Study on the stereoselective reactions of vinyl(phenyl)iodonium salts with sodium selenide, sodium sulfide, sodium azide and potassium thiocyanate

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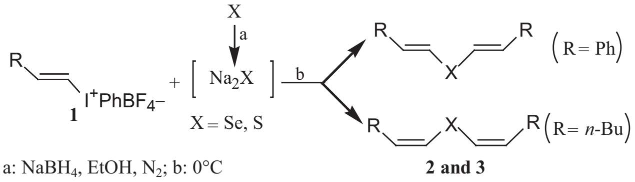
The reactions of vinyl(phenyl)iodonium salts with sodium selenide, sodium sulfide, sodium azide and potassium thiocyanate have been studied. Divinylic selenides, divinylic sulfides, vinylic azides and vinylic thiocyanates were synthesised stereoselectively in good yields.

Keywords: divinylic selenides, divinylic sulfides, vinylic azides, vinylic thiocyanates, vinyl(phenyl)iodonium salts

During the past few years the chemistry of hypervalent iodine compounds has experienced an unprecedented growth.[1] As powerful electrophilic reagents, the hypervalent iodine compounds, in particular, hypervalent iodonium salts have found synthetic applications due to their high reactivity toward various nucleophiles and their ready availability as well as their nontoxic properties. Having the excellent leaving-group ability of the phenyliodanyl group, vinyl(phenyl)iodonium salts can react with a series of nucleophilic reagents under mild conditions and many useful synthetic reactions using vinyl(phenyl)iodonium salts as vinylic synthons have been reported.[2] However, there is not a procedure for the synthesis of divinylic selenides, divinylic sulfides, vinylic azides or vinylic thiocyanates using vinyl(phenyl)iodonium salts. Therefore, in order to extend the usefulness of vinyl(phenyl)iodonium salts and to develop a simple and convenient method for synthesis of divinylic selenides, divinylic sulfides, vinylic azides and vinylic thiocyanates, the reactions of vinyl(phenyl)iodonium salts with sodium selenide, sodium sulfide, sodium azide and potassium thiocyanate have been investigated. We now report a novel and efficient method for the preparation of divinylic selenides, divinylic sulfides, vinylic azides and vinylic thiocyanates with high stereoselectivities.

Following our findings that vinylic selenides and vinylic tellurides can be prepared stereoselectively by the reaction of sodium selenolides and sodium tellurolates with vinyl(phenyl)iodonium salts,[3] we firstly investigated the possibility of extending the Se-vinylation and Te-vinylation reactions to sodium selenide, sodium telluride and sodium sulfide. We found that the reactions of sodium selenide, sodium telluride and sodium sulfide with vinyl(phenyl)iodonium salts readily occurred under mild conditions and gave the expected divinylic selenides and divinylic sulfides in good yields (Table 1). Unfortunately, the reaction products of vinyl(phenyl)iodonium salts with sodium telluride decomposed rapidly under workup and we did not obtain the expected divinylic tellurides.



Scheme 1

Table 1 Divinylic selenides and divinilic sulfides

Products	R	X	Configuration	Yield/%
2a	Ph	Se	*E, E*	82
2b	*n*-Bu	Se	*Z, Z*	78
3a	Ph	S	*E, E*	91
3b	*n*-Bu	S	*Z, Z*	73

There are two kinds of vinyl(phenyl)iodonium salts and *Z*-isomers are unstable. In the reactions, we selected (*E*)-(β-phenylvinyl)phenyliodonium tetrafluoroborate and (*E*)-(β-*n*-butylvinyl) phenyliodonium tetrafluoroborate[4] as the representatives of vinyl(phenyl)iodonium salts and two different stereochemical results were obtained. It was found that the reactions of (*E*)-(β-phenylvinyl)phenyliodonium tetrafluoroborate with sodium selenide and sodium sulfide were stereoselective reactions and the products **2a** (*E*, *E*)-divinylic selenide and **3a** (*E*, *E*)-divinylic sulfide were formed with retention of the configuration. However, a different result with complete inversion of the configuration for products **2b** (*Z*, *Z*)-divinylic selenide and **3b** (*Z*, *Z*)-divinylic sufide was obtained after using (*E*)-(β-*n*-butylvinyl)phenyliodonium salt in the reaction. The configurations of products **2** and **3** were assigned using ^1H NMR spectroscopy: the protons of the vinyl group showed a *J* value of 15 Hz for the *E*-isomers, in contrast with 10 Hz for the *Z*–isomers, which were consistent with our previous reports (Scheme 1).[5]

