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Electrophilic Reactions of Aromatic and Heteroaromatic Compounds in Ionic Liquids

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Abstract—The review summarizes and analyzes published data on electrophilic aromatic substitution reactions performed in ionic liquids.

1. INTRODUCTION

Ecological and economic problems impose more severe requirements on the application of alternative solvents in technology and large-scale organic synthesis [1]. An ideal solvent should be nonvolatile and low-toxic, highly resistant to chemical agents and temperature, and reusable. In addition, it should ensure high rate, yield, and selectivity (up to 100%) of a chemical process. Ionic liquids [1–37] meet the above requirements to a considerable extent. Up to now, ionic liquids have been successfully applied to effect a wide series of organic reactions, such as carbonylation, etherification, reduction of aldehydes and ketones, rearrangements, cycloaddition, polymerization, etc. [1–37].

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The goal of the present review is to analyze and systematize available data on the use of ionic liquids in electrophilic aromatic substitution reactions.

2. PROPERTIES OF IONIC LIQUIDS

In keeping with the generally accepted views, ionic liquids are electrolytes consisting of only cationic and anionic species and melting below 100°C. They can also be referred to as *low-melting salts*, *liquid organic salts*, and *salts fused at room temperature*. In the recent years, the term *novel solvents* has been introduced to emphasize the novelty of this kind of solvents or unusual application of salt systems as solvents. Ionic liquids possess a unique combination of properties which make them approaching *green solvents*. These properties are as follows: (1) high thermal stability (400°C and higher) and the possibility of using them in a wide temperature range (more than 500°C); (2) high chemical and electrochemical stability;

(3) high polarity; (4) low volatility; (5) high electric conductivity; and (6) low toxicity.

As a rule, ionic liquids are salts consisting of an organic cation and inorganic or organic anion. A large number of cations are used to built up ionic liquids: ammonium (**1**) [38, 39], pyrrolidinium (**2**) [39–41], phosphonium (**3**) [42], sulfonium (**4**) [43], imidazolium (**5**) [29, 39, 40, 44–47], oxazolium (**6**) [48, 49], thiazolium (**7**) [49, 50], triazolium (**8**) [51–55], pyrazolium (**9**) [56], benzotriazolium (**10**) [52], pyridinium (**11**) [57, 58], isoquinolinium (**12**) [59], and pyrimidinium (**13**) [60]. Ionic liquids may also include dications, e.g., imidazolium **14** [61] or ammonium **15–19** [62]. Anionic species may be both mononuclear [Cl^-, Br^-, NO_3^-, BF_4^-, PF_6^-, $AlCl_4^-$, SbF_6^-, $ZnCl_3^-$, $CuCl_2^-$, $SnCl_3^-$, $CH_3SO_3^-$, $CF_3SO_3^-$, $CF_3CO_2^-$, ClO_4^-, $(CF_3SO_2)_2N^-$] and bi- and polynuclear anions ($Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Fe_2Cl_7^-$, $Sb_2F_{11}^-$, $Au_2Cl_7^-$) [1, 11]. The latter are formed via reactions of Lewis acids with the corresponding mononuclear anions, e.g., by reaction of $AlCl_3$ with $AlCl_4^-$.
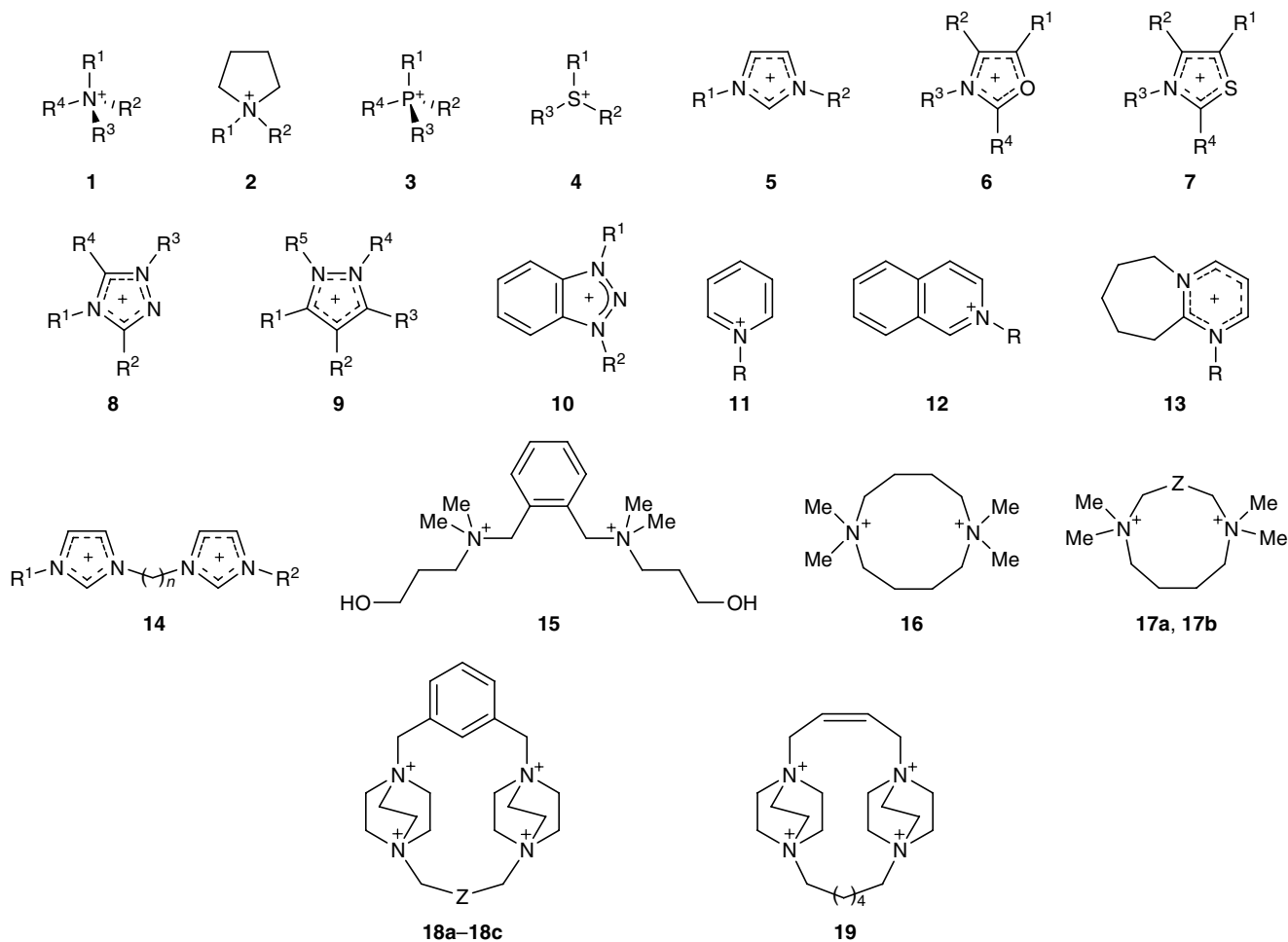

17, Z = CH=CH (**a**), C≡C (**b**); **18**, Z = $(CH_2)_6$ (**a**), $(CH_2)_8$ (**b**), C≡C (**c**).

Some physical parameters of 1-R-3-methylimidazolium ionic systems [1, 11, 24]

R	Anion	mp, °C	Density, g/cm³ (temperature, °C)	Viscosity, MPa s (temperature, °C)	Conductivity, S/m (temperature, °C)	E_T^N
Me	Cl⁻	125				
Et	Cl⁻	87				
Et	AlCl₄⁻	7				
Et	NO₃⁻	38				
Et	BF₄⁻	15	1.240 (25)	34 (25)	1.4 (25)	
Et	PF₆⁻	62			0.52 (26)	
Et	CF₃SO₃⁻	–9	1.390 (20)	45 (20)	0.92 (25)	
Et	NTf₂⁻	–3	1.520 (20)	34 (20)	0.57 (25)	
Et	CF₃CO₂⁻	–14	1.285 (20)	35 (20)	0.96 (20)	
Bu	Cl⁻	65				
Bu	AlCl₄⁻		1.238 (25)	27 (25)	1.0 (25)	
Bu	BF₄⁻		1.17 (30)	233 (30)	0.173 (25)	0.673
Bu	PF₆⁻	–61	1.363 (20)	207 (25)	0.146 (25)	0.667
Bu	CF₃SO₃⁻	16	1.290 (20)	90 (20)	0.37 (20)	0.667
Bu	CF₃CO₂⁻		1.209 (20)	73 (20)	0.32 (20)	0.620
Bu	C₃F₇CO₂⁻		1.333 (20)	182 (20)	0.1 (20)	
Bu	NTf₂⁻	–4	1.429 (20)	52 (20)	0.39 (20)	0.642

Such anions are very sensitive to water. Ionic liquids possessing a cationic and anionic center in a single molecule, e.g., sulfonamides **20a**, **20b**, and **21**, were synthesized [63].

20a, 20b

Me

21

20, *n* = 2 (**a**), 3 (**b**).
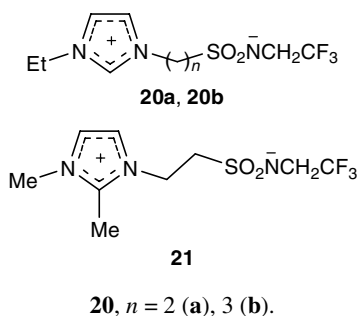
As a rule, ionic liquids containing an asymmetric cation melt at a lower temperature. In addition, their melting points strongly depend on the anion nature (see table). An important parameter of ionic liquids is their viscosity which also strongly depends on the anion (see table). Ionic liquids like [bmim][X]* give rise to the following anion series with respect to their viscosity: $AlCl_4^- < (CF_3SO_2)_2N^- < CF_3CO_2^- < CF_3SO_3^- < C_3F_7CO_2^- < PF_6^- < BF_4^-$; thi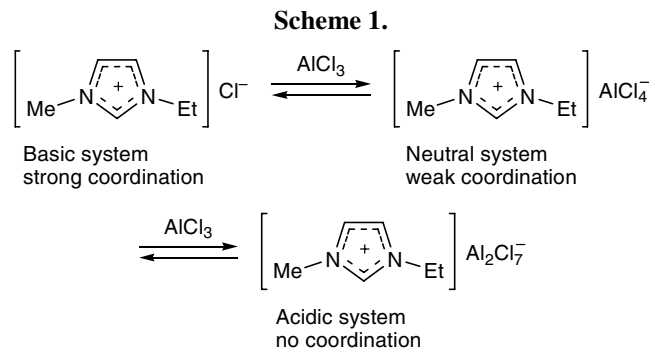s series is determined by the ability of anions to form hydrogen bonds and by the strength of their van der Waals interactions [34].

The density of ionic liquids approaches that typical of organic compounds; it increases as the number of heavy atoms therein rises. For example, in going from [emim][AlCl₄]* to [emim][Al₂Cl₇] and then to [emim][Al₂Br₇], the density increases from 1.294 to 1.389 and 2.219 g/cm³, respectively [11]. An analogous pattern is observed for [bmim][CF₃CO₂] and [bmim][CF₃SO₃] (see table). Within a series of structurally related ionic liquids, the density decreases as the size of the cation increases. For example, in the series of $1\text{-}R^1\text{-}3\text{-}R^2$-imidazolium tetrachloroaluminates, the density decreases as the number of carbon atoms in the alkyl groups (R^1 and R^2) increases, g/cm³: 1.31 ($R^1 = R^2 = $ Me), 1.27 ($R^1 = $ Me, $R^2 = $ Et), 1.23 ($R^1 = $ Me, $R^2 = $ Pr), 1.21 ($R^1 = $ Me, $R^2 = $ Bu), 1.14 ($R^1 = R^2 = $ Bu) [45].

Ionic liquids are usually characterized by high electric conductivity and polarity (see table). The polarity of [bmim][X] ionic liquids, estimated by the Reichardt electrophilicity parameter E_T^N [64], lies between those of water and acetonitrile ($E_T^N = 1$ and 0.46, respectively) [11]. In this respect, ammonium ionic liquids like [RNH₃][NO₃] are closer to water ($E_T^N = 0.954$ for R = Et and $E_T^N = 0.923$ for R = Pr) or even more polar ([Pr₂NH₂][SCN], $E_T^N = 1.006$) [11].

