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Decarbopalladation of π-Allylpalladium Intermediates Formed from Palladium-Catalyzed Arylations of 3-Allen-1-ols

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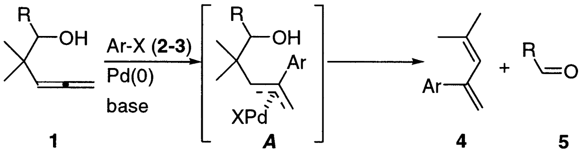
ABSTRACT



Unusual palladium-catalyzed arylative fragmentations of acyclic 3-allen-1-ols were observed. Oxidative addition of Pd(0) to aryl halides would form the arylpalladium halides, which added to the central carbon of allenes via carbopalladation to form the π-allylpalladium intermediates. The π-allylpalladium intermediates would be reductively eliminated via carbon–carbon cleavage to give the arylated dienes and the α-hydroxyalkylpalladium intermediates, which were further reductively eliminated to the corresponding aldehydes.

Palladium-catalyzed reactions involving nucleophilic attack on π-alkene- and π-allylpalladium complexes provide convenient and powerful tools for organic synthesis, and a large number of selective organic transformations have been reported.[1] Compared to alkynes, olefins, and 1,3-dienes, allenes have attracted considerable interest only in recent years. Many examples of palladium-catalyzed carbopalladations,[2] carbonylations,[3] dimerizations,[4] oxidations,[5] and hydropalladations[6] involving allenes were reported together with a variety of intramolecular variants.[7]

Mechanistically, allenes are capable of undergoing 1,2-addition under palladium catalysis with both electrophiles and nucleophiles with opposite regioselectivities, where electrophiles attach to the central carbon and nucleophiles to the 1- or 3-carbon of the allene.[8] In addition to these, several transition metal catalysts associated with ruthenium,[9] titanium,[10] and lanthanides[11] were developed to mediate a

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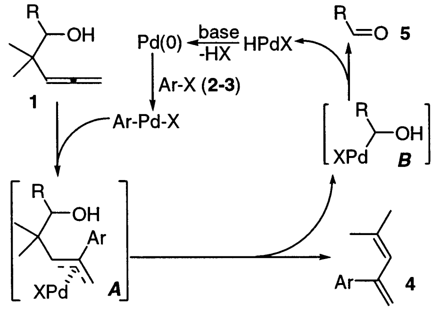
variety of transformations of allenes. During our study on Pd-catalyzed cyclization of allenynes,[12] we found an unusual carbon−carbon cleavage of π-allylpalladium intermediates (Scheme 1).

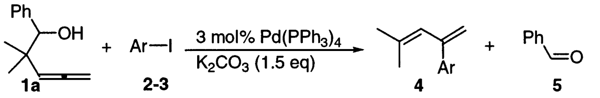
Scheme 1



Here we report these Pd-catalyzed carbon−carbon bond cleavages of hydroxy-containing π-allylpalladium intermediates (***A***).[13] It was expected that the initially formed π-allylpalladium intermediate might be cyclized with the internal nucleophile, OH, to form either the oxetane or the oxane heterocycle,[14] but the π-allylpalladium intermediate (***A***) was reductively eliminated to form the arylated 1,3-diene product **4** and the aldehyde **5** in excellent yields, respectively (eq 1 and Table 1). First, we examined this reaction in various solvents using allenol **1a** and iodobenzene (**2a**) in the presence of K_2CO_3 (entries 1−6).

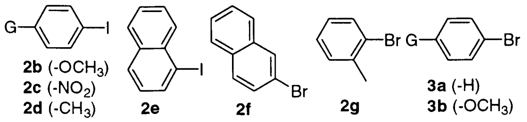
Among the various solvents we tested, the highest yield of the product diene **4a** (87%) and its counterpart, benzaldehyde (**5**, 82%), was obtained in refluxing 1,4-dioxane.[15] Next, we carried out the Pd-catalyzed arylative fragmentations with various aryl iodides **2b**−**e** and aryl bromides **2f,g**, **3a,b** in 1,4-dioxane. The allenol **1a** under these conditions were cleanly coupled separately with 4-iodoanisole (**2b**), 4-nitroiodobenzene (**2c**), 4-iodotoluene (**2d**), and 1-iodonaphthalene (**2e**) and subsequently cleaved to the arylated conjugated dienes **4b**−**e** in 81%, 85%, 80%, and 90% yields, respectively (entry 7−10). Aryl bromides such as 2-bromonaphthalene (**2f**), 2-bromotoluene (**2g**), bromobenzene (**3a**), and 4-bromoanisole (**3b**) also worked well to give **4f**, **4g**, **4a**, and **4b** in 89%, 78%, 79%, and 81% yields, respectively (entries 11−14). Note that sterically hindered 2-bromotoluene also gave the product **4g** in high yield (78%), despite its steric hindrance (entry 12).

