Stille Cross-Coupling Reaction of an α-Stannyl Enamide

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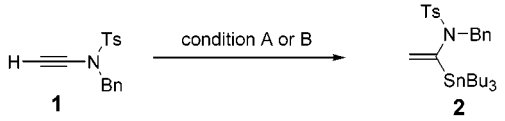
The Stille cross-coupling reaction of an *N*-tosyl α-stannyl enamine is clearly exemplified for the first time with a wide range of halogeno derivatives. This gives access to functionalized α-substituted enamines in fair yields.

Introduction

Enamines are versatile tools in organic synthesis.[1] They have been used mainly as nucleophiles in Michael addition reactions[2] but also to a lesser extent as electrophiles via conversion to iminium ions,[3] as functionalized dienophiles in cycloaddition reactions,[4] and as intermediates in the total synthesis of natural products and analogues.[5] Besides this synthetic aspect, the enamine moiety is also incorporated in a wide range of natural products.[6]

Methods for the preparation of enamines include condensation of a primary or secondary amine with ketones or aldehydes[1,7] and addition of Grignard reagents bearing an α-hydrogen to formamides.[1,8] Nevertheless, such methods do not allow the synthesis of highly functionalized enamines. Recently, Witulski described an elegant approach based on hydroboration followed by the Suzuki−Miyaura cross-coupling reaction of an ynamine to give substituted enamines.[9] Unfortunately, this approach is limited to the formation of the *β*-substituted isomer since the hydroboration occurs in a regiospecific manner. Moreover, examples were restricted to the synthesis of arylenamides.

Scheme 1. Preparation of α-Stannyl Enamine 2



condition A : $Bu_3SnH/Pd(PPh_3)_4$, THF 50°C, 65%
condition B : 1) $Bu_6Sn_2/Pd(PPh_3)_4$, 2) CF_3CO_2H/MeOH, 68% over 2 steps

Results and Discussion

We have recently reported the hydrostannation of ynamine **1**,[10] which affords the α-isomer as the major product.[11] This was cleanly achieved via reaction of *N*-benzyl, *N*-tosyl amino acetylene with 2 equiv of tributyltin hydride in the presence of a catalytic amount of palladium(tetrakis(triphenylphosphine)) to give a mixture of α- and *β*-isomers in a 91:9 ratio as determined by ^{1}H NMR spectrometry. Pure α-isomer is then easily obtained by column chromatography on silica gel. Meanwhile, we discovered that pure α-**2** can also be obtained following a two-step procedure involving cis addition of hexabutylditin to ynamine **1**[11] followed by protodestannylation using trifluoroacetic acid in methanol (condition B in Scheme 1). Exclusive protodestannylation of the *β*-position occurs under these conditions.

We then tried to apply the palladium-catalyzed cross-coupling reaction starting from **2**. The reaction of PhI with **2** under the originally described Stille conditions ($Pd(PPh_3)_4$) failed to afford the expected product as seen in the crude ^{1}H NMR spectrum. In the recent literature, the use of copper salts, in conjunction with soft ligands such as $AsPh_3$, has been highly recommended for acceleration of the rate of cross coupling,[12] especially in the case of sterically congested vinyltins. We therefore tested a wide variety of palladium catalysts ($Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $BnPdCl(PPh_3)_2$, and Pd_2dba_3) with or without

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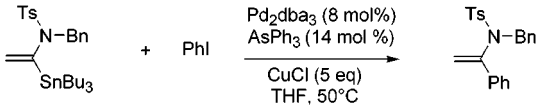
additive ligands, copper salts (CuI and CuCl), and solvents (THF, DMF, NMP, benzene, and toluene) in the reaction of iodobenzene with **2**. The best results were

Scheme 2. Cross-Coupling of 2 with PhI



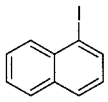
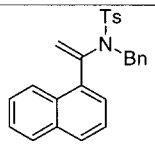
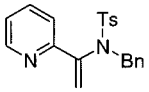
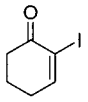
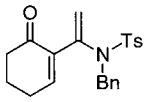
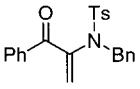
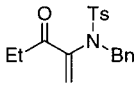
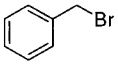
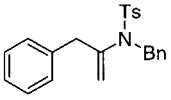
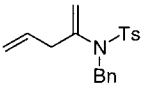
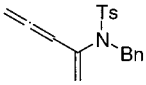
2 **3**

obtained when the reaction was performed in the presence of $Pd_2dba_3/AsPh_3$ and CuCl in THF to give compound **3** cleanly in 87% yield. With this encouraging result in hand, we then applied the above-described conditions to various electrophiles, and the results are summarized in Table 1.

