Synthesis of multi-substituted dihydrofurans via palladium-catalysed coupling between 2,3-alkadienols and pronucleophiles

doi: 10.1039/C8CC02589D

Journal Name

COMMUNICATION

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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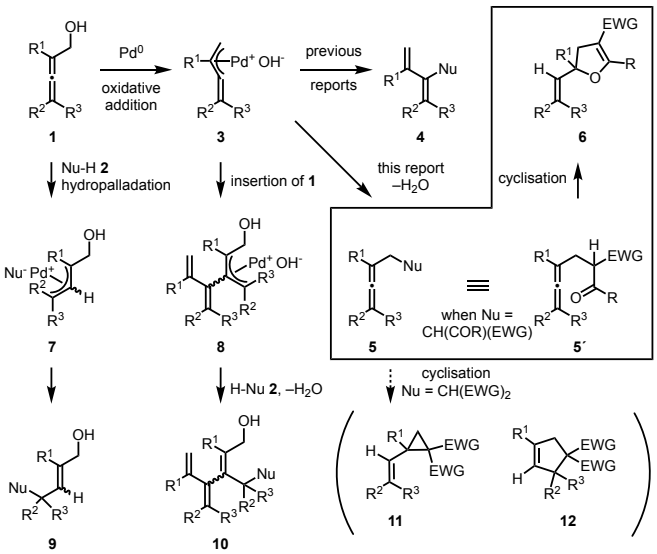
Multiple-substituted dihydrofurans were obtained by palladium-catalysed coupling reaction between 2,3-alkadienols and ketones bearing an electron-withdrawing group at the α-position. Methanol as a solvent was essential for the initial dehydrative substitution to suppress competitive hydroalkylation of the diene moiety. The substitution would be followed by intramolecular hydroalkoxylation under the same catalysis.

A nucleophilic substitution of a hydroxyl group without transforming it into a leaving group such as halide and sulphonate is very attractive in modern organic synthesis in terms of step-economy and waste minimisation.[1] Although Mitsunobu reaction[2] is classified as a dehydrative substitution applicable to a wide range of alcohols, it generates a stoichiometric amount of side products that are difficult to remove. On the other hand, Friedel-Crafts and Tsuji-Trost reactions, using transition metal-catalysed dehydrative substitutions of π-activated alcohols including allylic, propargylic and benzylic ones have recently received considerable attention because these reactions form only water as a byproduct.[3, 4] Tsuji-Trost reaction using allylic alcohol, instead of its acetate that is commonly utilised for this reaction, can exclude a base additive for the catalyst turnover but requires certain reaction conditions including special ligands[5], acidic additives[6], or protic media[7] to improve the low leaving ability of hydroxide ion. In contrast to allylic alcohol[4–8], the transformation of allenic alcohol, which can also lead to a π-allylpalladium intermediate upon activation,[9–12] has received only scattered attention (Scheme 1). To the best of our knowledge, Tsuji-Trost-type substitution reaction of allenic alcohol **1** with pronucleophile **2** leading to the formation of dehydration product **5** via *exo*-alkylidene-π-allylpalladium intermediate **3**[13] has never been developed, although a couple of transformations of **1** into 1,3-diene **4** have been reported (Scheme 1).[9–11] The dehydrative allenylation of **2** would be more difficult than simple allylation owing to two possible side reactions: 1) hydroalkylation of allene under palladium catalysis to give **9**;[14–16] 2) insertion of allene **1** into **3** to give dimerisation product **10**.[17] Herein, we report the reaction conditions for the dehydrative allenylation of **2**, which can suppress the side reactions. Moreover, we also demonstrate that the dehydrative allenylation of ketone **2**, substituted by an electron-withdrawing group at the α-position, accompanied the cyclisation of the resulting allenic ketone **5'** to give multiple-substituted dihydrofuran **6** in a single step. Here, it should be noted that other possible carbocyclic products **11** and **12** were hardly obtained. The single-step procedure has a great advantage over a three-step synthesis of dihydrofuran **6** from the common allenic alcohol **1** through 1) phosphorylation, 2) palladium-catalysed substitution of the phosphate with sodium salt of activated ketone and 3) intramolecular hydroalkoxylation of the resulting allenic β-ketoesters under the catalysis of mercury oxide and *p*-toluenesulfonic acid, as reported by Delair and Doutheau.[18, 19]



Scheme 1 Coupling Reactions between Allenic Alcohol **1** and **2**.

