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The hydrostannation of a propargylglycine derivative

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Abstract

The hydrostannation of methyl (*R,S*)-2-(*N*-diphenylmethylidene) aminopent-4-ynoate induced by a wide variety of transition metal complexes has been studied. The resulting isomeric α-amino acid derivatives featured a tributylvinylstannane in the side-chain and were separated by chromatography. A total of 24 different conditions were screened for this reaction in an attempt to effect a regioselective addition of tributyltin hydride to the alkyne group. Regioisomeric mixtures were formed in all cases and for some catalysts reduction to the allylglycine derivative was also significant.

Keywords: Stannyl; Tin; Catalysis

1. Introduction

The hydrostannation of alkynes with tributyltin hydride to produce vinylstannanes can be induced by free radicals [1] or a transition metal complex [2]. Furthermore, the hydrostannation may also proceed via the hydrogen atom of the tributyltin hydride adding as a nucleophile to an electron-deficient alkyne [3]. Among these different reaction modes the transition metal catalysed variant can be carried out under mild conditions and offers the additional advantage that different transition metal complexes may be screened in order to optimise the stereochemical outcome with regard to the formation of several isomeric vinylstannanes [4].

During a methodological study of the elaboration of the side-chain of α-amino acid derivatives using palladium catalysed chemistry, we required isomerically pure (tri-butylstannyl)allylglycine derivatives as precursors for Stille reactions [5,6]. The desired vinylstannanes were previously synthesised via a radical or a palladium induced hydrostannation of a suitable propargylglycine derivative [6,7]. However, each method afforded a mixture of regioisomeric stannanes. One of these mixtures was separated by laborious chromatography [7] and thus provided the starting materials for the Stille reactions.

A previous report had shown that the nitrogen of the diphenylmethylene protecting group of an amino acid had coordinated to the palladium catalyst and resulted in a regioselective reaction during the Stille coupling [6]. By analogy, it was anticipated that the imine nitrogen of propargylglycine derivative **1** would interact with the transition metal catalyst during the hydrostannation as in **2** (Scheme 1). Such a coordination between substrate and catalyst may have directed the hydrostannation in a regioselective manner, as indicated in Scheme 1 (many examples of the directing ability of a heteroatom in a suitable position are known [8]; *ortho*-lithiation of heteroatom substituted aromatics [9]). A recent report has demonstrated the efficacy of a regioselective, heterogeneous palladium-catalysed hydrostannation of alkenes [10].

Although **2b** would place the tributylstannane and one of the phenyl groups in close proximity, molecular models indicate that the diphenylimine group can rotate to minimize steric interactions with the bulky stannane.

2. Results and discussion

Propargylglycine derivative **1** was treated with tributyltin hydride in benzene in the presence of 0.5 mol.% $Pd(PPh_3)_4$ at ambient temperature and the product vinylstannanes **3** and **4** (formed in a 1:1 ratio) were separated by medium pressure liquid chromatography on a commercial silica column (Scheme 2). This is the

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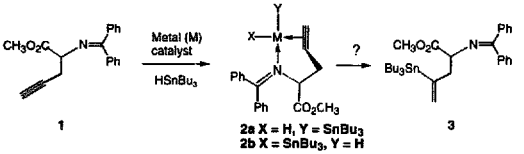


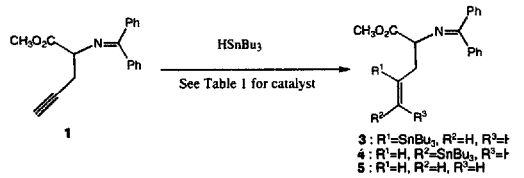
Scheme 1.

same ratio that was observed for the analogous *N*-acetyl propargyl glycine complex reported previously [6]. A decrease in the reaction temperature from 25 to −20 °C produced slightly more of the 4-(tributylstannyl)allylglycine derivative **3**, however, the regioselectivity was still very modest (2 to 1 in favour of **3**). Addition of $HSnBu_3$ to a solution of 0.5 mol.% $Pd(PPh_3)_4$ and a 1:1 mixture of **3** and **4** at ambient temperature does not change the ratio of the vinylstannanes, and produces only Sn_2Bu_6.

