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Consecutive Stille-coupling–hydrosilylation–Diels–Alder reaction of 17-iodo-5α-androst-16-ene

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Abstract

Homogeneous catalytic hydrosilylation of pregn-16-en-20-yne (produced from 17-iodo-5α-androst-16-ene by Stille-coupling) with triethylsilane is investigated in the presence of various Pt, Pd and Rh complexes. The stereoselective Diels–Alder reaction of one of the main products (21-triethylsilyl-pregna-16,20-diene, **3b**) led to a new pentacyclic steroidal derivative. The other steroidal diene (20-triethylsilyl-pregna-16,20-diene, **3a**) undergoes cycloaddition only in the presence of a hydrosilylation catalyst, giving the same cyclization product. The catalytic isomerization of **3a** and **3b** as precondition for cycloaddition was supposed.

Keywords: Hydrosilylation; Tandem reactions; Cycloaddition; Steroids; Isomerization

1. Introduction

Silicon plays an important role in the biosphere and is present in many living organisms, especially in bacteria and algae. It is also important for the higher plants, animals and man, although its biochemical mode of action is not understood yet. In drugs, replacement of carbon atoms with silicon results in changes in the chemical, physicochemical properties and structural features. As a consequence, pharmacological properties, selectivity and toxicity may be affected [1–3]. There are many examples of silylated steroidal derivatives with biological activity. Silylated steroids, with sex-hormone activity, have been converted into the corresponding pro-drugs, both via O- and C-silylation. Some (trialkylsilyl)ethynyl estradiol analogues which possess very high antifertility effects and reduced estrogenic activity [4] are particularly noteworthy. Another example is a trimethylsilyl analogue of a steroid hormone, 20-(2-(trimethylsilyl)ethyl)-5-pregnen-3,20-diol that behaves as an efficient mechanism-based inhibitor of cytocrome P-450 [5].

Hydrosilylation of 1-alkynes is a convenient method for the preparation of various silylated products [6,7]. However, the reaction has a selectivity problem due to the difficulty in controlling regio- and stereo-selectivity. This problem can be solved by the use of the appropriate catalyst in most cases. Hydro-

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silylation catalyzed by neutral rhodium complexes have been reported to be (Z)-selective [8], while cationic rhodium catalysis was proved to be (E)-selective [9,10]. In the latter case dehydrogenative silylation was also observed [11]. The most commonly used hydrosilylation catalyst, chloroplatinic acid (Speier's catalyst) usually gave mixtures of isomers [12–14]. There are only a few examples of Pd-catalyzed hydrosilylation of alkynes [15].

Here we describe the synthesis of new silylated steroidal dienes and a triethylsilyl-substituted pentacyclic steroid in a homogeneous catalytic coupling–hydrosilylation reaction sequence and in a consecutive, highly stereoselective Diels–Alder reaction, respectively. The steroidal enyne obtained in the first step has been hydrosilylated in the presence of various catalysts. The effect of the reaction conditions on the selectivity of the hydrosilylation step as well as Diels–Alder reactions of the products (silylated steroidal dienes) were also investigated.

2. Experimental

2.1. Chemicals

Solvents were dried by standard procedures and distilled under argon. Palladium catalysts [16,17] and the steroidal enyne (**2**) [18] were prepared as described previously, other complexes were of commercial source.

2.2. General method for the hydrosilylation

In a typical experiment, a mixture of 1 mmol pregn-16-en-20-yne, 0.02 mmol of catalyst and 2 mmol triethyl silane was heated under argon atmosphere in 10 ml toluene. Toluene and unreacted silane were removed in vacuum. The products were separated by column chromatography on silica gel with hexane/ethyl acetate as eluent and were characterized by MS and ^{1}H NMR.

2.3. One-pot coupling and hydrosilylation reaction

1 mmol 17-iodo-androst-16-ene, 0.02 mmol of catalyst, 1.1 equivalent of ethynyltributyltin and 2 mmol triethyl silane was heated under argon atmosphere in 10 ml toluene at 100°C. The reaction was followed by GC and GC-MS.

