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# Halo- and Azidodediazoniation of Arenediazonium Tetrafluoroborates with Trimethylsilyl Halides and Trimethylsilyl Azide and Sandmeyer-Type Bromodediazoniation with Cu(I)Br in $[BMIM][PF_6]$ Ionic Liquid[§]

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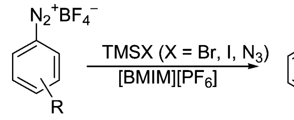
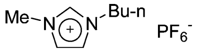


**1** (R = *p*-*t*-Bu) **5** (R = *p*-Br)
**2** (R = *p*-Cl) **6** (R = *p*-OMe)
**3** (R = *p*-Me) **7** (R = *m*-$NO_2$)
**4** (R = H) **8** (R = 2,4,6-$Me_3$)

Reaction of $[ArN_2][BF_4]$ salts immobilized in $[BMIM][PF_6]$ ionic liquid (IL) with TMSX (X = I, Br) and $TMSN_3$ represents an efficient method for the preparation of iodo-, bromo-, and azido-derivatives via dediazoniation. The reactions can also be effected starting with $ArNH_2$ by in situ diazotization with $[NO][BF_4]$ followed by reaction with TMSX or $TMSN_3$. Depending on the substituents on the benzenediazonium cation, competing fluorodediazoniation (ArF formation) and hydrodediazoniation (ArH formation) were observed. Dediazoniation with $TMSN_3$ and with TMSI generally gave the highest chemoselectivity toward $ArN_3$ and ArI formation. The IL was recycled and reused up to 5 times with no appreciable decrease in the conversions. Multinuclear NMR monitoring of the interaction of $[ArN_2][BF_4]$/TMSX, $[BMIM][PF_6]$/TMSX, and $[BMIM][PF_6]$/TMSX/$[ArN_2][BF_4]$ indicated that TMSF is formed primarily via $[ArN_2][BF_4]$/TMSX, generating $[ArN_2][X]$ in situ, which gives ArX on dediazoniation. Competing formation of ArF in Sandmeyer-type bromodediazoniation of $[ArN_2][BF_4]$ with Cu(I)Br immobilized in the IL points to significant involvement of heterolytic dediazoniation.

The remarkable leaving group ability of $-N_2^+$ enables two high-energy reactive intermediates namely aryl cation and aryl radical to be generated via heterolytic and homolytic dediazoniation processes, respectively. The mechanistic aspects of dediazoniation of $ArN_2^+$ salts have been extensively studied.[1−6] The heterolytic versus homolytic pathways are greatly influenced by the nature of solvent/nucleophile and substituent(s) on the diazonium cation.[1,4] Heterolytic dediazoniation dominates in low nucleophilicity/highly ionizing solvents, in protic superacids or in aqueous acids, and with electron-donating substitutents, whereas homolysis is promoted in more nucleophilic solvents, and in the presence of electron-withdrawing substitutes that increase the electron-demand at $N_\beta$.[1,2] For thermal dediazoniation of $R-C_6H_4-N_2^+\ BF_4^-$, whereas formation of Ar-Nu and ArF is indicative of a heterolytic process ($Ar^+$ formation and trapping), the presence of ArH (hydrodediazoniation) implies intervention by a homolytic pathway.[1]

We had earlier shown that various $R-C_6H_4-N_2^+\ BF_4^-$ salts are immobilized in imidazolium ILs and upon thermal dediazoniation produce the corresponding ArF in high yields.[7] In continuation of our studies focusing on onium ion chemistry and electrophilic aromatic substitution in ILs,[7−13] we report on dediazoniation of $R-C_6H_4-N_2^+\ BF_4^-$ salts in $[BMIM][PF_6]$ (Formula 1) in the presence of TMSX (TMS = trimethylsilyl; X = Cl, Br, I) and $TMSN_3$ as convenient, easy to perform, economical processes to prepare $R-C_6H_4-Br$, $R-C_6H_4-I$, and $R-C_6H_4-N_3$ in one pot, with easy workup and recycling of the IL. The reactions could also be carried out starting with the anilines, by generating the diazonium salts in situ. Interactions of TMSI and $TMSN_3$ with $[PhN_2][BF_4]$ and with $[BMIM][PF_6]$ were directly monitored by multinuclear NMR. Immobilization of Cu(I)Br in $[BMIM][PF_6]$[14] enabled the IL version of the classical Sandmeyer bromodediazoniation[14] to be examined.



