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Hannah Artz
Messiah University

Roseann K. Sachs
Messiah University

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Ionic Liquids as Both Solvent and Reagent in Electrophilic Addition Reactions

Hannah Artz and Dr. Roseann Sachs

I. ABSTRACT

Ionic Liquids (ILs) are an environmentally friendly alternative to organic and aqueous reaction solvents. ILs do not emit hazardous gasses, are readily recycled and reused, and often do not require an excess volume of harmful reagents and purification solvents. The IL anion's capacity to participate in a reaction as the nucleophile source is a much less understood area of this research, and it may advance the use of ILs in organic synthesis, particularly for addition and substitution reactions. Markovnikov hydrohalogenation of alkenes is one addition reaction that is generally taught as an introduction to organic chemical reactions; however, this reaction is difficult to successfully complete in the laboratory. ILs overcome the challenges posed in those traditional methods and can be used as both a reaction solvent and halogen source to successfully complete the Markovnikov addition of H-X across a double bond. The hydrohalogenation reaction was completed over 100 times using a variety of ionic liquids including imidazolium, pyridinium, pyrrolidinium, and piperidinium cations. Products were isolated using organic extraction and analyzed with NMR and GC-MS. Bromide anion ILs were consistently successful with all substrates, iodide was most efficient under nitrogen, and chloride was successful with additional heat. Hydrohalogenation of styrene was successful in all ILs used and most successful in the imidazolium-based bromide ILs. Reactions with cyclic aliphatic substrates were less successful with lower yields. Finally, hydrohalogenation of styrene derivatives was recently investigated with moderate success after modification of reaction conditions.

II. INTRODUCTION

Most organic chemical reactions require volatile organic solvents, and some utilize large quantities of hazardous acids. These compounds are hazardous because they pose flammability and irritation risks for organic chemists and may require hazardous disposal, creating environmental concerns. These concerns have been partially resolved by advancements in utilizing water as a reaction solvent. An aqueous solvent, however, is limited by organic reagent solubility properties and reaction conditions
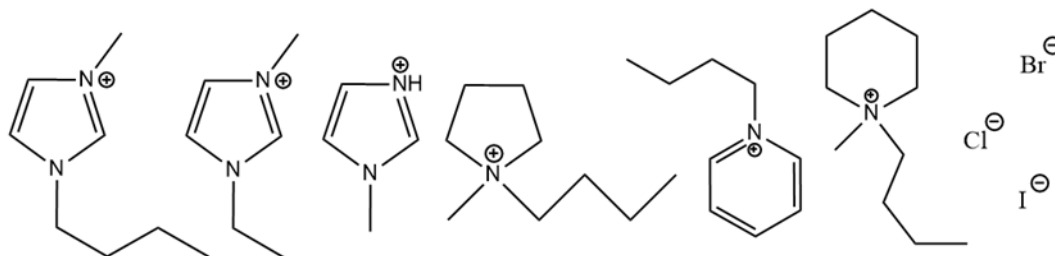

Figure 1. Ionic liquid cations and anions used this summer including: imidazolium, pyrrolidinium, pyridinium, piperdinium, bromide, chloride, and iodide.

requiring extreme temperatures. Organic chemists have responded to the concern to establish environmentally friendly solvents by investigating and developing ionic liquids (ILs) as reaction solvents.[1] ILs are important because their chemical and physical properties offer a more environmentally friendly approach to organic chemistry in the laboratory, and they alter traditional reaction mechanisms in strange and potentially useful ways.[1,2]

ILs are molten salts typically comprised of an organic cation and an organic or inorganic anion.[2] The ILs employed for this project involved various cations, including imidazolium, pyrrolidinium, pyridinium, and piperidinium with a halogen anion consisting of either a bromide, chloride, or iodide (Figure 1). The cation and anion often have a low degree of symmetry which reduces the salt's melting point by decreasing its lattice energy, allowing it to exist in the liquid phase at or slightly above room temperature.[1] ILs are efficient solvents because their ionic character enables them to dissolve polar and nonpolar substances.[2]

ILs have multiple beneficial features and therefore offer a more environmentally friendly approach to organic chemistry. ILs are a "greener" alternative to typical organic solvents because they have no measurable vapor pressure and do not emit volatile compounds.[1] In addition, ILs can be recycled and reused following a reaction.[3-5] As more methods to utilize ILs as reaction solvents are developed, the volume of laboratory waste may be significantly reduced. Finally, ILs are an advantageous compound to use in the laboratory because their properties include low flammability, high conductivity, and thermal stability.[1]
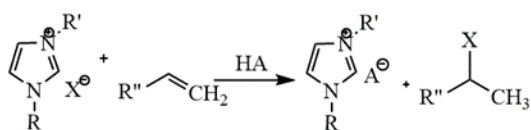

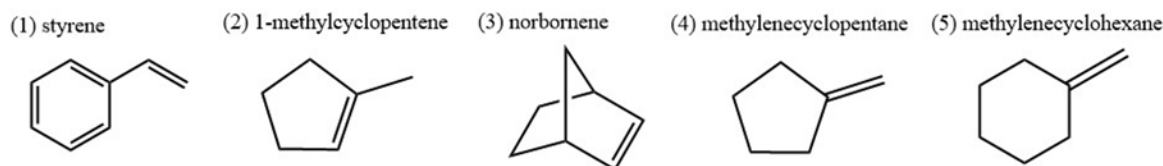**Figure 2.** General reaction for electrophilic addition using an imidazolium-based IL.

Hydrohalogenation addition reactions are one area of organic chemistry in which ILs can be utilized as an alternative solvent. The preparation of an alkyl halide from an alkene using two phase solvent mixtures is very simple in theory but has proven enormously difficult and hazardous in the laboratory. Alternatively, organic chemists have shown that this reaction may be carried out with silica gel or alumina; however, ILs are a more environmentally friendly approach which offers reusability.[6] Previous research has shown that ILs with halide anions may be used to accomplish substitution reactions to convert simple alcohols to alkyl halide compounds.[2] This concept can be applied to hydrohalogenation addition reactions using the IL as both a solvent and halide source (Figure 2).

Previous research projects at Messiah University conducted by Micah Ohlhausen and Jacob Bender have demonstrated that ILs, specifically the imidazolium-based 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) IL, can be used to as a solvent and as a reagent supplying the halide anion in hydrohalogenation reactions. Their research developed experimental methodologies to complete this reaction in aromatic and aliphatic substrates and confirmed product formation using GC/MS and ^{1}H NMR analysis.[3,4]

In Bender's methodology, five equivalents of the IL were utilized in order to obtain a high yield of a pure hydrohalogenated product. The use of excess IL enables the exploration of the IL's green characteristics with the possibility for IL reuse and recycling. If all the substrate molecules reacted, four equivalents of halide should be available in the IL solvent for four further reuse reactions. Once completely depleted of its halide anions, the IL could in theory be recycled through a series of reactions based on solubility principles.[5]

The primary goals of this research project were to confirm the procedure developed by

Successful Substrates

(1) styrene (2) 1-methylcyclopentene (3) norbornene (4) methylenecyclopentane (5) methylenecyclohexane

Unsuccessful Substrates

(6) *trans*-methylstyrene (7) *cis*-stilbene (8) 4-phenylbut-3-en-2-one (9) 2-cyclohexen-1-one (10) (R)-carvone (11) 2-ethylbutene
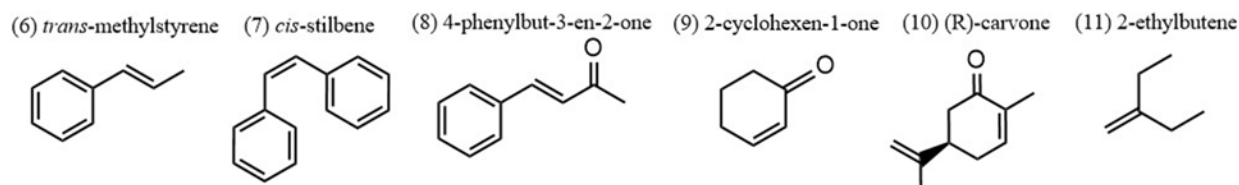
Figure 3. Successful and unsuccessful substrates used to investigate hydrohalogenation reactions in a variety of ILs.

