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Preliminary communication

The first example of α-organoseleno arsonium ylides and its Wittig-type reaction

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Abstract

α-Organoseleno arsonium ylide **3** was synthesized for the first time by a phenylselenenylation-transylidation reaction. It has sufficient activity to carry out the Wittig-type reaction, affording a novel method for the stereoselective synthesis of (Z)-α-phenylseleno-α,β-unsaturated esters **6**.

Keywords: Selenium; Arsenic

1. Introduction

Nowadays organoselenium compounds are playing more and more important roles in organic synthesis. If an organoselenium group is introduced into ylide, it may be possible to connect the organoselenium group onto many organic molecules by the Wittig reaction, obtaining a lot of organoselenium compounds, such as α-seleno-α,β-unsaturated compounds. Recently α-selenophosphonium ylides were synthesized [1,2], but it was found that the Wittig reaction did not occur with α-electron-attracting-group substituted α-seleno phosphonium ylides [3]. Although α-carbanions of phosphonates are more active than the corresponding phosphonium ylides, α-electron-attracting-group substituted α-selenophosphonates can not also be used for the Horner–Wadsworth–Emmons reaction [4]. The inactivity of these α-selenophosphonium ylides or α-carbanion of phosphonates are mainly due to the carbonyl conjugation with α-carbon and the orbital overlap of α-carbon with selenium, which restricts their applications in organic synthesis. Seeing that the reactivities of arsonium ylides are fairly higher than that of the corresponding phosphonium ylides and α-carbanion of phosphonates [5], we started to synthesize α-phenylseleno α-methoxycarbonylmethylene triphenylarsorane and tried to explore its Wittig-type reaction.

2. Results and discussion

Considering that arsonium ylide is a strong nucleophile and phenylselenenyl halide is a good electrophile, we reacted methoxycarbonylmethylene triphenylarsorane (**1**) with phenylselenenyl halide and found the phenylselenenylation-transylidation reaction took place. Among phenylselenenyl halides, phenylselenenyl chloride, phenylselenenyl bromide and presumed phenylselenenyl iodide [6], the less known phenylselenenyl iodide has the best reactivity and selectivity. Thus, in the mixed solvent of ether with methanol, methoxycarbonylmethylene triphenylarsorane (**1**) could react with phenylselenenyl iodide (**2**) smoothly to produce α-phenylseleno methoxycarbonylmethylene triphenylarsorane (**3**) in the yield of 92%. Meanwhile, almost quantitative arsonium salt **4** which can be reused was formed through the transylidation reaction. The white crystalline of α-phenylseleno methoxycarbonylmethylene triphenylarsorane (**3**) is the first example of α-organoseleno arsonium ylides and can be stored for following reaction beneath 0°C, although it is sensitive to heat, light and moisture.

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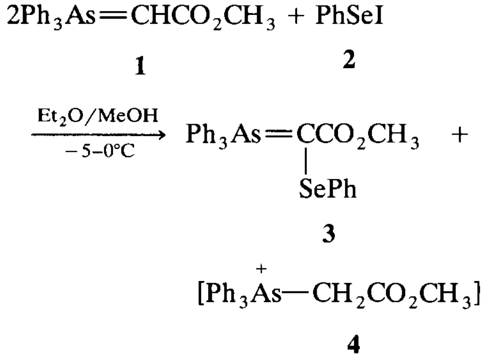
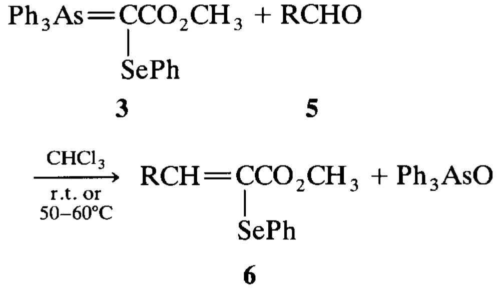


$$\underset{\mathbf{1}}{2Ph_3As{=}CHCO_2CH_3} + \underset{\mathbf{2}}{PhSeI} \xrightarrow[-5\text{–}0°C]{Et_2O/MeOH} \underset{\mathbf{3}}{Ph_3As{=}\underset{\substack{|\\ SePh}}{C}CO_2CH_3} + \underset{\mathbf{4}}{[Ph_3\overset{+}{As}{-}CH_2CO_2CH_3]I^-}$$