On the basis of the results summarized in the above table, it appears that the modified Stille coupling procedure outlined herein has broad applicability. Indeed, we have been able to transfer the enamine moiety to a wide range of halides. Coupling with iodoaromatics is very efficient (entry 1), as is the coupling with heteroaromatics (entry 2). In the latter case, the lower yield is attributed to a somewhat lower reactivity of the bromo derivatives compared to that of the iodides, as has already been frequently stated. We also reacted the 2-iodo cyclohex-2-enone with compound **2**. The reaction proceeded in an excellent yield to give a 1,3-diene that might have synthetic potential in a cycloaddition or in a 1,4-conjugate addition reaction (entry 4). This approach also allows the reaction of both aromatic (entry 4) and aliphatic (entry 5) acyl chlorides to afford α-amino α-enones that may serve as 2-functionalized Michael acceptors. The cross-coupling with benzyl or allyl bromide was also investigated, and the expected products were obtained in fair yields (entries 6 and 7). Noteworthy is the coupling process with propargyl bromide. The reaction occurred with complete transposition to give a unique enaminoallene **11** as the sole isomer (entry 8).

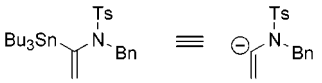
To confirm the Bu_3Sn/Cu transmetalation step, a mixture of stannyl enamine **2** and CuCl (5 equiv) was heated at reflux in THF for 2 h before adding ^2H_2O.[13] We isolated the 2-deutero *N*-benzyl, *N*-tosyl enamine 2-[^{2}H]-**12** (i.e., 70%) in 32% yield (Scheme 3). The low yield might be due to a propensity of the postulated copper intermediate to undergo β-elimination. Under the same conditions with no CuCl present, **2** remained unchanged. Thus, we postulate the catalytic cycle shown in Scheme 3 for the Pd(0)/CuCl-promoted coupling of **2** with halides.

Table 1. Cross-Coupling Reaction of 2

entry	EX	product		yield (%)
1			**4**	83
2			**5**	51
3			**6**	91
4			**7**	77
5			**8**	65
6			**9**	64
7			**10**	78
8			**11**	53

Finally, from the reactivity shown in this paper, the α-stannyl enamine **2** can be considered as a new d1 umpolung synthon, as depicted in Scheme 4.

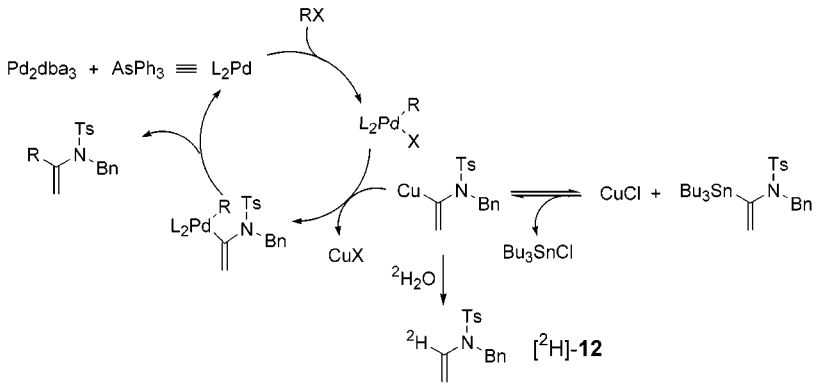
Scheme 4. 2 as a New Umpolung Synthon



Conclusion

In summary, we describe here an original route to α-substituted enamines based on a palladium/copper

Scheme 3. Proposed Catalytic Cycle for the Cross-Coupling Reaction



cross-coupling reaction of halogeno derivatives with sterically hindered α-stannyl enamines. Except for a report describing a few cross-couplings of an α-stannylated ene carbamate with acyl chlorides,[14] to the best of our knowledge, this is the first time that the Stille cross-coupling reaction of α-stannyl enamines with a wide range of halides has been clearly exemplified. This reaction efficiently complements the Suzuki−Miyaura approach in which only *β*-isomers could be obtained. The related cross-coupling reaction of the α,*β*-bisstannylated congener of **2** will be reported soon.

