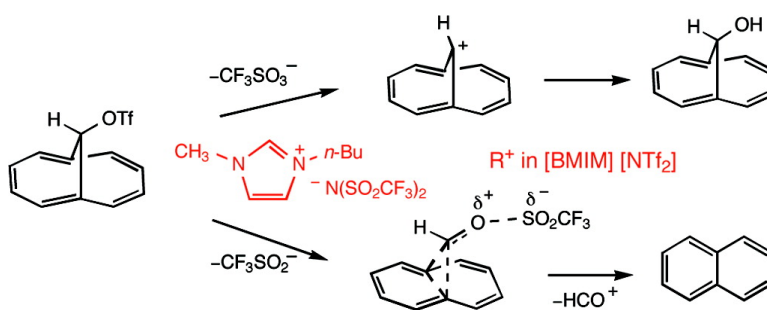


Carbocation-Forming Reactions in Ionic Liquids

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Carbocation-Forming Reactions in Ionic Liquids

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Abstract: A number of trifluoroacetates, mesylates, and triflates have been studied in ionic liquids. Several lines of evidence indicate that all of these substrates react via ionization to give carbocationic intermediates. For example, cumyl trifluoroacetates give mainly the elimination products, but the Hammett ρ^+ value of -3.74 is consistent with a carbocationic process. The analogous *exo*-2-phenyl-*endo*-3-deutero-*endo*-bicyclo[2.2.1]hept-2-yl trifluoroacetate gives an elimination where loss of the *exo*-hydrogen occurs from a cationic intermediate. 1-Adamantyl mesylate and 2-adamantyl triflate react to give simple substitution products derived from capture of 1- and 2-adamantyl carbocations by the residual water in the ionic liquid. The triflate derivative of pivaloin, *trans*-2-phenylcyclopropylcarbonyl mesylate, 2,2-dimethoxycyclobutyl triflate, the mesylate derivative of diethyl (phenylhydroxymethyl)-thiophosphonate, and *Z*-1-phenyl-5-trimethylsilyl-3-penten-1-yl trifluoroacetate all give products derived carbocation rearrangements (k_A processes). *anti*-7-Norbornenyl mesylate gives products with complete retention of configuration, indicative of involvement of the delocalized 7-norbornenyl cation. 1,6-Methano[10]annulen-11-yl triflate reacts in [BMIM][NTf₂] to give 1,6-methano[10]annulen-11-ol, along with naphthalene, an oxidized product derived from loss of trifluoromethanesulfinate ion. Analogous loss of CF₃SO₂⁻ can be seen in reaction of PhCH(CF₃)OTf. Ionic liquids are therefore viable solvents for formation of carbocationic intermediates via k_C and k_A processes.

Introduction

The effect of solvent on rates of reactions where carbocations are involved is profound. Thus model substrates such as *tert*-butyl chloride and 2-adamantyl tosylate show solvolysis rate differences of $10^{4.5}$ and $10^{5.4}$ respectively as solvent is varied from ethanol to the more "highly ionizing" hexafluoroisopropyl alcohol.¹ The increased ability of polar protic solvents to solvate (and stabilize) developing cations and anions accounts for these large rate effects. While dimethyl sulfoxide (DMSO) has long been recognized as an outstanding solvent for S_N2 reactions, we have recently found that this polar aprotic substance is also a reasonable solvent for S_N1-type reactions.² Thus a variety of carbocationic intermediates could be generated in DMSO despite the inability to solvate the developing anion via hydrogen bonding. Certain triflates were especially prone to give carbocation chemistry in DMSO.³ We are therefore interested in the ability of novel or unusual solvents to support carbocationic intermediates.

Ionic liquids are an emerging class of solvents that are of much recent interest for organic reactions.⁴ As nonvolatile, nonflammable, nontoxic, and potentially recyclable liquids, these substances have potential as environmentally benign "green" solvents. Among the many reactions that have now been carried

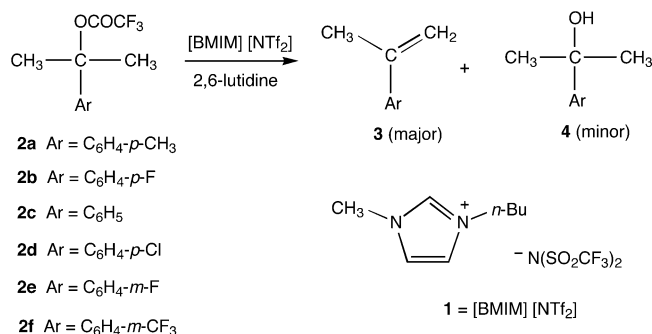
out in ionic liquids, a number of classic reactions have been reported. These include Grignard,⁵ Reformatsky,⁶ Friedel-Crafts,⁷ Beckmann,⁸ aromatic nitration,⁹ and S_N2 reactions.^{10–12} In a study of nucleophilic reactions of azide ion with various substrates in ionic liquids, 1-iodoadamantane was reported to react to form 1-azidoadamantane, presumably via the 1-adamantyl cation.¹² We have now carried out a number of studies designed to evaluate whether carbocations can be generated via S_N1 reactions in ionic liquids. Reported here are the results of these studies.