Table 1. Palladium-Catalyzed Arylative Fragmentations of 2,2-Dimethyl-1-phenyl-3,4-pentadien-1-ol with Aryl Halides **2** and **3**



(1)

entry	ArX	Solvents	temp (°C)/time (h)	product	% yield
1	**2a**	toluene	reflux/24	**4a**	55
2	**2a**	$CHCl_3$	reflux/24	**4a**	45
3	**2a**	1,4-dioxane	reflux/6	**4a**	87
4	**2a**	DMF	110/6	**4a**	74
5	**2a**	DMSO	110/6	**4a**	62
6	**2a**	ethanol	reflux/4	**4a**	73
7	**2b**	1,4-dioxane	reflux/6	**4b**	81
8	**2c**	1,4-dioxane	reflux/6	**4c**	85
9	**2d**	1,4-dioxane	reflux/6	**4d**	80
10	**2e**	1,4-dioxane	reflux/6	**4e**	90
11	**2f**	1,4-dioxane	reflux/6	**4f**	89
12	**2g**	1,4-dioxane	reflux/6	**4g**	78
13	**3a**	1,4-dioxane	reflux/6	**4a**	79
14	**3b**	1,4-dioxane	reflux/6	**4b**	81



Structural variations of the allenol **1** were tested to see whether the fragmentation of π-allylpalladium intermediates ***A*** might be affected by groups attached to the OH group. The phenyl group was replaced by H (**1b**), *n*-butyl (**1c**), vinyl (**1d**), and alkynyl (**1e**) for systematic study (eq 2 and Table 2).[16] All allenols possessing a hydroxyl group smoothly underwent the present reactions with iodobenzene (**2a**) to give the phenyl-substituted diene **4a** and the corresponding aldehydes. The simple allenol **1b** gave a slightly lower yield (45%) of the product **4a**. Allenol **1c** also underwent the present reactions with aryl iodides **2a**−**d** and aryl bromides **3a,b** but less efficiently than the phenyl-substrate **1a** to the aryl-substituted dienes **4a**−**d** in 71−88% yields. Allenol **1d** with iodobenzene (**2a**) gave the products **4a** in 69% yield. Allenol **1e** bearing an alkynyl group was less efficient than the other allenols **1a**−**d** under these conditions to give the expected products **4** and in some cases (**6g**) the cyclized

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(15) When K_2CO_3 was replaced by triethylamine, the reaction did not occur at all in toluene and 1,4-dioxane even after refluxing for 12 h and a low conversion in DMF was obtained at 110 °C.

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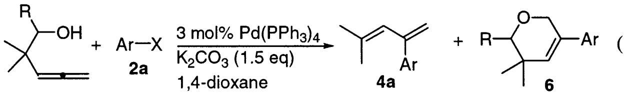
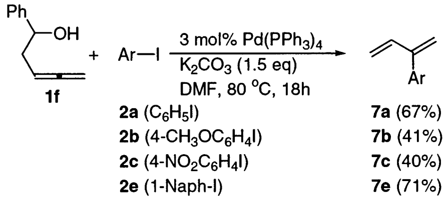
Table 2. Arylative Fragmentations of Allenol **1** with Aryl Halides **2** and **3**



R = H- (**1b**), *n*-Bu- (**1c**), CH_2=CH- (**1d**), *t*-C_4H_9—C≡C—(**1e**)

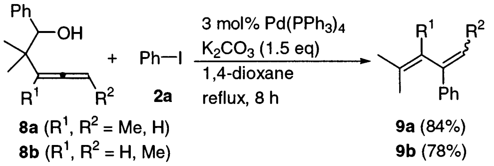
allenol	Ar-X	temp (°C)/time (h)	product	% yield
1b	**2a**	reflux/12	**4a**	45
1c	**2a**	reflux/6	**4a**	88
1c	**2b**	reflux/24	**4b**	71
1c	**2c**	reflux/6	**4c**	87
1c	**2d**	reflux/12	**4d**	71
1c	**3a**	reflux/10	**4a**	78
1c	**3b**	reflux/24	**4b**	71
1d	**2a**	80/14	**4a**	69
1e	**2a**	80/16	**4a**	77
1e	**2d**	80/10	**4d**	43
1e	**2f**	80/10	**4f**	47
1e	**2 g**	80/10	**4g, 6g**	34, 21

products along with some unidentified polymeric products. Our attention was then paid to the simple allenol **1f**. The arylative fragmentation of the allenol **1f** with iodobenzene (**2a**), 4-iodoanisole (**2b**), 4-nitroiodobenzene (**2c**), and 1-iodonaphthalene (**2e**) were carried out under the similar conditions except the reaction solvent. These reactions worked better in DMF than in 1,4-dioxane to give the expected products **7a**−**e** in good yields (eq 3).



(3)

Finally, the methyl substituents in both allenols **8a** and **8b** did not prevent the arylative fragmentations with iodobenzene (**2a**) to give **9a** and **9b** in 84% and 78% (an *E*/*Z* mixture of 1:3 ratio) yields, respectively.



(4)

A mechanistic interpretation is proposed as shown in Scheme 1. Oxidative addition of Pd(0) to aryl halides is now a generally accepted process to form arylpalladium halides, whose aryl group added to the central carbon of allene **1** via carbopalladation to form the intermediate ***A***. The π-allylpalladium intermediate ***A*** might be decarbopalladated to form the fragmentation products **4** and α-hydroxyalkylpalladium intermediate ***B***. The intermediate ***B*** can be β-eliminated to form the carbonyl compound **5** and HPdX species, which can reform Pd(0) species by reaction with a base.

In summary, we have shown highly unusual decarbopalladations of π-allylpalladium intermediates formed from acyclic 3-allen-1-ols. These new reactions involve π-allylpalladium intermediates ***A***, which were reductively eliminated via carbon−carbon cleavage to the arylated dienes and the resulting α-hydroxyalkylpalladium intermediates ***B***, which were further reductively eliminated to the corresponding aldehydes (Scheme 1).

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Supporting Information Available: Characterization data for compounds **4a**−**g**, **6g**, **7a,b,c,e**, and **9a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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