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Pd-Promoted Homocoupling Reactions of Unsaturated Silanes in Aqueous Micelles

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Palladium-promoted homocoupling reaction of vinyl- and polyenylsilanes in aqueous conditions has been investigated. The reaction is catalyzed by $PdCl_2$ in the presence of the reoxidizing system $CuCl_2$/LiCl and occurs at room temperature in aqueous solutions containing nonionic amphiphiles. Symmetrically α,ω-disubstituted stereodefined *all-trans* polyenes have been obtained in mild conditions and in good yields (65–87 %), higher than those previously reported for the same reactions carried out in methanol or HMPA. A comparison between two commercially available surfactants, Triton X-100 and PTS, has been performed.

Introduction

In recent years the use of water as solvent for organic reactions has been actively investigated[1] since aqueous conditions combined with efficient catalyst recycle could strongly reduce the environmental impact of several synthetic sequences. In many cases the use of surfactants in water effectively improves the reaction outcome compared with the same processes carried out in pure water, an effect which is called micellar catalysis.[2] A micellar system is composed of spherical amphiphilic aggregates of surfactant molecules having nanometric dimension range suspended in water or in media similar to water, and it can be considered a nano-heterogeneous two-phase system. In fact, such supramolecular structures create an environment that can accelerate the reactions by hydrophobic and concentration effects, due to the segregation of the reagents in the nanocores of the micellar structures. In particular, micellar catalysis represents a possible approach to convert common transition-metal catalyzed cross-coupling reactions into *green chemistry* processes carried out in water and appropriate experimental protocols have been set up for efficient Heck,[3] Sonogashira,[4] and Suzuki–Miyaura[5] reactions.

In spite of the well-recognized synthetic utility of metal catalyzed coupling reactions of unsaturated silanes,[6] due to the easy handling and low toxicity of organosilicon compounds, to the best of our knowledge micellar versions of these processes have never been investigated so far. In recent years, in connection with our continuous interest in development of synthetic methodologies for organic materials for photonics and electronics,[7] we have disclosed several efficient and selective protocols based on coupling reactions of unsaturated silanes to obtain stereodefined conjugated oligomers and polymers.[8] Therefore, we considered interesting to investigate whether aqueous micellar conditions can positively affect the outcome of some of these processes. Accordingly, as a first exploration in this direction, we report herein our study on the micellar version of a Pd-promoted homocoupling process of vinyl- and polyenylsilanes that we had previously shown to be an efficient methodology to synthesize extended stereodefined *all-trans* polyenes up to eight conjugated double bonds long, by doubling in one step the conjugated system of the starting unsaturated silanes.[9]

The significance of polyenes in studies dealing with organic electronics is manifold: conjugated polyenes have been investigated as molecular conductors[10] and switches,[11] optical conductors,[12] optical diodes,[13] and nonlinear optical (NLO) materials.[14] Moreover, due to their well-defined chemical structure and possibility of selective functionalization, they represent valuable model systems for validation of predictions based on theoretical calculations and for developing new concepts in organic electronics.[15]

Results and Discussion

We report here the application of micellar aqueous conditions to homocoupling reactions of vinyl- and polyenyltrimethylsilanes promoted by $PdCl_2$ in the presence of $CuCl_2$ and LiCl.

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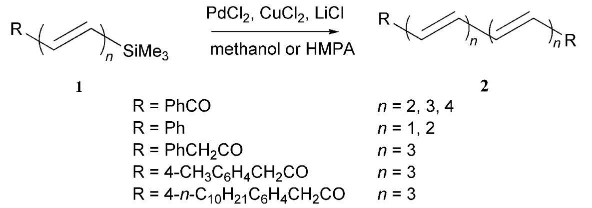
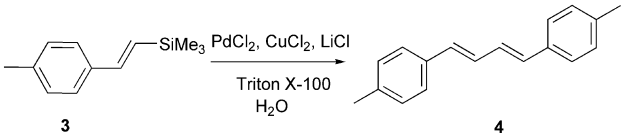
As previously reported,[9,16] silanes **1** afford dimerization products **2** (Scheme 1) with yields ranging from 30 to 61% by treatment with catalytic[16] to substoichiometric[9] amounts of $PdCl_2$ in methanol or HMPA, in the presence of a large excess of $CuCl_2$ and LiCl, which are necessary to reoxidize the Pd^0 generated in the reductive elimination step leading to the new carbon–carbon bond formation. The reaction is highly stereoselective, affording only the *all-E* stereoisomer of the product polyenes.



