

Electrophilic Nitration of Aromatics in Ionic Liquid Solvents

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Potential utility of a series of 1-ethyl-3-methylimidazolium salts [emim][X] with X = OTf⁻, CF₃COO⁻, and NO₃⁻ as well as [HNEtPr₂][CF₃COO] (protonated Hünig's base) ionic liquids were explored as solvent for electrophilic nitration of aromatics using a variety of nitrating systems, namely NH₄NO₃/TFAA, isoamyl nitrate/BF₃·Et₂O, isoamyl nitrate/TfOH, Cu(NO₃)/TFAA, and AgNO₃/Tf₂O. Among these, NH₄NO₃/TFAA (with [emim][CF₃COO], [emim][NO₃]) and isoamyl nitrate/BF₃·Et₂O, isoamyl nitrate/TfOH (with [emim][OTf]) provided the best overall systems both in terms of nitration efficiency and recycling/reuse of the ionic liquids. For [NO₂][BF₄] nitration, the commonly used ionic liquids [emim][AlCl₄] and [emim][Al₂Cl₇] are unsuitable, as counterion exchange and arene nitration compete. [Emim][BF₄] is ring nitrated with [NO₂][BF₄] producing [NO₂-emim][BF₄] salt, which is of limited utility due to its increased viscosity. Nitration in ionic liquids is surveyed using a host of aromatic substrates with varied reactivities. The preparative scope of the ionic liquids was also extended. Counterion dependency of the NMR spectra of the [emim][X] liquids can be used to gauge counterion exchange (metathesis) during nitration. Ionic liquid nitration is a useful alternative to classical nitration routes due to easier product isolation and recovery of the ionic liquid solvent, and because it avoids problems associated with neutralization of large quantities of strong acid.

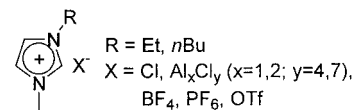
Introduction

Electrophilic nitration of aromatics is a fundamental reaction of great industrial importance, whose products are key organic intermediates or energetic materials. The mechanistic and synthetic aspects of nitration chemistry have been very thoroughly studied over the years.^{1–4} Depending on the reactivity of the nucleophile substrates and the desired chemo- and regioselectivity, a host of nitrating systems have been developed. These range from protic nitrations with mixed acids and superacids to nitril halides, acyl- and alkyl nitrates, metal nitrates, nitronium salts, as well as supported nitration and transfer-nitration reagents.¹

From a preparative perspective, whereas these methods have greatly contributed to enhancing the scope of nitration, there is continuing concern, especially for large-scale production of nitro compounds, regarding environmental aspects, disposal problems, and regeneration of the used acids. The ArNO₂ product(s) are usually soluble in concentrated HNO₃, and this creates problems in product recovery. Moreover, the water byproduct, formed during mixed acid nitration, lowers the acidity and hence the efficiency for continuous operations.

The past few years have witnessed a growing interest in ionic liquids as solvent and catalyst for certain organic

reactions in which 1-ethyl-3-methylimidazolium [emim] and 1-butyl-3-methyl-imidazolium [bmim] chloroaluminates are typically used as ionic liquids.⁵



Their utility in alkylation, acylation, hydrogenation, Diels–Alder, and Heck reactions has been demonstrated.^{6–10} Although [emim][X] with X = BF₄, PF₆, OTf, and Cl are commercially available, they are quite expensive. Therefore, the recycling and reuse are important issues for further investigation.

An early study of catalysis of electrophilic aromatic substitution reactions in acidic [emim] chloroaluminates included examples of nitration in particular with KNO₃.¹¹ It was proposed that KNO₃ reacts with the ionic liquid to generate NO₂⁺ in situ. However, there have been no

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(1) Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration, Methods and Mechanisms*; VCH: New York, 1989.

(2) Olah, G. A. In *Chemistry of Energetic Materials*; Olah, G. A., Squire, D. R., Eds.; Academic Press: New York, 1991; Chapter 7.

(3) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998; Chapter 2.

(4) Behnische, R. In *Methoden der Organischen Chemie (Houben-Weyl)*; Thieme Verlag: Stuttgart, New York, 1992; Vol. E16d, pp 262–361.

(5) (a) Freemantle, M. *Chem. Eng. News* **1998**, March, 32–37. (b) Freemantle, M. *Chem. Eng. News* **1998**, August, 12. (c) Freemantle, M. *Chem. Eng. News* **1999**, January, 23–24. (d) Carmichael, H. *Chem. Britain* **2000**, 36, 36–38.

(6) Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Chem. Commun.* **1998**, 2245.

(7) Stark, A.; MacLean, B. L.; Singer, R. D. *J. Chem. Soc., Dalton Trans.* **1999**, 63.

(8) Adams, C. J.; Earle, M. J.; Seddon, K. R. *Chem. Commun.* **1999**, 1043.

(9) (a) Fischer, T.; Sethi, A.; Welton, T.; Woolf, J. *Tetrahedron Lett.* **1999**, 40, 793. (b) Howarth, J.; Hanlon K.; Fayne, D.; McCormac, P. *Tetrahedron Lett.* **1997**, 38, 3097.

(10) Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Org. Lett.* **1999**, 1, 997.

