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HYPERVALENT IODINE IN SYNTHESIS 45: A SIMPLE METHOD FOR STEREOSELECTIVE SYNTHESIS OF VINYLIC TELLURIDES

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

Vinyl(phenyl)iodonium salts have recently drawn increasing attention as synthons of vinyl cations in vinylic nucleophilic substitutions[1]. Following our finding that vinylic selenides can be prepared stereoselectively by the reaction of sodium selenolates with vinyl(phenyl)iodonium salts[2], we investigated the possibility of extending the Se-vinylation reaction to sodium tellurolates. We found the reaction of sodium tellurolates with vinyl(phenyl)iodonium salts readily occurred in mild conditions and gave the expected vinylic tellurides, which afforded a simple method for synthesis of vinylic tellurides.

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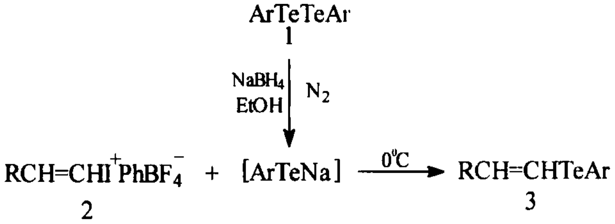
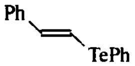
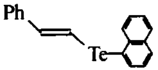
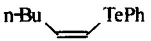
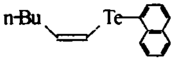
Analogous to Se-vinylation[2], the sodium tellurolates, prepared by reduction of diaryl ditellurides with sodium borohydride were used immediately in the reaction under an inert N_2 atmosphere. Stirring diaryl ditellurides (1) with sodium borohydride in ethyl alcohol for a short time until a light yellow solution was obtained, then adding vinyl(phenyl)iodonium salts (2), gave the corresponding vinylic telluride (3) immediately (Scheme 1). The products were characterized by IR, ^{1}H-NMR and MS as summarized in Table 1.

Scheme 1



We selected (E)-(β-phenylvinyl)phenyliodonium tetrafluoroborate and (E)-(β-n-butylvinyl)phenyliodonium tetrafluoroborate[3] as the representatives of vinyl-(phenyl)iodonium salts in the reaction and 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[4,5]. 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[5]. The configurations of products 3 were assigned using ^{1}H-NMR spectroscopy: the protons of vinyl showed a J of 15Hz for the E-isomers, in contrast with 9Hz for the Z-isomers.

Table 1 Vinylic Tellurides 3

Prodact	Yield[a] (%)	m.p.℃[b] (Lit.)	IR(KBr or film) ν (cm^{-1})[c]	^{1}H-NMR, ppm (CCl$_4$/TMS)[d]	MS, m/z[e]
	52	oil[6]	3040, 1580, 950, 730, 680	6.89 (1H, d, J=15Hz), 7.15-7.80 (11H, m)	
	48	66-67 (68-69)[6]	3030, 1570, 950, 810, 730, 685	3.79 (3H, s), 6.80 (2H, d, J=9Hz), 6.90 (1H, d, J=15Hz), 7.15-7.80 (8H, m)	
	43	oil	3040, 1590, 960, 790, 770, 730, 690	6.95-8.17 (14H, m)	358 (M$^+$,8.85), 360 (M+2, 9.37), 204 (100)
	49	oil[7]	3040, 1590, 730, 680	0.93 (3H, t, J=6Hz), 1.16-1.68 (4H, m), 1.90-2.33 (2H, m), 6.10-6.50 (1H, m), 6.56 (1H, d, J=9Hz), 7.02-7.30 (3H, m), 7.40-7.75 (2H, m)	288 (M$^+$, 64.32), 290 (M+2, 74.01), 117 (100)
	55	oil	3050, 1590, 810, 730, 680	0.97 (3H, t, J=6Hz), 1.17-1.66 (4H, m), 1.90-2.35 (2H, m), 2.36 (3H, s), 5.91-6.13 (1H, m), 6.56 (1H, d, J=9Hz), 6.87 (2H, d, J=8Hz), 7.43 (2H, d, J=8Hz)	302 (M$^+$, 48.57), 304 (M+2, 51.32), 131 (100)
	52	oil	3040, 1590, 810, 730, 685	0.98 (3H, t, J=6Hz), 1.15-1.62 (4H, m), 1.92-2.38 (2H, m), 3.80 (3H, s), 5.91-6.39 (1H, m), 6.60 (1H, d, J=9Hz), 6.90-7.30 (4H, m)	318 (M$^+$, 34.17), 320 (M+2, 37.02), 147 (100)
	51	oil	3040, 1570, 790, 770, 730	0.97 (3H, t, J=6Hz), 1.17-1.66 (4H, m), 1.93-2.40 (2H, m), 5.90-6.40 (1H, m), 6.60 (1H, d, J=9Hz), 7.00-8.13 (7H, m)	338 (M$^+$, 46.90), 340 (M+2, 52.44), 167 (100)

a. Yield of isolated pure product based on (1). b. Melting point is uncorrected. c. IR spectra were determined on a PE-683 spectrometer. d. ^{1}H-NMR spectra were recorded on a PMX-60 spectrometer. e. Mass spectra were measured on a HP5989B mass spectrometer.

In literature a variety of synthetic methods for vinylic tellurides have been reported, such as the reaction of elemental tellurium with acetylenes in basic medium[8], addition of organotelluro radicals to alkynes[9], reduction of acetylenic tellurides[10], nucleophilic substitution of unactivated vinyl halides with tellurolate anions[11] and so on. However, using vinyl(phenyl)iodonium salts as starting materials for synthesis of vinylic tellurides has not been reported. The present method has the advantages of mild reaction conditions, simple operation and easy availability of starting materials. Furthermore, the range of useful application of vinyl(phenyl)iodonium salts as vinylating agents in organic synthesis has been extended.

A general procedure for synthesis of vinylic telurides 3 is as follows:

Under N_2 atmosphere, a mixture of appropriate diaryl ditelluride (1) (0.2 mmoL) and sodium borohydride (0.41 mmoL) in ethyl alcohol (5 mL) was stirred at room temperature until a light yellow color solution was obtained. 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 completed 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 vinylic tellurides 3. All relevant data are summarized in the Table 1.

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