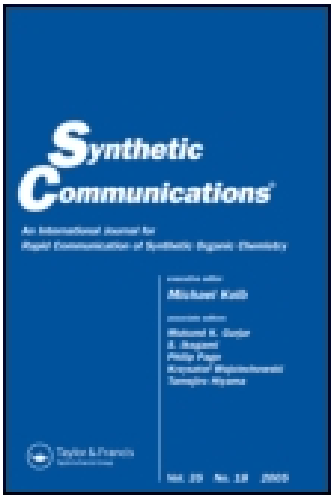

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ONE-POT STEREOSELECTIVE SYNTHESIS OF (*Z*)-α-ARYLTHIO-α,β-UNSATURATED KETONES BY HYDROSTANNYLATION–STILLE TANDEM REACTION OF ACETYLENIC SULFIDES

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(Z)-α-Arylthio-α,β-unsaturated ketones can be stereoselectively synthesized in one pot under mild conditions, in good yields, by the palladium-catalyzed hydrostannylation of acetylenic sulfides with tributyltin hydride, followed by Stille coupling with acyl chlorides.

Keywords: Acetylenic sulfide; hydrostannylation; Stille coupling; tandem reaction; α,β-unsaturated ketone

INTRODUCTION

α,β-Unsaturated ketones are useful synthetic intermediates, and a variety of synthetic methods for the synthesis of α,β-unsaturated ketones have been developed. Of these methods, the aldol condensation is one of the most powerful synthetic tools.[1] The hydrozirconation of alkynes, followed by aluminum chloride–promoted acylation of the resulting vinylzirconium compounds, has provided a convenient method for stereoselective synthesis of α,β-unsaturated ketones.[2] The synthesis of heteroatom-containing α,β-unsaturated ketones has also attracted considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of heteroatom functions. Sung et al. reported that hydrozirconation of acetylenic tellurides, followed by the reaction with acyl chlorides in the presence of CuI, gave α-organotelluro-α,β-unsaturated ketones.[3] Zhao et al. described the synthesis of (*Z*)-β-selenyl-α,β-unsaturated ketones by CuX-catalyzed selenocarbonylation addition reaction of selenoesters to nonactivated terminal alkynes.[4] (*Z*)-α-Selenyl-α,β-unsaturated ketones could be prepared by utilizing either a Wittig-type reaction of α-phenylselanyl arsonium ylides with carbonyl compounds[5] or through palladium-catalyzed acylation of (*E*)-α-selanylvinylstannanes with acyl halides.[6] α-Arylthio- or alkylthio-α,β-unsaturated ketones are very useful synthetic intermediates.[7] For example, they have been used in the preparation of 2,3-dihydrofurans[8] and 1,4- and 1,5-dicarbonyl compounds[9]

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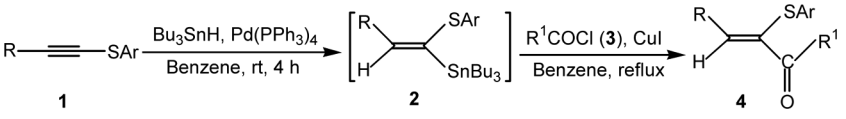
as well as in the regioselective alkylation of cyclohexanones.[7c] Some methods for the synthesis of α-arylthio- or alkylthio-α,β-unsaturated ketones have been developed, including Pummerer rearrangement of 2-arylsulfinyl ketones,[10] the NaOH-catalyzed thiolysis of α,β-epoxyketones,[11] and the Rh-catalyzed diazo decomposition of β-thio group α-diazo ketones.[12] Despite considerable methodological differentiation, the reported procedures usually require starting materials that are not readily available, and thus there still exists a need for new, selective, and convenient methods. Herein, we report that (*Z*)-α-arylthio-α,β-unsaturated ketones can be stereoselectively synthesized in one pot under mild conditions, in good yields, by the palladium-catalyzed hydrostannylation of acetylenic sulfides with tributyltin hydride, followed by Stille coupling with acyl chlorides.