Scheme 1. Homocoupling reactions of unsaturated silanes.

Competing proton-[17] and chlorodesilylation[18] processes are side reactions which decrease the yield of dimerized products. The former process is promoted by the hydrogen chloride derived from the methanolysis of the trimethylsilyl chloride generated in the reaction medium, while chlorodesilylation is due to $CuCl_2$.[9]

We started our investigation by reacting (*E*)-1-*p*-tolyl-2-(trimethylsilyl)ethene (**3**) (Scheme 2) in water with different amounts of the catalytic system composed of $PdCl_2$, $CuCl_2$, LiCl, in the presence of the commercially available nonionic amphiphile Triton X-100 (Figure 1).



Scheme 2. Homocoupling reaction of (*E*)-1-*p*-tolyl-2-(trimethylsilyl)ethene **3**.

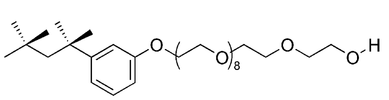


Figure 1. Structure of Triton X-100.

A minimum 25% palladium catalyst with respect to the starting silane **3** was necessary to reach the complete conversion (Table 1, entry 3). In these conditions, the reaction produces stereoselectively the dimerization product (1*E*,3*E*)-1,4-bis(*p*-tolyl)butadiene **4** with unexpectedly high yield (87%) compared with the yields obtained when the reactions were carried out in MeOH or HMPA.[9,16] The increased yield is due to the suppression of proto- and chlorodesilylation side reactions which negatively affect the process in non-micellar conditions.[9,16] Inhibition of protodesilylation can be attributed to the lipophilic nano-environment of the micellar core which protects the organic substrate from the reaction with HCl and likely reduces or eliminates its formation. Similarly, the $CuCl_2$ salt responsible for the chlorodesilylation reaction would not enter the lipophilic core of the micelles. Moreover, the $CuCl_2$ promoted halogenation of olefins is favoured by solvents that can coordinate copper, and this does not occur in the case of the long polyether chain of the Triton X-100 surfactant.[17]

Table 1. Homocoupling reaction of **3** in the presence of Triton X-100.[a]

Entry	Catalyst[b] (% $PdCl_2$)	Time [h]	GC conversion [%]	Yield[c] [%]
1	3	24	45	n.d.[e]
2	10	24	60	36
3	25	24	100	87
4[d]	25	24	45	n.d.[e]
5[f]	100	6	100	87

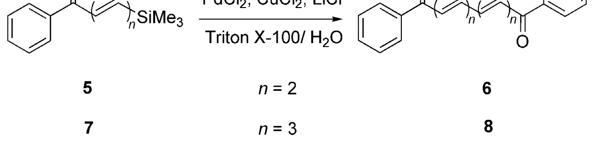
[a] Reactions carried out at room temperature in 15 wt.-% Triton X-100/$H_2$0. [b] Molar ratio $PdCl_2$/$CuCl_2$/LiCl, 1:8:3. [c] Based on isolated materials. [d] Reaction carried out "on water": without the presence of surfactant. [e] n.d.: not determined. [f] In this case the reoxidant system $CuCl_2$/LiCl was obviously not required.