Experimental Section

General Considerations. All reactions were performed in flame-dried Schlenk tubes under an atmosphere of nitrogen. Aryl iodides were from Aldrich or Acros and used without further purification. Tris(dibenzylideneacetone)dipalladium-(0), triphenyl arsine, and copper chloride were from Aldrich. 2-Iodo cyclohex-2-enone was prepared according to literature procedures.[15] THF was distilled under nitrogen from sodium benzophenone ketyl. Yields in Table 1 refer to isolated compounds of greater than 95% purity as determined by ^{1}H NMR. All new compounds were fully characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, MS, and IR), HR-MS, and, in the case of crystalline compounds, melting point.

Representative Procedure for *N*-Benzyl, *N*-(2-Styryl)-tosylamide 3. A flame-dried Schlenk tube was charged with CuCl (128 mg, 1.3 mmol) and $AsPh_3$ (9 mg, 0.03 mmol), and the mixture was degassed three times under vacuum with a dry nitrogen purge. Anhydrous THF (10 mL) was introduced with concomitant stirring, and the resulting mixture was again degassed twice by the freeze−thaw process. Pd_2dba_3 (12 mg, 0.012 mmol) was then introduced, and the mixture was degassed once. When the solution was warmed to room temperature (30 min), PhI (31 μL, 0.27 mmol) was added; the mixture turned brownish, and the resulting suspension was stirred for 30 min before adding **2** (139 mg, 0.24 mmol). After being stirred at room temperature for an additional hour, the mixture was heated to 60 °C and the reaction completion was monitored by TLC. The reaction mixture was cooled, filtered over a plug of Celite (1 cm), and rinsed five times with 10 mL of ether, × and the solution was concentrated to a residue that was purified by flash chromatography over silica gel and recrystallized from pentane/ether to give 77 mg (87% yield) of **3** as colorless crystals.

R_f: 0.32 (80:20 pentane/EtOAc).

^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.76 (bd, *J* = 8.5 Hz, 2H), 7.3−7.15 (m, 12H), 5.45 (s, 1H), 5.03 (s, 1H), 4.57 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.72, 53.19, 114.63, 126.89, 127.86, 128.05, 128.44, 128.73, 129.18, 129.67, 136.24, 136.72, 137.21, 143.71, 145.03. MS (CI/NH_3) *m/z*: 364 (M + 1, 100), 381 (M + 18, 24). HR-MS (EI) *m/z*: calcd for $C_{22}H_{21}NO_2S$ [M^+], 363.1293; found, 363.1296. FTIR (KBr) *ν*: 1621, 1599, 1493, 1455, 1351, 1164. Mp: 100.3−100.4 °C.

***N*-Benzyl, *N*-(1-Naphthalen-1-yl-vinyl)-tosylamide 4.** Colorless crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.8−7.7 (m, 3H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.4 (bt, *J* = 7.9 Hz, 1H), 7.3−7.2 (m, 7H), 7.15−7.08 (m, 2H), 7.03 (d, *J* = 7.3 Hz, 1H), 5.65 (s, 1H), 5.10 (s, 1H), 4.57 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.72, 52.45, 114.11, 124.95, 125.24, 125.85, 126.27, 126.85, 127.6, 128.05, 128.34, 128.47, 129.02, 129.64, 131.87, 133.81, 134.84, 137.11, 137.4, 142.25, 143.77. MS (ESI) *m/z*: 414 (M + 1, 69), 415 (18), 436 (M + 23, 100), 437 (24). HR-MS (EI) *m/z*: calcd for $C_{26}H_{23}NO_2S$ [M^+], 413.14495; found, 413.1456. FTIR (KBr) *ν*: 1595, 1345, 1163. Mp: 117.5−117.8 °C.