RESULTS AND DISCUSSION

Palladium-catalyzed hydrostannylation of arylthioalkynes has been reported to be highly regio- and stereoselective, giving (*E*)-α-arylthiovinylstannanes in excellent yields.[13] (*E*)-α-Arylthiovinylstannanes are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfides. Vinylstannanes can undergo the Stille coupling with organic halides.[14] The tandem reaction has recently been of interest for organic synthesis because it offers a convenient and economical method with which to prepare target organic molecules.[15] The palladium-catalyzed hydrostannylation of alkynes and the Stille reaction are acknowledged as useful tools for constructing complex organic molecules. However, to the best of our knowledge, there have been no reports on palladium-catalyzed tandem hydrostannylation–Stille coupling reaction of tributyltin hydride with acetylenic sulfides and acyl halides to date. Considering the fact that both the hydrostannylation and Stille reaction were catalyzed by $Pd(PPh_3)_4$, we tried to combine the two reactions, in one pot, to stereoselectively prepare (*Z*)-α-arylthio-α,β-unsaturated ketones (Scheme 1).

Initially, to determine the optimum tandem reaction conditions, after the hydrostannylation of 1-phenylthio-1-hexyne with Bu_3SnH in benzene in the presence of 5 mol% $Pd(PPh_3)_4$ at room temperature for 4 h as described by Magriotis et al.,[13] the Stille cross-coupling reaction of the intermediate (*E*)-1-phenylthio-1-tributylstannyl-1-hexene (**2a**) with benzoyl chloride (1.1 equiv) in benzene was examined under various reaction conditions. It was found that the Stille reaction of the intermediate **2a** with benzoyl chloride in benzene at room temperature did not occur in the presence of 10 mol% CuI cocatalyst; however, the same reaction at reflux temperature could proceed to give (*Z*)-1-benzoyl-1-phenylthio-1-hexene (**4a**) in 45% yield after 48 h. The amount of CuI cocatalyst affected the reaction rate of the Stille coupling.



Scheme 1. Hydrostannylation–Stille tandem reaction of acetylenic sulfides with Bu_3SnH and acyl chlorides.

Table 1. Synthesis of (*Z*)-α-arylthio-α,β-unsaturated ketones **4a–k**

Entry	R	Ar	R^1	Time (h)[a]	Product	Yield[b] (%)
1	n-C_4H_9	Ph	Ph	10	**4a**	74
2	n-C_4H_9	Ph	4-$O_2NC_6H_4$	8	**4b**	75
3	n-C_4H_9	4-$CH_3C_6H_4$	Ph	10	**4c**	77
4	n-C_4H_9	4-$CH_3C_6H_4$	4-ClC_6H_4	9	**4d**	71
5	CH_3OCH_2	Ph	Ph	10	**4e**	68
6	CH_3OCH_2	Ph	4-$CH_3C_6H_4$	12	**4f**	73
7	CH_3OCH_2	Ph	4-ClC_6H_4	9	**4g**	67
8	CH_3OCH_2	Ph	4-$O_2NC_6H_4$	8	**4h**	68
9	CH_3OCH_2	4-$CH_3C_6H_4$	Ph	11	**4i**	70
10	Ph	Ph	Ph	11	**4j**	80
11	Ph	4-ClC_6H_4	4-ClC_6H_4	9	**4k**	74

[a]Required for the Stille reaction.
[b]Isolated yield based on the acetylenic sulfide **1**.

When 75 mol% CuI was used, the Stille reaction of the intermediate **2a** with benzoyl chloride in benzene proceeded smoothly at reflux temperature to afford the **4a** in 74% yield after 10 h. We found that hydrostannylation of acetylenic sulfides **1** with tributyltin hydride using 5 mol% $Pd(PPh_3)_4$ in benzene at room temperature for 4 h, followed by reaction with acyl chlorides **3** and 75 mol% CuI at reflux, gave the (*Z*)-α-arylthio-α,β-unsaturated ketones **4** in good yields. The typical results are summarized in Table 1. As shown in Table 1, the tandem hydrostannylation–Stille reaction of tributyltin hydride with a variety of acetylenic sulfides and aromatic acyl chlorides proceeded smoothly, under very mild conditions, to afford the corresponding (*Z*)-α-arylthio-α,β-unsaturated ketones **4** stereoselectively. The nature of the substituents in aromatic acyl chlorides has no influence on the Stille reaction, and both strongly electron-withdrawing and electron-donating substituents can be present. However, when aliphatic acyl chlorides were used as the electrophiles, the Stille coupling reaction of the intermediates **2** did not occur at all.