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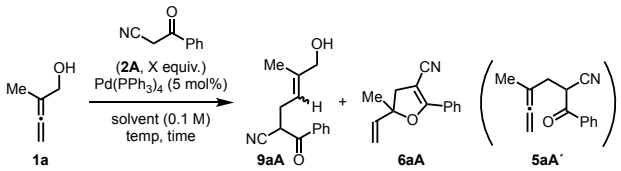
Electronic Supplementary Information (ESI) available: Detailed experimental procedures, spectroscopic data and copies of NMR spectra. See DOI: 10.1039/x0xx00000x

At first, 2-methyl-2,3-butadien-1-ol (**1a**, 1 equiv) was examined as an allenylating reagent for benzoylacetonitrile (**2A**, 2 equiv) on heating at 65 °C in the presence of 5 mol% tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (Scheme 2, Table 1, entries 1–5).[9] Aprotic solvents including toluene, THF, 1,4-dioxane, and dichloromethane resulted in a hydroalkylation of **1a** to give ca. 1:1 isomeric mixture of allylic alcohol **9aA** in moderate to good yield (Table 1, entries 1–4). Interestingly, the use of methanol as a solvent switched the reaction mode from addition to substitution to afford dihydrofuran **6aA** as a major product (entry 5).[20] The formation of allenylated product **5aA'** was not observed and would be followed by the intramolecular hydroalkoxylation of allene to give dihydrofuran **6aA** instead (vide infra). The reaction temperature was also a major reason for preferring the substitution reaction with 80 °C, leading to the best yield of **6aA** (entries 5–7). The molar ratio of pronucleophile **2A** to allenic alcohol **1a** was also crucial, and the use of 2 equiv of **2A** to **1a** turned out to be the best for the predominant formation of **6aA** (entries 7–10). In contrast, the use of an excess amount of **1a** to **2A** completely shut the reaction (entry 10). Instead of triphenylphosphine ligand, biaryl-based diphosphines such as BINAP and MeO-BIPHEP with allyl(cyclopentadienyl) palladium(II) led to the formation of a trace amount of **6aA** (data not shown).



Scheme 2 Pd(0)-Catalysed Coupling Reaction between **1a** and **2A**

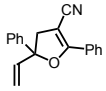
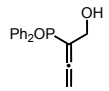
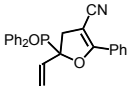
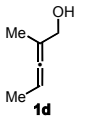
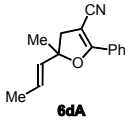
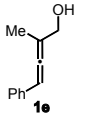
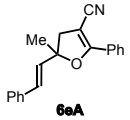
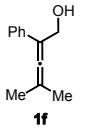
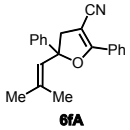
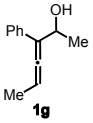
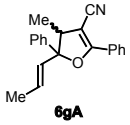
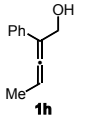
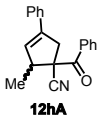
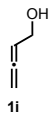
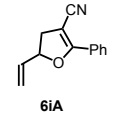
Table 1 Optimisation of Reaction Conditions for the Coupling Reaction between **1a** and **2A**

entry	solvent	X (equiv)	temp (°C)	time (h)	yield of **9aA** (%)[a]	yield of **6aA** (%)
1	toluene	2.0	65	4	54	trace
2	THF	2.0	65	2	70	trace
3	1,4-dioxane	2.0	65	2	64	trace
4	CH_2Cl_2	2.0	65	2	63	5
5	MeOH	2.0	65	4	18	58
6	MeOH	2.0	50	36	7	22
7	MeOH	2.0	80	1.5	12	68
8	MeOH	1.5	80	28	12	38
9	MeOH	3.0	80	1	25	42
10	MeOH	0.2	80	24	0	0

[a] *E*- and *Z*-**9aA** were obtained in the ratio of ca. 1.2:1 in entries 1–9.

