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Isothiouronium salts as useful and odorless intermediates for the synthesis of thiaalkylimidazolium ionic liquids

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ABSTRACT

A simple and odorless route for the synthesis of monocationic and dicationic thiaalkylimidazolium ionic liquids (ILs) is reported. Our approach starts with the selective monoalkylation of dihalogenated substrates by methylimidazole derivatives, followed by the synthesis of odorless isothiouronium salts *via* reaction with thiourea. The target ILs are obtained after sequential hydrolysis-alkylation of the isothiouronium salts followed by anion metathesis in water. After extraction, the novel thiaalkylimidazolium ILs are obtained with high purity, without the requirement of additional purification steps. In order to demonstrate their applicability, two of these task-specific ILs were employed as ligands in Ullmann and Suzuki couplings and also as charged probes to detect copper intermediates *via* ESI(+)-MS.

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Imidazolium-based ionic liquids (ILs) are among the most studied media for organic and inorganic reactions.¹ The facile modulation of the physical-chemical properties either by anion exchange or alkyl chain transformations has allowed a huge growth in the applications of these ionic fluids.² These compounds are widely applied for a plethora of purposes, as media for homogeneous and nanoparticle catalysis,³⁻⁶ CO₂ capture,⁷ electrochemistry.⁸ Moreover, these features in combination with their very low vapor pressure, non-flammability and recyclability render these materials ideal media for green chemistry transformations.⁹

In recent years, the development of task-specific ILs has been reported.¹⁰⁻¹² These compounds can be used as task specific acidic¹³ and basic¹⁴ ILs, ionophilic ligands and/or reaction media for various catalytic transformations, including cross-coupling reactions,^{15, 16} oxidation reactions,¹⁷ olefin metathesis,^{18, 19} and hydrogenation reactions.^{20, 21} They also allow the detection of catalytic intermediates *via* electrospray ionization mass spectrometry (ESI-MS) experiments.²² Besides their applications in homogeneous catalysis, N-, O-, P- and S-substituted imidazolium ILs have also been employed to modulate the stability and the reactivity of metallic nanoparticles.²³

In particular, thiaalkylimidazolium ILs have been applied in the extraction of heavy metal cations from water,²⁴ in electrochemical studies,²⁵ as recyclable and odorless Swern reagents²⁶ and as ligands for transition-metal complexes.²⁷ However, the synthesis of these compounds has some drawbacks, mainly related to the limited synthetic routes for their production and the toxicity and

odor of the synthetic intermediates, thiols or haloalkylsulfides (Scheme 1).^{24, 25, 28} Taking into account these drawbacks, herein we describe a simple and odorless route to produce various monocationic and dicationic thiaalkylimidazolium ILs. Our approach is based on the selective monoalkylation of dihalogenated substrates (1,2-dibromoethane and 1,3-dibromopropane) by methylimidazole derivatives followed by the synthesis of odorless isothiouronium salts. These sulfur-based salts can be hydrolyzed and alkylated *in situ*, furnishing the corresponding thiaalkylimidazolium salts. Finally, after *in situ* anion metathesis and extraction, the target ILs can be obtained with reasonable to high yields and high purity, without additional purification steps.

Scheme 1. Strategies used to synthesize thiaalkylimidazolium ILs: this work *versus* the literature.

After preparation, in order to illustrate the applicability of these compounds, the thiaalkylimidazolium ILs were applied as ligands in Ullmann and Suzuki coupling reactions.

Results and Discussion

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In our approach to prepare the thiaalkylimidazolium ILs, initially 1-methylimidazole or 1,2-dimethylimidazole were reacted with 1,2-dibromoethane or 1,3-dibromopropane in order to obtain the monoalkylated products. Selective monoalkylation was only achieved using specific conditions for each imidazolium/alkyl bromide pair (Scheme 2).



Scheme 2. Synthetic procedure for the preparation of bromo-substituted imidazolium salts **1a-c**.

In order to convert the brominated imidazolium salts into isothiouronium imidazolium salts **2**, intermediates **1** were reacted with thiourea in ethanol at reflux. Under these conditions, compounds **2a-c** were obtained in 65-81% yield (Scheme 3). It is noteworthy that the isothiouronium salts are odorless compounds and the work-up is very simple, since the addition of diethyl ether to the reaction mixture induces product crystallization.



Scheme 3. Synthesis of isothiuronium imidazolium salts 2a-c.

