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Selenium- and tellurium-based ionic liquids and their use in the synthesis of octahydroacridines

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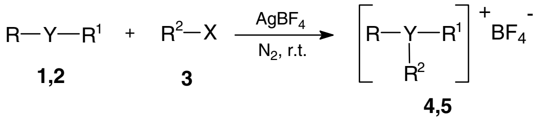
Abstract—A general and easy method for the synthesis of several selenonium and telluronium salts is described. These compounds are acidic liquids at room temperature and were obtained in excellent yields. Phenyl butyl ethyl selenonium tetrafluoroborate was employed in the hetero-Diels–Alder cyclization of aryl imines derived from citronellal, affording octahydroacridines in good yields.

Room-temperature ionic liquids are receiving much attention in organic chemistry as reaction solvents and catalysts.[1] Also called as molten salts, this new class of highly polar solvents is constituted by ions, and due to their low volatility, they are regarded as environmentally friendly green solvents. Product isolation or catalyst recycling is very easy in ionic liquids and in some cases, rate accelerations and/or selectivity improvements are also observed. Therefore, the preparation and study of the chemical and physical properties of new ionic liquids is of great interest, in order to design modulated solvents that are optimized for the chemical transformation to be accomplished.

In spite of the dozens of new ionic liquids described in the last years, the great majority presents imidazolium, pyridinium or phosphonium groups as cationic units, with major modifications on the anionic fragments.[1] On the other hand, in spite of the great development of the chemistry of selenium and tellurium compounds in the last years,[2] the preparation and characterization of Se- and Te-ionic liquids was scarcely explored.[3] Selenonium and telluronium ions are positively charged compounds of trivalent selenium and tellurium.[2b,4] Synthetic applications of onium salts of Se and Te include reactions with carbonyl compounds to afford olefins,[4,5a] alcohols,[4] oxiranes[4,5b] and cyclopropanes,[4] [2,3]-sigmatropic rearrangements[6], and substrate in Michael additions.[7] To our knowledge, the use of selenonium and telluronium salts as ionic liquids or acidic catalyst is still unexplored.

Our major research goal has been the development of new methods for the preparation and synthetic applications of organochalcogenium compounds[8] and the development of new cleaner protocols for classical reactions.[9] In continuation of these studies, we decided to explore the preparation of new Se and Te salts that are liquid at room temperature and can be used as solvents and/or catalysts in organic synthesis. Thus, we report here the results of the reaction of diorganyl chalcogenides **1**, **2** (Se, Te) with alkyl halides **3** in the presence of $AgBF_4$ to afford the respective selenonium **4** and telluronium tetrafluoroborates **5** (Scheme 1, Table 1).[10]

A detailed study was performed with the aim to obtain liquid salts at room temperature. Thus, several tests



Scheme 1.

Keywords: Selenonium and telluronium salts; Ionic liquids; Microwave irradiation.

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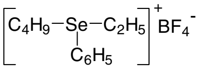
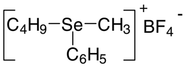
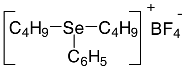
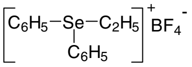
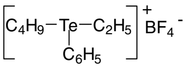
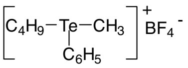
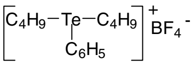
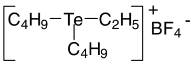
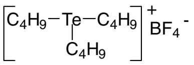
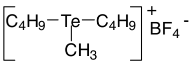
Table 1. Synthesis of ionic liquids **4** and **5**

