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Hypervalent Iodine in Synthesis 44: Stereoselective Synthesis of Vinylic Selenides by the Reaction of Sodium Selenolates with Vinyl (Phenyl) Iodonium Salts

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HYPERVALENT IODINE IN SYNTHESIS 44: STEREOSELECTIVE SYNTHESIS OF VINYLIC SELENIDES BY THE REACTION OF SODIUM SELENOLATES WITH VINYL (PHENYL) IODONIUM SALTS

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Abstract: Vinylic selenides have been prepared stereoselectively by the reaction of sodium selenolates with vinyl(phenyl)iodonium salts with retention or inversion of the configurations.

In recent years, vinylic selenides have been received much attention because of their special reactivity of selenium and the promising valuable application in organic synthesis[1,2]. Many methods exist for the synthesis of vinylic selenides, they can be prepared with acetylenes, acetylenic selenides, seleno ketals, olefins and vinyl halides as starting materials[1-3]. However, using vinyl(phenyl)iodonium salts as starting materials for synthesis of vinylic selenides has not been reported. The versatility of vinyl(phenyl)iodonium salts in organic synthesis has been recognized[6]. They serve as vinyl cation equivalent species and react readily with

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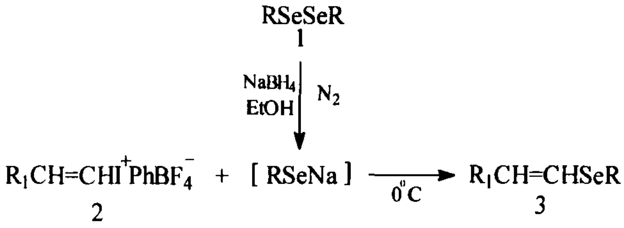
a wide range of nucleophiles, such as lithium dibutylcuprate, potassium cyanide, potassium halides, potassium 2-hexyl-1,3-indanedionate, sodium phenylthiolate and so on and a variety of substituted olefins were synthesized[6]. In order to increase the synthetic utility of this important class of compounds furthermore, we selected sodium selenolates as nucleophiles to examine their reactivity with vinyl(phenyl)iodonium salts. We found the reaction readily occurred in mild conditions and gave the expected vinylic selenides, which afforded a convenient method for synthesis of vinylic selenides.

Because of the exceptional propensity to oxidation of selenolates, we prepared them by reduction of the corresponding diselenides and used them immediately in the reaction under an inert N_2 atmosphere. Stirring of the diselenide (1) with sodium borohydride in ethyl alcohol for a short time, then adding the vinyl(phenyl)iodonium salt (2), gave the corresponding vinylic selenide (3) immediately (Scheme 1). The products were characterized by IR, ^{1}H-NMR, and MS, and the experimental results are summarized in Table 1.

We selected (E)-(β-phenylvinyl)phenyliodonium tetrafluoroborate and (E)-(β-n-butylvinyl)phenyliodonium tetrafluoroborate[7] as the representatives of vinyl-(phenyl)iodonium salts in the reaction. Two different kinds of result were obtained. When we used (E)-(β-phenylvinyl)phenyliodonium tetrafluoroborate, the products 3 with retention of the configuration were observed, which probably via an addition-elimination or a ligand coupling mechanism according to Ochiai[8,9]. However, the different result with complete inversion of the configuration for products 3 was obtained for using (E)-(β-n-butylvinyl)phenyliodonium salt in the reaction, probably via a S_N2 transition state[9]. The configurations of products 3



$$\begin{array}{c} \text{RSeSeR} \\ \mathbf{1} \end{array} \xrightarrow[\text{EtOH}]{\text{NaBH}_4,\ \text{N}_2} [\text{RSeNa}]$$

$$\underset{\mathbf{2}}{\text{R}_1\text{CH=CHI}^{+}\text{PhBF}_4^{-}} + [\text{RSeNa}] \xrightarrow[0^{\circ}\text{C}]{} \underset{\mathbf{3}}{\text{R}_1\text{CH=CHSeR}}$$

Scheme 1

Table 1. Vinylic Selenides 3

Product	R	R_1	Configuration	Yield(%)
3a	Ph	Ph	E	65
3b	p-ClC_6H_4	Ph	E	51
3c	p-MeC_6H_4	Ph	E	55
3d	p-$MeOC_6H_4$	Ph	E	62
3e	$PhCH_2$	Ph	E	58
3f	Ph	n-Bu	Z	57
3g	p-ClC_6H_4	n-Bu	Z	63
3h	p-MeC_6H_4	n-Bu	Z	64

were assigned using ^{1}H-NMR spectroscopy: the protons of vinyl showed a J of 15Hz for the E-isomers, in contrast with 10Hz for the Z-isomers.

