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A General Palladium-Catalyzed Carbonylative Sonogashira Coupling of Aryl Triflates

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Alkynones represent an interesting structural motif found in various bioactive molecules.[1] More importantly, they constitute key intermediates in the synthesis of natural products[2] and, especially, heterocycles.[3] Traditionally, alkynones have been synthesized by cross-coupling reactions of carboxylic acid chlorides and terminal alkynes.[4] However, the stability and functional group tolerance of the respective acid chlorides has limited the applications of this methodology. Since the first report by Tanaka in 1981,[5a] palladium-catalyzed carbonylative Sonogashira reactions of aryl halides have become an interesting alternative for the synthesis of alkynones and notable improvements have been achieved.[5,6] For example, Mori and co-workers reported carbonylation reactions at room temperature and with an ambient pressure of CO.[5c] Xia[5b] and Ryu[5j] developed recyclable catalyst systems based on heterogenization with Fe_3O_4 particles or in the presence of ionic liquids. Moreover, the latter group demonstrated the synthesis of alkynones from iodoalkenes by applying a combination of a palladium catalyst and UV irradiation.[5m] Recently, in addition to palladium-based catalysts, copper has been described as an active metal for carbonylative Sonogashira reactions by Bhanage and co-workers.[5n]

Unfortunately, most of these synthetic developments were only demonstrated with aryl iodides or iodoalkenes as the substrates. Clearly, this has significantly limited the substrate scope for this interesting methodology. Considering the advantages of (hetero)aryl bromides compared with those of the corresponding iodides, we very recently developed a general procedure for carbonylative Sonogashira reactions of this class of substrates.[7] Key to its success was the application of a palladium/$BuPAd_2$ (Ad = adamantyl) catalyst system[8] in the presence of potassium carbonate as a base. Based on this work, we became interested in further expanding the substrate scope of this methodology to aryl sulfonates. To the best of our knowledge, carbonylative Sonogashira reactions utilizing aryl sulfonates as the starting material have not been described before.

In addition to aryl halides, hydroxylated arenes are easily available and frequently found in pharmaceuticals, agrochemicals, and polymers, as well as biologically active natural compounds.[9] It is known that phenols can be transformed into their corresponding aryl triflates, which contain a highly reactive leaving group. This principle has often been used for the preparation of versatile intermediates in modern organic synthesis, particularly in palladium-catalyzed coupling reactions.[10]

Recently, some of us developed reductive carbonylation and carbonylative vinylation reactions of aryl/vinyl triflates.[11] Herein, in a continuation of this and other palladium-catalyzed carbonylation reactions,[12] we wish to report a general palladium-catalyzed synthesis of alkynones utilizing aryl and alkenyl triflates.

Initially, we investigated the carbonylative Sonogashira reaction of phenyl triflate and phenyl acetylene in the presence of $[\{Pd(cinnamyl)Cl\}_2]$ (1 mol %) and different ligands (2 mol %) at 10 bar carbon monoxide with NEt_3 as a base. Selected results are shown in Table 1. Whereas monodentate ligands did not give an appreciable amount of the product, several bidentate phosphines converted phenyl triflate into 1,3-diphenylpropynone in moderate to good yield. No product was detected in the presence of DPPM (1,1-bis(diphenylphosphino)methane), DPPE (1,2-bis(diphenylphosphino)ethane), DPPP (1,3-bis(diphenylphosphino)propane), or DPPPe (1,5-bis(diphenylphosphino)pentane) as the ligand (Table 1, entries 1–3 and 5). Applying ligands with theoreti-

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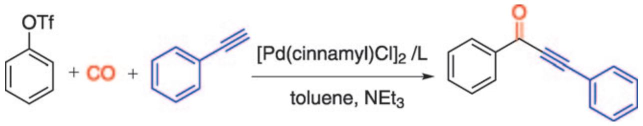
Table 1. The carbonylation of phenyl triflate with phenyl acetylene: the testing of different ligands.[a]



Entry	Ligand	Bite Angle	Yield [%][b]
1	DPPM	72	0
2	DPPE	78	0
3	DPPP	86	0
4	DPPB	98	28
5	DPPPe	–	0
6	DPPF	96	48
7	D*t*BPF	96	49
8	BINAP	92	19
9	DIOP	98	35
10	DPEphos	102	46
11	Xantphos	111	71
12	DBFphos	132	0