$[BMIM][PF_6]$

Keumi et al.[15] reported some years ago that dediazoniation of 2-fluorenediazonium tetrafluoroborate in DMF−THF mixed

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[§] Part of the undergraduate honors thesis of Abigail Hubbard. Halogen Introduction Strategies through Onium Ion Chemistry in Ionic Liquid Solvents, Kent State University, May 2007.

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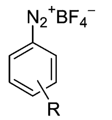
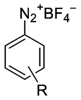
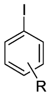
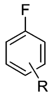
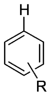


**1** (R = *p*-*t*-Bu)
**2** (R = *p*-Cl)
**3** (R = *p*-Me)
**4** (R = H)
**5** (R = *p*-Br)
**6** (R = *p*-OMe)
**7** (R = *m*-$NO_2$)
**8** (R = 2,4,6-$Me_3$)

**FIGURE 1.** Arenediazonium tetrafluoroborate salts studied.

**TABLE 1. Product Distribution in Dediazoniation Reactions in the Presence of TMSI**

| Substrate | Temp | Product Distribution %$^{a,b,c}$ | | |
|---|---|---|---|---|
|  | |  |  |  |
| **1** (R = *p*-*t*-Bu) | 65 ºC | 85 | | 1 |
| | RT | 94 | | |
| **2** (R = *p*-Cl) | 65 ºC | 87 | | 13 |
| | RT | 87 | | 11 |
| **3** (R = *p*-Me) | 65 ºC | 98 | | 1 |
| | RT | 93 | | 2 |
| **4** (R = H) | 65ºC | 100 | | |
| | RT | 97 | 3 | |
| **5** (R = *p*-Br) | 65 ºC | 95 | | 5 |
| | RT | 95 | | 5 |
| **6** (R = *p*-$CH_3O$) | 65 ºC | 92 | | 5 |
| | RT | 96 | | 4 |
| **7** (R = *m*-$NO_2$) | 65 ºC | 94 | | |
| | RT | 100 | | |
| **8** (R = 2,4,6-$Me_3$) | 65 ºC | 24 | 56 | 20 |
| | RT | 5 | 45 | 50 |

[a] Products confirmed by GC coinjection with authentic samples, GC-MS, or by $^1$H NMR. [b] Yields determined by GC (traces of unidentified materials were detectable by GC in some cases). [c] No literature data are available under classical/conventional conditions (without IL) for comparison.

solvent in the presence of TMSCl led to hydrodediazoniation forming fluorene, but in DMF (or DMA) as solvent, 2-halofluorenes were formed. Several other arenediazonium compounds were also studied in these solvents. Halodediazoniation efficiency increased in the order TMSCl < TMSBr < TMSI ≈ $TMSN_3$. Addition of MeI, NBS, or NCS increased the halodediazoniation conversions at the expense of protodediazoniation.

The efficacy of TMSX and $TMSN_3$-induced dediazoniations would be greatly enhanced if the reactions could be carried out without resorting to volatile/hazardous organic solvents (such as those used in ref 15), and provided they could be applied to readily available/widely employed diazonium salts. These considerations formed the basis for the present survey study in which diazonium salts (**1**−**8**) shown in Figure 1 were used.

**Halodediazoniation with TMSX in [BMIM][$PF_6$].** Diazonium salts listed in Figure 1 can be immobilized in [BMIM]-[$PF_6$] by mixing and/or by sonication. In line with an earlier study of Keumi et al.,[15] the TMSCl-induced chlorodediazoniations were found to be inefficient, giving low yields of the chloroarenes. Chemoselectivity toward halodediazonation increased in going to TMSBr. Table S1 (Supporting Information) summarizes the bromodediazoniation outcomes. Reactions were performed at rt and at 55 °C, with the former giving generally better results. Except for **4** (R = H) and **1** (R = *p*-*t*-Bu) for which ArF, "Schiemann product",[1,7] formation was dominant, other diazonium salts gave the bromoarenes in the 70−90% yield range. In the case of **8** (R = 2,4,6-$Me_3$), selectivity toward ArBr formation was significantly higher in the rt dediazoniation. With **2** (*p*-Cl), **5** (*p*-Br), **7** (*m*-$NO_2$), **1** (*p*-*t*-Bu), and **3** (*p*-Me), the corresponding ArH compounds were also observed. However, the extent of hydrodediazoniation products formed via **1** and **3** was quite minor.

