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Homogeneous catalytic dehalodimerization of 17-iodo-Δ^{16} steroids

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17-Iodo-Δ^{16} steroids undergo selective dimerization and carbonylative dimerization in the presence of palladium catalysts in dimethylformamide which result in 16-17'-coupled dienes and 17-carboxylic anhydrides, respectively. Moderate to good yields have been obtained for both types of dimers. (*Steroids* **60:**786–790, 1995)

Keywords: dehalodimerization of steroids; steroidal anhydrides; conjugated dimeric dienes; homogeneous palladium(0) catalysts

Introduction

Despite the potential pharmacological interest in *bis*-steroids, only a few examples of dimerization of steroids have been published in the literature. A simple procedure was found to dimerize cross-conjugated dienones to the corresponding olefins in the presence of zinc dust,[1] and 17-β-acetoxy-19-norandrosta-4,6-dien-3-one treated with allyltrimethylsilane in the presence of $TiCl_4$ yielded the 6β,6'β dimer.[2] Although the dehalodimerization of aryl halides in the presence of water, reducing agents, halogen acceptors, and catalysts is a well known method for the synthesis of biphenyls,[3,4] and although palladium-catalyzed coupling of alkyl iodides with hydrazine as a reducing agent has been reported,[5] to our knowledge no such catalytic method has been published yet for steroids.

The various types of steroidal dimers are not only of direct practical importance,[1] especially with respect to the anhydrides and acids available in facile reactions, but more significantly, they are potential minor or trace products in any functionalization of steroids which possess enol-triflate or halogeno-vinyl moieties. Therefore, trace analysis of these reaction mixtures requires full knowledge of the structures of the minor products to be identified. The compounds described in this paper could be crucial for many pharmacologically important classes of compounds. The easily available, novel types of dimers, which are produced by selective homogeneous catalytic reactions, could serve as important reference compounds in various syntheses.

This paper describes efficient new homogeneous catalytic methods for the dehalodimerization and carbonylative dimerization of steroidal alkenyl-iodides (17-iodo-androst-16-ene **(1),** 17-iodo-4-aza-4-methyl-androst-16-en-3-one **(3),** 17-iodo-4-aza-androst-16-en-3-one **(3b),** Scheme 1) to form 16-17'-coupled dienes and 17-carboxylic anhydrides.

Experimental

$Pd(PPh_3)_4$ and $Pd_2(dba)_3 \cdot CHCl_3$ (where dba is dibenzylideneacetone) were prepared as described previously.[6,7] Dimethylformamide was dried over molecular sieves and distilled under argon.

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard on a Varian Unity 300 spectrometer at 300 and 75.4 MHz, respectively. Mass spectra were recorded on a VG-16F mass spectrometer. Infrared spectra were recorded in KBr pellets on a Specord-IR 75 instrument.

General method for dehalodimerization and carbonylative dimerization

In a typical experiment, 0.5 mmol of the steroid **(1, 3a, 3b)** in 2 mL dimethylformamide was heated at 110°C in the presence of 1.5 mmol Et_3N and 0.0035 mmol $Pd_2(dba)_3 \cdot CHCl_3$ (or 0.07 mmol $Pd(PPh_3)_4$ or 0.07 mmol $Pd(OAc)_2$) under an argon (dehalodimerization) or carbon monoxide (carbonylative dimerization) atmosphere. The precipitate formed during the reaction was filtered from the hot mixture. The solid was washed with DMF and hexane and dried in vacuum. All products were characterized by ^1H NMR, ^{13}C NMR, MS, elemental analysis, and IR.