(11) Boon, J. A.; Lander, S. W., Jr.; Levisky, J. A.; Pflug, J. L.; Skrznecki-Cooke, L. M.; Wilkers, J. S. *Proceedings of the Joint International Symposium on Molten Salts*, 6th, 1987, Honolulu, Hawaii, 979–990.

detailed surveys of nitrating systems and ionic liquid systems to establish efficacy. In view of the recent excitement in exploring the industrial potential of green chemistry using room-temperature ionic liquids as “designer solvent”,¹² and the fundamental importance of nitration, we report here our exploratory studies aimed at determining the utility of ionic liquids as solvent for aromatic nitration. The scope and limitations have been determined for several nitrating systems using various [emim][X] compounds and aromatic substrates. The scope of the available ionic liquids is extended and [HNEtPr₂][CF₃COO] is introduced as a new ionic liquid. Simple workup and ionic liquid recycling procedures have also been devised.

Results and Discussion

Scope of the Available Ionic Liquids. 1-Ethyl-3-methylimidazolium salts with the chloroaluminate counterions, which are prepared by addition of appropriate amounts of AlCl₃ to [emim]Cl, have become standard ionic liquids, which depending on the amounts of the added AlCl₃, produce Lewis basic [emim]Cl, neutral [emim][AlCl₄] or Lewis acidic [emim][Al₂Cl₇] systems.^{5a} The [emim][X] salts with X = PF₆, BF₄, and OTf are commercially available. In the present study, we prepared [emim][CF₃COO], [emim][OTs], and [emim][FSO₃] in near-quantitative yields from [emim]Cl by reaction with CF₃COONa, AgOTs, and FSO₃K, respectively, in acetonitrile solvent. These are pale yellow free-flowing liquids (X = FSO₃ is more viscous). The [bmim][X] salts with X = BF₄ and PF₆ are known.^{10,13} In the present study, [bmim][CF₃COO] was prepared in good yields by counterion exchange (metathesis) from [bmim]Cl. Interestingly, whereas [bmim][PF₆] is stable to aqueous workup conditions (it is water immiscible and is isolated unchanged),¹⁰ [bmim][CF₃COO] and [bmim][BF₄] are both water soluble!

The observed counterion dependency of the NMR chemical shifts of the imidazolium core is a useful tool in determining whether metathesis accompanies nitration. Apart from these imidazolium-based ionic liquids, we found that [HNEtPr₂][CF₃COO] (protonated Hünig's base) melts at 92–93 °C and becomes an ionic liquid at room temperature after adding NH₄NO₃ and the aromatic compound. This provided an excellent medium for NH₄NO₃/TFAA nitration of arenes (see the following text).¹⁴

Nitronium Tetrafluoroborate [NO₂][BF₄] Nitration of Toluene. Aromatic nitrations with nitronium salts especially [NO₂][BF₄] have been extensively studied by Olah and co-workers from both mechanistic and synthetic angles.^{1,2} The [NO₂][BF₄] salt is a highly effective nitrating agent which reacts with a wide variety of arenes. We wondered if it is suitable for ionic liquid nitration.

Nitronium tetrafluoroborate was added to [emim]Cl (1:1) initially at –50 °C (both are solids). Upon raising the temperature to about –16 °C, a yellow liquid was formed (accompanied by gas evolution; NO₂Cl!). The mixture then remained a liquid when re-cooled. Subse-

quent addition of cold toluene (excess) at low temperature (inside a Schlenk tube) led to arene nitration (nitrotoluene ortho/para ratio = 1.50) in 21% yield. For comparison, an independent nitration of toluene with [NO₂][BF₄] in CH₂Cl₂ at rt gave an 83% yield with an ortho/para ratio of 1.45 (very close to the literature value).¹⁵ Formation of the yellow liquid and concomitant gas evolution are indicative of metathesis prior to arene nitration. Formation of [emim][BF₄] was confirmed by NMR following nitration and after recovery of the ionic liquid (see the Experimental Section). In a control experiment, when the evolved gas was allowed to escape the reaction mixture (nitration in an open system under nitrogen), the nitration yield decreased (ca. 15%). We surmise that [NO₂][BF₄] and NO₂Cl both acted as nitrating agent. It is known that the NO₂Cl nitration of benzene and toluene is rather sluggish in the absence of a Lewis acid.

A literature example reports a 35% yield of nitrobenzene from benzene after reflux for 15 h.¹⁶ NO₂Cl does become an effective nitrating agent in the presence of suitable Lewis acids.¹⁷ Taken together, the data suggest that the imidazolium salt catalyzes NO₂Cl nitration. However, since NO₂Cl/Lewis acid halide nitration and NO₂⁺ nitration have very similar regioselectivities in ionizing polar media,¹ the contribution of NO₂Cl nitration to the overall process cannot be determined. Clearly though the overall yield of nitrotoluenes (21%) is unattractive.

[NO₂][BF₄] slowly reacts with [emim][AlCl₄] to give a yellow suspension. Toluene is nitrated in this mixture in improved yields as compared to [emim]Cl/[NO₂][BF₄] system (47%; ortho/para ratio = 1.31). The recovered ionic liquid solvent was shown to be [emim][BF₄] (>95%) by comparison of its ¹⁹F NMR spectrum with an authentic sample (additional tiny fluorine resonances observed in fluoroborate anion region may be due to minor ligand exchange, i.e., [BF₃Cl]). This establishes [emim][BF₄] formation by counterion exchange as the main competing process. Nitration with the Lewis acidic [emim][Al₂Cl₇] actually lowered the yield of nitrotoluenes (32%) and [emim][BF₄] was again formed.

