Archive for
Organic Chemistry

The Free Internet Journal
for Organic Chemistry

Paper

Arkivoc **2018**, part ii, 50-59

Ring-closure reaction of 2-benzoylbenzenediazonium salts in 1-butyl-3-methylimidazolium ionic liquids

Takao Okazaki,* Hiroyuki Yamamoto, and Toshikazu Kitagawa*

Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan

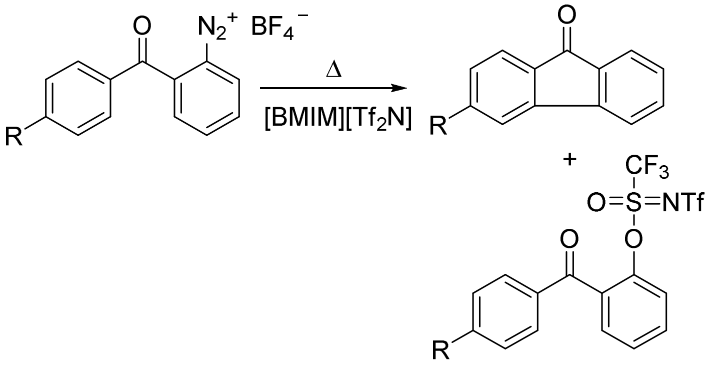
Email: okazaki@chem.mie-u.ac.jp

Dedicated to Professor Kenneth K. Laali on the occasion of his 65th birthday

Received 05-29-2017 **Accepted** 08-11-2017 **Published on line** 10-12-2017

Abstract

A ring-closure reaction by thermal dediazoniation of 2-substituted benzenediazonium tetrafluoroborates in imidazolium-based ionic liquids was investigated. Dediazoniation of 2-(4-R-benzoyl)benzenediazonium tetrafluoroborates (R = H, Me, OMe, Cl) in ionic liquid [BMIM][TfO] gave 3-R-9-fluorenones as ring-closure products and 2-(4-R-benzoyl)phenyl trifluoromethanesulfonates as substitution products. Dediazoniation in [BMIM][Tf$_2$N] afforded 3-R-9-fluorenones and R-C_6H_4-CO-C_6H_4-OSO(CF_3)(NSO_2CF_3). Yields of the ring-closure products were higher in [BMIM][Tf$_2$N] than in [BMIM][TfO]. 2-Benzylbenzenediazonium and 2-phenoxybenzenediazonium tetrafluoroborates exclusively produced substitution products in both ionic liquids. DFT calculations suggest that electron transfer from the anion to render homolytic process should be induced more readily in [BMIM][Tf$_2$N] than in [BMIM][TfO]. This ability may be responsible for the higher yields of the ring-closure products via homolytic pathway and the smaller yields of the substitution products via heterolytic pathway in [BMIM][Tf$_2$N].



Keywords: Ionic liquids, diazonium ions, dediazoniation, arylation, Pschorr reaction, fluorenone

DOI: https://doi.org/10.24820/ark.5550190.p010.195

©ARKAT USA, Inc

Introduction

Ionic liquids have recently attracted much attention because of their great potential as novel solvents for organic reactions.[1] They usually consist of organic cations and anions, and have melting points of 100 °C or below. Their properties as reaction media have been exploited in organic syntheses. Reaction products in ionic liquids can be separated by simple liquid-liquid extraction with organic solvents, since ionic liquids are immiscible in many organic solvents. In an imidazolium-based ionic liquid with tetrafluoroborate ([BMIM][BF_4], Figure 1), dediazoniation of arenediazonium tetrafluoroborates (ArN_2BF_4) was reported to afford Schiemann reaction products (Ar-F) as shown in Figure 2.[2] Dediazoniation in an imidazolium-based ionic liquid with bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]) produced $ArOSO(CF_3)(NSO_2CF_3)$ with a small amount of $ArNTf_2$ due to the ambident nucleophilic character of Tf_2N^-.[3] These successes suggest that the scope of their application could be expanded to the dediazoniative arylation of arenediazonium ions in ionic liquids.

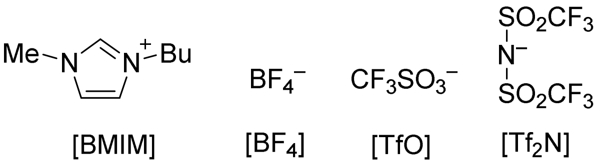


Figure 1. Abbreviation for an imidazolium-based cation and anions of ionic liquids.