Jacob Bender, evaluate the reusability of ILs, and apply the methodology to a variety of substrates and ILs.

III. RESULTS AND DISCUSSION

The experimental method developed by Bender was confirmed using styrene as the principal substrate (Figure 3, Structure 1).[3] When in excess, the IL was successfully reused three times, but could not be recycled to its original halide form. The methodology was successfully applied to a variety of substrates and ILs with a

few successful substrates and many failed substrates.

The success of a substrate in the IL hydrohalogenation reaction was determined according to its physical appearance, GC/MS purity, and ^{1}H NMR spectral quality. Styrene was the most consistently successful substrate investigated. Other moderately successful substrates included: 1-methylcyclopentene, norbornene, methylenecyclopentane, and methylenecyclohexane (Figure 3, Structures 2-5). The average yields and purities for each IL tested are shown in Table 1.

The substrates which yielded unsuccessful hydrohalogenation reactions in ILs included: *trans*-methylstyrene, *cis*-stilbene, 4-phenybut-3-en-2-one, 2-cyclohexen-1-one, (R)-carvone, and 2-ethylbutene (Figure 3, Structures 6-11). These reactions failed with minimal or no product formation or yielded an undesired product as confirmed by GC/MS and ^{1}H NMR spectral analysis.

Aromatic Substrates

Styrene was the primary successful aromatic substrate, and reactions of styrene with the imidazolium-based bromide ILs demonstrated the highest yields and purities overall (Table 1). The typical reaction of styrene with [BMIM][Br] was conducted with no adjustments to

Table 1. Average yield and purity for successful substrates

Substrate	Cation	Anion	Avg Yield	Avg Purity
(1) Styrene	BMIM	Br	95%	96%
	EMIM	Br	89%	96%
	BMIM	Cl	68%	63%
	EMIM	Cl	68%	62%
	EMIM	I	68%	50%
	pyrrolidinium	Br	77%	93%
	pyridinium	Br	-	73%
	piperidinium	Br	65%	62%
(2) 1-methylcyclopentene	BMIM	Br	16%	86%
	EMIM	Br	13%	65%
	BMIM	Cl	27%	90%
	BMIM	I	6%	27%
	EMIM	I	29%	11%
	pyrrolidinium	Br	-	76%
	pyridinium	Br	14%	67%
	piperidinium	Br	45%	90%
(3) norbornene	BMIM	Br	43%	95%
	EMIM	Br	49%	95%
	BMIM	Cl	29%	96%
	BMIM	I	75%	98%
(4) methylenecyclopentane	BMIM	Br	26%	89%
(5) methylenecyclohexane	BMIM	Br	30%	65%
	EMIM	Br	29%	14%
	BMIM	I	32%	63%
	pyridinium	Br	49%	90%

Bender's methodology and yielded a 90% pure product with minimal spectral contamination (Supp. Figures 1, 2).[8] The results of this typical reaction in [BMIM] [Br] confirmed Bender's methodology and was applied to styrene in the other halide ILs.

Styrene in the chloride ILs was significantly less successful than the bromide ILs with inconsistent yields and purities amongst various trials. The first reaction with chloride ILs failed but yield and purity significantly improved upon the addition of heat. The IL unsuccessfully used in styrene with [BMIM] [Cl] was reused to yield a very pure product according to the GC/MS with a ^{1}H NMR spectrum demonstrating product (Supp. Figures 3, 4). The NMR contained significant ethyl acetate contamination and subsequent products were rotary evaporated for longer durations under higher temperatures.

Similar to the chloride IL system, styrene was less successful in the iodide ILs with moderate yields and inconsistent purities. Preliminary reactions with iodide were unsuccessful until methodological adjustments were made, including a nitrogen atmosphere and methane sulfonic acid in place of concentrated sulfuric acid. These adjustments were consistent with literature recommendations from halide IL substitution reactions with alcohol substrates.[2] Styrene with [EMIM] [I] run with the experimental modifications was moderately successful with 57% purity with a significant amount of starting material (Supp. Figure 5). The ^{1}H NMR was well resolved with a few unknown impurity peaks, but no identifiable starting material peaks. (Supp. Figure 6). The excess starting material noted on the GC/MS may have been due to an elimination reaction in the injector.

IL reuse was successful up to three times when the IL was in five times excess for the bromide, chloride, and iodide imidazolium based ILs. Theoretically, the IL was expected to be reusable for five reactions; however, there was typically minimal, or no product yielded on the fourth reuse. After each workup, the IL was evaporated under reduced pressure to remove any additional extraction solvents and purity was confirmed using ^{1}H NMR. Supplemental Figure 7 demonstrates the efficacy of the workup as the IL shown in NMR B was utilized for two hydrohalogenation reactions and the spectrum shows very limited impurities with correct IL coupling and integrations.

Bender's experimental method instructed the use of five equivalents of IL which was proven successful with the capacity for reuse for three additional runs. Although five equivalents of IL yield a high purity product, it was also demonstrated that styrene can be successfully hydrohalogenated with just two equivalents. The ^{1}H NMR of this product was comparable to that obtained previously from styrene with [BMIM] [Br] and was quite clean with limited contamination (Supp. Figure 8). The reduced solvent volume necessary to complete a reaction was more cost-effective and applied to further reactions testing a variety of ILs and substrates.

The success of the styrene substrate with all ILs prompted the investigation of styrene derivatives containing electron-withdrawing and electron-donating groups in the para position with respect to the vinyl substituent. Figure 4 shows the four derivatives studied with preliminary reactions carried out in [BMIM] [Br].

The electron donating derivatives were expected to produce higher yields with greater purity in reaction conditions similar to the typical styrene method because the donating group should stabilize the carbocation intermediate. The electron-withdrawing derivatives were expected to require higher temperatures or a longer reaction time because they have a destabilized intermediate.[6]

Substrates 12, 13, and 14 were studied using the typical styrene in [BMIM] [Br] method. Reactions with substrates 12 and 14 yielded the

desired addition product and significant amounts of a 1,2-dibromo byproduct. When substrate 12 was run for 48 hours at 60°C in attempt to maximize product formation, the product was extremely viscous, and it did not yield the desired addition product. Additionally, substrate 13 was run for 48 hours, but similar to the second trial with substrate 12, the product was viscous and sticky, and the ^{1}H NMR spectrum did not demonstrate any observable product. The physical characteristics of those products and the broadening of the ^{1}H NMR spectra peaks for both reactions suggested that the starting materials may have polymerized.