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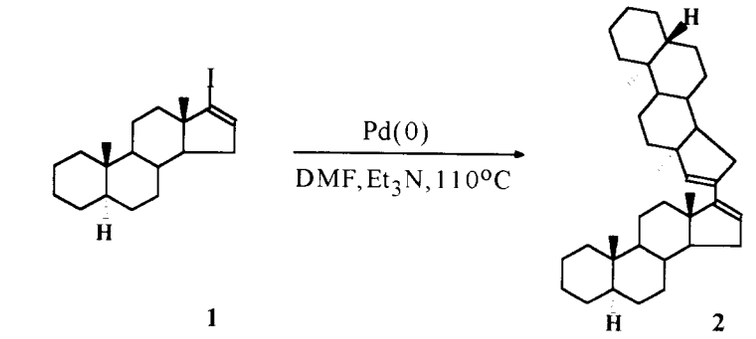
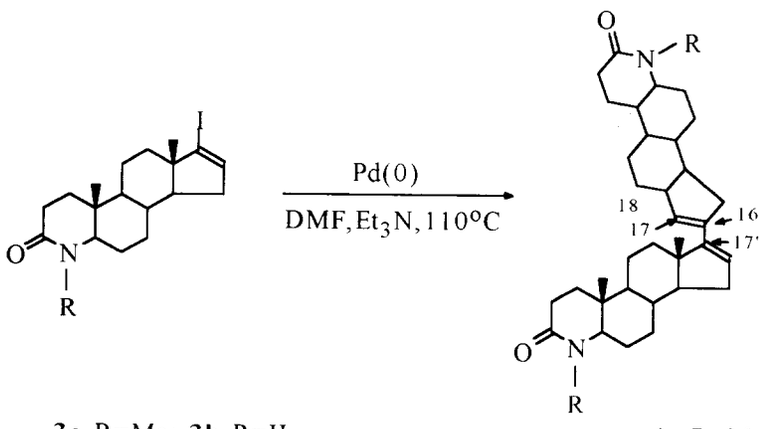




Scheme 1 Palladium-catalyzed dehalodimerization of **1, 3a, 3b.**

Formation of androsta-16-en-17-carboxylic acid (7)

17-Iodo-androsta-16-ene (**1**; 0.5 mmol) in 2 mL dimethylformamide (0.733 mg water/mL DMF, reaction vessels were not flame-dried) was heated at 110°C in the presence of 1.5 mmol Et_3N and 0.0035 mmol $Pd_2(dba)_3 \cdot CHCl_3$ under a CO atmosphere. Precipitation of androsta-16-en-17-carboxylic anhydride (**5**) began after a few minutes. After a couple of hours, the precipitate seemed to dissolve again. After heating the reaction mixture for 24 h, the solvent was removed in vacuum and the residue was analyzed by IR, ^1H NMR, ^{13}C NMR, and MS. The spectra showed two components: a small amount of androsta-16-en-17-carboxylic anhydride (**5**) and another compound identified as androsta-16-en-17-carboxylic acid (**7**), according to the spectroscopic data.

Characterization of the products

16-(Androst-16′-en-17′-yl)-androst-16-ene(*2*). ^1H NMR (δ, $CDCl_3$): 5.82 (s, 1 H, 17-H); 5.56 (s, 1 H, 16′-H); 0.9–2.4 (m, 44 H, ring protons); 0.86 (s, 3 H, 18′-H_3); 0.79 (s, 6H, 19-H_3 + 19′-H_3); 0.75 (s, 3 H, 18-H_3). MS (m/z, relative intensity): 514/83 (M^+); 499/100; 297/22; 109/23; 95/25; 81/25; 67/23; 55/23. Analysis calculated for $C_{38}H_{58}$ (514.88): C 88.65; H 11.35; Found: C 88.56, H 11.44. m.p. > 250°C. Yield 60%.

16-(4′-Methyl-4′-aza-androst-16′-en-3′-on-17′-yl)-4-methyl-4-aza-androst-16-en-3-one (*4a*). ^1H NMR (δ, $CDCl_3$): 5.83 (s, 1 H, 17-H); 5.57 (s, 1 H, 16′-H); 3.03 (dd, *J* = 6 Hz, 15 Hz, 2 H, 5-H + 5′-H); 2.90 (s, 6 H, N-CH_3 + N′-CH_3); 2.43 (m, 4 H, 2-H_2 + 2′-H_2); 2.26 (dd, *J* = 6.5 Hz, 12 Hz, 1 H, 15′α-H); 2.16 (m, 1 H, 15α-H); 2.08 (m, 1 H, 12′β-H); 2.04 (m, 1 H,15β-H); 2.02 (m, 2 H, 6α-H + 6′α-H); 1.87 (m, 1 H, 15′β-H); 1.84 (m, 2 H, 7 α-H + 7′α-H); 1.80 (m, 2 H, 1β-H + 1′β-H); 1.78 (m, 1 H, 12′α-H); 1.54 (m, 2 H, 11α-H + 11′α-H); 1.50 (m, 2 H, 8-H + 8′-H); 1.42 (m, 2 H, 12α-H + 12β-H); 1.38 (m, 2 H, 6β-H + 6′β-H); 1.36 (m, 2 H, 11β-H + 11′β-H); 1.34 (m, 2 H, 14-H + 14′-H); 1.32 (m, 2 H, 1α-H + 1′α-H); 1.02 (m, 2 H, 7β-H + 7′β-H); 0.90 (s, 6 H, 19-H_3 + 19′-H_3); 0.88 (s, 3 H, 18′-H_3); 0.86 (m, 2 H, 9-H + 9′-H); 0.76 (s, 3 H, 18-H_3). ^{13}C NMR (δ, $CDCl_3$): 170.8 (N-CO + N′-CO); 151.8 and 137.0 (16-C, 17′-C); 136.8 and 126.4 (16′-C, 17-C); 65.84 and 65.81 (5-C, 5′-C); 56.7 and 54.3 (14-C, 14′-C); 52.7 and 52.3 (9-C, 9′-C); 47.1 and 46.5 (13-C, 13′-C); 36.7 and 36.6 (10-C, 10′-C); 35.9*; 33.7; 33.1 (8-C, 8′-C); 32.9; 32.8; 31.0; 30.2; 30.1; 29.1 (N-CH_3, N′-CH_3); 29.07*; 25.4*; 21.2; 21.0; 17.3 and 16.4 (19-C, 19′-C); 12.42 and 12.36 (18-C, 18′-C). MS (m/z, relative intensity): 572/24 (M^+); 557/32; 302/100; 248/92; 233/77; 44/87; 41/75. UV: λ_{max} 248 nm (ε 7650). Analysis calculated for $C_{38}H_{56}N_2O_2$ (572.87): C 79.67; H 9.85; N 4.89; Found: C 79.55, H 9.91, N 4.75. m.p. > 250°C. Yield 40%. *Two signals coincide.

