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Letter

Green SN2: A Novel Ionic Liquid-Mediated Finkelstein Reaction for Safer, Superior Alkyl Halide Synthesis in Undergraduate Organic Chemistry

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Abstract

We present the development of a novel, environmentally friendly Finkelstein reaction conducted in ionic liquids, which provides a safer and more efficient alternative to the conventional halide exchange reaction employing sodium bromide in sulfuric acid. By leveraging the unique properties of ionic liquids—including high thermal stability, negligible vapor pressure, and tunable solvation characteristics—this new methodology enables an SN2 mechanism under significantly milder conditions, while achieving superior yields and selectivity. Comparative studies demonstrate that the ionic liquid-mediated process not only minimizes the generation of hazardous byproducts and corrosive waste but also enhances reaction reproducibility and efficiency. The improved safety profile and operational simplicity of this approach render it particularly suitable for incorporation into undergraduate organic chemistry curricula, where it serves as an effective pedagogical tool for illustrating SN2 kinetics, stereochemical inversion, and the principles of green chemistry. The reaction provides excellent yields (up to 93%) with high product purity, as confirmed by NMR and mass spectrometry. Additionally, the method is cost-effective due to the recyclability of ionic liquids and is scalable, offering advantages for both small-scale academic laboratories and larger-scale synthesis. Consequently, this synthetic strategy holds significant promise for broader adoption within the synthetic organic community.

Keywords

Ionic Liquids, Green Finkelstein Reaction, SN2 Mechanism, Undergraduate Organic Chemistry, Halide Exchange, Green Chemistry, Nucleophilic Substitution, Sustainable Synthesis, Solvent Effects, Pedagogical Laboratory Experiment

1. Introduction

Halide exchange reactions are fundamental to organic synthesis and are frequently utilized in undergraduate laboratories to illustrate the principles of the SN2 reaction mechanism [1-3]. The conventional Finkelstein reaction, which typically employs NaBr in concentrated H₂SO₄, effectively demonstrates nucleophilic substitution; however, its applica-

tion in educational laboratories is often limited by safety concerns, harsh reaction conditions, and the generation of corrosive byproducts, including hydrobromic acid (HBr) and sulfur dioxide (SO₂), which pose significant safety risks and contribute to environmental toxicity [1-4]. These challenges have prompted educators and researchers to investigate

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greener and safer alternatives that preserve the pedagogical value of demonstrating SN2 reactivity while mitigating associated hazards.

Ionic liquids (ILs) have emerged as a promising medium for organic transformations due to their unique physicochemical properties, including negligible vapor pressure, high thermal stability, and potential for structural modification [5, 6], as recently reviewed in the context of green synthetic design and material innovation [21-23]. Recent studies have highlighted the efficacy of ILs in facilitating various reaction pathways, including halide exchange processes, under mild conditions [7, 8]. In this context, we present a novel "Green Finkelstein Reaction" that employs a tailored ionic liquid system as a substitute for the traditional NaBr/H₂SO₄ methodology. Our approach not only enhances reaction yield and selectivity but also significantly improves operational safety and environmental sustainability. Furthermore, the low solvent consumption and recyclability of the ionic liquids make this approach cost-effective and suitable for scale-up in academic or industrial settings.

The newly developed protocol capitalizes on the enhanced solvation and ion mobility characteristics of the ionic liquid to facilitate efficient halide exchange via an SN2 mechanism under considerably milder conditions [9, 10], supported by investigations into ion mobility and dynamic behavior in ionic liquid media [24]. Comparative studies indicate that the IL-mediated reaction yields alkyl iodides with superior yields and reduced byproduct formation compared to the classical method [10, 11] on ionic liquids in sustainable synthesis [16, 19]. Additionally, the recyclability and low toxicity of the ionic liquid underscore its suitability for implementation in educational settings [12, 13], consistent with recent toxicological assessments [25]. These characteristics are particularly advantageous in an educational context, where safety and reproducibility are paramount, facilitating the demonstration of SN2 kinetics and stereochemical inversion without exposing students to hazardous reagents [14, 15], in alignment with recent advancements in SN2 reactivity and pedagogical strategies [26, 27].