Results and Discussion

k_C Substrates. In evaluating the viability of forming carbocations in ionic liquids, kinetic studies would be of great value. The first decisions involved choices of solvent and substrates. We initially chose the ionic liquid 1-butyl-3-methylimidazolium triflamide, [BMIM][NTf₂], **1**.¹³ It is relatively easy to prepare, recover, and recycle. Additionally, this

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Scheme 1. Reaction of Cumyl Trifluoroacetates in [BMIM][NTf₂]

ionic liquid is also one of the least viscous, and recording ¹H and ¹⁹F NMR spectra in this solvent are therefore quite easy. Although somewhat hygroscopic, the amount of water present can be easily determined by NMR. Hence kinetic studies can be conveniently carried out in essentially neat [BMIM][NTf₂] by ¹H or ¹⁹F NMR in the unlocked mode (recently termed No-D NMR).¹⁴

The cumyl system is classic in the history of carbocation chemistry¹⁵ and for this reason, the cumyl trifluoroacetates **2** were chosen for study. We wanted to compare the behavior of **2** in ionic liquids to that of classic cumyl systems in more traditional polar protic solvents. When the trifluoroacetates **2a**–**2f** were dissolved in [BMIM][NTf₂] containing buffering 2,6-lutidine, reaction occurred smoothly to give the alkenes **3** as the major product. Also formed were varying amounts of the alcohols **4**, which arise from traces of water (0.2–0.5%) in the solvent. For example, in “dry”[BMIM][NTf₂], α-methylstyrene, **3c**, is the sole product from **2c**, while 24% of cumyl alcohol, **4c**, is formed when the ionic liquid contains 0.5% water. The methyl signal of the 2,6-lutidine, which becomes increasingly protonated by the developing trifluoroacetic acid, shifts downfield as the reaction proceeds. This allows the first-order rate constant for the reaction to be determined (Figure 1).¹⁶ Alternatively, first order rate constants could be readily obtained from ¹⁹F NMR data. Although the solvent [BMIM][NTf₂] is fluorinated, solvent suppression routines allow accurate determination by ¹⁹F NMR of the amount of substrates **2** remaining relative to trifluoroacetate ion formed as the reaction proceeds.¹⁷

Rate data for the substrates **2** are summarized in Table 1. There is a large change in rate constant as the electronic character of the substituents is varied. The corresponding Hammett ρ value is –3.74 and is indicative of a large amount of cationic character in the transition state. For comparison purposes, the ρ values for substituted cumyl chlorides in methanol, ethanol, 2-propanol, and 90% aqueous acetone are –4.82, –4.67, –4.43, and –4.54, respectively.^{15e} These data implicate carbocation intermediates when substrates **2** react in [BMIM][NTf₂].

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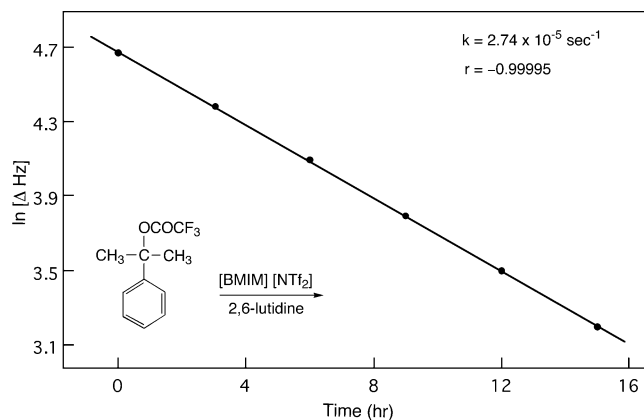
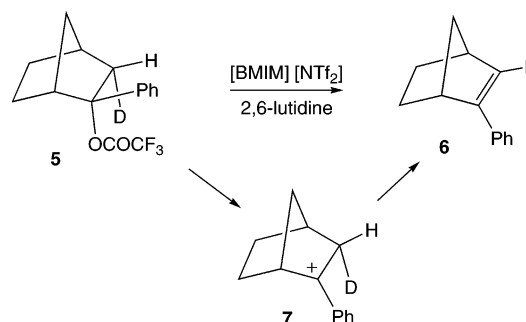


Figure 1. First-order plot for the reaction of **2c** in [BMIM][NTf₂] by ¹H NMR at 25.0 °C.

Table 1. Solvolysis Rate Constants for Cumyl Trifluoroacetates **2** in [BMIM][NTf₂] at 25.0 °C

substrate	k (s ⁻¹) ^a
2a Ar = <i>p</i> -CH ₃ C ₆ H ₄	3.67 × 10 ⁻⁴
2b Ar = <i>p</i> -F-C ₆ H ₄	4.04 × 10 ⁻⁵
2c Ar = C ₆ H ₅	2.74 × 10 ⁻⁵
2c Ar = C ₆ H ₅	1.13 × 10 ^{-3b}
2c Ar = C ₆ H ₅	3.71 × 10 ^{-4c}
2d Ar = <i>p</i> -Cl-C ₆ H ₄	8.41 × 10 ⁻⁶
2e Ar = <i>m</i> -F-C ₆ H ₄	1.17 × 10 ⁻⁶
2f Ar = <i>m</i> -CF ₃ -C ₆ H ₄	2.93 × 10 ⁻⁷

^a See Experimental section for kinetic method. ^b CH₃OH solvent; ref 17. ^c HOAc solvent; ref 17.

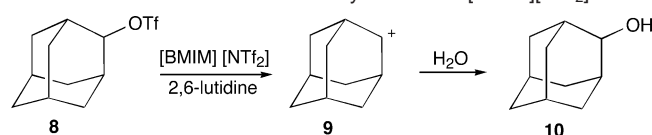
Scheme 2. Mechanism for Elimination Reaction of Trifluoroacetate **5** in [BMIM][NTf₂]

Since the ρ value in solvolyses of **2** in [BMIM][NTf₂] was less than that of cumyl chlorides in protic solvents, the possibility of a concerted elimination process was considered. The bicyclic trifluoroacetate **5**, which we have previously used as a probe for concerted elimination,^{2,18} was therefore solvolyzed in [BMIM][NTf₂], where it undergoes facile elimination to give the deuterated alkene **6** exclusively. This stereochemical result is consistent with involvement of cation **7**, which preferentially loses the *exo*-H. A concerted ester type pyrolytic elimination of trifluoroacetic acid is ruled out since this would be a syn process involving loss of the *endo*-D.¹⁹ A bimolecular E2 type of elimination would also involve loss of *endo*-D since a 0° dihedral angle is preferred in bimolecular eliminations in norbornyl systems.²⁰ Attention was next turned to the adamantyl systems **8** and **11** which have been used as models for substrates

