N-(Trifluoromethylsulfonyl)aryloxytrifluoromethylsulfoximines [ArO−SO(CF_3)=NTf] and N-Aryltriflimides Ar−N($Tf)_2$ by Thermal and Photolytic Dediazoniation of [ArN_2][BF_4] in [BMIM][Tf_2N] Ionic Liquid: Exploiting the Ambident Nucleophilic Character of a "Nonnucleophilic" Anion

Kenneth K. Laali,* Takao Okazaki, and Scott D. Bunge

Department of Chemistry, Kent State University, Kent, Ohio 44242

klaali@kent.edu

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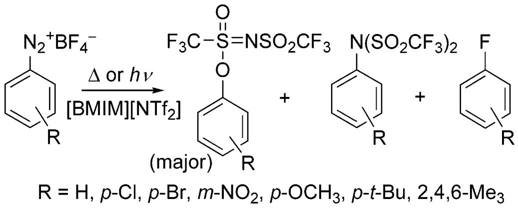

Arenediazonium tetrafluoroborate salts undergo metathesis on immobilization in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonato)amide [BMIM][Tf_2N]. The "noncoordinating", "nonnucleophilic" [Tf_2N] anion acts as an ambident nucleophile toward the aryl cations, formed via thermal dediazoniation, to give predominantly the oxy anion quenching products [ArO−SO(CF_3)=NTf], with minimal formation of ArN($Tf)_2$, irrespective of the nature of the substituent(s) on the ArN_2^+. Strong preference for the formation of oxygen trapping products did not change under photolytic conditions, where dediazoniation occurs at room temperature. A minimal amount of the Schiemann product ArF is also formed in both thermal and photolytic dediazoniation, depending on the substituent(s). Progress of dediazoniation in the IL (both thermal and photolytic) and the evolution of the products were directly monitored by ^1H and ^{19}F NMR. According to DFT (Density Functional Theory) calculations, PhN($Tf)_2$ is more stable than PhO−SO(CF_3)=NTf by 15−17 kcal/mol, depending on the basis set. Inclusion of solvation effects (PCM, with acetone and with CH_2ClCH_2Cl as solvent) did not change this preference. The [ArN_2][BF_4] dediazoniation in [BMIM][Tf_2N] resulted in synthesis and characterization of a series of hitherto unknown [ArO−SO(CF_3)=NTf] compounds. The X-ray structure of MesO−SO(CF_3)=NTf (Mes = mesityl) is reported. On the basis of extraction studies, suitable solvent systems have been identified that remove the products without dissolving [BMIM][NTf_2], thus overcoming product recovery difficulties typically associated with the use of this IL.

Introduction

We have previously reported[1] that arenediazonium tetrafluoroborates can be dissolved/immobilized in imidazolium ionic liquids (ILs) [EMIM][BF_4] (1-ethyl-3-methylimidazolium tetrafluoroborate) and [BMIM][PF_6] (1-butyl-3-methylimidazolium hexafluorophosphate), and subsequently undergo fluorodediazoniation upon heating, to give ArF in very high yield and selectivity. It is also possible to generate the diazonium salt in situ in the IL, by using nitrosonium salts. Immobilization of [ArN_2][BF_4] in [EMIM][CF_3COO], [EMIM][OTs], and [EMIM][OTf] resulted in metathesis, and subsequent dediazoniation gave the corresponding esters (nucleophile trapping products) ArOCOCF_3, ArOTs, and ArOTf, with little or no ArF being observed.

Ionic liquids (ILs), in particular imidazolium ILs, bearing [Tf_2N] counterion (**1**) have attracted recent interest due to their exceptional properties that combine hydrophobicity with low

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* Address correspondence to this author. Fax: 330-6723816. Phone: 330-6722988.

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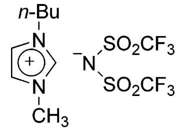
melting points, thermal and electrochemical stability, low viscosity, and high conductivity.[2−4]



[BMIM][NTf$_2$]

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Since $HN(Tf)_2$ is a remarkably strong Brønsted acid with a pK_a (in acetic acid) comparable to that of H_2SO_4,[5] its perfluorinated conjugate base is expected to be highly inert, possessing little or no coordinating and nucleophilic characteristics.