2.4. One-pot synthesis of the pentacyclic compound (**9**)

0.02 mmol of catalyst and 1 mmol steroidal enyne (**2**) were added to a Schlenk-tube equipped with a septum inlet. 2 mmol triethyl silane and 2 mmol diethyl fumarate were injected to the mixture through the septum inlet. The solution was stirred in inert atmosphere at 100°C. The solvent was removed in vacuo. The residue was subjected to column chromatography on silica gel with chloroform as eluent. The product was characterized by MS, ^{1}H NMR and various two-dimensional NMR techniques.

2.5. Characterization of the products

20-Triethylsilyl-pregna-16,20-diene (**3a**): yield: 74%. ^{1}H NMR (δ, $CDCl_3$): 6.0 (d, 2 Hz, 1H, 21-H_a); 5.94 (m, 1H, 16-H); 5.82 (d, 2 Hz, 1H, 21-H_b); 0.8–1.80 (m, 22H, ring protons); 0.98 (t, 9H, $SiCH_2C\mathbf{H}_3$), 0.87 (s, 3H, 18-H_3); 0.78 (s, 3H, 19-H_3); 0.48 (m, 6H, $SiC\mathbf{H}_2CH_3$). MS ((*m*/*z*)/relative intensity): 398 (M^+)/25; 383/32; 370/45; 258/10; 115/100; 87/95; 59/55.

21-Triethylsilyl-pregna-16,20-diene (**3b**): yield: 30%. ^{1}H NMR (δ, $CDCl_3$): 5.81 (m, 1H, 16-H); 5.51 (d, 13 Hz, 1H, 21-H); 5.30 (d, 13 Hz, 1H, 20-H); 0.8–1.80 (m, 22H, ring protons); 0.98 (t, 9H, $SiCH_2C\mathbf{H}_3$), 0.85 (s, 3H, 18-H_3); 0.78 (s, 3H, 19-H_3); 0.48 (m, 6H, $SiC\mathbf{H}_2CH_3$). MS ((*m*/*z*)/relative intensity): 398 (M^+)/22; 383/25; 369/22; 257/45; 115/90; 87/100; 59/52.

1′β,2′α-bis(Ethoxycarbonyl)-3′α-triethylsilyl-androstano-[16α,17-c]-cyclohex-4′-ene (**9**): yield: 59%. ^{1}H NMR (δ, $CDCl_3$): 5.12 (m, 1H, 4′-H); 4.15 (m, 4H, $OC\mathbf{H}_2CH_3$); 2.85 (m, 1H, 2′-H); 2.68 (m, 1H, 16-H); 2.25 (m, 1H, 1′-H); 2.1 (m, 1H, 3′-H); 1.2 (t, 7 Hz, 3H, $OCH_2C\mathbf{H}_3$); 1.18 (t, 7 Hz, 3H, $OCH_2C\mathbf{H}_3$); 0.8–1.80 (m, 22H, ring protons); 0.90 (t, 9H, $SiCH_2C\mathbf{H}_3$), 0.98 (s, 3H, 18-H_3); 0.82 (s, 3H, 19-H_3); 0.50 (m, 6H, $SiC\mathbf{H}_2CH_3$). MS (*m*/*z*)/relative intensity): 570 (M^+)/32; 555/5; 541/10; 382/10; 381/10; 367/13; 309/11; 143/16; 131/15; 115/50; 87/100; 59/41.

The other products were identified according to GC-MS measurements.

20-Triethylsilyl-pregn-16-ene (**4a** and **b**): MS ((*m*/*z*)/relative intensity): 400 (M^+)/6; 385/6; 371/8; 271/8; 257/15; 115/100; 87/60; 59/20 (probably two non-separable (20R/20S) epimers).

21-Triethylsilyl-pregn-16-ene (**4c**): MS ((*m*/*z*)/relative intensity): 400 (M^+)/40; 385/25; 371/64; 284/12; 258/45; 115/100; 87/82; 59/45.

