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3-Hydroxypropylammonium acetate (HPAA) ionic liquid: An effective acidic media in efficient conversion of anilines into aryl isocyanates

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ABSTRACT

A simple and mild procedure for the conversion of anilines into aryl isocyanates is described using 3-hydroxypropylammonium acetate (HPAA) ionic liquid as a novel and efficient media has been explored in the synthesis of aryl isocyanates from the reaction of substituted urea with sodium nitrite in a water immiscible solvent. This ionic liquid can be easily recovered and reused for several times without noticeable loss of activity.

***Keywords**: 3-Hydroxypropylammonium acetate, HPAA, Isocyanates, Ionic liquid, Aniline.*

1. Introduction

Isocyanates are versatile synthetic precursors used in various organic reactions such as nucleophilic additions with alcohols and amines, Diels-Alder cycloaddition reactions, and reactions with bifunctional compounds to produce a wide range of products including carbamates, polyurethanes, and heterocyclic compounds [1-2]. In addition, several important isocyanates [3] are produced as commercially important intermediates [4] used in the manufacture of thermoplastic foams, elastomers, adhesives, synthetic surface coatings, polyurethanes, agrochemicals, and herbicides [3,5]. Among the isocyanates used in polymer industry, the compounds including methylene 4,4-diphenyl diisocyanide (MDI) and 2,4-toluene diisocyanate (TDI) are important examples which are employed as starting materials in the synthesis of polyurethanes [3, 6-7]. Additionally, aromatic isocyanates such as phenyl isocyanate (PIC) and 3,4-dichlorophenyl isocyanate have often been used as key intermediates in the synthesis of specialty chemicals; their carbamate derivatives are engaged in the synthesis of various pesticides [8-13].

In 1849, Wurtz reported the synthesis of the first isocyantes from the reaction of organic sulphates with potassium cyanate [14]. Owing to their important biological activities and industrial applications, several approaches have been developed for the synthesis of isocyanates [15]. The most common synthetic approaches to isocyanates involve: (i) reaction of amines with phosgene [16], or its equivalents, e.g. diphosgene (trichloromethyl chloroformate) [17], and triphosgene [bis(trichloromethyl) carbonate] [18], (ii) thermal dissociation of carbamic acids using chloroformates [19], carbamates [20], or *N,N'*-carbonyldiimidazole [21], (iii) rearrangement of acyl azides using non-amine precursors (Curtius Rearrangement) [22-23] and hydroxamic acids (Lossen Rearrangement) [24-25]. Phenyl isocyanate has also been generated from aniline using oxalyl chloride which is extremely hazardous and prolonged exposure to the substance can cause target organs damage [26]. To eliminate the use of hazardous reagents such as phosgene, several other strategies have been developed including reductive [27], and oxidative carbonylation [28] using carbon monoxide as carbonyl source, and employing transition metal-based catalysts [29-39]. However, in oxidative carbonylation, the use of carbon monoxide is practically hampered by its poisonous and potentially explosive nature upon mixing with oxygen [40]. Moreover, the reactions of alcohols, thiols, and trimethylsilyl ethers with 2,4,6-trichloro[1,3,5] triazine/*n*-Bu_4NOCN [41], and the reactions of alkyl or aryl amines with di-*tert*-butyl dicarbonate, $(Boc)_2O$, in the presence of catalytic amount of 4-(dimethylamino) pyridine (DMAP) have led to the generation of sterically hindered alkyl and aryl isocyanates avoiding

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the use of phosgene [42]. However, many of the reported methods are subject to various drawbacks including the use of large amounts of dehydrating agents such as PCl_5, $POCl_3$, and extremely toxic and/or inflammable reagents like phosgene, oxalylchloride, trichloro[1,3,5]triazine, triphosgene, or relatively expensive catalysts such as $Pd(Py)_2Cl_2$, $PdCl_2$.

In recent years, much attention has been focused on the use of ionic liquids (ILs) in green synthetic organic reactions as promising non-aqueous solvents, phase transfer agents, or catalysts in various organic transformations [43]. The ionic liquids are made of positively and negatively charged ions which are immiscible with most of the organic solvents. Thus, these liquids can provide non-aqueous and polar alternative media for two-phase systems [44]. The green character of ionic liquids stems from their negligible vapor pressure and toxicity as claimed by many scientists in chemical literature [45]. In order to benefit the merits of ionic liquids in our research, we were encouraged, in continuation of the present work, to synthesize the aryl isocyanates from the reaction of substituted urea with sodium nitrite promoted by 3-hydroxypropylammonium acetate (HPAA), $[HOCH_2CH_2CH_2NH_3^+][AcO^-]$, as a new ionic liquid media (Scheme 1). The reactions proceeded smoothly at 0 ºC within 15-45 minutes to furnish the respective products with excellent yields. Also, this ionic liquid can be efficiently recycled and reused in several fresh runs without noticeable loss of activity.

