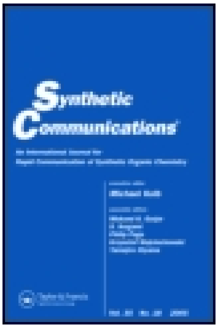

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A Stereoselective Synthesis of (E)-Divinyl Diselenides and (E)-Divinyl Ditellurides

Xian Huang [a] & Jun-Hua Wang [a]

[a] Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou, 310028, P.R., China

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A STEREOSELECTIVE SYNTHESIS OF (E)-DIVINYL DISELENIDES AND (E)-DIVINYL DITELLURIDES

Xian Huang* and Jun-Hua Wang

Department of Chemistry, Zhejiang University (Campus Xixi),
Hangzhou, 310028, P. R. China

Abstract: Insertion of elemental selenium or tellurium into the Csp^2-Zr bond of alkenylchlorozirconocenes followed by oxidation in air affords (E)-divinyl diselenides or (E)-divinyl ditellurides.

Although symmetrical diaryl- and dialkyl diselenides[1] or ditellurides[2] have become important synthetic reagents, divinyl diselenides[3] and divinyl ditellurides[4] are poorly described compounds, probably due to difficulties in their preparations. Recently we developed a novel methodology which involved the insertion of elemental selenium or tellurium into the Csp^2-Zr bond of alkenylchlorozirconocenes derived from hydrozirconation of alkynes, affording vinylseleno- or vinyltelluro zirconocenes as active intermediates. This method has been applied to the stereoselective synthesis of vinylic selenides and tellurides.[5]

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* To whom correspondence should be addressed.

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Given the promising synthetic potential which could be anticipated by the combination of the reactivity of diselenides or ditellurides and the reactivity associated with carbon-carbon double bond, herein we report a stereoselective synthesis of (E)-divinyl diselenides and (E)-divinyl ditellurides from alkynes and elemental selenium or tellurium.

Insertion of elemental selenium into the Csp^2-Zr bond of alkenylchlorozirconocenes proceeded smoothly in THF at room temperature and was usually complete in 30 minutes. In contrast to selenium, insertion of elemental tellurium into the Csp^2-Zr bond of alkenylchlorozirconocenes did not take place until the temperature of the reaction mixture was raised to 55℃ or so. The intermediate vinylseleno- or vinyltelluro zirconocenes in THF were exposed to air and formed (E)-divinyl diselenides or (E)-divinyl ditellurides, respectively. The results are summarized in the table.

The hydrozirconation reaction[6] is well-known for its excellent stereoselectivity, good yields and mild conditions. In addition to the 1-alkynes employed here, various internal alkynes and functionalized alkynes can undergo hydrozirconation reactions smoothly and stereoselectively. As a result, the present method provides a practical, stereoselective approach to various divinyl diselenides and divinyl ditellurides.

Experimental Section

IR spectra were recorded on a PE-683 spectrometer, and ^{1}H-NMR spectra were recorded on a JEOL-PMX60 spectrometer in CCl_4 solution using hexamethyldisilane as internal standard. MS were obtained on a HP5989B spectrometer. Melting points were not corrected. THF was newly distilled from sodium/benzophenone before use. $Cp_2Zr(H)Cl$ was prepared according to the literature procedure.[7]

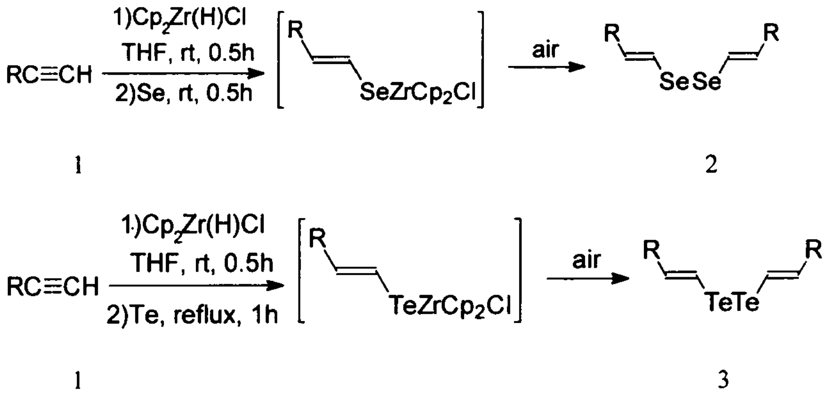
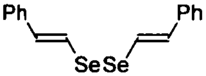
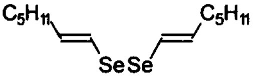
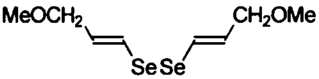
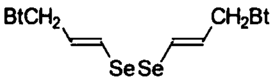
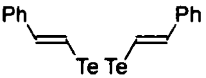
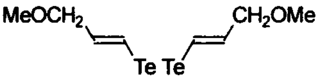


FIG. 1

Table Stereoselective synthesis of (E)-divinyl diselenides and ditellurides.