16-(4′-Aza-androst-16′-en-3′-on-17′-yl)-4-aza-androst-16-en-3-one (*4b*). ^1H NMR (δ, $CDCl_3$): 5.85 (s, 1 H, 17-H); 5.58 (s, 1 H, 16′-H); 5.44 (s, 2 H, NH + N′H); 3.08 (m, 2 H, 5-H + 5′-H); 2.42 (m, 4 H, 2-H_2 + 2′-H_2); 0.9–2.4 (m, 30 H, ring protons); 0.95 (s, 6 H, 19-H_3 + 19′-H_3); 0.9 (s, 3 H, 18′-H_3); 0.8 (s, 3 H, 18-H_3). MS (m/z, relative intensity): 544/98 (M^+); 529/100; 395/28; 312/37; 272/33; 258/21; 44/66; 41/66. Analysis calculated for $C_{36}H_{52}N_2O_2$ (544.82): C 79.36; H 9.62; N 5.14; Found: C 79.74, H 9.51, N 5.21. Yield 16%.

Androsta-16-en-17-carboxylic anhydride (*5*). ^1H NMR (δ, $CDCl_3$): 6.9 (s, 2 H, 16-H + 16′-H); 2.3 (m, 4 H, 15-H_2 + 15′-H_2); 0.9–2.2 (m, 40 H, ring protons); 0.94 (s, 6 H, 19-H_3 + 19′-H_3); 0.81 (s, 6 H, 18-H_3 + 18′-H_3). ^{13}C NMR (δ, $CDCl_3$): 160.3 (20-C, 20′-C); 148.1 (17-C, 17′-C); 146.5 (16-C, 16′-C);

56.6 (9-C, 9′-C); 55.2 (14-C, 14′-C); 47.3 (5-C, 5′-C); 46.1; 38.5; 36.5; 34.5; 33.9; 32.3; 31.9; 29.1; 28.9; 26.8; 22.2; 20.6; 16.0 (19-C, 19′-C); 12.2 (18-C, 18′-C). MS (m/z, relative intensity): 558/3 (M^+-28); 543/1; 285/100; 269/7; 109/7; 81/8; 55/8. IR (KBr, cm^{-1}): 1770 (ν C=O); 1580 (ν C=C). Analysis calculated for $C_{40}H_{58}O_3$ (586.90): C 81.86; H 9.96; Found: C 82.05, H 9.72. m.p. > 250°C. Yield 70%.