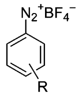
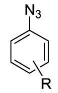
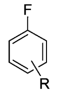
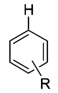
Table 1 summarizes the results of iododediazoniations with TMSI. For comparison, the reactions were run at rt and at 65 °C. Iodoarenes were formed in high yields (85−100%). With **8**, ArF and ArH were predominant. In other cases, these side products either were not detected or were present only in minor amounts.

A summary of the results of azidodediazoniations is presented in Table 2. For comparison, the reactions were performed at rt and at 65 °C. It can be seen that aryl azides were formed in high yields and high chemoselectivity in every entry. For **8**, the yield of mesityl azide was noticeably higher in the thermal reaction relative to that at rt. The ArF and ArH products were either absent or formed in small amounts. It should be noted that recycled/reused IL was used in numerous cases throughout this study, with only small changes in the conversions (less than 5%) being observed among reactions carried out in fresh IL versus those that utilized reused IL. In separate control studies it was established (by GC analysis) that for a given reaction, the fresh IL could be reused for up to five runs with no noticeable decrease in the conversions. Table S2 (Supporting Information) provides a summary of the product distribution results for in situ diazotization/iododediazoniation in representative cases. Slightly lower overall conversions were achieved in these two-step reactions as compared to the direct dediazoniations, but chemoselectivity continued to remain high (with ArF and ArH products remaining low). Minor amounts of the unreacted anilines were present (8% for *p*-*t*-Bu, 4% for *p*-Me, 19% for *p*-Br, and <1% for *p*-$CH_3O$).

**Dediazoniation with Cu(I)Br in [BMIM][$PF_6$].** The Sandmeyer reaction is a classical transformation for converting arylamine to aryl halides. Over the years, the mechanistic aspects of the Sandmeyer reaction have been extensively studied, and the topic has been critically reviewed and summarized by Zollinger.[1b] Involvement of the aryl radicals via homolytic dedidazoniation was established by kinetic studies and by product analysis. The copper salt functions as both electron-transfer agent and ligand-transfer oxidant. In some instances hydrodediazoniation accompanies halodediazionation.[1b]

Table S3 (Supporting Information) provides a summary of dediazoniations of the diazonium salts listed in Figure 1, in the presence of Cu(I)Br immobilized in [BMIM][$PF_6$]. Product analysis is indicative of heterolytic and homolytic dediazoniation pathways to variable degrees, depending on the substituents. With electron-donating substituents (*p*-Me, *p*-*t*-Bu, 2,4,6-trim-

**TABLE 2. Product Distribution in Dediazoniation Reactions in the Presence of $TMSN_3$**

| Substrate | Temp | Product Distribution %[a,b,c] | | |
|---|---|---|---|---|
|  | |  |  |  |
| **1** (R = *p*-*t*-Bu) | 65 °C | 95 | 0.5 | |
| | RT | 98 | 1 | 1 |
| **2** (R = *p*-Cl) | 65 °C | 99 | | |
| | RT | 93 | | |
| **3** (R = *p*-Me) | 65 °C | 95 | | |
| | RT | 93 | 4 | |
| **4** (R = H) | 65 °C | 90 | 3 | |
| | RT | 92 | 8 | |
| **5** (R = *p*-Br) | 65 °C | 97 | | |
| | RT | 97 | | |
| **6** (R = *p*-$CH_3O$) | 65 °C | 99 | | 1 |
| | RT | 98 | | <1 |
| **7** (R = *m*-$NO_2$) | 65 °C | 95 | | |
| | RT | 100 | | |
| **8** (R = 2,4,6-$Me_3$) | 65 °C | 93 | 6 | |
| | RT | 75 | 19 | 5 |