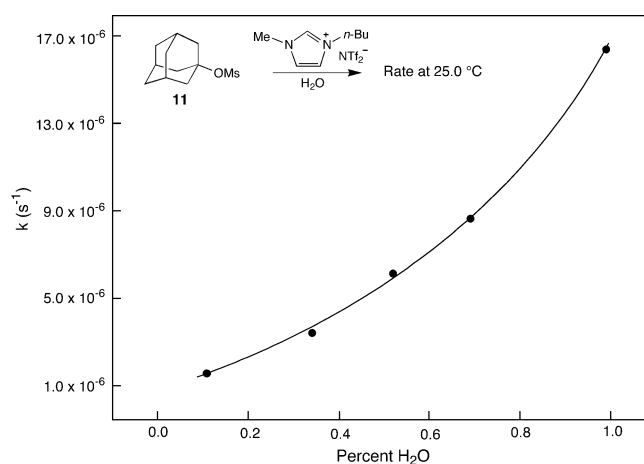
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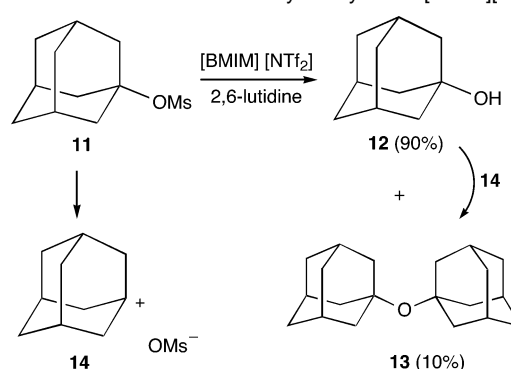
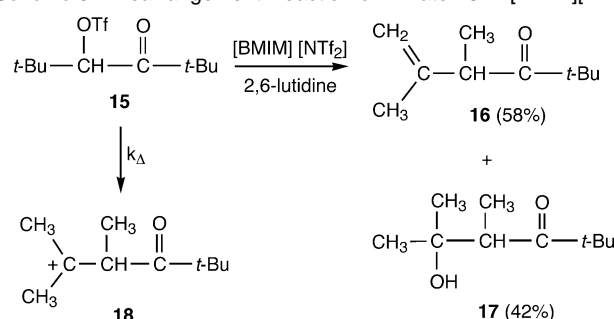
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Scheme 3. Reaction of 2-Adamantyl Triflate in [BMIM][NTf₂]**Table 2.** Solvolysis Rate Constants for 1-Adamantyl Mesylate, **11**, in Various Solvents at 25.0 °C

solvent	k (s ⁻¹)	γ_{OMs}
[BMIM][NTf ₂] (0.11% H ₂ O)	1.52×10^{-6}	-3.44
[BMIM][NTf ₂] (0.34% H ₂ O)	3.38×10^{-6}	-3.09
[BMIM][NTf ₂] (0.52% H ₂ O)	6.10×10^{-6}	-2.83
[BMIM][NTf ₂] (0.69% H ₂ O)	8.63×10^{-6}	-2.68
[BMIM][NTf ₂] (0.99% H ₂ O)	1.64×10^{-5}	-2.41
97% CF ₃ CH ₂ OH ^a	3.5×10^{-1}	1.92
80% EtOH/20% H ₂ O ^a	4.17×10^{-3}	0.00
CH ₃ OH ^a	2.81×10^{-4}	-1.17
CD ₃ CO ₂ D	6.58×10^{-4}	-0.80
DMSO- <i>d</i> ₆ ^b	4.21×10^{-7}	-4.00

^a Reference 21. ^b Reference 2.**Figure 2.** A plot of rate of reaction of **11** in [BMIM][NTf₂] at 25.0 °C vs % water in the solvent.

that react via k_C routes.^{1,21} 2-Adamantyl triflate, **8**, is a highly reactive substrate in protic solvents.^{22,23} We have now found that **8** is also quite reactive in [BMIM][NTf₂]. At 25 °C it readily converts in a first-order fashion to the alcohol substitution product **10** with a half-life of 5.4 min. This high reactivity contrasts with that of 2-bromoadamantane, which is reported to be unreactive in ionic liquids at 80 °C.¹² This is undoubtedly due to the much greater leaving group ability of the triflate nucleofuge, which has been estimated to react 10⁷ times faster than bromides.²⁴ The 2-adamantyl cation, **9**, is presumably the intermediate in this transformation. 1-Adamantyl mesylate, **11**, reacted in [BMIM][NTf₂] (containing 0.34% H₂O) to give a mixture of the alcohol **12** along with the ether **13**. First-order rate constants (Table 2), as well as product ratios, are quite dependent on the amount of water present in the solvent as illustrated in Figure 2. Activation parameters (0.11% H₂O in [BMIM][NTf₂]: $\Delta H = 22.7$ kcal/mol; $\Delta S = -9$ eu) are in line with a carbocation mechanism. Of interest is the unusually large rate effect induced by only small amounts of water in the ionic liquid. An increase in water concentration of less than 1%

Scheme 4. Reaction of 1-Adamantyl Mesylate in [BMIM][NTf₂]**Scheme 5.** Rearrangement Reaction of Triflate **15** in [BMIM][NTf₂]

resulted in a rate increase of more than a factor of 10. A reviewer has suggested that it may be due to rate determining trapping of a reversibly formed ion pair by water, i.e., formation of ion pair **14** may be reversible. This is the process originally suggested by Snee²⁵ in his controversial unified mechanism scheme, and we cannot rule out this possibility. Another possibility involves hydrogen bonding of water to the developing mesylate anion as the ionization proceeds. Since the ionic liquid is presumably less capable of hydrogen bonding to the developing mesylate anion, small amounts of water may exert an unexpectedly large effect on the developing mesylate anion, which demands solvation and hence dramatically increases solvolysis rates.