21-Triethylsilyl-pregn-16-en-20-yne (**5**): MS ((*m*/*z*)/relative intensity): 396 (M^+)/25; 381/20; 367/100; 339/15; 281/10; 55/10.

Three isomers of pregnene (**7a**–**c**): (i) MS ((*m*/*z*)/relative intensity): 286 (M^+)/42; 271/64; 257/8; 122/100; 81/54; 67/32; 55/10. (ii) MS ((*m*/*z*)/relative intensity): 286 (M^+)/45; 271/68; 257/16; 122/100; 81/58; 67/36; 55/32. (iii) MS ((*m*/*z*)/relative intensity): 286 (M^+)/10; 271/45; 257/100; 122/25; 81/20; 67/15; 55/10.

3. Results and discussion

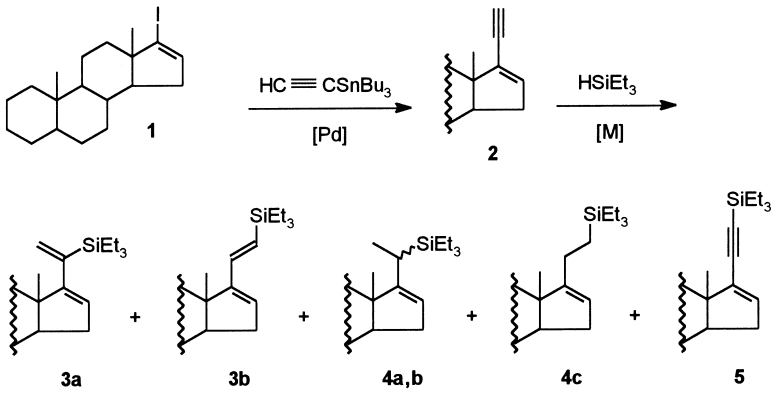
*3.1. Hydrosilylation of pregn-16-en-20-yne (**2**)*

The synthesis of silylated steroidal dienes was carried out in two routes.

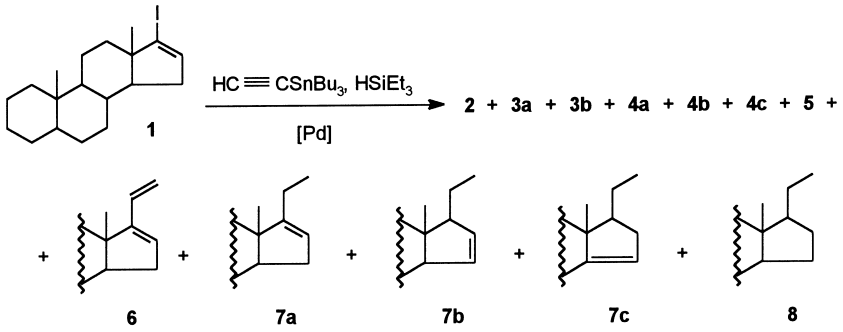
1. Pregn-16-en-20-yne was synthesized by Stille-coupling of 17-iodo-androst-16-ene and ethynyltributyltin. The isolated enyne was reacted with triethylsilane resulting in novel steroids possessing a silylated side chain (Scheme 1).
2. If the catalyst of hydrosilylation is identical with that of the Stille-coupling, the silylsteroids can be prepared by a tandem reaction (Scheme 2).