* Hereinafter, generally accepted abbreviations for ionic liquids are used: [bmim] stands for 1-butyl-3-methylimidazolium, and [emim], for 1-ethyl-3-methylimidazolium.

All ionic liquids can be divided into hydrophilic and hydrophobic [2]. The latter usually contain per-fluorinated anions. Most tetraalkylammonium, alkyl-pyridinium, and 1,3-dialkylimidazolium ionic liquids having bis(trifluoromethylsulfonyl)amide [65–67], bis-(pentafluoroethylsulfonyl)amide [59], trifluoromethyl-trifluoroborate [68], and hexafluorophosphate(V) anions [65, 69–73] are hydrophobic. These ionic liquids favor removal of water from reaction mixture and its transfer to another phase or evaporation at appropriate temperature; therefore, they are used in reactions with hygroscopic reagents or in those involving formation of moisture-sensitive intermediates. Most typical hydrophilic ionic liquids are salts formed by organic cations with the following anions: chloride [74], acetate [75], trifluoroacetate [74], *p*-toluenesulfonate [76], methanesulfonate [76], thiocyanate [77], and dicyanamide [39, 78]. It should be noted that the strength of hydrogen bonds formed by 1-butyl-3-methylimidazolium ionic liquids increases in the following series of anions: $PF_6^- < SbF_6^- < BF_4^- < (CF_3SO_2)_2N^- < ClO_4^- < CF_3SO_3^- < NO_3^- < CF_3CO_2^-$ [74]; this series reflects to some extent hydrophilic–hydrophobic properties of ionic liquids.

The acidity of ionic liquids and their ability to coordinate metal ions depend mainly on the anion nature. This may be illustrated by the equilibrium shown in Scheme 1. Chloroaluminate [emim][X] (X = Cl, AlCl₄, Al₂Cl₇) may be regarded as a base or acid at a AlCl₃-to-[emim][X] molar ratio of <0.5 or >0.5 [34]. The

Scheme 1.

Basic system
strong coordination

Neutral system
weak coordination

Acidic system
no coordination

acidity increases as the amount of AlCl₃ rises, and such chloroaluminate ionic liquids acquire superacidic properties upon addition of strong mineral acids (e.g., HCl; see figure) [34, 79, 80]. Unlike common superacids, superacidic ionic liquids are more convenient to handle with [79], and they are widely used at present to carry out electrophilic reactions [1–5, 7, 11, 13, 17, 18, 20–24, 31–34].
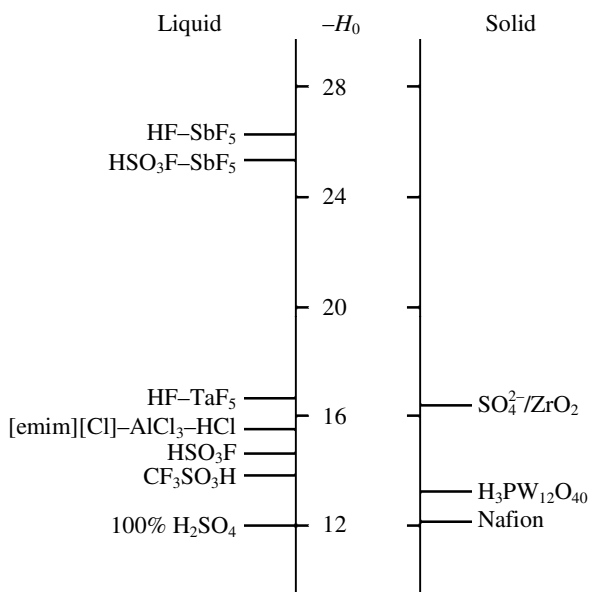
3. ELECTROPHILIC AROMATIC SUBSTITUTION

3.1. Alkylation and Related Reactions

Alkylation of aromatic compounds is one of the most important large-scale processes. More than 6000000 tons of alkyl-substituted arenes is produced worldwide per annum [81]. Many alkylation processes are performed in the presence of such acids as HF, H₂SO₄, and AlCl₃ as catalysts, thus creating serious ecological problems. Over many years, much effort was made to develop ecologically benign alkylation processes. A promising way of solving this problem is replacement of the above acids by solid acid catalysts (heteropolyacids, zeolites, etc.; see, e.g., [82–85]). However, these catalysts are not free from some disadvantages. For instance, solid acids undergo fast deactivation and give rise to pitch. In the recent time, ionic liquids have been proposed as promising solvents and catalysts for alkylation of arenes [81, 86–106].
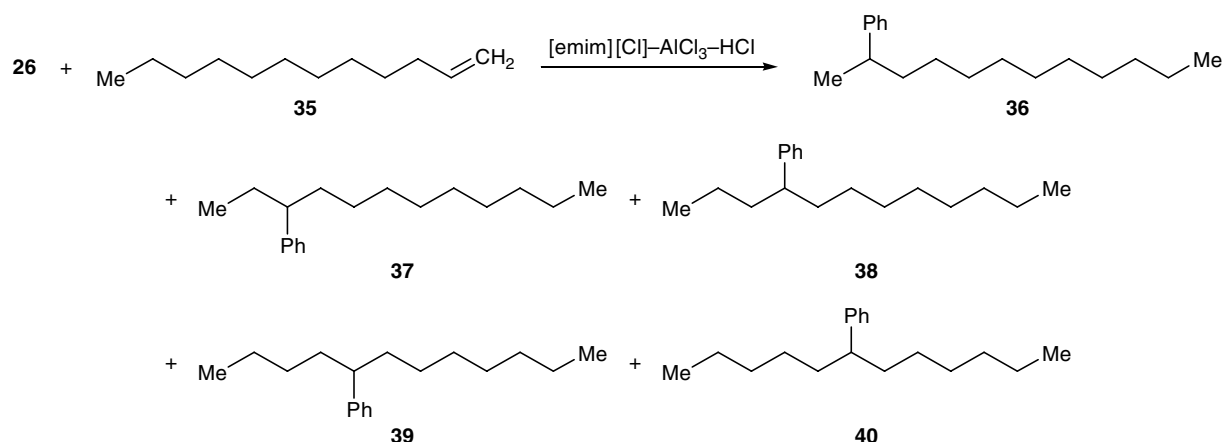
Koch et al. [101] were the first to report on the use of low-melting ionic liquids to effect alkylation of arenes. Electrochemical oxidation of hexamethylbenzene (**22**) in the system *N*-ethylpyridinium bromide–AlCl₃ in the presence of benzene at room temperature gave an equimolar mixture of pentamethylbenzene (**23**) and diphenylmethane (**24**) (Scheme 2).

Boon et al. [102] later proposed another ionic liquid, 1-ethyl-3-methylimidazolium [emim] tetra-chloroaluminate–AlCl₃, to perform alkylation of benzene (**26**) with alkyl chlorides **27a–27f**; as a result,
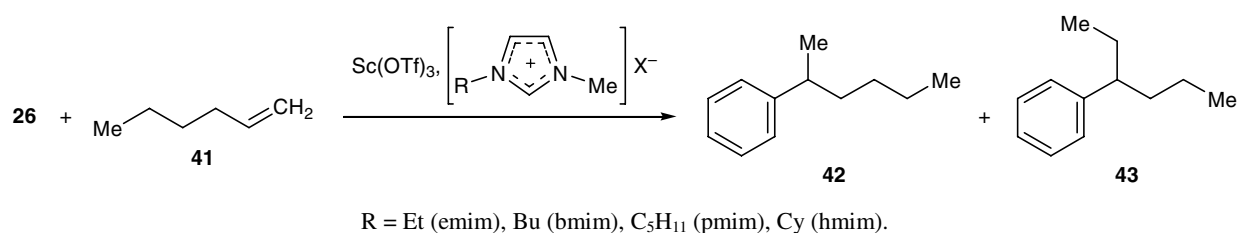

Liquid	$-H_0$	Solid
	28	
HF–SbF₅		
HSO₃F–SbF₅		
	24	
	20	
HF–TaF₅		SO₄²⁻/ZrO₂
[emim][Cl]–AlCl₃–HCl	16	
HSO₃F		
CF₃SO₃H		
		H₃PW₁₂O₄₀
100% H₂SO₄	12	Nafion

Hammett acidity functions H_0 of liquid and solid acids [34, 79]. Molar ratio AlCl₃/[emim][Cl] 55:45 [79].

Scheme 2.

various alkyl-substituted benzenes **28a–28f** were obtained (Scheme 3).

Scheme 3.

R = Me (**a**), Et (**b**), Pr (**c**), Bu (**d**), cyclohexyl (**e**), PhCH₂ (**f**).

In the reaction with excess methyl chloride or ethyl chloride, whole series of alkyl-substituted benzenes **28a** and **28b** were formed. For example, the alkylation with ethyl chloride gave 12% of mono-, 11% of di-, 33% of tri-, 24% of tetra-, 17% of penta-, and 2% of hexasubstituted derivatives. More bulky alkyl chlorides (R = Pr, Bu, Cy, PhCH₂) gave rise mainly to mono-, di-, and trialkylbenzenes **28c–28f**. The amount of polyalkylbenzenes can be reduced to a considerable extent by using excess benzene with respect to alkyl chloride. Thus the reaction of benzene with propyl chloride at a ratio of 10:1 led mainly to the formation of monoalkylation products (95%): 30% of propylbenzene and 70% of isopropylbenzene.

By alkylation of benzene (**26**) with methylene chloride (**29**) or chloroform (**30**) in ammonium, pyridinium, or imidazolium ionic liquids (IL) (trimethylammonium, 1-butylpyridinium, or 1-butyl-3-methylimidazolium chloride in a mixture with AlCl₃) in the

Scheme 4.

24, **29**, $n = 2$; **30**, **31**, $n = 3$.

presence of hydrogen chloride, di- and triphenylmethanes **24** and **31** were obtained, respectively (Scheme 4) [81]. The yield of diphenylmethane in ionic liquids was considerably greater (95–97%) than in the system HCl–AlCl₃–CH₂Cl₂ (38%). The formation of triphenylmethane from benzene and chloroform in ionic liquids is strongly hindered (the maximal conversion in the system [bmim][Cl]–AlCl₃ was only 23%), and the major product is diphenylmethane (yield 90%). It should be noted that the yield of diphenylmethane almost does not depend on the structure of the cationic part of ionic liquid.

The alkylation of *o*-xylene (**32**) with 1,2-dichloroethane (**33**) in ionic liquids based on ammonium or pyridinium salts and AlCl₃ gave 40–60% of 1,2-bis-(3,4-dimethylphenyl)ethane (**34**) [100] (Scheme 5).

Scheme 5.

The catalytic system [emim][Cl]–AlCl₃, as well as [emim][Cl]–AlCl₃–HCl, was used to catalyze alkylation of benzene (**26**) with 1-dodecene (**35**) (Scheme 6) [81]. The reaction is characterized by almost 100% conversion of 1-dodecene; however, it is accompanied by isomerization of intermediate dodecyl cation, so

Scheme 6.

Scheme 7.

R = Et (emim), Bu (bmim), C$_5$H$_{11}$ (pmim), Cy (hmim).

Scheme 8.

Scheme 9.

that a mixture of five isomeric dodecylbenzenes is formed, 2-phenyldodecane (**36**) slightly prevailing (35–40%). The alkylation of benzene with 1-decene in ionic liquids like [Rmim][HSO$_4$] or [Rmim][B(HSO$_4$)$_4$] (R = Bu, C$_8$H$_{17}$) occurs in a similar way [89].

Interesting data were reported in [91] on the alkylation of benzene (**26**) with 1-hexene (**41**) in the presence of scandium trifluoromethanesulfonate; the latter is known as a water-insensitive Lewis acid. The reaction did not occur in organic solvents (CH$_2$Cl$_2$, MeCN, MeNO$_2$, PhNO$_2$), water, and hydrophilic ionic liquids

([emim][BF$_4$], [emim][OTf], [bmim][BF$_4$], [bmim]· [OTf]), whereas hydrophobic ionic liquids ([emim]· [SbF$_6$], [bmim][SbF$_6$], [bmim][PF$_6$], [pmim][PF$_6$], [hmim][PF$_6$]) ensured formation of the corresponding alkyl-substituted benzenes in high yield (93–96%) (Scheme 7). The ratio of alkyl-substituted benzenes weakly depends on the nature of ionic liquid [**42**:**43** = (1.5–2):1].

