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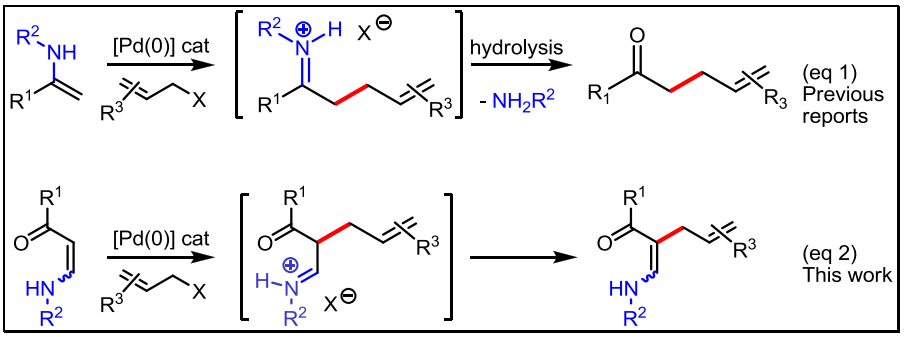
Abstract: A new palladium-catalyzed approach for the C-allylation of β-enaminones under microwave irradiation is reported. This methodology provides an easy access to a variety of α-allylated enaminones. The reaction takes place with the preservation of the enamine function, which is poised for further transformations towards nitrogen-containing heterocycles.

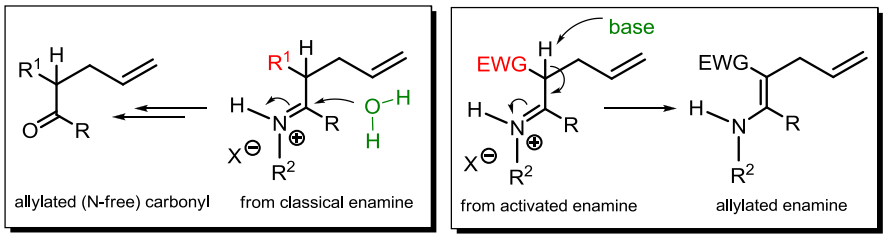
Key words: enaminone, palladium, allylation, allyl acetate, microwave irradiation.

Palladium-catalyzed transformations have gained an important place in the toolbox of synthetic chemists.[1] During the last 30 years, the Tsuji-Trost allylation arose as a versatile method for the functionalization of a wide array of scaffolds.[2,3] In particular, enamines have been amongst the first nucleophiles shown to smoothly react with a η^3-allylpalladium complex, as reported by Tsuji *et al.* in their seminal paper.[4] Indeed, such structures can be efficiently allylated at carbon, leading to the corresponding γ,δ-unsaturated carbonyls after hydrolysis of the iminium ion intermediate (Scheme 1, eq 1).[5] On the other hand, C-allylation of enamines with conservation of the nitrogen atom is a hitherto unsolved and challenging transformation,[6] of high potential interest for the synthesis of nitrogen-containing frameworks. To reach this goal, and in keeping with our ongoing interest in η^3-allylpalladium chemistry,[7] we herein report a new protocol of allylation of β-enaminones,[8] wherein the enamine function is preserved (Scheme 1, eq 2).



Scheme 1 Pd-mediated allylation of enamine derivatives

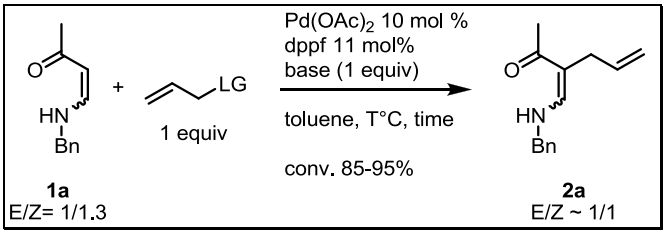
Due to their particular reactivity, which combines the nucleophilicity of enamines with the electrophilicity of enones, β-enamino carbonyl scaffolds are versatile nitrogen-containing building blocks,[9] which have been employed for transition metal-catalyzed syntheses of various heterocyclic derivatives.[10] We thought that such structures could keep the conventional carbonucleophilic reactivity toward transiently generated η^3-allylpalladium complexes, yet, derailing from the classical reactivity in the subsequent evolution of the iminium ion generated. Indeed, due to the increased acidity of the newly allylated carbon atom, elimination to regenerate the enamine function can be predicted (Scheme 2, right) instead of the classical iminium ion hydrolysis (Scheme 2, left).