4-Methyl-4-aza-androst-16-en-3-on-17-carboxylic anhydride (*6a*). ^{1}H NMR (δ, $CDCl_3$): 6.9 (s, 2 H, 16-H + 16′-H); 3.07 (dd, *J* = 6 Hz, 15 Hz, 2 H, 5-H + 5′-H); 2.93 (s, 6 H, N-CH_3 + N′-CH_3); 2.46 (m, 4 H, 2-H_2 + 2′-H_2); 2.36 (m, 4 H, 15-H_2 + 15′-H_2); 1.0–2.2 (m, 26 H, ring protons); 0.96 (s, 6 H, 19-H_3 + 19′-H_3); 0.92 (s, 6 H, 18-H_3 + 18′-H_3). ^{13}C NMR (δ, $CDCl_3$): 170.6 (NCO, N′CO); 160.0 (20-C, 20′-C); 147.8 (17-C, 17′-C); 146.1 (16-C, 16′-C); 65.7 (5-C, 5′-C); 55.8 (9-C, 9′-C); 52.3 (14-C, 14′-C); 46.1 (13-C, 13′-C); 36.6 (10-C, 10′-C); 34.2 (2-C, 2′-C); 32.7 (8-C, 8′-C); 32.1; 29.9; 29.1 (N-CH_3, N′-CH_3); 29.0; 25.2; 20.8; 16.0 (19-C, 19′-C); 12.3 (18-C, 18′-C). MS (m/z, relative intensity): 331/43; 316/14; 124/21; 112/11; 70/100; 57/26; 55/10; 42/10. IR (KBr, cm^{-1}): 1770 (ν C=O); 1640 (ν NC=O); 1580 (ν C=C). Analysis calculated for $C_{40}H_{56}N_2O_5$ (644.90): C 74.50; H 8.75; N 4.34; Found: C 74.62, H 8.67, N 4.51 m.p. > 250°C. Yield 75%.

4-Aza-androst-16-en-3-on-17-carboxylic anhydride (*6b*). ^{1}H NMR (δ, $CDCl_3$): 6.9 (s, 2 H, 16-H + 16′-H); 6.05 (s, 2 H, NH + N′H); 3.08 (m, 2 H, 5-H + 5′-H); 2.86 (m, 8 H, 2-H_2 + 2′-H_2 + 15-H_2 + 15′-H_2); 1.0–2.2 (m, 26 H, ring protons); 0.96 (s, 6 H, 19-H_3 + 19′-H_3); 0.92 (s, 6 H, 18-H_3 + 18′-H_3). ^{13}C NMR (δ, $CDCl_3$); 172.3 (NCO, N′CO); 160.0 (20-C, 20′-C); 147.8 (17-C, 17′-C); 146.1 (16-C, 16′-C); 60.7 (5-C, 5′-C); 55.9 (9-C, 9′-C); 51.6 (14-C, 14′-C); 46.1 (13-C, 13′-C); 35.9 (10-C, 10′-C); 34.1 (2-C, 2′-C); 33.4; 33.2 (8-C, 8′-C); 32.1; 29.3; 28.5; 27.1; 20.9; 16.0 (19C, 19′-C); 11.3 (18-C, 18′-C). MS (m/z, relative intensity): 317/39; 302/100; 272/55; 124/25; 98/24; 91/30; 79/22; 55/29; 41/31. IR (KBr, cm^{-1}): 3180 (ν NH); 1760 (ν C=O); 1660 (ν NC=O); 1580 (νC=C). Analysis calculated for $C_{38}H_{52}N_2O_5$ (616.84): C 73.99; H 8.50; N 4.54; Found: C 72.82, H 8.35, N 4.62. Yield 61%.

Androsta-16-en-17-carboxylic acid (*7*). ^{1}H NMR (δ, $CDCl_3$): 6.9 (s, 1 H, 16-H); 2.25 (m, 2 H, 15-H_2); 0.9–2.2 (m, 20 H, ring protons); 0.88 (s, 3 H, 19-H_3); 0.8 (s, 3 H, 18-H_3). ^{13}C NMR (δ, $CDCl_3$): 170.1 (20-C); 146.4 (17-C); 146.1 (16-C); 56.7 (9-C); 55.2 (14-C); 47.2 (5-C); 45.8; 38.4; 36.4; 34.8; 33.9; 32.0; 31.9; 29.0; 28.9; 26.8; 22.1; 20.6; 16.0 (19-C); 12.1 (18-C). MS (m/z, relative intensity): 302/27 (M^+); 287/100; 269/22; 257/51; 109/42; 95/29; 81/33; 67/32; 55/31; 41/31. IR (KBr, cm^{-1}): 1670 (ν C=O); 1580 (ν C=C).

Table 1 Dehalodimerization of 17-iodo-androst-16-ene (**1**) in dimethylformamide

Catalyst	Et_3N/**1**	Isolated yield (%)
$Pd_2(dba)_3 \cdot CHCl_3$	1	43
$Pd_2(dba)_3 \cdot CHCl_3$	3	60
$Pd_2(dba)_3 \cdot CHCl_3$	10	Traces
$Pd(PPh_3)_4$	3	52
$Pd(OAc)_2$	3	35

Reaction conditions: Pd/**1** = 0.03; 110°C; 14 h.