[a] Products confirmed by GC coinjection with authentic samples, GC-MS, or $^1H$ NMR. [b] Yields determined by GC (traces of unidentified materials were detectable by GC in some cases). [c] No literature data are available under classical/conventional conditions (without IL) for comparison (reaction of in situ generated $[HOOCC_6H_5N_2][Cl]$ with $TMSN_3$ was reported to give 82% of the corresponding azide: Tisler, M.; Stanovnik, B.; Zrimsek, Z.; *Kem. Drus.* **1979**, *26*, 163−71).

ethyl, and *p*-OMe) the Schiemann products were predominant. With *p*-Cl, hydrodediazoniation (chlorobenzene formation) and the Schiemann product (*p*-bromofluorobenzene) were major. With *p*-Br and *m*-$NO_2$, the Sandmeyer-derived products along with hydrodediazoniation products were formed, with no Schiemann products being detected. The substituent effect on product distribution can be visualized via Charts S1 and S2 (Supporting Information), showing increased formation of ArF with electron-donating substituents and increased hydro- and halodediazoniation with increasing electron-withdrawing power of the substituents. Significant involvement of heterolytic dediazonation (ArF formation) under the conditions of Sandmeyer chemistry is noteworthy, and may stem from increased stability of an incipient $Ar^+$ formed via $[ArN_2^+][BF_4^-]$ as a tight ion pair in the IL, relative to the aryl radical.

**NMR Monitoring of the $[ArN_2^+][BF_4^-]$, TMSX, and $[BMIM][PF_6]$ Interactions**. Returning to the earlier discussion on the nature of interaction between the diazonium salt, TMSX, and the IL, the binary systems $[BMIM][PF_6]$/TMSI, $[BMIM][PF_6]$/$TMSN_3$, $[PhN_2^+][BF_4^-]$/$[BMIM][PF_6]$, and $[PhN_2^+][BF_4^-]$/$TMSN_3$ and the ternary systems $[PhN_2^+][BF_4^-]$/TMSI/$[BMIM][PF_6]$ and $[PhN_2^+][BF_4^-]$/$TMSN_3$/$[BMIM][PF_6]$ were studied directly by multinuclear NMR ($^1H$, $^{19}F$, $^{29}Si$, and $^{13}C$). The samples were studied by NMR immediately or shortly after preparation (representative spectra in the Supporting Information).

Addition of TMSI to the IL at rt rapidly resulted in the formation of TMSF, with no TMSI remaining after a few minutes. The $^1H$ NMR (Figure S1, Supporting Information) shows the peaks for the IL and TMSF (no TMSI present). The same information could be deduced via $^{13}C$ NMR (Figure S2, Supporting Information). The $^{19}F$ NMR (Figure S3, Supporting Information) exhibits the signals for $[PF_6]$ and TMSF. By contrast, no reaction occurred when $TMSN_3$ was added to the IL. The $^{13}C$ NMR (Figure S4, Supporting Information) shows peaks for the IL and the unreacted $TMSN_3$ (and the added TMS). This was verified via $^{29}Si$ NMR (Figure S5, Supporting Information), showing $TMSN_3$ and TMS.

When $[PhN_2][BF_4]$ is immobilized in excess IL in the NMR tube, only resonances due to the IL and the diazonium cation are observed [$^{13}C$ NMR spectrum (Figure S6, Supporting Information); $^1H$ NMR (Figure S7, Supporting Information), $^{19}F$ NMR (Figure S8, Supporting Information)]. The control experiment to monitor the interaction between $[PhN_2][BF_4]$ and $TMSN_3$ had to be performed under heterogeneous conditions in $CDCl_3$ due to low solubility of the diazonium salt. The $^1H$ NMR (Figure S9, Supporting Information) showed the formation of TMSF, which was also verified via the $^{29}Si$ NMR spectrum (Figure S10, Supporting Information). The data pointed to eq 1 as the primary source of TMSF.

$$[PhN_2][BF_4] + TMSN_3 \rightarrow TMSF + [PhN_2][N_3] + BF_3 \quad (1)$$

Focusing on the ternary systems, upon addition of excess TMSI to the diazonium salt immobilized in the IL, TMSF was quickly formed and dediazoniation ensued. Signals due to PhI began to appear at the expense of the diazonium salt (NMR spectra: Figure S11, Supporting Information, $^1H$ NMR; Figure S12, Supporting Information, $^{13}C$ NMR; Figure S13, Supporting Information, $^{19}F$ NMR). Figure S14 (Supporting Information) is the $^{29}Si$ NMR for the $[PhN_2^+][BF_4^-]$/$TMSN_3$/$[BMIM][PF_6]$ in $CDCl_3$ (under heterogeneous conditions) showing the TMSF and unreacted $TMSN_3$.

