Catalytic alkynylation of 6-bromosteroids

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An efficient method for synthesis of 6-alkynyl-substituted androstane derivatives was developed *via* the Pd-catalyzed Sonogashira—Hagihara coupling reaction. The use of AgCl as the cocatalyst (instead of traditionally used CuI) was shown to increase the activity of the catalytic system in several cases.

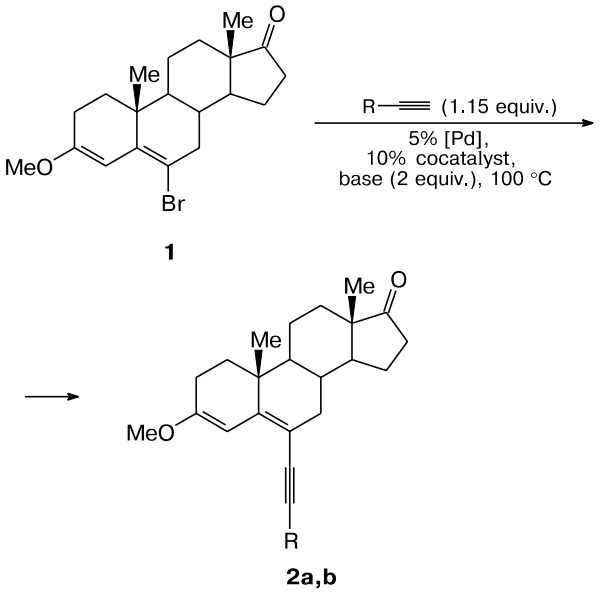
Key words: alkynylation, steroids, Sonogashira—Hagihara reaction, dienynes.

The palladium-catalyzed reaction of terminal alkynes with aryl or vinyl halides (Sonogashira—Hagihara coupling reaction)[1] is a convenient method for the introduction of the C≡C bond into complicated organic molecules. This reaction was successfully used for the synthesis of new alkynyl derivatives of steroids.[2] The starting compounds were 3- and 17-enol triflates of steroids, which are smoothy transformed, under standard conditions, into the ethynylation products in yields from moderate to high. The use of this reaction involving a series of *ortho*-substituted arylacetylenes followed by ring closure makes it possible to obtain steroid molecules with heterocyclic substituents, such as indole,[3] benzofuran,[4] quinolone,[5] and butenolide.[6] The initial steroid triflates can easily be synthesized using the Stang method[7] from the corresponding carbonyl compounds. At the same time, this method has several drawbacks: the enol triflate group is formed only in the carbonyl group site in the molecule, and the enolization of the carbonyl group of steroid is not always regioselective.

Until the recent time, halosteroids have not been used in the Sonogashira—Hagihara reaction. We have recently shown[8,9] that 4(6)-bromo(chloro)-substituted derivatives of steroids of the androstane and pregnane series, which were described in the literature or obtained by us for the first time,[9] can successfully be used in the Pd-catalyzed Suzuki reaction to introduce functionally substituted aryl and hetaryl fragments into positions 4 and 6. In the present work, we report the successful use of 6-bromosteroids in the Sonogashira—Hagihara coupling reaction.

Although the regularities of the Pd-catalyzed alkynylation of aryl and vinyl halides were studied rather widely, the standard protocol should almost always be modified to choose the best reaction conditions. The cross-couping conditions were optimized using as an example 6-bromo-3-methoxyandrosta-3,5-dien-17-one (**1**) (Scheme 1) containing the electron-donating methoxy group, which decreases the reactivity of the substrate in the step of oxidative addition to the Pd catalyst. The study of the activity of various sources of the Pd catalysts in the reaction of compound **1** with phenylacetylene in the presence of CuI and Et_3N in aqueous dioxane shows[10] that the ligand environment on palladium exerts a strong effect on the yield of alkynylation product **2a**.

