

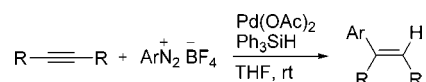
Palladium-Catalyzed Hydroarylation of Alkynes with Arenediazonium Salts

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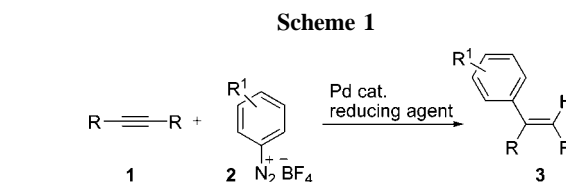
ABSTRACT

The palladium-catalyzed hydroarylation of arenediazonium tetrafluoroborates with alkynes in the presence of triphenylsilane affords stereoselectively hydroarylation products in moderate to high yields. The reaction tolerates a variety of substituents including keto, ester, cyano, and nitro groups and can be performed as a one-pot procedure generating the arenediazonium salt in situ. With ethyl phenylpropynoate as the starting alkyne, the hydroarylation affords ethyl (*Z*)-2-arylcinnamates stereo- and regioselectively.

After the first palladium-catalyzed arylation of olefins with arenediazonium salts reported by Matsuda et al.,¹ arenediazonium salts have been used as aryl partners in a variety of palladium-catalyzed reactions including Mizoroki–Heck reactions,² Suzuki–Miyaura^{2g,3} and Stille⁴ cross-couplings, and carbonylation reactions.^{2h,i,5} They have also been used as precursors of sulfinic acids⁶ and boronic esters.⁷ Indeed, their higher reactivity, the utilization of mild conditions, aqueous medium, their availability from inexpensive anilines, and the absence of added bases in several applications make them an attractive alternative to aryl halides or triflates.⁸ Nevertheless, very little has been done with alkynes. To the best of our knowledge, the sole attempt to involve alkyne partners in a reaction with arenediazonium salts was made by Genêt et al.,⁹ who described the palladium-catalyzed cross-coupling of potassium 1-hexenyltrifluoroborate with *p*-toluenediazonium tetrafluoroborate. However, only small amounts of the desired cross-coupling derivative were observed, the starting diazonium salt being quantitatively reduced.

Because of our ongoing interest in alkyne-based palladium-catalyzed processes,¹⁰ we decided to investigate the palladium-catalyzed hydroarylation of internal alkynes with arenediazonium salts (Scheme 1).

The palladium-catalyzed hydroarylation of alkynes with aryl and vinyl halides or triflates^{10b,c,11} has been shown to



be a useful tool for the preparation of substituted olefins. With alkynes containing nucleophilic and electrophilic centers close to the carbon–carbon triple bond, the reaction affords cyclic derivatives.^{10c} The intramolecular version of the reaction has also been described.¹¹ The extension of the hydroarylation protocol to arenediazonium salts would widen significantly the synthetic scope of this chemistry. Herein we report the results of this study.

The reaction of diphenylacetylene with *p*-methoxybenzenediazonium tetrafluoroborate was initially examined as the model system. Phosphine-free conditions were selected on the basis of the known detrimental effect of phosphine ligands in many palladium-catalyzed reactions of arenediazonium salts¹² and our previous experience with the hydrovinylation of vinyl triflates wherein phosphines were found to hamper the coordination of the alkyne to the palladium atom of vinylpalladium intermediates (an event which precedes the carbopalladation step) and favor the reduction of vinyl triflates to alkenes via displacement of