An exception to its noncoordinating nature was the finding that it coordinates to Yb^{2+}.[6] A qualitative sequence of cation/anion association tendencies was derived recently by Chiappe and associates[7] for a group of ammonium and imidazolium cations bearing various counterions including [OTf], [PF_6], and [Tf_2N] by using ESI-MS, based on MS/MS measurements on mixed complexes. This work demonstrated that [Tf_2N] was the least interacting anion among the counterions studied. Whereas dediazoniation of $PhN_2^+\ BF_4^-$ (**1a**) in a 1:1 mixture of [BMIM]-[Br] and [BMIM][PF_6] gave only PhBr, the same reaction in [BMIM][Br] and [BMIM][Tf_2N] (1:1) gave the Tf_2N trapping products.[8] It was suggested that this stems from differences in metathesis and pre-association abilities of different anions, which infer that the following process (eq 1) is highly efficient:

$$[ArN_2][BF_4] + [EMIM][Tf_2N] \rightarrow [ArN_2][Tf_2N] + [EMIM][BF_4] \quad (1)$$

Phenyldiazonium bis(trifluoromethylsulfonyl)amide was previously synthesized and isolated by Yagupolskii et al.[9] via the following reaction (eq 2):

$$PhN_2^+\ Cl^- + XN(SO_2CF_3)_2 \rightarrow PhN_2^+\ {}^-N(SO_2CF_3)_2 + XCl\ (X = H \text{ or } Na) \quad (2)$$

Upon heating, N-(trifluoromethylsulfonyl)phenoxytrifluoromethylsulfoximine (**3a**) and $PhN(Tf)_2$ (**2a**) were formed in ca. 12:1 ratio. The same approach was used by Zhu and DesMarteau,[10] who prepared the parent (R = H) as well as the p-F and p-OH diazonium salts. The ratio of O versus N trapping products formed via thermal dediazoniation was reported to be variable depending on solvent, temperature, and reaction time.[10]

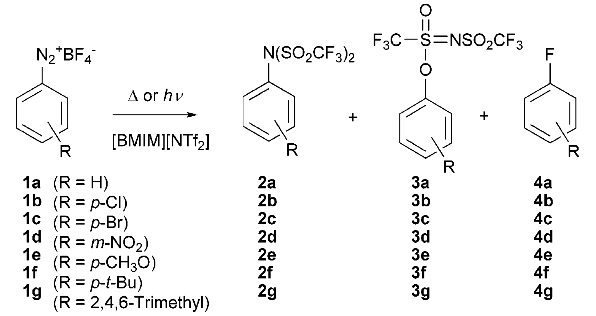

FIGURE 1. Dediazoniation products in [BMIM][Tf_2N].

The metathesis approach in imidazolium ILs, as shown in our earlier work,[1] makes it possible to tailor-make diazonium salts for various studies and eliminates the need for independent synthesis and isolation of targeted salts.

Parent N-phenyltriflamide and some of its ring-substituted derivatives have been known in the literature since the early studies of Hendrickson and Bergeron[11a,b] and Yagopolskii and associates[11c,d] on the synthesis of triflamides via the conjugate base of amines and Tf_2O. Whereas parent $PhN(Tf)_2$ is commercially available, the ring-substituted derivatives are unavailable. As for the [$ArO{-}SO(CF_3){=}NTf$] class of compounds, no published synthetic methods are available. Therefore, access to these compounds via dediazoniation protocol, starting from readily available aryldiazonium tetrafluoroborates in [BMIM]-[Tf_2N], represents a useful and remarkably simple approach.

In continuation of our studies focusing on onium ion chemistry and electrophilic aromatic substitution in ionic liquids,[1,12−17] and inspired by recent work of Chiappe,[7,8] and earlier studies by DesMarteau[10] and Yagupolskii,[9] we have performed a substituent effect study on dediazoniation to explore the O- versus N-trapping product dependency, under both thermal and photolytic conditions, by NMR monitoring. In the context of this study, we have synthesized and characterized several hitherto unknown [$ArO{-}SO(CF_3){=}NTf$] compounds (**3**) (Figure 1), and have determined the X-ray structure for $MesO{-}SO(CF_3){=}NTf$ (**3g**). Relative stabilities of the O- versus N-trapping products were also investigated by the DFT (Density Functional Theory) method for **2a** and **3a** (Ar = Ph).

