First application of ionic liquid to reactions involving organotellurium compounds as intermediates

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The condensation reaction of telluronium salts **1** with aldehydes and dibutyl telluride **4**, bromide **5** with aldehyde **2** proceeded smoothly in the ionic solvent [bmim][BF_4], affording a novel method for the stereoselective synthesis of *(E)*-α,β-unsaturated compounds **3** in high purity, excellent yields and high stereoselectivity.

Keywords: ionic liquid, organotellurium compounds, α,β-unsaturated compounds

Ionic liquids have the advantage of low volatility, immiscibity with many organic solvents, good solvating properties for both inorganic and organic compounds and produce enhancements in reaction rates, yields and selectivities.[1,2] Their applications in organic synthesis have been reported in Heck reaction,[3] Beckmann rearrangement,[4] Friedel–Crafts reaction,[5] hydrogenation,[6] and Wittig reactions.[7] Recently reactions using organotellurium compounds as intermediates have been studied and applied in organic synthesis. These methods have advantages over previous methods.[8-11] However, there has been no report on the application of ionic liquids to these reactions. Here we report our investigation on the application of ionic liquid in some important reactions via organotellurium compounds as intermediates.

It was reported that telluronium salts themselves **1** can condense directly with aldehydes and an one-pot reaction of dibutyl telluride **4**, bromide **5** and aldehyde **2** could also proceed smoothly, affording a facile method for the synthesis of *(E)*-α,β-unsaturated compounds **3**.[12] We chose 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (Fig. 1) as an ionic liquid for these studies. This can be easily prepared from 3-methylimidazole.

Our experiments show that both the condensation reaction (Eqn (1), Scheme 1) (Method A) and the one-pot reaction (Eqn (2), Scheme 1) (Method B) proceeded smoothly in the ionic solvent [bmim][BF_4] and faster than in common organic solvent reported in literature with the similar yields and stereoselectivities.[12] Moreover the isolation of the products **3** was greatly simplified when the ionic liquid is used. The extraction of the reaction mixture with hexane removed the decomposition products of dibutyl telluroxide with a trace amount of (*E*)-α,β-unsaturated compounds **3**. Further extraction with ethyl ether and then evaporation of solvent gave desired (*E*)-α,β-unsaturated compounds **3** with high purity, good yields and high stereoselectivities. In some cases the purity can be 100%

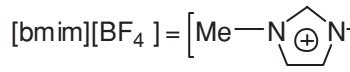


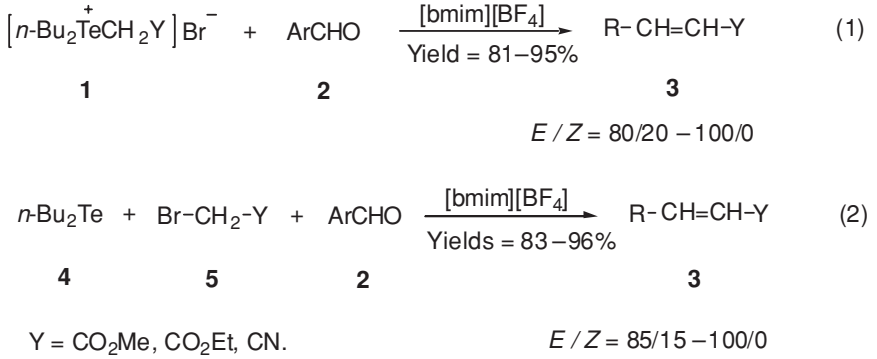
Fig. 1

and in other cases less than 3% aldehydes **2** were detected by ^{1}H NMR. In order to recycle the used [bmim][BF_4], it was treated with anhydrous potassium carbonate and then extracted with dichloromethane to separate the unreacted telluronium salts **1**. In some cases less than 2% salts **1** were detected in the extract. When the clean ionic solvent [bmim][BF_4] was reused for five times, no changes were observed in rates, purities, yields and stereoselectivities of the condensation reaction and the one-pot reaction. To our knowledge, there is only one report on the stereoselective synthesis of (*E*)-α,β-unsaturated compounds via ylides in ionic solvent.[7] Our synthetic method is preferred over the literature method because the preparations of ylides, and the corresponding salts can be omitted.