Scheme 1



1

2a,b

R = Ph (**a**), CH_2OH (**b**)

The yields (according to the ^1H NMR data) of alkynylation product **2a** (5% [Pd], 10% CuI, 2 equiv. Et_3N, dioxane—H_2O (3 : 1), 100 °C, 4 h) on different catalysts

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are presented below (dppb is 1,4-bis(diphenylphosphino)butane, dppf is 1,1′-bis(diphenylphosphino)ferrocene).

Catalyst	Yield (%)	Catalyst	Yield (%)
$Pd(MeCN)_2Cl_2$	0	$Pd/C + PPh_3$	21
$Pd(dppb)Cl_2$	12	$Pd(PPh_3)_2Cl_2$	23
$Pd(dppf)Cl_2$	21	$Pd(PPh_3)_4$	53

The most efficient catalyst was $Pd(PPh_3)_4$ (53%), whereas the use of $Pd(PPh_3)_2Cl_2$ as the catalyst results in a considerably lower yield of product **2a**. Interestingly, the $Pd/C + PPh_3$ catalytic system, in which the concentration of active palladium is very low (it is considered that only soluble catalyst complexes are involved in the reaction[11]) and, hence, the PPh_3 : "active Pd" ratio substantially exceeds 4 : 1, exhibits the activity comparable to that in the case of $Pd(PPh_3)_2Cl_2$. At the same time, the "ligand-free" catalyst $Pd(MeCN)_2Cl_2$ gives no even trace amounts of **2a**, and the Pd catalysts with bidentate ligands are somewhat less efficient than $Pd(PPh_3)_2Cl_2$.

It should be mentioned that for all the catalysts used the only conversion product of steroid **1** is alkynylated product **2a**. At the same time, in this case we failed to separate product **2a** and starting steroid **1** by chromatography. Therefore, for the preparative synthesis of **2a** it was necessary to find conditions for the full completion of the cross-coupling.

The cross-couping catalyzed by the $Pd(PPh_3)_4$/CuI system is very sensitive to the nature of the solvent and base used in the reaction. For instance, no product **2a** is formed when the solvent is either Et_3N widely used for this purpose or THF that has been introduced in practice of the Sonogashira reaction rather recently[12] (Table 1). At the same time, the reaction occurs with moderate yields in both polar acetonitrile (32%) and less polar piperidine[13] (55%). The addition of $Bu_4N^+I^-$ favoring[14–16] the formation of anionic palladium complexes to the reaction mixture induces no changes in the yield of alkynylation product **2a**. To the contrary, the addition of water increases considerably the yield of compound **2a**. The highest yields of the product are observed in aqueous piperidine (78%) and aqueous dioxane (53%). It should be mentioned that the optimum volume fraction of water depends substantially on the nature of the organic cosolvent and its increase can result in a sharp decrease in the yield of compound **2a**.

The use of potassium carbonate or ammonia as bases in aqueous dioxane (3 : 1) insignificantly affects the yield of the coupling product compared to that of triethylamine. Meanwhile, the reaction in the presence of piperidine affords product **2a** in 95% yield. The further elongation of the reaction duration does not allow one to achieve the complete conversion of steroid **1** to compound **2a**.

As reported recently,[17] silver salts can be used as cocatalysts instead of copper(I) iodide in the Sonogashira reaction. In our case, the replacement of copper(I) iodide by silver salts (AgCl or AgBr) results in the 100% conversion of steroid **1**. However, to suppress the formation of by-products, the amount of piperidine in the reaction mixture should be increased. The yield of coupling product **2a** after column chromatography on silica gel was 80%. The coupling of compound **1** with propargyl alcohol (Table 2) in aqueous dioxane (3 : 1) in the presence of piperidine and the $Pd(PPh_3)_4$/CuI catalytic system, unlike a similar reaction of steroid **1** with phenylacetylene, gives no even trace amounts of alkynylation product **2b**. At the same time, the use of AgCl as the cocatalyst makes it possible to obtain a good yield of the product with some elongation of the reaction time. The further increase in the activity of the catalytic system is achieved by the addition of 40 mol.% $Bu_4N^+Br^-$, providing the complete conversion of the starting halide **1**.