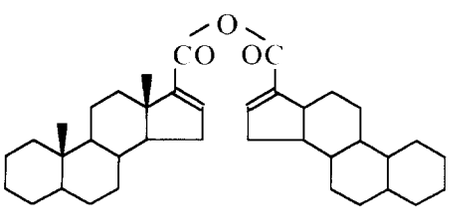
Results and discussion

Dehalodimerization

Reaction of the substrates (17-iodo-androst-16-ene, **1**; 17-iodo-4-aza-4-methyl-androst-16-en-3-one, **3a**; 17-iodo-4-aza-androst-16-en-3-one, **3b**) in dimethylformamide in the presence of triethylamine and a preformed Pd(0) catalyst resulted in the precipitation of dimeric steroidal products (Scheme 1).

The unexpected formation of the non-symmetrical 16-17′ coupled products was shown by NMR. Only **4a** was soluble enough for investigation by all of the NMR technics (^{1}H NMR, ^{13}C NMR, DNOE, ^{1}H-^{1}H-COSY, DQF-COSY, MQF-COSY) required for full structural characterization. The differential NOE experiments showed that saturation of 17-H at 5.83 ppm resulted in enhancement of the singlets at 0.88 ppm and 0.76 ppm (18′-H_3 and 18-H_3) and of the multiplet at 2.16 ppm (15α-H). At the same time, irradiation of the other sp^2 proton signal at 5.57 ppm (16′-H) caused an increase of the 15′α-H (2.26 ppm, dd) and the 15α-H (2.16 ppm, m) signals and only a slight increase of the low-field singlet at 0.88 ppm (18′-H_3). These observations support the structure given in Scheme 1 in which C-16 of one of the steroid skeletons is connected with C-17 of the other. The duplication of most of the signals in ^{1}H NMR and ^{13}C NMR is in agreement with the proposed non-symmetrical structure.

A possible explanation for the formation of **4a** is as follows: The dehalogenation of the iodo-alkenyl bond of **3a** results in the formation of 4-methyl-4-aza-androsta-16-en-3-one. This compound can be detected in the reaction mixture by gas chromatography-mass spectroscopy (GC-MS) measurements. The alkene may react with alkenyl-iodide **3a** in a Heck-type coupling reaction which involves the palla-



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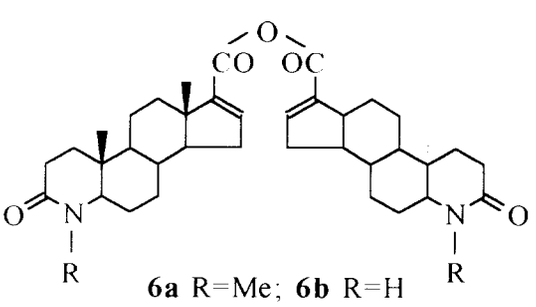
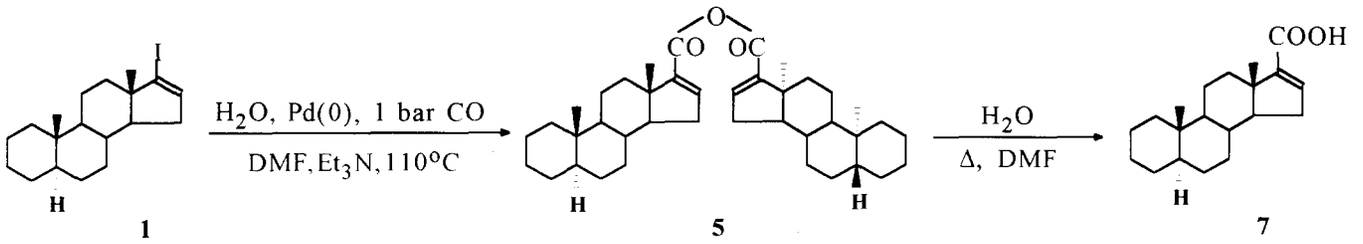


6a R=Me; **6b** R=H

Scheme 2 Structure of steroidal anhydrides.