Different from α-electron-attracting group substituted α-seleno phosphonium ylides and phosphonates, the α-phenylseleno methoxycarbonylmethylene triphenylarsorane (**3**) has sufficient activity to carry out Witting-type reaction. It can react with aromatic, aliphatic or α,β-unsaturated aldehydes under very mild conditions to produce α-phenylseleno-α,β-unsaturated esters **6** in excellent yields (Method A). The product **6** is a new type of vinyl selenides, which are important intermediates owing to the versatile reactivities of seleno group and carbon–carbon double bond. It was not necessary to isolate the ylide **3** which reacted in situ with aldehydes as a one-pot reaction (Method B). The one-pot method simplified the manipulation procedures and gave similar results.



$$\underset{\mathbf{3}}{Ph_3As{=}\underset{\substack{|\\ SePh}}{C}CO_2CH_3} + \underset{\mathbf{5}}{RCHO} \xrightarrow[\substack{r.t.\ or\\ 50\text{–}60°C}]{CHCl_3} \underset{\mathbf{6}}{RCH{=}\underset{\substack{|\\ SePh}}{C}CO_2CH_3} + Ph_3AsO$$

It is also noteworthy that this Wittig-type reaction has high stereoselectivity to form Z-type of α-phenylseleno-α,β-unsaturated esters **6** predominantly. For assignment of configuration of two isomers, we utilized the empirical fomula on the chemical shift of olefinic hydrogen [7] to calculate the chemical shift of olefinic hydrogen of α-thioaryl α,β-unsaturated esters and obtained that, its chemical shift of Z-isomer was around 7.86 and that of E-isomer was around 6.89. Compared the calculated result of α-thioaryl α,β-unsaturated ester with the chemical shift of α-arylseleno α,β-unsaturated ester by 300 MHz ^{1}H-NMR, we inferred that the configuration of the major isomer whose olefinic hydrogen absorbed at the range of δ 7.3–8.2 was Z-type and that of minor isomer whose olefinic hydrogen absorbed at the range of δ 6.3–7.1 was E-type. This is in agreement with the stereochemistry of the Wittig-type reaction of α-iodo-methoxycarbonylmethylene triphenylarsorane [8].

The method described above constituted the synthesis of α-phenylseleno methoxycarbonylmethylene triphenylarsorane (**3**) with the advantages of simple procedure, mild reaction condition and high yield. As expected, this α-seleno arsonium ylide **3** has sufficient activity to undergo Wittig-type reaction smoothly, offering the first method for the stereoselective synthesis of (Z)-α-seleno-a,β-unsaturated esters **6**. The reaction has the advantages of mild reaction conditions, convenient manipulations, excellent yield and high stereoselectivities. Thus it will be worth applying this Wittig-type reaction into organic synthesis.

Table 1

The Wittig-type reaction of α-phenylseleno arsonium ylides **3** with aldehydes **5**

Entry	R in **5**	Reaction Time (h) [a] Method A (Method B)	Isolated Yield (%) Method A (Method B)	Z/E [b]
6a	4-$NO_2C_6H_4$-	4 (8)	92 (91)	90/10
6b	4-Cl C_6H_4-	18 (19)	91 (88)	84/16
6c	C_6H_5-	25 (26)	95 (93)	82/18
6d	4-$CH_3C_6H_4$-	34 (35)	94 (90)	81/19
6e	$C_6H_5CH{=}CH$-	15 (18)	95 (96)	95/5
6f	CH_3-CH=CH-	18 (24)	90 (91)	98/2
6g	$CH_3(CH_2)_6CH_2$-	24 (28)	86 (81)	99/1
6h	$(CH_3)_2CHCH_2$-	21 (27)	85 (84)	99/1

[a] α-Phenylseleno arsonium ylides **3** react with aromatic aldehydes at r.t. and aliphatic or α,β-unsaturated aldehydes at 50–60°C.

3. Experimental details

^{1}H-NMR spectra were recorded on a AZ-300 MHz and Varian EM-360 (60 MHZ) with TMS as internal standard. Mass spectra were determined by a Finigan 8230 mass spectrometer. IR spectra were obtained as neat capillary cells (liguid products) or KBr disks (solid products) on a Shimadzu IR-408 instrument.

All solvents were dried and redistilled before use. Methoxycarbonylmethylene triphenylarsorane (**1**) and phenylselenenyl iodide (**2**) were prepared according to the literature methods of Refs. [9] and [6] respectively. All reactions were carried out under nitrogen.