2. Results and Discussion

We propose that the tetrafluoroborate anion exhibits a lower coordinating capacity than both chloride and acetate, which may diminish its effectiveness in stabilizing ionic intermediates. This reduced solvation capacity correlates with the observed lower yields. It is essential to highlight that the distinctive properties of ionic liquids—including high thermal stability, tunable polarity, and exceptional solvation capabilities—significantly enhance reaction kinetics. Their ability to promote improved ion mobility and stabilize transition states more effectively leads to accelerated and more complete reactions. Furthermore, the high yields achieved in ionic liquids contribute to the minimization of side reactions and the formation of unwanted byproducts, thereby underscoring

their advantages over traditional solvents such as acetone. We anticipate that these improvements in yield and safety render ionic liquids particularly appealing for undergraduate organic chemistry laboratories. The yields observed (ranging from 88% to 93%) not only exemplify the critical importance of solvent selection in SN2 reactions but also present a safer, more environmentally sustainable, and pedagogically sound alternative to conventional methodologies. By adopting the ionic liquid-mediated protocol, educators can provide students with a tangible demonstration of contemporary green chemistry principles, emphasizing essential concepts such as reaction mechanisms, solvent effects, and sustainable practices. Furthermore, we assert that the superior efficacy of ionic liquids in the green Finkelstein reaction is primarily attributable to their remarkable capacity to stabilize ionic intermediates and optimize transition state energies. These advantages result in significantly enhanced product yields compared to acetone, establishing ionic liquids as invaluable tools for both advanced synthetic applications and the instruction of organic chemistry [17, 18].

Efficiency and Sustainability of the Green Finkelstein Reaction: Ionic Liquids vs. Conventional Solvents

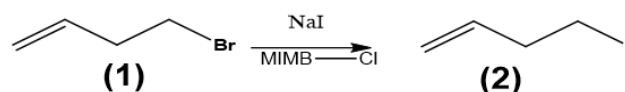


Figure 1. Reaction via Finkelstein Reaction.

Table 1. Green Finkelstein Reaction in Ionic Liquids vs. Conventional Solvents.

Solvent	Yield of Alkyl Iodide (%)	Reaction Time (min)	Recyclability (% Retained Yield After 3 Cycles)
[BMIM][OAc]	91	30	87
[BMIM][Cl]	93	30	89
[BMIM][BF ₄]	88	30	85
Acetone	67	30	-

We propose that the tetrafluoroborate anion exhibits lower coordinating capacity than both chloride and acetate, which may reduce its effectiveness in stabilizing ionic intermediates. This diminished solvation capacity is correlated with the observed lower yields. It is essential to highlight that the unique properties of ionic liquids—including high thermal stability, tunable polarity, and exceptional solvation capabilities—significantly enhance reaction kinetics. Their ability to promote improved ion mobility and stabilize transition states more effectively leads to accelerated and more complete reactions. Moreover, the high yields achieved in ionic liquids

contribute to the minimization of side reactions and the formation of unwanted byproducts, thereby underscoring their advantages over traditional solvents such as acetone. We anticipate that these enhancements in yield and safety make ionic liquids particularly attractive for undergraduate organic chemistry laboratories. The yields observed (ranging from 88% to 93%) not only exemplify the critical importance of solvent selection in SN2 reactions but also present a safer, more environmentally sustainable, and pedagogically sound alternative to conventional methodologies. By adopting the ionic liquid-mediated protocol, educators can provide students with a tangible demonstration of contemporary green chemistry principles, emphasizing essential concepts such as reaction mechanisms, solvent effects, and sustainable practices. Furthermore, we assert that the superior efficacy of ionic liquids in the green Finkelstein reaction is primarily attributable to their remarkable capacity to stabilize ionic intermediates and optimize transition state energies. These advantages result in significantly enhanced product yields compared to acetone, establishing ionic liquids as invaluable tools for both advanced synthetic applications and the instruction of organic chemistry.

4-Iodobut-1-ene (2)

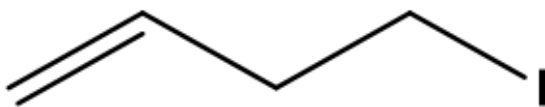


Figure 2. Preparation of 4-iodobutene.

Procedure A

To a stirred solution of sodium iodide (8.88 g, 59.2 mmol, 1.00 equiv) and acetone (47 mL) was added 4-bromobut-1-ene (237) (4.00 g, 29.6 mmol, 0.50 equiv) and the resulting solution was heated to reflux for 30 minutes. After cooling, three quarters of the acetone was removed, water (30 mL) was added to the residue and the resulting mixture was extracted with ether (15 mL). The organic phase was washed with saturated sodium sulfite solution (6 mL) to remove any coloration, dried over MgSO_4 and concentrated *in vacuo* to afford the title compound as a pale yellow oil (3.6 g, 67%); ν_{max} (thin film/ cm^{-1}) 2967, 1460, 112, 802, 753, 672; δ_{H} (250 MHz, CDCl_3) 5.73 (1H, dt, J 3.8 Hz, $\text{CH}=\text{CH}_2$), 5.18 (1H, bd, J 1.5 Hz, $\text{CH}=\text{CH}$), 5.14 (1H, dd, J 3.6 Hz, $\text{CH}=\text{CH}$), 3.19 (2H, t, J 7.2 Hz, CH_2I), 2.64 (2H, q, J 6.9 Hz, $\text{CH}_2\text{CH}_2\text{I}$). δ_{C} (62.5 MHz, CDCl_3) 136.9, 118.0, 37.5, 4.5; m/z (C.I) 182 (MH^+ , 100%), 56 (16 %) $\text{C}_4\text{H}_8\text{I}$, requires 182.9671, found 182.9672.