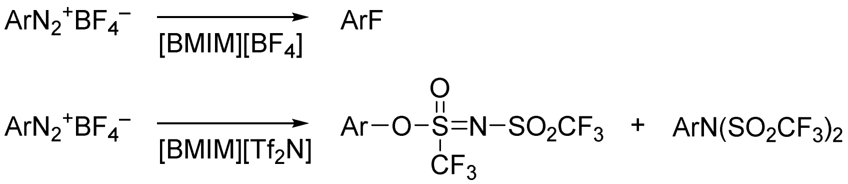


Figure 2. Products of the dediazoniation of arenediazonium ions in ionic liquids.

The dediazoniative arylation of arenediazonium salts has been examined in common solvents as a method for the synthesis of polycyclic aromatic compounds.[4-9] Dediazoniation of arenediazonium ion ArN_2^+ potentially gives aryl cation Ar^+ via a heterolytic pathway (Figure 3). The aryl cation Ar^+ reacts with a nucleophile (X^-) to produce a substitution product ArX. Alternatively, reduction of ArN_2^+ via one-electron transfer from a nucleophile (X^-) affords an intermediate $Ar\text{-}N_2^\bullet$, which, with a loss of a molecular of nitrogen, produces an aryl radical $Ar^\bullet$ (a homolytic pathway). The radical $Ar^\bullet$ abstracts a hydrogen atom from solvent to give ArH. When arene molecules are present, the radical intermediate $Ar^\bullet$ can react with arenes to form arylated compounds by homolytic aromatic substitution. This arylation is known as the Gomberg-Bachmann reaction, and its intramolecular analogue is referred to as the Pschorr reaction. Dediazoniative intramolecular cyclization of 2-benzoylbenzenediazonium gave 9-fluorenone (**2a** in Figure 4) as a ring-closure product with/without Cu catalyst.[4] In addition, 2-benzylbenzenediazonium and 2-phenoxybenzenediazonium afforded fluorene (**2e**) and dibenzofuran (**2f**), respectively, in aqueous acids.[5-7] Dediazoniation of 2-benzoylbenzenediazonium tetrafluoroborate (**1a**) in the presence of KOAc in Freon-113 (CCl_2FCClF_2) was reported to give **2a** in 73% yield.[8] Dediazoniation of **1a** in the presence of Cu_2O catalyst in aqueous sulfuric acid produced **2a** in 93% yield.[9] The ring-closure products in the presence of the catalyst are believed to be produced predominantly via homolytic dediazoniation process.

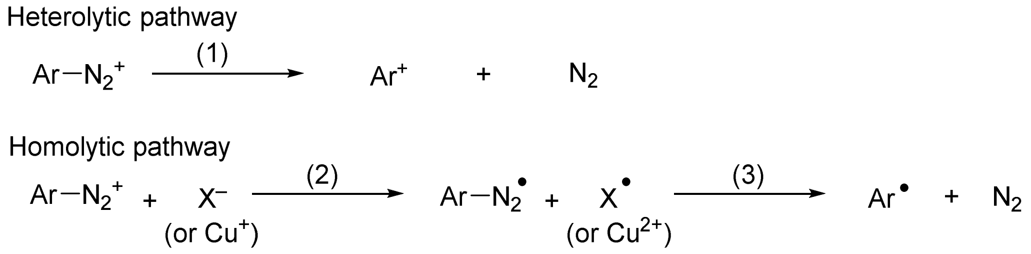


Figure 3. Heterolytic and homolytic dediazoniation mechanisms of arenediazonium ions: (1) Heterolytic dissociation of the C-N bond, (2) electron-transfer process, and (3) homolytic dissociation of the C-N bond.