The present protocol offers a simple and benign procedure for the synthesis of aryl isocyanates in high yields with eliminating phosgene or any other toxic materials used in previously reported methods. Therefore, this approach can be considered as a convenient alternative to phosgene-based methods for the synthesis of aryl isocyanates. The advantages allocated to this procedure are: cleaner reaction, easier workup, reduced reaction times, high yields and eco-friendly.

2. Experimental

2.1. General

F Solvents, reagents, and chemical materials were obtained from Aldrich and Merck chemical companies and purified prior to use. Nuclear magnetic resonance spectra were recorded on a JEOL FX 90Q spectrometer using tetramethylsilane (TMS) as internal standard. Infrared spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer (KBr pellets).

2.2. Preparation of the Task-Specific Ionic Liquid (HPAA)

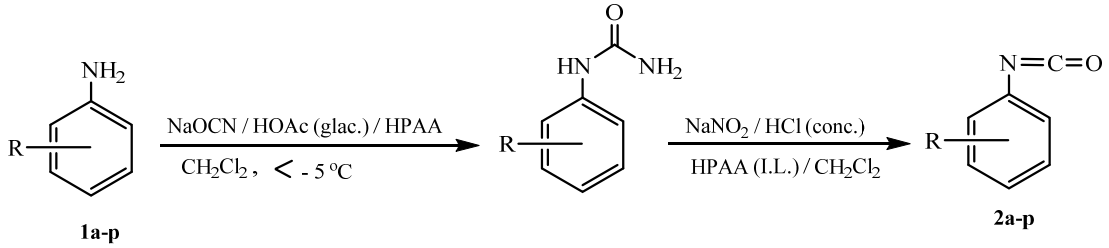
The ionic liquid HPAA was synthesized following the reported procedure [46]. In a 250 mL three-necked flask containing ethanol (25 mL), was added 3-aminopropan-1-ol (3.79 ml, 50 mmol). To the resulting solution was added dropwise with stirring a solution of glacial acetic acid (3 ml, 50 mmol) in 25 ml of ethanol at room temperature during 60 min, and the resulting mixture was allowed to stir at room temperature for 24 h. Then, ethanol was removed to leave an oily residue which was dried under reduced pressure at 50 °C for 48 h to provide $[HO(CH_2)_3NH_3^+]$ $[CH_3COO^-]$ as a colorless and viscous liquid.

2.3. General procedure for the preparation of aryl-substituted urea

The aryl-substituted urea derivatives were synthesized from respective anilines according to the literature [47]. In a 100 mL flask charged with arylamine (10 mmol) was added a mixture of glacial acetic acid (10 mL) and distilled water (20 mL). To the resulting solution was added a solution of sodium cyanate (0.65 g, 10 mmol) in warm water (50 mL) with stirring. The resulting reaction mixture was allowed to stand for 30 min and then cooled in iced water. The white crystals formed were filtered, dried and recrystallized from hot water to yield the respective aryl-substituted ureas in 95-99% yields.

2.4. Typical procedure for the preparation of aryl isocyanates using 3-hydroxypropylammonium acetate ionic liquid

To a mixture of concentrated hydrochloric acid (37%) (2 mL) and 6 drops of 3-hydroxypropylammonium acetate (0.12 g, 0.9 mmol) in CH_2Cl_2 (10 mL), were added phenyl urea (0.136 g, 1 mmol) and a solution of sodium nitrite (0.138 g, 2 mmol) in water (1 mL) below -5 ºC. The resulting mixture was stirred for an appropriate time (Table 1), and then left to separate



Scheme 1. 3-Hydroxypropylammonium acetate-promoted conversion of anilines into aryl cynates.

into the layers. The organic layer was separated from the aqueous layer and filtered to separate the solid materials. The organic filtrate was dried over anhydrous sodium sulfate, filtered and the filtrate was evaporated under reduced pressure to afford the pure phenyl isocyanate in 91% yield. To recover and reuse the ionic liquid, the isolated aqueous layer was filtered and evaporated under reduced pressure. Other aryl isocyanates were synthesized following the same procedure. All the products were characterized on the basis of their physical and spectral (FT-IR, ^{1}H NMR, and ^{13}C NMR) data that were consistent with those reported [16-26]. Some selected spectral data are given below.

