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Pyrylium sulfonate based ionic liquids

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ABSTRACT

Pyrylium salts represent a new group of ionic liquids (ILs) containing a positive charge on the oxygen atom. The novel ILs were obtained starting with 4-pyrones from petroleum feedstock and renewable resources and sulfonic acids. The use of carboxylic acids instead of salts resulted in the formation of cocrystals. The synthesized pyrylium ionic liquids were stable in air and in contact with water and common organic solvents. The permanganate indices which are characteristic for prepared sulfonates were also investigated. The pyrylium ionic liquids were useful as immobilizers and dissolving agents in hydrosilylation reactions.

Oxonium ions are widely known as reactive intermediates in organic reactions or as highly reactive chemical reagents. Trialkyloxonium salts with inert counterions (such as BF_4^- or PF_6^-) are very powerful alkylating agents. Oxatriquinane and oxatriquinacene, as water-stable versions of these highly reactive salts, have been synthesized recently.[1] The pyrylium cation as a fully unsaturated six-membered heterocycle with one oxygen atom bearing a positive charge is much less reactive than a trialkyloxonium ion. For example, it is stable in nucleophilic solvents when the reaction medium is strongly acidic. However, pyrylium salts are water unstable. In the literature, different methods are described for synthesizing pyrylium salts, for example, one of the first reactions was heterocyclization of 1,5-diketones.[2–4] The Balaban–Nenitzescu–Praill synthesis[5] from tertiary butanol and an acid anhydride in the presence of tetrafluoroboric, perchloric, hexafluorophosphoric, or trifluoromethanesulfonic acids is the best method for the preparation of pyrylium salts with alkyl substituents.[6–8] 2,6-Dialkyl-4-methylpyrylium hexafluorophosphates termed ionic liquids (ILs) by Balaban[9] were obtained in good yields between 60–70% and characterized by their sharp melting point.[10]

ILs, depending on the cation, are divided into: imidazolium, ammonium, pyridinium, phosphonium, piperidinium, morpholinium, and sulfonium ILs.[11–13] The positive charge is localized on the nitrogen, phosphorus, or sulfur atom. Pyrylium salts represent a new group of ILs containing the positive charge on the oxygen atom. The pyrylium ILs described by Balaban include anions of inorganic origin.[10] Herein, we report the synthesis and properties of pyrylium salts with organic anions. According to our knowledge, pyrylium ILs have not been used as reaction solvents.

Table 1
Prepared 4-hydroxypyrylium sulfonates

Salt	R^1	R^2	R^3	R^4	Yield (%)	Mp (°C)	I_{Mn}[c]
1	Me	H	Me	MePh	96	115–117	9.27
2	Me	OH	H	MePh	92	145–147	7.13
3	Me	H	Me	Ph	93	97–99	7.31
4	Me	OH	H	Ph	96	143–145	6.36
5	Et	OH	H	Ph	98	72–74	3.28
6	Me	H	Me	Me	93	Liquid[a]	14.96
7	Me	OH	H	Me	94	75–78	10.88
8	Me	H	Me	Et	97	Liquid[b]	12.36
9	Me	OH	H	Et	91	77–79	10.18

[a] Density at 20 °C = 1.26 g mL^{-1}.
[b] Density at 20 °C = 1.22 g mL^{-1}.
[c] Permanganate index in $mgO_2\ L^{-1}$ indicates the quantity of oxygen required for the chemical oxidation of organic matter present in water.

New 4-hydroxypyrylium sulfonates were synthesized in one step with very good yields of over 90%. 2,6-Dimethyl-4-pyrone, 3-hydroxy-2-methyl-4-pyrone (maltol) and 2-ethyl-3-hydroxy-4-pyrone (ethyl maltol) were used as bases. Maltol is found in the bark of young larch trees, pine needles, chicory wood, oils, and roasted malt. It is used as a fragrant, caramel-like flavor for addition in foods, imparts a ‘freshly-baked’ flavor (E number E636) to bread and cakes and the roasting of cocoa and coffee beans. Four strong sulfonic acids: benzenesulfonic ($pK_a = 0.7$[14]) and *p*-toluenesulfonic ($pK_a = -1.34$[14]), methanesulfonic ($pK_a = -1.2$[14]) and ethanesulfonic ($pK_a = -1.61$[15]) were used as acids.