The reaction of compound **1** with acetylenes containing withdrawing substituents in an aqueous dioxane—piperidine system is complicated by the conjugated addition of amine to the triple bond. This process is the only route of the reaction in the case of 4-nitrophenylacetylene.

Table 1. Effect of the nature of the solvent and base on the yield of alkynylation product **2a**[a]

Solvent	Base	Yield[b] (%)	Solvent	Base	Yield[b] (%)
Benzene	Et_3N	0	THF	Et_3N	0
$CHCl_3$	Et_3N	0	Dioxane—H_2O (19 : 1)	Et_3N	10
Et_3N	Et_3N	0	Dioxane—H_2O (3 : 1)	Et_3N	53
MeCN	Et_3N	32	Piperidine	Piperidine	55
MeCN—H_2O (19 : 1)	Et_3N	44	Piperidine—H_2O (19 : 1)	Piperidine	78
MeCN—H_2O (3 : 1)	Et_3N	12	Piperidine—H_2O (3 : 1)	Piperidine	30
MeCN/Bu_4NI (2 equiv.)	Et_3N	31	Dioxane—H_2O (3 : 1)	Piperidine	95
Dioxane—H_2O (3 : 1)	NH_3 (aqueous)	66		K_2CO_3	43

[a] 5% $Pd(PPh_3)_4$, 10% CuI, 4 h, 100 °C.
[b] According to the ^1H NMR data.

Table 2. Yields of the alkynylation products in the reaction of steroid **1** with terminal acetylenes[a]

Product	Catalyst	*t*/h	Yield[b] (%)
2a	$Pd(PPh_3)_4$/CuI	4	95
	$Pd(PPh_3)_4$/AgCl	4	100 (80)
2b	$Pd(PPh_3)_4$/CuI	4	0
	$Pd(dppf)Cl_2$/AgCl	4	22
	$Pd(PPh_3)_4$/AgCl	4	51
	$Pd(PPh_3)_4$/AgCl	24	78
	$Pd(PPh_3)_4$/AgCl/40% $Bu_4N^+Br^-$	24	100 (66)

[a] 5% $Pd(PPh_3)_4$, 10% CuI, dioxane—H_2O (3 : 1), 2 equiv. piperidine, 100 °C or 5% $Pd(PPh_3)_4$, 10% AgCl, dioxane—H_2O—piperidine (2 : 1 : 1), 100 °C.
[b] According to the ^1H NMR data, the preparative yield is given in parentheses.

Table 3. Yields of the products of alkynylation of bromosteroid **3** by various acetylenes[a]

Product	R	Cocatalyst	*t*/h	Yield[b] (%)
4a	Ph	CuI	4	100 (86)
4b	CH_2OH	CuI	4	100 (72)
4c	n-C_5H_{11}	CuI	4	95
			7	100
		AgCl	4	100 (58)
4d	Bu	AgCl	4	100 (72)
4e	CH_2NMe_2	CuI	4	100 (91)

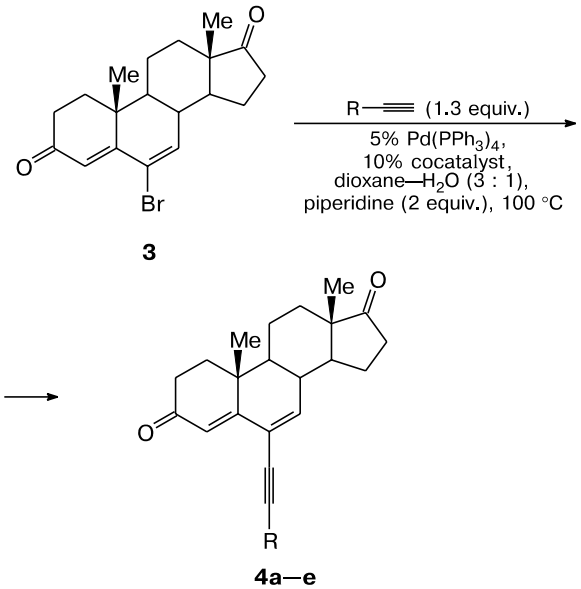
[a] 5% $Pd(PPh_3)_4$, 10% CuI (AgCl), 2 equiv. piperidine, dioxane—H_2O (3 : 1), 100 °C.
[b] According to the ^1H NMR data, the preparative yield is given in parentheses.