The reaction was then repeated with a variety of transition metal complexes as catalysts under the conditions outlined in Scheme 2. The ^1H NMR spectra of the crude products were analysed and compared with the spectra of pure vinylstannanes **3** and **4**. The ^1H NMR spectrum of vinylstannane **3** was diagnostic of a 1,1-disubstituted vinylstannane, as the two olefinic resonances at $\delta = 5.67$ ppm and at $\delta = 5.17$ ppm were coupled with a coupling constant of $J = 3$ Hz. A tin–hydrogen coupling of approximately $J = 136$ Hz for the proton at $\delta = 5.67$ ppm indicated a *trans*-stereochemical relationship relative to the stannyl moiety, whilst the coupling of approximately $J = 62$ Hz indicated a *cis*-stereochemical relationship for the proton at $\delta = 5.16$ ppm [11]. On the basis of the appearance of the ^1H NMR spectrum of vinylstannane **4**, the olefinic coupling constant for the *trans* protons could not be measured directly by inspecting the line-splitting, as the chemical shift separation of two resonances at $\delta = 5.98$ ppm (d) and $\delta = 5.76$ ppm (dt) was not sufficiently large to allow for a first order analysis of this spin system.

Among the catalysts, palladium and platinum complexes stabilised by triphenylphosphine were more active than their nickel and rhodium counterparts (Table 1, entries 2, 15, 17 and 19). Furthermore, it was evident that triphenylphosphine was a better ligand than trialkylphosphines or tri-*o*-tolylphosphine on palladium with regard to the activity of the resultant complexes (Table 1, entries 1 to 5). There was no obvious relationship between the cone angle [12] of the ligand and the regioselectivity, as both bulky and small tertiary phosphines favoured the formation of vinylstannane **4**, whilst triphenylphosphine, which in this context is a ligand with a medium-sized cone angle, afforded relatively more vinylstannane **3**. Triphenylarsine stabilised palladium complexes constituted inferior catalysts for the hydrostannation of **1** (Table 1, entries 7 and 8). Chelating phosphines did not catalyse the reaction well (Table 1, entry 6).

On the basis of previous studies, palladium complexes lacking a strongly coordinating tertiary phosphine ligand were expected to coordinate to the imine nitrogen of propargylglycine derivative **1** during the hydrostannation [6]. Therefore, the 'ligand-free' complexes derived from palladium(II) acetate, bis(benzonitrilo)palladium(II) chloride and bis(acetonitrilo)pal-



Conditions : 2.0 eq of $HSnBu_3$, 5 mol% transition metal complex, benzene, 2 h, 25 °C

Scheme 2.

Table 1
Results of the hydrostannation of propargylglycine **1**

Entry	Transition metal complex	 **4** %Yield	 **3** %Yield	 **1** %Yield	 **5** %Yield
1	$Pd(PPh_3)_4$	43	46	0	0
2	$PdCl_2(PPh_3)_2$	35	50	9	0
3	$PdCl_2[P(o\text{-}tolyl)_3]$	30	15	43	0
4	$PdCl_2(PMe_3)_2$	3	2	89	2
5	$PdCl_2(PBu_3)_2$	24	16	48	0
6	$PdCl_2$dppe	15	15	59	3
7	$PdCl_2(AsPh_3)_2$	0	0	92	0
8	"$Pd(AsPh_3)_4$" in THF	0	0	88	4
9	Pd on polyimine	5	1	33	44
10	Pd on polymer supported PPh_3	37	38	0	19
11	$PdCl_2(CH_3CN)_2$	21	16	38	21
12	$PdCl_2(PhCN)_2$	25	11	32	13
13	$Pd(OAc)_2$	25	5	49	16
14	10% Pd on carbon	0	0	92	0
15	$RhCl(PPh_3)_3$	13	8	65	10
16	Cp_2ZrHCl	0	0	77	8
17	$NiBr_2(PPh_3)_2$	8	8	79	0
18	Ni(0)	28	23	44	0
19	$PtCl_2(PPh_3)_2$	8	31	49	4
20	PPh_3	0	0	98	0
21	10% Pd on carbon, THF	7	0	28	54
22	10% Pd on carbon, THF piperidine	33	5	43	11
23	aged $Pd(PPh_3)_4$ THF	28	14	0	41
24	aged $Pd(PPh_3)_4$ THF piperidine	31	18	24	0