Selected spectral data

(Entry d, Table 1):

Oil. IR (KBr): $\bar{\nu}$= 3064, 2240, 1501, 1384, 1098 cm^{-1}. ^{1}HNMR (90 MHz, $CDCl_3$): δ= 3.69 (s, 3 H), 6.79-7.18 (m, 4 H) ppm. ^{13}CNMR (22.5 MHz, $CDCl_3$): δ= 55.5, 114.8, 125.16, 125.9, 157.4 ppm.

(Entry e, Table 1):

Oil. IR (KBr): $\bar{\nu}$= 3062, 2249, 1709, 1579, 809 cm^{-1}. ^{1}HNMR (90 MHz, $CDCl_3$): δ= 2.32 (s, 3 H), 7.08-7.48 (m, 4 H) ppm. ^{13}CNMR (22.5 MHz, $CDCl_3$): δ= 125.9, 129.7, 131.1, 132.0 ppm.

(Entry g, Table 1):

Oil. IR (KBr): $\bar{\nu}$= 2267, 1627, 1548, 1091, 827 cm^{-1}. ^{1}HNMR (90 MHz, $CDCl_3$): δ= 6.97-7.25 (m, 4 H) ppm. ^{13}CNMR (22.5 MHz, $CDCl_3$): δ= 22.4, 125.6, 130.2, 134.9 ppm.

3. Results and Discussion

To make a contribution towards the elimination of the aforementioned drawbacks in the synthesis of aryl isocyanates, herein, we are encouraged to report the simple and environmentally benign procedure for the conversion of aryl amines **1a-p** into corresponding aryl isocyanates **2a-p** (Scheme 1). In this procedure, the anilines are converted into respective ureas with sodium cyanate and glacial acetic acid, followed by reaction with nitrous acid promoted by 3-hydroxypropylammonium acetate (HPAA) as an ionic liquid. The reaction was conducted smoothly under mild conditions and reduced reaction times (15-45 min) to afford the products in high yields (65-92%, Table 1).

As shown in Table 1, the rate of reaction with the aryl ureas bearing electron-releasing groups at *ortho* and/or *para* positions appears higher than the reaction rate for the aryl ureas carrying electron-withdrawing groups. This implies that the release of N_2 molecule in the second step of the reaction occurs more readily in the former case. However, using this method, the anilines substituted with strong withdrawing groups such as NO_2 group located at *ortho, meta* or *para* positions (entries b, c and n) failed to produce their intermediate ureas and, as a result, no conversion to the expected isocyanates was noticed. In addition, the reaction with heteroaryl amines such as 2-aminopyridine or 2-aminothiazole is believed to involve the isocyanate intermediates which actively undergo rapid dimerization and trimerization [48-50] with no detectable formation of the expected isocyanates (entries m and n). Likewise, this approach proved to be unsuccessful in attempted reactions with the aliphatic amines such as benzylamine and ethylamine (entries o and p) possibly due to their insufficient reactivity to produce the respective substituted ureas.

It is interesting to know that, this method eliminates the phosgene or any other toxic materials used in previously reported methods. Also, the low melting point of HPPA ionic liquid (-88 °C) used as a promoter in the present reactions allowed the conversions to occur at low temperature. Commercially inexpensive and easily prepared HPPA combined with its easy separation from the reaction mixture and its potent reusability have made it to be considered as a useful ionic liquid media for the conversion of anilines into isocyanates under mild conditions with high yields.