The addition to less electron-deficient 4-cyanophenylacetylene is slower, and the yield of the alkynylation product is 17% (according to the ^1H NMR data).

Enol ether **2a** in aqueous ethanol in the presence of HCl or HBr is hydrolyzed very slowly. For instance, at room temperature the HCl-catalyzed reaction occurs for 3 days and affords a complicated mixture of poorly separable products, which were not identified.

In the most cases, the Sonogashira reaction of 6-bromoandrosta-4,6-diene-3,17-dione (**3**) with various terminal acetylenes (Scheme 2) proceeds better than that with halide **1** (Table 3). For instance, its cross-coupling with phenylacetylene occurs with catalysis by $Pd(PPh_3)_4$ with the CuI cocatalyst in aqueous dioxane in the presence of piperidine as a base for 4 h. Similarly, the reaction with propargyl alcohols requires no use of AgCl as the cocatalyst.

Scheme 2



The cross-coupling products of bromosteroid **3** with phenylacetylene and propargyl alcohol were obtained in 86 and 72% yields, respectively. The reaction with hept-1-yne was completed in the presence of CuI in 50% excess acetylene with an elongation of the process duration. When AgCl is used as the cocatalyst, the cross-coupling reactions of bromosteroid **3** with hept-1-yne and hex-1-yne proceed for 4 h with 30% excess acetylene. *N*,*N*-Dimethylpropargylamine reacts with bromosteroid **3** with 100% conversion under the conditions similar to those used in the case of phenylacetylene or propargyl alcohol.

In summary, we developed an efficient method for the synthesis of earlier unknown 6-alkynyl-substituted androstane derivatives by the palladium-catalyzed Sonogashira—Hagihara reaction. The use of AgCl as the cocatalyst in aqueous dioxane was shown to increase considerably the activity of the catalytic system.

Experimental

The course of the reactions was monitored by thin layer chromatography on Silufol-254 plates and ^1H NMR spectroscopy. The yields of alkynylation of 6-halosteroids were determined by ^1H NMR spectroscopy. ^1H NMR spectra were recorded on a Varian VXR-400 instrument with a working frequency of 400 MHz in $CDCl_3$. Chemical shifts are presented in the δ scale and were measured relative to HMDS (δ = 0.05). The ratio of products in reaction mixtures was determined from the ratios of signals of vinylic protons at the C(4) atom. MALDI-TOF spectra were measured on a Bruker Daltonics UltraFlex instrument in dithranol. Starting halosteroids **1** and **3** were synthesized according to earlier described[9] procedures. Products were isolated by column chromatography on silica gel (Merck, 0.040—0.063 mm). After the eluent was evaporated *in vacuo*, the resulting oil was dissolved in ether. The repeated

evaporation gives compounds **2a,b** and **4a,b** as solid crystalline substances. After evaporation on a rotary evaporator, compounds **4c—e** congeal as very hard glassy products well soluble in organic solvents.

Alkynylation of 6-bromo-3-methoxyandrosta-3,5-dien-17-one (1). Bromo steroid **1** (56.9 mg, 0.15 mmol), $Pd(PPh_3)_4$ (8.7 mg, 7.5 μmol), AgCl (2.1 mg, 15 μmol), dioxane (1 mL), water (0.5 mL), piperidine (0.5 mL), and the corresponding acetylene (0.195 mmol) were placed under argon in a hermetically closed glass vessel. The reaction mixture was heated for 4—24 h at 100 °C. The obtained suspension was diluted with dichloromethane and washed with water, and the organic layer was separated and dried with anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. Crystals of compounds **2a,b** can be obtained by slow precipitation with petroleum ether from a dichloromethane solution.