All yields were determined by ^1H NMR analysis of the crude reaction product and an internal standard. Vinylstannanes **3** and **4** were isolated as a mixture by chromatography for entries 1, 2, 3, 4, 10, 11, 18, 19. The reaction conditions are depicted in Scheme 2.

ladium(II) chloride were screened (Table 1, entries 11 to 13). These catalysts were less reactive than those derived from triphenylphosphine, and gave considerable quantities of the reduced compound **5**.

In several reactions the allylglycine derivative **5** was observed as a by-product (Table 1, entries 9 to 13). This by-product may have arisen via a protodestannylation of **3** or **4**, or via a hydrogenation of **1**. When a pure mixture of vinylstannanes **3** and **4** was submitted to the hydrostannation conditions ($Pd(CH_3CN)_2Cl_2$ and $HSnBu_3$), allylglycine **5** was not detected and unchanged vinylstannanes **3** and **4** were isolated. This experiment suggested that allylglycine **5** was formed from propargylglycine derivative **1** directly, and not through the intermediacy of vinylstannanes **3** and **4**. Catalysts that afforded a relatively large amount of allylglycine **5** were distinguished by a possible aggregation of several palladium atoms. Such an aggregation may have occurred when palladium was adsorbed on a solid support during the synthesis of palladium on polymer supported triphenylphosphine or when palladium atoms aggregate in solution due to the absence of a stabilising tertiary phosphine ligand, as in palladium(II) acetate. The hydrostannation of **1** in the presence of 'aged $Pd(PPh_3)_4$' gave considerable quantities of the allylglycine **5** (Table 1, entry 23). When the same reaction was performed in a mixture of THF and piperidine, no allylglycine was formed. Presumably the strong ligand piperidine prevented the aggregation of palladium atoms in solution or, alternatively, suppressed the hydrogenation catalysed by oligomeric palladium species directly. In contrast to these results, the addition of palladium on carbon to a pure mixture of **3** and **4** in THF gave predominantly the destannylated allylglycine **5**. The addition of piperidine to the palladium on carbon catalyst also suppressed the formation of the allylglycine **5** (Table 1, entry 22).

In summary, 19 transition metal complexes have been screened as catalysts for the addition of tributyltin hydride to propargylglycine derivative **1**, however, a regioselective formation of the product vinylstannanes was not achieved.

3. Experimental

THF was distilled from sodium/benzophenone, other solvents were fractionated through a 30 cm long column

packed with glass helices. 'Hexane' refers to the fraction of light petroleum boiling between 67 and 69 °C. Pd on polyimine, $PdCl_2(CH_3CN)_2$, $PdCl_2(PhCN)_2$, $PdCl_2(PBu_3)_2$, $PdCl_2(PPh_3)_2$, $PdCl_2$dppe and $Pd(OAc)_2$ was purchased from Aldrich. The following compounds were prepared from literature procedures: methyl *N*-diphenylmethyleneimine glycinate [13], $PdCl_2(PMe_3)_2$ [14], amorphous Pd-metal [15], $RhCl(PPh_3)_3$ [16], $NiBr_2(PPh_3)_2$ [17], $PtCl_2(PPh_3)_2$ [16], Cp_2ZrHCl [18], $PdCl_2[P(o\text{-tolyl})_3]_2$ [19] and $PdCl_2(AsPh_3)_2$ [19]. Reactions were performed under an atmosphere of nitrogen unless otherwise mentioned.