The reaction of pent-2-ene (**44**) with benzene (**26**) in another ionic system (AlCl$_3$–Et$_3$SBr) gave isomeric alkylbenzenes: pentylbenzene (**45**), 2-phenylpentane

(**46**), and 3-phenylpentane (**47**) (Scheme 8) [92], as well as di- and trisubstituted products whose fraction increased with rise in the amount of AlCl$_3$ in the ionic liquid. Analogous results were obtained in the reaction of oct-1-ene (**48**) with benzene in the same catalytic system [92]. The reaction of *p*-xylene (**49**) with styrene (**50**) in 1-methyl-3-[3-(chlorosulfonyl)propyl]imidazolium trifluoromethanesulfonate was more selective: monosubstituted compound **51** was formed in 88% yield [95] (Scheme 9).

High yield and selectivity (>98%) were attained in the alkylation of benzene with ethylene (**52**) in ionic liquids modified with Brønsted acids [96]. The selectivity was slightly lower (79–83%) when chloroaluminate ionic liquids on the basis of 1-R-3-methylimidazolium chlorides were used (R = Et, Bu, C$_8$H$_{17}$, C$_{12}$H$_{25}$) [23]. Sun et al. [93] studied the mechanism of this reaction using labeled atoms. In the alkylation of deuterobenzene with ethylene in the system [bmim]·[Cl]–FeCl$_3$, deuterium atom was found in position *2* of 1-butyl-3-methylimidazolium; therefore, it was presumed that the process is initiated (at least partially) by elimination of proton from the 2-position of the imidazolium ring, i.e., the ionic liquid acts here as Brønsted acid.

Chen et al. [97] examined the effect of the composition of [Et$_3$NH][Cl]–FeCl$_3$–HCl on the alkylation of benzene with hex-1-ene. No alkylation occurred in the presence of only the Lewis acid (FeCl$_3$), while modification of the acid system [Et$_3$NH][Cl]–FeCl$_3$ with hydrogen chloride resulted in 100% conversion of hex-1-ene and exclusive formation of monoalkylation products. Similar results were obtained in the alkylation of benzene with hex-1-ene in another ionic system, [bmim][Cl]–FeCl$_3$ [98].

The alkylation of benzene with pent-1-ene (**53**) in chloroaluminate ionic liquids ([emim][Cl]–AlCl$_3$, [bmim][Cl]–AlCl$_3$, [Me$_3$NHCl]–AlCl$_3$, 1-butylpyridinium chloride–AlCl$_3$) was studied in [99]. The conversion reached 100% in a few minutes at room temperature, and the maximal selectivity for monoalkylation (98.6%) was observed with [Me$_3$NHCl]–AlCl$_3$. The alkylation of benzene with ethylene and other related reactions were performed with the use of Lewis acids like R$_n$MX$_{3-n}$ (R = C$_{1-6}$-alkyl; M = Al, Ga; X = Hlg) in various ionic liquids (alkylammonium, imidazolium, pyridinium, and phosphonium halides) [94]. Cycloalkenes **54a** and **54b** were involved in reaction with benzene (**26**) in [bmim][SbF$_6$] in the presence of Sc(OTf)$_3$; as a result, the corresponding monocyclo-

alkylbenzenes **55a** and **55b** were obtained in high yield (84–92%) [91] (Scheme 10).
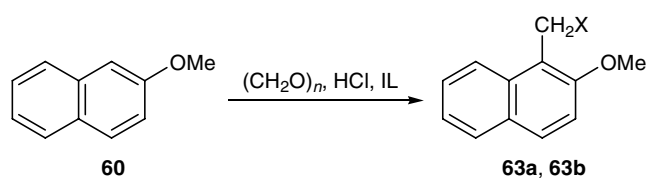
Scheme 10.

R = Bu; *n* = 3 (**a**), 4 (**b**).
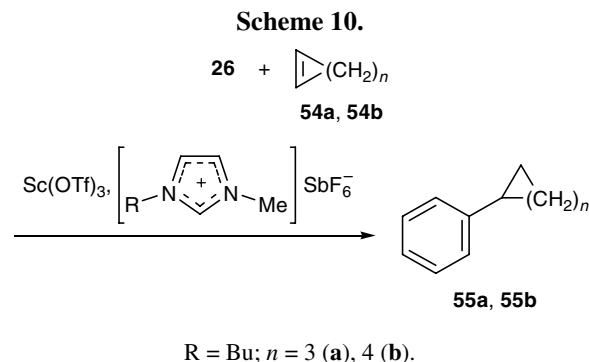
Under analogous conditions, the reaction of cyclohexene (**54b**) with phenol (**56**) and anisole (**57**) gave cyclohexyl-substituted phenol **58** and anisole **59**, the *ortho–para* isomer ratio being 2.5:1 and 1.8:1, respectively (Scheme 11)] [91].

Scheme 11.

R = Bu; **56**, **58**, X = HO; **57**, **59**, X = MeO.
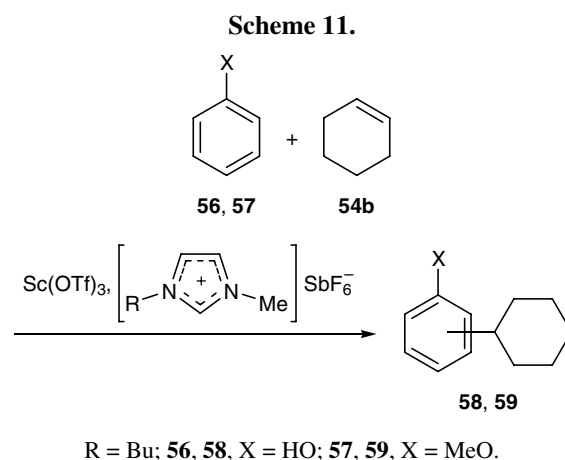
In some cases, the use of ionic liquids instead of conventional solvents allows the selectivity and the rate of arene alkylation to be increased to a considerable extent. In the hydroxymethylation of 2-methoxynaphthalene (**60**) and 2-methylfuran (**61**) with para-formaldehyde (**62**) in 1-ethyl-3-methylimidazolium chloride or 1-butyl-3-methylimidazolium hexafluorophosphate(V), catalyzed by HCl, monoalkylation products **63a**, **63b**, **64a**, and **64b** were formed (>97%) (Schemes 12, 13), whereas the reaction with 2-methoxynaphthalene in ethanol gave exclusively dialkylation product **65** (Scheme 14); 2-methylfuran showed extremely low reactivity (conversion <5%) [90].
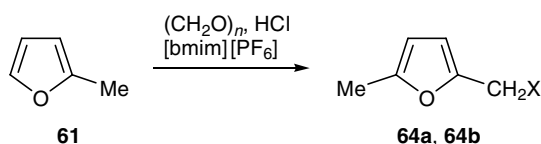
Acid-catalyzed alkylation of phenol (**56**) with *tert*-butyl alcohol (**66**) in 1-butyl-3-methylimidazolium hexafluorophosphate(V) [86] or 1-hexyl-3-(4-sulfo-
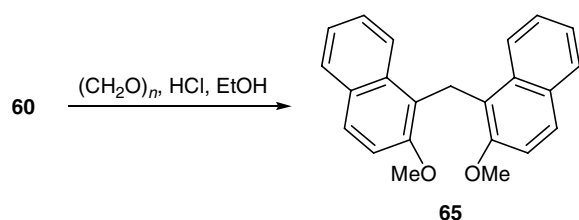
Scheme 12.

IL = [emim][Cl], [bmim][PF$_6$]; X = HO (**a**), Cl (**b**).
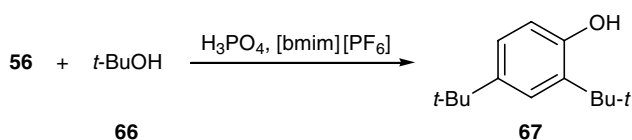
Scheme 13.

X = HO (**a**), Cl (**b**).

Scheme 14.

butyl)imidazolium hydrogen sulfate [106] was reported to produce 2,4-di-*tert*-butylphenol (**67**) with a selectivity of >75 and 61%, respectively (Scheme 15); unlike common organic solvents (e.g., CCl$_4$), neither *m-tert*-butylphenol (**68**) nor *tert*-butyl phenyl ether (**69**) was formed [86].
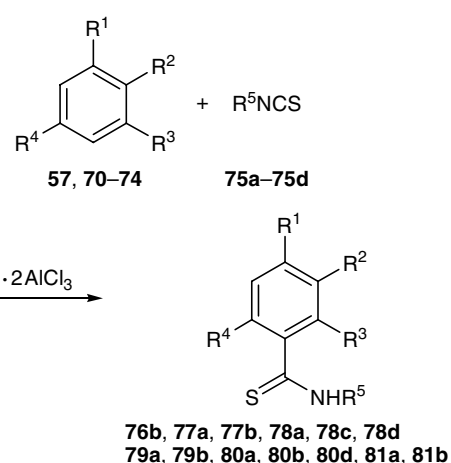
Scheme 15.

Compound **69** was obtained with a high selectivity (>99%) using other ionic liquids, 1-hexyl- and 1-octyl-3-methylimidazolium tetrafluoroborates [87]. High *para* selectivity was observed in the reactions of activated arenes **57** and **70–74** with isothiocyanates **75a–75d** in [bmim][Cl]·2AlCl$_3$ (Scheme 16); the yields of **76–81** (R = Ph, *p*-ClC$_6$H$_4$, Et, Cy) were 66–92% [88].

The key stage in the synthesis of indoles according to Fischer is intramolecular alkylation of aromatic ring. The reactions of arylhydrazines **82** with ketones **83** in choline chloride (ChCl) as ionic liquid in the presence of ZnCl$_2$ gave indoles **84** with high yield and regio-

Scheme 16.

57, **76**, R^1 = MeO, R^2 = R^3 = R^4 = H; **70**, **77**, R^1 = HO, R^2 = Me, R^3 = R^4 = H; **71**, **78**, R^1 = HO, R^2 = R^3 = Me, R^4 = H; **72**, **79**, R^1 = HO, R^3 = Me, R^2 = R^4 = H; **73**, **80**, R^1 = HO, R^2 = R^4 = Me, R^3 = H; **74**, **81**, R^1 = R^3 = Me, R^2 = R^4 = H; R^5 = Ph (**a**), *p*-ClC$_6$H$_4$ (**b**), Et (**c**), Cy (**d**).

selectivity [103] (Scheme 17). Likewise, Bischler–Napieralski cyclization of amides **85a–85c** in ionic liquid [bmim][PF$_6$] ensures higher yield and purity of

Scheme 17.
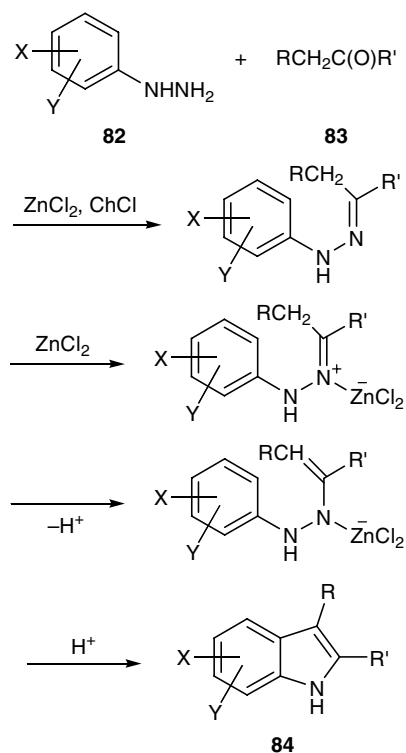
82, X = Y = H; X = 2-Cl, Y = 5-Cl; X =H, Y = 4-Cl; X =H, Y = 2-Me; **83**, R = R' = Me; R = Et, R' = Me; **84**, R = R' = Me: X = 4-Cl, Y = 7-Cl; X = H, Y =5-Cl; X = H, Y =7-Me; R = Et, R' = Me, X = Y = H.