Collectively, the control experiments suggest that whereas in the case of $TMSN_3$, the major source of TMSF is via eq 1, in the case of TMSI, TMSF could be formed via both eqs 2 and 3.

$$[PhN_2][BF_4] + TMSN_3 \rightarrow TMSF + [PhN_2][N_3] + BF_3 \quad (1)$$

$$[PhN_2][BF_4] + TMSI \rightarrow TMSF + [PhN_2][I] + BF_3 \quad (2)$$

$$[BMIM][PF_6] + TMSI \rightarrow TMSF + [BMIM][I] + PF_5 \quad (3)$$

Given that the IL was used in large excess over TMSX in halo- and azidodediazoniations, it is unlikely that eq 3 could contribute to any significant extent to the formation of ArI, since this would require a statistically unfavorable second metathesis (as in eq 4), which is much more likely to produce ArF instead!

$$[ArN_2][BF_4] + [BMIM][PF_6]\ (major) + [BMIM][I]\ (minor) \rightarrow [ArN_2][I] \quad (4)$$

The picture that emerges is that TMSI, TMSBr, and $TMSN_3$ react with the diazonium tetrafluoroborates immobilized in $[BMIM][PF_6]$ to produce TMSF, and this leads to the formation of $[ArN_2][X]$ via metathesis, as a tight ion-pair. The latter conveniently undergoes dediazoniation in the IL at rt (or by mild heating) to give ArX. The $TMSN_3$ and TMSI reactions

(Tables 1 and 2) produced the highest chemoselectivites and are, therefore, viable synthetic methods to prepare ArX via the readily available [$ArN_2$][$BF_4$] salts, without resorting to organic solvents like DMF and THF to perform these reactions. Product distributions data for these reactions imply no significant substituent effect dependency, except for **8** (due to steric effects). Increased formation of hydrodediazoniation products (ArH) was observed in TMSBr reactions (Table S1, Supporting Information) with electron-withdrawing substitutents (**2**, **5**, and **7**). The halo- and azidodediazoniations could also be carried out starting from the corresponding amines by in situ diazotization (Table S2, Supporting Information), with no significant substituent effect dependency in the studies cases. The rather unique nature of the IL as solvent for electrophilic/cationic chemistry is manifested in attempted Cu(I)Br homolytic halodediazonation in Sandmeyer-type reactions (Table S3, Supporting Information), in which significant amounts of the Schiemann products were formed, indicating notable involvement by the aryl cation.

## Experimental Section

**Dediazoniation Procedure with TMSX.** The Schlenk tube equipped with a magnetic stirring bar was charged with [BMIM][$PF_6$] (3.52 mmol, 0.66 mL) under a nitrogen atmosphere. The arenediazonium salt (0.141 mmol) was added and the mixture was stirred or sonicated until immobilized. TMSX (0.169 mmol) was added and the reaction mixture was stirred either overnight at room temperature or for 2 h with heat (50−60 °C for TMSBr, and 60−70 °C for TMSI and $TMSN_3$ reactions). Completion of the dediazoniation reactions was indicated when $N_2$ evolution was ceased. The reaction mixture was extracted three times with diethyl ether (0.5 mL × 3) to ensure complete extraction of the products from the IL. The combined ether extract was neutralized with sodium bicarbonate and quickly filtered prior to analysis by GC, GC-MS, IR, or NMR. Since some of products, specially the ArF compounds, were rather volatile, GC analyses to determine product distribution were performed carefully, and each reaction mixture was injected 3 times to ensure reproducibility.

**Supporting Information Available:** Tables S1−S3; experimental details; plots of substituent effects on heterolytic and homolytic dediazoniation products in the presence of Cu(I)Br immobilized in the IL; multinuclear NMR spectra of [$ArN_2$][$BF_4$]/TMSX, [BMIM][$PF_6$]/TMSX, and [BMIM][$PF_6$]/TMSX/[$ArN_2$][$BF_4$] systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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