Using a slight excess of [NO₂][BF₄] relative to the ionic liquid (1.2-fold), nitration of toluene was examined in [emim][BF₄]. An orange viscous oil was formed upon addition of [NO₂][BF₄] to [emim][BF₄] and subsequent addition of toluene gave only a 5% yield of nitrotoluenes isomers. NMR analysis of the ionic liquid layer following nitration showed that the imidazolium core undergoes ring nitration to produce [NO₂-emim][BF₄] (3-nitro and 4-nitro isomers) (Scheme 1). The resulting nitrated imidazolium core in [NO₂-emim][BF₄] exhibits increased viscosity (yellow oil rather than a liquid) and this feature limits its potentials. Nevertheless, [NO₂-emim][BF₄] could be used for [NO₂][BF₄] nitration of toluene in good yield (71%; ortho/para ratio = 1.17).

[Emim][PF₆] was allowed to react with excess [NO₂][BF₄] (4.7-fold). A colorless oil was formed (it contained some undissolved nitronium salt), to which toluene was added. In this case, once again, toluene nitration and imidazolium nitration occurred. The resulting [NO₂-emim][BF₄] could be reused for arene nitration by addi-

(12) Freemantle, M. *Chem. Eng. News* **2000**, May, 37–50.

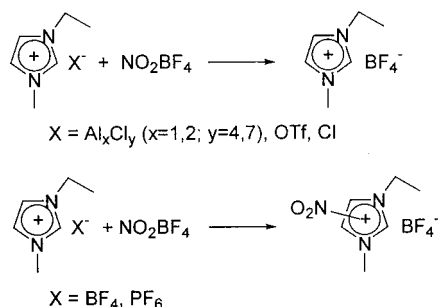
(13) Huddelton, J. G.; Willauer, H. D.; Swatboski, R. P.; Nisser, A. E.; Roger, R. D. *Chem. Commun.* **1998**, 1765.

(14) Whether this a consequence of metathesis with NH₄NO₃ or formation of a binary system which induces ionic liquid property is presently an open question.

(15) Coon, C. L.; Blucher, W. G.; Hill, M. E. *J. Org. Chem.* **1973**, *38*, 4243.

(16) Price, C. C.; Sears, C. A. *J. Am. Chem. Soc.* **1953**, *75*, 3276

(17) Kuhn, S. J.; Olah, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 4564.

Scheme 1. Reaction of [NO₂][BF₄] with [emim]X Salts

tion of fresh nitronium salt followed by the aromatic (at least two cycles were tried) where the nitrotoluenes yield did not decrease.

An exothermic reaction occurred upon mixing [emim]-[OTf] and [NO₂][BF₄] (1:1.2 ratio). Subsequent addition of toluene resulted in nitrotoluenes formation in low yield (19%). NMR analysis of the ionic liquid phase after workup showed that in this case nitration of imidazolium core did not occur but metathesis took place to form [emim][BF₄]. These results are unexpected in view of the powerful nitrating ability of [NO₂][OTf].^{1,15}

Nitration with Isoamyl Nitrate. Nitration of aromatics with alkyl nitrates requires protic or Lewis acid activation.^{1,2} In the present study, a survey of various [emim][X] ionic liquids showed that [emim][OTf] is the optimal ionic liquid for RONO₂ nitration catalyzed by BF₃·Et₂O or TfOH (Scheme 2). With BF₃·Et₂O heating of the reaction mixture was necessary (69% yield; ortho/para ratio = 1.0), whereas with in TfOH-catalyzed reaction nitration could be effected at 0 °C (60% yield; ortho/para ratio = 1.45).

Toluene nitration with isoamyl nitrate/TfOH/Tf₂O system in [emim][NO₃] ionic liquid was also successful but gave lower yields of nitrotoluene isomers (36%; ortho/para ratio = 1.43). NMR analysis of the recovered ionic liquid was consistent with the formation of [emim][OTf] via counterion exchange.

Using [emim][CF₃COO] as ionic liquid solvent, isoamyl nitrate/TFA/TFAA nitrating system did not react with toluene.

Regeneration/recycling of the [emim][OTf] ionic liquid used in RONO₂ nitration was accomplished by heating the used ionic liquid under vacuum, followed by NMR assay.

Survey of Nitration with M_x(NO₃)_y/TFAA Systems.

(a) In [emim][NO₃]. The Cu(II)nitrate/acetic anhydride system has been used for nitration of activated systems such as annulenes and cyclophanes.¹⁸ Using Cu(II)nitrate/TFAA in the present study, we find that toluene is nitrated in [emim][NO₃] ionic liquid solvent in reasonable yield (59% isolated yield; ortho/para ratio = 0.92). The low ortho/para ratio is indicative of nitration with a bulky polarized complex similar to that proposed by Olah et al. for AgNO₃/BF₃.¹⁹ An unattractive feature of Cu(II)nitrate nitration in [emim][NO₃] is the difficulty in removing the residual copper compound(s) from the ionic liquid following nitration. Addition of 18-crown-6

to complex Cu²⁺ ion and chromatographic purification were ineffective.

Toluene is similarly nitrated with an AgNO₃/Tf₂O system in [emim][NO₃] to give nitrotoluenes (58% isolated yield; ortho/para ratio = 1.16). In this case, metathesis is a competing process forming [emim][OTf], and AgOTf is a byproduct that is easily removed. The NH₄NO₃/TFAA system is an in situ source of trifluoroacetyl nitrate (Scheme 2), it is an interesting nitrating reagent that has not been widely exploited. NH₄NO₃ dissolves in [emim]-[NO₃], allowing homogeneous nitration which ensues when TFAA is introduced following the addition of toluene. The nitrotoluene isomers are obtained in 59% isolated yield with an ortho/para ratio of 1.15.

(b) In [emim][CF₃COO]. NH₄NO₃ is soluble in [emim]-[CF₃COO] and following the addition of the aromatic, addition of TFAA brings about arene nitration, which after a short reaction time at r.t. resulted in a 65% isolated yield of nitrotoluene isomers with an ortho/para ratio of 1.02.