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Table 1. Reducing Agents, Solvents, and Temperature in the Palladium-Catalyzed Hydroarylation of Diphenylacetylene with *p*-Methoxybenzenediazonium Tetrafluoroborate^a

entry	reducing agent	solvent	T (°C)	time (h)	yield ^b of 3a (%)	E/Z
1	Et ₃ SiH	THF	rt	24	19	>99:1
2	Et ₃ SiH	THF	40	24	traces	
3	Et ₃ SiH	THF/MeOH ^c	rt	6	13	>99:1
4	Et ₃ SiH	DMF	rt	24		
5	Et ₃ SiH	MeCN	rt	24	21	>99:1
6	Oct ₃ SiH	THF	rt	24	32	>99:1
7	<i>i</i> -Pr ₃ SiH	THF	rt	24	53	>99:1
8	Ph ₃ SiH	THF	rt	24	62	>99:1
9	Ph ₃ SiH	THF	40	2	25	97:3
10	Ph ₃ SiH	MeCN	rt	2	35	97:3
11	Ph ₃ SiH	DMF	rt	0.75	62	>99:1
12	Ph ₃ SiH	THF	rt	3.5	82 ^d	>99:1
13	<i>i</i> -Pr ₃ SiH	THF	rt	1.5	71 ^d	>99:1

^a Unless otherwise stated, reactions of entries 7–19 were carried out on a 0.5 mmol scale, under argon, using 1 equiv of diphenylacetylene, 1.5 equiv of *p*-methoxybenzenediazonium tetrafluoroborate, 2 equiv of R₃SiH, and 0.02 equiv of Pd(OAc)₂ in 4 mL of solvent. ^b Yields are given for isolated products. ^c THF/MeOH 1:1. ^d In the presence of 4 equiv of *p*-methoxybenzenediazonium tetrafluoroborate.

the triflate anion by formate.¹³ Assuming that some similarity might exist between arylpalladium intermediates derived from the reaction of arenediazonium salts with Pd(0) and vinylpalladium intermediates derived from the oxidative addition of vinyl triflates to Pd(0) (at least as far as the intermediacy of cationic organopalladium complexes is concerned), the utilization of phosphine-free conditions appeared appropriate to our study. Representative optimization experiments are summarized in Table 1.

Potassium formate is commonly used in hydroarylation reactions with aryl halides, but no evidence of alkene

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formation was obtained using diphenylacetylene and *p*-methoxybenzenediazonium tetrafluoroborate with HCO₂K and Pd(OAc)₂ in THF, EtOH, or DMF as the solvent at temperatures ranging from rt to 60 °C. Surmising that in the presence of formate anions the reduction of the alkyne and the arylpalladium intermediate is faster than the carbopalladation reaction, we decided to explore the utilization of other, possibly more selective, reducing agents and focused our attention on trialkylsilanes. After a number of experiments, success was finally encountered under the conditions reported in Table 1, entry 12, which allowed for the isolation of **3a** in 82% yield.¹⁴

These “optimal” conditions were then applied to other arenediazonium tetrafluoroborates (Table 2). Hydroarylation

Table 2. Palladium-Catalyzed Hydroarylation of Diphenylacetylene with Arenediazonium Tetrafluoroborates **2^a**

entry	R ¹	2	time (h)	yield of 3^{b,c} (%)
1	<i>p</i> -MeO-	2a	3.5	82, 3a
2	<i>m</i> -CF ₃ -	2b	7	58, 3b
3	<i>p</i> -Me-	2c	5	86, 3c
4	<i>p</i> -MeCO-	2d	8	59, 3d
5	<i>m</i> -MeO-	2e	22	77, 3e
6	<i>o</i> -MeO-	2f	24	56, ^d 3f
7	3,4,5-(MeO) ₃ -	2g	24	51, 3g
8	2-Me,4-F-	2h	24	66, ^d 3h
9	<i>p</i> -CN-	2i	24	54, 3i
10	<i>p</i> -NO ₂ -	2j	24	42, 3j
11	2,4-Me ₂ -	2k	24	89, 3k
12	<i>p</i> -MeO ₂ C-	2l	24	53, 3l

^a Reactions were carried out under argon on a 0.5 mmol scale using 1 equiv of diphenylacetylene, 4 equiv of **2**, 2 equiv of Ph₃SiH, 0.02 equiv of Pd(OAc)₂ in 4 mL of anhydrous THF at rt. ^b Yields are given for isolated products. ^c E/Z ratios were calculated by NMR analyses and were usually found to be higher than 99:1. ^d E/Z = 96:4.