Whereas the widely utilized [BMIM] and [EMIM] ILs with TfO and BF_4 counterions are insoluble in Et_2O, allowing phase separation and easy workup, the corresponding [Tf_2N] ILs are soluble, not only in ether but also in a host of other organic solvents, and this creates practical difficulties for product removal from the IL. This problem has been addressed and

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TABLE 1. Dediazoniation Outcomes, Product Ratios, and Yields for Thermal Decomposition of Diazonium Salts in [BMIM][NTf$_2$][a]

diazonium salt **1**	temp (°C)	reaction time	conversion of **1** (%)	products distribution **2**:**3**:**4** (%)[b]		yields (%)[c]
				in IL	after recovery from IL[d]	
a: R = H	rt	2 days	32	7:93:−		
	90	13 min	100	6:84:19	4:96:−[e]	36
b: R = *p*-Cl[f]	90	1 h	85	8:70:22		
	90	2.5 h	100	7:74:19	10:90:−[g]	36
	90	13 h	100	5:66:29		
c: R = *p*-Br	rt	2 days	0			
	50	2 h	0			
	90	13 h	100	5:72:23	8:92:−[e]	61
d: R = *m*-NO$_2$	90	22.5 h	100	6:80:14	14:86:−[e]	29
e: R = *p*-CH$_3$O	70	1 day	0			
	80	1 day	31	−:−:trace		
	90	12 h	84	−:−:trace		
		27 h	100	−:−:trace		
f: R = *p*-*t*-Bu	90	14 min	100	4:84:12	3:97:−[e]	64
g: R = 2,4,6-trimethyl	90	13 min	100	2:72:26	1:99:−[h]	56

[a] Reaction condition: 0.12 mmol of **1**; 0.60 mmol of IL. [b] By NMR. [c] Amount of crude mixture of products after recovery from IL. [d] Extraction with hexane−ether (19:1) and evaporation at rt under reduced pressure. [e] Colorless oil. [f] Reaction condition: 0.24 mmol of **1**; 1.20 mmol of IL. [g] Pale-yellow oil. [h] Pale-pink crystals.

resolved in the framework of this study, by identifying solvents that selectively extract the products without dissolving the IL.

Results and Discussion

NMR Monitoring of Dediazoniation in [BMIM][Tf$_2$N]. (a) Initial Studies and Search for Suitable Solvents for Product Recovery from IL. Parent **1a** underwent slow dediazoniation at room temperature to give **2a** and **3a** in 1:13 ratio, with 68% of **1a** remaining unreacted after 2 days. Dediazoniation proceeded to completion when the sample was briefly heated to ca. 70 °C (for just 15 min), at which point the **2a**:**3a** ratio was 1:14.

By using Et$_2$O (the most commonly employed solvent for preparative chemistry in ILs), the products were completely extracted, but the ether layer contained significant amounts of the IL. Product extraction with hexane (a solvent that does not dissolve the IL) was only effective/acceptable when several extractions were performed and the extracts were combined. These initial tests underscored the need for finding suitable solvents for extraction and product recovery, without dissolving/removing the IL.

Diazonium salt **1c** was immobilized in [BMIM][NTf$_2$] and heated by ca. 70 °C for 2 h. At this point, dediazoniation was complete and the **2c** to **3c** ratio was 1:22. Suitability of *tert*-butyl methyl ether, benzene, nitromethane, and CS$_2$ as potential solvents for extraction was tested. With *t*-BuOMe the organic extract contained significant amounts of the IL. Benzene appeared more suitable, but still removed some of the IL. MeNO$_2$ was miscible with the IL and gave just one phase, but CS$_2$, on the other hand, was able to extract the products with no contamination from the IL.