In conclusion, we found a novel and convenient method for stereoselective synthesis of vinylic selenides. Mild reaction conditions, simple operation and good yields make it attractive. Furthermore, the range of useful application of vinyl(phenyl)iodonium salts as vinylating agents in organic synthesis has been extended.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on PMX-60 Spectrometer, using CCl_4 as the solvent with TMS as an internal standard. IR spectra were determined on PE-683 Spectrophotometer. Mass spectra were measured on a HP5989B mass spectrometer.

General procedure for synthesis of vinyl selenides 3

Under N_2 atmosphere, a mixture of appropriate diselenide (1) (0.2 mmoL) and sodium borohydride (0.41 mmoL) in ethyl alcohol (5 mL) was stirred at room temperature until the yellow color disappeared. Then, the reaction mixture was cooled to 0°C, a solution of vinyl(phenyl)iodonium tetrafluoroborate (2) (0.4 mmoL) in ethyl alcohol (2 mL) was added slowly. The reaction was fast and complete immediately (monitored by TLC), water (10 mL) was added to the resulting mixture and extracted with dichloromethane (2×10 mL). The extract was washed with water (10 mL) and dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica gel plate using hexane as developer to give the pure vinyl selenides 3

3a[10]**:** oil, IR(film)ν: 3040, 1580, 1460, 950, 725, 685cm^{-1}. ^{1}H-NMR δ: 6.75 (1H, d, J=15Hz), 7.00-7.60 (11H, m).

3b[11]**:** m.p. 50-52°C, IR(KBr)ν: 3020, 1595, 1480, 1090, 950, 810, 730, 690 cm^{-1}. ^{1}H-NMR δ: 6.87 (1H, d, J=15Hz), 7.06 (1H, d, J=15Hz), 7.15-7.67 (9H, m). MS, m/z: 294 (M$^+$, 100).

3c: oil, IR(film)ν: 3040, 1595, 1490, 945, 800, 730, 685cm^{-1}. ^{1}H-NMR δ: 2.38 (3H, s), 6.61 (1H, d, J=15Hz), 6.80 (1H, d, J=15Hz), 7.00-7.51 (9H, m). MS, m/z: 274 (M$^+$, 21.8), 194 (100).

3d: oil, IR(film)ν: 3020, 2850, 1595, 1480, 1250, 940, 820, 730, 685cm^{-1}. ^{1}H-NMR δ: 3.80 (3H, s), 6.53 (1H, d, J=15Hz), 6.90 (1H, d, J=15Hz), 7.00-7.53 (9H, m). MS, m/z: 290 (M$^+$, 31.9), 210 (100).

3e: oil, IR(film)ν: 3050, 1610, 1465, 950, 730, 690cm^{-1}. ^{1}H-NMR δ: 3.93 (2H, s), 6.60 (1H, d, J=15Hz), 7.00-7.40 (11H, m). MS, m/z: 274 (M$^+$, 33.5), 91 (100).

3f[12]**:** oil, IR(film)ν: 3040, 1590, 1450, 730, 690, 665cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, t, J=6Hz), 1.20-1.66 (4H, m), 2.00-2.40 (2H, m), 5.90-6.30 (1H, m), 6.41 (1H, d, J=10Hz), 7.00-7.55 (4H, m).

3g: oil, IR(film)ν: 3020, 1620, 1485, 1345, 1090, 810, 670cm^{-1}. ^{1}H-NMR δ: 0.98 (3H, t, J=6Hz), 1.20-1.65 (4H, m), 1.95-2.45 (2H, m), 5.85-6.30 (1H, m), 6.38 (1H, d, J=10Hz), 7.10-7.50 (4H, m). MS, m/z: 274 (M$^+$, 29.1), 57 (100).

3h: oil, IR(film)ν: 3020, 1640, 1475, 1310, 800cm^{-1}. ^{1}H-NMR δ: 0.97 (3H, t, J=6Hz), 1.18-1.65 (4H, m), 2.00-2.40 (2H, m), 2.35 (3H, s), 5.90-6.25 (1H, m), 6.37 (1H, d, J=10Hz), 7.00 (2H, d, J=8Hz), 7.33 (2H, d, J=8Hz). MS, m/z: 254 (M^+, 100).

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