For the synthesis of the desired thiaalkylimidazolium ILs, sequential hydrolysis-alkylation reactions were performed in water followed by in situ anion metathesis. With respect to dicationic ILs (Scheme 4), initially, 2a-c were heated at reflux with KOH in water for 15 minutes. Afterwards, 1,2-dibromoethane, bis(2-chloroethyl)ammonium 1,3-dibromopropane or hydrochloride were added and the mixture was heated at reflux for an additional 15 minutes. For ILs 3a-c, the final solution was adjusted to pH = 6 and the water was evaporated before extraction of the ILs with methanol. For ILs 4a-c, 5b, 6b and 7b, LiNTf₂ (or KPF₆ for IL **5a**) was added to the reaction mixture and the ILs were extracted from water with ethyl acetate, affording the thiaalkylimidazolium ILs in 69-99% yield. Regarding the monocationic ILs (Scheme 5), after hydrolysis, monoalkylation and anion exchange afforded compounds 8b and 9b in 74% and 52% yield, respectively, after direct extraction.



Scheme 5. Isothiouronium salts as intermediates in the synthesis of monocationic thiaalkylimidazolium ILs.

In terms of physical-chemical properties, ILs **3a-c** are highly hygroscopic, due the nature of bromine anion and also the NH group in the center of the structure, which enables hydrogen bonding between water and the ILs. The NH group also induces the hygroscopicity in ILs with anions such as NTf_2^- , a classical anion of hydrophobic ILs.

Differential scanning calorimetry (DSC) analysis was performed to determine the influence of the ILs structure on their thermal behavior. The anion influence is observed when **4a** (NTf₂⁻) and **5a** (PF₆⁻) are compared, where the PF₆⁻ anion confers a lower T_m value to the IL than NTf₂⁻. The influence of a substituent at the C2 position of the imidazolium ring was also evaluated by comparing **4a** (H) and **4b** (CH₃), where compound **4b** has a lower

 $T_{\rm m}$ temperature. This behavior can be regarded as being due to the methyl group, which hampers the formation of H-bonds between the cations and anions of the IL. The influence of chain length **4a** (2C) and **4c** (3C) cannot be verified because the $T_{\rm m}$ and $T_{\rm f}$ for **4c** were not obtained from DSC analysis.

ILs **4a-c** are liquids at room temperature, while **5a** exhibit wax aspect at the same temperature. As shown in Table 1, ILs **4a** and **5a** have a T_m above 100 °C, although they are liquid and wax respectively at room temperature even after being dried at 100 °C under vacuum for several hours. This can be explained by the hygroscopicity of these ILs because of strong H-bonds involving water and both the NH of the side chain and the C2H on the imidazolium ring. This behavior allows the confinement of water

2

molecules that are trapped inside the ionic network constituted of contact ion pairs on the IL and hampers the removal of water even under vacuum.²⁹ The T_m for IL **4b** is lower than the T_m for **4a** and 5a due to the absence of H-bonds since the C2 position of the imidazolium ring of 4b is protected by a CH₃ substituent. Thermogravimetric analysis (TGA) of the ILs were performed in order to determine the thermal stability of the compounds (Table 1). As depicted in Table 1, the thermal stability was $6b \ge 4c > 4b$ > 7b > 4a > 8b > 5a. In general, monocationic ILs displayed lower Tonset than dicationic ones. This result is in agreement with the literature since the observed higher thermal stability of dicationic ILs is attributed to the greater charge and intermolecular interactions, their higher molecular weight, higher density, smaller free volume and higher shear viscosity.³⁰ The reversibility of the breakdown reactions allows recombination of the fragments which do not move away due to this "cage effect".

Table 1. Thermal properties	of ILs obtained by DSC and TGA
-----------------------------	--------------------------------

4a286133.5168.55a268124.24b30589.653.74c340n.o.n.o.7b2896b3508b $<$ 300	LI	Tonset (°C) ^a	T _f (°C) ^b	T _m (°C) ^b
5a268124.2 $4b$ 30589.653.7 $4c$ 340n.o.n.o. $7b$ 289 $6b$ 350 $8b$ < 300	4 a	286	133.5	168.5
4b 305 89.6 53.7 4c 340 n.o. n.o. 7b 289 - - 6b 350 - - 8b < 300 - -	5a	268		124.2
4c 340 n.o. n.o. 7b 289 - - 6b 350 - - 8b <300	4 b	305	89.6	53.7
7b 289 - - 6b 350 - - 8b <300 - -	4 c	340	n.o.	n.o.
6b 350 8b <300	7b	289	-	-
8h <300	6b	350	-	-
00 000	8b	<300	-	-

^aTGA; ^bDSC; n.o. = not observed.