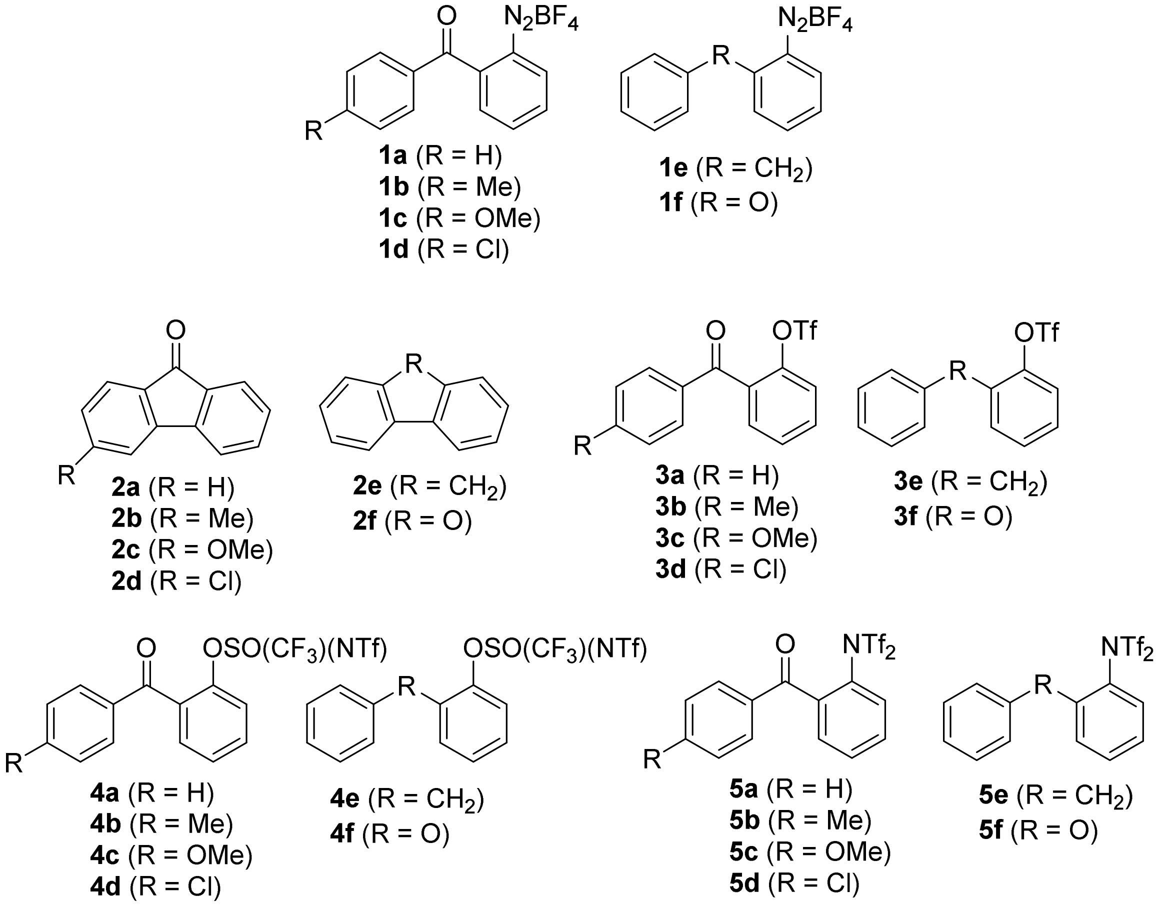


Figure 4. Structures of diazonium salts and dediazoniation products. Tf denotes a CF_3SO_2 group.

Hoping to expand the scope of the application of ionic liquids to dediazoniation, we explored the ring-closure reactions by the dediazoniation of arenediazonium salts **1a**-**1f** in ionic liquids, [BMIM][TfO] and [BMIM][Tf_2N] (Figure 4). The effect of substituents on the yield of ring-closure products was also examined. In addition, the efficiency of electron transfer from the ionic liquids was investigated by the DFT (density functional theory) calculations to examine selectivity in the heterolytic and homolytic processes of the dediazoniation.

Results and Discussion

The ionic liquids, [BMIM][Tf_2N] and [BMIM][TfO], were prepared by methods similar to those described in the literature.[10-12] A reaction of 1-methylimidazole with 1-chlorobutane in acetonitrile gave [BMIM][Cl],[10] the anion of which could be exchanged with either LiOTf or $LiNTf_2$ to afford [BMIM][TfO][11] or [BMIM] [Tf_2N],[12] respectively.

Solutions of **1a**-**1f** in the ionic liquids were heated, and then the extracted products were analyzed by NMR measurements. The product distributions are summarized in Table 1. Dediazoniation of **1a** afforded a mixture of ring-closure product **2a** and substitution product **3a** in [BMIM][TfO]. Their yield ratio was 66:34. In [BMIM][NTf_2], **2a**, **4a**, and **5a** were formed at a ratio of 85:15:<1. It is noteworthy that the ring-closure product was produced more selectively in [BMIM][Tf_2N] than in [BMIM][TfO]. The preferential formation of **4a** over **5a** is attributed to the preference for O-attack over N-attack, which is consistent with that reported in the earlier studies.[3]

To investigate the effect of substituents on benzoyl group, product distributions of dediazoniation of the diazonium ions with Me, OMe, and Cl groups (**1b**-**d**) were examined. The yields of ring-closure products **2b**-**d** were found to be higher in [BMIM][Tf_2N] than in [BMIM][TfO], and substitution products **3b**-**d** and **4b**-**d** were formed in considerable yields. The substituent groups had only a small effect on the product distributions. It is likely that the substituents have little influence on the product-forming step.