(b) Larger Scale Dediazoniations and Product Recovery. Following the above-mentioned exploratory experiments (on 3−5 mg scale), dediazoniation of **1b** in [BMIM][NTf$_2$] was carried out on a larger scale (500 mg) (with **1b**: IL molar ratio of 1:5). Figure S1 in the Supporting Information shows the ^{1}H NMR spectrum at the onset, prior to dediazoniation (signals due to the IL and the diazonium ion are marked on the spectrum and on the inset). The immobilized diazonium salt was heated at 90 °C for 2.5 h. Figures S2 and S3 in the Supporting Information show the proton and fluorine NMR spectra, following the completion of dediazoniation and prior to extraction (with signals due to the products **2b** and **3b** marked on the spectrum and on the inset; traces of **4b** are also detectable).

Product recovery tests (for a more complete list and outcomes see Table S1 in the Supporting Information) were performed with CS$_2$, and with hexane−ether mixtures (in 1:1, 8:2, and 19:1 ratios) (2 × 1 mL). It was confirmed that CS$_2$ could extract the products with negligible contamination with the IL. Similarly, the NMR spectrum of the IL phase following product extraction with hexane-ether (19:1) showed no detectable peaks due to products.

Figures S4 and S5 (Supporting Information) illustrate the proton and fluorine NMR spectra of the reaction mixture following extraction with hexane/ether (19:1), and after solvent removal under reduced pressure. It is noted that a trace of **4b**, observed in the reaction mixture prior to extraction, is no longer present after extraction and solvent removal. Loss of the volatile **4b** was also corroborated based on material balance, and from relative NMR integrals before and after dediazoniation, which also implied partial decomposition of **2b**/**3b** under thermal dediazoniation.

Based on a number of test studies, hexane/ether (19:1) was selected as the optimal solvent system for workup, and the method was used for product isolation in subsequent runs.

Table 1 summarizes the product ratios at various intervals (in the IL before extraction and after extraction and product recovery) for the thermal dediazoniation of diazonium tetrafluoroborate salts **1a** through **1g**, immobilized in [BMIM][Tf$_2$N]. Isolated product yields were typically in the 30−60% range, depending on the diazonium salt. NMR monitoring of the progress of dediazoniation in the IL, and product analysis before and after extraction, indicated that all dediazoniations were heterolytic (absence of any detectable ArH),[18] and that aryl cation trapping by [Tf$_2$N] anion was very predominant relative to Schiemann product (ArF) formation, irrespective of the substituent on the diazonium ion. These findings are in concert with earlier dediazoniation studies in ILs.[1]

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TABLE 2. Dediazoniation Outcomes, Product Ratios, and Yields for Photolytic Decomposition of Selected Diazonium Salts in [BMIM][NTf_2][a]

diazonium salt **1**	temp (°C)	reaction time[b]	conversion of **1** (%)	products distribution **2**:**3**:**4** (%)[c] in IL	products distribution **2**:**3**:**4** (%)[c] after recovery from IL[e]	yields (%)[d]
b: R = *p*-Cl	rt	10 d[f]	100	6:77:17	7:93:−[g]	38
d: R = *m*-NO_2	rt	1.5 d[h]	100	4:86:10	18:82:−[g]	12
e: R = *p*-OMe	rt	4 d[f] + 4 h[h]	100	3:64:33		<5
f: R = *p*-*t*-Bu	rt	9.5 h[h]	100	2:86:12	18:82:−[g]	32
	rt	3 h[h]	87	8:64:28	8:92:−[g]	41

[a] Reaction condition: 0.12 mmol of **1**; 0.60 mmol of IL. [b] d (day); h (hour). [c] By NMR. [d] Amount of crude mixture of products after recovery from IL. [e] Extraction with hexane−ether (19:1) and evaporation at rt under reduced pressure. [f] 0.2 W low-pressure mercury lamp. [g] Pale-yellow oil. [h] 15 W low-pressure mercury lamp.

In thermal dediazoniations described, nucleophilic trapping by the [Tf_2N] anion resulted in predominant formation of [ArO−SO(CF_3)═NTf] over the alternative ArN($Tf)_2$, and preference for trapping at oxygen over trapping at nitrogen remained unchanged by changing the nature of the substitutents on PhN_2^+ (electron withdrawing or donating).