This side reaction is probable because literature demonstrates that organic and inorganic chemists utilize ILs as efficient solvents for radical polymerization reactions.[7] Running these reactions at lower temperatures, in the dark, and in an inert nitrogen atmosphere may reduce this side reaction by limiting the activation of any polymerization initiators. Additionally, investigating reduced reaction times and monitoring the reaction after 6, 12, and 24 hours with ^{1}H NMR would be beneficial to observe progression of product formation and polymerization. Finally, a variety of temperatures should be investigated to fully evaluate the parameters to maximize yield and minimize byproduct formations. Another method to prevent polymerization is the addition of radical scavengers to react with any radicals formed throughout the reaction. Two common scavengers utilized in commercial and food products include butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). The structure of these compounds indicates that they will not interfere with the electrophilic addition reaction and will reduce O_2 concentrations and quench oxygen radicals to inhibit polymerization.[8]

Substrate 14, an electron-withdrawing derivatives, yielded a thin, light-yellow product. The product ^{1}H NMR spectrum was well resolved, but contained significant amounts of starting material, 1,2-dibromo byproduct, and product. When the reaction was run for 48 hours, more starting material was observed in the spectrum compared to the 24-hour reaction. The 24- and 48-hour reactions suggest that longer reaction times may allow some product to revert to starting material; therefore, the reaction should be limited to 24 hours and monitored at 6 and 12 hours to evaluate product formation. Additionally, running this reaction in an inert nitrogen atmosphere may reduce byproduct formation. Finally, additional heating at 30, 45, and 60°C may be an important factor to overcome the activation energy and utilize more starting material. These methodological modifications can be applied to substrate 15 as it is evaluated in addition to the other three derivatives.

Reactions manipulating temperature, time, and atmosphere should be carried out in the bromide, chloride, and iodide ILs to fully evaluate these substrates. Additionally, it would be valuable to study the mechanism for addition reactions in ILs in order to appropriately apply expectations for the effects of electron-donating
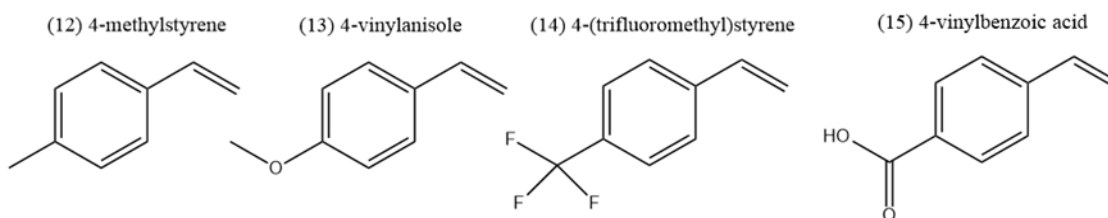

Figure 4. Styrene derivatives investigated in [BMIM] [Br] to study the effects of electron donating (12 and 13) and electron withdrawing (14 and 15) groups on addition reactions in ILs.

and withdrawing-groups on this reaction, as it may deviate from the traditional mechanism understood in organic solvents.

Aliphatic Substrates

The primary aliphatic substrate investigated, 1-methylcyclopentene, demonstrated low yields with inconsistent purities ranging from 11%-90% (Table 1). The 1-butyl-1-methylpiperidinium bromide IL produced the highest yield and purity of any IL tested. 1-Methylenecyclopentene with [1-butylpyridinium] [Br] IL yielded a moderate purity with the most well resolved ^{1}H NMR (Supp. Figures 9, 10). The other monocyclic aliphatic substrates were similar to 1-methylcyclopentene with lower yields, inconsistent purities, and poorly resolved ^{1}H NMR spectra (Table 1, Figure 3, Structures 4-5). In addition to the methodological adjustments made with each halide IL, the aliphatic substrates which were liquid at room temperature required the melted IL to be slightly cooled. Otherwise, the hot IL evaporated some starting material, lowering the product yield.

As demonstrated in Supplemental Figure 10, the NMRs for the aliphatic substrates were not well resolved. Additionally, the GC/MS library did not contain the expected product structure. Instead, mass spectra were used to confirm product structures. Hydroiodination of 1-methylcyclopentene in [BMIM] [I] was one instance of this issue. The mass spectrum for this reaction was used to confirm the product structure because the molecular ion peak at 209.9 m/z was consistent with the expected product molecular weight. This spectrum also contained an iodine cation peak at 126.9 m/z, and a methylcyclopentyl cation peak at 83.1 m/z, confirming the structure (Supp. Figure 11). This technique was applied for any product structure not found in the MS database and structures were confirmed according to the presence of the expected molecular ion and peaks attributable to the fragmented product.

The secondary aliphatic substrate investigated was norbornene. This substrate was expected to be similar to 1-methylcyclopentene; however, it produced high purities across the various halide ILs with moderate yields (Table 1). The typical reaction of norbornene with [BMIM] [Br] was particularly successful with a purity of 93% (Table 1, Supp. Figure 12). The ^{1}H NMRs for the hydrohalogenated products were quite complicated due to W-coupling and non-traditional peak splitting. One trial of this typical reaction yielded an extremely clean ^{1}H NMR spectrum with correct integrations, good resolution, and limited impurities (Supp. Figure 13).

Initially, the bromine substituent was expected to be in the *exo* position because the ^{1}H NMR chemical shifts were consistent with that of the *exo* product in spectral databases.[9–11] Additionally, mass spectral studies in the literature suggested that the *exo*-Br is fragmented more easily than the *endo*-Br.[12,13] This was consistent with the mass spectrum for 2-bromonorbornane which demonstrated extremely small molecular ion peaks (Supp. Figure 14).

Upon further analysis using ^{13}C NMR, the product spectrum demonstrated two sets of seven peaks, indicating that the product may be a mixture of *endo*- and *exo*-2-bromonorbornane. The higher set of peaks are consistent with the spectral database peaks for the *exo* product (Supp. Figure 15).[9–11] There are no database spectra for the *endo* product; therefore, more analysis must be completed to confirm the mixture of these stereoisomers.

Future Directions

Future research will complete the investigation of the norbornene substrate with non-imidazolium based ILs. These products may be used to analyze the *endo* and

exo-2-bromonorbornane product mixture. Additionally, investigations with styrene derivatives will be completed. Preliminary reactions with two electron-donating derivatives and one of the two electron-withdrawing derivatives were completed in [BMIM] [Br]. The temperature, reaction time, and atmospheric parameters will be adjusted to optimize product yield and purity for the bromide, chloride, and iodide ILs. Radical scavengers like BHA and BHT also will be added to quench radicals and inhibit polymerization reactions.[8]

A third category of substrates that will be investigated is vinyl aromatic heterocycles. These substrates retain the aromaticity of the successful styrene substrate while incorporating nitrogen heteroatoms to resemble natural products. Substrates that will be investigated include: 4-vinylpyridine, 2-vinlypyridine, 1-vinylimidazole, and 1-vinyl-1, 2, 4-triazole. Previous research demonstrates that ILs can be used to successfully extract a wide variety of natural products from their biological sources.[14] Once these compounds are extracted, we could apply addition and substitution reactions to these substrates as an environmentally friendly technique that can be incorporated into synthetic schemes with natural products.

IV. EXPERIMENTAL

Each reaction was carried out using either of the two methods described for aromatic and aliphatic substrates respectively. The aromatic method served as the primary method and was refined from the [BMIM] [Br] and styrene reaction with specific adaptions to the temperature, atmosphere, or acid in order to optimize the results for an alternative IL or substrate. The most optimal reactions were selected from the 112 completed throughout the past seven months and are outlined below.