It is well documented that the Stille coupling reaction of vinylstannanes with organic halides, in the presence of a palladium catalyst, retains configuration.[14] In addition, the *Z*-configuration of compound **4c** was confirmed by nuclear Overhauser effect spectroscopy (NOESY) experiments. An enhancement of the allylic protons was observed as the vinylic proton of **4c** was irradiated. A correlation between the allylic protons and the aromatic protons ($\delta = 7.14$) of the (4-methylphenyl)thio group was observed. The NOE results indicate that compound **4c** has the expected *Z*-configuration and that the cross-coupling reaction of (*E*)-α-arylthiovinylstannanes **2** with acyl halides **3** retains configuration.

EXPERIMENTAL

General

Benzene was distilled from sodium immediately prior to use. Infrared (IR) spectra were obtained with a Perkin-Elmer 683 instrument as neat films. ^1H NMR spectra were recorded with a Bruker AC-400 (400-MHz) spectrometer using $CDCl_3$

as solvent. ^{13}C NMR spectra were recorded with a Bruker AC-400 (100-MHz) spectrometer using $CDCl_3$ as solvent. Mass spectra (EI) were determined with a Finnigan 8230 mass spectrometer. Microanalyses were measured with a Yanaco MT-3 CHN microelemental analyzer. $Pd(PPh_3)_4$ was prepared according to a literature procedure.[16]

General Procedure for the Synthesis of (*Z*)-α-Arylthio-α,β-unsaturated Ketones 4a–k

A 25-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar under an argon atmosphere was charged sequentially with acetylenic sulfide **1** (1 mmol), benzene (4 mL), $Pd(PPh_3)_4$ (0.05 mmol), and Bu_3SnH (1.1 mmol). The mixture was stirred at room temperature for 4 h, acyl chloride (1.1 mmol) and CuI (0.75 mmol) were added, and the mixture was stirred at reflux for 8–12 h. The reaction mixture was cooled to room temperature and diluted with light petroleum. The supernatant was filtered through a short plug of silica gel, and the filtrate was evaporated. The residue was purified by preparative thin-layer chromatography (TLC) on silica gel to afford the corresponding compounds.

Data

(*Z*)-1-Benzoyl-1-phenylthio-1-hexene (4a). Oil. IR (film): ν (cm^{-1}) 3060, 2928, 1665, 1597, 1447, 1258, 741, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.49–7.47 (m, 1H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.24–7.10 (m, 5H), 6.73 (t, $J = 7.2$ Hz, 1H), 2.61–2.55 (m, 2H), 1.52–1.48 (m, 2H), 1.43–1.38 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.11, 149.69, 137.45, 135.72, 134.40, 132.34, 129.88, 129.39, 128.93, 128.12, 126.63, 30.69, 30.33, 22.54, 13.89; MS (EI, 70 eV): m/z 296 (M^+, 100), 105 (93), 77 (45). Anal. calc. for $C_{19}H_{20}OS$: C, 77.00; H, 6.80. Found: C, 76.74; H, 6.61.

(*Z*)-1-(4-Nitrobenzoyl)-1-phenylthio-1-hexene (4b). Oil. IR (film): ν (cm^{-1}) 2928, 1670, 1592, 1519, 1345, 848, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 8.8$ Hz, 2H), 7.18–7.06 (m, 5H), 6.55 (t, $J = 7.2$ Hz, 1H), 2.63–2.57 (m, 2H), 1.55–1.50 (m, 2H), 1.45–1.37 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.52, 147.01, 143.50, 134.72, 132.38, 129.32, 128.93, 128.58, 128.13, 126.07, 123.53, 31.31, 30.99, 22.50, 13.97; MS (EI, 70 eV): m/z 341 (M^+, 9.3), 109 (100), 57 (35). Anal. calc. for $C_{19}H_{19}NO_3S$: C, 66.85; H, 5.61. Found: C, 66.56; H, 5.69.