3.1. Synthesis of α-phenylseleno methoxycarbonylmethylene triphenylarsorane (3)

To a stirred suspension of methoxycarbonylmethylene triphenylarsorane (**1**) (0.756 g, 2 mmol) in $MeOH-Et_2O$ (0.6 ml, v/v = 1 : 1) was added dropwise the solution of phenylselenenyl iodide (**2**) (1 mmol) in $MeOH-Et_2O$ (2.8 ml, v/v = 1 : 1) at −5–0°C. With the drop of the solution of phenylselenenyl iodide, the reaction mixture changed from suspension to clear solution and turned to suspension again. After the suspension was filtered, the residue was washed with ether and a small amount of methanol to yield 0.45 g of **3** as a white crystal. The filtrate of the suspension was evaporated and its residue was extracted with benzene. Evaporation of benzene gave another part of **3** (0.04 g). Thus the totall yield was 93%. mp 203–205°C. ^{1}H-NMR δ(ppm): 7.72–7.10(m, 20H), 3.42(s, 3H). MS *m/e*: 534(m, 8.2), 152(100.0). IR ν(cm^{-1}): 1590(vs), 1290(vs), 740(s), 690(s). Anal. Calc. for $C_{27}H_{23}O_2Se$: C, 60.80; H, 4.35. Found: C, 60.67: H, 4.32.

3.2. General procedures for the synthesis of α-seleno-α,β-unsaturated esters **6**

Method A. When sunlight was blindered, the mixture of α-phenylseleno methoxycarbonylmethylene triphenylarsorane (**3**) (1.2 mmol) and aldehyde **5** (1.0 mmol) in chloroforn (3 ml) was stirred for the time indicated in Table 1. With the aromatic aldehydes, the reactions were carried out at r.t. and for another 1 h at 50–60°C. With the aliphatic and α,β-unsaturated aldehydes, the reactions were carried out at 50–60°C. The progress of reaction was monitored by TLC or ^{1}H-NMR. After the completion of the reaction, the mixture was concentrated and the residue was subjected to a flash chromatography on a silica gel column (petroleum ether/ether = 4 : 1 as eluent). The product **6** was isolated by preparative thin layer chromatography (petroleum ether/ether = 5 : 1 as eluent).

Method B. At −5–0°C, the solution of phenylselenenyl iodide (**2**) (1.5 mmol) in MeOH–Et_2O (4.2 ml, v/v = 1 : 1) was added dropwise into the stirred suspension of methoxycarbonylmethylene triphenylarsorane (**1**) (3 mmol) in MeOH–Et_2O (0.9 ml, v/v = 1 : 1). With the drop of the solution of phenylselenenyl iodide (**2**), the precipitate of α-phenylseleno methoxycarbonylmethylene triphenylarsorane (**3**) was formed. After addition, the reaction mixture was stirred for another 0.5 h at room temperature. Then the ether in the mixture was evaporated off and chloroform (2 ml) was added to dissolve **3**. The reaction system was blindered and the solution of aldehyde **5** (1 mmol) in chloroform (1 ml) was injected. The reaction time was indicated in Table 1 and the remaining manipulations were analogous to that of Method A.

3.2.1. Methyl 2-phenylseleno-3-(4-nitrophenyl)-2-propenoate (**6a**)

Mp 69–78°C. ^{1}H-NMR δ(ppm); 8.20–8.12(m, 2H); 8.07(Z), 6.84(E) (s, Z + E = 1H); 7.73–7.64(m, 2H); 7.41–7.20(m, 5H); 3.66(Z) 3.59(E) (s, Z + E = 3H). MS *m/e*: 363(M, 100.0). IR ν(cm^{-1}): 1700(vs), 1590(s), 1500(vs), 1250(vs), 840(s), 750(s), 685(s). Anal. Calc. for $C_{16}H_{13}NO_4Se$: C, 53.05; H, 3.62; N, 3.87. Found: C, 53.25; H, 3.65; N, 3.84.

3.2.2. Methyl 2-phenylseleno-3-(4-chlorophenyl)-2-propenoate (**6b**)

Mp 54–63°C. ^{1}H-NMR δ(ppm): 8.08(Z), 6.95(E) (s, Z + E = 1H); 7.58(m, 2H); 7.42 ~ 7.19(m, 7H); 3.63(Z), 3.56(E) (s, Z + E = 3H). MS *m/e*: 352(M, 70.7), 57(100.0). IR ν(cm^{-1}): 1700(vs), 1590(s), 1250(vs), 810(s), 730(s), 680(s). Anal. Calc. for $C_{16}H_{13}O_2SeCl$: C, 54.64; H, 3.73. Found: C, 54.77; H, 3.75.