Scheme 2 Concept: expected different evolution in the allylation of classical *versus* EWG-activated enamines

With this idea in mind, we undertook an investigation of the Pd-catalyzed allylation using β-enaminone **1a**, (readily prepared from 4-(trimethylsilyl)-3-butyn-2one and benzylamine and isolated in 1/1.3 *E*/*Z* ratio)[11] as the model substrate. As recent studies showed that the combination of $Pd(OAc)_2$ with a phosphino-ferrocene ligand in a molecular ratio 1/1.1 allows efficient allylations of enamines,[5c,g-h] we decided to carry out our first reaction with 10 mol% of $Pd(OAc)_2$, 11 mol% of dppf [1,1'-bis(diphenylphosphino)ferrocene] and 1 equivalent of allyl phosphate in toluene at 60 °C or 40 °C. Pleasantly, the desired allylated enaminone **2a** could be obtained in 31% or 30% NMR yields[12] after 18 h at 60 °C or 65 h at 40 °C, respectively (Table 1, entries 1-2).[13]

Table 1 Allylation of enaminone **1a** under thermal conditions[a]



Entry	LG	Base	Temp (°C)	Time (h)	Yield (%)[b]
1	$OP(O)(OEt)_2$	-	60	18	31
2	$OP(O)(OEt)_2$	-	40	65	30
3	$OP(O)(OEt)_2$	proton sponge	60	18	52[c]
4	$OP(O)(OEt)_2$	lutidine	60	18	50
5	OAc	-	40	65	33
6	OAc	proton sponge	40	65	63

[a] Unless otherwise noted, all reactions were conducted in sealed tube under argon atmosphere at 0.5 M concentration with **1a** (1 equiv), allylic partner (1 equiv), $Pd(OAc)_2$ (10 mol%), dppf (11 mol%) and base (1 equiv) in toluene.

[b] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene).

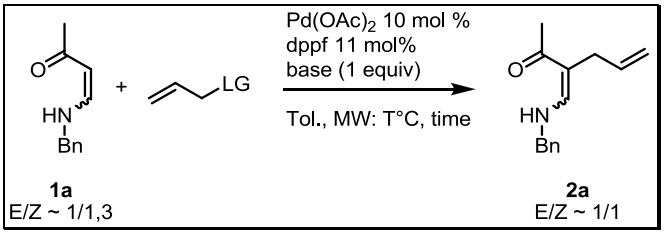
[c] The same yield was obtained in the presence of the following additives: I) 4Å molecular sieves, II) 10 equivalents H_2O.

However, we noticed some degradation, likely due to the hydrolysis of the iminium intermediate. Therefore, we hypothesized that the use of additives such as non-nucleophilic-amine bases could favor the regeneration of the enamine moiety by deprotonation at the α-position of the carbonyl (Scheme 2, right), and thus improve the efficiency of this transformation.

Indeed, adding proton sponge (1,8-bis(dimethylamino)naphthalene) or lutidine (2,6-dimethylpyridine) demonstrated a beneficial effect, and allylated enaminone **2a** was formed in 52% and 50% NMR yields, respectively, after 18 h at 60 °C (entries 3-4). The same effect was observed in the presence of 1 equivalent of proton sponge with allyl acetate as the allylic partner, in which case an improved 63% NMR yield was obtained after 65 h at 40 °C (compare entries 5 *vs* 6). Finally, experiment of entry 6, when run in the presence of 4Å molecular sieves, led to the same yield as when run without, demonstrating that traces of water do not play a role in the degradation process (entry 3).

Despite the yield improvement, the prolonged reaction time remained a drawback. Hence, in order to speed up the reaction, we decided to test microwave irradiation (Table 2).[14]

Table 2 Allylation of enaminone **1a** under microwave irradiation[a]



Entry	LG (equiv)	Base	T (°C)	Time	Yield (%)[b]
1	$OP(O)(OEt)_2$ (1)	proton sponge	100	1 h	-[c]
2	OAc (1)	proton sponge	100	1 h	68
3	**OAc (2)**	**proton sponge**	**100**	**1 h**	**72 (60)[d]**
4	OAc (2)	proton sponge	100	1 h 30	71
5	OAc (2)	proton sponge	130	1 h	41
6	OAc (2)	lutidine	100	1 h	31
7	OAc (2)		100	1 h	47
8	OAc (2)	DBU	100	1 h	42

[a] Unless otherwise noted, all reactions were conducted in sealed tube under argon atmosphere and microwave irradiation at 0.5 M concentration with **1a** (1 equiv.), allylic partner (1 or 2 equiv.), $Pd(OAc)_2$ (10 mol%), dppf (11 mol%) and base (1 equiv) in toluene.

