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A novel method for the synthesis of (*Z*)-α-selenyl-α,β-unsaturated ketones via acylation of (*E*)-α-selanylvinylstannanes

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Abstract

The (*E*)-α-selenylvinylstannanes react with acyl halides in presence of a catalytic amount of $Pd(PPh_3)_4$ to give the corresponding (*Z*)-α-selenyl-α,β-unsaturated ketones in good yield. © 1999 Elsevier Science S.A. All rights reserved.

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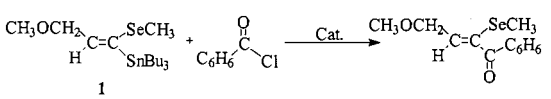
1. Introduction

A variety of synthetic methods for the syntheses of α,β-unsaturated ketones have been reported. Of these methods, the aldol condensation is one of the most powerful synthetic tools for them [1]. The Friedel–Crafts reaction of acyl chlorides, acids, or anhydrides with olefins is also an important route to the α,β-unsaturated ketones [2]. The hydrozirconation of acetylenes, followed by aluminium chloride promoted acylation of the resulting vinylzirconium compounds, has been added to the list to important methods for preparing α,β-unsaturated ketones [3]. However, the synthesis of heteroatom-containing α,β-unsaturated ketones has scarcely been addressed. The vinyl copper reagents, which were generated by cuprate reduction of α-alkoxycarbonylketene dithioacetals, can be acylated in good yields to methylthio α,β-unsaturated ketones [4]. Sung described that hydrozirconation of acetylenic tellurides, followed by the reaction with acyl halides in the presence of CuI, afforded organotelluro-α,β-unsaturated carbonyl compounds [5]. It is well known that α,β-unsaturated ketones are one of the most widely used synthetic building blocks and the organoselenium compounds are playing an increasing important role in organic syntheses [6]. Therefore, introducing organoselenium compounds into α,β-unsaturated ketones is potentially very significant. Our research group has reported a procedure based on α-phenylselanyl arsonium ylides which undergo Wittig-type reactions with carbonyl compounds, leading to the expected α-selenyl-α,β-unsaturated compounds with high steroselectivity [7]. Besides, (*Z*)-β-selenyl-α,β-unsaturated ketones have been produced by selenocarbonylation addition reaction of selenoesters to nonactivated terminal alkynes. These reactions are catalyzed by CuX with high selectivities and good yields [8]. Herein we describe a coupling reaction between (*E*)-α-selenylvinylstannanes and acyl halides in the presence of catalytic amounts of $Pd(PPh_3)_4$ to give (*Z*)-α-selenyl-α,β-unsaturated ketones.

Palladium-catalyzed hydrostannation of alkynes provides a simple general route for the synthesis of vinylstannanes [9]. Vinylstannanes are pivotal intermediates in a wide range of carbon–carbon bond-forming reactions [10]. Thus recently the hydrostannation of acetylenic selenides to afford (*E*)-α-selenylvinylstannanes have been described [11]. (*E*)-α-selenylvinylstannanes, which are convenient precursors were used for the stereoselective synthesis of trisubstituted alkenes



Scheme 1.

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Table 1
Effect of catalyst, temperature, time and solvents on the coupling reaction of substrate 1 with benzyl chloride

Catalyst [a]	Additive [b]	Solvent	Temperature (°C)	Reaction time (h)	Yield (%) [d]
$PdCl_2(PPh_3)_2$	CuI	DMF	r.t.(or 65°C)	72	0
$PdCl_2(PPh_3)_2$	CuI	C_6H_6	r.t. (or reflux)	72	0
$PdCl_2(PPh_3)_2$	CuI	C_6H_6	120 (sealed tube)	72	32
$PdBnCl(PPh_3)_2$	CuI	DMF	r.t. (or 65°C)	72	0
$PdBnCl(PPh_3)_2$	CuI	THF	120 (sealed tube)	72	Trace
$PdBnCl(PPh_3)_2$	CuI	C_6H_6	120 (sealed tube)	72	45
$Pd(PPh_3)_4$	CuI	DMF	r.t. (or 65°C)	72	0
$Pd(PPh_3)_4$	CuI	THF	120 (sealed tube)	72	0
$Pd(PPh_3)_4$	CuI	C_6H_6	r.t. (or reflux)	72	0
$Pd(PPh_3)_4$	CuI	CH_2Cl_2	120 (sealed tube)	72	0
$Pd(PPh_3)_4$		C_6H_6	120 (sealed tube)	72	63
$Pd(PPh_3)_4$	CuI	C_6H_6	120 (sealed tube)	72	80
$Pd(PPh_3)_4$	CuI	C_6H_6	120 (sealed tube)	4	73
$Pd(PPh_3)_4$	CuI	C_6H_6	120 (sealed tube)	7	82
$Pd(PPh_3)_4$	CuI [c]	C_6H_6	120 (sealed tube)	7	81
	CuI	C_6H_6	120 (sealed tube)	72	0

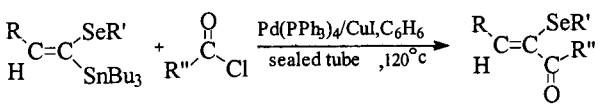
[a] 5 mol% of Pd $(PPh_3)_4$ was used.
[b] 0.75 (equiv.) CuI was used.
[c] 1 mmol CuI was used.
[d] Isolated yield.