products were isolated in moderate to high yields. The reaction tolerates a variety of substituents including keto, ester, cyano, and nitro groups (palladium-catalyzed reactions with the latter frequently fail because of their tendency to

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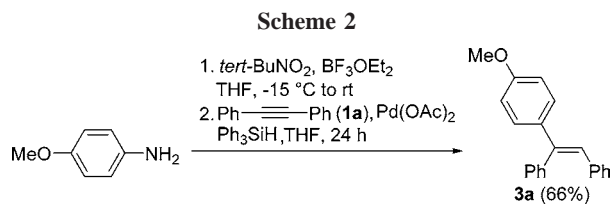
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decompose¹²). It is also highly stereoselective: *E/Z* ratios usually exceed 99:1. Only with *o*-methoxy- and 2-methyl-4-fluorobenzenediazonium tetrafluoroborates a lower stereoselectivity was attained (Table 2, entries 6 and 8). The (*E*) stereochemistry of **3a** was assigned by NOESY experiments which showed a strong cross-peak between the vinylic proton and the ortho hydrogens of the added aryl unit. That of the other hydroarylation derivatives was assigned based on this data and all our previous work on hydroarylation reactions in which the *cis* adduct has usually been the main product.

It is worth noting that arenediazonium salts containing ortho substituents can give hydroarylation products in good to high yields (Table 2, entries 6, 8, and 11), while ortho-substituted aryl iodides are reluctant to give the same derivatives. A remarkable example of this behavior is provided by the reaction of *o*-iodoanisole with diphenylacetylene. Under conditions that are known to afford the desired products with a variety of meta- and para-substituted aryl iodides (HCOOK, HCOOH/Et₃N, with and without PPh₃, in DMF or THF at rt –40 °C), the corresponding hydroarylation derivative was isolated in 7–17% yields.¹⁵

The hydroarylation reaction was also performed generating the arenediazonium salt in situ.¹⁶ This protocol was attempted with *p*-anisidine and diphenylacetylene (Scheme 2). The best



result was obtained by adding the reagents required for the hydroarylation step to the crude mixture resulting from the

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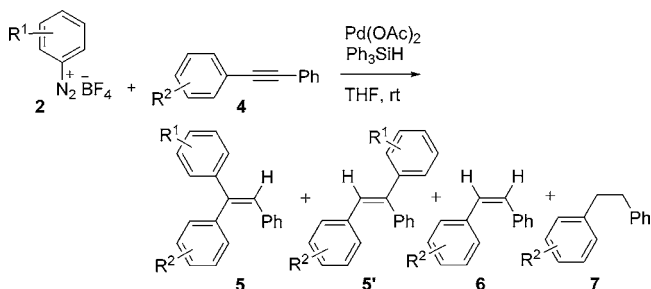
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(14) The utilization of a large excess of the arenediazonium salt is due to its tendency to undergo several competitive side reactions such as the formation of the corresponding arene and fluoroarene.

preparation of *p*-methoxybenzenediazonium tetrafluoroborate concentrated under reduced pressure.

The hydroarylation of diarylacetylenes asymmetrically substituted with electron-donating and electron-withdrawing groups was then explored to investigate the role of electronic effects on the regioselectivity of this hydroarylation process (Table 3). According to previous hydroarylations of aryl

Table 3



R ¹ , 2	R ² , 4	time (h)	5 + 5' yield (%)	yield of 6 (%)	yield of 7 (%)
<i>p</i> -MeO, 2a	<i>p</i> -MeO, 4a	7	71 (56/44)	15	7
<i>p</i> -Me, 2c	<i>p</i> -MeO, 4a	6	86 (53/47)		
<i>p</i> -MeO, 2a	<i>p</i> -MeCO, 4b	7	20 ^a (56/44)	31	

^a **4b** was recovered in 36% yield.

iodides¹⁷ and related palladium-catalyzed additions of “arylpalladium halides” to alkynes,¹⁸ the results obtained suggest that electronic effects play a minor role in controlling the regiochemistry of the reaction. Regioisomeric hydroarylation products (their regiochemistry was not assigned) were indeed isolated in almost equimolar amounts. The nature of the substituents on the alkyne partner, however, can influence the carbopalladation/reduction (of the C–C triple bond) ratio (Table 3).