***N*-Benzyl, *N*-(1-Pyridin-2-yl-vinyl)-tosylamide 5.** Slightly yellow amorphous solid. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 8.43 (m, 1H), 7.74 (bd, *J* = 7.9 Hz, 2H), 7.55 (td, *J* = 1.8, 7.9 Hz, 1H), 7.43 (bd, *J* = 7.9 Hz, 1H), 7.34−7.17 (m, 7H), 7.08−7.14 (m, 1H), 6.27 (s, 1H), 4.96 (s, 1H), 4.58 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.78, 54.78, 117.79, 121.26, 123.17, 128.05, 128.37, 128.54, 129.51, 129.64, 135.36, 135.68, 136.46, 143.87, 144.68, 148.95, 154.87. MS (CI, NH3) *m/z*: 344 (M + 1, 8), 361 (M + 18, 100). HR-MS (EI) *m/z*: calcd for $C_{21}H_{20}N_2$ [$M^+ - SO_2$], 300.16265; found, 300.1633. FTIR (NaCl) *ν*: 1585, 1348, 1163.

***N*-Benzyl, *N*-[1-(6-Oxo-cyclohex-1-enyl)-vinyl]-tosylamide 6.** Colorless crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.72 (d, *J* = 8.2 Hz, 2H), 7.35−7.15 (m, 7H), 7.01 (t, *J* = 4.2 Hz, 1H), 5.72 (s, 1H), 4.78 (s, 1H), 4.47 (s, 2H), 2.41 (s, 3H), 2.25 (m, 4H), 1.79 (m, 2H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 20.65, 21.33, 25.34, 38.31, 53.84, 116.73, 126.92, 127.08, 127.37, 127.41, 128.25, 128.51, 128.76, 134.88, 134.98, 138.99, 142.64, 149.21, 196.21. MS (ESI) *m/z*: 414 (M + 23, 100), 415 (17), 805 (dimer, 10). HR-MS (EI) *m/z*: calcd for $C_{22}H_{23}NO$ [$M^+ - SO_2$] 317.17796, found 317.1769; calcd for $C_{15}H_{16}NO$ [M^+ − Tos] 226.12319, found 226.1236. FTIR (KBr) *ν*: 1679, 1595, 1457, 1349, 1164. Mp: 90.4−90.6 °C.

***N*-Benzyl, *N*-(1-Oxo-1-phenylprop-2-en-2-yl)-tosylamide 7.** Colorless crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.84 (d, *J* = 8.5 Hz, 2H), 7.5−7.2 (m, 12H), 5.84 (s, 1H), 5.5 (s, 1H), 4.62 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.78, 51.35, 123.88, 128.05, 128.7, 129.9, 129.7, 129.8, 135.33, 135.75, 136.82, 142.03, 144.1, 192.49. MS (CI/NH_3) *m/z*: 392 (M + 1, 7), 409 (M + 18, 100). HR-MS (EI) *m/z*: calcd for $C_{16}H_{14}NO$ [M^+ − Tos], 236.10754; found, 236.1065. FTIR (KBr) *ν*: 1679, 1598, 1345, 1159. Mp: 125.2−125.5 °C.

***N*-Benzyl, *N*-(3-Oxopent-1-en-2-yl)-tosylamide 8.** Colorless crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.70 (bd, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.3−7.2 (m, 5H), 5.92 (s, 1H), 5.29 (s, 1H), 4.46 (s, 2H), 2.51 (q, 2H, *J* = 7.4 Hz), 2.43 (s, 3H), 0.92 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 8.1, 21.75, 31.71, 52.8, 122.52, 128.7, 129.21, 129.7, 134.84, 135.17, 143.8, 144.19, 199.48. MS (CI/NH_3) *m/z*: 361 (M + 18, 100). HR-MS (EI) *m/z*: calcd for $C_{16}H_{16}NO_2S$ [M^+ − EtCO], 286.09018; found, 286.0905. FTIR (KBr) *ν*: 1705, 1602, 1455, 1348, 1163. Mp: 87.8−88.1 °C.