[12]. The coupling reaction of (*E*)-α-selenylvinylstannanes with vinylic halides was conducted in the presence of a palladium-copper cocatalyst and gave β-selenyl substituted 1,3-dienes [13]. With the extended application of the (*E*)-α-selenylvinylstannanes in organic synthesis, we attempted to carry out the coupling reaction of (*E*)-α-selenylvinylstannanes with acyl halides in the presence of a palladium(0) catalyst.

2. Results and discussion

It was found that the reaction of (*E*)-α-selenylvinylstannanes with acyl halides was efficiently catalyzed by $Pd(PPh_3)_4$ in the presence of CuI at 100–120°C under sealed-tube conditions. The corresponding (*Z*)-α-selenyl-α,β-unsaturated ketones were obtained in good yields (Scheme 1). Among the palladium–phosphine complexes screened, $Pd(PPh_3)_4$ showed the best catalytic activity (yield 82%); while the yields were lower in the presence of other palladium–phosphine complexes such as $PdCl_2(PPh_3)_2$ (32%) and $PdBnCl(PPh_3)_2$ (trace). On the other hand, the reaction did not occur in the presence of CuI without any catalyst after 72 h under sealed-tube conditions. Moreover, the yield was only 63% without the co-catalyst (CuI). Various solvents and catalysts were tested at different temperatures in the model reaction under the influence of a catalytic amount of $Pd(PPh_3)_4$ (5 mol%) and the results are summarized in Table 1. It was found that benzene was the best solvent among those tested, such as CH_2Cl_2, THF and DMF.

The reactions of several (*E*)-α-selenylvinylstannanes and acyl halides were examined in the presence of a catalytic amount (5 mol%) of $Pd(PPh_3)_4$ and CuI (0.75 equiv.) in benzene under sealed tube condition and the results are listed in Table 2. In all cases, the reaction proceeded smoothly to give the corresponding compounds.



In conclusion, a new method for the synthesis of (*Z*)-selenyl-α,β-unsaturated ketones has been presented based on the cross-coupling reaction of (*E*)-α-selenylvinylsannanes with acyl halides. This shows the usefulness of (*E*)-α-selenylvinylstannanes for the synthesis of highly functionalized organoselenium compounds. The investigation of the synthetic application of (*Z*)-α-selenyl-α,β-unsaturated ketones are in progress.

Table 2
Synthesis of (*Z*)-α-selenyl-α,β-unsaturated ketones

Entry	R	R′	R″	Yield (%) [a]
1	CH_3OCH_2	CH_3	Ph	82
2	CH_3OCH_2	Ph	Ph	75
3	n-C_5H_{11}	Ph	Ph	78
4	CH_3OCH_2	*p*-Cl-C_6H_4	Ph	65
5	CH_3OCH_2	CH_3	*p*-Cl-C_6H_4	68

[a] Isolated yield.

3. Experimental

^{1}H-NMR spectra were recorded in $CDCl_3$ at AZ-300 instrument. IR spectra were obtained on FTS-185 as neat films. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Solvents were dried, deoxygenated and distilled before use. All reaction was carried out under nitrogen.

*3.1. General procedure for the synthesis of (Z)-α-selenyl unsaturated ketones **1–5**:*

To a solution of (*Z*)-α-selenylvinylstannanes (1.0 mmol) and acyl halides (1.1 mmol) in benzene (2.0 ml) under nitrogen, Pd $(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were added, then tube was sealed, the resulting mixture was stirred at 120°C for 7 h, cooled to room temperature, and diluted with light petroleum. The supernatant was filtered through a short plug of silica gel and the filtrate evaporated. The residue was purified by preparative TLC on silica gel to afford the corresponding compounds.

Compound 1. ^{1}H-NMR: δ 7.71–7.86 (m, 2H, Ar), 7.30–7.52 (m, 3H, Ar), 6.26 (t, *J* 6.60 Hz, 1H, HC=C), 4.18 (d, *J* 6.60 Hz, 2H, OCH_2), 3.30 (s, 3H, CH_3O), 2.03(s, 3H, $SeCH_3$); MS: 270 (M^+ 100), 239 (7), 175 (18); 105(74),77(60), 45(36); IR (neat) ν/cm^{-1}: 3060, 2985, 1660, 1594,1448 and 1120; HRMS: Anal. Calc. for $C_{12}H_{14}O_2Se$, 270.0159 Found: 270.0130.