(c) Tf_2N-Derived Product Ratios Under Photolytic Dediazoniation. To determine whether preference for trapping at oxygen could change if dediazoniations were effected at room temperature under photolytic conditions[19] (by UV irradiation), diazonium salts **1b**, **1d**, **1e**, and **1f** were immobilized in [BMIM]-[Tf_2N] and subjected to UV irradiation in quartz NMR tubes.

As in earlier cases, dediazoniation progress was monitored directly by NMR. Product ratios were determined in each case after specified intervals, both prior to extraction (directly in the IL) and after product recovery (data summarized in Table 2). The corresponding [ArO−SO(CF_3)═NTf] compounds were found to be the major product in every case, whereas ArN($Tf)_2$ compounds were consistently present in minor amounts. As observed in the thermal reactions, the corresponding ArF was also formed in minor amounts (detected in the reaction mixtures prior to workup). The use of very low power UV source (a 0.2 W low-pressure mercury lamp used in the laboratory to visualize spots in TLC) in the case of **1b** (a diazonium salt whose thermal dediazoniation was relatively slow) resulted in very slow dediazoniation. After 10 days **1b** had fully reacted. The [Tf_2N]-derived products were obtained in 38% isolated yield (in 93:7 ratio). Dediazoniation rates were accelerated when a higher power UV lamp was employed. For example, in the case of **1f** (R = *t*-Bu) NMR monitoring indicated that after 3 h, only 13% unreacted diazonium salt was present in the reaction mixture. Under photolytic conditions, and with the more powerful UV lamp, shorter reaction times resulted in higher isolated yields as compared to longer reactions, suggesting that prolonged irradiation resulted in product degradation. This problem was especially significant in the case of **1e** (*p*-OMe).

Strong preference for trapping at oxygen versus nitrogen was therefore also established in photolytic dediazoniations in the IL. The presence of the corresponding Schiemann products (ArF) and absence of the protio-dediazoniation products (ArH) (at the NMR detection limit) argue in favor of heterolytic dediazoniation for both thermal and photolytic dediazoniation reactions in the IL.

Table S2 in the Supporting Information summarizes the multinuclear NMR data (^{1}H, ^{13}C, and ^{19}F) as well as IR data for the Tf_2N-derived products synthesized in this study. Spectral data for **2a**,[10,20a] **3a**,[9,10] **2c**,[20b] and the corresponding ArF products **4a**−**g**[1,21] agree with the reported data in the literature. NMR data for **2d**[11c] and **2e**[11d,e] are also included. As can be seen in the representative NMR spectra (Supporting Information), ^{19}F NMR provides the simplest and most direct assay for monitoring the evolution of Tf_2N-derived products upon dediazoniation, with [ArO−SO(CF_3)═NTf] exhibiting two well-resolved singlets (1:1 ratio) and ArN($Tf)_2$ a slightly more deshielded singlet (see Figure S5, Supporting Information).

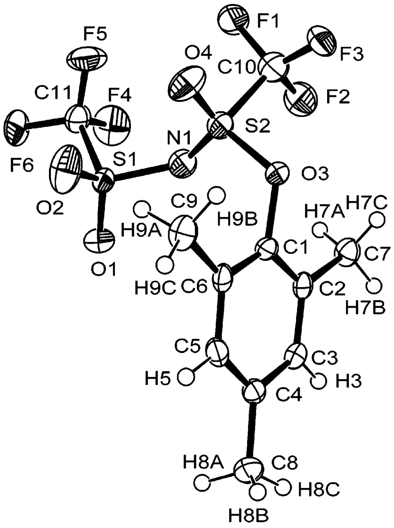

FIGURE 2. Thermal ellipsoid plot of **3g** (ellipsoids are drawn at the 50% level).

(d) X-ray Structure of 3g. The novel MesO-SO(CF_3)═NTf product **3g**, formed via thermal dediazoniation of diazonium salt **1g** in the IL, was isolated as pale pink crystals, and its X-ray structure was determined. The thermal ellipsoid plot is shown in Figure 2 (for detailed structural data see the Supporting Information). The two N−S bonds are noticeably short [1.493-(7) Å] and long [1.625(6) Å]. The Ar−O−SO angle is 120.7-(4)°. Bond angles for N−SO_2−CF_3, N═SO_2−CF_3, and the S−N−S moieties are 100.9(3)°, 105.8(4)°, and 127.9(4)° respectively.