To further explore the effect of the ionic liquids, we examined the dediazoniation of diazonium salts **1e**-**1f**, which have a more strongly electron-donating substituent on the benzenediazonium ring. Dediazoniation of **1e** significantly decreased the yield of the ring-closure product, and predominantly gave **3e** and **4e**. **1f** reacted slowly even at 100 °C—although most of **1f** remained intact after 24 h, substitution products **3f**, **4f**, and **5f** were detected by NMR. However no ring closure product **2f** could be found. These results suggest that **1e**-**1f** predominantly reacted via a heterolytic mechanism in the ionic liquids.

Table 1. Product Distribution of Dediazoniation of Diazonium Salts in Ionic Liquids

Substrate	Ionic liquid	Temp, Time	Product (yield ratio)[a]	Total yield of **2**-**5**, %[a]
1a	[BMIM][TfO]	50 °C, 6 h	**2a**, **3a** (66:34)	79
	[BMIM][Tf_2N]	50 °C, 6 h	**2a**, **4a**, **5a** (85:15:<1)	91
1b	[BMIM][TfO]	80 °C, 1.5 h	**2b**, **3b** (58:42)	84
	[BMIM][Tf_2N]	80 °C, 1.5 h	**2b**, **4b**, **5b** (75:24:1)	94
1c	[BMIM][TfO]	80 °C, 2 h	**2c**, **3c** (53:47)	78
	[BMIM][Tf_2N]	80 °C, 2 h	**2c**, **4c**, **5c** (72:27:1)	84
1d	[BMIM][TfO]	80 °C, 1 h	**2d**, **3d** (42:58)	74
	[BMIM][Tf_2N]	80 °C, 1 h	**2d**, **4d**, **5d** (78:22:<1)	72
1e	[BMIM][TfO]	80 °C, 6 h	**2e**, **3e** (11:89)	88
	[BMIM][Tf_2N]	80 °C, 6 h	**2e**, **4e**, **5e** (9:86:5)	85
1f	[BMIM][TfO]	100 °C, 24 h	**3f**	9
	[BMIM][Tf_2N]	100 °C, 24 h	**4f**, **5f** (84:9)	14

[a] After extraction with hexane. The yield ratio was determined by ^1H and ^{19}F NMR.

DFT calculations[13] were employed to estimate reaction energies for understanding the effect of the ionic liquids on the dediazoniation of the arenediazonium ions. The first chemical process of the heterolytic mechanism in dediazoniation is heterolytic cleavage of the C-N bond to give aryl cations Ar^+ (equation 1 in Figure 3). The reactions between aryl cations and X^- ($CF_3SO_3^-$ or Tf_2N^-) give the substitution products (**3**-**5**). In the homolytic process, the reduction of the diazoniums by one electron transfer from X^- gives radicals (equation 2) and the subsequent homolytic dissociation of the C-N bond generates aryl radicals $Ar^{\bullet}$ (equation 3).

To take the solvent effect into account, the widely used PCM (Polarizable Continuum Model)[14] method was employed, with ethanol chosen as a model solvent for ionic liquids.[15] Calculated Gibbs free energies of reactions were summarized in Table 2.

Table 2. Gibbs Free Energy of Reaction (Δ*G*) for the Dediazoiation by the DFT Calculations

ArN_2^+	Δ*G* (EtOH), kcal/mol[a]			
	eq. 1[b]	eq. 2 (X = TfO)[b]	eq. 2 (X = Tf_2N)[b]	eq. 3[b]
1a	13.2	57.8	54.7	-19.2
1b	12.7	57.8	54.7	-19.6
1c	–[c]	57.5	54.5	-19.2
1d	13.6	57.2	54.1	-19.1
1e	12.2	60.8	57.7	-15.8
1f	24.5	62.4	59.3	-14.7

[a] PCM(EtOH)-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). Structures and energies of the diazonium ions were computed without counter anion (BF_4^-).

[b] The reactions of eqs. 1-3 were shown in Figure 3.

[c] The aryl cation could not be obtained due to isomerization into the ring-closure product during the structural optimization.

The Gibbs free energies of reactions for heterolytic dediazoniation (eq. 1) were calculated to be 13.2 kcal/mol for **1a**, 12.2 kcal/mol for **1e**, and 24.5 kcal/mol for **1f** by PCM(EtOH)-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). The reaction energies of equation 2 for **1e**-**f** were higher than that for **1a**. These energies can be interpreted as reflecting relative stabilities of diazonium ions.