Method A: Aromatic Substrates

Styrene with [BMIM] [Br]. 1-Butyl-3-methylimidazolium bromide (2.201 g, 10.0 mmol) was added to a 25 mL round-bottomed flask and melted. Styrene (230 μL, 2.0 mmol) was added and the reaction solution was stirred in an ice bath for 15 minutes. The flask was equipped with a condenser and the apparatus was covered in foil. Chilled, concentrated sulfuric acid (210 μL, 3.94 mmol) was added and the reaction was stirred for 24 hours. The flask was uncovered to reveal a cloudy, pale-yellow solution. The mixture was extracted 3 times with 5 mL portions of 2:1 hexane: ethyl acetate and 3 times with 5 mL portions of 1:1 hexane: ethyl acetate. The extract was analyzed with GC/MS and evaporated under reduced pressure at 35°C to a thin, clear, yellow oil (Supp. Figure 1). The IL was evaporated under reduced pressure at 45°C. The product and IL were analyzed with ^{1}H NMR (Supp. Figure 2). GC/MS R_t=8.702 min. ^{1}H NMR (CDCl$_3$): δ 7.454-7.248 (m, 5H), δ 5.2 (q, 1H), δ 2.05 (d, 3H).

Reuse of [BMIM] [Cl] with styrene. The viscous, clear, pale green IL used in styrene with [BMIM] [Cl] was re-heated. That reaction was run with 1-butyl-3-methylimidazolium chloride (1.794 g, 10.3 mmol) in a 25 mL round-bottomed flask. Styrene (230 μL, 2.0 mmol) was added and the reaction solution was stirred in an ice bath for 15 minutes. The flask was equipped with a condenser and the apparatus was covered in foil. Chilled concentrated sulfuric acid (210 μL, 3.94 mmol) was added. The reaction was stirred for 24 hours in a sand bath at ~50°C. The flask was uncovered to reveal a cloudy, pale green viscous solution. The mixture was extracted 3 times with 5 mL portions of 2:1 hexane: ethyl acetate and 3 times with 5 mL portions of 1:1 hexane: ethyl acetate. The extract was analyzed with GC/MS and evaporated under reduced pressure at 35°C

to a clear, colorless oil (Supp. Figure 3). The IL was evaporated under reduced pressure at 45°C. The product and IL were analyzed with ^{1}H NMR (Supp. Figure 4). GC/MS R_t=6.490 min. ^{1}H NMR (CDCl$_3$): δ 7.426-7.248 (m, 5H), δ 5.09 (q, 1H), δ 1.85 (d, 3H).

Styrene with [EMIM] [I]. 1-Ethyl-3-methylimidazolium iodide (2.385 g, 10.0 mmol) was added to a 3 necked 50 mL round-bottomed flask and heated. The melted IL was degassed under N$_2$ for ~20 minutes. The flask was equipped with a condenser and the apparatus was covered in foil. Styrene (230 µL, 2.0 mmol) was added and the reaction solution was stirred in an ice bath for 15 minutes. Chilled methane sulfonic acid (260 µL, 4.0 mmol) was added. The reaction was stirred for 24 hours. The flask was uncovered to reveal a dark yellow-brown solution. The mixture was extracted 3 times with 5 mL portions of 2:1 hexane: ethyl acetate and 3 times with 5 mL portions of 1:1 hexane: ethyl acetate. The extract was analyzed with GC/MS and evaporated under reduced pressure at 35°C to a thin, dark yellow-brown oil (Supp. Figure 5). The IL was evaporated under reduced pressure at 45°C. The product and IL were analyzed with ^{1}H NMR (Supp. Figure 6). GC/MS R_t=12.704 min. ^{1}H NMR (CDCl$_3$): δ 7.45-7.206 (m, 5H), δ 5.40 (q, 1H), δ 2.2 (d, 3H).

Method B: Aliphatic Substrates

1-Methylenecyclopentene with [1-butylpyridinium] [Br]. 1-Butylpyridinium bromide (0.889 g, 4.1 mmol) was added to a 25 mL round-bottomed flask and melted. The reaction flask was stirred at room temperature until the flask was slightly warm, 1-methylcyclopentene (210 µL, 2.0 mmol) was added, and the reaction was stirred in an ice bath for 15 minutes. The flask was equipped with a condenser and the apparatus was covered in foil.

Chilled concentrated sulfuric acid (110 µL, 2.12 mmol) was added. The reaction was stirred for 24 hours. The flask was uncovered to reveal a clear yellow solution. The mixture was extracted 3 times with 5 mL portions of 2:1 hexane: ethyl acetate and 3 times with 5 mL portions of 1:1 hexane: ethyl acetate. The extract was analyzed with GC/MS and evaporated under reduced pressure at 35°C to a dark blue-black product (Supp. Figure 9). The IL was evaporated under reduced pressure at 45°C. The product and IL were analyzed with ^{1}H NMR (Supp. Figure 10). GC/MS R_t=4.346 min. ^{1}H NMR (CDCl$_3$): δ 1.6 (q, 4H), δ 1.029 (s, 3H), δ 0.851 (q, 2H).

Norbornene with [BMIM] [Br]. 1-Butyl-3-methylimidazolium bromide (2.249 g, 10.3 mmol) was added to a 25 mL round-bottomed flask and melted. Norbornene (0.189 g, 2.0 mmol) was added, and the reaction was stirred in an ice bath for 15 minutes. The flask was equipped with a condenser and the apparatus was covered in foil. Chilled concentrated sulfuric acid (210 µL, 3.94 mmol) was added and the reaction was stirred for 24 hours. The flask was uncovered to reveal a dark yellow-brown solution. The mixture was extracted 3 times with 5 mL portions of 2:1 hexane: ethyl acetate and 3 times with 5 mL portions of 1:1 hexane: ethyl acetate. The extract was analyzed with GC/MS and evaporated under reduced pressure at 35°C to a thin, dark yellow-tan oil (Supp. Figure 12). The IL was evaporated under reduced pressure at 45°C. The product and IL were analyzed with ^{1}H NMR (Supp. Figure 13). GC/MS R_t=6.382 min. ^{1}H NMR (CDCl$_3$): δ 3.9 (m, 1H), δ 2.5 (d, 1H), δ 2.297 (s, 1H), δ 2.03 (q, 2H), δ 1.8 (dt, 1H), δ 1.62 (m, 1H), δ 1.45 (m, 1H), δ 1.27 (dt, 1H), δ 1.164 (m, 1H), δ 1.65 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 54.3 (m, 1H), δ 46.6, δ 44.1, δ 37.2, δ 35.7, δ 28.3, δ 27.7.

Instrumentation

Product and IL samples were analyzed using a Nuclear Magnetic Resonance Spectrometer (JEOL, 400 MHz). Extract samples were analyzed using the Gas Chromatograph/Mass Spectrometer (Agilent Technologies, 8890 GC/5977B MS). The table below provides the GC/MS parameters used for the most successful substrates.