Scheme 18.

$R = R' = H$ (**a**), MeO (**b**), $R = $ MeO, $R' = H$ (**c**).

Scheme 19.

$R = Pr, C_5H_{11}, C_7H_{15}; X = Cl, Br, BF_4.$
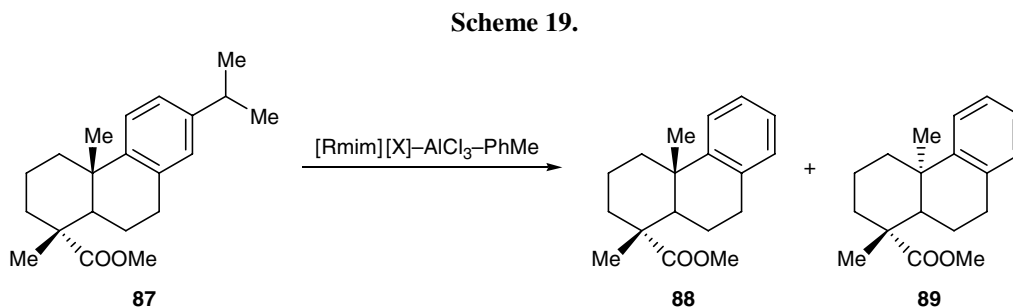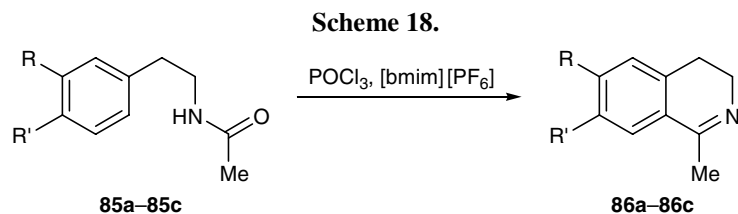
the products and shorter reaction time, as compared to the reactions carried out in common solvents [104] (Scheme 18).

Ionic liquids based on imidazolium salts with various alkyl groups and counterions were used to effect dealkylation of methyl dehydroabietate (**87**) [105] (Scheme 19). The selectivity of the process strongly depended on the medium. In going from [pmim][Cl] to [pmim][BF$_4$]–PhMe, the ratio of compounds **88** and **89** changed from 27:73 to 85:15.

The above data indicate that ionic liquids provide a convenient tool for controlling alkylation of aromatic and heteroaromatic compounds.

3.2. Acylation and Carbonylation

Acylation of aromatic compounds is an important process in manufacture of drugs [107, 108], dyes [109–111], pesticides [112], and various intermediate products in fine organic synthesis [113]. Acylation of arenes is usually characterized by higher selectivity than their alkylation, for introduction of an acceptor RCO group deactivates the aromatic ring and hampers subsequent electrophilic substitution. For example, in
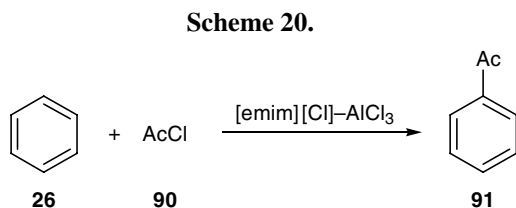
Scheme 20.

the reaction of benzene with acetyl chloride (**90**) in the system [emim][Cl]–AlCl$_3$ only monosubstitution product, acetophenone (**91**) was formed [102] (Scheme 20). The rate of acylation depends on the [emim][Cl]-to-AlCl$_3$ molar ratio (N); almost no reaction occurs if $N \leq 0.5$.

Csihony et al. [114, 115] performed a detailed spectral study on the mechanism of acylation of benzene with acetyl chloride in the systems [bmim][Cl]–MCl$_3$ (M = Al, Fe). As shown by Mössbauer spectroscopy, addition of FeCl$_3$ to [bmim][Cl] led to the formation of an equilibrium mixture containing FeCl$_3$, [bmim]·[Fe$_2$Cl$_7$], Fe$_2$Cl$_6$, and/or [bmim][FeCl$_4$], depending on the molar ratio of FeCl$_3$ and [bmim][Cl] [114]. After addition of MeCOCl to the system [bmim][Cl]–AlCl$_3$, the IR spectrum contained absorption bands corresponding to acetyl cation **A** and acetyl chloride complexes with AlCl$_3$ (**C–D**) [115]. These bands disappeared after addition of benzene, in keeping with the acylation mechanism shown in Scheme 21. It was found that [(MeCO)$_2$CHCO]$^+$[MCl$_4$]$^-$ species does not participate in the acylation of benzene [114].

High regioselectivity in the acylation of monosubstituted benzenes PhX [X = Me (**92**), Cl (**93**), MeO (**57**)], naphthalene (**94**), 3-isopropyl-1,1,2,6-tetramethylindan (**95**), and methyl dehydroabietate (**87**) with acetyl chloride in chloroaluminate ionic liquids was reported in [105, 116] (Schemes 22–27). The acylation of toluene (**92**), anisole (**57**), and *m*-xylene (**74**) with acetyl chloride or acetic anhydride in the systems [bmim][Cl]–MCl$_n$ (M = Al, Sn, Fe) was also
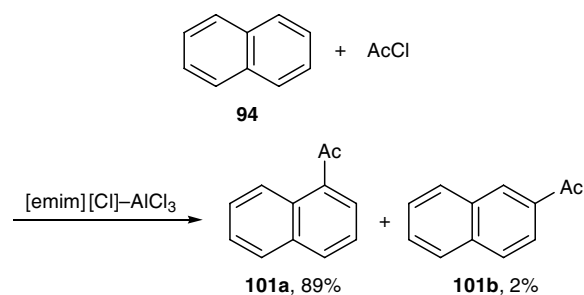
Scheme 21.
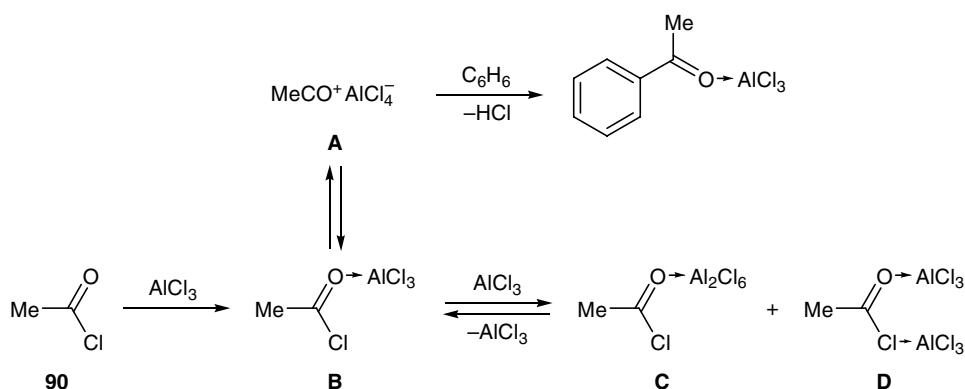
characterized by high regioselectivity [117]. The selectivity in the acylation of *m*-xylene with acetyl chloride increased as the temperature rose. In all reactions, the lowest conversion was observed in the system [bmim][Cl]–AlCl₃, while the best results were obtained with [bmim][Cl]–FeCl₃ [117]. Chloroaluminate ionic liquid [bmim][Cl]–AlCl₃ was used as solvent and catalyst in the synthesis of 4-aryl-4-oxobutanoic acids **106a–106d** and **108–110** and *o*-benzoylbenzoic acids **112a–112d** and **113–115** [118] (Schemes 28–31).

The classical version of Friedel–Crafts acylation of arenes implies catalysis by typical Lewis acids (AlCl₃,

FeCl₃, etc.) which are taken in an amount equivalent to the amount of aromatic substrate, for the catalyst is bound by the ketone thus formed [119]. The use of

Scheme 25.

Scheme 22.
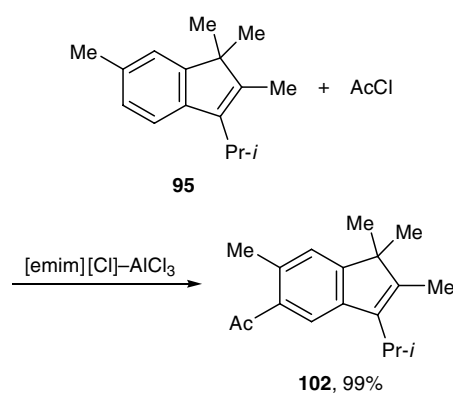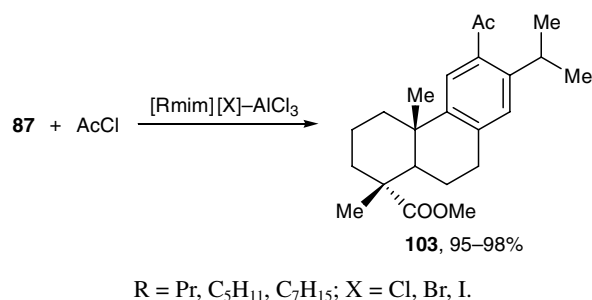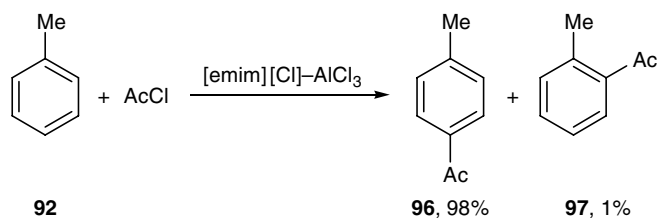
Scheme 26.

Scheme 23.

Scheme 24.

Scheme 27.

R = Pr, C₅H₁₁, C₇H₁₅; X = Cl, Br, I.
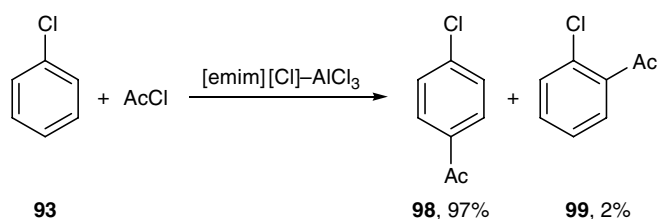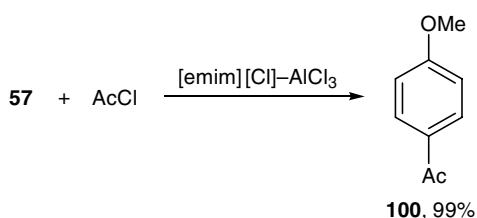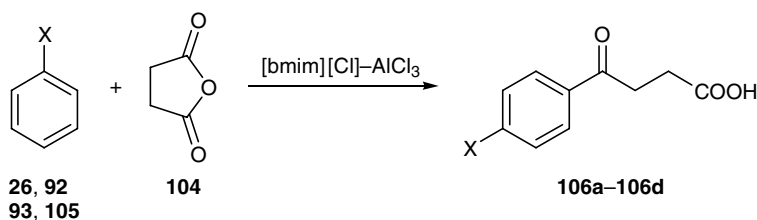
Scheme 28.

26, X = H; **92**, X = Me; **93**, X = Cl; **105**, X = Br; **106**, X = H (**a**), Me (**b**), Cl (**c**), Br (**d**).
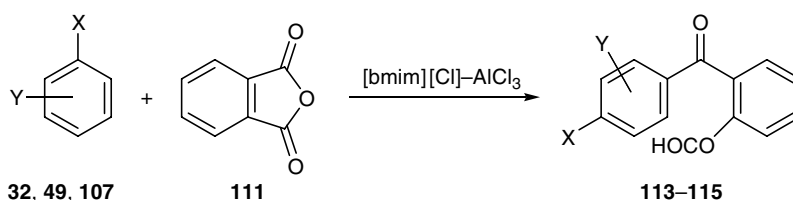
Scheme 29.
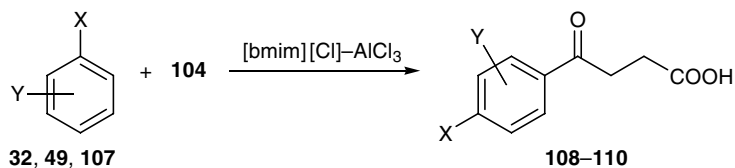
32, X = Me, Y = 2-Me; **49**, X = Me, Y = 4-Me; **107**, X = Cl, Y = 2-Cl; **108**, X = 3-Me, Y = 4-Me; **109**, X = 2-Me, Y = 5-Me; **110**, X = 3-Cl, Y = 4-Cl.