The energies of the electron transfer from the anions to diazonium ions **1a** (eq. 2) were estimated to be 57.8 kcal/mol for X = CF_3SO_3 and 54.7 kcal/mol for X = Tf_2N. These energies were significantly higher than that of the heterolytic dediazoniation (eq. 1). Since a large amount of ring-closure product via the homolytic process was experimentally formed, the high Gibbs free energy of reaction might be attributed to the overestimation of the solvation energies for ionic species ArN_2^+ and X^-. Comparison of the energies of the electron transfer suggests that the ability of the electron-transfer from TfO^- to the diazonium is higher than that from Tf_2N^-. The arenediazonium ions could be reduced to the radical more rapidly in [BMIM][Tf_2N] than in [BMIM][TfO]. Consequently, the ring-closure products from the aryl radical by intramolecular C-C bond formation could become more dominant in [BMIM][Tf_2N]. This result could rationalize the experimental trend.

The formations of the aryl radicals (eq. 3) for **1a**-**1f** were found to be exergonic. It is likely that the $ArN_2^{\bullet}$ radicals immediately decompose to aryl radicals and nitrogen. Moreover, the energies (eqs. 1-3) for **1b**-**d** were similar to that for **1a**. This is consistent with the experimentally found small substituent effect on the product distribution. A change in Δ*G* from **1f** to **1a** (= Δ*G*(**1f**) - Δ*G*(**1a**)) for eq. 1 was larger than those for eq. 2, suggesting that **1f** should react via the heterolytic process more dominantly than **1a**. However, experimentally the ring-closure product from **1a** via the homolytic process was formed more significantly. The reason for this discrepancy remains unclear.

Conclusions

The product distributions of dediazoniation of diazonium salts **1a**-**f** in ionic liquids were examined. **1a**-**d** afforded both ring-closure products and substituted compounds, while **1e**-**f** predominantly reacted via the heterolytic process to give the substituted products. The yields of the ring-closure products in [BMIM][NTf_2] were higher than those in [BMIM][TfO]. This was attributed to the higher ability of the electron-transfer from Tf_2N^-, indicating that [BMIM][Tf_2N] was an adequate solvent for the formation of the ring-closure products. The effect of substituents on the benzoyl group on the product distribution was not significant.

Experimental Section

General. NMR spectra were recorded on a 300 MHz spectrometer at room temperature. IR data were collected using an FT-IR instrument. High-resolution mass spectral data were recorded with electron impact ionization at 70 eV. Diazonium tetrafluoroborates **1a**,[8] **1b**,[18,19] **1c**,[18] **1d**,[18] **1e**,[20] and **1f**[21] were synthesized by the reaction of their corresponding anilines with sodium nitrite in aqueous HBF_4 solution. Ionic liquids [BMIM][Cl],[10] [BMIM][TfO],[11] and [BMIM][Tf_2N][12] were prepared using methods similar to those reported in the literature. The other reagents were commercially available and were used as received.

General procedure for product analysis of the dediazoniation of diazonium salts in ionic liquid

The diazonium tetrafluoroborates (10–20 mg) were dissolved in ionic liquids (0.4 mL). The solution was heated using the conditions shown in Table 1. The ionic liquids were extracted with hexane. After removal of the solvent, the residues were analyzed by NMR, and the product distributions are summarized in Table 1. Compounds **2a**,[22] **2b**,[23] **2c**,[24] **2d**,[23] **2e**,[22] **3a**,[25] **3d**,[26] **3e**,[27] and **3f**[27] were identified by comparing their NMR spectra with those reported in the literature. The isomers ArOSO(CF_3)(NTf) (**4a**-**4f**) and $ArNTf_2$ (**5a**-**5f**) were attempted to be purified with SiO_2 column chromatography using hexane–CH_2Cl_2 or hexane–ether as an eluent. However, they could not be separated by chromatography.

4a: pale yellow oil (mixture of **4a** and **5a**, 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2H, *J* 7.2 Hz), 7.70–7.40 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4 (CO), 144.9 (C), 135.9 (C), 134.0 (CH), 132.9 (CH), 132.4 (C), 131.8 (CH), 130.1 (2CH), 129.2 (CH), 128.6 (2CH), 122.9 (CH), 118.4 (CF_3, q, *J* 320 Hz), 118.1 (CF_3, q, *J* 320 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.5 (s, 3F), -78.3 (s, 3F).

5a: ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.9 (s, 6F).

