SHORT PAPER

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Stereoselective synthesis of (*Z*)-ketene selenothioacetals *via* hydrozirconation of alkylacetylenic selenides†

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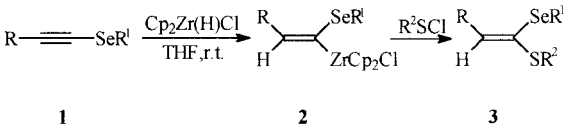
Hydrozirconation of internal acetylenic selenides afforded (*E*)-α-zirconated vinylic selenide intermediates, which react with alkylsulfenyl chlorides to give (*Z*)-ketene slenothioacetals in good uield.

Keywords: Hydrozirconation of internal acetylenic selenides

Organoselenium chemistry is of current interest from a synthetic and structural point of view.[1] Recently, many 1,1-, or 1,2-bimetalloalkenes have been used in the stereoselective syntheis of trisubstituted alkenes. However, there are only a rew reports on the preparation of ketene selenothioacetals.[2–4] The alkylation of Se-alkyl carboxylic thionoselenoesters enethiolates lead to a mixture of (*E*)- and (*Z*)-ketene thioselenoacetals.[2] The reaction of lithium alkyneselenolates gave rise to lithium eneselenolates, which were trapped with alkyhalides to afford (*Z*)-ketene selenothiothiacetals, whereas trapping with allylic bromides yielded γ,δ-unsaturated seleothioesters *via* a seleno-Claisen rearrangement.[3] Selenothioic acid *S*-alkyl eesters were treated with Et_3N and $Cd(OAc)_2{\cdot}2H_2O$ to give symmetrically substituted seleophenes, whereas the similar reaction in the presence of alkyl halides afforded ketene selenothioacetals.[4] In this paper, we have studied the hydrozirconation of internal acetylenic sleenides, in order to develop a new method for stereoselective synthesis of (*Z*)-ketene thioselenoactals.

Internal acetylenic selenides react with $Cp_2Zr(H)Cl$[5] in THF at room temperature to give the α-zirconated vinyl selenides **2**,[6,7] which afford (*Z*)-ketene selenothioacetals **3** in good yields when treated with alkyl sulfenyl chlorides.[8]



1 **2** **3**

R = Ph, n-C_6H_{13}; R^1 = CH_3, CH_3CH_2, i-Bu; R^2 = CH_3, CH_3CH_2, i-Bu, PhCH2

Scheme 1

The compounds **3a**[2], **3b**[3], **3c**, **3d**[3], **3e**[2], **3f**[2], **3g**[2] and **3h**[2] were purified by preparative TLC on silica gel and fully characterised by ^{1}H NMR spectroscopy.

In summary, the present reaction provides a new synthetic route to (*Z*)-ketene selenothioacetals. Further synthetic applications of (*Z*)-ketene selenothioacetals are in progress.

Experimental

^{1}H NMH spectra were recorded on Bruker AC-300 spectrometer in $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra were detemined using a PE-683 as neat films. Mass spectra were obtained on Finigan 8230 mass spectrometer. Silica gel 60 GF_{254} was used for analytical and preparative TLC. All reactions were carried out in pre-dried glassware (150°C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. Internal acetylenic slenides and alkyl sulfenyl chlorides were prepared according to the literature methods.[9,8]

General procedure for the synthesis of **3a–f**: A mixture of $Cp_2Zr(H)Cl$[5] (1 mmol) and terminal alkyne **1** (1 mmol) in THF (5 ml) was stirred at room temperature for 30 min. The resulting solution was cooled to 0°C and into it was injected freshly prepared R^2SCl[8] (1 mmol). The mixture was stirred at room temperature for 30 min and the solvent was removed subsequently under reduced presure. The residue was extracted with light petroleum (3 × 6 ml) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel using light petroleum as eluent.

Table 1 Synthesis of (*Z*)-ketene selenothioacetals **3**

Entry	R	R^1	R^2	Yield[a]/%
3a	Ph	CH_3	CH_3	79
3b	Ph	CH_3	*i*-Bu	73
3c	Ph	CH_3	$PhCH_2$	81
3d	Ph	CH_2CH_3	*i*-Bu	73
3e	Ph	*i*-Bu	CH_3	69
3f	*n*-C_6H_{13}	CH_3	CH_3	76
3g	*n*-C_6H_{13}	CH_3	CH_2CH_3	71
3h	*n*-C_6H_{13}	CH_3	$PhCH_2$	82

[a]Isolated yield.

3a: Oil. IR (film): ν = 2978, 2953, 2872, 1610, 1550, 1495, 1270, 1242, 1065, 1020, 915, 750, 685; ^{1}H NMR ($CDCl_3$): δ = 7.50–7.20 (m, 5H), 6.90 (s, 1H, PhC*H*), 2.41 (s, 3H, SCH_3), 2.21 (s, 3H, SeCH_3); MS: *m/z* =244 (M^+). Anal. Calcd. for $C_{10}H_{12}SSe$: C, 49.18; H, 4.92; Found C, 49.48, H, 4.93.

