ease of use, unique reaction profile, and potential for larger-scale application with the appropriate experimental setup, mechanical grinding has become an essential tool in the synthetic organic chemistry paradigm.

II. RESULTS AND DISCUSSION

As illustrated in Scheme 1, herein, we reported using metathesis and a grinding technique to prepare the two ionic liquids (1-butyl-3-methylimidazolium perchlorate [bmim]ClO₄ and 1-butyl-3-methylimidazolium hydroxide [bmim]OH) in this brief message. The matching halide-based ionic liquid precursors and the desired inorganic/organic salt containing the target anion underwent a metathesis reaction to successfully create the target ionic liquids. Under mild reaction conditions, the metathesis strategy demonstrated is straightforward, effective, and high-yielding method for anion exchange that produced the necessary ionic liquids.

Scheme 1. Synthesis of ILs using grinding approach

The reactions were typically carried out in polar aprotic solvents such as acetonitrile or dichloromethane, facilitating effective ion exchange. The formation of an insoluble inorganic salt (e.g., MX) acted as the driving force for the reaction, allowing easy separation of the product by filtration. After solvent removal and purification, the ionic liquids were obtained as clear viscous liquids. Overall yields ranged from 68% (4a) and 75% (4b), indicating the high efficiency of the metathesis process. The absence of starting halide ions in the final products, as confirmed by qualitative halide tests, demonstrated the completeness of the anion exchange. FT-IR spectra of the synthesized ionic liquids showed

characteristic absorption bands corresponding to both the organic cation and the exchanged anion. The disappearance of bands associated with halide-containing precursors and the emergence of new bands attributable to the target anions confirmed successful metathesis. Typical bands observed include: C–H stretching vibrations of alkyl chains in the range of 2850–3150 cm^{-1} . C–N or C=N stretching vibrations of the cationic moiety around 1600–1650 cm^{-1} . Anion-specific bands, such as S=O stretching (for sulfonate-based anions) or P–F stretching (for fluorinated anions), appearing in the expected regions. These spectral features are consistent with the proposed ionic liquid structures. ^1H and ^{13}C NMR spectra further confirmed the successful synthesis of the ionic liquids. The chemical shifts and splitting patterns correspond well with the expected structures of the cationic frameworks. No residual peaks associated with halide precursors were observed, indicating high purity. Compared to direct synthesis methods, metathesis allows greater flexibility in designing ionic liquids with tailored properties by simply varying the anion. This makes the approach particularly suitable for developing task-specific ionic liquids for catalytic, electrochemical, or separation applications. The synthesized ionic liquids show physicochemical properties comparable to or better than previously reported ionic liquids with similar cationic frameworks. The ability to fine-tune properties such as viscosity and thermal stability by anion selection highlights the versatility of the metathesis method. The results confirm that metathesis is a reliable and scalable synthetic route for producing novel ionic liquids with controlled composition and desirable performance characteristics.

III. CONCLUSION

In summary, two ionic liquids were successfully synthesized via the metathesis method using grinding approach with high yields and purity. Spectroscopic and thermal analyses confirmed the successful anion exchange and structural integrity of the products. The observed physicochemical properties suggest that these ionic liquids hold significant potential for advanced applications in green chemistry and materials science, useful for synthetic applicability in organic synthesis.

Experimental Section

Step-A

In a dry flask 1-methylimidazole (1) (4.1gm, 50mmol) and 1.2 equivalents of butyl bromides (6.5 ml, 60 mmol) (2) was added, sealed

and heated in an oil bath maintained at 120 °C for 20 minutes and cooled down to room temperature. Further, the reaction mixture was heated at same temperature (120 °C) for 10 minutes, and then cooled down to room temperature. The obtained ionic liquid was washed several times with ethyl acetate (5×25 mL) to remove the unreacted starting materials, dried under vacuum to give 1-butyl-3-methylimidazolium bromide (3.9gm) (3) and characterized.

Step-B

Metathesis reaction:

Synthesis of 1-butyl-3-methylimidazoliumhydroxide[bmim]OH (4a):

[bmim]Br (3, 5.0g, 22.8 mmol) was dissolved in methanol, and Amberlyst A-26 (30 mmol) was added and grinding was done for 6 h. The reaction mixture was then filtered through funnel. Solvent was evaporated with rotary evaporator and the product was dried under high vacuum.

Synthesis of 1-butyl-3-methylimidazoliumperchlorate-[bmim]ClO₄

(4b):

[bmim]Br (3, 5.0 g, 22.8 mmol) was dissolved in methanol, and sodium perchlorate (3.7g, 30 mmol) was added and grinding was done for 4 h. The reaction mixture was then filtered through funnel. Solvent was evaporated with rotary evaporator and the product was dried under high vacuum.