Scheme 30.
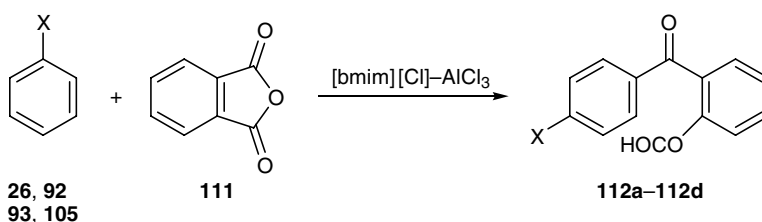
26, X = H; **92**, X = Me; **93**, X = Cl; **105**, X = Br; **112**, X = H (**a**), Me (**b**), Cl (**c**), Br (**d**).

Scheme 31.

32, X = Me, Y = 2-Me; **49**, X = Me, Y = 4-Me; **107**, X = Cl, Y = 2-Cl; **113**, X = 3-Me, Y = 4-Me; **114**, X = 2-Me, Y = 5-Me; **115**, X = 3-Cl, Y = 4-Cl.

metal trifluoromethanesulfonates in combination with ionic liquids makes it possible to considerably reduce the relative amount of the catalyst. Ross and Xiao [119] and Earle et al. 120] demonstrated high efficiency of the systems [bmim][BF$_4$]–M(OTf)$_2$ (M = Cu, Zn, Sc) and [bmim][NTf$_2$]–M(OTf)$_n$ (M = Zn, Co, In, Hf) in the acylation and benzoylation of aromatic compounds **57**, **60**, **93**, **119**, **120**, and **124** in the presence of a small amount of metal trifluoromethanesulfonate with respect to the substrate (Schemes 32–35). Benzoylation of anisole in the catalytic system [bmim]·[BF$_4$]–Cu(OTf)$_2$ occurs at a higher rate and with higher

regioselectivity (*para/ortho* ratio 96:4) than in common organic solvents such as acetonitrile or 1,2-dichloroethane [119].

Unlike monocyclic arenes, reactions with polycyclic hydrocarbons are characterized by lower selectivity. In the acylation of anthracene (**127**) with acetyl chloride in the system [emim][Cl]–AlCl$_3$ (N = 0.67) at 0°C, 69% of 9-acetylanthracene (**128**) was formed in 5 min; after 24 h, a mixture of 1,5- and 1,8-diacetyl-anthracenes **129** and **130** (32 and 24%, respectively) was obtained, while a considerable amount of initial anthracene remained unchanged [116] (Scheme 36).
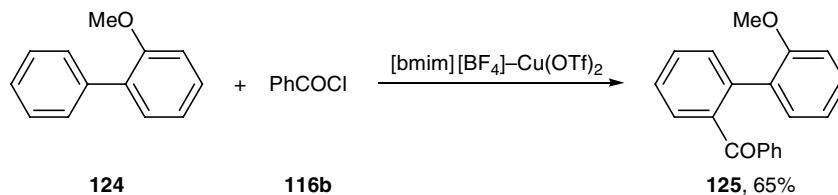
Scheme 32.
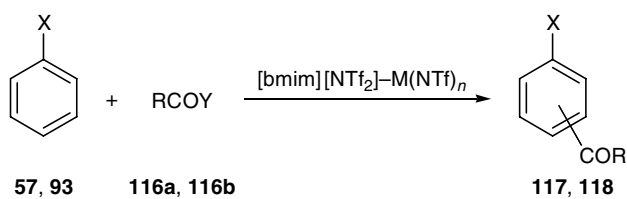
57, X = MeO; **93**, X = Cl; **116**, R = Ph, Y = PhCOO (**a**), Cl (**b**); **117**, R = Ph, X = MeO; **118**, R = Ph, X = Cl; 55–95%.

Scheme 33.
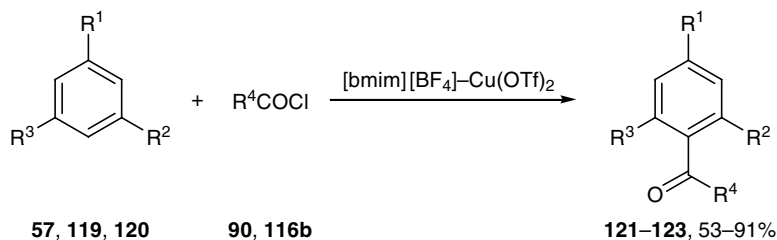
57, **121**, R^1 = MeO, R^2 = R^3 = H; **119**, **122**, R^1 = MeO, R^2 = R^3 = Me; **120**, **123**, R^1 = R^2 = R^3 = Me; **121**, R^4 = Me; **122**, **123**, R^4 = Ph.

Scheme 34.

Scheme 35.

Scheme 36.

These results may be rationalized in terms of reversibility of the acylation reaction in the [emim][Cl]–AlCl$_3$ system (transacylation). Thus keeping of 9-acetylanthracene (**128**) in the above system at 0°C leads to the formation of anthracene (**127**), 2-acetylanthracene (**131**), and 1,5- and 1,8-diacetylanthracenes **129** and **130**. Pyrene (**132**) was converted into 1-acetylpyrene (**133**, 13%) and a mixture of 1,6- and 1,8-diacetylpyrenes **134** and **135** (55%) in the system AcCl–[emim][Cl]–AlCl$_3$ [116] (Scheme 37). Under analogous conditions, 9- and 1-acetylphenanthrenes **137** and **138** were obtained from phenanthrene (**136**) [116] (Scheme 38).

Taking into account that polycyclic arenes could give rise to π complexes and that paramagnetic species could be formed in the system AcCl–[emim][Cl]–AlCl$_3$, Adams et al. [116] believe that the classical acylation mechanism should be revised.

Acid-catalyzed acyl group transfer from sterically hindered aromatic ketones **123a** and **139a–139d** to activated monosubstituted benzenes **57** and **92** in imidazolium ionic liquids ([emim][BF$_4$], [emim][OTf], [bmim][BF$_4$], [bmim][PF$_6$], [bmim][OTf]) was effected under fairly mild conditions [121] (Scheme 39). In the absence of an activated arene, the initial aromatic ketone underwent deacetylation by the action of

Scheme 37.

Scheme 38.

137, 55%   **138**, 30%

Scheme 39.

123a, R^1 = R^3 = R^5 = Me, R^2 = R^4 = H; **139**, R^1 = R^2 = R^4 = R^5 = Me, R^3 = H (**a**), MeCO (**b**); R^1 = R^2 = R^3 = R^4 = Me, R^5 = H (**c**); R^1 = R^2 = R^3 = R^4 = R^5 = Me (**d**); **57**, **140**, X = MeO; **92**, **141**, X = Me; **142**, R^1 = R^2 = R^4 = R^5 = Me, R^3 = H (**a**); R^1 = R^2 = R^3 = R^4 = Me, R^5 = H (**b**).

Scheme 40.

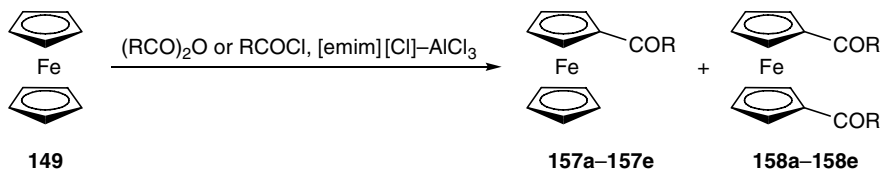**144**, R = MeO; **145**, R = H (**a**), MeO (**b**); IL = [emim][Cl]–AlCl$_3$, [bmim][PF$_6$].
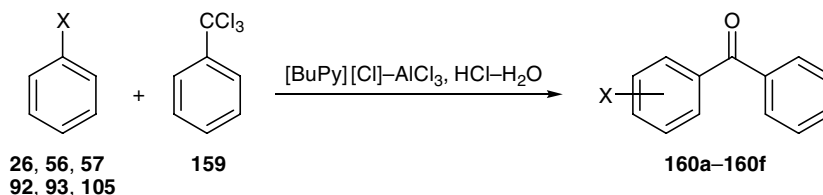
Scheme 41.

146, E = CH, X = 4-O$_2$N (**a**), 4-Cl (**b**), 5-CN (**c**), 6-F (**d**), 7-Br (**e**); E = N, X = H (**f**); **147**, R = 3-MeOC$_6$H$_4$ (**a**), 4-MeOC$_6$H$_4$ (**b**),
4-O$_2$NC$_6$H$_4$ (**c**), HOCO (**d**); **148**, E = CH, R = Me, X = 4-O$_2$N (**a**), R = Ph, X = 4-Cl (**b**), R = 3-MeOC$_6$H$_4$, X = 5-CN (**c**), R =
4-O$_2$NC$_6$H$_4$, X = 6-F (**d**), R = 4-O$_2$NC$_6$H$_4$, X = 7-Br (**e**); E = N, X = H, R = 4-MeOC$_6$H$_4$ (**f**), Me (**g**), HOCO (**h**).

Scheme 42.

R = Me (**a**), Ph (**b**), Pr (**c**), Bu (**d**), *t*-Bu (**e**).

Scheme 43.

X = H (**a**), Cl (**b**), Br (**c**), Me (**d**), OH (**e**), MeO (**f**).

Scheme 44.
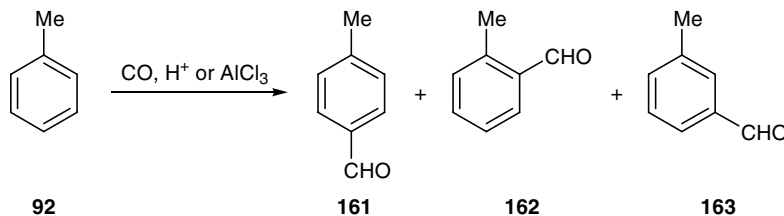
trofluoromethanesulfonic acid [121]. Ionic liquids are also effective as solvents in the acylation of heterocyclic compounds [122, 123] (Schemes (40, 41). Ionic liquids were used to carry out acylation of metal–aromatic compounds. The acylation of ferrocene (**149**) with carboxylic acid anhydrides (RCO)$_2$O [**116a**, R = Ph; **150**, R = Me; **151**, R = Pr; **152**, R = Bu; **153**, R = *t*-Bu) and chlorides RCOCl [**90**, R = Me; **116b**, R = Ph; **154**, R = Pr; **155**, R = Bu; **156**, R = *t*-Bu) in [emim][Cl]–AlCl$_3$ gave the corresponding mono- and disubstituted ferrocene derivatives **157a–157e** and **158a–158e** [124] (Scheme (42). The fraction of the disubstituted product increases in parallel with the amount of the acylating agent with respect to ferrocene and with the AlCl$_3$–[emim][Cl] ratio.

Benzoylation of arenes in chloroaluminate ionic liquids may be performed using aryltrichloromethanes as reagents [125]. By reaction of trichloromethylbenzene **159** and arenes **26**, **56**, **57**, **92**, **93**, and **105** in the system *N*-butylpyridinium chloride–AlCl$_3$, benzophenones **160a–160f** were obtained [125] (Scheme 43).