Entry	Chalcogenide **1** and **2**	Halide **3**	Products **4** and **5**	Time (h)	Yield[a,b] (%)
1	$C_4H_9SeC_6H_5$ **1a**	C_2H_5Br **3a**	 $[C_4H_9-\underset{C_6H_5}{Se}-C_2H_5]^{+}\,BF_4^{-}$ **4a**	5.0	94
2	$C_4H_9SeC_6H_5$ **1a**	CH_3I **3b**	 $[C_4H_9-\underset{C_6H_5}{Se}-CH_3]^{+}\,BF_4^{-}$ **4b**	4.0	97
3	$C_4H_9SeC_6H_5$ **1a**	C_4H_9Br **3c**	 $[C_4H_9-\underset{C_6H_5}{Se}-C_4H_9]^{+}\,BF_4^{-}$ **4c**	6.5	87
4	$C_6H_5SeC_6H_5$ **1b**	C_2H_5Br **3a**	 $[C_6H_5-\underset{C_6H_5}{Se}-C_2H_5]^{+}\,BF_4^{-}$ **4d**	2.0	99
5	$C_4H_9TeC_6H_5$ **2a**	C_2H_5Br **3a**	 $[C_4H_9-\underset{C_6H_5}{Te}-C_2H_5]^{+}\,BF_4^{-}$ **5a**	3.0	95
6	$C_4H_9TeC_6H_5$ **2a**	CH_3I **3b**	 $[C_4H_9-\underset{C_6H_5}{Te}-CH_3]^{+}\,BF_4^{-}$ **5b**	3.0	98
7	$C_4H_9TeC_6H_5$ **2a**	C_4H_9Br **3c**	 $[C_4H_9-\underset{C_6H_5}{Te}-C_4H_9]^{+}\,BF_4^{-}$ **5c**	3.5	93
8	$C_4H_9TeC_4H_9$ **2b**	C_2H_5Br **3a**	 $[C_4H_9-\underset{C_4H_9}{Te}-C_2H_5]^{+}\,BF_4^{-}$ **5d**	3.5	91
9	$C_4H_9TeC_4H_9$ **2b**	C_4H_9Br **3c**	 $[C_4H_9-\underset{C_4H_9}{Te}-C_4H_9]^{+}\,BF_4^{-}$ **5e**	4.5	81
10	$C_4H_9TeC_4H_9$ **2b**	CH_3I **3b**	 $[C_4H_9-\underset{CH_3}{Te}-C_4H_9]^{+}\,BF_4^{-}$ **5f**	2.5	98

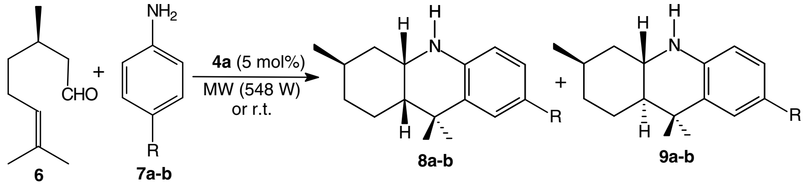
[a] Yields of pure products.

[b] All the synthesized salts were characterized by ^{77}Se (for **4a–d**), ^{125}Te (for **5a–f**), ^{13}C and ^{1}H NMR.[4,12]

were accomplished by varying the diorganyl chalcogenide **1** or **2** as well as the alkyl halides **3**, and the best results are described in Table 1. The experimental procedure is very easy, and a complete conversion of starting materials to products was observed after stirring a few hours at room temperature (Table 1).

With the aim to promote the nucleophilic substitution in **3**, several reaction conditions were tested, and the best results were obtained when an equimolar amount of silver tetrafluoroborate and diorganyl chalcogenide **1** or **2** was stirred at room temperature in the presence of an excess (5 equiv) of alkyl halide **3**.[10] The remaining volatile alkyl halides were easily removed by distillation and reused after the reaction. Selenonium **4** and telluronium salts **5** described here were easily purified[10] and characterized by NMR techniques (^{1}H, ^{13}C, ^{77}Se, and ^{125}Te). All the Se and Te salts show chemical shifts at downfield with respect to the dicoordinated selenides and tellurides precursors **1** and **2**. Thus, for instance, the ^{77}Se chemical shift of phenyl butyl ethyl selenonium tetrafluoroborate (**4a**) appears in 420 ppm, while the phenyl butyl selenide (**1a**) precursor shows a peak at 288 ppm.[11] The ^{125}Te chemical shift of tributyl telluronium tetrafluoroborate (**5e**) is 560 ppm, while a peak at 248 ppm for the dibutyl telluride (**2b**) was observed.[11] These observed downfield chemical shifts for salts **4** and **5** are in agreement with those reported for the Se and Te onium salts analogs.[4,12] All of the synthesized onium salts are liquid at room temperature, and although the melting points of **4** and **5** were not precisely established, compounds **4b**, **5d**, and **5f** are solids at 0 °C, while the other compounds are still liquids at −20 °C. With respect to the stability of the onium salts, it was observed that the selenonium derivatives are stable and can be stored at 5 °C for several weeks or days at room temperature without decomposition. However, the telluronium analogs are relatively unstable, and the decomposition to diorganyl tellurides occurs within a few days, even at −5 °C. The relative stability (or decomposition rate) can be easily observed by thin layer chromatography analysis.