6-(2-Phenylethynyl)-3-methoxyandrosta-3,5-dien-17-one (2a). The eluent was CH_2Cl_2. The yield was 48 mg (80%), m.p. 115—116 °C. Found (%): C, 83.50; H, 8.42. $C_{28}H_{32}O_2$. Calculated (%): C, 83.96; H, 8.05. ^{1}H NMR, δ: 7.42 (m, 2 H); 7.28 (m, 3 H); 5.96 (d, 1 H, H(4), J = 1.5 Hz); 3.67 (s, 3 H, OMe); 2.48, 2.35 (both m, 1 H each); 2.07 (m, 4 H); 1.86 (m, 3 H); 1.72 (m, 1 H); 1.64—1.08 (m, 7 H); 1.03, 0.90 (both s, 3 H each, Me).

6-(3-Hydroxyprop-1-yn-1-yl)-3-methoxyandrosta-3,5-dien-17-one (2b) was synthesized by the general procedure with the addition of $Bu_4N^+Br^-$ (19.3 mg, 0.06 mmol). The eluent was a CH_2Cl_2—Et_2O (20 : 1) mixture. The yield was 35 mg (66%), m.p. 193—195 °C. Found (%): C, 77.91; H, 8.70. $C_{23}H_{30}O_3$. Calculated (%): C, 77.93; H, 8.53. ^{1}H NMR, δ: 5.79 (s, 1 H, H(4)); 4.46 (s, 2 H); 3.64 (s, 3 H, OMe); 2.39 (m, 3 H); 2.10 (m, 2 H); 2.00—1.20 (m, 12 H); 1.05 (m, 1 H); 0.99, 0.89 (both s, 3 H each, Me). ^{13}C NMR, δ: 220.8, 159.0, 147.3, 107.3, 96.8, 91.2, 86.1, 54.6, 51.7, 51.6, 47.7, 47.5, 35.8, 35.8, 35.0, 33.5, 31.3, 31.0, 25.2, 21.7, 20.3, 18.9, 13.6.

Alkynylation of 6-bromoandrosta-4,6-diene-3,17-dione (3). Bromosteroid **3** (0.15 mmol), $Pd(PPh_3)_4$ (8.7 mg, 7.5 μmol), CuI (2.9 mg, 15 μmol), dioxane (1.5 mL), water (0.5 mL), the corresponding acetylene (0.195 mmol), and piperidine (30 μL, 0.3 mmol) were placed under argon in a hermetically closed glass vessel. The reaction mixture was heated for 4 h at 100 °C. The resulting suspension was diluted with dichloromethane and washed with water, and the organic layer was separated and dried with anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. Compounds **4a,b** were obtained as crystalline products by reprecipitation with petroleum ether from dichloromethane. Compounds **4c—e** are noncrystallizing solid glassy products.

6-(2-Phenylethynyl)androsta-4,6-diene-3,17-dione (4a). The eluent was a CH_2Cl_2—Et_2O (20 : 1) mixture. The yield was 50 mg (86%), m.p. 113—114 °C. Found (%): C, 84.47; H, 7.34. $C_{27}H_{28}O_2$. Calculated (%): C, 84.34; H, 7.34. ^{1}H NMR, δ: 7.46 (m, 2 H); 7.32 (m, 3 H); 6.63 (d, 1 H, H(4), J = 2.4 Hz); 6.45 (s, 1 H, H(7)); 2.52 (m, 4 H); 2.19 (m, 2 H); 2.05, 1.90 (both m, 1 H each); 1.74 (m, 3 H); 1.48, 1.32 (both m, 2 H each); 1.16, 0.97 (both s, 3 H each, Me).