3b: pale yellow oil; IR (KRS-6) 2923, 2849, 1668, 1212, 1141 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* 8.1 Hz, 2H), 7.62 (td, *J* 7.2, 2.0 Hz, 1H), 7.57 (dd, *J* 7.7, 2.0 Hz, 1H), 7.49 (t, *J* 7.1 Hz, 1H), 7.42 (d, *J* 8.1 Hz, 1H), 7.28 (d, *J* 6.9 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2 (C=O), 146.7 (C), 144.9 (C), 133.9 (C), 132.7 (C), 132.4 (CH), 131.1 (CH), 130.4 (2CH), 129.3 (2CH), 128.0 (CH), 122.4 (CH), 21.8 (CH_3); HRMS (EI, 70 eV) Calc'd for $C_{15}H_{11}F_3O_4S$ 344.0323, Found 344.0330.

4b: pale yellow crystals (mixture of **4b** and **5b**, 20:1); IR (KRS-6) 3021, 2921, 2851, 1668, 1396, 1219 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* 8.1 Hz, 2H), 7.70–7.66 (m, 1H), 7.63–7.59 (m, 1H), 7.56 (d, *J* 7.8 Hz, 1H), 7.53 (d, *J* 8.1 Hz, 1H), 7.29 (d, *J* 8.1 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0 (C=O), 145.3 (C), 145.1 (C), 133.5 (C), 132.9 (C), 132.7 (CH), 131.7 (CH), 130.4 (2CH), 129.4 (2CH), 129.2 (CH), 123.0 (CH), 21.8 (CH_3); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -73.5 (s, 3F, CF_3), -78.3 (s, 3F, CF_3); HRMS (EI, 70 eV) Calc'd for $C_{16}H_{11}F_6NO_5S_2$ 474.9982, Found 474.9982.

5b: ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.8 (s, 6F).

3c: pale yellow oil; IR (KRS-6) 2918, 2848, 1662, 1211, 1139, 1027 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, *J* 6.9, 2.1 Hz, 2H), 7.61 (td, *J* 7.7, 2.0 Hz, 1H), 7.56 (td, *J* 7.7, 2.0 Hz, 1H), 7.48 (t, *J* 7.5 Hz, 1H), 7.41 (d, *J* 8.1 Hz, 1H), 6.95 (d, *J* 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8 (C=O), 164.2 (C), 146.6 (CH), 132.9 (C), 132.6 (2CH), 132.2 (CH), 130.9 (CH), 129.3 (C), 128.0 (CH), 122.4 (C), 113.9 (2CH), 55.6 (CH_3); HRMS (EI, 70 eV) Calc'd for $C_{15}H_{11}F_3O_5S$ 360.0279; Found 360.0272.

4c: colorless oil (mixture of **4c** and **5c**, 10:1); IR (KRS-6) 3019, 2923, 2849, 1662, 1394, 1211 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (dd, *J* 6.9, 2.1 Hz, 2H), 7.68 (td, *J* 7.4, 2.1 Hz, 1H), 7.60 (td, *J* 7.8, 2.4 Hz, 1H), 7.58 (d, *J* 7.8 Hz, 1H), 7.53 (d, *J* 8.1 Hz, 1H), 6.96 (dd, *J* 6.3, 2.0 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0 (C=O), 164.4 (C), 133.1 (C), 132.7 (2CH), 132.5 (CH), 131.5 (C), 131.4 (CH), 129.2 (CH), 128.9 (C), 123.0 (CH), 114.0 (2CH), 55.6 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.6 (s, 3F), -78.3 (s, 3F); HRMS (EI, 70 eV) Calc'd for $C_{16}H_{11}F_6NO_6S_2$ 490.9931, Found 490.9934.

5c: ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.9 (s, 6F).

3d:[26] IR (KRS-6) 2926, 1673, 1213, 1139, 1089 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* 8.1Hz, 2H), 7.65 (td, *J* 7.7, 2.0 Hz, 1H), 7.55 (td, *J* 7.2, 2.1 Hz, 1H), 7.52 (d, *J* 7.2 Hz, 1H), 7.47 (dd, *J* 6.7, 1.9 Hz, 2H), 7.43 (d, *J* 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5 (C=O), 146.5 (C), 140.4 (C), 134.8 (C), 132.9 (C), 132.0 (CH), 131.5 (2CH), 131.1 (CH), 129.0 (2CH), 128.2 (CH), 122.6 (CH): HRMS (EI, 70 eV) Calc'd for $C_{14}H_8ClF_3O_4S$ 363.9784; Found 363.9788.