Hydrosilylation of pregn-16-en-20-yne resulted in the formation of five products (Scheme 1). The structures were determined by MS and NMR measurements. Beside the two dienes (**3a** and **b**), 20-triethylsilyl-pregn-16-ene (probably as two non-separable epimers **4a** and **b**), 21-triethylsilyl-pregn-16-ene (**4c**) and 20-triethylsilyl-pregn-16-en-20-yne (**5**) were also formed. The pregnene derivatives (**4a**–**c**) are produced by the hydrogenation of the silylated dienes. Hydrogenation as a side reaction is usually observed under hydrosilylation conditions [11,19,20]. Metal-hydride complexes as potential hydrogenation catalysts can be formed either in hexaethyldisilane-forming reaction by the activation of two triethylsilane molecules, or in an enyne–triethylsilane reaction leading to **5**. It should be mentioned that in these reactions pregna-16,20-diene (**6**) and other hydrogenated derivatives of **2** (**7a**–**c**, **8**, Scheme 2) could be detected only in traces, their total amount being <2%. The presence of Z-21-triethylsilyl-pregna-16,20-diene was not observed. Hydrosilylation of the 16-ene functionality did not take place.

H_2PtCl_6 and cationic rhodium complexes showed the highest activity (Table 1, entries 1, 5, 7). Using palladium-phosphine or neutral rhodium complexes longer reaction times were necessary for complete conversion (entries 3, 8, 10). The $Pd_2dba_3 + 8AsPh_3$ system was not active.



Scheme 1. Synthesis and hydrosilylation of pregn-16-en-20-yne (**2**).



Scheme 2. One-pot Stille-coupling–hydrosilylation of 17-iodo-androst-16-ene (**1**).

The ratio of the products is determined by the reaction conditions, first of all by the catalyst used. Surprisingly, chloroplatinic acid was found to be one of the most selective catalysts, which gave diene **3a** with 76% yield (entry 1). The $[Rh(nbd)Cl]_2 + 2PPh_3$ catalytic system was equally selective (entries 8, 9). In the presence of the cationic rhodium complexes, also **3a** was the main product. At the same time, these catalysts led to products obtained by dehydrogenative silylation and hydrogenation (entries 5, 6) in considerable quantity. The use of neutral rhodium complexes or $Pd(PPh_3)_4$ resulted in mixtures of isomers. $Rh(CO)_2(acac)$ + phosphine systems and $Pd(PPh_3)_4$ gave **3a** and **3b** in almost equal amounts.

The changes in the temperature (compare entries 5 and 6) or the use of bidentate ligands (compare entries 11, 12) did not alter the ratio of **3a** and **b** considerably. However, in $Rh(CO)_2(acac)$ + phosphine systems the use of higher temperature resulted in higher amounts of hydrogenated products and in the decrease of the amount of **3b**.

3.2. One-pot reaction of 17-iodo-androst-16-ene with ethynylstannane and triethylsilane

As $Pd(PPh_3)_4$ was proved to be an efficient catalyst for both Stille-reaction and hydrosilylation, one-pot synthesis of silylated products was attempted using

Table 1
Hydrosilylation of pregn-16-en-20-yne[a]

Entry	Catalyst	Reaction time (h)	Reaction temperature (°C)	Conversion (%)	Ratio of products (%)			
					3a	**3b**	**4a–c**	**5**
1	H_2PtCl_6	0.5	100	93	76	10	8	6
2	$Pt(DPPB)_2$[b]	8	100	66	71	8	9	12
3	$Pd(PPh_3)_4$	24	100	98	41	29	16	14
4	$Pd_2(dba)_3 + AsPh_3$	18	100	–	–	–	–	–
5	[Rh(cod)MOP]BF_4[c]	0.5	100	100	54	9	18	19
6	[Rh(cod)MOP]BF_4[c]	5	25	100	56	5	20	19
7	$[Rh(nbd)_2]OTf + 2PPh_3$	0.5	100	100	48	8	33	11
8	$[Rh(nbd)Cl]_2 + 2PPh_3$	5	100	95	81	4	7	8
9	$[Rh(nbd)Cl]_2 + 2PPh_3$	24	25	99	66	3	14	17
10	$Rh(CO)_2(acac) + 2PPh_3$	18	100	96	26	29	34	11
11	$Rh(CO)_2(acac) + 2PPh_3$	18	60	97	29	39	20	10
12	$Rh(CO)_2(acac)$ + DIOP[d]	18	60	98	32	37	22	8

[a] Reaction conditions: pregn-16-en-20-yne /triethylsilane/catalyst: 1/2/0.02, in toluene.
[b] DPPB: 1,4-bis(diphenylphophino)-butane.
[c] MOP: 2-methoxy-2′-diphenylphosphino-1,1′-binaphtyl.
[d] DIOP: (+)-2,3-*O*-*iso*-propylidene-2,3-dihydroxy-1,4-bis(diphenylphophino)-butane.