3.1. Methyl (R,S)-2-(N-diphenylmethylidene)aminopent-4-ynoate (1)

A stirred solution of diiso-propylamine (5.109 g, 51.00 mmol) in THF (80 ml) was cooled to −80 °C under an atmosphere of nitrogen. To this was added *n*-butyl lithium in hexanes (2.3 M, 52.00 mmol), a solution of methyl (*R,S*)-*N*-diphenylmethylideneglycinate (8.81 g, 50.00 mmol) in THF (20 ml), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone (10 ml, 82.70 mmol) and freshly distilled propargyl bromide (8.92 g, 75.00 mmol). Each addition lasted for 2 min and was followed by a waiting period of 10 min. After the addition was complete the mixture was stirred for 1 h and quenched by the addition of sat. NH_4Cl (10 ml) at −80 °C. The flask was removed from the cooling bath and stirring was continued for 10 min. The contents were poured onto sat. NH_4Cl (100 ml) and the aqueous phase was extracted with a 1:1 mixture of hexane/ether (3 × 50 ml). The combined organic phase was washed with water (2 × 50 ml), dried ($MgSO_4$) and the solvent evaporated to yield an oily residue which was stirred at 50 °C under reduced pressure (0.5 Torr). The title compound **1** was obtained (10.44 g, 97% yield). Anal. Found: C, 78.61; H, 5.88; N, 4.37. $C_{19}H_{17}NO_2$ Calc.: C, 78.33; H, 5.88; N, 4.81%. ^{1}H NMR: δ 8.29 (bs, 1H, N=CH), 7.77–7.31 (m, 5H, ar), 4.09 (m, 1H, H2), 3.63 (s, 3H, CH_3), 2.95–2.68 (m, 2H, H3), 2.14 (t, J = 2.6 Hz, 1H, H5). ^{13}C NMR: δ 169.9, 163.9, 134.7, 130.6, 127.9, 127.8, 79.6, 70.8, 70.7, 51.4, 22.4. IR (neat) ν_{max} 3300, 1740, 1620, 1450, 1290, 1210, 1180, 705 cm^{-1}. MS (EI) m/z 215 (M^+).

3.2. Methyl (R,S)-2-[N-(diphenylmethylidene)amino]-4-(tributylstannyl)but-4-enoate (3) and methyl (2RS,4E)-2-[N-(diphenylmethylidene)amino]-5-(tributylstannyl)-but-4-enoate (4)

To a degassed solution of propargylglycine derivative **1** (867 mg, 2.976 mmol) in benzene (50 ml) was added $Pd(PPh_3)_4$ (17 mg, 0.015 mmol). When the solution became homogeneous, tributyltin hydride (1.039 g, 3.571 mmol) was added dropwise from a syringe over a period of 20 min at ambient temperature. After 10 min of stirring the solvent was evaporated and the residue analysed by ^{1}H NMR spectroscopy. Resonances at δ = 5.16 ppm (**3**) and δ = 5.98 ppm (**4**) were detected in a ratio of 1.3:1.0. The crude product was purified by MPLC (1:4 ethyl acetate/hexane) to afford **3** (641 mg, 37%) and **4** (555 mg, 32%) as isomerically pure compounds. Anal. Found: C, 64.03; H, 6.99; N, 3.37. $C_{31}H_{45}NO_2Sn$ (**3**) Calc.: C, 63.93; H, 7.79; N, 2.41%.

3.2.1. Data for vinylstannane 3

^{1}H NMR: δ 7.65–7.15 (m, 10H, ar), 5.67 (d and tin satellites, J = 3 Hz, 1H, J_{SnH} = 136 Hz, $H5_{pro\text{-}E}$), 5.16 (d and tin satellites, J = 3 Hz, J_{SnH} = 62 Hz, 1H, $H5_{pro\text{-}Z}$), 4.20 (dd, J = 6 Hz, J = 7 Hz, 1H, H2), 3.69 (s, 3H, CH_3), 2.96 (dd, J = 13 Hz, J = 6 Hz, 1H, H3), 2.65 (dd, J = 13 Hz, J = 7 Hz, 1H, H3), 1.48–0.78 (m, 27H, Bu). ^{13}C NMR: δ 172.0, 171.0, 150.1, 140.0, 136.5, 130.3, 128.9, 128.7, 128.6, 128.5, 128.1, 128.0, 65.7, 51.9, 44.8, 29.0, 27.3, 13.7, 9.3. IR (neat) ν_{max} 2948, 1740, 1632, 1452, 1203, 1185, 700 cm^{-1}. MS (EI) m/z 582 (M^+ for ^{119}Sn).