(c) In [HNtPr₂][CF₃COO]. The trifluoroacetate salt of Hünig's base melts between 92 and 93 °C. This ionic liquid proved to be ideal for the NH₄NO₃/TFAA nitrating system producing high yield of nitroaromatics. NH₄NO₃ is soluble and nitration is effected at rt, it is complete within minutes. Toluene nitration gave a 58% yield and an ortho/para ratio of 1.27.

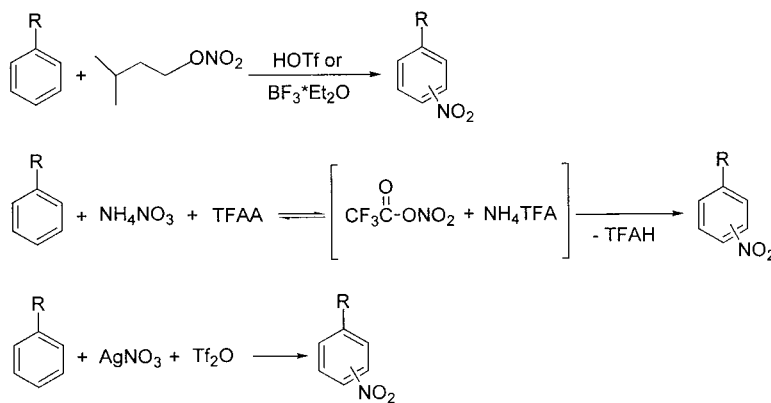
Comparative Assessment and Regeneration/Recycling Issues. Among [emim][X] salts, [emim][OTf] and [emim][CF₃COO] are most suited for ionic liquid nitration. Among various nitrating systems examined, M_x(NO₃)_y/TFAA and AgNO₃/Tf₂O provide the best regeneration/recycling potential because the organics form a separate phase and are removed by a simple extraction. From the nitration efficiency perspective, the NH₄NO₃/TFAA system is superior, but there is no phase separation. This can be induced by addition of the Hünig's base NEtPr₂, whose salt [HNtPr₂][CF₃COO] cannot be removed from [emim][CF₃COO] initially. However, this does not diminish the physical characteristics of the ionic liquid which can be reused several times, allowing [HNtPr₂][CF₃COO] to build up in the [emim][X]. At this point, most of [HNtPr₂][CF₃COO] can be removed by simple filtration or centrifuge, allowing [emim][X] to be reused.

Our work identifies NH₄NO₃/TFAA/[HNtPr₂]-[CF₃COO] as an overall superior system for aromatic nitration. Following nitration, addition of free Hünig's base brings about the desired phase separation so the organics can be removed. Then NH₄TFA is removed by heating under vacuum, leaving behind [HNtPr₂]-[CF₃COO]. Thus, the "byproduct" of nitration is the ionic liquid. Alternatively, in both cases, *n*-Bu₂O can be used to extract the organics and the ionic liquid is purified by heating under vacuum.

Scope of Aromatic Nitration Using the Optimal Systems. Having established NH₄NO₃/TFAA/[HNtPr₂]-[CF₃COO], NH₄NO₃/TFAA/[emim][CF₃COO], and isoamyl nitrate/TfOH/[emim][OTf] as promising systems, a series of arenes were studied to determine the scope and limitation of ionic liquid nitration. The results are summarized in Table 1. Nitration of anisole, *p*-methylanisole, *tert*-butylbenzene, mesitylene, fluorobenzene, *p*-fluorotoluene, toluene, benzene, and naphthalene were effected in good to excellent yields by using the above systems. Trifluoromethylbenzene was nitrated albeit in

(18) (a) Mitchell, R. H.; Yan, J., S.-H. *Tetrahedron Lett.* **1979**, 1289. (b) Tashiro, M.; Mataka, M.; Takeshita, M.; Arimura, T.; Tsuge, A.; Yamato, T. *J. Org. Chem.* **1989**, *54*, 451.

(19) Olah, G. A.; Fung, A. P.; Narang, S. C.; Olah, J. A. *J. Org. Chem.* **1981**, *46*, 3533.

Scheme 2. Most Promising Nitrating Systems for Ionic Liquid Nitration of Aromatics**Table 1. Nitration of Arenes in Ionic Liquids^a**