When the reactants were stirred in aqueous suspension (entry 4) in the absence of surfactant, a protocol denoted as "on water" conditions,[19] only 45% conversion was achieved after 24 hours and a black colloidal palladium precipitate was formed in the reaction mixture.

Equally good yield (87%) was obtained with a stoichiometric amount of $PdCl_2$, in the absence of the reoxidizing system ($CuCl_2$/LiCl) (entry 5, Table 1). The same reaction carried out in methanol occurred with a slightly lower yield (79%), but the addition of one equivalent of dicyclohexylethylamine was necessary to prevent protodesilylation of the starting silane by HCl generated in the reaction environment.[16]

Complete conversion of the reactants in the stoichiometric conditions was fast (6 h), likely due to the higher availability of the palladium(II) in the nano-confined micellar environment.

The investigation was then extended to the homocoupling reaction of keto-polyenylsilanes (Scheme 3). The conjugated polyenic carbonyl compounds are useful structural intermediates in organic synthesis,[20] especially in the field of natural products.[21] The use of these starting compounds enables a straightforward comparison with the results obtained in our previous studies dealing with the same reaction carried out in methanol or HMPA.[9]



Scheme 3. Homocoupling reactions of keto-polyenylsilanes **5** and **7** in the presence of Triton X-100.

All the reactions were carried out in surfactant/water media, at room temperature and in conditions ranging from catalytic to substoichiometric in $PdCl_2$ and the results are summarized in the Table 2.

Table 2. Homocoupling reactions of keto-polyenylsilanes in the presence of Triton X-100.[a]

Entry	Silyl ketone	Catalyst[b] (% $PdCl_2$)	Time [h]	GC Conversion [%]	Product	Yield[c] [%]
1	**5**	3	12	30	**6**	8
2	**5**	10	12	45	**6**	20
3	**5**	25	12	100	**6**	85
4	**7**	25	24	100	**8**	65

[a] Reactions carried out at room temperature in 15 wt.-% Triton X-100/H_2O. [b] Molar ratio $PdCl_2$/$CuCl_2$/LiCl, 1:8:3. [c] Based on isolated materials.

Three experiments were carried out using the silylated ketone **5** as the substrate to give (2*E*,4*E*)-1,6-diphenyl-2,4-butadiene-1,6-dione (**6**). The results for these reactions are similar to those recorded with **3**: the highest yield in the polyene **6** was obtained performing the homocoupling reaction with 25% $PdCl_2$ (Table 2, entry 3), while complete conversion was not reached with catalytic percentages (3%, 10%, Table 2, entries 1, 2) of the Pd^{II} salt. Again, no side reactions (protodesilylation and chlorodesilylation) of the starting silyl ketone **5** were detected. Finally, in the optimized conditions, the conjugated triene **7** afforded the diketo-polyene **8** in 65% yield (Table 2, entry 4).

Among the wide number of nonionic micelle-forming surfactants employed in micellar catalysis, the Lipshutz's group[22] reported studies on the vitamin-E-based amphiphile PTS (polyoxyethanyl α-tocopheryl sebacate) (Figure 2) which can be employed as micelle-forming system in transition-metal catalyzed cross-coupling reactions carried out in neat water. Recently, aqueous solutions containing small amounts of PTS were also used as reaction media for efficient olefin cross-metathesis[23] and ring closing metathesis[24] reactions.

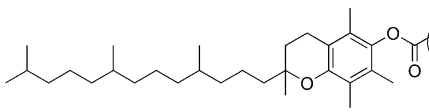
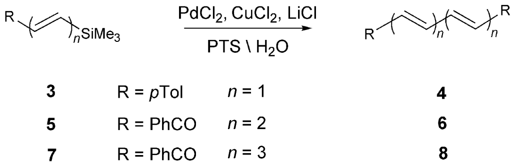


Figure 2. Structure of PTS ($n \approx 13$; MW ≈ 1200).