Table 2. GC/MS Parameters

	styrene	methylcyclopentene	norbornene	methylenecyclohexane
Inlet temp	250°C	250°C	250°C	250°C
Quadrople	150°C	150°C	150°C	150°C
Flow rate	1.2 mL/min	1.2 mL/min	1.2 mL/min	1.2 mL/min
Column/inlet pressure	10.42 psi	10.42 psi	10.42 psi	10.42 psi
Oven temperature ramping sequence	60°C hold 2 min, ramp to 100°C, hold 10 min	60°C hold 2 min, ramp to 75°C, hold 12 min	60°C hold 2 min, ramp to 100°C, hold 10 min	60°C hold 2 min, ramp to 100°C, hold 6 min
Ramp rate	20°C/min	20°C/min	20°C/min	60°C hold 2 min, ramp to 100°C, hold 6 min
Solvent delay	2.5 min	1.80 min	2 min	2 min

V. SUPPLEMENTAL FIGURES
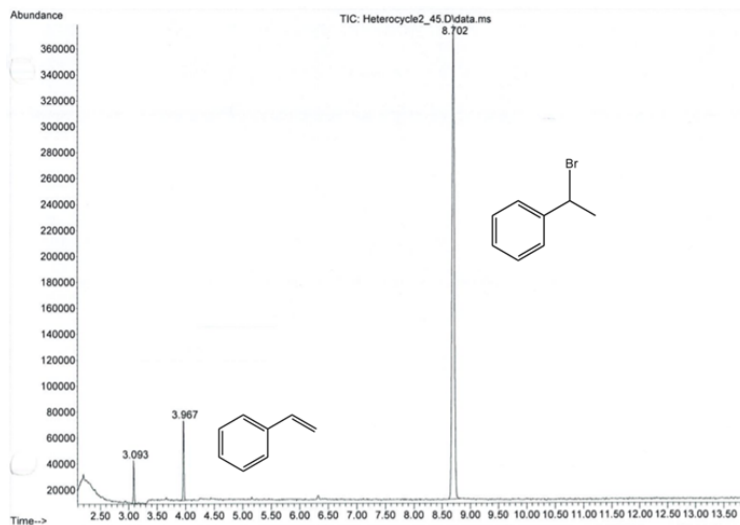
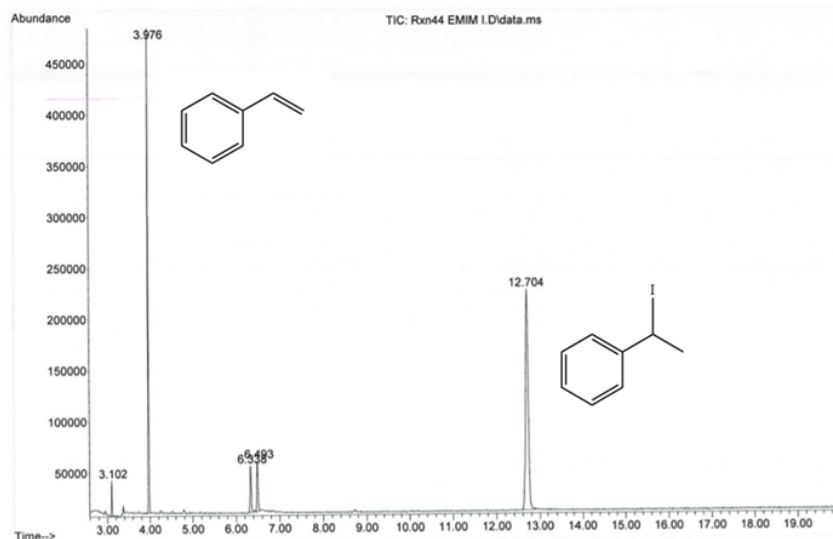**Figure 1.** GC/MS spectrum of styrene with [BMIM] [Br] extract showing 90% purity of (1-bromoethyl)benzene product, R_t=8.702 min. The other notable peaks are ethyl acetate (R_t=3.093 min) and styrene starting material (R_t=3.967 min).
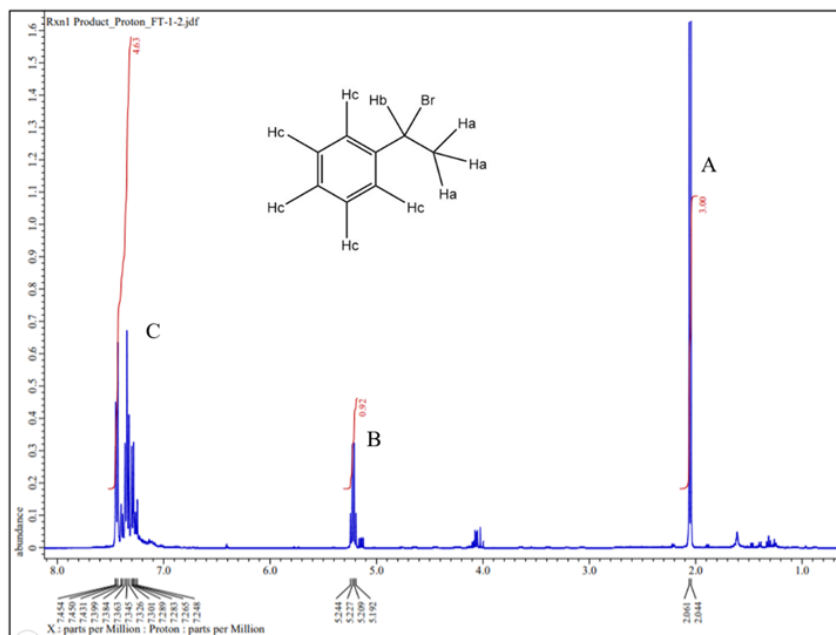
Figure 2. ^{1}H NMR spectrum of styrene with [BMIM] [Br] product: (1-bromoethyl)benzene. The product is fairly clean with very little ethyl acetate and small amounts of the (1,2-dibromoethyl)benzene byproduct. ^{1}H NMR (CDCl$_3$): δ 7.45-7.25 (m, 5H), δ 5.2 (q, 1H), δ 2.05 (d, 3H).
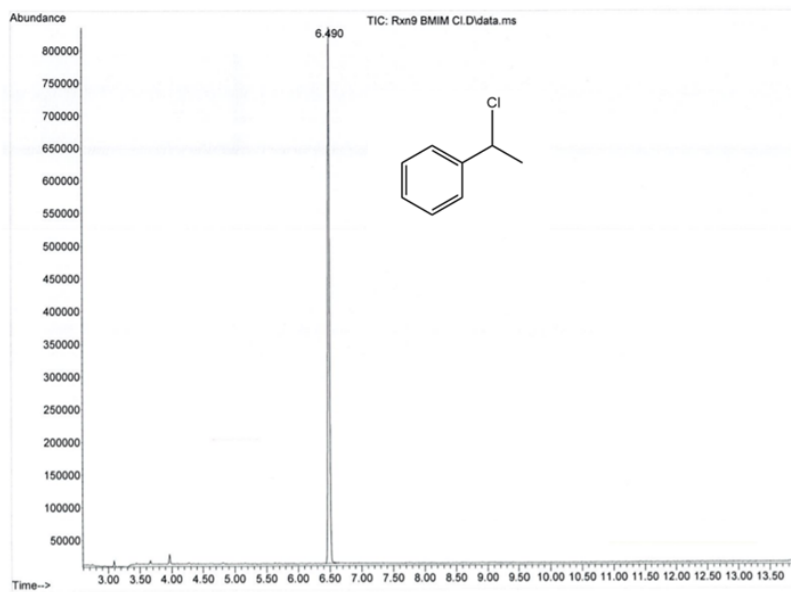
Figure 3. GC/MS spectrum of reuse of [BMIM] [Cl] with styrene extract showing 100% purity of (1-chloroethyl)benzene product, R_t=6.490 min.
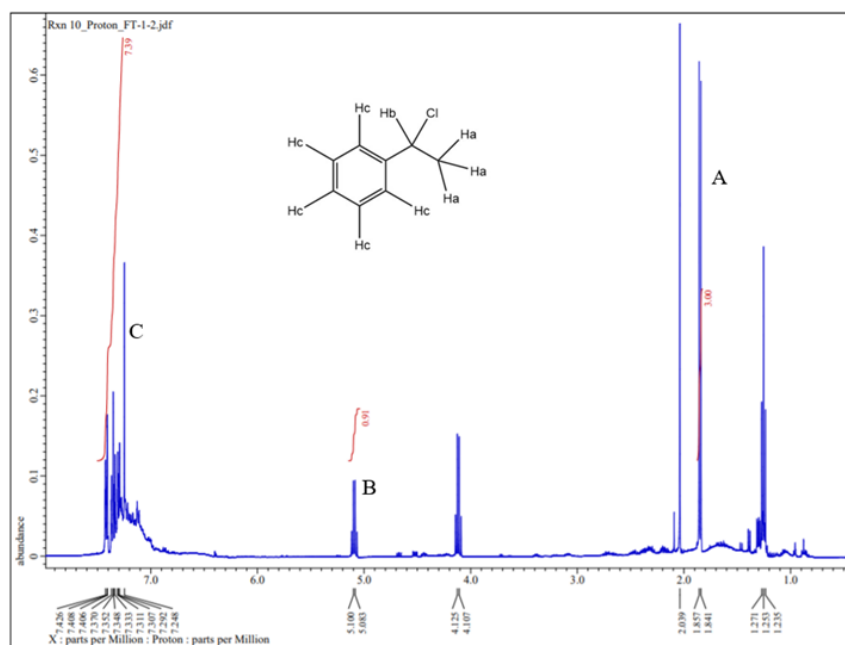
Figure 4. ^{1}H NMR spectrum of reuse of [BMIM] [Cl] with styrene product: (1-chloroethyl)benzene. The spectrum shows significant amounts of ethyl acetate in the product. ^{1}H NMR (CDCl$_3$): δ 7.43-7.25 (m, 5H), δ 5.09 (q, 1H), δ 1.85 (d, 3H).

