A Novel Regio- and Stereoselective Formal Cross-Coupling Reaction of Unsaturated Silanes with Arenediazonium Tetrafluoroborates

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Introduction

Palladium-catalyzed cross-coupling reactions between organometallic reagents and electrophilic aromatic partners represent a powerful synthetic tool for carbon−carbon bond formation.[1] Besides aryl halides and triflates, arenediazonium salts have been employed as electrophiles for palladium-catalyzed cross-coupling reactions with stannyl derivatives.[2] Related processes also involving arenediazonium salts are represented by palladium-catalyzed reactions with alkenes,[3] or with germyl derivatives,[4] carboxylation,[5] formylation,[6] and carbonylation[7] reactions.

Recently, Genêt and co-workers[8] have reported the cross-coupling reaction between arenediazonium tetrafluoroborates and aryl or alkenyl boronic acids[8a] or potassium trifluoroborates[8b] in the presence of catalytic amounts of palladium(II) acetate. The process appears of special interest since it occurs under mild conditions and in the absence of both base and ligand. After the work of the Genêt group, similar results involving boronic acids have been reported also by Sengupta and Bhattacharyya.[9]

Alkenylsilanes are absent among the array of organometallic compounds used in palladium-catalyzed cross-coupling reactions with arenediazonium salts. Actually, Kikukawa and co-workers reported a palladium-catalyzed aryldesilylation of alkenylsilanes by arenediazonium salts,[10] but the lack of regio-and stereospecificity in this reaction is more compatible with an addition−elimination mechanism rather than with a cross-coupling process.

On the other hand, it is known that unsaturated silanes cannot be easily subjected to palladium-catalyzed cross-coupling reaction because of the low reactivity of the silicon−carbon bond toward transmetalation. The difficulty of performing these reactions with simple trimethylsilyl compounds has been stressed,[11] and the use of alkenyl-fluoro or -alkoxysilanes in the presence of fluoride ion[12] is required in the reaction with unsaturated organic halides. More recently, (*E*)- and (*Z*)-1-alkenyl-1-methylsilacyclobutanes have been employed in stereospecific cross-coupling reactions with aryl iodides in mild conditions.[13]

In our previous work,[14] we overcame the drawback of the poor reactivity of trimethylsilyl derivatives disclosing a novel and efficient protocol for the formal cross-coupling reaction of alkenyl and polyenyl silanes with aryl or vinyl halides consisting of an *ipso*-borodesilylation with boron trichloride and subsequent in situ palladium-catalyzed coupling reaction of the resulting boron derivative with organic halides. The overall procedure, described in Scheme 1, represents a formal Suzuki−Miyaura cross-coupling reaction starting with unsaturated silanes.

In this paper we report our work dealing with the use of alkenylsilanes as starting materials for an efficient, formal Genêt cross-coupling reaction with arenediazonium salts.

Results and Discussion

Alkenylsilanes **1a**−**c** and (1*E*,3*E*)-1,4-bis(trimethylsilyl)-1,3-butadiene **1d** were subjected to reaction with boron trichloride in methylene chloride solution to perform the easy *ipso*-borodesilylation described above. After removal of the solvent, the intermediates deriving from the transmetalation step were used directly in a cross-coupling procedure, adding the solvent (dioxane), palladium acetate as the catalyst, and diazonium tetrafluoroborates **2a**−**e** to the crude product. The results, reported in Table 1 (entries 1−8), clearly show that, in contrast with the direct aryldesilylation of vinylsilanes

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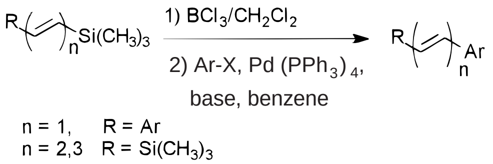
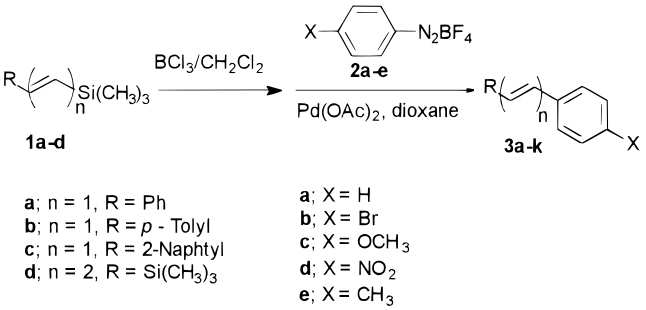
Scheme 1



Scheme 2



with arenediazonium salts, our protocol allows a stereoselective and regioselective arylation of vinylsilanes affording the cross-coupling products with various arenediazonium tetrafluoroborates, in acceptable to good yields.