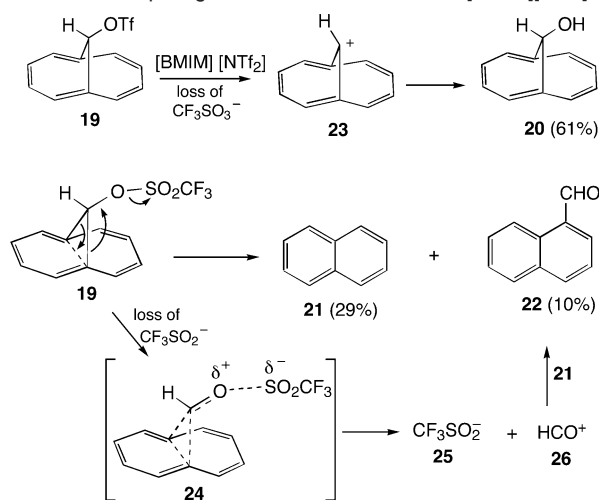
Of interest is the reactivity of mesylate **11** in [BMIM][NTf₂] relative to protic solvents. Data in Table 2 allows this comparison. The reactivity of **11** is less than in typical polar protic solvents, but greater than in DMSO-*d*₆, a polar aprotic solvent recently found to support carbocation forming reactions.²

Carbocation Rearrangements and k_A Processes. One of the fundamental processes that carbocations can undergo is rearrangement. To obtain further evidence for the involvement of carbocationic intermediates in ionic liquids, as opposed to S_N2 reactions with cationic character in the transition state, substrates capable of rearrangement were therefore investigated. The substrates examined include those with a range of leaving groups. They also reflect the historic nature of carbocation chemistry, ranging from carbocations of very recent interest to some of the old classic rearrangements. Substrates have also been chosen that reflect the interests of our laboratory. The α -keto triflate **15**²⁶ was dissolved in [BMIM][NTf₂] where it undergoes first-order reaction at convenient rates at room temperature to give mixtures of the rearranged alkene **16** and

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Table 3. Solvolysis Rate Constants for Triflate **15** in Various Solvents at 25.0 °C

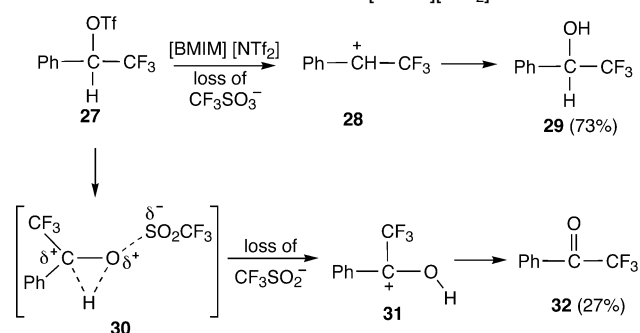
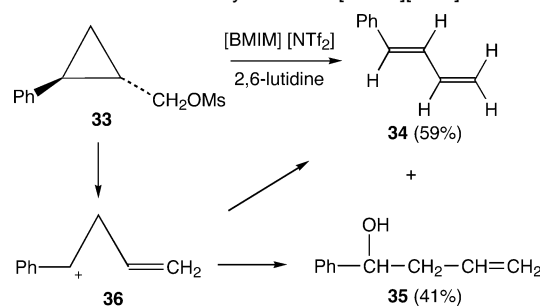
solvent	k (s ⁻¹)	k_{relative}
[BMIM][NTf ₂] (0.17% H ₂ O)	4.08×10^{-5}	1.00
[BMIM][NTf ₂] (0.30% H ₂ O)	4.36×10^{-5}	1.07
[BMIM][NTf ₂] (0.78% H ₂ O)	4.83×10^{-5}	1.18
[BMIM][NTf ₂] (1.40% H ₂ O)	5.49×10^{-5}	1.35
[BMIM][BF ₄] (0.2% H ₂ O)	3.93×10^{-4}	9.63
[BMIM][PF ₆]	1.54×10^{-4}	3.77
[BMIM][N(CN) ₂]	5.20×10^{-4}	12.7
[MeN(<i>n</i> -Bu) ₃][NTf ₂]	2.00×10^{-5}	0.49
[<i>n</i> -Bu-Pyridinium][NTf ₂]	4.95×10^{-5}	1.21
CF ₃ CH ₂ OH	4.36×10^{-5}	1.07
CH ₃ CH ₂ OH	5.98×10^{-6}	0.15
97% (CF ₃) ₂ CHOH	1.82×10^{-4}	4.46
CH ₃ CO ₂ H	4.15×10^{-6}	0.10
DMSO- <i>d</i> ₆	1.05×10^{-3}	25.7

Scheme 6. Competing Reactions of Triflate **19** in [BMIM][NTf₂]

alcohol **17**. Rate data are given in Table 3. Unlike the solvolysis of mesylate **11**, addition of small amounts of water have only minimal effects on reaction rate of triflate **15**. The rearranged products are consistent with involvement of the rearranged carbocation **18**. Table 3 also gives solvolysis rates of triflate **15** in five other ionic liquids as well as in other protic solvents. The rate of ionization of triflate **15** in all of the ionic liquids studied is quite facile and exceeds that in many common protic solvents used in solvolysis studies.