Figure 5. GC/MS spectrum of styrene with [EMIM] [I] extract showing 57% purity of (1-iodoethyl)benzene product R_t=12.704 min. Other significant peaks include styrene starting material (R_t=3.976 min) and oxidized byproducts (R_t=6.338 min and 6.493 min).
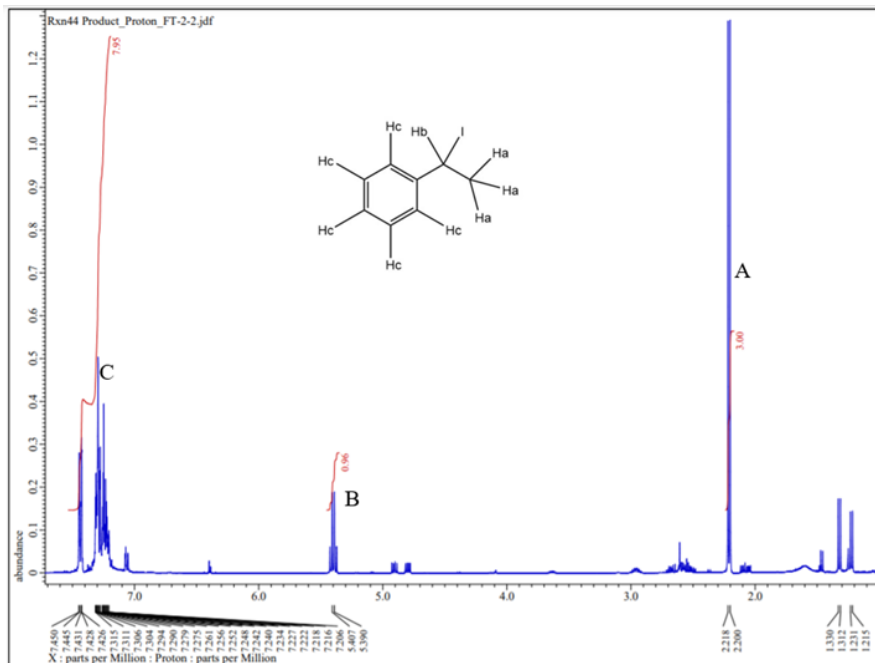
Figure 6. ^1H NMR spectrum of styrene with [EMIM] [I] product: (1-iodoethyl)benzene. Spectrum shows mostly product with some unknown byproducts and contaminants. ^1H NMR (CDCl$_3$): δ 7.45-7.21 (m, 5H), δ 5.40 (q, 1H), δ 2.2 (d, 3H).
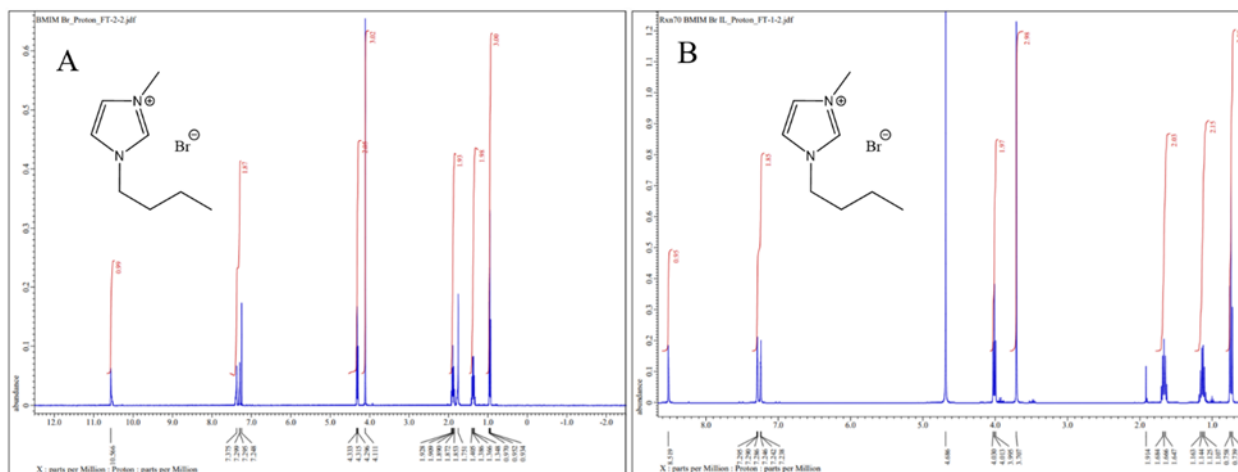
Figure 7. ^{1}H NMR spectral comparison of the 1-butyl-3-methylimidazolium bromide IL before use (A) and after it was used for two hydrohalogenation reactions (B). NMR (B) is extremely clean following the reaction workup with very minor impurities throughout the spectrum.
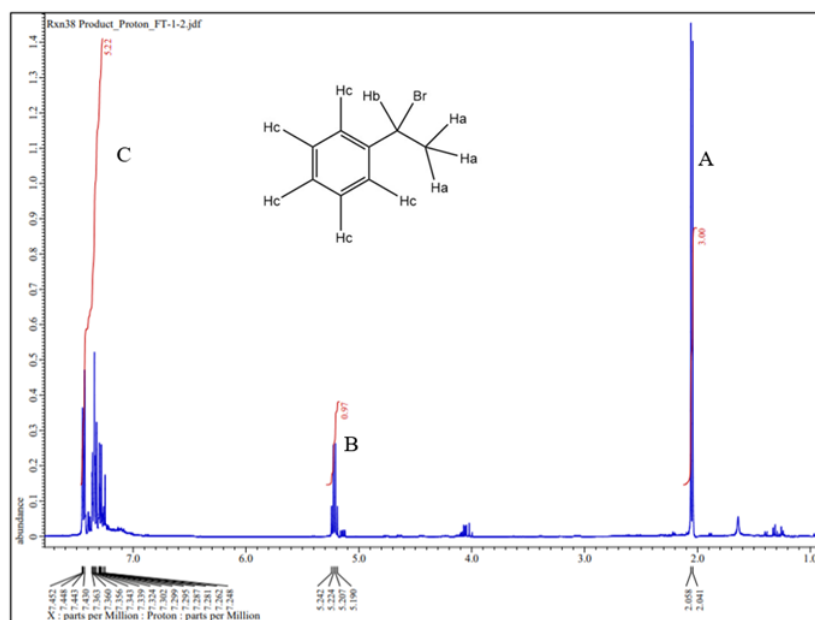
Figure 8. ^{1}H NMR spectrum of styrene with 2 equivalents [BMIM] [Br] product: (1-bromoethyl)benzene. This reaction was completed with 2 equivalents of [BMIM][Br] IL in contrast to the typical 5 equivalents used. The product is fairly clean with very little ethyl acetate and small amounts of the (di-1,2-bromoethyl)benzene byproduct. ^{1}H NMR (CDCl$_3$): δ 7.45-7.25 (m, 5H), δ 5.2 (q, 1H), δ 2.05 (d, 3H).
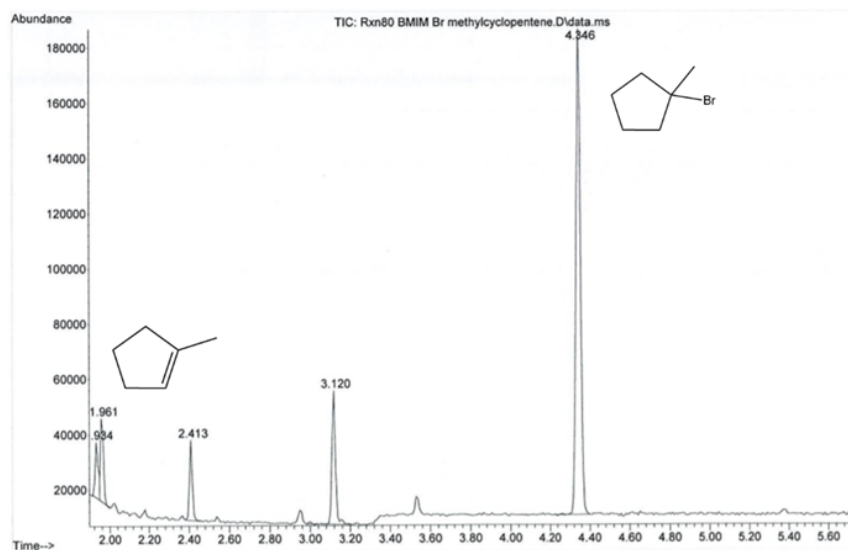
Figure 9. GC/MS spectrum of 1-methylenecyclopentene with [1-butylpyridinium] [Br] extract showing 67% purity of 1-bromo-1-methylcyclopentane product, R_t=4.346 min. Other notable peaks include 1-methylcyclopentene starting material (R_t=1.961 min) and ether compounds at R_t=2.413 min and 3.120 min.
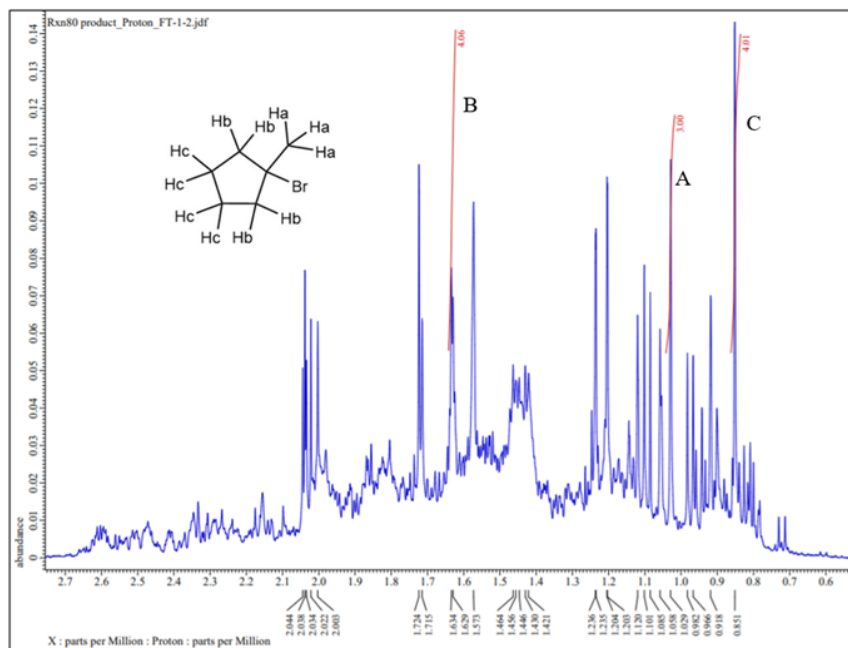