Table 2
Tandem Stille-coupling and hydrosilylation in the presence of $Pd(PPh_3)_4$[a]

Entry	Reaction time	Conversion	Ratio of products (%)							
	(h)	(%)	**2**	**3a**	**3b**	**4a–c**	**5**	**6**	**7a–c**	**8**
1	5	100	86	3	–	–	6	Traces	5	Traces
2	15	100	–	11	–	4	45	4	33	3
3[b]	15	100	–	52	19	14	15		Traces	

[a] Reaction conditions: 17-iodo-androst-16-ene/ethynylstannane/triethylsilane/catalyst: 1/1.1/2/0.02, in toluene at 100°C.
[b] Hydroquinone added.

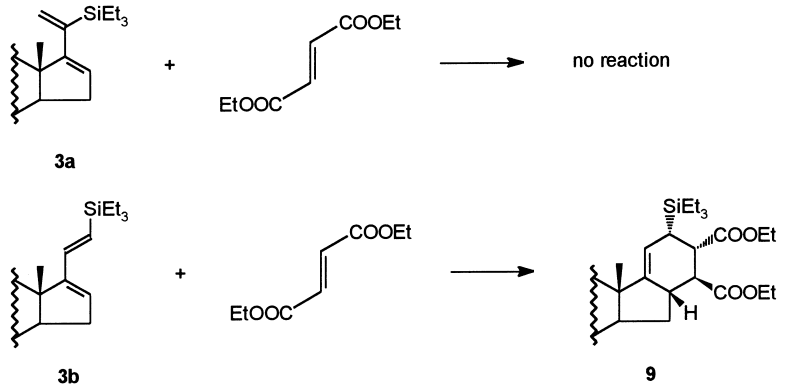
17-iodo-androst-16-ene as substrate (Scheme 2). The results were remarkably different from those of the two-step procedure (Table 2). The main product of the reaction was **5**. The hydrogenated silyl-derivatives (**4a–c**) were formed only in a few percent, but considerable amounts of products due to hydrogenation of enyne **2** were detected. The product ratio observed at short reaction times (Table 2, entry 1) shows that the first step is the coupling of the steroidal alkenyl iodide with the stannane. After 5 h no unreacted **1** could be detected in the reaction mixture. The enyne product (**2**) reacted further with the hydrosilane slowly. The different product distribution of the hydrosilylation reaction is due to a free-radical reaction or a free-radical reaction and a homogeneous catalytic reaction operating together. This is supported by the fact that on addition of hydroquinone as a radical inhibitor to the reaction mixture, the ratio of the products was similar to that observed in the hydrosilylation of the enyne (**2**) in the presence of $Pd(PPh_3)_4$ (Table 1, entry 3).

Radical reactions of organosilanes are well-known processes [21]. In this case, the presence of the organostannane derivatives which can easily produce free-radicals may initiate such reactions.

3.3. Cycloaddition of silylated steroidal dienes

Previously, the synthesis of various pentacylic steroids via tandem coupling and cycloaddition reactions has been reported [22,23]. These results induced us to investigate the possibility of a one-pot hydrosilylation–Diels–Alder reaction. The hydrosilylation–cycloaddition reaction sequence was carried out in two routes. (i) The dienophile is reacted with an isolated steroidal silylated diene (**3a** or **b**) (method A). (ii) The steroidal enyne (**2**) is reacted with triethylsilane and a dienophile in the presence of the hydrosilylation catalyst (method B). In the one-pot reactions examined before, diethyl fumarate was proved to be the dienophile of choice. It does not inhibit homogeneous catalysts, reactive and its cycloaddition proceeds with good stereoselectivity [22,23].