REFERENCES

- [1]. Kurul, F., Doruk, B., and S. N. Topkaya. (2025) Principles of green chemistry: building a sustainable future. *Discov. Chem.*, 2, 68. <https://doi.org/10.1007/s44371-025-00152-9>
- [2]. de Marco, B. A., Rechelo, B. S., Tófoli, E. G., Kogawa, A. C., Salgado, and H. R. N. (2019) Evolution of green chemistry and its multidimensional impacts: A review. *Saudi Pharm. J.*, 27(1), 1-8. <https://doi.org/10.1016/j.jsps.2018.07.011>.
- [3]. Ganesh, K. N., Zhang, D., Miller, S. J., Rossen, K., Voutchkova-Kostal, A. M. et al. (2021) Green Chemistry: A Framework for a Sustainable Future. *Org. Process Res. Dev.*, 25(7), 1455–1459. <https://doi.org/10.1021/acs.oprd.1c00216>
- [4]. Hessel, V., Tran, N. N., Asrami, M. R., Tran, Q. D., Van Duc Long, N., Escrivà-Gelonch, M., Tejada, J. O., Linke, S., and Sundmacher, K. (2022) Sustainability of

- green solvents – review and perspective. *Green Chem.* 24, 410-437, <https://doi.org/10.1039/D1GC03662A>
- [5]. Wagare, D. S., Shirsath, S. E., Shaikh, M. et al. (2021) Sustainable solvents in chemical synthesis: a review. *Environ Chem. Lett.*, 19, 3263–3282. <https://doi.org/10.1007/s10311-020-01176-6>
- [6]. Alreshidi, M. A., Yadav, K. K., Gunasekaran, S., Gacem, A., Sambandam, P. G. Etal. (2025) A review on the evolution of ionic liquids: Sustainable synthesis, applications, and future prospects. *Materials Today Sustainability* 31, 101160. <https://doi.org/10.1016/j.mtsust.2025.101160>
- [7]. Al-Bodour, A., Alomari, N., Perez-Duran, G., Rozas, S., Iglesias-Silva, G., Aparicio, S., Gutierrez-Vega, A., and Atilhan, M. (2025) Ionic Liquids as Multidimensional Materials: A Review from Fundamentals to Applications. *Energy Fuels*, 39(27), 12791–12829. <https://doi.org/10.1021/acs.energyfuels.5c01280>
- [8]. Zhuo, Y., Cheng, H.-L., Zhao, Y.-G., and Cui, H.-R. (2024) Ionic Liquids in Pharmaceutical and Biomedical Applications: A Review. *Pharmaceutics* 16, 151. <https://doi.org/10.3390/pharmaceutics16010151>
- [9]. Pereira, J., Souza, R., and Moita, A. (2024) A Review of Ionic Liquids and Their Composites with Nanoparticles for Electrochemical Applications. *Inorganics* 12, 186. <https://doi.org/10.3390/inorganics12070186>
- [10]. Yadav, S., Baweja, K., Kumar, C. et al. (2024) A Review: Applications of Ionic Liquids in Medicinal Chemistry. *Chemistry Africa* 7, 2975–2988. <https://doi.org/10.1007/s42250-024-00960-z>
- [11]. Lei, Z., Dai, C., Hallett, J., and Shiflett, M. (2024) Introduction: Ionic Liquids for Diverse Applications. *Chem. Rev.*, 124(12), 7533–7535. <https://doi.org/10.1021/acs.chemrev.4c00291>
- [12]. Matuszek, K., Piper, S. L., Brzeczek-Szafran, A., Roy, B., Saher, S., Pringle, J. M., and MacFarlane, D. R. (2024) Unexpected Energy Applications of Ionic Liquids. *Adv. Mater.*, 36(23), 2313023. <https://doi.org/10.1002/adma.202313023>
- [13]. Hu, Y., Xing, Y., Yue, H., Chen, T., Diao, Y., Wei, W., and Zhang, S. (2023) Ionic liquids revolutionizing biomedicine: recent advances and emerging opportunities. *Chem. Soc. Rev.*, 52, 7262-7293. DOI: [10.1039/D3CS00510K](https://doi.org/10.1039/D3CS00510K)
- [14]. Ferreira, B. L., Granato, D., and Nunes, I. L. (2023) Uses of ionic liquids to obtain bioactive compounds: insights from the main international regulations for technological applications. *Critical Reviews in Food Science and Nutrition*, 63(28), 9217–9232. <https://doi.org/10.1080/10408398.2022.2067115>
- [15]. Kaur, G., Kumar, H., and Singla, M. (2022) Diverse applications of ionic liquids: A comprehensive review. *J. Mol. Liq.*, 351, 118556. <https://doi.org/10.1016/j.molliq.2022.118556>
- [16]. Pešić, J., Watson, M., Papović, S., and Vraneš, M. (2021) Ionic Liquids: Review of their Current and Future Industrial Applications and their Potential Environmental Impact. *Recent Pat. Nanotechnol.*, 15(3), 225-244. doi: 10.2174/1872210513999190923121448
- [17]. Welton, T. (2018) Ionic liquids: a brief history. *Biophys. Rev.*, 10, 691–706. <https://doi.org/10.1007/s12551-018-0419-2>
- [18]. Lei, Z., Chen, B., Koo, Y.-M., MacFarlane, D. R. (2017) Introduction: Ionic Liquids. *Chem. Rev.*, 117(10), 6633–6635. <https://doi.org/10.1021/acs.chemrev.7b00246>
- [19]. Vekariya, R. L. (2017) A review of ionic liquids: Applications towards catalytic organic transformations, *J. Mol. Liq.*, 227, 44-60. <https://doi.org/10.1016/j.molliq.2016.11.123>
- [20]. Shamshina, J. L., and Rogers, R. D. (2023) Ionic Liquids: New Forms of Active Pharmaceutical Ingredients with Unique, Tunable Properties. *Chem. Rev.*, 123(20), 11894–11953. <https://doi.org/10.1021/acs.chemrev.3c00384>
- [21]. Ho, T.-L., Fieser, M., and Fieser, L. (2006) 1-Butyl-3-methylimidazolium salts (bmim). Fieser and Fieser's Reagents for Organic Synthesis. <https://doi.org/10.1002/9780471264194.fos02085>
- [22]. Gruzdev, M. S., Ramenskaya, L. M., Chervonova, U. V. et al. (2009) Preparation