Procedure B

To a stirred solution of sodium iodide (1.00 g, 6.67 mmol, 1.00 equiv) and [BMIM][Cl] (10 mL) was added 4-bromobut-1-ene (1) (450 mg, 3.33 mmol, 0.50 equiv) and the resulting solution was heated to reflux for 30 minutes.

After cooling, three quarters of the acetone was removed, water (8 mL) was added to the residue and the resulting mixture was extracted with ether (7 mL). The organic phase was washed with saturated sodium sulfite solution (6 mL) to remove any coloration, dried over MgSO_4 and concentrated *in vacuo* to afford the title compound as a pale-yellow oil (562 mg, 93%).

3. Conclusion

The findings of this study indicate that the Green Finkelstein Reaction utilizing ionic liquids represents a more advantageous alternative to the traditional synthesis of alkyl halides, exemplified by the preparation of 1-bromobutane from 1-butanol via reflux in H_2SO_4 [20]. The high yield (93%) of 4-iodobut-1-ene achieved in this investigation surpasses the efficiency associated with conventional halide substitution reactions typically conducted in undergraduate organic chemistry laboratories [16, 18].

In addition to the improved yield, this methodology significantly enhances safety and environmental sustainability. The traditional approach, which necessitates the in-situ generation of HBr from NaBr and concentrated H_2SO_4 , poses serious corrosive hazards, generates toxic acidic vapors, and requires prolonged heating under reflux conditions. In contrast, the ionic liquid-based reaction obviates the need for hazardous mineral acids, operates under milder conditions, and reduces volatile organic emissions, thereby rendering it a greener and safer experimental procedure for academic environments.

As demonstrated in Table 1, the use of [BMIM][Cl] yielded the highest product conversion (93%) and exhibited 89% recyclability after three cycles, outperforming traditional solvents such as acetone, which provided only a 67% yield and was non-recyclable. Even the lowest-yielding ionic liquid ([BMIM][BF₄], 88%) significantly exceeded acetone in performance. These results illustrate the superior solvation and ion-transport characteristics of ionic liquids, leading to enhanced SN2 reaction kinetics and minimal formation of side products. Notably, all ionic liquids employed in this study demonstrated excellent reusability, with only marginal decreases in yield over three cycles, indicating their cost-effectiveness and suitability for repeated instructional use.

Furthermore, the protocol's tolerance to ambient moisture, absence of toxic byproducts, and reduced flammability profile enhance its safety for instructional laboratories. The minimal purification requirements and high product purity, confirmed by NMR, IR, and MS analyses, further underscore the practicality of the method.

Considering these attributes—higher yield, reduced hazards, cost efficiency, and ease of scale-up—this ionic liquid-mediated Green Finkelstein Reaction represents a highly promising alternative for not only undergraduate organic chemistry curricula but also broader synthetic applications

where sustainability, efficiency, and safety are paramount.

Abbreviations

IL(s)	Ionic Liquid(s)
SN2	Bimolecular Nucleophilic Substitution
NaBr	Sodium Bromide
H ₂ SO ₄	Sulfuric Acid
[BMIM][OAc]	1-Butyl-3-methylimidazolium Acetate
[BMIM][Cl]	1-Butyl-3-methylimidazolium Chloride
[BMIM][BF ₄]	1-Butyl-3-methylimidazolium Tetrafluoroborate
NMR	Nuclear Magnetic Resonance
δH, δC	Chemical shift for protons (¹ H) and carbon (¹³ C)
MHz	Megahertz
J	Coupling Constant (Hz)
CDCl ₃	Deuterated Chloroform
MgSO ₄	Magnesium Sulfate
vacuo	Under Vacuum
C.I	Chemical Ionization (mass spectrometry)
υ _{max}	Maximum Absorption Frequency (IR, cm ⁻¹)

Author Contributions

Bello Y. Makama performed the experiments, analyzed the data, and drafted the manuscript, while Laurence M. Harwood conceived the project, proposed conducting the reaction in conventional solvents, and guided the initial studies.

Conflicts of Interest

The authors declare no conflicts of interest.

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