Following the above results, we further checked the reactions of vinyl(phenyl)iodonium salts with sodium azide and potassium thiocyanate, obtaining the expected vinylic azides and vinylic thiocyanates by simple procedures. The products showed that both reactions have different stereoselectivities.

We stirred the mixture of vinyl(phenyl)iodonium salts with a saturated aqueous solution of sodium azide in CH_2Cl_2. It was found that it was only necessary to stir the mixture for a short period of time at r.t. and the reaction afforded (*E*)-vinylic azides **4** after workup and isolation (Scheme 2). Although the reaction mechanism was not clarified, the method gave a novel and simple synthesis of (*E*)-vinylic azides in good yields (Table 2).

Following successful azidation, we then attempted the synthetic approach to vinylic thiocyanates. Under similar reaction conditions we found that the reaction of vinyl(phenyl)iodonium salts with potassium thiocyanate was difficult to achieve. But, after addition of catalytic amount tetrabutylammonium bromide (TBAB) and stirring the mixture for several hours at r.t., the reaction did give the expected vinylic thiocyanates (Table 2). It should be noted that when (*E*)-(β-phenylvinyl)phenyliodonium tetrafluoroborate was used to react with potassium thiocyanate, the product **5a** with retention of configuration was observed. However, complete inversion of configuration was observed during the formation of product **5b** from the (*E*)-(β-*n*-butylvinyl)phenyliodonium salt (Scheme 3).

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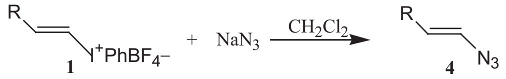
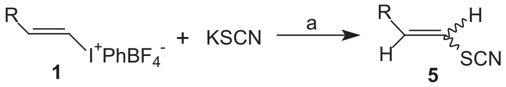


Scheme 2

Table 2 Vinylic azides and vinilic thiocyanates

Products	R	Reaction time/h	Configuration	Yield/%
4a	Ph	0.5	*E*	72
4b	*n*-Bu	0.2	*E*	78
5a	Ph	8	*E*	66
5b	*n*-Bu	2	*Z*	63



a. CH_2Cl_2, H_2O, TBAB

Scheme 2

Divinylic selenides, divinylic sulfides, vinylic azides and vinylic thiocyanates are important compounds of versatile utility[6] as well as theoretical interest.[7] Recently, Silveira *et al.*[8] reported that divinylic selenides were used to undergo direct coupling with terminal alkynes in the presence of a Ni/CuI catalyst to prepare important enyne systems in good yields and with complete retention of configuration. Divinylic selenides could be prepared by the reaction of selenium bisphosphonate with aldehydes.[9,10] There were other methods for preparation of divinylic selenides and divinylic sulfides, in which vinyl halides usually were used as starting materials to react with salts of selenide or sulfide under Pd catalysis.[11-13] Y. Masuda *et al.*[14] recently reported a method for preparation of vinylic azides and vinylic thiocyanates in a one-pot process from alkynes involving hydroboration. Other methods for the synthesis vinylic azides have been reported[15] e.g. from 2-iodoalkyl azides by elimination of hydrogen iodide to form 2-azidoalk-1-enes. The reaction between 1,2-epoxyalkylsilanes and azidotrimethylsilane only gave (*Z*)-vinylic azides,[16] whilst the *E*-isomers were produced in poor yields by the reaction of 1,2-epoxyalkylsilanes with sodium azide.[17] There has been a report about the preparation of (*E*)-vinylic thiocyanates by reaction of (*E*)-alkenylpentafluorosilicates with copper(‖) thiocyanate in DMF.[18] However, using vinyl(phenyl)iodonium salts as starting materials for synthesis of divinylic selenides, divinylic sulfides, vinylic azides and vinylic thiocyanates offers a novel alternative approach.