3.2.2. Data for vinylstannane 4

^{1}H NMR: δ 7.62–7.13 (m, 10H, ar), 5.98 (d and tin satellites, J_{SnH} = 74 Hz, 1H, H5), 5.76 (dt, 1H, H4), 4.19 (dd, 1H, H2), 3.71 (s, 3H, CH_3), 2.82–2.70 (m, 2H, H3), 1.48–0.78 (m, 27H, Bu). ^{13}C NMR: δ 172.5, 170.8, 144.3, 139.6, 136.4, 131.7, 130.3, 128.8, 128.6, 128.4, 128.0, 65.4, 52.0, 42.2, 29.0, 27.2, 13.6, 9.3 (tin satellites, J_{SnH} = 272 Hz, $SnCH_3$). IR (neat) ν_{max} 2953, 1738, 1635, 1460, 1198, 1185, 700 cm^{-1}. MS (EI) m/z 582 (M^+ for ^{119}Sn).

3.2.3. Screening of transition metal complexes as catalysts for the hydrostannation of propargylglycine 1

To a degassed solution of propargylglycine derivative **1** (98 mg, 0.336 mmol) in THF (5 ml) was added one of the transition metal complexes (0.017 mmol) listed in Table 1. Tributyltin hydride (196 mg, 0.672 mmol) was added dropwise from a syringe over a period of 2 h at ambient temperature using a syringe pump. After 10 min of stirring the solvent was evaporated and the residue and a known quantity of benzaldehyde (typically 30 mg, internal standard) were dissolved in $CDCl_3$ (approximately 1 ml). A portion of this sample (around 20%) was analysed by ^{1}H NMR spectroscopy. The intensities of the resonances at δ = 10.2 ppm (benzaldehyde), δ = 5.98 ppm (**4**), δ = 5.16 ppm (**3**), δ = 1.95 ppm (**1**), δ = 4.35 ppm (**1**) and at δ = 5.10–5.00 ppm (**5**) were measured and the amount of compounds **1**, **3**, **4** and **5** present in solution calculated. The results are listed in Table 1. In some cases the crude product was purified by MPLC (1:4 hexane/ethyl acetate) to afford vinylstannanes **3** and **4**.

This general procedure was used for the following

transition metal complexes: $PdCl_2(PPh_3)_2$, $PdCl_2[P(o\text{-tolyl})_3]_2$, $PdCl_2(PMe_3)_2$, $PdCl_2(PBu_3)_2$, $Pd(OAc)_2$, $PdCl_2$dppe, $PdCl_2(AsPh_3)_2$, Pd on polyimine, Pd on polymer supported PPh_3, $PdCl_2(CH_3CN)_2$, $PdCl_2(PhCN)_2$, amorphous Pd-metal, $RhCl(PPh_3)_3$, $NiBr_2(PPh_3)_2$, $PtCl_2(PPh_3)_2$, an aged sample of $Pd(PPh_3)_4$ and PPh_3 (control reaction).

3.2.4. '$Pd(AsPh_3)_4$' as a catalyst in the hydrostannation of 1

A yellow mixture was prepared by stirring Pd_2dba_3 (7 mg, 7.6 mmol) and triphenylarsine (37 mg, 0.122 mmol) in THF (5 ml) at ambient temperature. Propargylglycine **1** (89 mg, 0.306 mmol) was added followed by tributyltin hydride (178 mg, 0.612 mmol), which was introduced dropwise with a syringe over a period of 20 min. After stirring for 10 min the solvent was evaporated and the residue analysed in the presence of benzaldehyde by ^{1}H NMR spectroscopy. The resonances were consistent with **1** and a trace amount of **5**.