R-Ar	i.l.	yield (%)	isomer distribution (%)
OMe	[emim][OTf]	95 (GC)	67.1/-/32.9 (GC) ^b
	[emim][CF ₃ COO]	75 (NMR)	64.5/-/35.5 (NMR) ^b
	[HNEtPr ₂][CF ₃ COO]	99 (NMR)	74.3/-/25.7 (GC) ^b
1-MeO/4-Me	[emim][OTf]	90 (GC)	100 ^c
	[emim][CF ₃ COO]	70 (GC)	100 ^c
	[HNEtPr ₂][CF ₃ COO]	88 (GC)	100 ^c
<i>t</i> Bu	[emim][OTf]	80 (GC)	12.1/7.5/80.4
	[emim][CF ₃ COO]	81 (GC)	7.9/6.8/85.3 ^b
	[HNEtPr ₂][CF ₃ COO]	64 (GC)	8.4/6.2/85.4
1,3,5-tri-Me	[emim][OTf]	80 (NMR)	
	[emim][CF ₃ COO]	>66 (NMR)	
	[HNEtPr ₂][CF ₃ COO]	53 (NMR)	
F	[emim][OTf]	90 (GC)	9.4/3.2/87.4 (GC) ^b
	[emim][CF ₃ COO]	54 (GC)	6.6/-/93.4 (GC) ^b
	[HNEtPr ₂][CF ₃ COO]	97 (GC)	3.8/3.4/92.8 (GC) ^b
Me	[emim][CF ₃ COO]	65	49.5/2.0/48.5 (GC) ^b
	[emim][OTf]	60	58.0/2.1/39.9 (GC) ^b
	[HNEtPr ₂][CF ₃ COO]	58 (NMR)	54.0/3.6/42.4 (GC) ^b
H	[emim][CF ₃ COO]	50 (GC)	
	[emim][OTf]	84 (GC)	
	[HNEtPr ₂][CF ₃ COO]	56 (GC)	
CF ₃	[emim][CF ₃ COO]	~3 (GC)	14.8/66.8/18.4 (GC) ^b
	[emim][OTf]	24 (GC)	9.3/89.2/1.5 (GC) ^b
	[emim][OTf]	57 (NMR)	13.0/79.1/7.9 (GC) ^d
4-F/1-Me	[emim][CF ₃ COO]	<56 ^e	9.9/3.9/86.2 (GC) ^d
	[HNEtPr ₂][CF ₃ COO]	42-62 (GC)	17.7/15.0/62.3 (GC) ^f
	[emim][CF ₃ COO]		
NO ₂	[emim][OTf]		
	[HNEtPr ₂][CF ₃ COO]		
	[emim][CF ₃ COO]		
naphthalene	[emim][OTf]		
	[HNEtPr ₂][CF ₃ COO]	100 (GC)	92.9/7.1(GC) ^g

^a For [emim][OTf], the nitration system was isoamyl nitrate/TfOH. For [emim][CF₃COO] and [HNEtPr₂][CF₃COO], the nitration system was NH₄NO₃/TFAA. ^b Ortho-/meta-/para-. ^c 4-Methyl-2-nitroanisole. ^d 3-Nitro- and 2-nitro-4-F-toluene plus a skeletally rearranged fluoronitrotoluene isomer. ^e Small impurity present. ^f Rearrangement increases with increased reaction times. ^g 1-Nitro/2-nitro.

lower yields, but nitrobenzene could not be further nitrated. With *p*-fluorotoluene, apart from the two expected isomers, a minor product was formed which increased in the mixture with time. On the basis of NMR analysis of the isomeric mixture (¹H and ¹⁹F), it was tentatively identified as another isomer of fluoronitrotoluene (methyl disproportionation). In most cases, the yields and isomer distributions of nitration in ionic liquids are comparable to those of the conventional systems.¹

In summary, the utility of ionic liquids solvents for electrophilic nitration of arenes has been studied. Whereas imidazolium chloroaluminates are unsuitable, [emim][OTf], [emim][CF₃COO] and [HNEtPr₂][CF₃COO] are quite promising. Ionic liquid nitration using [NO₂][BF₄] is problematic because the imidazolium core itself is nitrated in competition, and the resulting C-nitrated imidazolium salt is a viscous oil not an ionic liquid. Optimal systems are NH₄NO₃/TFAA and isoamyl nitrate/TfOH or isoamyl nitrate/BF₃·Et₂O.

The present systems do not require large quantities of strong acids, they offer simple workup procedure and do not need aqueous workup. Relatively simple operations have been devised to regenerate and recycle the ionic liquids.

Experimental Section

Starting Materials and Reagents. [Emim][X] (X = Cl, PF₆, BF₄, OTf), NO₂BF₄, isoamyl nitrate, TFAA, TfOH, BF₃·Et₂O, AlCl₃, AgNO₃, Cu(II) nitrate, NH₄NO₃, NEtPr₂, sodium *p*-toluenesulfonate, potassium fluorosulfate, sodium trifluoroacetate, 1-methylimidazole, 1-chlorobutane, and the arenes were all high purity commercial samples (all from Aldrich) which were used without further purification. Tf₂O was prepared from TfOH and P₂O₅. [HNEtPr₂][CF₃COO] was prepared by adding CF₃COOH (1 equiv) to an ether solution of NEtPr₂. The resulting precipitate was washed with ether. [Bmim][Cl] was prepared according to a literature procedure.¹³ Ether was dried over sodium. Other solvents were used without purification.

(a) Synthesis of New Imidazolium Ionic Liquids by Counterion Exchange. (a1) 1-Ethyl-3-methyl-1H-imidazolium Trifluoroacetate. To a solution of [emim]Cl (1.47 g, 10.0 mmol) in acetonitrile/ether (15 mL, 2:1) was added a solution of sodium trifluoroacetate (1.36 g, 10.0 mmol) in ether/acetone (6 mL, 1:1), whereupon a white solid continually formed. The mixture was allowed to stir for 1 h to ensure complete reaction. The solution was separated from the precipitate, and the solvents were removed, leaving 2.24 g (100%) of a pale yellow oil: IR (film) ν 3080 (s, br), 2260 (br), 1780 (s, br), 1575 (s) cm^{-1} ; ^1H NMR (acetone- d_6 , 300.14 MHz) δ 1.56 (t, 3H, $J = 7.2$, CH_3CH_2), 4.10 (s, 3H, CH_3), 4.46 (q, 2H, $J = 7.2$, CH_3CH_2), 7.86 (s, 1H, CH), 7.95 (s, 1H, CH), 9.77 (s, 1H, N_2CH); ^{13}C { ^1H } NMR (acetone- d_6 , 75.47 MHz) δ 15.84 (s), 36.62 (s), 45.54 (s), 116.39 (q, $J = 288$, CF_3), 123.02 (s), 124.61 (s), 137.89 (s), 158.93 (q, $J = 39$, CO).