In summary, we report a novel and efficient method for stereoselective synthesis of divinylic selenides, divinylic sulfides, vinylic azides and vinylic thiocyanates by the reactions of vinyl(phenyl)iodonium salts with sodium selenide, sodium sulfide, sodium azide and potassium thiocyanate. The present reactions have some advantages namely the use of the easily obtainable vinyl(phenyl)iodonium salts, mild reaction conditions, simple operational procedure and good yields. Furthermore, the range of useful application of vinyl(phenyl)iodonium salts as vinylating agents in organic synthesis has been extended.

Experimental

Melting points were determined on a digital m.p. apparatus and were not corrected. IR spectra were recorded on a FT-170 SX instrument, ^1H NMR spectra were measured on a Bruker AM-400 FT-NMR spectrometer, and mass spectra were determined on an HP5989A mass spectrometer. The vinyl(phenyl)iodonium salts were prepared according to the literature procedures.[4] Sodium selenide, sodium sulfide, sodium azide and potassium thiocyanate were commercially available.

The reaction of vinyl(phenyl)iodonium salts with sodium selenide or sodium sulfide, general procedure

Under a N_2 atmosphere, a mixture of selenium powder or sulfur powder (0.25 mmol) and sodium borohydride (0.50 mmol) in anhydrous ethyl alcohol (5 ml) was stirred at room temperature until a light yellow solution was obtained. Then the reaction mixture was cooled to 0°C and a solution of vinyl(phenyl)iodonium tetrafluoroborate **1** (0.5 mmol) in anhydrous ethyl alcohol (2 ml) was added slowly. The reaction was fast and completed immediately (monitored by TLC), sat. aq. NaCl (15 ml) was added to the resulting mixture and which was then extracted with dichloromethane (2×10 ml). The extract was washed with water (10 ml) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subject to preparative TLC on a silica gel plate using hexane as developer to give the pure divinylic selenides **2** or divinylic sulfides **3.**

The reaction of vinyl(phenyl)iodonium salts with sodium azide, general procedure

Sodium azide (0.5 mmol) was dissolved in water (5 ml). Then a solution of vinyl(phenyl)iodonium tetrafluoroborate **1** (0.5 mmol) in dichloromethane (5 ml) was added slowly at room temperature. The reaction was fast and completed in about 0.5 h (monitored by TLC). After reaction was finished, sat. aq. NaCl (15 ml) was added and the resulting mixture was extracted with dichloromethane (2×10 ml). The extract was washed with water (10 ml) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subject to preparative TLC on a silica gel plate using hexane as developer to give the pure vinylic azides **4**.

The reaction of vinyl(phenyl)iodonium salts with potassium thiocyanate, general procedure

Potassium thiocyanate (0.6 mmol) was dissolved in water (5 ml). Then a solution of vinyl(phenyl)iodonium tetrafluoroborate **1** (0.5 mmol) in dichloromethane (5 ml) and phase transfer catalyst TBAB (0.02 mmol) were added at room temperature. The mixture was stirred until the reaction was completed (monitored by TLC). After reaction was finished, sat. aq. NaCl (15 ml) was added and the resulting mixture was extracted with dichloromethane (2×10 ml). The extract was washed with water (10 ml) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subject to preparative TLC on a silica gel plate using hexane as developer to give the pure vinylic thiocyanates **5**.

(E, E)-Distyryl selenide (**2a**): M.p. 42–43°C (Lit.[10] 43–44°C). ^1H NMR ($CDCl_3$): $\delta = 6.75$ (d, $J = 15$ Hz, 2H,), 7.10–7.50 (m, 12H); IR (film, cm^{-1}): 3040, 1580, 1480, 950, 730, 685; EI-MS (*m/z*, %): 286 (M^+, 42.8), 183 (100); HRMS calcd for $C_{16}H_{14}Se$ 286.0261, found 286.0235.