In order to evaluate the potential applicability of these thiaalkylimidazolium ILs, selected compounds were applied as ionophilic ligands for stabilizing the active species in coppercatalyzed Ullmann C-O coupling and as charged probes to detect copper intermediates in the same reaction. The coupling between 4-bromoacetophenone and 4-*tert*-butylphenol in the presence of CuI and ligand **8b** were used as a model (Table 2). Initially, conditions screening was performed and reasonable results were attained using Cs₂CO₃ in toluene at 100 °C (Entry 3). Excellent conversion and selectivity were observed with ligand **6b** (Entry 5, Table 2), while low conversion was attained without the ligand (Entry 6, Table 2). Therefore, the presence of an IL as ligand provides a significant positive effect on the catalytic process.

 Table 2. Coupling reaction between 4-bromoacetophenone and 4-tertbutylphenol in the presence of CuI employing thiaalkylimidazolium ILs as ligands

Br	+ [Base gand plvent		
Entry	Ligand	Base	Solvent	Conv.	Sel. ^a
				(%)	(%)
1	8b	K ₃ PO ₄	Dioxane	10	>99
2	8h	V.DO	Toluono	21	>00

-	0.0	11)1 04	1010010	01	
3	8b	Cs_2CO_3	Toluene	64	>99
4 ^b	8b	Cs_2CO_3	Toluene	71	94
5	6b	Cs_2CO_3	Toluene	90	>99
6	-	Cs_2CO_3	Toluene	11	>99
Reagents	and condition	s: 4-bromo	acetophenone	(0.5 mm	ol), 4-tert
1 / 1 1	1 (0 (1) 1	(1 1	1. 1. 1.(10	10() C I	(1.0 10/)

butylphenol (0.6 mmol), base (1 mmol), ligand (10 mol%), CuI (10 mol%), solvent (2 mL), 100 °C, 24 h. Conversion and selectivity determined by GC. "By-products: homocoupling and aryl halide reduction. ^bReaction performed at 125 °C in a resealable Schlenk tube.

A reaction under the optimized conditions (Entry 5, Table 2) was monitored by ESI-MS experiments in positive mode for the detection of intermediates with ligand **6b** as an ionophilic probe. First, the solution of CuI and ligand **6b** was analyzed and the free ligand with one counter-anion unity (m/z = 621), the doubly charged free ligand (m/z = 170) and the ligand coordinated at the Cu metal center (m/z = 964) were detected (ESI, Fig. S31). Continuing the experiment, the base, 4-bromoacetophenone and *tert*-butylphenol were added and the solution was analyzed by ESI-

MS after two hours (ESI, Fig. S32). One peak was observed related to a structure with the characteristic isotope distribution of a copper species (m/z = 340). This peak was attributed to the copper-nucleophile species [Cu(**6b**)OAr]⁺I⁻, which has a double positive charge due to the ionophilic probe. Copper-nucleophile species have been reported as being capable of reacting with aryl halides under mild conditions.³¹⁻³⁷ This finding suggests that the formation of copper-nucleophilic species precedes activation of the aryl halide, as observed in the literature.³⁸

Taking into account that various organosulfur ligands have been synthesized and applied in Suzuki cross-coupling reactions³⁹ with advantages (thermal stability and air/moisture insensitivity) over classic phosphines or *N*-heterocyclic carbenes (NHCs), the applicability of the thiaalkylimidazolium ILs was extended to the Suzuki reaction. Initially, the Pd precursor [PdCl₂(**6b**)] was prepared by reacting PdCl₂ with LiCl to generate the [PdCl₄]²⁻ anion, and then the dicationic ligand was added to form the desired complex (ESI, Fig. S34). The [PdCl₂(**6b**)] complex was applied as the catalyst precursor to promote the C-C coupling between bromotoluene and phenylboronic acid (Table 3).

Table 3. Suzuki coupling reaction between 4-bromotoluene and phenylboror	nic
acid promoted by [PdCl ₂ (6b)] as the catalyst precursor	

B(OH) ₂ [PdCl ₂ (6b)] Base Solvent					
Entry	Solvent	Base	Temp.	time	Conv.
			(°C)	(h)	(%)
1	H_2O	KOH	80	2	0
2	THF	KOH	80	2	0
3	THF	K_2CO_3	100	18	>99
4	Toluene	KOH	80	2	99
5	Toluene	K_2CO_3	100	2	99
6	Toluene	K_2CO_3	100	18	>99
7	Toluene	KF·2H ₂ O	100	2	99
8 ^a	Toluene	K_2CO_3	100	18	77

Reagents and conditions: bromotoluene (0.25 mmol), phenylboronic acid (0.275 mmol), base (1.0 mmol), $[PdCl_2(6b)]$ (0.5 mol%), degassed solvent, anisole as an internal standard. Conversion determined by GC. ^aPd(OAc)₂ without ligand and diphenylether as an internal standard.