With the optimised reaction conditions in hand (Table 1, entry 7), the scope of allenic alcohols **1b–i** was investigated (Table 2). Substitution of the methyl group at C-2 in **1a** by a phenyl group did not affect the efficiency of the coupling reaction with **2A** to give 2,5-diphenyl-5-vinyl-4,5-dihydrofuran-3-carbonitrile (**6bA**) in 71% yield (entry 1). Diphenylphosphine oxide as the substituent was also compatible with the reaction conditions to give **6cA** in moderate yield (entry 2). Two substituents at C-2 and C-4 in 2,3-butadien-1-ol **1** were also tolerated and transferred to the C-5 position and the terminal carbon of vinyl group at C-5 of 4,5-dihydrofuran, respectively (entries 3 and 4). The use of 2,4,4-trisubstituted allenic alcohol **1f** also resulted in dehydrative allenylation of **2A** and concomitant cyclisation to give **6fA** in 65% yield (entry 5). The use of secondary alcohol **1g** resulted in the formation of 4-substituted 4,5-dihydrofuran **6gA** as a diastereomeric mixture (entry 6). It should be noted that the parent primary alcohol **1h** was converted into *C*-cyclisation product **12hA** instead of *O*-alkylation product **6hA** (entry 7, vide infra). Unfortunately, unsubstituted 2,3-butadien-1-ol (**1i**) did not undergo dehydrative allenylation of **2A** at all (entry 8).

Table 2 Scope of Allenic Alcohols[a]

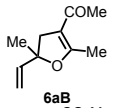
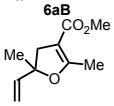
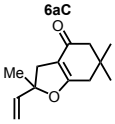
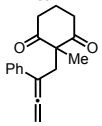
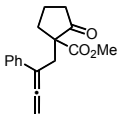
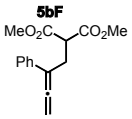
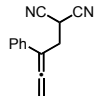
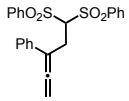
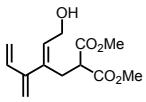
entry	substrate	product	yield (%)
1	 **1b**	 **6bA**	71
2	 **1c**	 **6cA**	47
3	 **1d**	 **6dA**	45
4	 **1e**	 **6eA**	43
5	 **1f**	 **6fA**	65
6	 **1g**	 **6gA**	74 (*dr* = 1 : 1)
7	 **1h**	 **12hA**	80 (*dr* = 1.3 : 1)
8	 **1i**	 **6iA**	0

[a] Reaction conditions: **1b–i** (1 equiv), **2A** (2 equiv), $Pd(PPh_3)_4$ (5 mol%), MeOH (0.1 M), 80 °C, 1. 5 h (entries 1–6), 2 h (entry 7), or 24 h (entry 8).

Next, the scope of pronucleophiles was also investigated (Table 3). Instead of benzoylacetonitrile (**2A**), acetylacetone (**2B**) and methyl acetoacetate (**2C**) also underwent dehydrative allenylation with **1a** and concomitant cyclisation to provide 4-substituted 2,5-dimethyl-2-vinyl-2,3-dihydrofurans **6aB** and **6aC** in fair yields (entries 1 and 2). Cyclic 1,3-diketone **2D** also participated in the tandem reaction to give tetrahydrobenzofuranone **6aD** in 43% yield (entry 3). α-substituted cyclic ketones **2E** and **2F,** as well as active methylene compounds **2G–I** bearing no ketone functionality, underwent dehydrative substitution of **1b**, which was not

followed by cyclisation to furnish 1,1-disubtituted allenes **5bE–I** in moderate to good yields (entries 4–8). In contrast, the coupling reaction between 2,3-butadienol (**1i**) and dimethyl malonate (**2G**) took place, but the major product was not allene **5iG** but triene **10iG** (entry 9).

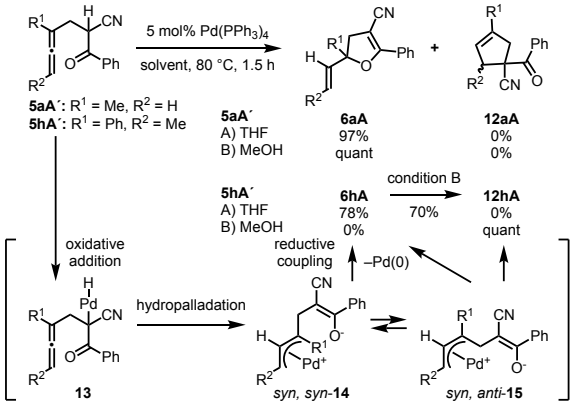
Table 3 Scope of Pronucleophiles[a]