6-(3-Hydroxyprop-1-yn-1-yl)androsta-4,6-diene-3,17-dione (4b). The eluent was a CH_2Cl_2—Et_2O (4 : 1) mixture. The yield was 37 mg (72%), m.p. 206—207 °C. Found (%): C, 78.05; H, 7.87. $C_{22}H_{26}O_3$. Calculated (%): C, 78.07; H, 7.74. ^{1}H NMR, δ: 6.56 (d, 1 H, H(4), J = 1.5 Hz); 6.34 (s, 1 H, H(7)); 4.42 (d, 2 H, J = 5.0 Hz); 2.47 (m, 5 H); 2.16 (m, 2 H); 2.02, 1.89 (both m, 1 H each); 1.72 (m, 3 H); 1.46, 1.28 (both m, 2 H each); 1.12, 0.95 (both s, 3 H each, Me).

6-(Hept-1-yn-1-yl)androsta-4,6-diene-3,17-dione (4c). The eluent was CH_2Cl_2. The yield was 33.2 mg (58%). The product was a slightly yellowish solid glassy mass. ^{1}H NMR, δ: 6.46 (br.s, 1 H, H(4)); 6.36 (s, 1 H, H(7)); 2.62—2.37 (m, 4 H); 2.32 (t, 2 H, J = 7.2 Hz); 2.22—1.21 (m, 14 H); 1.12 (s, 3 H, Me); 0.95—0.90 (m, 9 H). ^{13}C NMR, δ: 219.2, 199.5, 161.0, 142.4, 124.2, 122.4, 92.7, 76.5, 50.0, 48.5, 48.2, 37.0, 36.0, 35.6, 34.0, 33.7, 31.2 (2 C), 28.4, 22.1, 21.3, 19.9, 19.2, 16.2, 13.9, 13.6. MS MALDI-TOF, m/z: 379.24 $[M + H]^+$. Calculated for $C_{26}H_{35}O_2$: M 379.26.

6-(Hex-1-yn-1-yl)androsta-4,6-diene-3,17-dione (4d). The eluent was CH_2Cl_2. The yield was 39.3 mg (72%). The product was a slightly yellowish solid glassy mass. ^{1}H NMR, δ: 6.47 (d, 1 H, H(4), J = 2.1 Hz); 6.35 (s, 1 H, H(7)); 2.62—2.32 (m, 6 H); 2.21—2.00 (m, 3 H); 1.88 (m, 1 H); 1.77—1.21 (m, 10 H); 1.12 (s, 3 H, Me); 0.95—0.90 (m, 7 H). ^{13}C NMR, δ: 219.2, 199.5, 161.0, 142.4, 124.2, 122.3, 92.6, 76.5, 50.0, 48.5, 48.2, 36.9, 36.0, 35.5, 33.9, 33.7, 31.1, 30.7, 22.0, 21.3, 19.8, 18.9, 16.2, 13.6 (2 C). MS MALDI-TOF, m/z: 365.23 $[M + H]^+$. Calculated for $C_{25}H_{33}O_2$: M 365.25.

6-(3-Dimethylaminoprop-1-yn-1-yl)androsta-4,6-diene-3,17-dione (4e). The eluent was a CH_2Cl_2—MeOH (50 : 1) mixture. The yield was 49.9 mg (91%). The product was a slightly yellowish solid glassy mass. ^{1}H NMR, δ: 6.54 (d, 1 H, H(4), J = 2.1 Hz); 6.35 (s, 1 H, H(7)); 3.40 (s, 2 H); 2.63—2.30 (m, 4 H); 2.32 (s, 6 H, NMe_2); 2.21—2.00 (m, 2 H); 1.88 (m, 1 H); 1.73 (m, 3 H); 1.54—1.23 (m, 4 H); 1.13, 0.96 (both s, 3 H each, Me); 0.84 (m, 1 H). ^{13}C NMR, δ: 219.1, 199.3, 160.5, 143.6, 124.2, 121.8, 86.8, 81.2, 49.8, 48.4, 48.3, 48.1, 44.3 (2 C), 37.0, 35.9, 35.5, 33.8, 33.6, 31.1, 21.2, 19.8, 16.2, 13.6. MS MALDI-TOF, m/z: 366.23 $[M + H]^+$. Calculated for $C_{24}H_{32}NO_2$: M 366.24.

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