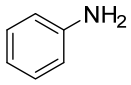
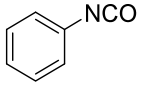
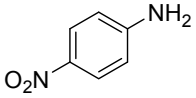
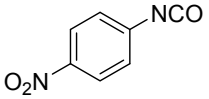
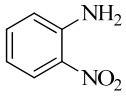
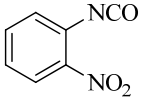
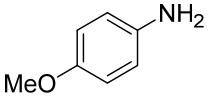
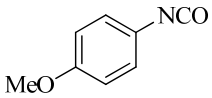
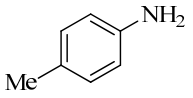
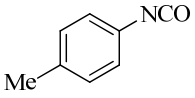
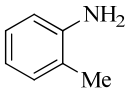
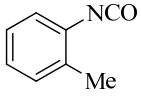
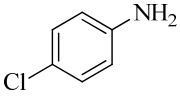
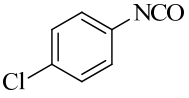
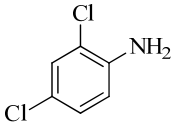
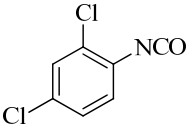
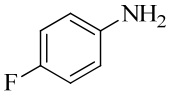
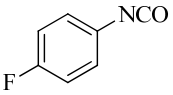
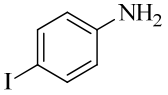
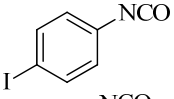
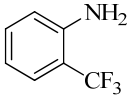
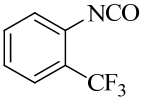
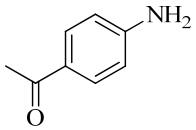
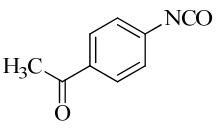
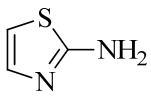
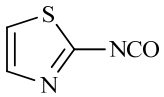
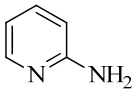
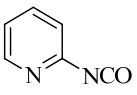
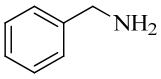
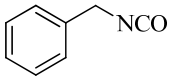
To study the effect of solvent on the reaction, several solvents including H_2O, MeCN, $HCCl_3$, and CH_2Cl_2 were examined in the model conversion of aniline into respective isocyanate under identical conditions. The use of water or acetonitrile as solvents resulted in large amounts of by-products including mainly phenol, and the corresponding phenyl isocyanate was obtained in very low yield. Among the solvents tested, dichloromethane provided the best result in terms of the yield and reaction time. As shown in Table 2, satisfactory results were obtained using concentrated HCl in HPAA/CH_2Cl_2 for this method (entry 5).

Formation of the products was confirmed by the appearance of a signal at about 125 ppm assigned to the N=C=O group in their ^{13}C-NMR spectra, and also by the absence of the signals for NH_2 group in their ^{1}H-NMR and IR spectra at about 6 ppm and 3300-3400 cm^{-1} respectively which are present in the spectra of the starting anilines.

4. Conclusions

In summary, a simple and efficient approach was developed for non-phosgene direct synthesis of aryl isocyanates. The reactions were promoted by 3-hydroxypropylammonium acetate (HPAA) as a new and hitherto unreported ionic liquid in the titled reactions. Simple procedure, mild reaction conditions, short reaction times and high yields, commercial availability and reusability of HPAA, and elimination of harmful chemicals such as phosgene or oxalyl chloride in the reaction are the main advantages of the present protocol.

Table 1. Conversion of anilines **1a-p** into respective isocyanates **2a-p** with sodium cyanate in glacial HOAc followed by reaction with $NaNO_2$/HCl (conc.) (37%) in the presence of HPPA.[a]

Entry	Substrate **1**	Product **2**	Time (min)	Yield (%)[b]	m.p. (°C)		Ref.
					Found	Reported	
a			20	91	Oil	Oil	[20]
b			240	trace	-	-	
c			240	trace	-	-	
d			20	89	Oil	Oil	[51]
e			15	89	Oil	Oil	[52]
f			20	85	Oil	Oil	[53]
g			20	90	Oil	Oil	[51]
h			30	88	61-63	62	[56]
i			25	75	Oil	Oil	[54]
j			15	92	45-47	48	[55]
k			45	65	Oil	Oil	[54]
l			30	89	Oil	Oil	[52]
m			120	-	-	-	
n			120	-	-	-	
o			240	-	-	-	
p			240	-	-	-	

[a]Conditions: phenyl urea (1 mmol), $NaNO_2$ (2 mmol), 37% HCl (2 mL), HPPA (0.9 mmol), CH_2Cl_2, < -5 °C temperature.
[b]Isolated yield.

Table 2. Optimization of the model conversion of aniline into phenyl isocyanate.

Entry	condition	Time (min)	Yield (%)
1	$NaNO_2$/HCl (conc.)/no I.L /CH_2Cl_2	180	0
2	$NaNO_2$/HCl (conc.)/HPAA/H_2O	60	Trace
3	$NaNO_2$/HCl (conc.)/HPAA/CH_3CN	60	Trace
4	$NaNO_2$/HCl (conc.)/HPAA/$CHCl_3$	60	35
5	$NaNO_2$/HCl (conc.)/HPAA/CH_2Cl_2	20	98

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