4d: pale yellow crystals (mixture of **4d** and **5d**, 40:1); mp 56.7–57.1 °C; IR (KBr) 1671, 1394, 1211, 1134, 1091 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* 8.4 Hz, 2H), 7.74–7.70 (m, 1H), 7.62–7.59 (m, 2H), 7.55 (d, *J* 8.1 Hz, 1H), 7.48 (d, *J* 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3 (C=O), 144.9 (C), 140.8 (C), 134.3 (C), 133.3 (CH), 132.2 (C), 131.6 (CH), 131.5 (2CH), 129.4 (CH), 129.1 (2CH), 123.0 (CH), 118.6 (CF_3, q, *J* 320 Hz), 118.5 (CF_3, q, *J* 320 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.5 (s, 3F), -78.3 (s, 3F); HRMS (EI, 70 eV) Calc'd for $C_{15}H_8ClF_6NO_5S_2$ 494.9436; Found 494.9436.

5d: ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.8 (s, 6F)

4e: pale yellow oil (mixture of **4e** and **5e**, 20:1); IR (KRS-6) 3031, 2924, 1232, 1135, 1141 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.36 (m, 3H), 7.32 (t, *J* 7.1 Hz, 1H), 7.30 (t, *J* 6.9 Hz, 2H), 7.26–7.22 (m, 1H), 7.20 (d, J 6.6 Hz, 2H), 4.07 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5 (C), 137.8 (C), 134.2 (C), 132.5 (CH), 129.7 (CH), 129.0 (2CH), 128.8 (2CH), 128.6 (CH), 126.8 (CH), 121.8 (CH), 35.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.8 (s, 3F), -78.4 (s, 3F); HRMS (EI, 70eV) Calc'd for $C_{15}H_{11}F_6NO_4S_2$ 447.0033, Found 447.0035.

5e: ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.5 (s, 6F).

4f: pale yellow crystals (mixture of **2f**, **4f**, and **5f**, trace:10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (t, *J* 8.0 Hz, 3H), 7.34 (t, *J* 7.8 Hz, 1H), 7.23 (t, *J* 8.7 Hz, 1H), 7.17 (d, *J* 8.1 Hz, 1H), 7.09 (d, *J* 7.5 Hz, 2H), 6.96 (d, *J* 8.4 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.3 (s, 3F), -78.5 (s, 3F).

5f: ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.7 (s, 6F).

DFT calculations

Structures were optimized using a C_1 molecular point group by the density function theory (DFT) method[13] at B3LYP/6-31G(d) level using the Gaussian 03 package.[28] All computed geometries were verified by frequency calculations to have no imaginary frequencies. The solvent effects were calculated using the Polarizable

Continuum Model (PCM)[14] for the optimized structures with ethanol (relative static permittivity, ε = 24.852) at the B3LYP/6-311+G(2d,p) level.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (C) (15K05474), Japan.

Supplementary Material

Energies of the Optimized Structures by the DFT Calculations.

References and Notes

1. Hallett, J. P.; Welton, T. *Chem. Rev.* **2011**, *111*, 3508−3576. https://doi.org/10.1021/cr1003248 Chiappe, C. In *Ionic Liquids in Synthesis*, 2nd ed., Ed. by Wasserscheid, P.; Welton, T. Wiley-VCH, Weinheim, 2008, Chapter 5.1; Earle, M. In *Ionic Liquids in Synthesis*, 2nd ed., Ed. by Wasserscheid, P.; Welton, T. Wiley-VCH, Weinheim, **2008**, Chapter 5.2; Wasserscheid, P.; Schulz, P. In *Ionic Liquids in Synthesis*, 2nd ed., Ed. by Wasserscheid, P.; Welton, T. Wiley-VCH, Weinheim, **2008**, Chapter 5.3.
2. Laali, K. K.; Gettwert, V. J. *J. Fluorine Chem.* **2001**, *107*, 31–34. https://doi.org/10.1016/S0022-1139(00)00337-7
3. Laali, K. K.; Okazaki, T.; Bunge, Scott. D. *J. Org. Chem.* **2007**, *72*, 6758–6762; Okazaki, T.; Laali, K. K.; Bunge, S. D.;Adas, S. K. *Eur. J. Org. Chem.* **2014**, 1630–1644. https://doi.org/10.1021/jo0708801
4. Cohen, T.; Dietz, A. G., Jr.; Miser, J. R. *J. Org. Chem.* **1977**, *42*, 2053–2058. https://doi.org/10.1021/jo00432a003
5. DeTar, D. F. *Org. React.* **1957**, *9*, 409–462.
6. Zollinger, H. *Diazo Chemistry I*, VCH Weinheim, **1994**. https://doi.org/10.1002/3527601724
7. Reichardt, C.; Welton, T. *Solvents and Solvent Effects in Organic Chemistry*, 4th Ed., Wiley-VCH, Weinheim, 2011.
8. Beadle, J. R.; Korzeniowski, S. H.; Rosenberg, D. E.; Garcia-Slanga, B. J.; Gokel, G. W. *J. Org. Chem.* **1984**, *49*, 1594–1603. https://doi.org/10.1021/jo00183a021
9. Lewin, A. H.; Cohen, T. *J. Org. Chem.* **1967**, *32*, 3844–3850. https://doi.org/10.1021/jo01287a027
10. Dupond, J.; Consorti, C. S.; Suarez, P. A. Z.; Souza, R. F. *Org. Synth.* **2002**, *79*, 236–241. https://doi.org/10.15227/orgsyn.079.0236
11. Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Sedden, K. R.; Welton, T. *Anal. Chem.* **2007**, *79*, 758–764. https://doi.org/10.1021/ac061481t
12. Creary, X.; Wills, D. E.; Gagnon, M. *J. Am. Chem. Soc.* **2005**, *127*, 18114–18120. https://doi.org/10.1021/ja0536623

13. Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; 2nd Ed., Wiley-VCH, Weinheim, 2000.
14. Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3094; Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041.
15. Empirical solvent polarity scale $E_T(30)$, which is defined by using the solvatochromic shifts of Reichardt's dye,[7] was reported to be 52.3 for [BMIM][TfO] and 51.5 for [BMIM][Tf_2N].[16] These values are comparable to that of ethanol (51.9). In addition, solvolytic studies suggested that the solvent effect of ionic liquids is similar to that of alcohols.[12,17]
16. Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2* **2001**, 433–435 https://doi.org/10.1039/b101449h Welton, T. In *Ionic Liquids in Synthesis*, 2nd ed., Edited by Wasserscheid, P.; Welton, T. Wiley-VCH, Weinheim, 2008, Chapter 3.5, pp. 130–141; Ohano, H. In *Electrodeposition from Ionic Liquids*, Edited by F. Endres, A. P. Abbott, D. R. MacFarlane, Wiley-VCH, Weinheim, **2008**, Chapter 3, pp. 47–82.
17. Okazaki, T.; Ito, K.; Kitagawa, T. *Tetrahedron Lett.* **2015**, *56*, 6066–6068.
    https://doi.org/10.1016/j.tetlet.2015.09.056
18. Schmidt, B.; Elizarov, N.; Schilde, U.; Kelling, A. *J. Org. Chem.* **2015**, *80*, 4223–4234.
    https://doi.org/10.1021/acs.joc.5b00272
19. Chandler, S. A.; Hanson, P.; Taylor, A. B.; Walton, P. H.; Timms, A. W. *J. Chem. Soc., Perkin Trans. 2* **2001**, 214–228.
    https://doi.org/10.1039/b006184k
20. Schmidt, R. R.; Schneider, W.; Karg, J.; Burkert, U. *Chem. Ber.* **1972**, *105*, 1634–1645.
    https://doi.org/10.1002/cber.19721050519
21. Wassmundt, F. W.; . Pedemonte, P. *J. Org. Chem.* **1985**, *60*, 4991–4994.
    https://doi.org/10.1021/jo00121a016
22. Aldrich/ACD Library of FT NMR Spectra Pro, Aldrich Chemical Co., Milwaukee, WI; Advanced Chemistry Development, Toronto, ON, Canada, **2002**.
23. Thirunavukkarasu, V. S.; Cheng, C.-H. *Chem. Eur. J.* **2011**, *17*, 14723–14726.
    https://doi.org/10.1002/chem.201102996
24. Coelho, P. J.; Carvalho, L. M.; Rodrigues, S.; Oliveira-Campos, A. M. F.; Dubest, R.; Aubard, J.; Samat, A.; Guglielmetti, R. *Tetrahedron* **2002**, *58*, 925–931.
    https://doi.org/10.1016/S0040-4020(01)01187-5
25. a,Xu, M.; Lukeman, M.; Wan, P. *Photochem. Photobiol.* **2006**, *82*, 50–56.
    https://doi.org/10.1562/2005-02-17-RA-444
    b. Sapountzis, I.; Lin, W.; Kofink, C. C.; Despotopoulou, C.; Knochel, P. *Angew. Chem. Int. Ed.* **2005**, *44*, 1654–1658.
    https://doi.org/10.1002/anie.200462013
26. Tian, Y.; Qi, J.; Sun, C.; Yin, D.; Wang, X.; Xiao, Q. *Org. Biomol. Chem.* **2013**, *11*, 7262–7266.
    https://doi.org/10.1039/c3ob41680a
27. Wang, J.-Q.; Harvey, R. G. *Tetrahedron* **2002**, *58*, 5927–5931.
    https://doi.org/10.1016/S0040-4020(02)00534-3
28. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.

E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.