- of 1-butyl-3-methylimidazolium salts and study of their phase behavior and intramolecular interactions. *Russ. J. Gen. Chem.*, 79, 1720–1727. <https://doi.org/10.1134/S1070363209080246>
- [23]. Swapnil, A., Dharaskar, Kailas Wasewar, L., Varma, M. N., Shende, D. Z., and Yoo, C. (2016) Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel. *Arab. J. Chem.*, 9(4), 578-587. <https://doi.org/10.1016/j.arabjc.2013.09.034>
- [24]. Tanaka, K., and Toda, F. (2000) Solvent-free organic synthesis. *Chem. Rev.*, 100(3), 1025-1074. <https://doi.org/10.1021/cr940089p>
- [25]. Li, M-Y., Gu, A., Li, J., and Liu, Y. (2025) Advanced green synthesis: Solvent-free and catalyst-free reaction. *Green Synthesis and Catalysis*, 6(1),36-66. <https://doi.org/10.1016/j.gresc.2024.11.001>
- [26]. Zangade, S., and Patil, P. (2019) A review on solvent-free methods in organic synthesis. *Curr. Org. Chem.*, 23(21), 2295-2318. DOI:10.2174/1385272823666191016165532
- [27]. Wang, G-W. (2013) Mechanochemical organic synthesis. *Chem. Soc. Rev.*, 42, 7668-7700. <https://doi.org/10.1039/C3CS35526H>
- [28]. Jean-Louis, D., and Tomislav, F. (2017) Mechanochemistry: A force of synthesis. *ACS Cent. Sci.*, 3(1), 13-19. <https://doi.org/10.1021/acscentsci.6b00277>
- [29]. Kishore, K., Sinha, M. K., Singh, A., Archana, R., Gupta, M. K., and Korkmaz, M. E. (2022) A comprehensive review on the grinding process: Advancements, applications and challenges. *Proceed. Institution Mechanical Engineer. Part C: J. Mechan. Engineer. Sci.*, 236(22), 10923-10952. DOI:10.1177/09544062221110782
- [30]. Leonardi, M., Villacampa, M., and Menéndez, J. C. (2018) Multicomponent mechanochemical synthesis. *Chem. Sci.*, 9, 2042-2064. <https://doi.org/10.1039/C7SC05370C>
- [31]. Ardila-Fierro, K. J., and Hernandez, J. G. (2021) Sustainability assessment of mechanochemistry by using the twelve principles of green chemistry. *ChemSusChem*, 14, 2145-2162. <https://doi.org/10.1002/cssc.202100478>
- [32]. Friščić, T., Mottillo, C., and Titi, H. M.(2020) Mechanochemistry for synthesis. *Angew. Chem. Int. Ed. Engl.*, 59(3), 1018-1029. <https://doi.org/10.1002/anie.201906755>