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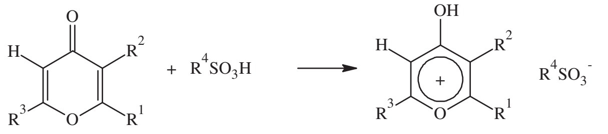


Scheme 1. Prepation of the pyrylium sulfonates.

Several examples are presented in Table 1, which were prepared according to the reaction shown in Scheme 1. Of the nine sulfonates synthesized, seven were crystalline compounds and the other two were liquids. Six are ILs and three are solids, with melting points above 100 °C. The liquid products obtained were dried under vacuum and stored over P_4O_{10}. The water content, determined by Karl-Fischer measurements was found to be less than 500 ppm.

All the synthesized sulfonates were characterized by ^1H and ^{13}C NMR and elemental analysis. The structure of sulfonate **4** was confirmed by two-dimensional NMR. The crystal structure of **4** was determined (Fig. 1). Furthermore, the autostereographic projection was investigated for the same compound (see Supplementary data).

The sulfonates synthesized were insoluble in diethyl ether, hexane, and tetrachloromethane, but were soluble in chloroform, DMSO, acetone, water, DMF, and low-molecular weight alcohols. Furthermore, they were poorly soluble in toluene. The physicochemical properties of the prepared sulfonates are presented in Table 2. The pyrylium sulfonates obtained were thermally stable and all showed 50% thermal decomposition at around 250 °C (Table 2).

In the case of differential scanning calorimetry analysis (DSC) only the two liquid salts **6** and **8** exhibited glass transition temperatures at −57.5 and −65 °C, respectively.

The synthesized ILs were air- and moisture-stable salts. The dynamically growing application of ILs induces misgivings as to their utilization. We regard their oxidation in an aqueous solution of $KMnO_4$ as an effective medium. For each of the sulfonates we were able to investigate the permanganate index (I_{Mn}), according to the analytical standard (EN ISO 8467:2001). The results are listed in Table 1. For comparison, the estimated values for urea and pyridine were, respectively, 2.13 and 19.89 [$mgO_2\ L^{-1}$]. The values I_{Mn} presented were characteristic for the prepared sulfonates.

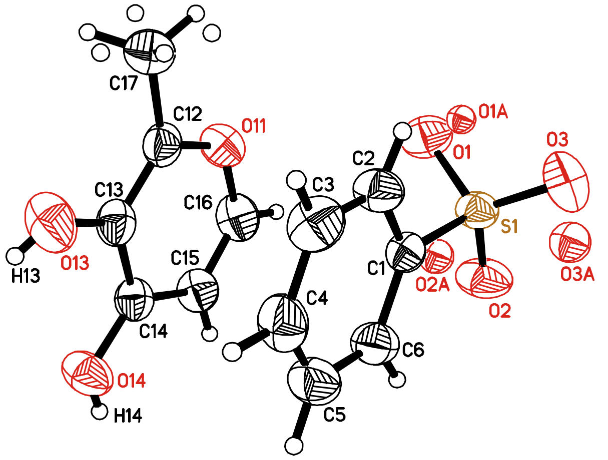


Figure 1. The ORTEP drawing of the ionic pair of 3,4-dihydroxy-2-methylpyrylium benzenesulfonate **4** as present in the crystal. The disordered positions of the sulfonate and methyl groups are indicated by showing one set of atoms bonded and the other not bonded to the central atom. The thermal ellipsoids are drawn at the 50% probability level. The CCDC reference number for this IL is 798798.

Table 2
The physicochemical properties of the synthesized sulfonates

Sulfonate	T_g[a]	T_m[b]	T_{onset}[c]
1	–	146.5	297
2	–	83	270
3	–	102.5	320
4	–	120	168
5	–	78	270
6	−57.5	–	293
7	–	77.5	242
8	−65	–	280
9	–	63	248

[a] Glass transition temp determined by DSC.
[b] Melting point on heating determined by DSC.
[c] Decomposition temp determined from onset to 50 wt % mass loss.