(a2) 1-Ethyl-3-methyl-1H-imidazolium *p*-Toluene-sulfonate (Tosylate). To a solution of [emim]Cl (293 mg, 2.0 mmol) in acetonitrile (10 mL) was added silver *p*-toluene-sulfonate (594 mg, 2.0 mmol), and the above procedure was followed: yield 559 mg (99%) of a pale yellow oil; IR (film) ν 3120 (m), 3080 (s), 2960 (m), 1760 (s), 1480 (w), 1440 (m), 1380, 1480 (w) cm^{-1} ; ^1H NMR (acetone- d_6 , 300.14 MHz) δ 1.40 (t, 3H, $J = 7.2$, CH_3CH_2), 2.29 (s, 3H, CH_3), 3.93 (s, 3H, NCH_3), 4.27 (q, 2H, $J = 7.2$, CH_3CH_2), 7.13 (d, 2H, $J = 7.9$, CCH), 7.67 (d, 2H, $J = 7.9$, CCH), 7.73 (s, 1H, NCH), 7.82 (s, 1H, NCH), 9.48 (s, 1H, N_2CH); ^{13}C { ^1H } NMR (acetone- d_6 , 75.47 MHz) δ 15.83, 21.22, 36.38, 45.30, 122.95, 124.54, 126.66, 129.05, 138.10, 139.01, 146.95.

(a3) 1-Ethyl-3-methyl-1H-imidazolium Fluorosulfonate. To a solution of [emim]Cl (146 mg, 1.0 mmol) in acetone/acetonitrile (1:1; 6 mL) was added potassium fluorosulfate (138 mg, 1.0 mmol), and the same procedure as above was followed: yield 210 mg (100%) of a yellow viscous oil; IR (film) ν 3080 (m), 2940 (s), 2840 (m), 1715 (m), 1560 (m), 1375 (w), 1270 (s) cm^{-1} ; ^1H NMR (acetone- d_6 , 300.14 MHz) δ 1.56 (t, 3H, $J = 7.3$, CH_3CH_2), 4.08 (s, 3H, CH_3), 4.43 (q, 2H, $J = 7.2$, CH_3CH_2), 7.77 (s, 1H, CH), 7.84 (s, 1H, CH), 9.73 (s, 1H, N_2CH); ^{13}C { ^1H } NMR (MeCN- d_3 , 75.47 MHz) δ 15.60, 36.68, 45.64, 122.82, 124.54, 137.25.

(a4) 1-Butyl-3-methyl-1H-imidazolium Trifluoroacetate. To a solution of [bmim]Cl (3.49 g, 20.0 mmol) in CH_3CN (10 mL) was added a solution of sodium trifluoroacetate (2.72 g, 20.0 mmol) in ether/acetone (1:1; 6 mL), whereby a white solid was continually formed. The mixture was allowed to stir for 1 h to ensure complete reaction. The solution was separated from the precipitate, and the solvent was removed leaving 4.79 g (95%) of a yellow liquid: IR (film) ν 3060 (s), 2960 (s), 2860 (m), 2700–1850 (br), 1760 (m), 1660 (s, br), 1465 (m) cm^{-1} ; ^1H NMR (acetone- d_6 ; 300.14 MHz) δ 0.88 (t, 3H, $J = 7.5$, CH_3CH_2), 1.31 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 4.10 (s, 3H, NCH_3), 4.42 (t, 2H, $J = 7.3$, NCH_2), 7.97 (pt, 1H, $J = 1.7$, CH), 8.06 (pt, 1H, $J = 1.7$, CH), 9.90 (s, 1H, N_2CH); ^{13}C { ^1H } NMR (acetone- d_6 ; 75.47 MHz) δ 13.86, 19.86, 36.68, 49.88, 123.34, 124.56, 138.07.

(b1) Reaction of $[\text{NO}_2][\text{BF}_4]$ with Ionic Liquids and Nitration of Toluene. (b1) [emim]Cl. $[\text{NO}_2][\text{BF}_4]$ (414 mg, 3.1 mmol) was added to [emim]Cl (440 mg, 3.0 mmol) at -50°C , and the solid mixture was allowed to warm to around -16°C whereby a yellow liquid was formed (minor gas evolution was noted; NO_2Cl !). After the liquid was cooled to -50°C , cold toluene (5 mL) was added. The mixture was stirred at ca. -50°C for 30 min, followed by 2 h at rt. The toluene phase was separated by extraction with ether and with CH_2Cl_2 . Removal of solvent left 91 mg (21%) of nitrotoluene isomers. GC analysis: 58.7% ortho, 2.4% meta, 38.9% para. The ^1H NMR spectrum of the recovered ionic liquid (in CD_3CN) showed complete counterion exchange (\rightarrow [emim][BF_4]).

(b2) [emim]Cl/ AlCl_3 (emim AlCl_4). Mixing [emim]Cl (439 mg, 3.0 mmol) and commercial "anhydrous" AlCl_3 (400 mg, 3.0 mmol) (not sublimed) gave a pale yellow oil to which $[\text{NO}_2][\text{BF}_4]$ (466 mg, 3.5 mmol) was added, whereby a slow reaction ensued inside the yellow suspension (gas evolution). After 5 min, toluene (6 mL) was slowly added whereby an orange fluid and a white precipitate were formed (the latter is mostly AlCl_3

possibly with minor amounts of AlF_3 or AlCl_xF_y) (see also further). The suspension was stirred for 2 h and extracted with ether and with CH_2Cl_2 . Work up similar to b1. Yield: 228 mg (47%) yellow oil. Nitrotoluene isomer distribution: 54.9% ortho, 3.2% meta, 41.9% para. Extraction of the white precipitate with CH_3CN yielded [emim][BF_4], which was identified by ^1H NMR. Formation of [emim][BF_4] by counterion exchange ($>95\%$) was further confirmed in an independent run via ^{19}F NMR in comparison with an authentic sample, showing that most of $[\text{BF}_4]$ ends up in the recovered ionic liquid).