Besides $AgBF_4$, a variety of silver salts ($AgNO_3$, $AgNO_3/KBF_4$, and $AgNO_3/NaBF_4$) were tested. However, in spite of high conversion rates (>95%), only solid chalcogenonium salts at room temperature were obtained. When $AgSO_4$ was employed as a reaction promoter, no consumption of starting diorganylchalcogenides (**1** and **2**) was observed. Although most experi-



Scheme 2.

Table 2. The reaction of (*R*)-citronellal (**6**) with anilines **7a**, **b** at room temperature or under MW

Entry	R, **7**	Method[a]	Reaction time (min)[b]	Yield (%) **8** + **9**
1	H, **7a**	A	60	76
2	H, **7a**	B	6	73
3	CH_3, **7b**	A	60	74
4	CH_3, **7b**	B	5	80

[a] Method A: The reaction mixture was stirred at room temperature. Method B: The experiments were performed under MW (548 W).

[b] The reaction progress was monitored by TLC.

ments were performed in a 2.0 mmol scale, phenyl butyl ethyl selenonium tetrafluoroborate (**4a**) was prepared starting from higher amounts of reagents (30 mmol) in 95% yield.

In continuation of our studies on the development of new protocols under solvent-free conditions, we decided to investigate the use of these new ionic liquids as green solvents and/or catalysts in organic synthesis. Thus, we studied their use in the preparation of 1,2,3,4,4a,9,9a,10-octahydroacridines (OHAs) **8** and **9** by hetero-Diels–Alder reaction involving (*R*)-citronellal (**6**) and arylamines **7**.[13] In view of the high stability, facile preparation and low viscosity, we decided to use phenyl butyl ethyl selenonium tetrafluoroborate (**4a**) as the catalyst in this reaction (Scheme 2, Table 2).

We examined the reaction time, the amount of ionic liquid and the effect of irradiation with microwaves.[13] It was found that by using 3 mol % of **4a**, at room temperature, the reaction proceeded slowly and in 53% yield after stirring for 1 h. However, by using 5 mol % of **4a**, the desired products **8a** and **9a** (R = H) were obtained in good yields (76%) after stirring for the same time (Table 2, entry 1). Aiming to reduce the reaction time, the mixture was irradiated with microwaves (548 W). Complete consumption of the starting materials was observed after 6 min and the products were obtained in comparable yields (Table 2, entry 2). When the same protocol was performed at reduced MW power (353 W), incomplete consumption of aniline (**7a**, R = H) was observed after 10 min, yielding 51% of the product. The same procedures were employed using toluidine (**7b**, R = CH_3) as starting material, affording a mixture of the OHAs **8b** and **9b** in 74% and 80% yields at room temperature and under MW (548 W), respectively (Table 2, entries 3 and 4). A cis and trans mixture of OHAs was formed with a 1:1 ratio (determined by ^1H NMR). The products are easily separable by column chromatography, with the more polar isomer showing the trans-configuration.[13] The decomposition of **4a** to phenyl butyl selenide **1a** that can be easily purified to prepare new selenonium salt, was also observed.

In conclusion, we have presented here an easy and general method for the synthesis of selenonium and telluronium ionic liquid salts. The new phenyl butyl ethyl selenonium tetrafluoroborate **4a** can be used as a catalyst in the atom-economic synthesis of OHAs. The procedure is very simple, and it makes use of easily available starting materials and no solvent is necessary. The use of microwaves accelerates the reaction with comparable yields. Studies looking for other applications of the ionic liquids described here in other reactions are in course at our laboratory.