The triflate **19**²⁷ shows unusual behavior in [BMIM][NTf₂]. Reaction at 70 °C leads to the alcohol **20** in addition to the fragmentation products naphthalene, **21**, and 1-naphthaldehyde, **22**. These products are all consistent with cationic processes, with the alcohol **20** being derived from reaction of the carbocation **23** with water in the solvent. Competing with this k_C process is a process where the S–O bond of the triflate fragments via transition state **24** to give the trifluoromethanesulfinate anion **25**, which can be identified by ¹⁹F NMR. Further fragmentation leads to the product naphthalene, **21**, along with the formyl cation **26**, which is the source of the 1-naphthaldehyde, **22**, via formylation of **21**.

This unusual S–O cleavage process in solvolysis of **19** can also be seen when triflate **27**²⁸ reacts in [BMIM][NTf₂]. Major products are alcohol **29** and trifluoroacetophenone **32**. The

Scheme 7. Reaction of Triflate **27** in [BMIM][NTf₂]**Scheme 8.** Reaction of Mesylate **33** in [BMIM][NTf₂]

alcohol **29** is derived from carbocation **28**, while the ketone **32** is proposed to arise via S–O bond cleavage of **27** along with hydride migration. As before, the trifluoromethanesulfinate ion **25** can be observed by ¹⁹F NMR spectroscopy.

Other rearrangement processes attest to the involvement of carbocations when certain substrates are dissolved in ionic liquids. The rearrangement propensity of the 2-phenylcyclopropylcarbonyl cation^{29,30} has made this system of interest with respect to the mechanism of enzyme catalyzed hydroxylation of methylcyclopropanes.^{31,32} We have now examined mesylate **33** in [BMIM][NTf₂] where it readily reacts at room temperature to give a rearranged set of products, **34** and **35**, derived from the homoallylic cation **36**. This classic rearrangement of **33** in the ionic liquid is consistent with relatively facile carbocation formation. The triflate **37**³³ and the mesylate **40**³⁴ represent additional k_A substrates that have been studied in our laboratory. These substrates react in [BMIM][NTf₂] by first-order processes to give rearranged products **38** and **41**. Additionally the Taylor laboratory has recently studied the rearrangement of silyl activated homoallylic alcohols to cyclopropanes via carbocation intermediates.³⁵ In situ conversion of **45** (a mixture of *E* and *Z* isomers) to the mesylate led to the vinylcyclopropanes **44**, presumably via a k_A process.³⁶ We have now studied the *Z*-trifluoroacetate **43** in [BMIM][BF₄] since a side reaction

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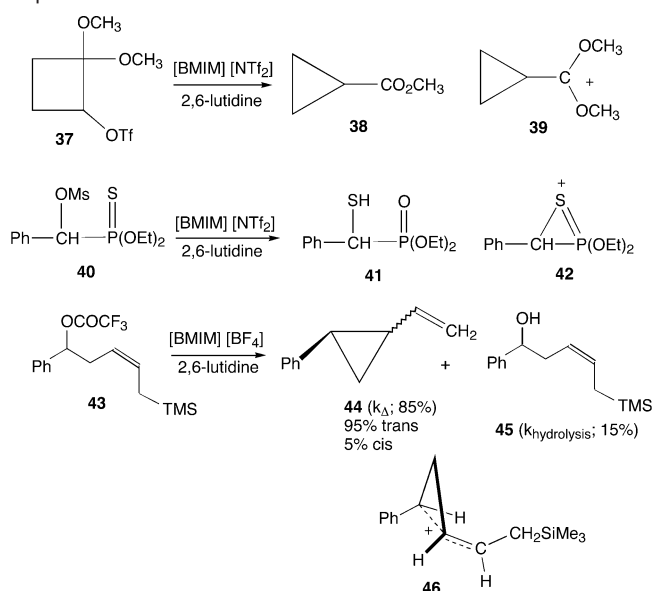
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Scheme 9. Rearrangement Reactions of k_A Substrates in Ionic Liquids

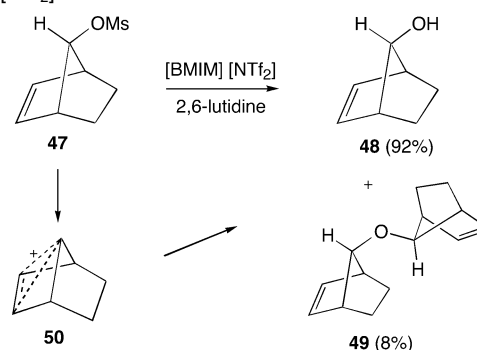
involving hydrolysis of the trifluoroacetate group of **43** by acyl-oxygen cleavage to give the alcohol **45** occurs more readily in [BMIM][NTf₂]. At 70 °C trifluoroacetate **43** reacts in [BMIM][BF₄] to give the rearranged cyclopropanes **44** (trans:cis ratio = 95:5) along with a smaller amount of the ester hydrolysis product, the unrearranged alcohol **45**.

These structurally rearranged products attest to the formation of cationic intermediates **39**, **42**, and **46** in ionic liquids. Neighboring cyclobutane σ -bond participation in **37** leads to methoxy stabilized cation **39**, while neighboring sulfur participation gives the cyclized intermediate **42**, the precursor to the sulfur migration product **41**. Homoallylic π -participation by the silyl activated double bond of **43** leads to silyl stabilized cation **46**, the precursor of the cyclopropanes **44**.