[b] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene).

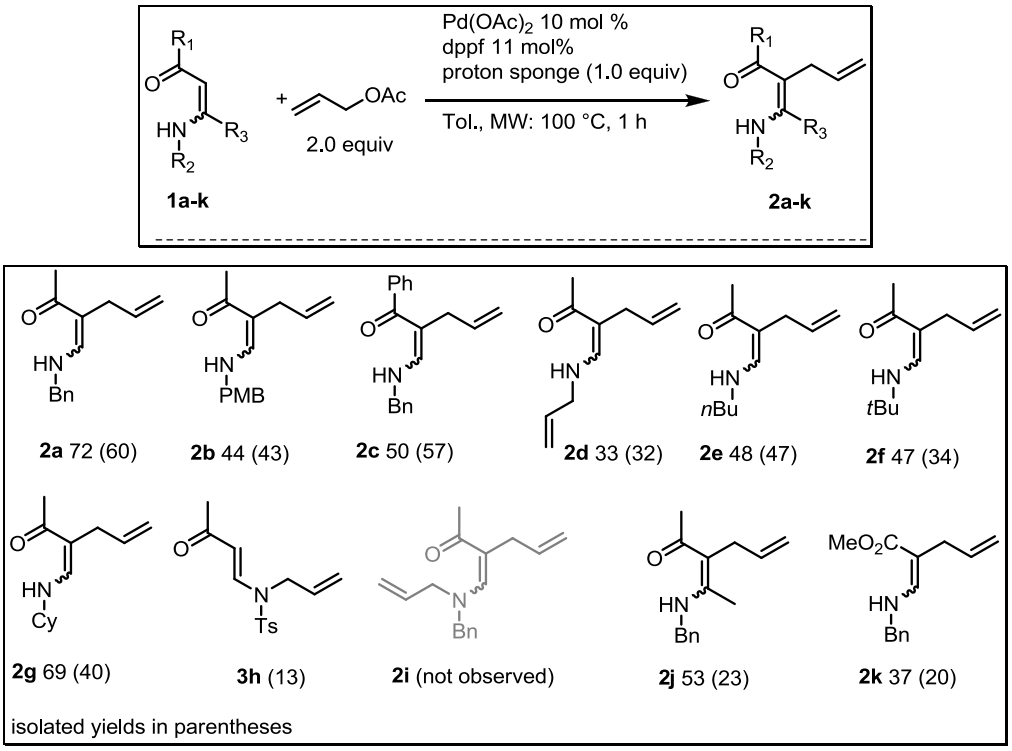
[c] Degradation.

[d] Isolated yield in parentheses.

While allyl phosphate only gave degradation after 1 h at 100 °C under microwave irradiation (Table 2, entry 1), allyl acetate afforded the desired allylated enaminone **2a** in 68% NMR yield (entry 2). An improved (72% ^{1}H-NMR) yield was obtained when 2 equivalents of allylic partner were used (entry 3). The time (entry 4), the temperature (entry 5) and the nature of the base (entries 5-8) were also screened, and the best result was obtained with 1 equivalent of proton sponge after 1 h of microwave irradiation at 100 °C. An investigation of the influence of the solvent (toluene, dioxane, DMF, EtOH, DMSO, THF) and the nature of both the Pd-catalyst and the ligand was also undertaken.[15] We found the optimal yield for allylation of enaminone **1a** (^{1}H-NMR yield 72%, isolated yield 60%) was obtained in the presence of 2 equivalents of allyl acetate with 10

mol% of $Pd(OAc)_2$, 11 mol% of dppf and 1 equivalent of proton sponge in toluene after 1 h, under microwave heating at 100 °C (entry 3).[16,17]

