Alkylation of naphthalene using three different ionic liquids

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Abstract

It is well known that room temperature ionic liquids (Ils) have the potential for serving as efficient reaction media in the Friedel–Crafts reactions of naphthalene. In this work, three ionic liquid systems prepared with AlCl$_3$ were used as reaction media for the alkylation of naphthalene with different reagents. The following cations were used to prepare the chloroaluminate(III) ionic liquids: 1-butyl-3-methylimidazolium [Bmim]; 8-butyl-1,8-diazabicyclo[5,4,0]-undec-7-enium [bDBU] and 5-butyl-1,5-diazabicyclo[4,3,0]-non-5-enium [bDBN]. Ionic liquid systems are easy to prepare and show interesting catalytic properties. The thermal stability and structural NMR spectra of the ionic liquids were studied. The Ils rendered this reaction green characteristics. The conversions and reaction yields produced by the alkylation reaction of naphthalene with ethyl bromide and isopropyl chloride in the three ionic liquid systems were compared.
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1. Introduction

The majority of organic syntheses carried out in industry are generic reactions, such as oxidation, alkylation, isomerization, sulfonation, nitration, etc. Alkylation, of which the petroleum industry is by far the largest practitioner, is a process that is widely used for the manufacture of a large number of products. Alkylation is frequently carried out in liquid phase at temperatures higher than 200 °C and at above atmospheric pressures [1]. The Friedel–Crafts alkylation of aromatic compounds with alkyl halides, alcohols, alkenes or ethers as alkylating reagents is an important reaction that has been used in the production of pharmaceuticals and fine chemicals for more than a century [2].

Since most conventional industrial processes are performed with volatile and hazardous halogenated solvents, their replacement with ionic liquids could lower the environmental risks involved considerably [3–6]. Room temperature ionic liquids have been increasingly employed as green solvents, since they are easy to recycle, they possess a remarkably high thermal stability and show no effective vapour pressure [7,8], thus providing a way of avoiding the generation of contaminated waste and its subsequent treatment [9,10]. Notable examples of the application of ionic liquids include the use of chloroaluminate(III) ionic liquids in catalyst and solvent combinations for a number of organic Friedel–Crafts [11–13] and related organometallic reactions [14,15]. Ionic liquids such as the (bmim)Cl–AlCl$_3$ system have also been shown to demonstrate catalytic activity in reactions such as Friedel–Crafts acylations, alkylation, the isomerization of alkenes and the alkylation of isobutane with butene [16–19].

Although many Friedel–Crafts reactions have already been performed using ionic liquids, most studies have focused on those derived from imidazole [11,20,21]. In this paper, the preparation of alkylnaphthalenes using a typical ionic liquid [bmim]Cl–AlCl$_3$ and two new ionic liquids[22] [bDBU]Cl–AlCl$_3$ and [bDBN]Cl–AlCl$_3$ as the solvent and Lewis catalyst is described.

The cations used to prepare the chloroaluminate(III) ionic liquids were 1-butyl-3-methylimidazolium [Bmim]; 8-butyl-1,8-diazabicyclo[5,4,0]-undec-7-enium [bDBU] and 5-butyl-1,5-diazabicyclo[4,3,0]-non-5-enium [bDBN] (See Fig. 1).

2. Experimental

2.1. Synthesis of ionic liquids

All the aluminium ionic liquids (Al-IL) were synthesized using the same standard procedures [21,23]. The Al-ionic

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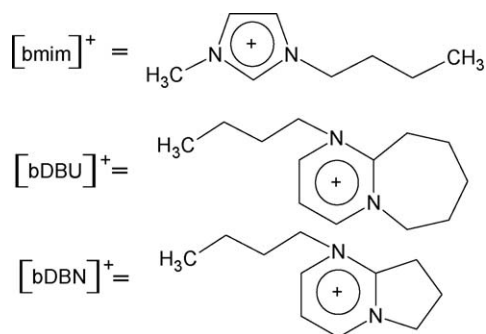*E-mail address:* carlosgb@incar.csic.es (C.G. Blanco).