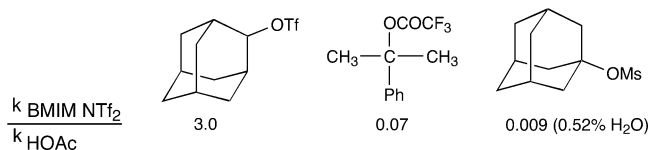
Attention was finally turned to the *anti*-7-norbornenyl system, a classic k_A system of perhaps the most renown. *anti*-7-Norbornenyl tosylate exhibits an extraordinary large acetolysis rate relative to the saturated analogue and products form with complete retention.³⁷ Reaction of 7-norbornenyl mesylate, **47**, in [BMIM][NTf₂] at room temperature gives the alcohol **48** (complete retention) along with smaller amounts of the ether **49**. As in protic solvents, the delocalized bishomoaromatic 7-norbornenyl cation **50** accounts for these products and provides additional evidence for the involvement of carbocationic intermediates in [BMIM][NTf₂].

“Solvent Ionizing Power” of Ionic Liquids. While our studies show that carbocations form in ionic liquids, rates of ionization of typical substrates are, in general, not extraordinarily rapid. Thus triflates **8**, **15**, **27**, and **37** are slightly more reactive in [BMIM][NTf₂] than in acetic acid, a commonly used solvent for S_N1 reactions. Trifluoroacetates **2c** and **5** are about an order of magnitude less reactive in BMIM NTf₂ than in acetic acid, while mesylates **11** and **40** are roughly 100 times less reactive.

These studies suggest that *Y* values for ionic liquids are quite dependent on leaving group. The ionizing power of [BMIM][NTf₂] can be classified as “low” for mesylates, where reactivity

Scheme 10. Reaction of *anti*-7-Norbornenyl Mesylate **47** in [BMIM][NTf₂]**Table 4.** Solvolysis Rate Constants in [BMIM][NTf₂] at 25.0 °C

substrate	k (s ⁻¹)
8	2.13×10^{-3} (0.57% H ₂ O)
19	3.00×10^{-7} (0.50% H ₂ O)
27	9.54×10^{-6} (0.33% H ₂ O)
33	3.32×10^{-5} (0.42% H ₂ O)
37	6.02×10^{-3} (0.75% H ₂ O)
40	1.87×10^{-7} (0.33% H ₂ O)
47	3.48×10^{-5} (0.40% H ₂ O)

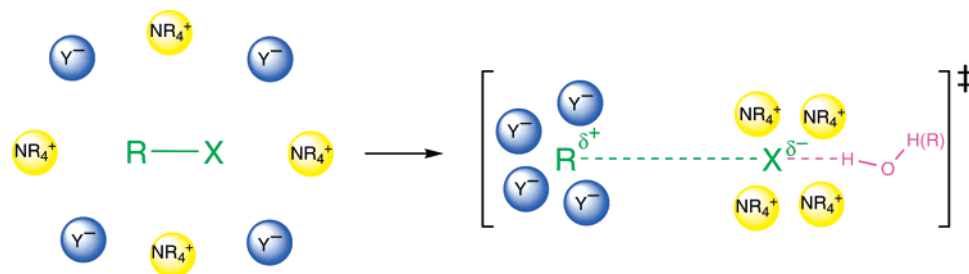
Chart 1. Solvolysis Rates in [BMIM][NTf₂] Relative to Rates in Acetic Acid

is comparable to that in ethanol. However, for triflates, the ionizing power of [BMIM][NTf₂] is “moderate” and can exceed that of common polar protic solvents such as acetic acid, ethanol, and methanol.

Given the nature of ionic liquids (cations and anions), why are *Y* values for solvolysis reactions, where carbocations and anions are formed, not incredibly large? It is suggested that ionic liquids have a decreased ability to hydrogen bond to the developing anion in the transition state (relative to polar protic solvents) and this is, in part, responsible for the generally low *Y* values for ionic liquids. In the case of the triflate leaving group, where the demand for stabilization of the developing triflate anion is much less, and there is decreased demand for hydrogen bonding, then the ionizing power of ionic liquids is higher.

Welton has carried out kinetic studies on S_N2 reactions in ionic liquids.¹⁰ He has concluded that nucleophiles such as halide are fully coordinated in ionic liquids and that one face of the halide must become uncoordinated before S_N2 reaction can occur. In the case of neutral amine nucleophiles, hydrogen bonding of the ionic liquid with the emerging ammonium ion leads to increased reactivity of amines in ionic liquids. With these findings in mind, some further speculation concerning the nature of the involvement of ionic liquids in cationic solvolyses is therefore in order. We envisage a developing transition state (leading to an ion-pair) where the loosely organized ionic liquid becomes much more ordered as charge develops (Chart 2). The importance of trace amounts of water in determining rates of 1-adamantyl mesylate, **11**, as well as the significant amount of ether product, suggests a role of water (or alcohol) in the

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Chart 2. Schematic Representation of Reorganization of an Ionic Liquid in the Transition State during an S_N1 Process

transition state. It is suggested that the function of trace amounts of water (or alcohol) is to more effectively hydrogen bond to the developing anion. As the reaction proceeds and alcohol product builds up, the hydrogen bonding of alcohol to the developing mesylate anion results in alcohol being present in the vicinity of the initially formed ion pair. This leads to facile ether formation. In the case of triflates such as **15**, the decreased need for hydrogen bonding for anion stabilization results in a much smaller rate effect of added water.

Conclusions. A wide variety of substrates undergo clean first-order solvolysis reactions in ionic liquids. Cationic intermediates are involved as evidenced by a Hammett ρ^+ value of -3.74 for reaction of cumyl trifluoroacetates. 1-Adamantyl mesylate and 2-adamantyl triflate also react readily by cationic mechanisms. Further evidence for cationic intermediates comes from the observation of cationic rearrangement processes in a number of triflates, mesylates, and trifluoroacetates. Rates of reaction of substrates in ionic liquids are not extraordinarily high relative to rates in polar protic solvents. Certain triflates react in [BMIM]-[NTf₂] to give products derived from competing loss of CF₃SO₂⁻. This unusual S—O fragmentation, as well as facile ether formation, suggests that carbocation chemistry in ionic liquids is not only viable but also somewhat different from the chemistry observed in protic solvents.