Using method A (Scheme 3), it was proved that only one of the two silylated dienes was able to give a

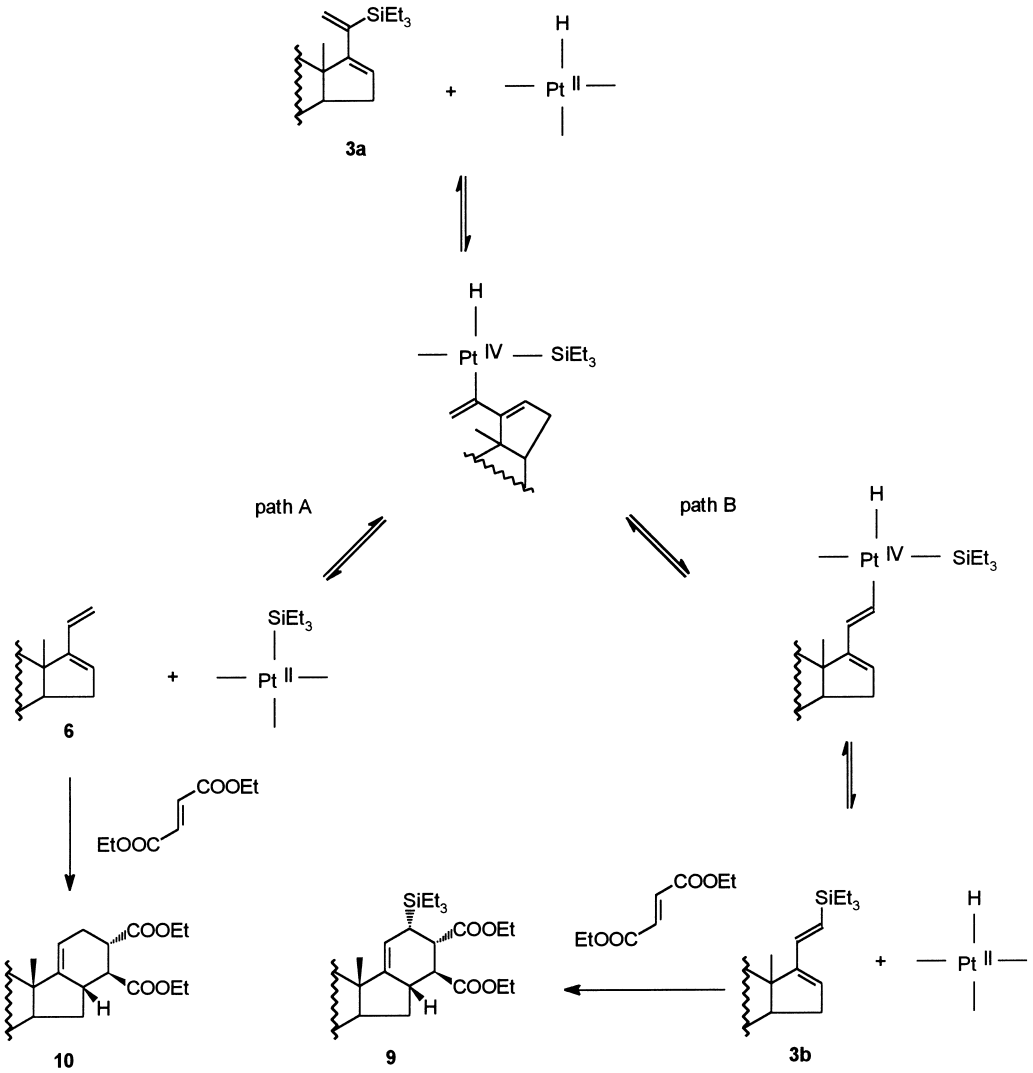


Scheme 3. Cycloaddition reactions of steroidal dienes **3a** and **b**.