As observed in Table 3, except for the reactions in THF and water at 80 °C (Entries 1 and 2), all experiments showed satisfactory conversion. In addition, a control experiment using Pd(OAc)₂ showed lower conversion (Entry 8) when compared to the reactions employing the IL ligand (see Entries 5 and 6). Indeed, by comparing entries 5 and 8 it is clear that the complex [PdCl₂(6b)] allowed almost full conversion in only 2 h whereas Pd(OAc)₂ led to only 77% conversion over 18 h. These results indicate that the sulfur-based IL ligand has an important role for the efficiency of the reaction. This is probably related to the stabilizing effect provided by the IL ligand avoiding the aggregation of Pd particles in the reaction medium. Further substrates were evaluated with the intention to widen the scope of the reaction. Indeed, the catalytic system produced the coupling products with high conversions and, in particular, could activate the C-Cl bond in chloroacetophenone (Table 4).

Table 4. Suzuki coupling reaction of different substrates and phenylboronic acid promoted by $[PdCl_2(6b)]$ in toluene

na I	promoted by	[PdCl ₂ (ob)] in toluene	
	R	+ $(PdCl_2(6b))$ K_2CO_3 Toluene	R
	X = Br, Cl; R	= OAc, OMe, CF ₃	
	Entry	Substrate	Conv. (%) ^a
	1	Bromoacetophenone	99
	2	Bromoanisole	99
	3	Bromobenzotrifluoride	97

4			Tetrahedron Letters		
	4	Chloroacetophenone	99	[12] C.B. Y	
	5	Chloroanisole	16	99-121.	

Reagents and conditions: aryl halide (0.25 mmol), phenylboronic acid (0.275 mmol), K2CO3 (1.0 mmol), [PdCl2(6b)] (0.5 mol%), 100 °C, 18 h, degassed solvent (2 mL), anisole as an internal standard. Conversion determined by GC.

Due to these promising results, imidazolium-based ILs were used as media for the Suzuki coupling reaction. In these tests, the system from entry 6 (Table 3) was employed under biphasic conditions (toluene/IL). Among the ILs tested, the best conversion was achieved using BMI·BF4, but it was less active when compared to the homogeneous reaction conducted in toluene (compare Tables 3 and 5). Unfortunately, attempts to recycle the biphasic catalytic system failed, since the conversion dropped in the second run (Entry 1, Table 5).

Table 5. Suzuki coupling reaction between 4-bromotoluene and phenylboronic acid promoted by [PdCl₂(6b)] under biphasic conditions



Reagents and conditions: bromotoluene (0.25 mmol), phenylboronic acid $(0.275 \text{ mmol}), \text{ K}_2\text{CO}_3 (1.0 \text{ mmol}), [PdCl_2(\textbf{6b})] (0.5 \text{ mol}\%), \text{ toluene (1.0 mL)},$ IL (0.5 mL), 100 °C, 18 h, degassed solvent, anisole as an internal standard; ^aConversion determined by GC after each run.

In summary, we have described a practical, useful and odorless synthesis of mono and dicationic sulfur-containing imidazoliumbased ILs. Our strategy based on a key isothiouronium salt intermediate allowed the generation of ten new ILs with yields ranging from 52% to 99%, which represents an excellent alternative to the protocols already described in literature for the synthesis of thiaalkylimidazolium ILs. Moreover, these compounds were applied as ligands and ionic tags for the detection of reaction intermediates in Ullmann and Suzuki coupling reactions, opening new possibilities to apply these ILs in several catalytic transformations. A more comprehensive scope evaluation as well as the application of these ILs in other metal-catalyzed reactions are underway in our groups and it will be published in due course.

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Δ

- Synthesis of thiaalkylimidazolium ionic liquids from odorless isothiouronium salts.

- Mono and dicationic thiaalkylimidazolium ionic liquids were prepared and characterized.

Accepter - These ionic compounds were applied as ligands in Ullman and Suzuki coupling reactions.

- They can also be employed as charged probes to detect intermediates by ESI-MS.





- Odorless synthesis
- Ionically tagged ligands
- Ligands for metal-catalyzed C-C and C-O couplings





a: for **1a** = diethyl ether, r.t., 4 d, 10 eq. dibromide. *b*: for **1b** = ethyl acetate, reflux, 24 h, 5 eq. dibromide. *c*: for **1c** = CH_3CN , reflux, 24 h, 5 eq. dibromide.