Experimental Section

Preparation of Ionic Liquids. The ionic liquids used in these studies were prepared by the general procedures previously described.^{38–40} Thus, in a typical procedure for the preparation of [BMIM][NTf₂], 11.3 g of 1-butyl-3-methylimidazolium chloride was dissolved in 35 mL of distilled water and 20.2 g of lithium triflamide was added with vigorous stirring. After 30 min, the phases were allowed to separate and the upper aqueous phase was decanted. Distilled water (20 mL) was added to the ionic liquid phase and the mixture was stirred for 15 min. The upper aqueous phase was removed, and 40 mL of CH₂Cl₂ was added to the remaining ionic liquid. A small amount of Na₂SO₄ was added to the solution followed by MgSO₄. After filtration, the solvent was removed using a rotary evaporator. The last traces of CH₂Cl₂ were removed by heating the residue at 50 °C at 15 mm pressure until the weight of the residue remained constant. The yield of [BMIM][NTf₂] was 26.8 g (99% yield), and the ¹H NMR spectrum showed no trace of CH₂Cl₂. The water content was <0.03% (as can be determined by integration of the water signal which appears between δ 2.6 and 2.8). Ionic liquids are hygroscopic, and the amount of water present was determined by NMR. In certain studies, trace amounts of water were added to the ionic liquid.

Preparation of Substrates. The preparations of **2**,⁴¹ **5**,¹⁸ **8**,²³ **11**,^{22,42} **15**,²⁶ **19**,²⁷ **27**,²⁸ and **40**³⁴ have previously been described. Mesylates **33** and **47** were prepared by reaction of CH₃SO₂Cl and Et₃N with the appropriate alcohols, *trans*-2-phenylcyclopropylcarbinol²⁹ and *anti*-7-norbornenol.⁴³ Triflate **37** was prepared by reaction of 1-hydroxy-2,2-dimethoxycyclobutanol³³ with triflic anhydride and 2,6-lutidine in CH₂Cl₂. Trifluoroacetate **43** was prepared by reaction of alcohol **45**^{36a} with trifluoroacetic anhydride and 2,6-lutidine in ether.

Reaction of 106 mg of *trans*-2-phenylcyclopropylcarbinol²⁹ with 100 mg of CH₃SO₂Cl and 105 mg of Et₃N gave mesylate **33** as an unstable oil. ¹H NMR of **33** (CDCl₃) δ 7.27 (t, J = 8 Hz, 2 H), 7.19 (t, J = 8 Hz, 1 H), 7.09 (d, J = 8 Hz, 2 H), 4.24 (m, 2 H), 3.021 (s, 3 H), 2.00 (m, 1 H), 1.57 (m, 1 H), 1.13 (m, 1 H), 1.07 (m, 1 H). ¹³C NMR of **33** (CDCl₃) δ 140.9, 128.5, 126.2, 126.0, 73.8, 38.1, 22.3, 21.4, 14.1.

Reaction of 201 mg of 1-hydroxy-2,2-dimethoxycyclobutanol³³ with 490 mg of (CF₃SO₂)₂O and 225 mg of 2,6-lutidine gave triflate **37** as an unstable oil. ¹H NMR of **37** (CDCl₃) δ 5.09 (t, J = 7.6 Hz, 1 H), 3.323 (s, 3 H), 3.262 (s, 3 H), 2.8 (m, 2 H), 2.10 (m, 1 H), 1.78 (m, 1 H). ¹³C NMR of **37** (CDCl₃) δ 118.4 (q, J = 319 Hz), 103.2, 83.0, 49.7, 49.5, 25.7, 22.2.

Reaction of 77 mg of alcohol **45**^{35a} with 90 mg of (CF₃CO)₂O and 53 mg of 2,6-lutidine gave trifluoroacetate **43** as an oil. ¹H NMR of **43** (CDCl₃) δ 7.42–7.34 (m, 5 H), 5.88 (d of d, J = 8, 6 Hz, 1 H), 5.58 (m, 1 H), 5.17 (m, 1 H), 2.78 (m, 1 H), 2.60 (m, 1 H), 1.48 (m, 2 H), 0.015 (s, 9 H). ¹³C NMR of **43** (CDCl₃) δ 156.8 (q, J = 42 Hz), 114.6 (q, J = 286 Hz), 138.0, 130.1, 128.9, 128.8, 126.6, 119.9, 80.4, 33.7, 18.8, -1.8 .

Reaction of 114 mg of *anti*-7-norbornenol⁴³ with 165 mg of CH₃SO₂Cl and 183 mg of Et₃N gave *anti*-7-norbornenyl mesylate **47** as an unstable oil. ¹H NMR of **47** (CDCl₃) δ 6.02 (t, J = 2.3 Hz, 2 H), 4.27 (br s, 1 H), 3.00 (s, 3 H), 2.88 (m, 2 H), 1.88 (m, 2 H), 1.13 (m, 2 H). ¹³C NMR of **47** (CDCl₃) δ 133.5, 86.7, 44.2, 38.4, 21.4.

Solvolyses in Ionic Liquids. Kinetics Procedures. Rates of reaction of triflates, mesylates, and trifluoroacetates were determined by ¹H and ¹⁹F NMR methods. Spectra were recorded in the unlocked mode using recently described methods.¹⁴

Method 1:¹⁶ Approximately 5 mg of substrate was dissolved in 0.7 mL of the appropriate ionic liquid with stirring and approximately 5 mg of 2,6-lutidine was added. The sample was placed in an NMR tube, and the tube was placed in a constant-temperature bath at the appropriate temperature or in the probe of the NMR at 25.0 °C. At appropriate time intervals, the tube was withdrawn from the bath and analyzed by ¹H NMR and the shift of the singlet due to the 2,6-lutidine was determined. The shift of the 2,6-lutidine, which moves downfield as a function of time, was monitored. After 10 half lives, a final reading was taken. First-order rate constants were calculated by standard least squares procedures. Rates of **2c**, **2f**, **8**, **11**, **15**, **19**, **27**, **37**, and **47** were measured by this method.