Table 3
The prepared 4-pyrone/carboxylic acid cocrystals

Cocrystal	R^1	R^2	R^3	Acid	Yield (%)	Mp (°C)
10	Me	H	Me	Sal	95	65–67
11	Me	OH	H	Sal	97	82–84
12	Et	OH	H	Sal	98	76–78
13	Me	OH	H	Mal	96	81–83
14	Me	OH	H	Ox	97	135–137
15	Me	OH	H	Lac	95	127–129
16	Me	H	Me	Gly	93	55–57

When we used carboxylic acids: oxalic (Ox) ($pK_a = 1.27$[14]), D,L-malic (Mal) ($pK_a = 3.40$[16]), salicylic (Sal) ($pK_a = 2.98$[17]), glyconic (Gly) ($pK_a = 3.83$[17]), and lactic (Lac) ($pK_a = 3.83$[17]) instead of sulfonic acids we obtained cocrystals. The prepared cocrystals are presented in Table 3. These cocrystals manifested sharp melting points.

The structures of cocrystals were confirmed by ^1H and ^{13}C NMR and elemental analysis. In addition, for 2,6-dimethyl-4-pyrone/salicylic acid **10**, two-dimensional NMR, solid-state NMR, and crystallographic analysis were performed (Fig. 2). These solid cocrystals crystallized from stoichiometric amounts of carboxylic acid and the 4-pyrone base.

The synthesized cocrystals were stable up to 180 °C and glass transition temperatures were observed for only two of the cocrystals: **10** and **13** (Table 3).

In these two reactions (using sulfonic or carboxylic acids), proton transfer took place to give a salt or a cocrystal. The acid ionization constant (pK_a) is employed for predicting solid form molecular ionization states.[18] In the case of the synthesis of a pyrylium salt with an organic anion, the pK_a value is important: organic acids with a pK_a less than 1 form salts, and those with a pK_a more than 1 yield cocrystals.

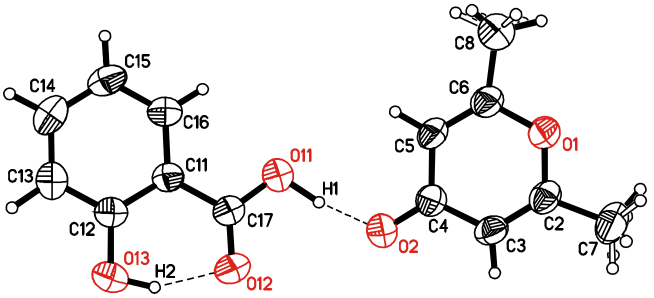
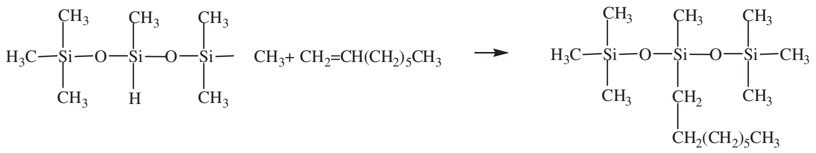


Figure 2. The ORTEP drawing of the H-bonded molecule of salicylic acid and 2,6-dimethyl-4-pyrone **10**, as present in the cocrystal structure. The CCDC reference number for this cocrystal is 798797.



Scheme 2. Hydrosilylation of 1-octene.

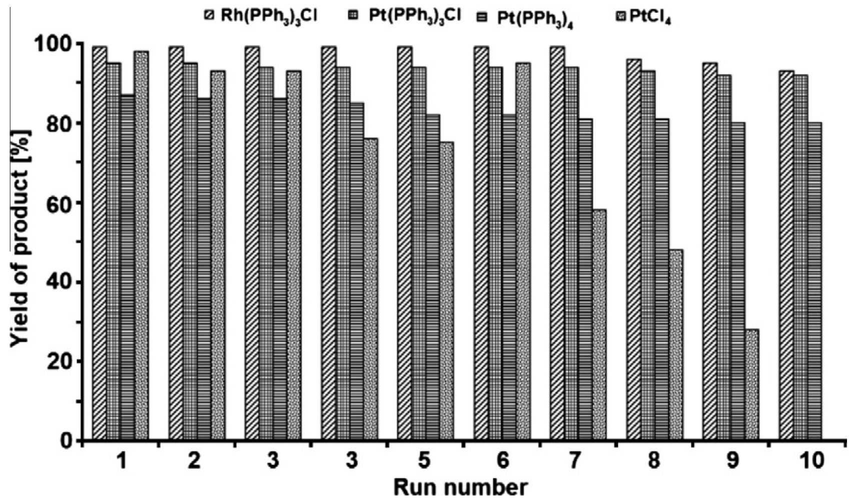


Figure 3. The yield of product over 10 runs with the recovered catalytic system for the hydrosilylation of 1-octene catalyzed by Pt or Rh complexes immobilized in pyrylium IL **6**.