Fig. 1. Structure of cations used to prepare chloroaluminate(III) ionic liquids.

liquids were prepared by gradually adding the appropriate amount of aluminium chloride to the selected cation. The reaction was subjected to continuous stirring overnight at 0 °C in order to allow the perfect homogenization of the resulting Al-IL. The whole process was kept under an argon atmosphere to avoid the hydrolysis of $AlCl_3$. The proton and carbon shifts (d/ppm, J/Hz), were down field relative to the external $SiMe_4$.

The NMR spectrum for BmimIL ($CDCl_4$, ppm) consists of the following peaks: ^1H NMR dH: 0.86 (t, 3H), 1.28 (s, 2H), 1.80 (q, 2H), 3.90 (s, 3H), 4.13 (t, 2H), 7.32 (m, 2H), 8.56 (s, 1H); ^{13}C NMR dC: 13.76, 19.87, 32.34, 37.29, 50.64, 123.11, 124.42, 135.73.

The NMR spectrum for DBUIL consists of: ^1H NMR dH: 0.97 (t, 3H), 1.36 (s, 2H), 1.63 (q, 2H), 1.76–1.84 (m, 6H), 2.14 (q, 2H), 2.77 (s, 2H), 3.44–3.65 (m, 8H); ^{13}C NMR dC: 14.29, 20.43, 20.67, 23.76, 26.69, 29.08, 31.35, 39.77, 47.97, 49.96, 54.94, 56.21, 167.00.

The NMR spectrum for DBNIL consists of: ^1H NMR dH: 0.95 (t, 3H), 1.32 (s, 2H), 1.63 (q, 2H), 2.15 (q, 2H), 2.24 (q, 2H), 2.98 (t, 2H), 3.33–3.44 (m, 6H), 3.76 (t, 2H); ^{13}C NMR dC: 14.26, 18.69, 19.53, 20.40, 30.12, 31.12, 43.14, 45.26, 54.21, 55.10, 164.50.

The thermogravimetric analyses (TGA) of the sample were performed by heating it from 25 to 600 °C at a rate of 3 °C min^{-1}. The TGA data show that all three ionic liquids were pure and free of any of the starting materials. It was also established that the compounds were thermally stable up to 270 °C.

The imidazolium cations tended to be thermally less stable than the bDBU and bDBN cations. In consequence, the aluminium ionic liquid from bDBU and bDBN was thermally more stable than the imidazolium aluminium ionic liquid. (See Table 1).

Table 1
Thermogravimetric analysis results comparing the T_{onset} (°C) of the cations and the aluminium ionic liquids

	Cation (°C)	Al-IL (°C)
Bmim	274.9	400.6
bDBU	333.8	480.0
bDBN	353.4	497.0

2.2. Alkylation reaction conditions

The reactions were carried out under an inert atmosphere due to the sensitivity of the catalyst towards moisture. All the reactions were performed according to the literature [20]. The solvents were dried in accordance with the standard procedures [14]. The batch reactor consisted of a dry round-bottomed flask (slurry reactor) equipped with a reflux cooler, gas-inlet valve, and sampling exit. The temperature was kept stable at 70 °C by means of a silicon oil bath equipped with a thermostat and a magnetic stirrer. The temperature was measured in the oil bath. The same stirring speed 900 rpm was used for all of the experiments. The catalyst was weighed in the reactor under the reflux of an inert gas and then naphthalene was added. Samples were taken periodically, and distilled water has been used to stop the reaction completely. The ionic liquid action is inhibited in the water phase, and the organic phase, with the soluble compounds, is analyzed by gas chromatography to allow the degree of conversion and reaction yields to be quantified. The reaction products were identified by GC-MS, and by comparing the mass spectra with the library data. For undocumented compounds, a close examination of the mass spectra fragmentations and peak profiles was performed.