Method 2:⁴⁴ Approximately 5 mg of substrate was dissolved in 0.7 mL of the appropriate ionic liquid with stirring and approximately 5 mg of

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2,6-lutidine was added. The sample was placed in an NMR tube, and the tube was placed in a constant-temperature bath at the appropriate temperature or in the probe of the NMR spectrometer at 25.0 °C. At appropriate time intervals, the NMR tube was analyzed by ¹⁹F NMR and the relative areas of unreacted trifluoroacetate and trifluoroacetate anion were determined. A solvent suppression routine was used to eliminate most of the signal due to the triflamide anion of the ionic liquid. Rates of **2a**, **2b**, **2d**, and **2e** were measured by this method.

Method 3: A sample of substrate in the appropriate ionic liquid prepared as described above was placed in an NMR tube, and the tube was placed in a constant-temperature bath at the appropriate temperature. At appropriate time intervals, the tube was analyzed by 600 MHz ¹H NMR and areas due to unreacted mesylate and mesylate anion were measured. Rates of **33** and **40** were measured by this method.

Solvolyses in Ionic Liquids. Product Studies. Approximately 5–10 mg of the appropriate substrate was dissolved in 1 mL of the ionic liquid and 2,6-lutidine was added. The mixture was kept at the appropriate temperature for 8 half lives and then analyzed by ¹H NMR spectroscopy. All products (except ether **49**) were identified by spectral comparisons with authentic samples. In certain cases, the reaction mixture was extracted into hexane or C₆D₆ before recording NMR spectra. Product ratios were determined by integration of the appropriate signals in the ¹H NMR spectra. The following procedures for solvolyses of trifluoroacetate **5**, mesylate **11**, triflate **19**, and mesylate **33**, are representative.

A solution of 10 mg of trifluoroacetate **5**¹⁸ (99% D incorporation) and 8 mg of 2,6-lutidine in 1.0 mL of [BMIM][NTf₂] containing 0.3% H₂O was kept at room temperature for 8 h. The mixture was then extracted with 3 mL of hexane, and the hexane was filtered through a small amount of silica gel in a pipet. The solvent was removed using a rotary evaporator and the residue was dissolved in CDCl₃ and analyzed by ¹H and ¹³C NMR. The ¹H NMR showed only alkene **6**, which contained 99% deuterium as determined from the residual undeuterated alkene signal at δ 6.59.

A solution of 11.3 mg of 1-adamantyl mesylate, **11**, and 9 mg of 2,6-lutidine in 1.1 mL of [BMIM][NTf₂] containing 0.1% H₂O was heated at 70 °C for 6.5 h. ¹H NMR analysis showed a mixture of 1-adamantanol, **12**, and di-1-adamantyl ether, **13**,⁴⁵ in a 4:1 ratio. The mixture was then extracted with 3 mL of hexane, and the hexane was

filtered through a small amount of silica gel in a pipet. The solvent was removed using a rotary evaporator. The residue was identified as di-1-adamantyl ether, **13**,⁴⁵ by ¹H NMR and mass spectrometry which showed *m/e* = 286. The 1-adamantanol did not extract into the hexane. In a separate run containing 0.35% H₂O, extraction of the solvolysis mixture with two 3 mL portions of ether and analysis by ¹H NMR showed **12** and **13** in a 90:10 ratio.

A solution of 4.6 mg of triflate **19** and 4.5 mg of 2,6-lutidine in 1.1 mL of [BMIM][NTf₂] containing 0.5% H₂O was heated at 70 °C for 3 h and then heated at 80 °C for 3 h. At the completion of the reaction, the mixture was analyzed by ¹⁹F NMR which showed CF₃SO₃⁻ located 0.47 ppm downfield from the solvent NTf₂⁻ signal and CF₃SO₂⁻ located 8.31 ppm upfield from the solvent signal. ¹H NMR analysis showed alcohol **20**, naphthalene, **21**, and 1-naphthaldehyde, **22**, in a 61:29:10 ratio. These products were identified by spectral comparisons with authentic samples run in [BMIM][NTf₂].

A solution of 8.4 mg of mesylate **33** and 8.2 mg of 2,6-lutidine in 1.5 g of [BMIM][NTf₂] containing 0.4% H₂O was kept at 25 °C for 24 h and then heated at 45 °C for 5 h. During the course of the reaction, the solution was analyzed by ¹H NMR which showed the starting mesylate at δ 3.04 as well as a signal due to mesylate ion (CH₃SO₃⁻) which grows in at δ 2.7. Also appearing is a transient signal which grows in at δ 2.87 which is due to a rearranged and reactive mesylate tentatively identified as 1-phenyl-3-buten-1-yl mesylate. At the completion of the reaction ¹H NMR analysis showed only 1-phenyl-1,3-butadiene, **34**,⁴⁶ and 1-phenyl-3-buten-1-ol, **35**,⁴⁷ in a 59:41 ratio. These products were identified by spectral comparisons with authentic samples.

Supporting Information Available: ¹NMR spectra illustrating the determination of water content in ionic liquids, ¹NMR and ¹⁹F NMR spectra showing the kinetic methods, the Hammett plot for the data in Table 1, and ¹H and ¹³C NMR spectra of compounds **33**, **37**, **43**, and **47**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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