Therefore, we extended our investigation to homocoupling of **3** in the presence of this alternative surfactant (Scheme 4). When using 7 wt.-% PTS in water and 25% $PdCl_2$, no substantial difference in the reaction outcome between Triton X-100 and PTS was observed, except a slight reduction of the yield (80%, Table 3 entry 4).



Scheme 4. Homocoupling reaction of unsaturated silyl ketones in PTS.

Reducing the concentration of the surfactant to 2 wt.-% PTS/H_2O resulted in a lower rate of the dimerization reaction (Table 3, entries 1, 2). As with Triton X-100, the conversion critically depends on the amount of catalyst employed (Table 3, entries 1,3). Increasing the amount of the surfactant to 15 wt.-% PTS/H_2O (Table 3, entry 5), no substantial improvement of the reaction yield was observed compared with the use of 7 wt.-% PTS/H_2O (Table 3, entry 4) and a very viscous reaction mixture was generated that was difficult to stir without heating.

Finally, conjugated diketo-polyenes with four and six double bonds have been obtained in good yield by dimerization of the keto-polyenylsilanes **5** and **7** in the optimized conditions (Table 3, entries 7, 8), while reducing the amount of surfactant in the case of the substrate **5** resulted in longer reaction time and lower yield (Table 3, entry 6).

Conclusions

In summary, we have reported here a study on the use of micellar conditions applied to the palladium-catalyzed homocoupling reactions of trimethylsilyl polyenes, as a first example of studies directed towards the investigation of reactivity of unsaturated silanes in coupling processes in aqueous environment and in the presence of surfactants.

Table 3. Homocoupling reactions of unsaturated silyl ketones in the presence of PTS as surfactant.

Entry	Silyl ketone	Catalyst[b] (% $PdCl_2$)	Surfactant (PTS/H_2O % weight)	Time [h]	GC Conversion [%]	Yield[c] [%]
1[a]	**3**	10	2	48	45[e]	36
2[a]	**3**	25	2	48	100[e]	65
3[a]	**3**	10	7	24	86[e]	55
4[a]	**3**	25	7	24	100[e]	80
5[d]	**3**	25	15	24	100[e]	80
6[a]	**5**	25	2	48	100[e]	60
7[a]	**5**	25	7	24	100[e]	65
8[a]	**7**	25	7	24	100[e]	65

[a] Reactions carried out at room temperature. [b] Molar ratio $PdCl_2$/$CuCl_2$/LiCl, 1:8:3. [c] Based on isolated materials. [d] Good stirring with a slight heating (40 °C) is needed for solubilizing the reactants due to the high viscosity of the mixture. [e] Determined by GLC analysis.

The results of our experiments demonstrate that under micellar conditions the reactions afford dimerization products in higher yields compared with those obtained using methanol or HMPA as the solvent, maintaining the high stereoselectivity. The observed improvement is likely due to suppression of proto- and chlorodesilylation side reactions in the nano-segregated lipophilic micellar environment. Studies are in progress in our laboratory to extend the micellar conditions to other transition metal-catalyzed reactions of unsaturated silanes.

Experimental Section

General: All chemicals were purchased from Aldrich, Alfa Aesar and Acros and used without further purification. TRITON X-100 and PTS are commercially available from Sigma–Aldrich. Commercially available copper(II) chloride and anhydrous lithium chloride were used without further purification. (2*E*,4*E*)-1-phenyl-5-(trimethylsilyl)penta-2,4-dien-1-one (**5**), (2*E*,4*E*,6*E*)-1-phenyl-7-(trimethylsilyl)hepta-2,4,6-trien-1-one (**7**) were prepared as reported in the literature.[25]

Column chromatography was performed using silica gel 60 (0.04–0.063 mm) from Merck. Petroleum ether was the 40–70 °C boiling fraction. Thin-layer-chromatography analysis was conducted using Merck Silica gel 60 F254 aluminium sheets. GLC analysis was performed with Varian 3900 (dimethylpolysiloxane, 30 m × 25 mm × 0.25 µm). MS spectra were acquired on a Shimadzu GC–MS-QP 5000 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 500 spectrometer at 500 MHz and 125.7 MHz, respectively. The residual $CHCl_3$ signal at δ = 7.24 ppm and the $CDCl_3$ signal at δ = 77.0 ppm were used as standards for ^{1}H NMR and ^{13}C NMR spectra, respectively.