Carbonylation of arenes with carbon(II) oxide requires strongly acidic medium [126]. The possibility of using chloroaluminate imidazole- and pyridine-based ionic liquids as catalytic media for carbonylation of arenes was demonstrated in [126–128]. High solubility of AlCl$_3$ in [RNC$_5$H$_5$][(CF$_3$SO$_2$)$_2$N] made it possible to effect carbonylation of toluene [126]. The reaction gave *p*-methylbenzaldehyde (**161**) as the major product (selectivity 85–86%), and the overall

yield of aldehydes **161–163** strongly depended on the substituent R in the pyridine ring (R = Me, 22%; R = Et, 30%; R = C$_6$H$_{13}$, 13%; Scheme 44).
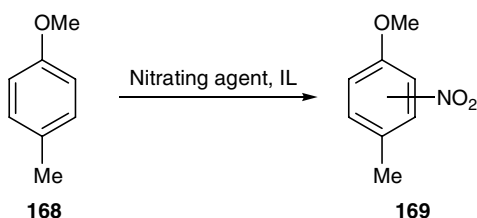
3.3. Nitration

Nitration is one of the main processes in the treatment of aromatic raw materials, which leads to high-energy substances [129], drugs [107, 108], and important intermediate products for a number of chemical technologies [109–113]. Boon et al. [130] were the first to report on the use of ionic liquids in the nitration of arenes; the catalytic system was [emim][Cl]–AlCl$_3$. Laali and Gettwert [131] demonstrated successful application of ionic liquids like [emim][Y] (Y = OTf$^-$, CF$_3$COO$^-$, NO$_3^-$) and [Et(i-Pr)$_2$NH][CF$_3$COO] in the nitration of aromatic compounds **26**, **57**, **92**, **94**, **164–166**, and **168** with various nitrating agents (NH$_4$NO$_3$–CF$_3$COOH, isopentyl nitrate–BF$_3 \cdot$Et$_2$O, isopentyl nitrate–CF$_3$SO$_3$H, CuNO$_3$–CF$_3$CO$_2$H, AgNO$_3$–Tf$_2$O) (Schemes 45–47).

Scheme 45.
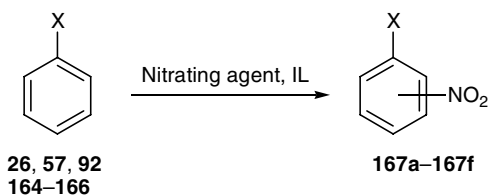
26, X = H; **57**, X = MeO; **92**, X = Me; **164**, X = t-Bu; **165**, X = F; **166**, X = CF$_3$; **167**, X = H (**a**), Me (**b**), t-Bu (**c**), CF$_3$ (**d**), MeO (**e**), F (**f**).

Scheme 46.

Scheme 47.
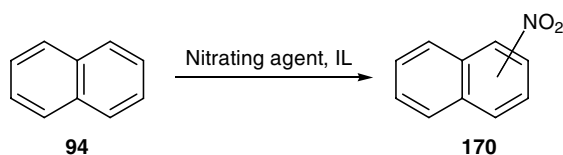
The yield and selectivity in the nitration processes strongly depended on the substrate structure. Substituted benzenes **164** and **165** give rise mainly to the corresponding *para*-substituted product, whereas intro-

duction of electron-withdrawing substituents (X = CF$_3$, NO$_2$) inhibits the reaction. The nature of ionic liquid also affects the regioselectivity of nitration but not so strongly. Analogous results were reported in [132, 133]. In the nitration of toluene with HNO$_3$–Ac$_2$O in CH$_2$Cl$_2$ the *ortho/para* isomer ratio was equal to 1.4, while in ionic liquids it was 1.5, 1.4, and 1.3 for [bmim][Y] (Y = BF$_4$, NTf$_2$), 1-butyl-2,3-dimethyl-imidazolium bis(trifluoromethylsulfonyl)amide [bm$_2$im][NTf$_2$], and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [bmpy][NTf$_2$], respectively [132]. A different ratio of isomeric *ortho*- and *para*-nitrotoluenes (0.8) was obtained in the nitration of toluene with 62% HNO$_3$ in the presence of a catalytic amount of ionic liquid of another type, 3-methyl-1-(3-sulfopropyl)imidazolium trifluoro-methanesulfonate [133]. The best yield of nitrotoluenes (93%) was attained using [bmpy][NTf$_2$] [132], presumably due to high resistance of that ionic liquid toward nitrating systems. It should be noted that ionic liquids like [emim][Y] undergo nitration themselves [131]. The use of ionic liquids instead of traditional solvents enhances the reactivity of aromatic compounds [132]. For instance, the nitration of bromo- and chlorobenzenes in [bmpy][[NTf$_2$] gave the corresponding nitro derivatives in 63 and 50% yield, respectively, whereas no nitration occurred in methylene chloride. In addition, [bmpy][[NTf$_2$] ensured fairly high regioselectivity in the nitration of bromo- and chlorobenzenes: in both cases, the *ortho/para* isomer ratio was 0.28 [132]. A high *para*-selectivity was also attained in the nitration of phenols with Fe(NO$_3$)$_3$ in 1,3-dibutyl-imidazolium tetrafluoroborate [134] and ethylammonium nitrate [135] (in the latter case, ultrasonic activation was applied).

Various ammonium and phosphonium ionic liquids were used in the nitration of naphthalene with HNO$_3$ in

Scheme 48.
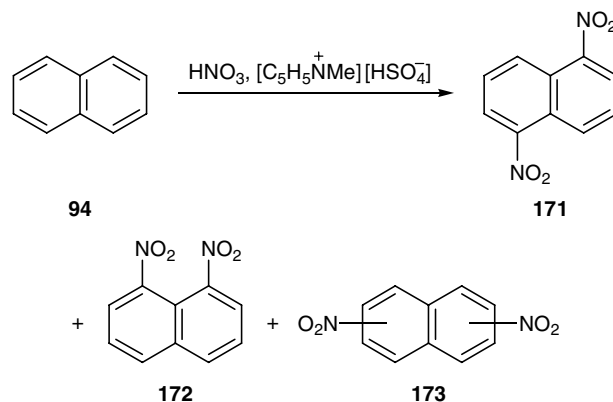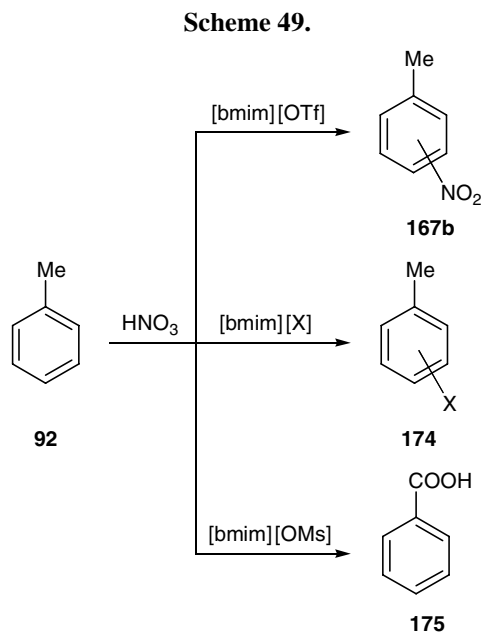
Scheme 49.

the presence of H_2SO_4 or H_3PO_4 [136]. Treatment of naphthalene with 98% HNO_3 in N-methylpyridinium hydrogen sulfate gave a mixture of 1,5-dinitronaphthalene (38%), 1,8-dinitronaphthalene (53%), and other dinitronaphthalenes (9%) (Scheme 48).
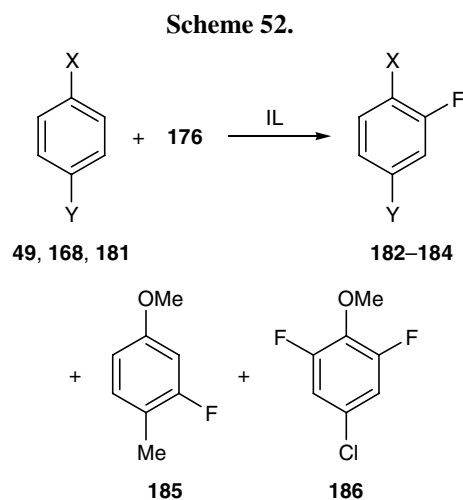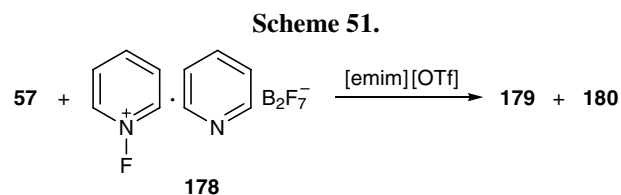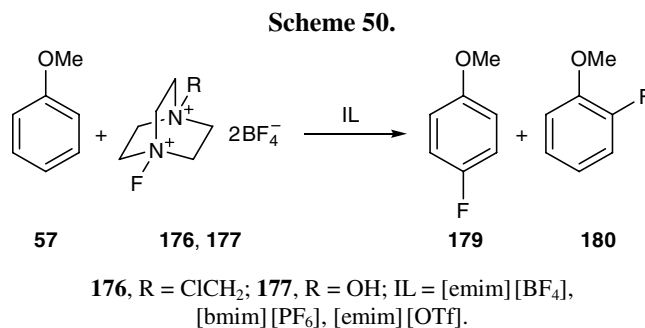
The nature of ionic liquid strongly affects the reaction direction. In the nitration of toluene with HNO_3 in [bmim][OTf] the expected nitrotoluenes **167b** were formed, while in [bmim][X] (X = Cl, Br, I) halogenation of the aromatic ring occurred to give halogen-substituted toluenes **174**, and [bmim][OMs] promoted oxidation of toluene to benzoic acid (**175**) [137] (Scheme 49). Thus, under certain conditions, ionic liquid can act not only as solvent but also as reagent.

3.4. Halogenation

Halogenation of aromatic compounds is an important process in large-scale organic synthesis of drugs [107, 108], pesticides [112], dyes, liquid crystals, photographic materials [109–111], and other compounds [113]. Laali and Borodkin [138] were the first to report on electrophilic fluorination in ionic liquids. Using a broad series of N–F reagents **176–178** and imidazolium ionic liquids, it was shown that the latter are effective in fluorination of various aromatic and heterocyclic compounds (Schemes 50–54).

In all cases, the *ortho/para* isomer ratio in the fluorination of anisole was close to unity. Low selectivity was also observed in the fluorination of dibenzofuran (**195**:**196**:**197** = 19:42:40), whereas *p*-methyl-

and *p*-chloroanisoles gave rise mainly to fluoro derivatives in which the halogen atom was located in the *ortho*-position with respect to the more electron-donor substituent, MeO group (93–95%). The high substrate selectivity both in acetonitrile and in [emim][OTf] ($k_{mesitylene}$:k_{durene} = 6 and 10, respectively) is consistent with the polar fluorination mechanism.
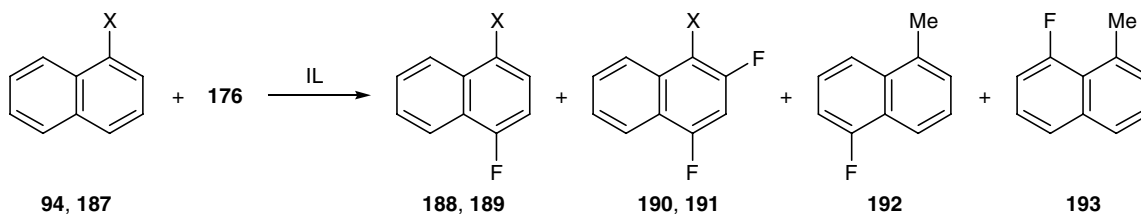
Scheme 50.

176, R = ClCH$_2$; **177**, R = OH; IL = [emim][BF$_4$], [bmim][PF$_6$], [emim][OTf].

Scheme 51.

Scheme 52.

49, **182**, X = Y = Me; **168**, **183**, X = MeO, Y = Me; **181**, **184**, X = MeO, Y = Cl; IL = [emim][BF$_4$], [emim][OTf].

Electrophilic fluorination of indole derivatives in [bmim][Y] ionic liquids occurred predominantly at the nitrogen-containing ring; in the presence of phenylmethanethiol PhCH$_2$SH (**200**), sulfide **201** was formed [139] (Schemes 55, 56).
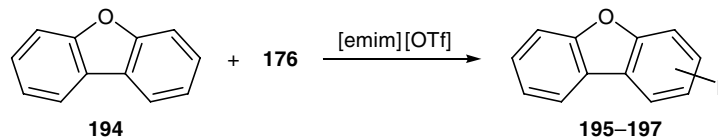
Although 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**176**) is a very effective fluorinating agent for aromatic com-

Scheme 53.