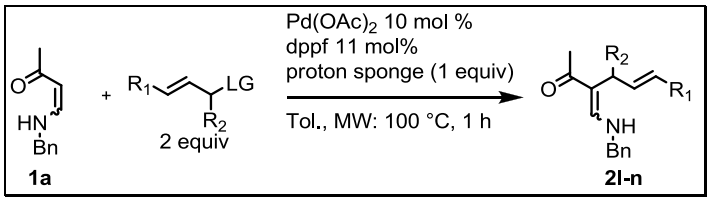
With these optimized conditions in hand, we began to explore the scope of the allylation with allyl acetate on a series of β-enaminones (Scheme 3). Benzyl (**2a-2c**), allyl (**2d**) and alkyl groups (**2e-2g**) on the secondary amine moiety were well tolerated and provided the target allylated enaminones in good to moderate yields. A less nucleophilic enaminone, such as *N*-tosyl-enaminone **1h** only gave 13% of *N*-allylated product **3h**, which proved that the electron-richness of the nitrogen atom is crucial for reaction at carbon. Moreover, the tertiary enaminone **1i**, was unreactive. The presence of a methyl substituent at the C3-position was also investigated, in which case a 23% yield (53% ^{1}H-NMR yield) was obtained for the allylated enaminone **2j**. Finally, a β-enamino ester could be used, leading to **2k** in a low yield (20%). We speculate that in this case the weakly acidic character of the α-proton favors degradation of the iminium intermediate over enamine regeneration.



Scheme 3 Scope of the allylation with allyl acetate

Next, we studied the reaction between β-enaminone **1a** and various allylic partners (Table 3). While but-3-en-2-yl acetate (entry 1) only afforded the corresponding branched allylated enaminone (**2l**) with low yield, crotyl acetate gave no reaction (entry 3). The corresponding phosphates led only to degradation (entries 2 and 4). On the other hand, the use of cinnamyl acetate, gave exclusively the linear product **2n** with 29% ^{1}H-NMR yield without trace of the branched isomer (entry 5). Nevertheless, an improved (68% ^{1}H-NMR, 42% isolated) yield was obtained when 2 equivalents of cinnamyl phosphate were used (entry 6).

Table 3 Scope of the allylation with different allylic partners



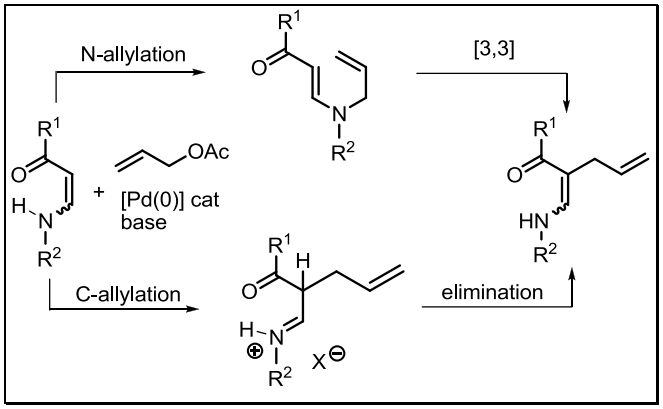
Entry	LG	R_1	R_2	Yield (%)[a]
1	OAc	H	Me	**2l**: 13 (14)[b]
2	$OP(O)(OEt)_2$	H	Me	-[c]
3	OAc	Me	H	**2m**: 0
4	$OP(O)(OEt)_2$	Me	H	-[c]
5	OAc	Ph	H	**2n**: 29
6	$OP(O)(OEt)_2$	Ph	H	**2n**: 68 (42)[b]

[a] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene).

[b] Isolated yield in parentheses.

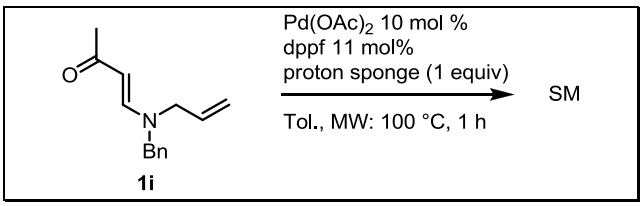
[c] Degradation.

Finally, we wished to verify that this transformation takes place *via* a direct C-allylation as opposed to a N-allylation / [3,3]-sigmatropic rearrangement (Scheme 4).