2.3. Naphthalene purification

The naphthalene used in these experiments was purified using a technique developed by our group. The starting material was a naphthalene of technical grade [24] (96.5% of purity). The impurities had been previously extracted with acetic acid. The process consisted in mixing the melted naphthalene with the acetic acid, and then cooling it down to room temperature. At this temperature the naphthalene crystallizes to form two phases, a solid phase with the pure naphthalene and a liquid phase which consists of the acetic acid with the extracted impurities. The naphthalene was cleaned with water that swept the acid remains away. The acetic acid can be reutilized after distillation.
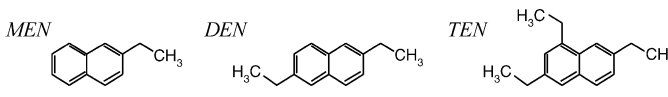
3. Results

The effectiveness of the ionic liquids BmimIL, DBUIL and DBNIL was investigated in alkylation of naphthalene with ethyl bromide and with isopropyl chloride.

3.1. Alkylation with ethyl bromide in different ionic liquid systems

Monoethylnaphthalenes (MEN); diethylnaphthalenes (DEN) and triethylnaphthalenes (TEN) were the main products obtained from the reaction of naphthalene with ethyl bromide. Since the reactivity and the degree of conversion of naphthalene depend on the reaction temperature, an "ideal" reaction temperature must first be established. To determine this temperature, the alkylation of naphthalene with three different ionic liquids was attempted at three different temperatures, 30, 60 and 80 °C. Table 2 shows the variation in conversion efficiency and alkyl derivate compounds yields with temperature and the duration of the reaction when

Table 2

Alkylation reactions at three temperatures with ethylbromide as reagent using BmimIL

MEN   *DEN*   *TEN*

T (°C)	Time	% Conversion	% MEN	% DEN	% TEN
30	1 min	58	83	17	–
	1 h	93	12	61	27
	2 h	94	9	59	32
	3 h	94	8	52	40
	24 h	98	4	39	57
60	1 min	69	49	49	3
	1 h	94	8	35	57
	2 h	95	7	34	59
	3 h	96	6	33	61
	4 h	97	5	32	63
	24 h	98	3	35	62
80	1 min	51	56	39	5
	1 h	96	13	35	52
	2 h	100	7	39	54
	3 h	100	4	51	45
	4 h	100	–	55	45
	24 h	100	–	54	45

Table 3

Conversion and selectivity products for the alkylation of naphthalene with ethylbromide at 70 °C with different ionic liquid systems

MEN   *DEN*   *TEN*

Ionic liquid	Time	% Conversion	% MEN	% DEN	% TEN
BmimIL	1 min	69	49	48	3
	1 h	94	8	35	57
	2 h	93	7	34	59
	3 h	95	6	33	61
	4 h	97	5	32	63
	24 h	98	3	35	62
DBUIL	1 min	65	41	51	8
	1 h	85	9	30	61
	2 h	83	7	28	65
	3 h	93	6	23	71
	4 h	88	5	23	72
	24 h	90	–	24	76
DBNIL	1 min	52	59	41	–
	1 h	80	14	39	47
	2 h	86	14	38	48
	3 h	90	11	37	51
	4 h	73	11	41	48
	24 h	84	6	45	49

the alkylation reactions were carried out in BmimIL at different temperatures.

A high degree of conversion (approx. 93%), was observed independently of the temperature after 1 h of reaction. Furthermore, the conversion increased with increasing temperature and reaction time. As the reaction progressed, the alkyl derivative compounds yields changed with reaction time, most of the MEN becoming DEN and TEN by the end of the reaction. It was thought that at 80 °C, TEN would outnumber DEN. However, the results were not as expected, possibly due to the sublimation of naphthalene at this temperature. As a certain amount of the reactant was in the gas phase, the reaction was carried out in heterogeneous conditions, which resulted in a decrease in reactivity. The same behaviour was found when DBUIL and DBNIL were used as the alkylation reaction media.
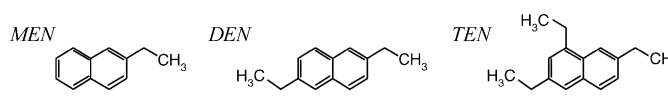
Since the degree of conversion increased with increasing temperature and the reaction at 80 °C was not as effective as expected, the temperature for the alkylation of naphthalene in the different ionic liquids was fixed at 70 °C.