94, **188**, **190**, X = H; **187**, **189**, **191**, X = Me; IL = [bmim][PF$_6$], [emim][OTf].
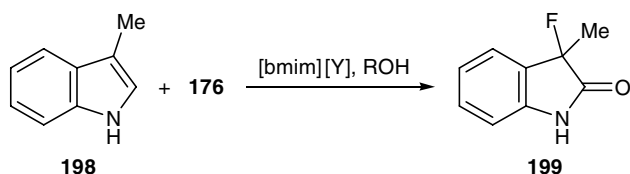
Scheme 54.

195, 1-F; **196**, 2-F; **197**, 3-F.

pounds, reactions in ionic liquids in the presence of iodine result in iodination rather than fluorination [140] (Schemes 57–59). Ionic liquids can act simultaneously as reaction medium and electrophilic halogenating agents toward aromatic compounds [141, 142]. For example, treatment of arenes **57**, **94**, **120**, **142a**, **218**, **223**, and **224** with 3-R-imidazolium tribromides

(R = H, Bu) leads to the formation of the corresponding bromo derivatives **219–222** and **225–230** in high yields [141] (Schemes 60–63). Another ionic liquid, *N*-pentylpyridinium tribromide, can also be used as a reagent for bromination of arenes [142].

Apart from molecular halogens, electrophilic halogenation of aromatic compounds may be effected with *N*-halosuccinimides. The latter are more advantageous, for the reaction releases no hydrogen halide which promotes corrosion. Rajagopal et al. [143] studied bromination of benzene and naphthalene derivatives
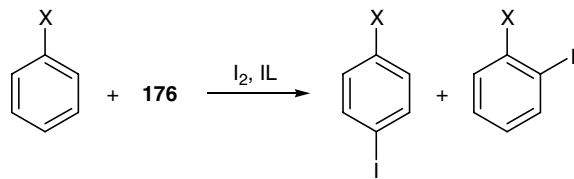
Scheme 55.
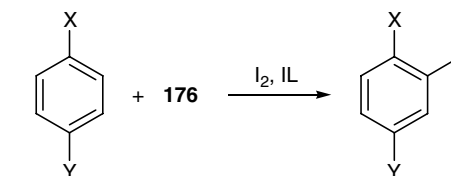

Y = BF$_4$, PF$_6$; R = Me, Et.

Scheme 56.
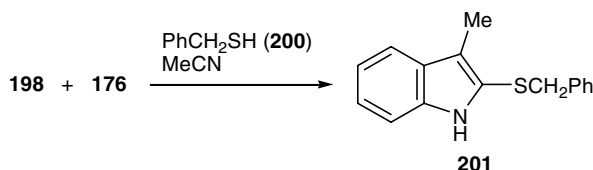
Scheme 57.

92, **203**, **207**, X = Me; **56**, **204**, **208**, X = HO; **57**, **205**, X = MeO; **202**, **206**, X = NH$_2$; IL = [bmim][PF$_6$] or [bpyr][BF$_4$].

Scheme 58.

49, **211**, X = Y = Me; **209**, **212**, X = HO, Y = Me; **210**, **213**, X = HO, Y = NO$_2$; IL = [bmim][PF$_6$] or [bpyr][BF$_4$].

Scheme 59.
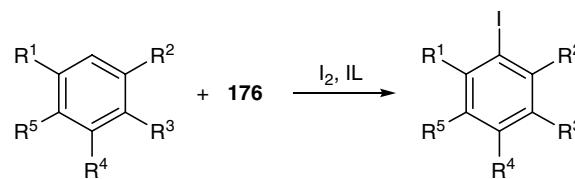
120, **215**, R^1 = R^2 = R^4 = Me, R^3 = R^5 = H; **214**, **216**, R^1 = R^2 = H, R^3 = R^5 = *i*-Pr, R^4 = OH; **142a**, **217**, R^1 = R^2 = R^3 = R^5 = Me, R^4 = H; IL = [bmim][PF$_6$] or [bpyr][BF$_4$].

Scheme 60.
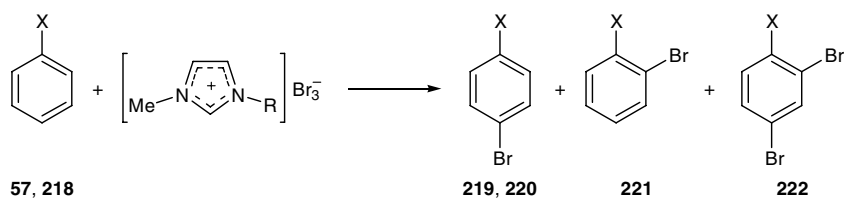
57, 219, X = MeO; **218, 220–222**, X= MeNH; R = H, Bu.

Scheme 61.
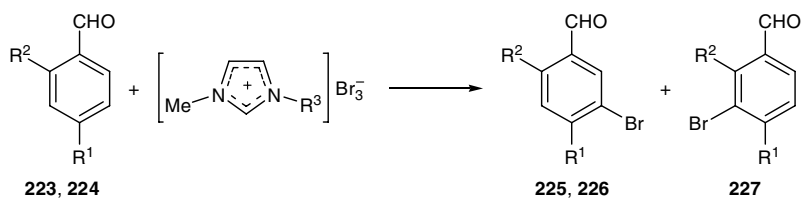
223, 225, 227, R^1 = H, R^2 = Me; **224, 226**, R^1 = MeO, R^2 = H; R^3 = H, Bu.

Scheme 62.
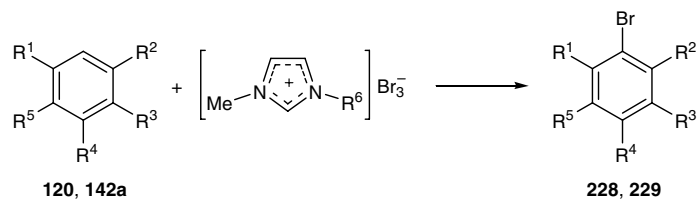
120, 228, R^1 = R^2 = R^4 = Me, R^3 = R^5 = H; **142a, 229**, R^1 = R^2 = R^3 = R^5 = Me, R^4 = H; R^6 = H, Bu.

Scheme 63.
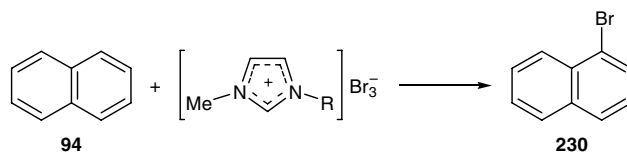
R = H, Bu.

Scheme 64.
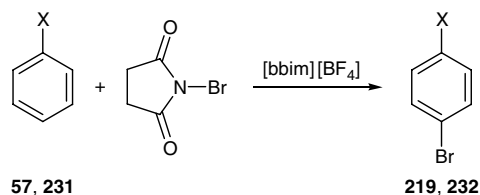
57, 219, X = MeO; **231, 232**, X = MeCONH.

Scheme 65.
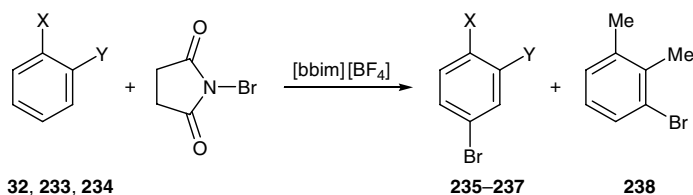
32, 235, 238, X = Y = Me; **233, 236**, X = Y = HO; **234, 237**, X = HO, Y = O$_2$N.

Scheme 66.
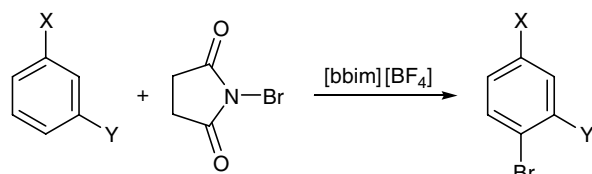
74, **239**, **240**　→　**241–243**

74, **241**, X = Y = Me; **239**, **242**, X = Y = HO;
240, **243**, X = MeO, Y = Me.

Scheme 67.
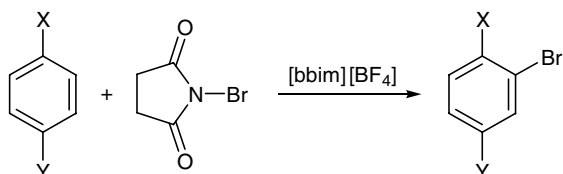
49, **244**　→　**245**, **246**

49, **245**, X = Y = Me; **244**, **246**, X = Y = MeO.

Scheme 68.
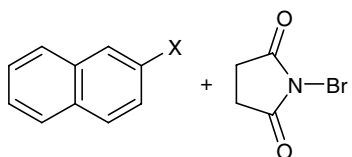
60, **247**
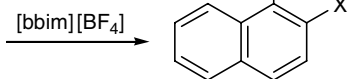
248, **249**

60, **248**, X = MeO; **247**, **249**, X = HO.

Scheme 69.
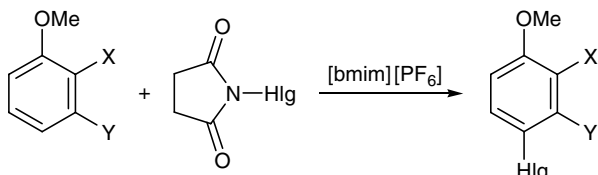
57, **250–252**　→　**181**, **205**, **219**
253–261

57, X = Y = H; **250**, X = MeO, Y = H; **251**, X = Me, Y = MeO; **252**, X = Y = MeO; **181**, X = Y = H, Hlg = Cl; **219**, X = Y = H, Hlg = Br; **205**, X = Y = H, Hlg = I; **253**, X = MeO, Y = H, Hlg = Cl; **254**, X = MeO, Y = H, Hlg = Br; **255**, X = MeO, Y = H, Hlg = I; **256**, X = Me, Y = MeO, Hlg = Cl; **257**, X = Me, Y = MeO, Hlg = Br; **258**, X = Me, Y = MeO, Hlg = I; **259**, X = Y = MeO, Hlg = Cl; **260**, X = Y = MeO, Hlg = Br; **261**, X = Y = MeO, Hlg = I.

Scheme 70.
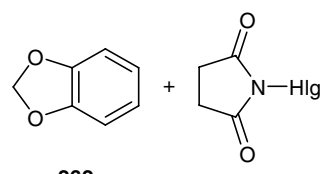
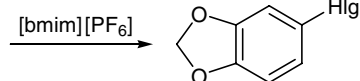
262

263–265

263, Hlg = Cl; **264**, Hlg = Br; **265**, Hlg = I.

Scheme 71.
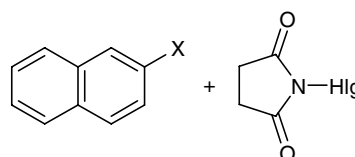
60, **247**, **266**
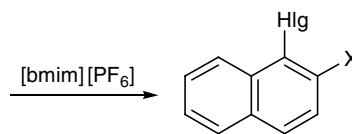
267–273

60, X = MeO; **247**, X = HO; **266**, X = Me; **267**, X = Me, Hlg = Cl; **268**, X = Me, Hlg = Br; **269**, X = Me, Hlg = I; **270**, X = HO, Hlg = Cl; **249**, X = HO, Hlg = Br; **271**, X = HO, Hlg = I; **272**, X = MeO, Hlg = Cl; **248**, X = MeO, Hlg = Br; **273**, X = MeO, Hlg = I.