ILs are recognized as potential media for the immobilisation of catalysts and were used with considerable success in a wide range of laboratory scale reactions.[19] Having experience with catalytic systems for hydrosilylation processes, based mainly on rhodium siloxide complexes immobilized in imidazolium and phosphonium ILs,[20–22] we decided to test pyrylium ILs. In the present study we employed a rhodium complex [Rh(PPh$_3$)$_3$Cl] and complexes of platinum at different oxidation states, namely [Pt(PPh$_3$)$_4$], [Pt(PPh$_3$)$_2$Cl$_2$], and [PtCl$_4$], immobilized in liquid pyrylium sulfonate **6**. The obtained systems were used as catalysts for the model reaction of octene hydrosilylation (Scheme 2).

Our studies showed that immobilisation of the complexes in sulfonate **6** gave biphasic systems which enabled easy separation of the products from the catalytic system and its reuse in subsequent catalytic runs. In all cases only one product was formed (the β addition product). Figure 3 shows the yields of product over 10 reaction cycles for the reaction catalyzed by a particular metal complex immobilized in pyrylium IL **6**.

The catalytic activity of most of the systems studied was high and enabled product yields above 50% to be obtained in subsequent runs, except for the catalytic system based on [PtCl$_4$]. However, the highest catalytic activity as well as high stability and reproducibility were shown by the systems based on [Rh(PPh$_3$)$_3$Cl] and [Pt(PPh$_3$)$_2$Cl$_2$], which made it possible to obtain the product in yields over 90% in 10 subsequent runs.

Pyrylium ILs are characterized by thermal stability and have very low, but not null vapor pressure. The hydrosilylation process, employed in our study as a test reaction, is usually carried out without a solvent. ILs chosen for such an application have to be of high purity (no contaminants able to poison the catalyst) and should dissolve and immobilize the metal complex, while maintaining its high catalytic activity.

The pyrylium IL used by us did not play the role of solvent, but that of a metal complex immobilizing agent. Moreover, the IL should form a bi- or multiphase system with substrates and products, be stable in the presence of reactive substrates and should not interact with the products. The ILs applied in this study have met all these requirements which resulted in a highly effective catalytic system for the reaction studied (particularly in the case of the rhodium siloxide complex). Another advantage of the IL was its immiscibility with the reactants and ability to form well-separated phases, which made isolation of the post-reaction mixture from the catalytic system very easy. The hydrosilylation in the presence of four different complexes of metals indicated differences in their catalytic performance, particularly when they were reused. In the case of [Rh(PPh$_3$)$_3$Cl] and [Pt(PPh$_3$)$_2$Cl$_2$] complexes, immobilization in the IL was excellent and they were well-protected against leaching and showed high catalytic activity. The two other complexes were not so efficiently immobilized in the IL, which resulted in their gradual leaching from the catalytic system as reflected by the decreasing product yield. This fact was confirmed by results of post-reaction mixture analysis performed by ICP-OES which showed no presence of Rh or Pt in the case of the former two complexes, whereas in that of the remaining two complexes the post-reaction mixture obtained after subsequent reaction runs contained platinum.

4-Pyrones, obtained from petroleum feedstock and renewable resources (maltol), are reactive cyclic compounds, capable of forming both oxonium cation and cocrystals with organic acids. Very strong sulfonic acids lead to pyrylium ionic liquids due to a protonation reaction. On the other hand, carboxylic acids are too weak to create ionic bonds, but are strong enough to yield hydrogen bond based cocrystals. Both kinds of product could be obtained in one step with high efficiency, and purity. These thermally-stable pyrylium ionic liquids are useful as immobilizers and dissolving agents in hydrosilylation reactions.

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Supplementary data

Supplementary data (synthetic and analytical details, NMR spectra, crystals) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.06.058.

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