Figure 10. ^{1}H NMR spectrum of 1-methylenecyclopentene with [1-butylpyridinium] [Br] product: 1-bromo-1-methylcyclopentane. The product peaks are not well resolved, but were identifiable based on correct integration, expected shifting, splitting, and chemical shift consistency throughout numerous reactions yielding this product. ^{1}H NMR (CDCl$_3$): δ 1.6 (q, 4H), δ 1.03 (s, 3H), δ 0.85 (q, 2H).
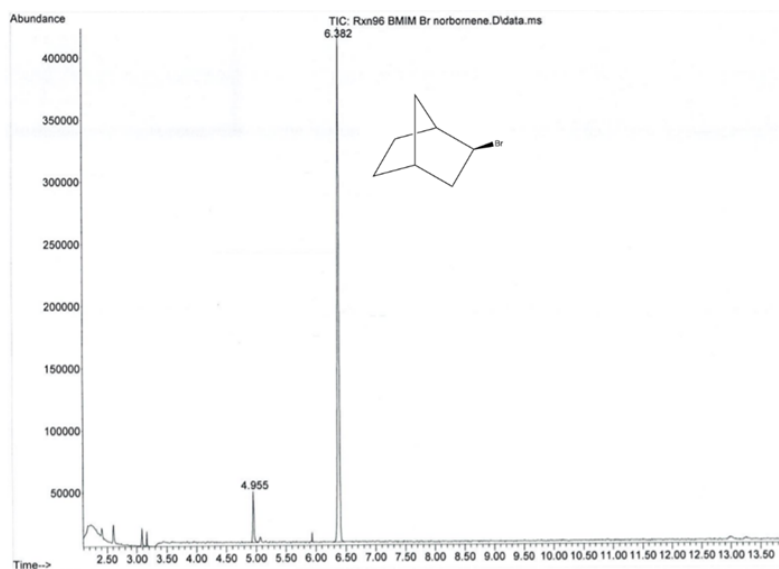
Figure 11. GC/MS spectrum of 1-methylenecyclopentene with [BMIM] [I] product. The 1-iodo-1-methylcyclopentane product was not found in the library database, but the mass spectrum was used to confirm the product structure according to the molecular ion peak at 209.9 m/z, an iodine cation peak at 126.9 m/z, and a methylcyclopentane cation peak at 83.1 m/z.
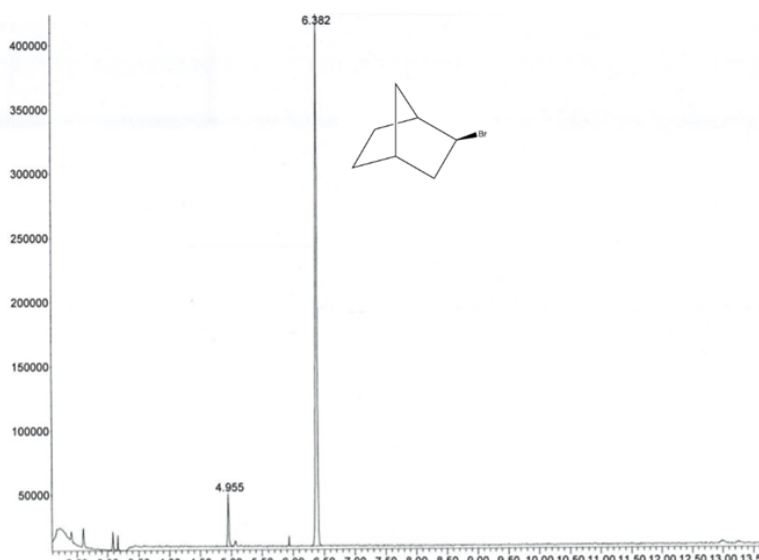