The alkylation of naphthalene using ethyl bromide as reagent was carried out at 70 °C. As can be seen in Table 3, conversion increases with increasing time in all the reactions and for the different ionic liquids used: BmimIL (system [bmim]Cl–AlCl$_3$), DBUIL (system [bDBU]Cl–AlCl$_3$) and DBNIL (system [bDBN]Cl–AlCl$_3$).

Although all the reactions exhibit a high reactive conversion, the BmimIL system shows a higher degree of naphthalene conversion (98%) than the DBUIL and DBNIL systems. The different compound yields from Friedel–Crafts alkylation depend on the reaction time and the ionic liquid used. Hence, the DBUIL system produces more tryethylnaphthalenes (TEN) than other ionic liquids and so is a good method for producing these com-

pounds. By using DBNIL the ratio between the production of diethyl- and triethylnaphthalenes, at the end of the reaction, is greater compared to the reactions carried out in the other systems, DEN being the compound with the highest yield (Table 3).

At the beginning of the reaction, monoethylnaphthalene (MEN) is more abundant and the selectivity is higher when an ionic liquid DBNIL is used as the reaction media (Table 3). Since instantaneous reaction with DBNIL gives major products MEN and DEN, the latter could be separated by distillation, in order to obtain MEN.

3.2. Alkylation with isopropyl chloride in different ionic liquid systems

Table 4 shows the conversions and selectivity products for the three ionic liquid systems used in the alkylation of naphthalene with isopropyl chloride as reagent. Previous studies on the ideal reaction temperature present similar behaviour to the ethyl bromide alkylation. Hence, the working temperature chosen for these experiments was 70 °C.

The main products of the reaction were monoisopropylnaphthalenes (MPrN); diisopropylnaphthalenes (DPrN) and triisopropylnaphthalenes (TPrN). In these reactions the conversion rate of naphthalene is significantly high for all three ionic liquid systems (Table 4). The selectivity for the most substituted naphthalene derivatives (TPrN) is not as remarkably high as in the ethyl bromide reactions. With reaction time MPrN is consumed, giving rise to higher alkyl derivative compounds (DPrN and TPrN). TPrN, which is thermodynamically the most stable of the three, was expected to be the main product. However, the distribution of the product concentrations was different to

Table 4
Conversion and selectivity products for the alkylation of naphthalene with iso-propylchloride at 70 °C with different ionic liquid systems

MPrN: DPrN: TPrN:

Ionic liquid	Time	% Conversion	% MPrN	% DPrN	% TPrN
BmimIL	1 min	65	23	29	48
	1 h	82	53	33	14
	2 h	84	54	35	11
	3 h	88	51	40	9
	4 h	89	47	41	12
	24 h	89	46	44	10
DBUIL	1 min	67	43	26	31
	1 h	82	45	37	18
	2 h	83	44	40	16
	3 h	85	35	45	20
	4 h	87	35	45	20
	24 h	85	33	46	21
DBNIL	1 min	67	41	25	34
	1 h	83	51	43	6
	2 h	83	53	40	7
	3 h	86	45	47	7
	4 h	90	34	52	13
	24 h	90	40	45	15

what was expected, MPrN being the main product followed by DPrN. The formation of TPrN may have been inhibited by steric hindrances.

The highest reactivity was achieved with the ionic liquid DBUIL system, as it generated the highest concentration of TPrN (21%), although the highest degree of naphthalene conversion was obtained with DBNIL (90%).

4. Conclusion

The preparation of different aluminium ionic liquid systems is feasible and quick. The ethylation of naphthalene using three ionic liquid systems was carried out at a high naphthalene conversion rate, compared to the traditional reaction that involves Lewis acids. The reaction and extraction of the products were performed without any difficulty. The results show that the Friedel–Crafts reactions of naphthalene using ionic liquids as catalysts can be achieved with a high degree of conversion and a good yield. By selecting the appropriate ionic liquid system and alkylation agent and by varying the temperature and the duration of the reaction, it is possible to develop different reactions with the aim of obtaining specific naphthalene derivatives, thereby opening up new perspectives in the field of naphthalene derivatives.

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