Acknowledgments

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10. *General procedure for the synthesis of ionic liquids* **4a**–**d** *and* **5a**–**f**. To a mixture of butyl phenyl selenide **1a** (0.428 g; 2.0 mmol) and ethyl bromide (0.540 g, 5.0 mmol), under nitrogen, was added AgBF$_4$ (0.388 g, 2.0 mmol) at room temperature. The reaction progress was followed by TLC, and after 5 h (see Table 1) CH$_2$Cl$_2$ was added (10 mL) and the crude was filtrate over celite. The filtrate was evaporated under reduced pressure and washed with dry ether (3 × 3 mL) for removing unreacted **1a**, yielding 0.620 g (94%) of pure **4a** as a light yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.82 (t, $J = 7.5$ Hz, 3H), 1.39 (t, $J = 7.5$ Hz, 3H), 1.22–1.73 (m, 4H), 3.57–3.82 (m, 4H), 757–7.68 (m, 3H), 7.79–7.83 (m, 2H); ^{77}Se NMR (57 MHz, CDCl$_3$) δ (ppm) 419.96 (PhSeSePh as reference compound).
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12. Matano, Y.; Suzuki, H.; Azuma, N. *Organometallics* **1996**, *15*, 3760, and references therein.
13. *General procedure for the synthesis of octahydroacridines* **8** *and* **9**. *Method A*: To a mixture of (+)-citronellal **6** (0.154 g, 1 mmol) and aniline **7a** (0.093 g, 1 mmol), **4a** (0.016 g, 5 mol %) was added and the solution stirred at room temperature for 1 h. The crude product was purified by column chromatography over silica gel (SiO$_2$) eluting with hexane/ethyl acetate (98:2), yielding the products **8a** (0.159 g, 38%) and **9a** (0.159 g, 38%). The spectral data were in perfect agreement with those reported in the literature.[9b] *cis*-**8a** (first eluted fraction): ^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 7.11 (dd, $J = 7.6$ and 1.4 Hz, 1H), 6.94 (ddd, $J = 8.0$, 7.5, and 1.5 Hz, 1H), 6.57 (dt, $J = 7.4$ and 1.2 Hz, 1H), 6.41 (dd, $J = 7.9$ and 1.1 Hz, 1H), 3.81–3.83 (m, 1H), 3.50 (br s, 1H), 1.56–1.77 (m, 5H), 1.31 (s, 3H), 1.21 (s, 3H), 1.07–1.31 (m, 3H), 0.88 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl$_3$) δ (ppm) 143.1, 128.1, 126.5, 126.1, 116.2, 112.8, 46.8, 44.5, 41.2, 35.6, 34.8, 34.1, 26.1, 25.5, 23.0, 22.2. *trans*-**9a** (second eluted fraction): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.21 (dd, $J = 7.6$ and 0.8 Hz, 1H), 6.94 (ddd, $J = 7.6$, 7.4, and 1.2 Hz, 1H), 6.63 (dd, $J = 7.6$ and 0.8 Hz, 1H), 6.41 (dd, $J = 8.0$ and 0.4 Hz, 1H), 3.55 (br s, 1H), 3.05 (ddd, $J = 10.4$, 10.3, and 4.0 Hz, 1H), 1.50–1.87 (m, 6H), 1.32 (s, 3H), 1.09 (s, 3H), 0.99–1.28 (m, 2H), 0.95 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 142.9, 131.0, 126.4 (2C), 116.6, 113.5, 50.4, 46.9, 43.2, 35.0, 34.7, 30.8, 27.1, 26.6, 24.6, 22.2. *Method B*: The aforementioned whole mixture was previously stirred for 1 min and then irradiated with microwave (a domestic Panasonic model Piccolo NN-S42BK, operating at 2.45 MHz) at 548 W[14] for 5–6 min and the product was purified according to the described on Method A.
14. The oven powers were determined as described by Kingston, H. M. In *Introduction to Microwave Sample Preparation—Theory and Practice*; Jassie, L. B., Ed.; American Chemical Society: DC, 1988.