Scheme 3 Reaction of 17-iodo-androst-16-ene in DMF under a CO atmosphere.

dium(0)-catalyzed coupling of vinylic halides with alkenes or dienes.[8,9] It is believed that the first step of this reaction is the oxidative addition of the vinylic halide to the palladium(0) catalyst. The resulting vinylic palladium halide then undergoes insertion of the alkene. Elimination of a hydridopalladium halide group from the adduct yields the diene. The reaction is conducted in the presence of a secondary or tertiary amine in order to convert the hydridopalladium complex back to the Pd(0) catalyst.

This explanation is supported by the fact that when a simple non-steroidal vinyl bromide derivative (1-bromovinyl)trimethylsilane) is used as substrate, the same reaction conditions lead to the formation of the corresponding dimers (*bis*(trimethylsilyl)butadienes, at least four isomers detected by GC-MS) and trimers. Although dimers can be produced by direct coupling of the substrate through activation of the bromo-carbon bond or by reaction of dehalogenated olefin and (1-bromovinyl)trimethylsilane, trimers are produced only by Heck-reaction of the diene dimer with vinyl bromide.

In the Heck-reaction, the regiochemistry of the addition of organopalladium compound to alkene appears to be sterically controlled. Therefore, the unexpected formation of the 16-17′ coupled products can be explained by the fact that reaction of the sterically less crowded position-16 of the Δ^{16} derivatives is much more favored than that of position-17.

The experiments carried out on **1** proved that both catalyst and amine are necessary for the above reaction. A three-fold excess of the amine increased the isolated yield (Table 1), but the use of 10 Eq stopped the reaction. The use of Pd(II) catalysts resulted in slightly lower yields of dimers.

Under the same reaction conditions (3 Eq amine, catalyst: $Pd_2(dba)_3 \cdot CHCl_3$), 40% and 16% yields were obtained by using **3a** and **3b** as substrates, respectively.

Table 2 Carbonylative dimerization of various steroids in DMF under CO

Substrate	Reaction time (h)	Isolated yield (%) (product)
1	3	70 **(5)**
1	5	70 **(5)**
1	14	27 **(5)**
1	22	18 **(5)**
3a	4	75 **(6a)**
3b	4	61 **(6b)**

Reaction conditions: $Pd_2(dba)_3 \cdot CHCl_3$; Pd/substrate = 0.03; 3 Eq Et_3N; solvent:DMF; 1 bar CO; 110°C.

Carbonylative dimerization

Running the above reaction under 1 bar of CO resulted in the synthesis of new compounds which proved to be the anhydrides of the substrates derived by carbonylative dehalodimerization (**5, 6a, 6b,** Scheme 2.). Under these conditions, the anhydride derivative could be isolated from the reaction mixture, but upon further heating, this compound disappeared and formation of the acid derivative was observed (Scheme 3). The reaction time was optimized in order to get the maximum isolated yields of the anhydrides (Table 2.).

Palladium-catalyzed carbonylation reactions are well known methods for the synthesis of carboxylic acids.[10] Under a carbon monoxide atmosphere, CO insertion into the Pd-carbon bond (formed by the oxidative addition of substrate) is very fast and leads to an acyl intermediate with high reactivity. Upon hydrolysis, the intermediate yields the corresponding carboxylic acid. This acid may react with another palladium-acyl complex to form the anhydride derivative.

Thus, it is thought that the presence of water is necessary for the synthesis of both steroidal anhydrides and acids. As dimethylformamide was dried before use, the water-content of the solvent (0.13 mg water/mL) was not enough for formation of the anhydride in moderate to good yields. Also, the reactions were carried out with a small amount of substrate (0.5 mmol); therefore, the moisture deposited in the glassware used may have been sufficient for the formation of anhydrides and acids. This assumption is supported by the fact that when the reaction vessels were flame-dried, the amount of anhydride formed increased with increasing water content in a series of experiments carried out in dimethylformamide containing different amounts of water (Table 3). However, the importance of dimethylformamide was shown by the fact that the same reaction took place only in traces when carried out in toluene containing water in the above concentrations.

Table 3 Effect of the water content of DMF on the formation of androsta-16-en-17-carboxylic anhydride **(5)**

Water content (mg/mL DMF)	Yield[a] (%)	Calculated yield[b] (%)
0.244	12	10.8
0.405	19	18.0
0.733	31	32.6

[a]Reaction conditions: $Pd_2(dba)_3 \cdot CHCl_3$; Pd/substrate = 0.03; 0.5 mmol of **1**; 3 Eq Et_3N; 2 mL DMF; 1 bar CO; 110°C; 3 h; the reaction vessel was flame-dried.
[b]Based on the water content of DMF.

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