In conclusion, the condensation reaction and the one-pot reaction via the organotellurium compounds takes place smoothly in the ionic solvent [bmim][BF_4] with high purity, excellent yields and high stereoselectivities. The isolation in this method is much simpler than the previous work-up by column chromatography. Moreover the ionic solvent [bmim][BF_4] can be efficiently reused. The application of the ionic solvent in the process of reactions and isolations can not only reduce the harmful effects of volatile solvent, but also decrease the quantity of volatile solvent needed in the process. This method is more user- and eco-friendly.

Experimental

All reactions were carried out under nitrogen atmosphere. Reactions were monitored by TLC. ^{1}H NMR spectra were determined in $CDCl_3$ on a Bruker Advance 400 (400MHZ) with TMS as internal standard.



Scheme 1 The condensation and one-pot reaction via the organotellurium compounds in [bmim][BF_4].

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Table 1 The condensation and one-pot reaction for the synthesis of α,β-unsaturated compounds **3** in [bmim][BF_4]

Entry	Y	Ar	Reaction time/h		Isolated yields/%		Purity/%		*E*/*Z*	
			Method A	Method B	Method A	Method B	Method A	Method B	Method A	Method B
3a	COOMe	4-$NO_2C_6H_4$	2		92		92		85/15	
3b	COOMe	4-FC_6H_4	3		91		90		100/0	
3c	COOMe	4-ClC_6H_4	6		81		85		100/0	
3d	COOMe	C_6H_5	4		90		91		98/2	
3e	COOMe	4-$CH_3C_6H_4$	5		86		96		80/20	
3f	COOEt	4- $NO_2C_6H_4$	2	2	95	93	100	92	100/0	100/0
3g	COOEt	4-FC_6H_4	3	3	94	95	98	92	85/15	90/10
3h	COOEt	C_6H_5	5	5	88	87	95	96	80/20	85/15
3i	COOEt	4-$CH_3C_6H_4$	6	7	90	91	96	91	99/1	100/0
3j	CN	4- $NO_2C_6H_4$	3	3	87	90	95	96	100/0	99/1
3k	CN	4-ClC_6H_4	4	4	90	91	100	95	85/15	90/10
3l	CN	C_6H_5	6	6	86	83	95	90	90/10	85/15
3m	CN	4-$CH_3C_6H_4$	7	8	82	84	91	88	100/0	98/2

[a]All products are confirmed by ^{1}H NMR, IR and MS.
[b]The ratios of *E*-isomer to *Z*-isomer are determined by ^{1}H NMR or GC**.**

Mass spectra (EI) were obtained on a HP5989B mass spectrometer. IR spectra were taken with a Bruker Vector 22 spectrometer. Melting points were uncorrected. Dibutyl telluride **4** was prepared according to the literature method.[13]

Synthesis of α,β-unsaturated compounds via organotellurium compounds as intermediates in ionic liquid

Method A: Under nitrogen, the mixture of telluronium salt **1** (2.0 mmol) and aldehyde (2.0 mmol) **2** in [bmim][BF_4] (10 ml) was stirred at 80 °C for the time indicated in Table 1. After extraction with hexane (10 ml × 2), the solution of [bmim][BF_4] was extracted with Et_2O (5 ml × 3). Evaporation of Et_2O gave α,β-unsaturated compounds 3.

Method B: Under nitrogen, the mixture of dibutyl telluride **4** (2.0 mmol), bromide **5** (2.0 mmol) and aldehyde **2** (2.0 mmol) in [bmim][BF_4] (10 ml) was stirred at 80 °C for the time indicated in Table 1. The work-up is similar to that in the Method A.

Methyl 3- (4-nitrophenyl)-2-propenoate (**3a**): m.p. 80–82 °C (lit.[14a] trans m.p. 160–161 °C). ^{1}H NMR δ (ppm): 8.41 (d, *J*=8.4Hz, 2H), 7.85 (d, *J*=8.4Hz, 2H), 7.60 (d, *J*=16.0Hz, E), 7.05 (d, *J*=12.6Hz, Z) (*E*+*Z*=1H), 6.75 (d, *J*=16.0Hz, E), 6.25 (d, *J*=12.6Hz, Z) (*E*+*Z*=1H), 4.45 (s, E), 4.10 (s, Z) ((*E*+*Z*=3H). IR ν (cm^{-1}): 3105, 2982, 1708, 1525, 1356, 862; MS *m/z*: 205 (M^+, 23), 77 (100).