3.2.3. Methyl 2-phenylseleno-3-phenyl-2-propenoate (**6c**)

Oil. ^{1}H-NMR δ(ppm): 8.18(Z), 7.08(E) (s, Z + E = 1H); 7.69–7.61(m, 2H); 7.42–7.19(m, 8H); 3.63(Z), 3.57(E) (s, Z + E = 3H). MS m/e: 318(M, 19.2), 317(M-1, 100.0). IR ν(cm^{-1}): 1710(vs), 1580(s), 1200(vs), 730(s), 690(s). Anal. Calcd. for $C_{16}H_{14}O_2Se$: C, 60.58; H, 4.45. Found: C, 60.71; H, 4.47.

3.2.4. Methyl 2-phenylseleno-3-(4-methylphenyl)-2-propenoate (**6d**)

Oil. ^{1}H-NMR δ(ppm): 8.20(Z), 7.13(E) (s, Z + E = 1H); 7.65–7.62(m, 2H); 7.43–7.18(m, 7H); 3.63(Z), 3.58(E) (s, Z + E = 3H); 2.36(Z), 2.32(E) (s, Z + E = 3H). MS *m/e*: 332(M, 58.9), 115(100.0), IR ν(cm^{-1}): 1710(vs), 1590(s), 1250(vs), 810(s), 735(s), 690(s). Anal. Calc. for $C_{17}H_{16}O_2Se$: C, 61.64; H, 4.87. Found: C, 61.78; H, 4.85.

3.2.5. Methyl 2-phenylseleno-5-phenyl-2,4-pentadienoate (**6e**)

Mp 49–56°C. ^{1}H-NMR δ(ppm) (4E, 2Z): 7.97 (d, *J* = 10 Hz, 1H); 7.66 (dd, *J* = 16 Hz, 1H); 7.56–7.05(m, 10H); 6.52(d, *J* = 10 Hz, 1H); 3.66(s, 3H). MS *m/e*: 344 (M, 8.1), 128(100.0). IR ν(cm^{-1}): 1690(vs), 1610(s), 1570(s), 1230(vs), 730(s), 680(s). Anal. Calc. for $C_{18}H_{16}O_2Se$: C, 62.98; H, 4.70. Found: C, 62.72; H, 4.69.

3.2.6. Methyl 2-phenylseleno-2, 4-hexadienoate (**6f**)

Oil. ^{1}H-NMR δ(ppm) (4E, 2Z): 7.75(d, *J* = 11 Hz, 1H); 7.36–7.15(m, 5H); 6.77(dd, *J* = 16 Hz, 1 H); 6.31(m, 1H); 3.67(s, 3H); 1.86(d, 3H). MS *m/e*: 282(M, 7.3), 283(M + 1, 100.0). IR ν(cm^{-1}): 1750(vs), 1630(s), 1570(s), 1230(vs), 730(s), 685(s). Anal. Calc. for $C_{13}H_{14}O_2Se$: C, 55.53; H, 5.02. Found: C, 55.64; H, 5.05.

3.2.7. Methyl 2-phenylseleno-2-undecenoate (**6g**)

Oil. ^{1}H-NMR δ(ppm) (2Z): 7.37(t, 1H), 7.35–7.18(m, 5H), 3.65(s, 3H), 2.45(q, 2H), 1.40–1.20(m, 12H), 0.87(t, 3H). MS *m/e*: 354(M, 100.0). IR ν(cm^{-1}): 1710(vs), 1605(s), 1240(vs), 730(s), 685(s). Anal. Calc. for $C_{18}H_{26}O_2Se$: C, 61.18; H, 7.42. Found: C, 61.03; H, 7.40.

3.2.8. *Methyl 2-phenylseleno-5-methyl-2-hexenoate* (**6h**)

Oil. ^{1}H-NMR δ(ppm) (2Z): 7.41(t, 1H), 7.40–7.12(m, 5H), 3.65(s, 3H), 2.39(t, 2H), 1.85–1.74(m, 1H), 0.94(d, 6H). MS *m/e*: 298(M, 18.8), 297(M-1, 100.0). IR ν(cm^{-1}): 1710(vs), 1605(s), 1245(vs), 730(s), 685(s). Anal. Calc. for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.82; H, 6.12.

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