(*E*)-1-*p*-Tolyl-2-(trimethylsilyl)ethene (3): A three-neck 250 mL round-bottomed flask equipped with a magnetic stir bar and 100 mL dropping funnel was charged with (*E*)-(2-bromovinyl)trimethylsilane (4.0 g, 22.3 mmol), $NiCl_2$(dppe) (0.36 g, 0.69 mmol) and 50 mL of freshly distilled THF, under a nitrogen atmosphere. The solution was cooled to 0 °C and *p*-tolylmagnesium bromide (0.37 N solution in THF, 80 mL, 29.2 mmol) was added dropwise. The solution was maintained at 0 °C during the addition and then warmed to room temperature overnight. The reaction mixture was then quenched with water and extracted twice with hexane. The organic layers were combined, dried with anhydrous Na_2SO_4, and the solvent was distilled under reduced pressure to yield a light yellowish liquid. Purification by column chromatography using petroleum ether as solvent afforded 4.54 g (yield 87%) of a colourless liquid. Spectroscopic characterizations of the product **3** are in agreement with the data reported in the literature.[26] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.3 (s, 9 H), δ = 2.4 (s, 3 H), δ = 6.56 (d, *J* = 19.1 Hz, 1 H), δ = 7.00 (d, *J* = 19.1 Hz, 1 H), δ = 7.24 (d, *J* = 8 Hz, 2 H), δ = 7.46 (d, *J* = 8 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 145.35, 137.65, 135.62, 129.10, 128.03, 126.17, 21.35, –0.70 ppm. MS (EI, 70 eV): *m*/*z* (%) = 190 (36) [M$^+$], 175 (100), 159 (63), 149 (53).

Procedure for the Homocoupling Reaction of the (*E*)-1(-*p*-Tolyl)-2-(trimethylsilyl)ethene (3) Using 25% of $PdCl_2$ in Aqueous Micelles with Triton X-100 (15 wt.-% Triton X-100/H_2O): A 25 mL round-bottomed flask was charged with (*E*)-1-(*p*-tolyl)-2-(trimethylsilyl)ethene (**3**) (0.1 g, 0.53 mmol), $PdCl_2$ (0.023 g, 0.13 mmol), $CuCl_2$ (0.143 g, 1.06 mmol), LiCl (0.017 g, 0.39 mmol) in 5 mL of surfactant water solution and the mixture was stirred at room temperature. The reaction was monitored by TLC or GC–MS analysis until the disappearance of **3**. The reaction mixture was quenched with a saturated aqueous sodium chloride solution and then extracted twice with ethyl acetate. The organic layers were combined and dried with anhydrous Na_2SO_4. After evaporation of the solvent at reduced pressure, the crude product was subjected to flash chromatography, using petroleum ether as eluent, and a white solid was isolated (0.054 g, 87% yield); m.p. 199–200 °C (ethanol) that was identified as **4** on the basis of the following spectroscopic data: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 6.58–6.68 (m, 2 H), 6.86–6.97 (m, 2 H), 7.14 (d, *J* = 7.9 Hz, 4 H), 7.34 (d, *J* = 8.0 Hz, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.32, 126.13, 128.38, 129.25, 132.13, 134.57, 137.22 ppm. MS (EI, 70 eV): *m*/*z* (%) = 234 (49) [M$^+$], 219 (100), 204 (37), 115 (10), 105 (15), 101 (4).