Methyl (E)-3- (4-fluorophenyl)-2-propenoate (**3b**): Oil (lit.[14b] oil). ^{1}H NMR δ (ppm): 7.74 (d, 2H, *J*=8.4Hz), 7.70 (d, 2H, *J*=15.6Hz), 7.38 (d, 2H, *J*=8.4Hz), 6.38 (d, 2H, *J*=15.6Hz), 3.95 (s, 3H); IR ν (cm^{-1}): 3130, 2980, 1711, 1605, 842; MS *m/z*: 180 (M^+, 21), 103 (100).

Methyl (E)-3- (4-chlorophenyl)-2-propenoate (**3c**): m.p. 74–75 °C (lit. [14c] 76–76 °C). ^{1}H NMR δ (ppm): 7.71 (d, 2H, *J*=8.4Hz), 7.69 (d, 1H, *J*=15.6Hz), 7.22 (d, 2H, *J*=8.4Hz), 6.36 (d, 1H, *J*=15.6Hz), 3.90 (s, 3H); IR ν (cm^{-1}): 3105, 2884, 1705,1552, 810; MS *m/z*: 196 (M^+, 32), 76 (100).

Methyl 3-phenyl-2-propenoate (**3d**): Oil (lit. [14d] trans 36 °C). ^{1}H NMR δ (ppm): 7.70 (d, *J*=16.0Hz, E), 6.97 (d, *J*=12.6Hz, Z) (*E*+*Z*=1H), 7.59–7.52 (m, 2H), 7.40–7.35 (m, 3H), 6.45 (d, *J*=16.0Hz, E), 5.98 (d, *J*=12.6Hz, Z) (*E*+*Z*=1H), 3.81 (s, E), 3.73 (s, Z) (*E*+*Z*=3H). IR ν (cm^{-1}): 3100, 2975, 1716, 1617, 1495, 769, 710; MS *m/z*: 162 (M^+, 21), 131 (100).

Methyl (E)-3- (4-methylphenyl)-2-propenoate (**3e**): m.p. 54–55 °C (lit. [14e] *trans* 55–56 °C). ^{1}H NMR δ (ppm): 7.77 (d, 2H, *J*=8.4Hz), 7.71 (d, 1H, *J*=15.6Hz), 7.28 (d, 2H, *J*=8.4Hz), 6.40 (d, 1H, *J*=15.6Hz), 3.94 (s, 3H), 2.18 (s, 3H); IR ν (cm^{-1}): 3086, 2984, 1656, 1605, 1264, 813; MS *m/z*: 176 (M^+, 37), 131 (100).

Ethyl (E)-3- (4-nitrophenyl)-2-propenoate (**3f**): m.p. 135–138 °C (lit.[14a] 138.5 °C). ^{1}H NMR δ (ppm): 8.28 (d, 2H, *J*=8.5Hz), 7.62 (d, 1H, *J*=15.6Hz), 7.44 (d, 2H, *J*=8.5Hz), 6.39 (d, 1H, *J*=15.6Hz), 4.27 (q, *J*=7.1Hz, 2H), 1.36 (t, *J*=7.1Hz, 3H); IR ν (cm^{-1}): 3105, 2965, 1725, 1632, 1542, 1355, 785; MS *m/z*: 205 (M^+, 38), 103 (100).

Ethyl (E)-3- (4-fluorophenyl)-2-propenoate (**3g**): Oil (lit. [14f] oil). ^{1}H NMR δ (ppm): 7.98 (d, 2H, *J*=8.4Hz), 7.62 (d, 1H, *J*=15.6Hz), 7.43 (d, 2H, *J*=8.4Hz), 6.38 (d, 1H, *J*=15.6Hz), 4.26 (q, *J*=7.1Hz, 2H), 1.37 (t, *J*=7.1Hz, 3H); IR ν (cm^{-1}): 3100, 1715, 1641, 1492, 870; MS *m/z*: 194 (M^+, 33), 102 (100).