(b3) [emim]Cl/2 AlCl_3 (emim Al_2Cl_7). Mixing [emim]Cl (439 mg, 3.0 mmol) and commercial "anhydrous" AlCl_3 (800 mg, 6.0 mmol) gave a gray liquid to which $[\text{NO}_2][\text{BF}_4]$ (393 mg, 3.0 mmol) was added (a green suspension). Addition of toluene (6 mL) gave a dark-red solution. After 10 min a white precipitate and a yellow liquid were formed. The suspension was stirred for 2 h and extracted with ether and CH_2Cl_2 . Work up similar to b1. Removal of the solvent left a yellow solid which was extracted again with ether. Product weight was 131 mg (32%). Nitrotoluene isomer distribution: 53.8% ortho, 3.2% meta, 43.0% para. Extraction of the white precipitate with CH_3CN yielded [emim][BF_4] (^1H NMR).

(b4) [emim][BF_4]. Addition of $[\text{NO}_2][\text{BF}_4]$ (500 mg, 3.76 mmol) to [emim][BF_4] (606 mg, 3.06 mmol) gave an orange viscous oil. After 1 h toluene (6 mL) was added and the mixture was stirred overnight. Work up analogous to b1). Product weight was 21 mg (5%). Nitrotoluene isomer distribution: 39.5% ortho, 33.5% meta, 27.0% para. The ^1H NMR spectrum of the ionic liquid showed [emim][BF_4] and two isomeric nitroimidazolium salts with nitration taking place at the 4 and 5 position of the imidazole ring. Additional $[\text{NO}_2][\text{BF}_4]$ (359 mg, 2.7 mmol) was added to bring about complete $[\text{NO}_2\text{-emim}][\text{BF}_4]$ formation which was washed with ether and CH_2Cl_2 to give a yellow viscous oil (4- NO_2 and 5- NO_2 -[emim][BF_4]): IR (film) ν 3140 (s), 3000 (w), 1740 (m), 1690 (m), 1650 (m), 1590 (s), 1525 (s), 1460 (m), 1400 (s), 1320 (s) cm^{-1} ; ^1H NMR (acetone- d_6 ; 300.14 MHz) δ 1.62 (q, 6H, $J = 7.3$, CH_3CH_2 , both isomers), 4.11 (s, 3H, NCH_3 , isomer 1), 4.27 (s, 3H, NCH_3 , isomer 2), 4.47 (q, 2H, $J = 7.3$, CH_3CH_2 , isomer 2), 4.73 (q, 2H, $J = 7.2$, CH_3CH_2 , isomer 1), 8.78 (s, 1H, CH, isomer 1), 8.85 (s, 1H, CH, isomer 2), 9.15 (s, 2H, N_2CH , isomer 1 + 2).

Isomer ratio (^1H NMR: NCH_3 group): 2/1 = 1.1.

(b5) $[\text{NO}_2\text{-emim}][\text{BF}_4]$. Addition of $[\text{NO}_2][\text{BF}_4]$ (500 mg, 3.76 mmol) to $[\text{NO}_2\text{-emim}][\text{BF}_4]$ (729 mg, 3.0 mmol) gave a yellow suspension to which toluene (5 mL) was slowly added. After the mixture was stirred overnight, the products were separated from the ionic liquid phase by addition of ether and CH_2Cl_2 . Removal of solvent gave a dark-green oil which was rinsed with ether. Removal of ether left 366 mg (71%) of isomeric nitrotoluene (56.8% ortho, 3.2% meta, 40.0% para). NMR assay of the recovered $[\text{NO}_2\text{-emim}][\text{BF}_4]$ salt (a viscous oil) showed it to be almost pure.

(b6) [emim][PF_6]. A colorless oil (containing some undissolved nitronium salt) was formed when [emim][PF_6] (623 mg, 2.43 mmol) and $[\text{NO}_2][\text{BF}_4]$ (995 mg, 7.49 mmol) were mixed. Slow addition of toluene (3 mL) led to a vigorous reaction. After stirring overnight the mixture was extracted with ether. GC analysis indicated a 45% yield of nitrotoluene isomers (59.2% ortho, 2.6% meta, 38.2% para). The ionic liquid phase was a yellow, highly viscous oil (with greenish precipitate inside). ^1H NMR showed imidazolium ring nitration and counterion exchange.

(b7) [emim][OTf]. A hot liquid was formed when [emim]-[OTf] (520 mg, 2.0 mmol) and $[\text{NO}_2][\text{BF}_4]$ (323 mg, 2.43 mmol) were mixed. After the liquid was cooled to rt, toluene (5 mL) was added. Extraction with ether and removal of unreacted toluene left 63 mg (19%) of nitrotoluene isomers (GC analysis: 59.4% ortho, 3.0% meta, 37.6% para). ^1H NMR assay of the ionic liquid phase showed that metathesis took place to give [emim][BF_4].

(c) Nitration with Isoamyl Nitrate. General Procedure. The aromatic compound (4.0 mmol) was added to a solution of the ionic liquid (3–7 mmol) and isoamyl nitrate (266 mg, 2.0 mmol).