Table 3
One-pot synthesis of **9** from 17-ethynyl-androst-16-ene (**2**)[a]

Entry	Catalyst	Reaction time (h)	Conversion (%)	Ratio of products				
				3a	**3b**	**4a–c**	**5**	**9**
1	$Pd(PPh_3)_4$	5	62	40	–	30	3	27
2	$Pd(PPh_3)_4$	48	75	16	–	37	7	40
3	$[Rh(cod)MOP]BF_4$[b]	18	>98	16	–	25	19	40
4	$Rh(CO)_2(acac) + 2PPh_3$	18	>98	6	–	31	24	39
5	H_2PtCl_6	18	98	18	–	8	8	66

[a] Reaction conditions: 17-ethynyl-androst-16-ene/triethylsilane/diethyl fumarate/catalyst: 1/2/2/0.02, in toluene at 100°C.
[b] MOP: 2-methoxy-2′-diphenylphosphino-1,1′-binaphtyl.



Scheme 4. Isomerization of steroidal diene **3a** and **b** in the presence of a dienophile and a catalyst.

cycloadduct with diethyl fumarate. **3b** could be totally converted into **9** in the presence of the dienophile. The compound depicted in Scheme 3 was the only isomer produced in detectable amount. The structure of the cycloadduct was determined by ^{1}H NMR, ^{1}H–^{1}H COSY and NOE experiments. In the reaction of **3a** with diethyl fumarate no cycloaddition products could be detected even at high temperature and after prolonged interaction. This can be explained only by the *s-trans* conformation of diene **3a** which is supported by geometry optimization with MM1 force field (DTMM 2.0). The *s-cis* conformation of the diene is disfavored due to the steric hindrance between the bulky triethylsilyl group and the 18-methyl group.

At the same time, the product distribution of the one-pot reaction (method B) was remarkably different from that that was expected (Table 3). After prolonged heating, the ratio of the cycloaddition product in the reaction mixture was higher than it could be calculated from the data of the previous hydrosilylation experiments. Besides, a considerable amount of **3a** seemed to have been consumed (compare data of Tables 1 and 3).

In order to clarify this reaction, isolated **3a** and diethyl fumarate was heated in the presence of H_2PtCl_6. In this case, the exclusive formation of another cycloaddition product (10 [22], Scheme 4) was observed. When a similar experiment was carried out in the presence of an excess of triethyl silane, cycloadduct **9** was produced (32% yield after 18 h heating). This can be explained by the oxidative addition of **3a** to a Pt-hydride (Scheme 4), followed either by the reductive elimination of pregna-16,20-diene (pathway A) or by the isomerization of the complex I into II and reductive elimination of **3b** (pathway B). The former pathway leads to cycloadduct **10**, while the latter gives **9** in the presence of the dienophile. The hydrogen that is necessary for the formation of **6** may evolve from the triethylsilyl moiety. This assumption is supported by the fact that various silicon containing-oligomers were detected in the reaction mixture by GC-MS.

The use of other hydrosilylation catalysts gave similar results. In the reaction of **3a**, triethylsilane and diethyl fumarate **9** was produced in 18 and 22% yields after 18 h heating, in the presence of $Rh(CO)_2(acac) + 2PPh_3$ and $Pd(PPh_3)_4$ catalysts, respectively.

4. Conclusions

Hydrosilylation of steroidal enyne **2** results in a number of products depending on the catalyst used. Silicon-containing steroidal dienes are the main products in most cases. In the tandem Stille-coupling–hydrosilylation reaction sequence the second reaction proceeds both via homogeneous catalysis and via a radical pathway leading to the silylated enyne **5** as the main product. One of the hydrosilylation products, 21-triethylsilyl-pregna-16,20-diene (**3b**) can be totally converted into a pentacyclic steroidal derivative via cycloaddition with diethyl fumarate. At the same time, in the presence of a catalyst 20-triethylsilyl-pregna-16,20-diene (**3a**) undergoes cycloaddition resulting in the same cyclization product. The catalytic isomerization of **3a** and **3b** as precondition for cycloaddition was supposed.

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