The nature of the arenediazonium tetrafluoroborate substituent does not exert a significant influence on the reactions of these substrates: similar yields are obtained either with electron-withdrawing (nitro) or electron-donating (methoxy or methyl) groups.

When the methodology is extended to the bis-silylated system **1d** (entries 9−11), the cross-coupling also occurs in a chemo- and stereoselective fashion, involving only one of the two trimethylsilyl groups, thus providing an alternative route to the synthesis of trimethylsilyl dienes. The chemoselectivity of the *ipso*-borodesilylation process, involving only one of the two trimethylsilyl groups of **1d**, may be ascribed to the electron-withdrawing effect of the boron group on the conjugated system,[15] which renders more difficult the electrophilic substitution of the second trimethylsilyl group.

Reactions involving arenediazonium tetrafluoroborates containing a bromine substituent (entries 2, 4) display high chemoselectivity, leading to bromo intermediates which can be used in further stepwise cross-coupling reactions. In fact, we have performed the sequential cross-coupling reaction on 4-bromoarenediazonium tetrafluoroborate **2b** as shown in Scheme 3. The bromostilbene **3d** was then allowed to couple with the styrylsilane **1a** according to our procedure,[14a,b] which, when halides are involved as substrates, requires the use of a Pd(0)−phosphine complex as catalyst. The unsymmetrical distyryl derivative **4a** was formed in the reaction.

Conclusions

In conclusion, our procedure opens the access to the use of vinyl and polyenyl silanes in highly regio- and stereoselective cross-coupling reactions with arenediazonium tetrafluoroborates. Furthermore, the possibility of employing the unsaturated silanes in sequential cross-coupling reactions with bromoarene diazonium salts enlarges the synthetic potential of these versatile substrates. Indeed, the preparation of conjugated structures of interest in the field of liquid crystals[16] and of NLO[17] and electroluminescent materials[18] can be easily envisaged.

Experimental Section

Silica gel 60 (particle size 0.040−0.063) for flash column chromatography and aluminum sheets with silica gel 60 F_{254} for TLC were used. GC analyses were performed on a gas chromatograph equipped with a SE-30 (methylsilicone, 30 m × 0.25 mm i.d.) capillary column. ^{1}H NMR spectra were recorded in $CDCl_3$ at 500 MHz and at 200 MHz using the residual $CHCl_3$ as the standard. To obtain reproducible results, it is recommended that commercial 1 M solutions of BCl_3 in methylene chloride be stored under nitrogen in a freezer over anhydrous Na_2CO_3. 1,4-Dioxane and benzene were distilled from benzophenone ketyl immediately prior to use. Dichloromethane was distilled over phosphorus pentoxide immediately prior to use. All reactions were performed under a nitrogen atmosphere. Arenediazonium tetrafluoroborates were generally prepared from commercial aromatic amines according to published methods.[19] If necessary, the salts were purified by several recrystallizations from acetone/diethyl ether and could be stored for several weeks at −4 °C.

(*E*)-Stilbene (3a). Typical Procedure. A 1 M methylene chloride solution of BCl_3 (2.3 mL, 2.3 mmol) was added dropwise under a nitrogen atmosphere to a stirred solution (5 mL) of the vinylsilane **1a** (0.30 g, 1.7 mmol) in dichloromethane at 0 °C. The reaction was monitored by GC until no more vinylsilane was detected (a small amount of protodesilylated product was present). After reaction completion, as detected by GC analysis (2 h), the solvent was removed under vacuum and the residue dissolved in anhydrous dioxane. The catalyst, $Pd(OAc)_2$ (0.02 g, 0.089 mmol), and phenyl diazonium tetrafluoroborate **2a** (0.27 g, 1.40 mmol) were then added. The resulting suspension was stirred at room temperature for 24 h. After completion, the reaction was quenched with water (15 mL), and the resulting mixture was extracted thrice with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated at reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether as eluent); 0.20 g (80% yield) of **3a** were recovered (mp 123−124 °C from ethanol; lit. 124−125 °C[20]).

(*E*)-4-Bromostilbene (**3b**),[21] (*E*)-4-methylstilbene (**3c**),[20,22] (*E*)-4-bromo-4′-methylstilbene (**3d**),[23](*E*)-4-methoxy-4′-methylstilbene (**3e**),[24,25](*E*)-4-methyl-4′-nitrostilbene (**3f**),[26](*E*)-4,4′-dimethylstilbene (**3g**),[23] (*E*)-1-(2-naphthyl)-2-phenylethene (**3h**),[27] (1*E*, 3*E*)-1-phenyl-4-trimethylsilyl-1,3-butadiene (**3i**),[28] (1*E*, 3*E*)-1-(4-nitrophenyl)-4-trimethylsilyl-1,3-butadiene (**3j**),[29] (1*E*, 3*E*)-4-(4-methylphenyl)-1-trimethylsilyl-1,3-butadiene (**3k**)[14b] were characterized comparing their physical properties and ^{1}H NMR spectra with those reported in the literature.