(a) HOTf (0.3 mL, 4.0 mmol) was added slowly at 0 °C. The mixture was extracted with ether and the extract was washed with NaHCO₃/water to give the products.

(b) BF₃·Et₂O (2 mL) was added, and the mixture was heated to 100 °C. The products were isolated by extraction with ether.

Regeneration/Recycling of the Ionic Liquid. This was accomplished by simply heating the ionic liquid to 100 °C under vacuum.

(d) Nitration with M_x(NO₃)_y/TFAA System in [emim]-[NO₃]. (d1) Cu(NO₃)₂·H₂O + TFAA + Toluene. Adding Cu(NO₃)₂·H₂O (250 mg, ~1.3 mmol) to [emim][NO₃] (281 mg, 1.6 mmol) led to an exothermic reaction with evolution of a brown gas. The resulting brown-green color changed to green during addition of TFAA (2.0 mL, 14.0 mmol) and subsequently toluene (5 mL) was slowly added. After stirring for 12 h a green solution and a brown precipitate were formed. Extraction with ether gave a green viscous oil, which was dissolved in ether again and extracted with water. Removal of the ether phase left 211 mg (59%) of nitrotoluene isomers (GC analysis: 46.9% ortho, 2.1% meta, 51.0% para). Following extraction the residue is a pale green solid. Attempts to remove the Cu compound from the ionic liquid with 18-crown-6 or chromatography were unsuccessful.

(d2) AgNO₃ + Tf₂O + Toluene. Tf₂O (0.5 mL, 3.0 mmol) was added to a suspension of [emim][NO₃] (800 mg, 4.6 mmol) and AgNO₃ (169 mg, 1.0 mmol) whereby a reaction occurred and a brown gas evolved. Addition of toluene (5 mL) gave a white solid and a yellow solution. After 12 h the suspension was extracted with ether and CH₂Cl₂. Removal of the solvents left a yellow oil and a small amount of a white solid (AgOTf). Yield of nitrotoluene isomers: 736 mg (58%); (GC analysis: 51.4% ortho, 4.6% meta, 44.0% para). Counterion exchange converted [emim][NO₃] to [emim][OTf].

(d3) NH₄NO₃ + TFAA + Toluene. Ammonium nitrate (160 mg, 2.0 mmol) was dissolved in emimNO₃ (1.16 g, 7.88 mmol), and toluene (2 mL) was added followed by TFAA (0.4 mL, 3.0 mmol). After 1 h, only one phase was observed. Excess TFAA was removed and the solution was neutralized with the Hünig base. The nitrotoluene products were removed by extraction with ether (ether phase washed with NaHCO₃/water): yield 59% (NMR); GC analysis 51.9% ortho, 3.3% meta, 44.9% para.

(e) Nitration with NH₄NO₃/TFAA System in [emim]-[CF₃COO]. General Procedure. NH₄NO₃ (160 mg, 2.0 mmol) was dissolved in [emim][CF₃COO] (1.75 g, 8.0 mmol) and the aromatic compound (4.0 mmol) was added. At 0 °C TFAA (1.4 mL, 10.0 mmol) was slowly added, which started the reaction. After 10–30 min the reaction was over and only one phase was observed.

Regeneration/Recycling of the Ionic Liquid. Procedure 1. After removal of excess TFAA under vacuum, ether was added followed by the Hünig base until a phase separation was observed. After extraction with ether, the ionic liquid contained [NH₄][CF₃COO] and [HNEtPr₂][CF₃COO]. The [NH₄][CF₃COO] salt could be removed by heating the ionic liquid/salt mixture to 130 °C in high vacuum. It was impossible to remove the [HNEtPr₂][CF₃COO] salt. After several nitration experiments, some [HNEtPr₂][CF₃COO] salt precipitated either during workup or during reaction and could be removed by filtration or more effectively by centrifuge. Based on NMR assay, the “recycled” ionic liquid containing up to 65% [HNEtPr₂][CF₃COO] is still an ionic liquid and can be reused.

Procedure 2. After the nitration, the ionic liquid was extracted with *n*Bu₂O (the extract was washed with NaHCO₃/water to remove CF₃COOH and TFAA). It was then heated to 130 °C in high vacuum to remove TFAA, CF₃COOH, *n*-Bu₂O, and [NH₄][CF₃COO].

(f) Nitration with [NH₄][NO₃]/TFAA System in [HNEtPr₂][CF₃COO]. General Procedure. [HNEtPr₂][CF₃COO] (1.83 g, 7.5 mmol) was heated until it melted (92–93 °C). Then NH₄NO₃ (160 mg, 2.0 mmol) was dissolved in the ionic liquid and the aromatic compound (4.0 mmol) was added. The mixture was cooled to rt, and TFAA (1.4 mL, 10.0 mmol) was slowly added which started the nitration reaction. After 10–30 min, the reaction was over and only one phase was observed.

Regeneration/Recycling of the Ionic Liquid. Procedure 1. After removal of excess TFAA under vacuum, ether was added followed by the Hünig base until a phase separation was observed. After extraction with ether the [NH₄][CF₃COO] salt and remaining ether were removed from the ionic liquid by heating the ionic liquid/salt mixture to 130 °C in high vacuum. This workup procedure created as “byproduct” the ionic liquid [HNEtPr₂][CF₃COO].

Procedure 2. Following the nitration reaction, the ionic liquid was extracted with *n*-Bu₂O (the *n*-Bu₂O phase was washed with NaHCO₃/water.) The ionic liquid was heated to 140 °C in high vacuum to remove TFAA, CF₃COOH, *n*-Bu₂O and [NH₄][CF₃COO].

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