(e) DFT Calculations. To get a handle on relative product stabilities, the Tf_2N-derived products **2a** and **3a** were calculated

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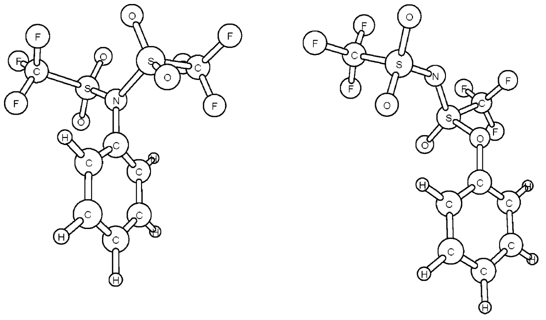

2a **3a**

FIGURE 3. Optimized structures for **2a** and **3a** by B3LYP/6-31G(d).

by DFT at various basis sets and the data are gathered in Table S5 (Supporting Information). Compound **2a** is 16.0 kcal/mol more stable than **3a** at the B3LYP/6-31G(d) level. The computed lowest energy structure for **3a** has a different conformation as compared to the X-ray geometry, which was calculated to be slightly less stable. The order of stability is similar at B3LYP/6-31++G(d,p) and B3LYP/6-311++G(d,p) levels. The optimized structures are shown in Figure 3.

The dielectric constant ($\epsilon = 11.6$) has been measured for [BMIM][NTf$_2$].[22] Since the dielectric constants for CH_2ClCH_2Cl and acetone are 10.36 and 20.7, respectively, and these solvents are available for PCM (polarizable continuum models) calculations in the Gaussian 03 program, solvation effects in the two solvents were estimated by PCM. The dielectric constant of acetone is larger than that of [BMIM][NTf$_2$], and it was anticipated that it could result in overestimation of the solvation effect. Nevertheless, relative stability differences between **2a** and **3a** were not affected by this test.

Clearly, the observed strong preference for oxy-anion trapping is related to the kinetics of nucleophilic quenching of the aryl cation via dediazoniation, which is opposite to the relative thermodynamic stabilities of the two types of products.

Summary

Immobilization of the readily available diazonium tetrafluoroborates in [BMIM][Tf$_2$N] and subsequent dediazoniation provided a simple and practical one-pot approach for the synthesis of the Tf$_2$N-derived products. Despite the “nonnucleophilic” and “noncoordinating” nature of the [Tf$_2$N] anion, nucleophilic quenching products were predominantly formed, with relatively minor formation of the Schiemann product. Oxygen-trapping product was greatly favored over N-trapping product, irrespective of the substituents, and this preference was observed in both thermal and photolytic dediazoniation reactions. The ^{19}F NMR provided the most convenient tool for monitoring the dediazoniation progress and the evolution of the products. DFT calculations at various basis sets showed that PhO−SO(CF$_3$)=NTf is consistently less stable than ArN(Tf)$_2$. The X-ray structure of MesO−SO(CF$_3$)=NTf provided the first glance into the structure of this class of molecules. Compound **1g** and related compounds, bearing other carbocation stabilizing groups on the aryl ring, represent intriguing probes for solvolytic studies, especially in ILs. Studies focusing on these aspects are ongoing in our laboratory.

Supporting Information Available: Experimental section, ^{1}H and ^{19}F NMR spectra of reaction mixtures and products (Figures S1−S15), results of product recovery studies from the ionic liquid (Table S1), multinuclear NMR and IR data (Table S2), data collection parameters (Table S3), selected bond distances and angles for **3g** from X-ray analysis (Table S4), computed energies (Table S5), and Cartesian coordinates for optimized structures by the DFT calculations (Tables S6−S11); the X-ray crystallographic file in CIF format for **3g**, also available from the Cambridge Data Base under CCDC 645183. This material is available free of charge via the Internet at http://pubs.acs.org.

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