3b: Oil. IR (film): ν = 2957, 2927, 2870, 1598, 1560, 1492, 1265, 1240, 1075, 1030, 920, 750, 690. ^{1}H NMR ($CDCl_3$): δ = 7.53–7.20 (m, 5H), 7.10 (s, 1H, PhC*H*), 2.70 (d, *J* = 6.8 Hz, 2H, SCH_2) 2,20 (s, 3H, SeCH_3), 1.93 (q, *J* = 6.7 Hz, 1H, C*H*Me_2), 1.05 (d, *J* = 6.7 Hz, 6H, CH_3). MS: *m/z* = 286 (M^+). Anal. Calcd. for $C_{13}H_{18}SSe$: C, 54.55; H, 6.29; Found C, 54.45, H, 6.31.

3c: Oil. IR (film): ν = 3050, 2960, 2955, 1665, 1605, 1550, 1500, 1450, 1020, 750, 690; ^{1}H NMR ($CDCl_3$); δ = 7.50–716 (m, 10H), 7.05 (s, 1H, PhC*H*), 3.97 (s, 2H, SCH_2), 2.30 (s, 3H, SeCH_3); *m/z* = 320 (M^+). Anal. Calcd. for $C_{16}H_{16}SSe$: C, 60.00; H, 5.00; Found C, 60.01, H, 5.02.

3d: Oil. IR (film) ν = 3055, 3020, 2960, 2920, 2860, 1655, 1600, 1560, 1485, 1030, 746, 695. ^{1}H NMR ($CDCl_3$); δ = 7.50–7.20 (m, 5H), 7.10 (s, 1H, PhC*H*), 2.83 (q, *J* = 7.5 Hz, 2H, SeCH_2), 2.73 (d, *J* = 6.8 Hz, 2H, SCH_2), 1.90 (q, *J* = 6.6 Hz, 1H, C*H*Me_2), 1.36 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.05 (d, *J* = 6.6 Hz, 6H, CH_3). MS: *m/z* = 300 (M^+). Anal. Calcd. for $C_{14}H_{20}SSe$: C, 56.00; H, 6.67. Found C, 56.29, H, 6.78.

3e: Oil. IR (film): ν = 2960, 2930, 2870, 1650, 1600, 1555, 1505, 1490, 1265, 1025, 920, 750, 690. ^{1}H NMR ($CDCl_3$): δ = 7.55–7.20 (m, 5H), 7.05 (s, 1H, PhC*H*), 2.72 (d, *J* = 6.8 Hz, 2H, SeCH_2), 2.40

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(s, 3H, SCH_3), 1.88 (q, J = 6.6 Hz, 1H, CHMe$_2$), 1.00 (d, J = 6.5 HZ, 6H, CH_3); MS: m/z = 286 (M^+). Anal. Calcd. for $C_{13}H_{18}SSe$: C, 54.55; H, 6.29. Found C, 54.33, H, 6.38.

3f: Oil. IR (film): ν = 2930, 2860, 1610, 1550, 1385, 1270, 1242, 920, 780, 680; ^{1}H NMR ($CDCl_3$) δ = 6.50 (t, J = 6.0 Hz, 1H, C = CH), 240 (s, 3H, SCH_3), 2.20 (s, 3H, SeCH_3), 2.10 (m, 2H), 1.50–0.90 (m, 11H); MS: m/z = 252 (M^+). Anal. Calcd. for $C_{10}H_{20}SSe$: C, 47.62; H, 7.94. Found C, 48.16, H, 7.97.

3g: oil. IR (Film): ν = 2925, 2865, 1605, 1555, 1382, 1280, 1240, 925, 790, 680; ^{1}H NMR ($CDCl_3$) δ = 6.47 (t, J = 6.0 Hz, 1H, C = CH, 2.70 (q, J = 6.5 Hz, 2H, SCH_2), 2.25 (s, 3H, SeCH_3), 2.10 (m, 2H), 1.55–0.95 (m, 14 H); MS: m/z = 266 (M^+). Calcd. for $C_{11}H_{22}SSe$: C, 49.62; H, 8.27. Found C, 49.97, H, 8.30.

3h: Oil. IR (film): ν = 3040, 2950, 2875, 1645, 1600, 1550, 1500, 1450, 1030, 750, 693; ^{1}H NMR ($CDCl_3$): δ = 7.50–7.18 (m, 5H), 6.55 (s, 1H, J = 6.0 Hz, 1H, C = CH), 3.95 (s, 2H, SCH_2), 2.25 (s, 3H, SeCH_3), 2.10 (m, 2H), 1.55–0.95 (m, 11 H); m/z = 328 (M^+). Anal. Calcd. for $C_{16}H_{24}SSe$: C, 58.54; H, 7.32; Found C, 58.41, H, 7.32.

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