Scheme 72.
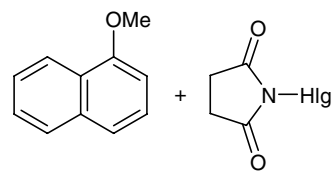
274
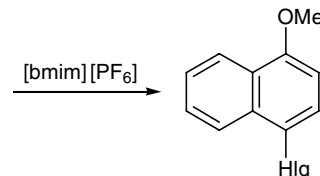
275–277

275, Hlg = Cl; **276**, Hlg = Br; **277**, Hlg = I.

with *N*-bromosuccinimide in 1,3-dibutylimidazolium tetrafluoroborate [bbim][BF$_4$]. In most cases, the reaction was quite selective, and the yields ranged from 80 to 98% (Schemes 64–68). Analogous results were ob-

tained by Yadav et al. [144] who performed halogenation of benzene and naphthalene derivatives with *N*-halosuccinimides (Hlg = Cl, Br, I) in [bmim][PF$_6$] (Schemes 69–72).

3.5. Sulfonation and Sulfenylation

Chloroaluminate ionic liquids were also reported as reaction media and catalysts in electrophilic sulfonation. As shown in [145], the reactions of *p*-toluenesulfonyl chloride (**278**) with benzene (**26**) and its methyl- and chloro-substituted derivatives in the system [bmim][Cl]–AlCl$_3$ gave 83–92% of diaryl sulfones (Schemes 73–76). The isomer ratio strongly depends on the substituents in the benzene ring (**280**:**282** = 34:66, **281**:**283** = 5:95, **284**:**285** = 11:89). Nitrobenzene failed to react under these conditions.

Study on the sulfonation of benzene and toluene showed that the conversion increases as the ratio AlCl$_3$–[bmim][Cl] changes from 0.5 to 0.67. According to the ^{27}Al NMR data, Al$_2$Cl$_7^-$ predominates in the system at N = 0.67; aft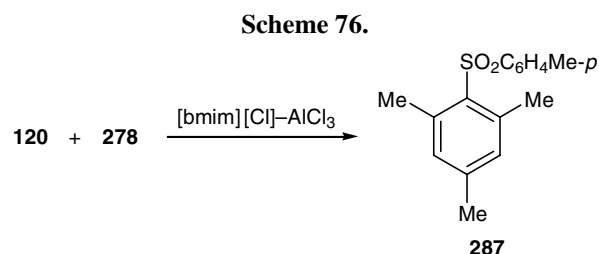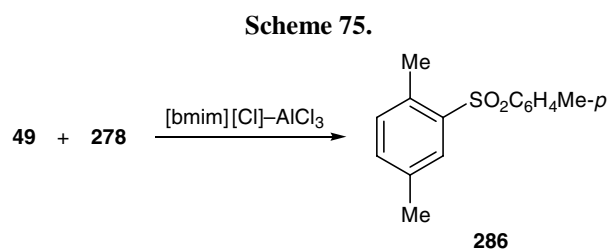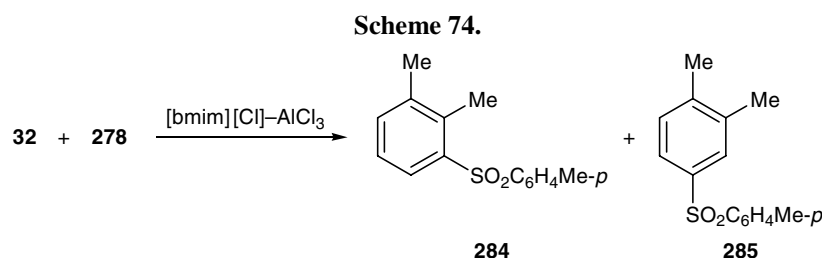er addition of equimolar amounts of *p*-toluenesulfonyl chloride and mesitylene and passing HCl, the major species was AlCl$_4^-$.

Sulfenylation of benzene, naphthalene, and their derivatives was performed with thionyl chloride in the system [bmim][Cl]–AlCl$_3$ (yield 85–96%) [146] (Schemes 77–79). The conversion in the sulfenylation of toluene smoothly increased in parallel with the AlCl$_3$–[bmim][Cl] ratio (N = 0.5–0.67); no reaction occurred at $N \leq 0.5$ even under fairly severe conditions (100°C, 3 h). Chloroaluminate ionic liquid [bmim]·[Cl]–AlCl$_3$ (N = 0.67) showed a high efficiency in the synthesis of aromatic sulfonamides [147].

Scheme 73.

26, **92**, **93**   **278**   **279–281**   **282**, **283**

26, **279**, X = H; **92**, **280**, **282**, X = Me; **93**, **281**, **283**, X = Cl.

Scheme 74.

32 + **278** [bmim][Cl]–AlCl$_3$

284   **285**

Scheme 75.

49 + **278** [bmim][Cl]–AlCl$_3$

286

Scheme 76.

120 + **278** [bmim][Cl]–AlCl$_3$

287
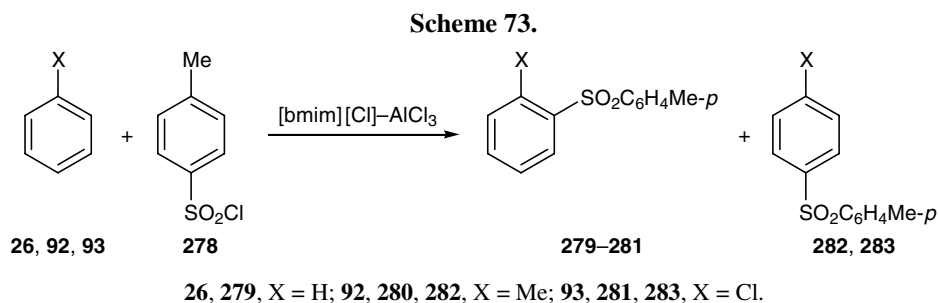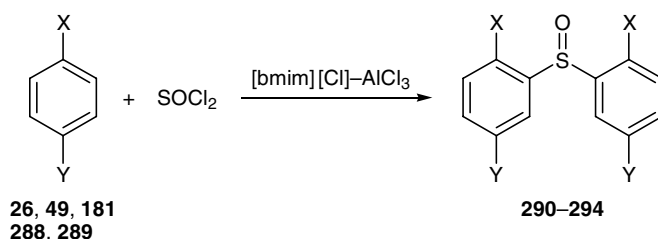
Scheme 77.

26, **290**, X = Y = H; **49**, **291**, X = Y = Me; **289**, **293**, X = Y = Cl; **288**, **292**, Y = Cl, X = Me; **181**, **294**, Y = Cl, X = MeO.

Scheme 78.
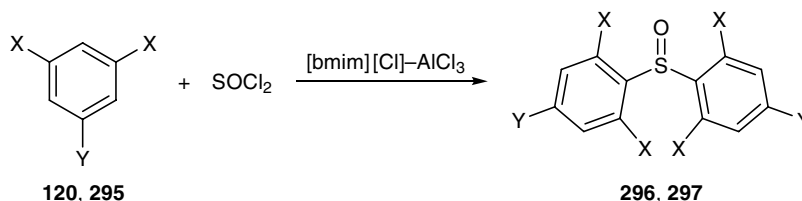
120, **296**, X = Y = Me; **295**, **297**, X = H, Y = Ph.

Scheme 79.

298, X = H; **299**, X = MeO.

3.6. Amination and Related Reactions

Only one publication [148] is available on the amination of arenes in ionic liquids. The amination of methylbenzenes was performed in [bmim][Cl]–AlCl$_3$; as noted above, this chloroaluminate ionic liquid acquires superacidic properties on passing hydrogen chloride. Strongly acidic system is necessary to generate reactive aminating species, NH$_2^+$, from NaN$_3$ as initial reagent (cf. [148–152]) (Scheme 80). The yields of the resulting amines were as follows: from o-xylene, 65% (ratio of 2,3-dimethyl- and 3,4-dimethylanilines 40:60); from m-xylene, 78% (ratio of 2,4-dimethyl-, 2,6-dimethyl-, and 3,5-dimethylanilines 71:24:5); and from mesitylene, 76%.

An analogous chloroaluminate ionic liquid, [BuPy][Cl]–AlCl$_3$ was used to obtain dichloro-(phenyl)phosphine (**306**) from benzene (**26**) and PCl$_3$

Scheme 80.
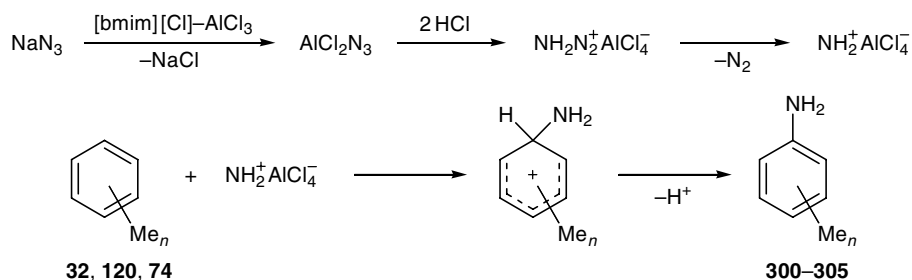
32, Me$_n$ = 1,2-Me$_2$; **74**, Me$_n$ = 1,3-Me$_2$; **120**, Me$_n$ = 1,3,5-Me$_3$; **300**, Me$_n$ = 2,3-Me$_2$; **301**, Me$_n$ = 2,4-Me$_2$; **302**, Me$_n$ = 2,6-Me$_2$; **303**, Me$_n$ = 3,4-Me$_2$; **304**, Me$_n$ = 3,5-Me$_2$; **305**, Me$_n$ = 2,4,6-Me$_3$.
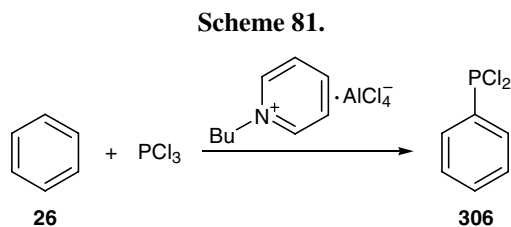
Scheme 81.

[153] (Scheme 81). The system [BuPy][Cl]–AlCl$_3$ is advantageous, for it ensures facile isolation of the product; in the classical version of this reaction, it is necessary to use excess AlCl$_3$ which forms a complex with dichloro(phenyl)phosphine.

4. PROSPECTS IN USING IONIC LIQUIDS IN ELECTROPHILIC PROCESSES

In the recent years, interest in ionic liquids as alternative ecologically benign solvents for both laboratory and large-scale applications increases. Their low volatility makes it possible to reduce or even avoid air pollutions with toxic wastes, and their high polarity ensures higher rates of electrophilic processes, as compared to reactions in conventional solvents. In some cases, electrophilic aromatic substitution reactions performed in ionic liquids are characterized by high selectivity. In this respect, development of processes taking advantage of ionic liquids in combination with solid supports and solid acids attracts specific interest.

Ionic liquids considerably enhance catalytic activity of Lewis acids. An illustrative example is enhancement of the catalytic activity of Sc(OTf)$_3$ in the alkenylation of benzene with 1-phenylprop-1-yne [154]. Under conventional conditions, this reaction is very slow, and the yield is very poor. The use of ionic liquids such as [bmim][PF$_6$] and [bmim][SbF$_6$] sharply increases the reaction rate, and the yield of 1,1-diphenylprop-1-ene attains 90% and more. As noted above, chloroaluminate ionic liquids are superacids which are more convenient to handle with than traditional superacids. Therefore, they can be used simultaneously as reaction medium and powerful acid catalysts in electrophilic reactions; moreover, the acidity of the medium can be controlled by varying the ratio of components of ionic liquids.

The nature of anionic and cationic parts of ionic liquids can strongly affect the reaction direction, and particular components can act as specific reagents. An example is the above discussed reaction of toluene with HNO$_3$ in [bmim][X] (X = OMs, OTf, Hlg), which gives different products (benzoic acid, isomeric nitro-toluenes, or halotoluenes) depending on the anionic component [137].

Despite numerous publications on the application of ionic liquids in chemical practice (more than 2000 articles have been published in the recent years), some aspects and potentials of their use still remain unexplored. In particular, the reason is diversity of ionic liquids. The number of commonly used solvents is quite limited (~600), while estimation of possible number of binary ionic liquids gives a huge value (~10^6), and the number of triple systems approaches 10^{18} [15]. Taking into account the diversity and unique properties of known ionic liquids, their wide potential as new effective and ecologically safe media for performing electrophilic reactions is beyond doubt.

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