Figure 12. GC/MS spectrum of norbornene with [BMIM] [Br] extract showing 93% purity of 2-exo-norbornane product R_t=6.382 min. The other notable peak on the spectrum is the oxidized byproduct (R_t=4.955 min).
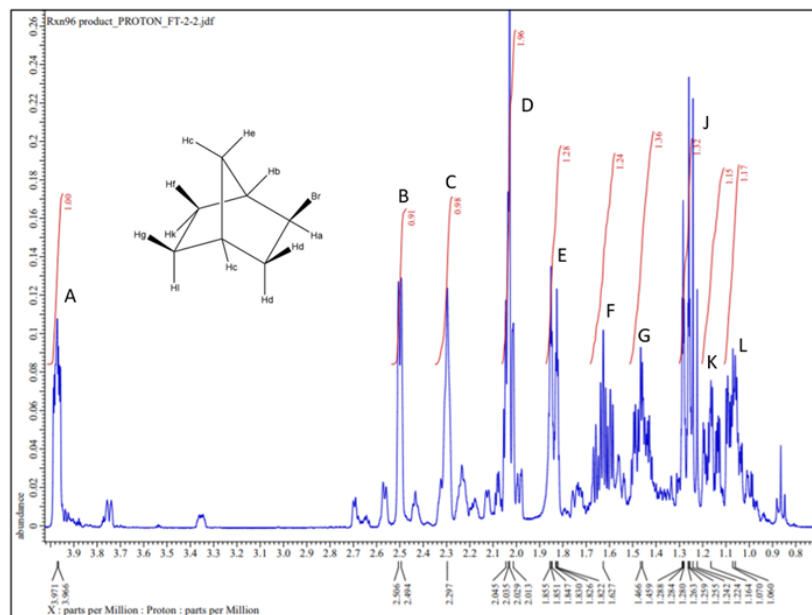
Figure 13. ^{1}H NMR spectrum of norbornene with [BMIM] [Br] product: 2-exo-bromonorbornane. The product peaks are well resolved despite contamination with ethyl acetate and various unknown impurities. ^{1}H NMR (CDCl$_3$): δ 3.9 (m, 1H), δ 2.5 (d, 1H), δ 2.30 (s, 1H), δ 2.03 (q, 2H), δ 1.8 (dt, 1H), δ 1.62 (m, 1H), δ 1.45 (m, 1H), δ 1.27 (dt, 1H), δ 1.16 (m, 1H), δ 1.65 (m, 1H).
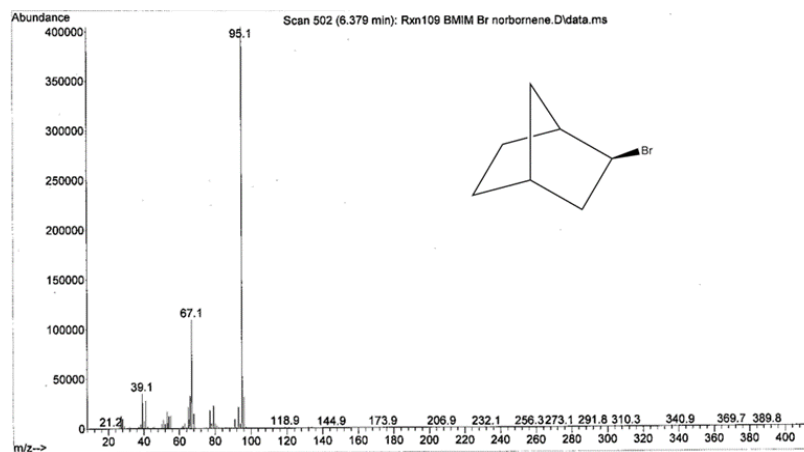

Figure 14. Mass spectrum of norbornene with [BMIM] [Br]. The instrument display of this spectrum demonstrates the characteristic bromine isotope peaks at 173 m/z and 175 m/z with the average signal provided as 173.9 m/z. These molecular ion peaks are extremely small, and the major fragment is the norbornyl cation at 95.1 m/z after a loss of the bromine substituent.
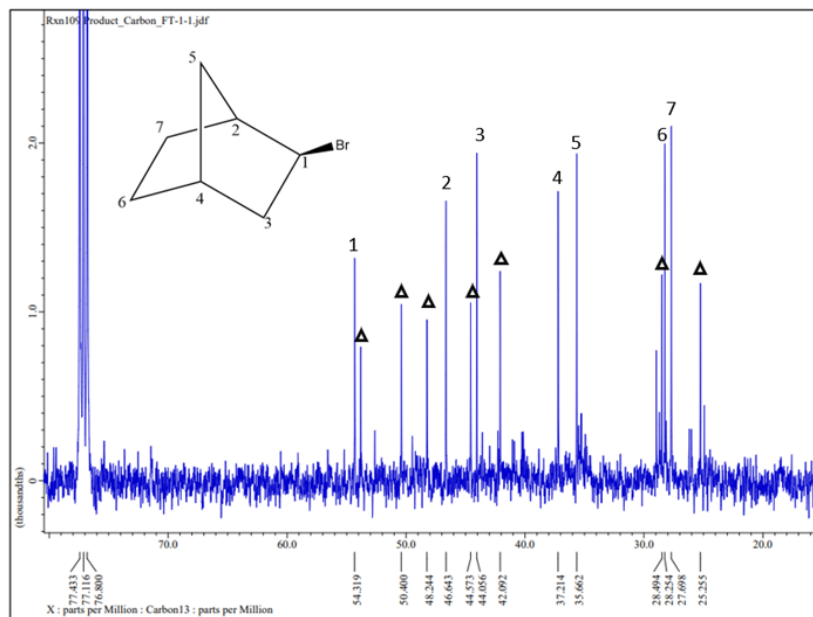
Figure 15. The ^{13}C NMR spectrum of norbornene with [BMIM] [Br] product: 2-bromonorborane. The larger set of seven peaks are consistent with the database spectrum for *exo*-2-bromonorbornane. The second set of seven smaller peaks identified with the triangles are likely the *endo*-2-bromonorbornane product, indicating that the product is a mixture of both stereoisomers. ^{13}C NMR (CDCl$_3$): δ 54.3 (m, 1H), δ 46.6, δ 44.1, δ 37.2, δ 35.7, δ 28.3, δ 27.7.

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