entry	substrate	pronucleophile	product	yield (%)
1	**1a**	$CH_3COCH_2COCH_3$ (**2B**)		49
2	**1a**	$CH_3COCH_2CO_2CH_3$ (**2C**)	**6aB** 	57
3	**1a**	dimedone (**2D**)	**6aC** 	43
4	**1b**	 **2E**	**6aD** 	51
5	**1b**	 **2F**	**5bE** 	53
6	**1b**	$CH_2(CO_2Me)_2$ (**2G**)	**5bF** 	60
7	**1b**	$CH_2(CN)_2$ (**2H**)	**5bG** 	58
8	**1b**	$CH_2(SO_2Ph)_2$ (**2I**)	**5bH** 	48
9	**1i**	$CH_2(CO_2Me)_2$ (**2G**)	**5bI**  **10jG**	58

[a] Reaction conditions: **1** (1 equiv), **2B–I** (2 equiv), $Pd(PPh_3)_4$ (5 mol%), MeOH (0.1 M), 80 °C, 1. 5 h (entries 1–5, 8) or 2 h (entries 6, 7, 9).

As reported in the literature on Tsuji-Trost reaction using allylic alcohols in protic media,[7] methanol is the best solvent for dehydrative coupling reaction between allenic alcohol **1** and **2,** which activate the poor leaving ability of the hydroxyl group in **1** via hydrogen-bond (Scheme 1). In methanol, the oxidative addition of allenic alcohol **1** to palladium(0) could predominate over that of pronucleophile **2**, and the latter leads to the formation of hydroalkylation product **9**. The substituent R^1 at C-2 would help to avoid the undesired carbopalladation of **1** with *exo*-alkylidene-π-allylpalladium intermediate **3** to give dimerisation product **10**.

To reveal the requirements for the concomitant cyclisation, allenylated ketone **5aA'**, prepared by allenylation of **2A** with methanesulfonate of **1a** under basic conditions, was subjected to the reaction conditions shown in Scheme 3. The *O*-cyclisation of **5aA'** proceeded under the palladium catalysis in either methanol or THF as a solvent, whereas no reaction took place in the absence of the catalyst (see supporting information). Hence, dihydrofuran **6aA** would be formed by intramolecular hydroalkoxylation of allene **5aA'** via either π-allylpalladium intermediates **14** or **15**.[21, 22] On the contrary, the palladium-catalysed cyclisation of phenyl-substituted allene **5hA'** was dependent on the solvent with THF and methanol, leading to dihydrofuran **6hA** and cyclopentene **12hA**, respectively. In addition, the exposure of **6hA** to the catalyst in methanol caused rearrangement to **12hA**. Although it is not clear yet, the exceptional *C*-cyclisation of **5hA'** takes place only in methanol through *syn*,*anti*-π-allylpalladium **15** with properly arranged substituents (R^1=Ph, R^2≠H, R^3=H)(Table 2, entry 7 vs. 1, 3, 5, 6).[23]



Scheme 3 Pd(0)-Catalysed Cyclisation of **5aA'** and **5hA'** Leading to Dihydrofuran **6aA**·**6hA** and Cyclopentene **12hA**

In summary, we have developed a Tsuji-Trost-type reaction using allenic alcohols with pronucleophiles under neutral conditions. Both methanol solvent and a substituent at C-2 in 2,3-butadienols turned out to be essential for the dehydrative coupling reaction. Palladium complex plays a dual role in the dihydrofuran synthesis to catalyse not only allenylation of enolisable ketone pronucleophiles but also the following *O*-cyclisation. Further studies on the asymmetric variant of the reaction are underway.

This work was partly supported by JSPS KAKENHI Grant Number JP15K07849, The Research Foundation for Pharmaceutical Sciences, SUNTRY FOUNDATION for LIFE SCIENCES and Platform Project for Supporting Drug Discovery and Life Science Research (Basis for Supporting Innovative Drug Discovery and Life Science Research (BINDS)) from AMED under Grant Number JP18am0101095 and JP18am0101100.

Conflicts of interest

There are no conflicts of interest to declare.

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