(*Z*)-1-Benzoyl-1-(*p*-tolylthio)-1-hexene (4c). Oil. IR (film): ν (cm^{-1}) 2927, 1666, 1596, 1448, 1258, 1089, 806, 717; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.51–7.49 (m, 1H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.64 (t, $J = 7.6$ Hz, 1H), 2.59–2.54 (m, 2H), 2.24 (s, 3H), 1.51–1.44 (m, 2H), 1.42–1.35 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.15, 148.43, 137.53, 136.80, 136.36, 132.28, 130.53, 129.70, 129.42, 128.00, 127.48, 30.73, 30.21, 22.53, 21.00, 13.89; MS (EI, 70 eV): m/z 310 (M^+, 37), 186 (25), 105 (100), 91 (43). Anal. calc. for $C_{20}H_{22}OS$: C, 77.39; H, 7.14. Found: C, 77.15; H, 6.95.

(*Z*)-1-(4-Chlorobenzoyl)-1-(*p*-tolylthio)-1-hexene (4d). Oil. IR (film): ν (cm^{-1}) 2926, 1667, 1588, 1492, 1253, 1091, 806, 756; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.61 (t, $J = 7.2$ Hz, 1H), 2.60–2.54 (m, 2H), 2.24 (s, 3H), 1.53–1.49 (m, 2H), 1.44–1.38 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.00, 147.82, 138.66, 137.04, 136.11, 135.74, 135.02, 130.76, 130.67, 129.76, 128.39, 30.74, 30.13, 22.53, 21.02, 13.90; MS (EI, 70 eV): m/z 346 (M^+, ^{37}Cl, 16), 344 (M^+, ^{35}Cl, 45), 139 (100), 91 (29). Anal. calc. for $C_{20}H_{21}OSCl$: C, 69.65; H, 6.14. Found: C, 69.38; H, 5.86.

(*Z*)-1-benzoyl-1-phenylthio-3-methoxypropene (4e). Oil. IR (film): ν (cm^{-1}) 3060, 2929, 1667, 1597, 1580, 1448, 1248, 1100, 745, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.53–7.34 (m, 3H), 7.27–7.14 (m, 5H), 6.69 (t, $J = 5.6$ Hz, 1H), 4.40 (d, $J = 5.6$ Hz, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.97, 143.20, 136.87, 136.73, 133.08, 132.72, 130.70, 129.46, 129.06, 128.26, 127.29, 70.08, 58.79; MS (EI, 70 eV): m/z 284 (M^+, 41), 253 (100), 144 (36), 109 (41), 105 (87). Anal. calc. for $C_{17}H_{16}O_2S$: C, 71.82; H, 5.67. Found: C, 71.55; H, 5.79.

(*Z*)-1-(4-Methylbenzoyl)-1-phenylthio-3-methoxypropene (4f). Oil. IR (film): ν (cm^{-1}) 3061, 2928, 1666, 1596, 1583, 1447, 1249, 1101, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, $J = 8.0$ Hz, 2H), 7.28–7.24 (m, 3H), 7.21–7.15 (m, 4H), 6.64 (t, $J = 5.6$ Hz, 1H), 4.39 (d, $J = 5.6$ Hz, 2H), 3.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.63, 143.67, 142.47, 136.87, 134.01, 133.16, 130.66, 129.72, 129.24, 128.99, 127.23, 70.03, 58.73, 21.66; MS (EI, 70 eV): m/z 298 (M^+, 6.8), 296 (100), 282 (85), 253 (34), 239 (40), 105 (58), 91 (62). Anal. calc. for $C_{18}H_{18}O_2S$: C, 72.47; H, 6.08. Found: C, 72.19; H, 5.87.