***N*-Benzyl, *N*-(3-Phenylprop-1-en-2-yl)-tosylamide 9.** Colorless crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.7 (d, *J* = 8 Hz, 2H), 7.3−7.1 (m, 10H), 6.86 (m, 2H), 4.66 (m, 2H), 4.42 (s, 2H), 3.3 (bs, 2H), 2.45 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.32, 42.99, 53.76, 115.2, 126.13, 127,49, 127.75, 128.78, 129.2, 129.4, 135.12, 135.51, 137.26, 143.28, 147.16. MS (CI/NH_3) *m/z*: 378 (M + 1, 100). HR-MS (EI) *m/z*: calcd for $C_{16}H_{16}N$ [M^+ − Tos], 222.12827; found, 222.1272. FTIR (KBr) *ν*: 1642, 1595, 1494, 1460, 1347, 1161. Mp: 89.4−89.8 °C.

***N*-Benzyl, *N*-(Buta-1,4-dien-2-yl)-tosylamide 10.** Slightly yellow crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.72 (d, *J* = 7.9 Hz, 2H), 7.35−7.25 (m, 7H), 5.46 (tdd, *J* = 7.3, 9.8, 17.1 Hz), 4.96 (s, 1H), 4.94 (bd, *J* = 9.8 Hz, 1H), 4.87 (bd, *J* = 17.1 Hz, 1H), 4.7 (s, 1H), 4.45 (s, 2H), 2.72 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.72, 40.87, 53.77, 114.79, 117.67, 127.89, 128.05, 128.50, 129.05, 129.6, 134.16, 135.88, 136.14, 143.64, 145.94. MS (CI/NH_3) *m/z*: 328 (M + 1, 100), 345 (M + 18, 48). HR-MS (EI) *m/z*: calcd for $C_{19}H_{21}NO_2S$ [M^+], 327.12930; found, 327.1289. FTIR (KBr) *ν*: 1637, 1600, 1494, 1453, 1350, 1161. Mp: 49.8−50 °C.

***N*-Benzyl, *N*-(Penta-1,3,4-trien-2-yl)-tosylamide 11.** Colorless crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) *δ*: 7.73 (d, *J* = 8.5 Hz, 2H), 7.35−7.25 (m, 7H), 5.57 (t, *J* = 6.7 Hz, 1H), 5.15 (dd, *J* = 1.2, 1.8 Hz, 1H), 4.82 (dd, *J* = 1.2, 1.8 Hz, 1H), 4.72 (ddd, *J* = 1.2, 1.8, 6.7 Hz, 2H), 4.52 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) *δ*: 21.72, 53.26, 79.4, 93.37, 118.18, 127.89, 128.08, 128.41, 129.12, 129.54, 136.43, 137.04, 139.24, 143.42, 210.38. MS (CI/NH_3) *m/z*: 326 (M + 1, 100), 327 (68), 343 (M + 18, 28). HR-MS (EI) *m/z*: calcd for $C_{19}H_{19}NO_2S$ [M^+],

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325.11365; found, 325.1142. FTIR (KBr) ν: 2361, 2340, 1598, 1344, 1161, 1091. Mp: 94.5 °C.

***N*-Benzyl, *N*-(1-Deuteriovinyl)-tosylamide 12.** White crystals. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 7.7 (d, J = 8.5 Hz, 2H), 7.4−7.2 (m, 7H), 6.95 (dd, J = 9.2, 15.9 Hz, residual H), 4.51 (s, 2H), 4.26 (d, J = 9.2 Hz, 1H), 4.25 (bs, ^{2}H compound), 4.13 (d, J = 15.9 Hz, 1H), 4.12 (bs, ^{2}H compound), 2.42 (s, 3H). ^{2}H NMR (46 MHz, $CDCl_3$) δ: 6.98. ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 21.75, 49.02, 94.60, 94.79 (residual ^{13}CH), 127.08, 127.18, 127.6, 128.73, 130.06, 132.42, 135.72, 136.46, 144.06. MS (CI/NH_3) m/z: 288 (44), 289 (100), 290 (39), 305 (13), 306 (26), 307 (12). FTIR (KBr) ν: 1628, 1609, 1495, 1450, 1349, 1160. Mp: 101−101.2 °C.

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