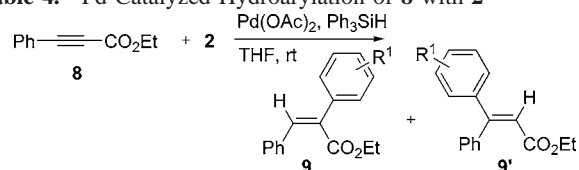
The same minor role of electronic effects on the regiochemistry of the reaction was observed with ethyl phenylpropynoate (Table 4). Apparently, the phenyl group exerts more influence on the direction of the addition than the ester groups does and regioisomeric derivatives **9'**, which would be expected to be favored by an electronic biased process, were isolated in small amounts, the main products being ethyl (*Z*)-2-arylcinnamates **9** (*E/Z* > 99:1). The latter were isolated in yields comparable to those obtained with aryl iodides,¹⁶ providing a simple straightforward route to this class of compounds.

(15) The reaction of *p*-iodoanisole with diphenylacetylene in the presence of Ph₃SiH, Pd(OAc)₂ at 40 °C using THF and DMF as solvents was also attempted, but no evidence of formation of the corresponding hydroarylation product was attained.

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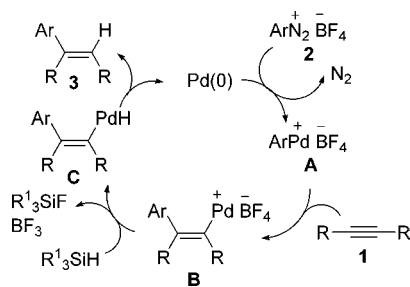
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Table 4. Pd-Catalyzed Hydroarylation of **8** with **2**

R ¹ , 2	time (h)	yield of 9 (%)	yield of 9' (%)	9/9'
<i>p</i> -MeO, 2a	7	55, 9a	9, 9a'	86:14
<i>m</i> -CF ₃ , 2b	9	55, 9b	5, 9b'	91:9
<i>p</i> -Me, 2c	8	44, 9c	6, 9c'	88:12
<i>m</i> -MeO, 2e	9	55, 9d	13, 9d'	81:19

As to the mechanism, we believe that the reaction proceeds through the basic steps outlined in Scheme 3: (a) stereose-

Scheme 3

lective addition of the initially formed σ -arylpalladium complex **A** to the C–C triple bond, (b) reaction of the resultant carbopalladation adduct **B** with trialkylsilyl fluoride, the presence of which has been evidenced in almost all the reactions investigated), (c) reductive elimination.

The alternative mechanism involving an hydrosilylation step to give vinyltrialkylsilane intermediates followed by their cross-coupling with arylpalladium complexes appears less

likely in view of the known¹⁹ reluctance of simple vinyltrialkylsilanes to enter transmetalation processes. This is due to the extremely low polarity of the C–Si bond. Vinylfluoro- or vinylalkoxysilanes in the presence of fluoride anions are usually required to perform palladium-catalyzed cross-coupling reactions.²⁰ Even an addition–elimination mechanism on vinyltrialkylsilane intermediates, as proposed for the palladium-catalyzed arylation of substituted vinylsilanes with arenediazonium tetrafluoroborates,^{3b,21} seems to be flawed by the stereo- and regioselectivity of the hydroarylation reaction. Indeed, a lack of stereo- and regioselectivity would be expected if an addition–elimination mechanism was operating.

In conclusion, we have described the first alkyne-based palladium-catalyzed synthetic application of arenediazonium salts. The reaction tolerates a variety of substituents including keto, ester, cyano, and nitro groups, is highly stereoselective, and can be performed as a one-pot process generating the arenediazonium salt in situ; and with ethyl phenylpropynoate a satisfactory regioselectivity is observed, comparable to that obtained with aryl iodides. Further studies on this chemistry are currently underway.

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Supporting Information Available: A complete description of experimental details and product characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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