The stereochemistry of the product **4** can not be directly derived from the ^{1}H NMR spectrum on the basis of the coupling constants of the protons of the diene moiety, because they appear as a second order AA′BB′ spin system. However, the analysis of the spin system by means of MestReC NMR software, as we previously reported for similar dienes,[27] enabled us to define the coupling constant values *J*(AB) = *J*(A′B′) = 17 Hz, *J*(BB′) = 9 Hz, *J*(AB′) ≈ 0.5 Hz, *J*(AA′) = 0 Hz which are characteristic for a (1*E*,3*E*)-diene structure.

Procedure for the Homocoupling Reaction of the (2*E*,4*E*)-1-Phenyl-5-(trimethylsilyl)-2,4-pentadien-1-one 5 Using 25% of $PdCl_2$ in Aqueous Micelles with Triton X-100 (15 wt.-% Triton X-100/H_2O): A 25 mL round-bottomed flask was charged with (*2E,4E*)-1-phenyl-5-(trimethylsilyl)-2,4-pentadien-1-one **5** (0.1 g, 0.43 mmol), $PdCl_2$ (0.019 g, 0.109 mmol), $CuCl_2$ (0.116 g, 0.86 mmol) LiCl (0.014 g, 0.327 mmol) in 5 mL of surfactant water solution and the mixture was stirred at room temperature. The reaction was monitored by TLC. The reaction mixture was quenched with saturated aqueous sodium chloride and the organic compound was extracted twice with ethyl acetate. The organic layers were combined and dried with anhydrous Na_2SO_4. After evaporation of the solvent at reduced pressure, the product **6** was isolated as a yellow solid after flash chromatography, using petroleum ether/diethyl ether (6:4) as eluent (0.057 g, 85% yield): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.59–6.75 (m, 2 H), 6.69–6.85 (m, 2 H), 7.15 (d, *J* = 14.8 Hz, 2 H), 7.38–7.59 (m, 8 H), 7.89–7.95 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 126.91, 128.48, 128.57, 132.9, 134.82, 137.96, 140.51, 143.52, 190.15 ppm. Mp: 213-214 °C (chloroform/diethyl ether). Spectroscopic characterizations of the product **6** are in agreement with the data reported in literature.[9]

Procedure for the Homocoupling Reaction of the (2*E*,4*E*,6*E*)-1-Phenyl-7-(trimethylsilyl)-2,4,6-heptatrien-1-one (7) Using 25% of $PdCl_2$ in Aqueous Micelles with Triton X-100 (15 wt.-% Triton X-100/H_2O): A 25 mL round-bottomed flask was charged with (2*E*,4*E*,6*E*)-1-phenyl-7-(trimethylsilyl)-2,4,6-heptatrien-1-one (**7**) (0.1 g, 0.391 mmol), $PdCl_2$ (0.017 g, 0.098 mmol), $CuCl_2$ (0.105 g, 0.78 mmol) LiCl (0.012 g, 0.292 mmol) in 5 mL of surfactant water solution and the mixture was stirred at room temperature. The reaction was monitored by TLC and quenched with a saturated aqueous sodium chloride solution. The mixture was then extracted twice with dichloromethane. The organic layers were combined and dried with anhydrous Na_2SO_4. Concentration of the solvent at reduced pressure gave a crude product that was recrystallized from chloroform/diethyl ether isolating **8** as an orange solid (0.046 g, 65% yield); m.p. 221–222 °C (chloroform/diethyl ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.40–6.55 (m, 6 H), 6.71 (dd, *J* = 14.8, 10.2 Hz, 2 H), 7.01 (d, *J* = 14.9 Hz, 2 H), 7.38–7.65 (m, 8 H), 7.88–

7.98 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 125.63, 128.26, 128.51, 132.33, 132.54, 134.61, 135.88, 138.50, 141.57, 144.21, 190.29 ppm. Spectroscopic characterizations of the product **8** are in agreement with the data reported in the literature.[9]

Acknowledgments

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