Ethyl 3-phenyl-2-propenoate (**3h**): Oil (lit.[14g] oil). ^{1}H NMR δ (ppm): 7.73 (d, *J*=16.0Hz, *E*), 6.90 (d, *J*=12.6Hz, *Z*) (*E*+*Z*=1H), 7.55–7.50 (m, 2H), 7.35–7.25 (m, 3H), 6.45 (d, *J*=16.0Hz, *E*), 5.85 (d, *J*=12.6Hz, *Z*) (*E*+*Z*=1H), 4.35–4.27 (m, 2H), 1.54 (t, *J*=7.1 Hz, *E*), 1.25 (t, *J*=7.0 Hz, *Z*) (*E*+*Z*=3H); IR ν (cm^{-1}): 3102, 1735, 1638, 1490, 765, 715; MS *m/z*: 176 (M^+, 38), 131 (100).

Ethyl (E)-3- (4-methphenyl)-2-propenoate (**3i**): Oil (lit.[14h] oil). ^{1}H NMR δ (ppm): 7.64 (d, 1H, *J*=15.5Hz), 7.47 (d, 2H, *J*=8.4Hz), 6.90 (d, 2H, *J*=8.5Hz), 6.41 (d, 1H, *J*=15.6Hz), 4.28 (q, *J*=7.0Hz, 2H), 2.36 (3H, s), 1.38 (t, *J*=7.1Hz, 3H); IR ν (cm^{-1}): 3052, 2980, 1719, 1607, 824; MS *m/z*: 206 (M^+, 100), 162 (97).

(E)-3- (4-nitrophenyl)-2-propenenitrile (**3j**): m.p. 196–198 °C (lit.[14i] *trans* m.p. 197–198 °C). ^{1}H NMR δ (ppm): 8.29 (d, 2H, *J*=8.8Hz), 7.64 (d, 2H, *J*=8.8Hz), 7.47 (d, 1H, *J*=16.7Hz), 6.06 (d, 1H, *J*=16.7Hz); IR ν (cm^{-1}): 3075, 2210, 1601, 1520, 1347, 745; MS *m/z*: 174 (M^+, 78), 101 (100).

3- (4-chlorophenyl)-2-propenenitrile (**3k**): m.p. 83–85 °C (lit.[14j] 84–85 °C). ^{1}H NMR δ (ppm): 7.70 (d, 2H, *J*=8.6Hz), 7.56 (d, *J*=15.8Hz, *E*), 7.12 (d, *J*=12.6Hz, *Z*) (*E*+*Z*=1H), 7.33 (d, 2H, *J*=8.6Hz), 6.38 (d, *J*=15.8Hz, *E*), 5.40 (d, *J*=12.6Hz, *Z*) (*E*+*Z*=1H); IR ν (cm^{-1}): 3069, 2216, 1625, 1285, 775; MS *m/z*: 163 (M^+, 62), 76 (100).

3-pheny)-2-propenenitrile (**3l**): Oil (lit.[14j] oil).^{1}H NMR δ (ppm): 7.50–7.30 (m, 5H), 7.15 (d, *J*=16.8Hz, *E*), 6.70 (d, *J*=12.6Hz, *Z*) (*E*+*Z*=1H), 5.88 (d, *J*=16.8Hz, *E*), 5.20 (d, *J*=12.6Hz, *Z*) (*E*+*Z*=1H); IR ν (cm^{-1}): 3065, 2215, 1622, 1450, 750, 713; MS *m/z*: 129 (M^+, 100), 76 (29).

(E)-3- (4-methylphenyl)-2-propenenitrile (**3m**): m.p. 78–79 °C (lit.[14k] 79–80 °C). ^{1}H NMR δ (ppm): 7.85 (d, 2H, *J*=8.8Hz), 7.56–6.96 (3H, m), 5.77 (d, 1H, *J*=16.4Hz), 2.32 (s, 3H); IR ν (cm^{-1}): 3065, 2217, 1687, 1605, 815, 770; MS *m/z*: 159 (M^+, 100), 77 (33).

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