(*Z*)-1-(4-Chlorobenzoyl)-1-phenylthio-3-methoxypropene (4g). Oil. IR (film): ν (cm^{-1}) 2929, 1669, 1593, 1580, 1402, 1093, 691; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.15–7.13 (m, 5H), 6.43 (t, $J = 5.6$ Hz, 1H), 4.39 (d, $J = 5.6$ Hz, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.27, 134.93, 134.33, 130.65, 129.44, 129.01, 128.94, 128.87, 128.69, 128.42, 126.18, 70.71, 58.48; MS (EI, 70 eV): m/z 318 (M^+, ^{35}Cl, 1.4), 259 (26), 123 (55), 111 (64), 109 (100). Anal. calc. for $C_{17}H_{15}O_2SCl$: C, 64.05; H, 4.74. Found: C, 63.77; H, 4.49.

(*Z*)-1-(4-Nitrobenzoyl)-1-phenylthio-3-methoxypropene (4h). Oil. IR (film): ν (cm^{-1}) 2928, 1672, 1595, 1521, 1404, 1346, 1093, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, $J = 8.8$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.16–7.07 (m, 5H), 6.56 (t, $J = 5.6$ Hz, 1H), 4.43 (d, $J = 5.6$ Hz, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.41, 145.63, 137.74, 134.97, 133.47, 130.19, 129.37, 129.06, 128.46, 126.70, 123.58, 70.68, 58.68; MS (EI, 70 eV): m/z 329 (M^+, 53), 298 (25), 115 (91), 109 (100). Anal. calc. for $C_{17}H_{15}NO_4S$: C, 62.00; H, 4.59. Found: C, 61.73; H, 4.73.

(*Z*)-1-Benzoyl-1-(*p*-tolylthio)-3-methoxypropene (4i). Oil. IR (film): ν (cm^{-1}) 2927, 1667, 1597, 1592, 1448, 1403, 1094, 808, 716; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.51–7.35 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H),

6.99 (d, $J = 8.0$ Hz, 2H), 6.59 (t, $J = 5.6$ Hz, 1H), 4.40 (d, $J = 5.6$ Hz, 2H), 3.43 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.08, 141.84, 137.57, 136.79, 133.46, 132.71, 131.33, 129.83, 129.54, 129.15, 128.23, 70.01, 58.75, 21.05; MS (EI, 70 eV): m/z 298 (M^+, 54), 267 (66), 105 (100). Anal. calc. for $C_{18}H_{18}O_2S$: C, 72.47; H, 6.08. Found: C, 72.64; H, 6.25.

(*Z*)-1-Benzoyl-1-phenylthio-2-phenylethene (4j). White solid. Mp. 75–76 °C (lit.[17] mp 74–75 °C). IR (KBr): ν (cm^{-1}) 3060, 1667, 1581, 1447, 1241, 745, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, $J = 7.6$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.50–7.34 (m, 6H), 7.27–7.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.47, 139.87, 137.38, 135.58, 134.63, 133.08, 132.50, 131.29, 130.42, 129.45, 128.96, 128.56, 128.48, 128.12, 127.38; MS (EI, 70 eV): m/z 316 (M^+, 8.3), 211 (17), 109 (34), 105 (100). Anal. calc. for $C_{21}H_{16}OS$: C, 79.73; H, 5.10. Found: C, 79.54; H, 5.23%.

(*Z*)-1-(4-Chlorobenzoyl)-1-(4-chlorophenyl)thio-2-phenylethene (4k). White solid. Mp 81–83 °C. IR (KBr): ν (cm^{-1}) 2925, 1665, 1587, 1475, 1092, 819, 762; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.76 (m, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.47–7.31 (m, 5H), 7.24–7.13 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.98, 140.42, 139.09, 137.18, 135.47, 134.51, 134.23, 133.43, 132.55, 130.92, 130.74, 130.45, 129.22, 129.03, 128.57; MS (EI, 70 eV): m/z 384 (M^+, ^{35}Cl, 39), 139 (45), 111 (66), 109 (100). Anal. calc. for $C_{21}H_{14}OSCl_2$: C, 65.63; H, 3.67. Found: C, 65.41; H, 3.85.

CONCLUSION

In conclusion, we have developed an efficient and stereoselective one-pot method for the synthesis of (*Z*)-α-arylthio-α,β-unsaturated ketones. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, and good yields.

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