Compound 2. ^{1}H-NMR: δ 7.15–7.79 (m, 10H, Ar), 6.36 (t, *J* 7.20 Hz, 1H, HC=C), 4.15 (d, *J* 7.20 Hz, 2H, OCH_2), 3.38 (s, 3H, CH_3O); MS: 332 (M^+, 62), 301 (48), 105 (99), 77(100), 45(58); IR (neat) ν/cm^{-1}: 3059, 2986, 1663, 1579, 1477 and 1118; HRMS: Anal. Calc. for $C_{17}H_{16}O_2Se$: 332.0316 Found: 332.0293.

Compound 3. ^{1}H-NMR: δ 7.10–7.89 (m, 10H, Ar), 6.48 (t, *J* 7.80 Hz, 1H, HC=C), 1.25–1.38 (m, 8H, $(CH_2)_4$), 1.89(t, *J* 5.60, 3H, CH_3); MS: 358 (M^+, 6), 182 (64), 105 (100), 77 (55); IR (neat) ν/cm^{-1}: 3060, 2957, 1661, 1598, 1477 and 1067; HRMS: Anal. Calc. for $C_{20}H_{22}OSe$: 358.0836, Found: 358.0806.

Compound 4. ^{1}H-NMR: δ 7.02–7.89 (m, 9H, Ar), 6.53 (t, *J* 7.00 Hz, 1H, HC=C), 4.17 (d, *J* 7.80 Hz, 2H, OCH_2), 3.30 (s, 3H, CH_3O); MS: 354 (M^+, 10), 249 (70), 105(74), 77(100), 45(33); IR (neat) ν/cm^{-1}: 3060, 3028, 1661, 1598, 1579 and 1045; HRMS: Anal. Calc. for $C_{17}H_{15}O_2SeCl$: 353.9926 Found: 353.9901.

Compound 5. ^{1}H-NMR: δ 7.32–7.93 (m, 4H, Ar), 6.24 (t, *J* 6.60 Hz, 1H, HC=C), 4.18 (d, *J* 6.60 Hz, 2H, OCH_2), 3.25 (s, 3H, CH_3O), 2.08 (s, 3H, $SeCH_3$); MS: 304 (M^+, 100), 239 (84), 237 (75), 209 (13), 111 (36), 45 (37); IR (neat) ν/cm^{-1}: 3052, 2931, 1663, 1587, 1485 and 1013; HRMS: Anal. Calc. for $C_{12}H_{13}O_2ClSe$: 303.9769 Found: 303.9765.

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References

[1] (a) A.T. Nielsen, W. Houlihan, Org. React. 16 (1968). (b) B.D. Chong, Y.I. Ji, S.S. Oh, J.D. Yang, W. Baik, S. Koo, J. Org. Chem. 62 (1997) 9323.
[2] C.D. Nenitzescu, A.T. Balaban, Friedel–Crafts Relat. React. 3 (1964) 1035.
[3] D.B. Carr, J. Schwartz, J. Am. Chem. Soc. 99 (1977) 639.
[4] M. Hojo, H. Harada, A. Hosomi, Chem. Lett. (1994) 437.
[5] J.W. Sung, W.B. Jang, D.Y. Oh, Tetrahedron Lett. 37 (1996) 7537.
[6] Z.Z. Huang, X. Huang, Y.Z. Huang, J. Chem. Soc. Perkin Trans. I 2 (1995) 95.
[7] C.Q. Zhao, X. Huang, Tetrahedron Lett. 39 (1998) 1933.
[8] J.V. Commaseto, J. Organomet. Chem. 253 (1983) 131.
[9] (a) H.X. Zhang, F. Guibe, G. Balavoine, J. Org. Chem. 55 (1990) 1857. (b) R. Rossi, A. Carpita, P. Cossi, Tetrahedron Lett., 33 (1992) 8801.
[10] (a) T.N. Mitchell, Synthesis (1992) 803. (b) J. Thibonnet, M. Abarbi, Synlett (1999) 141. (c) K. Lee, S.I. Kim, J.K. Cha, J. Org. Chem. 63 (1998) 9135.
[11] X. Huang, Y. Ma, Synth. Commun. 27 (1997) 2407.
[12] X. Huang, Y. Ma, Synthesis (1997) 417
[13] Y. Ma, X. Huang, J. Chem. Soc. Perkin Trans. I (1997) 2947.