Synthesis of 1-(4-Methyl-*trans*-styryl)-4-*trans*-styrylbenzene (4a). A 1 M dichloromethane solution of BCl_3 (1.5 mL, 1.5

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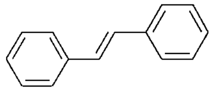
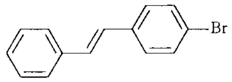
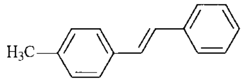
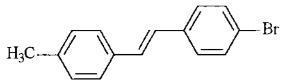
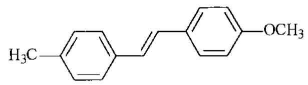
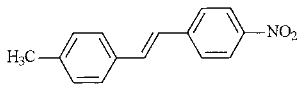
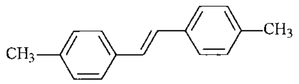
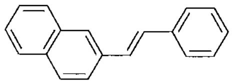
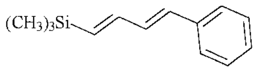
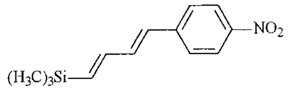
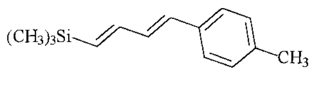
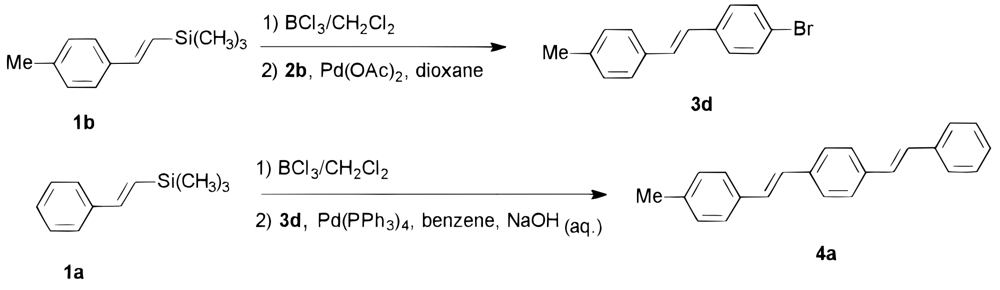
Table 1. Formal Cross-coupling Reactions of Vinylsilanes with Arenediazonium Tetrafluoroborates

Entry	Vinylsilane	Arenediazonium tetrafluoroborate	Coupling products		Yield (%)[a]
1	**1a**	**2a**		**3a**	80
2	**1a**	**2b**		**3b**	61
3	**1b**	**2a**		**3c**	72
4	**1b**	**2b**		**3d**	60
5	**1b**	**2c**		**3e**	65
6	**1b**	**2d**		**3f**	58
7	**1b**	**2e**		**3g**	62
8	**1c**	**2a**		**3h**	50
9	**1d**	**2a**		**3i**	45
10	**1d**	**2d**		**3j**	40
11	**1d**	**2e**		**3k**	42

[a] Yields refer to purified isolated products

Scheme 3



mmol) was slowly added under nitrogen to a stirred dichloromethane solution (3 mL) of **1a** (0.15 g, 0.85 mmol) at 0 °C. After reaction completion (2 h), the solvent was removed under vacuum and the residue dissolved in anhydrous benzene/ethanol

(2/1, 15 mL). Bromostilbene **3d** (0.22 g, 0.85 mmol) and the catalyst Pd(PPh_3)$_4$ (0.03 g, 0.026 mmol) were then added, and the mixture was stirred for a few minutes. A 2 M solution of NaOH (0.9 mL) was slowly dropped while stirring. The mixture was then refluxed for 24 h until no more **3d** was present (GC analysis). The reaction was quenched with water, and the resulting mixture was extracted with dichloromethane. The solvent was then evaporated at reduced pressure. The crude product **4a** was purified by chromatography on silica gel (petroleum ether/dichloromethane 6/4 as eluent) to give 0.20 g of a white solid (78% yield), mp 276−277 °C from chlorobenzene (lit. 276 °C[30]).

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Supporting Information Available: Characterization data are available for compounds **3i**−**k** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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