3.2.5. Cp_2ZrHCl as a catalyst in the hydrostannation of 1

To a stirred solution of propargylglycine **1** (103 mg, 0.354 mmol) in dry dichloromethane (2 ml) at ambient temperature was added Cp_2ZrHCl (5 mg, 18 mmol) under an atmosphere of nitrogen. Tributyltin hydride (206 mg, 0.708 mmol) was added over a period of 10 min. The mixture was stirred for 20 min and the solvent was evaporated. The ^{1}H NMR spectrum (with benzaldehyde as internal standard) was consistent with the presence of unchanged **1** and allylglycine **5** in a ratio 10:1.

3.2.6. 'Ligand-free Ni^0' as a catalyst in the hydrostannation of 1

To a stirred suspension of anhydrous orange $NiCl_2$ (4 mg, 12 mmol) in dry THF (3 ml) was added at ambient temperature lithium aluminium hydride (4 mg, 0.105 mmol). The mixture darkened and a solution of propargylglycine **1** (72 mg, 0.364 mmol) in THF (2 ml) was quickly added followed by tributyltin hydride (212 mg, 0.728 mmol), which was introduced dropwise with a syringe over a period of 5 min. The solvent was evaporated and the residue was analysed by ^{1}H NMR spectroscopy in the presence of benzaldehyde. The crude product was purified by MPLC to afford **4** (15 mg, 7%), **3** (59 mg, 28%) and **1** (29 mg, 40%).

3.3. Methyl (R,S)-2-[N-(didiphenylmethylidene)amino]but-4-enoate (5)

3.3.1. Method 1

To a stirred suspension of propargylglycine **1** (56 mg, 0.192 mmol) and 5% palladium on carbon (77 mg) in THF (5 ml) was added tributyltin hydride (447 mg, 1.536 mmol) from a syringe at 50 °C over a period of 3 h using a syringe pump. The mixture was filtered through Kenite and the solvent evaporated. The residue was purified by MPLC to afford pure **5** (30 mg, 54%). The ^{1}H NMR spectral data of **5** were in agreement with the reported values [20]. Other fractions contained **1** (15 mg, 28%) and **4** (8 mg, 7%).

^{1}H NMR: δ 7.65–7.15 (m, 10H, ar), 5.74–5.60 (m, 1H, H4), 5.10–5.00 (three bs, 2H, H5), 4.16 (m, 1H, H2), 3.72 (s, 3H, CH_3), 2.75–2.57 (m, 2H, H3). ^{13}C NMR: δ 172.4, 171.0, 139.8, 136.3, 134.2, 130.4, 128.9, 128.7, 128.5, 128.0, 127.9, 117.7, 65.3, 52.1, 38.2.

3.3.2. Method 2 (in THF)

To a solution of propargylglycine derivative **1** (56 mg, 0.192 mmol) and aged $Pd(PPh_3)_4$ (11 mg, 9.5 mmol) in THF (4 ml) was added tributyltin hydride (279 mg, 0.96 mmol) from a syringe at ambient temperature over a period of 3 h using a syringe pump. The solvent was evaporated and the crude product purified by MPLC to yield compounds **4** (31 mg, 28%), **3** (16 mg, 14%) and **5** (23 mg, 41%).

3.3.3. Method 3 (Pd on C as a catalyst for the destannylation of 3 and 4)

A 1:1 pure mixture of vinylstannanes **3** and **4** (51 mg, 0.175 mmol) was treated with tributyltin hydride (407 mg, 1.400 mmol) and 5% palladium on carbon (37 mg) in THF (5 ml) as described under Method 1. Signals at $\delta = 5.10–5.00$ ppm due to allylglycine **5** were prominent in the ^{1}H NMR spectrum of the crude reaction product. The crude product was not purified.

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