Scheme 4 Possible mechanistic paths toward the allylated product

To this purpose, tertiary enaminone **1i** was synthesized and submitted to the reaction conditions (in the absence of the allyl partner). After 1 h under microwave heating at 100 °C, only unreacted starting material (SM) was recovered (Scheme 3 and 5). Consequently, we assume that a direct C-allylation mechanism is operating, leading to an iminium intermediate, which would then undergo elimination to regenerate the enamine function (Scheme 1, eq 2; Scheme 2, right).[18]



Scheme 5 Control experiment

In summary, we have developed a Pd-catalyzed intermolecular C-allylation of β-enaminones under microwave irradiation, leading to the corresponding α-allylated substrate. The preservation of the nitrogen atom in this transformation is a new feature of high potential interest in relation to the synthesis of heterocyclic and biologically relevant targets. Extension of this methodology for the synthesis of nitrogen-containing frameworks is currently underway in our laboratory.

Acknowledgment

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(13) In general, the allylated product **2a** was obtained with an average 1/1 E/Z ratio (determined by ^{1}H NMR of the crude mixture). This ratio is variable and can change during silica gel purification.

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(15) See Supporting Information.

(16) When the reaction was carried out without either the pre-catalyst/ligand system or the pre-catalyst, only unreacted enaminone **1a** was recovered with traces of the corresponding imino-enol tautomer **1a'** (see Supporting Information).

(17) **General Procedure.** To a suspension of $Pd(OAc)_2$ (13 mg, 0.057 mmol, 10 mol %), dppf (35 mg, 0.063 mmol, 11 mol %) and proton sponge (0.12 g, 0.57 mmol, 1 equiv) in THF (0.5 mL) in a Schlenk flask equipped with a septum, under argon atmosphere, was added allyl acetate (0.12 mL, 1.14 mmol, 2.0 equiv). After 5 minutes stirring, a solution of enaminone **1a** (100 mg, 0.57 mmol, 1 equiv) in THF (0.5 mL) was added, the flask was sealed and the mixture was stirred during 1 hour under microwave irradiation at 100 °C. The resulting crude was filtered on a plug of silica gel. The solvent was removed and the mixture was purified by flash chromatography on silica gel (ethyl acetate/cyclohexane: 20/80) to afford 86 mg of the allylated enaminone **2a** as a mixture of *Z* and *E* isomers.

Analytical data for 2a. Yield= 60%; yellow oil; ratio (*Z*/*E*) = 1.7/1 (analysis of the crude ^{1}H NMR showed a *Z*/*E* ratio = 1/1); IR (film) 3272, 3030, 2920, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 10.24 (brs, 1H, N$\underline{H}_{(Z)}$), 7.42-7.25 (m, 11H, =C$\underline{H}$NH$_{(E)}$+ C$\underline{H}_{Ar(Z+E)}$), 6.66 (d, *J* = 12.4 Hz, 1H, =C$\underline{H}$NH$_{(Z)}$), 5.94-5.71 (m, 2H, $\underline{H}$C=CH$_{2(Z+E)}$), 5.10-4.99 (m, 4H, HC=C$\underline{H}_{2(Z+E)}$), 4.43 (d, *J* = 5.9 Hz, 2H, C$\underline{H}_2$Ph$_{(E)}$), 4.39 (d, *J* = 6.1 Hz, 2H, C$\underline{H}_2$Ph$_{(Z)}$), 3.12 (dt, *J* = 6.0, 1.6 Hz, 2H, C$\underline{H}_2$CH=CH$_{2(E)}$), 2.94 (dt, *J* = 5.8, 1.6 Hz, 2H, C$\underline{H}_2$CH=CH$_{2(Z)}$), 2.22 (s, 3H, C$\underline{H}_3$CO$_{(E)}$), 2.13 (s, 3H, C$\underline{H}_3$CO$_{(Z)}$); ^{13}C NMR (75 MHz, $CDCl_3$): 198.2, 194.2, 153.0, 149.5, 138.6, 138.5, 138.4, 136.0, 128.9, 128.8, 127.8, 127.6, 127.0, 126.9, 114.8, 114.6, 102.8, 52.5, 52.2, 35.6, 28.0, 27.6, 24.4; HRMS *m/z* calcd. for $C_{14}H_{17}NONa$ $(M+Na)^+$: 238.1208; found: 238.1204.

(18) Formation of the linear product, when using cinnamyl acetate, is a further proof of the direct C-allylation mechanism.