Entry	RC≡CH R	Se or Te	Products	Yields (%)[a]
2a	Ph	Se		74
2b	n-C_5H_{11}	Se		75
2c	$MeOCH_2$	Se		72
2d	$BtCH_2$[b]	Se		67
3a	Ph	Te		71
3b	$MeOCH_2$	Te		73

[a] Isolated yields. [b] Bt=benzotriazol-1-yl.

Typical procedure for divinyl diselenides: To a stirred suspension of $Cp_2Zr(H)Cl$ (0.308g, 1.2mmol) in THF (8ml) under N_2 atmosphere was added phenylacetylene (0.102g, 1mmol). The mixture was stirred until it turned into a clear solution, then was transferred *via* a syringe into a stirred suspension of elemental selenium (0.080g, 1mmol) in THF (2ml). The mixture turned gradually into a deep red solution, then was exposed to air at 0℃ for 0.5h followed by treatment with water (0.2ml) at the same temperature. The mixture was stirred for another 1h. The solvent was evaporated under reduced pressure, and the residue was extracted with Et_2O (4x10ml). The organic layer was dried with anhydrous $MgSO_4$ and evaporated. The residue was purified by preparative thin layer chromatography eluted with light petroleum ether-diethyl ether (10:1), affording 2a.

2a: [3b] Orange solid, mp56-58℃(lit.[3b] 62-64℃). ^{1}H-NMR: δ7.40-6.95(m, 6H), 6.78(d, J=16Hz, 1H). IR: ν_{max}(cm^{-1}) 3088, 3060, 1616, 1588, 1510, 952, 735, 690.

2b: Yellow oil. ^{1}H-NMR: δ6.50(d, J=15.6Hz, 1H), 5.80(dt, J=15.6 and 6.0Hz, 1H), 2.0(t, J=6.0Hz, 2H), 1.30(m, 6H), 0.90(t, J=4.6Hz, 3H). IR: ν_{max}(cm^{-1}) 3010, 1632. MS(m/z): 354(m$^+$, ^{80}Se), 314, 274, 231, 177, 147, 95. Anal. calcd for $C_{14}H_{26}Se_2$: C, 47.46; H, 7.34. Found: C, 47.71; H, 7.58.

2c: Yellow oil. ^{1}H-NMR: δ6.65(d, J=15.2Hz, 1H), 6.0(dt, J=15.2 and 5.4 Hz, 1H), 3.90(d, J=5.4Hz, 2H), 3.25(s, 3H). IR: ν_{max}(cm^{-1}) 3010, 1632. MS(m/z): 302(m$^+$, ^{80}Se), 224, 150. Anal. calcd for $C_8H_{14}O_2Se_2$: C, 31.79; H, 4.64. Found: C, 32.01; H, 4.74.

2d. Yellow solid, mp 156-160(dec.). ^{1}H-NMR: δ8.12-7.78(m, 1H), 7.70-7.02(m, 3H), 6.54(d, J=15.0Hz, 1H), 6.02(dt, J=15.0 and 6.0Hz, 1H), 5.20(d, J=6.0Hz, 2H). IR: ν_{max}(cm^{-1}) 1634, 1612, 1510, 1330, 1302, 1250, 1230, 952, 786, 760, 736. MS(m/z): 476(m$^+$, ^{80}Se), 396, 316, 277, 158, 119. Anal. calcd for $C_{18}H_{16}N_6Se_2$: C, 45.38; H, 3.36; N, 17.65. Found: C, 45.26; H, 3.33; N, 17.70.

Typical procedure for divinyl ditellurides: To a stirred suspension of $Cp_2Zr(H)Cl$ (0.308g, 1.2mmol) in THF (10ml) under N_2 atmosphere was added phenylacetylene (0.102g, 1mmol). The mixture was stirred until it turned into a clear solution, then elemental tellurium (0.127g, 1mmol) was added. Under refluxing the mixture turned gradually into a deep red solution, then was exposed to air at 0℃ for 0.5hr, followed by treatment with water (0.2ml) at the same temperature. The mixture was stirred for another 1h. The solvent was evaporated under reduced pressure, and the residue was extracted with Et_2O (4x10ml). The organic layer was dried with anhydrous $MgSO_4$ and evaporated. The residue was purified by preparative thin layer chromatography eluted with light petroleum ether-diethyl ether (12:1), affording 3a.

3a:[4b] Brown solid, mp 80-82℃. ^{1}H-NMR: δ7.58(d, J=16.0Hz, 1H), 7.40-7.0(m, 5H), 6.98(d, J=16.0Hz, 1H). IR: $\nu_{max}(cm^{-1})$ 3050, 1650, 1612, 1504, 964, 760, 736, 690,. MS(m/z): 464(m^+), 334, 206, 103.

3b: Brown oil. ^{1}H-NMR: δ6.90(d, J=16.0Hz, 1H), 6.12(dt, J=16.0 and 5.0Hz, 1H), 3.92(d, J=5.0Hz, 2H), 3.20(s, 3H). IR: $\nu_{max}(cm^{-1})$ 3010, 1615. MS(m/z): 398(m^+), 270, 141, 71. Anal. calcd for $C_8H_{14}O_2Te_2$: C, 24.24; H, 3.54. Found: C, 24.50; H, 3.71.

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