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

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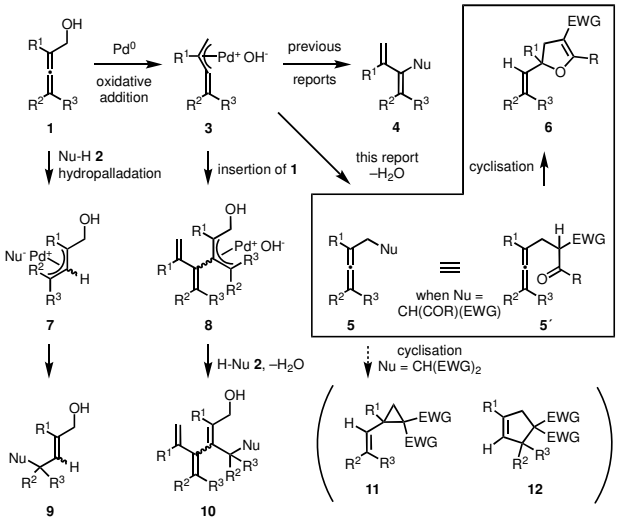
Multiple-substituted dihydrofurans were obtained by palladium-catalysed coupling reaction between 2,3-alkadienols and ketones bearing an electron-withdrawing group at the α-position. Methanol as a solvent was essential for the initial dehydrative substitution to suppress competitive hydroalkylation of 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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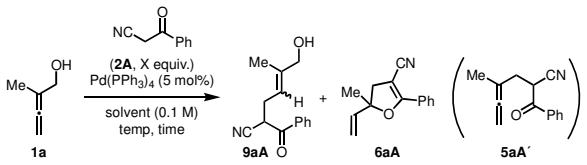
At first, 2-methyl-2,3-butadien-1-ol (**1a**, 1 equiv) was examined as an allenylating reagent for benzoylacetonitrile (**2A**, 2 equiv) on heating at 65 °C in the presence of 5 mol% tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (Scheme 2, Table 1, entries 1–5).[9] Aprotic solvents including 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**

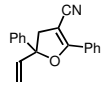
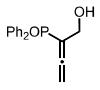
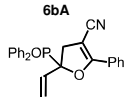
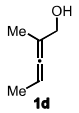
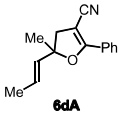
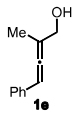
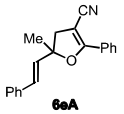
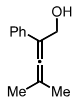
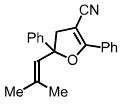
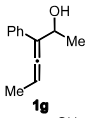
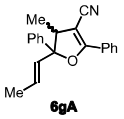
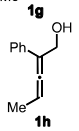
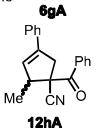
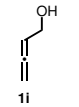
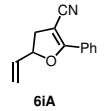
Table 1 Optimisation of Reaction Conditions for the Coupling Reaction between **1a** and **2A**

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 3-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

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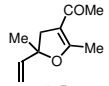
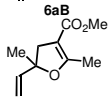
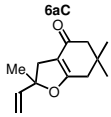
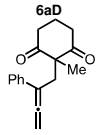
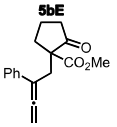
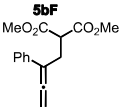
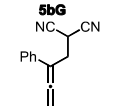
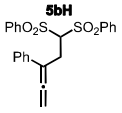
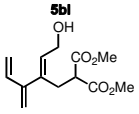
followed by cyclisation to furnish 1,1-disubtituted allenes **5bE–I** in moderate to good yields (entries 4–8). In contrast, the coupling reaction between 2,3-butadienol (**1i**) and dimethyl malonate (**2G**) took place, but the major product was not allene **5iG** but triene **10iG** (entry 9).

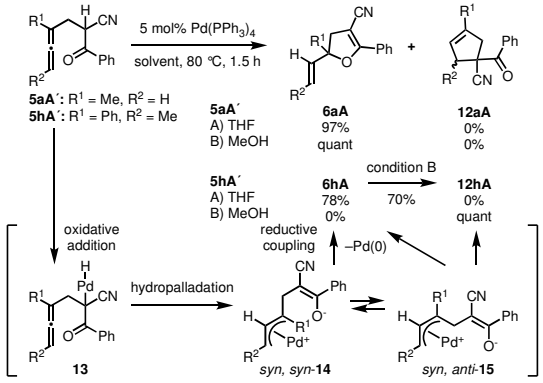
Table 3 Scope of Pronucleophiles[a]

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

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Conflicts of interest

There are no conflicts of interest to declare.

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