(Z,Z)-Di-hex-1-enyl selenide (**2b**): Oil. ^1H NMR ($CDCl_3$): $\delta = 0.95$ (t, $J = 6$ Hz, 6H), 1.16–1.60 (m, 8H), 1.90–2.37 (m, 4H), 5.60–6.00 (m, 2H), 6.41 (d, $J = 10$ Hz, 2H); IR (film, cm^{-1}): 3020, 1620, 1465, 1320; EI-MS (*m/z*, %): 246 (M^+, 5.3), 57 (100); HRMS calcd for $C_{12}H_{22}Se$ 246.0887, found 246.0843.

(E,E)-Distyryl sulfide (**3a**): Oil[12]. ^1H NMR ($CDCl_3$): $\delta = 6.77$ (d, $J = 15$ Hz, 2H), 7.01–7.42 (m, 12H); IR (film, cm^{-1}): 3040, 1580, 1480, 950, 725, 685; EI-MS (*m/z*, %): 238 (M^+, 41.2), 103 (100); HRMS calcd for $C_{16}H_{14}S$ 238.0816, found 238.0801.

(Z,Z)-Di-hex-1-enyl sulfide (**3b**): Oil. ^1H NMR ($CDCl_3$): $\delta = 0.93$ (t, 6H, $J = 6$ Hz), 1.16–1.67 (m, 8H), 1.95–2.40 (m, 4H), 5.70-5.91 (m, 2H), 6.13 (d, 2H, $J = 10$ Hz); IR (film, cm^{-1}): 3020, 1595, 1470, 1320; EI-MS (*m/z*, %): 198 ($M^{+,}$ 83.7), 83 (100); HRMS calcd for $C_{12}H_{12}S$ 198.1442, found 198.1433.

(E)-Styryl azide (**4a**): Oil[14]. ^1H NMR ($CDCl_3$): $\delta = 6.08$ (d, $J = 14$ Hz, 1H), 6.48 (d, $J = 14$ Hz, 1H), 7.10–7.13 (m, 5H); IR (film, cm^{-1}): 3020, 2105, 1650, 1460, 1270, 930, 750, 690; EI-MS (*m/z*, %): 145 (M^+, 27.1), 103 (100); HRMS calcd for $C_8H_7N_3$ 145.0640, found 145.0621.

(E)-Hex-1-enyl azide (**4b**): Oil.[14] ^1H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6$ Hz, 3H), 1.07–1.48 (m, 4H), 1.70–2.20 (m, 2H), 4.83–5.40 (m, 1H), 5.63 (d, $J = 13$ Hz, 1H); IR (film, cm^{-1}): 3020, 2115, 1670, 1580. 1480, 1260, 940; EI-MS (*m/z*, %): 125 (M^+, 18.3), 57 (100); HRMS calcd for $C_6H_{11}N_3$ 125.0953, found 125.0911.

(E)-Styryl thiocyanate (**5a**): Oil.[14] ^1H NMR ($CDCl_3$): $\delta = 6.36$ (d, $J = 15$ Hz, 1H), 6.93 (d, $J = 15$ Hz, 1H), 7.27–7.31 (m, 5H); IR (film, cm^{-1}): 3040, 2160, 1630, 1460, 950, 740, 690; EI-MS (*m/z*, %): 161 (M^+, 100); HRMS calcd for C_9H_7NS 161.0299, found 161.0278.

(Z)-Hex-1-enyl thiocyanate (**5b**): Oil. ^1H NMR ($CDCl_3$): $\delta = 0.90$ (t, $J = 6$ Hz, 3H), 1.13–1.57 (m, 4H), 1.93–2.43 (m, 2H), 5.87–6.02

(m, 1H), 6.04 (d, $J = 10$ Hz, 1H); IR (film, cm^{-1}): 3040, 2170, 1630, 1480, 1320, 750; EI-MS (m/z, %): 141 (M$^+$, 20.2), 57 (100); HRMS calcd for $C_7H_{11}NS$ 141.0612, found 141.0588.

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