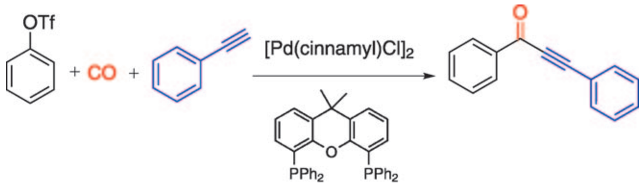
[a] Phenyl triflate (1.0 mmol), phenyl acetylene (1.2 mmol), CO (10 bar), $[\{Pd(cinnamyl)Cl\}_2]$ (1 mol %), ligand (2 mol %), toluene (2 mL), NEt_3 (2 mmol), 100 °C, 20 h. [b] Yield was determined by GC with hexadecane as the internal standard.

cal bite angles[13] between 96 and 98°, such as DPPB (1,4-bis(diphenylphosphino)butane), DPPF (1,1′-bis(diphenylphosphino)ferrocene), D*t*BPF (1,1′-bis(di-*tert*-butylphosphino)ferrocene), DIOP ((+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) or DPEphos ((oxydi-2,1-phenylene)bis(diphenylphosphino)) led to 1,3-diphenylpropynone in 28–49 % yield (Table 1, entries 4, 6, 7, 9, and 10). Best results were obtained with Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) as the ligand (Table 1, entry 11).[14] Notably, the product of the competing Sonogashira coupling (1,2-diphenylethyne) is not formed under these conditions. However, no reaction occurred with DBFphos (4,6-bis(diphenylphosphino)dibenzofuran), which has the largest bite angle among the ligands tested here (Table 1, entry 12).

Next, we investigated the influence of base, pressure, solvent, and temperature on the reaction (Table 2). The use of other common organic and inorganic bases resulted in lower yields (Table 2, entries 1–5). Variation of the solvent showed that heptane and NMP (*N*-methylpyrrolidone) are not suitable solvents (Table 2, entries 6 and 9), whereas DMF and dioxane gave product yields comparable to toluene (Table 1, entry 11; Table 2, entries 7 and 8). Increasing the temperature to 110 °C led to an 83 % yield, but further increases in the temperature resulted in the decomposition of phenyl triflate (Table 2, entries 10 and 11). The desired coupling reaction also took place at 5 bar CO pressure, although the yield of 1,3-diphenylpropynone was somewhat decreased to 63 % (Table 2, entry 12).

Once the optimized conditions were identified, we investigated the general applicability of this methodology (Table 3). To our delight, the new palladium-catalyzed carbonylative Sonogashira reaction took place in the presence of both electron-donating and electron-withdrawing sub-

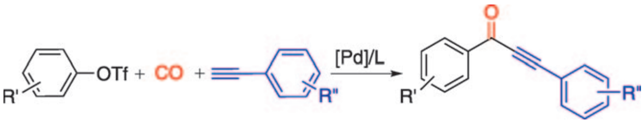
Table 2. The carbonylation of phenyl triflate with phenyl acetylene: the variation of the reaction conditions.[a]



Entry	Solvent	Base	Yield [%][b]
1	toluene	DBACO	0
2	toluene	TMEDA	20
3	toluene	DiPEA	37
4	toluene	K_2CO_3	13
5	toluene	K_3PO_4	0
6	heptane	NEt_3	9
7	dioxane	NEt_3	48
8	DMF	NEt_3	67
9	NMP	NEt_3	11
10	toluene	NEt_3	83[c]
11	toluene	NEt_3	0[d]
12	toluene	NEt_3	63[c,e]

[a] Phenyl triflate (1.0 mmol), phenyl acetylene (1.2 mmol), CO (10 bar), $[\{Pd(cinnamyl)Cl\}_2]$ (1 mol %), Xantphos (2 mol %), solvent (2 mL), base (2 mmol), 100 °C, 20 h. DBACO = 1,4-diazabicyclo[2.2.2]octane; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine; DiPEA = *N*,*N*-diisopropylethylamine. [b] Yield was determined by GC with hexadecane as the internal standard. [c] 110 °C. [d] 120 °C. [e] CO (5 bar).

Table 3. The palladium-catalyzed carbonylative Sonogashira reaction of aryl and alkenyl triflates.[a]



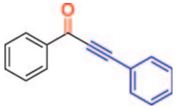
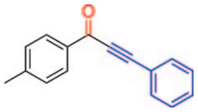
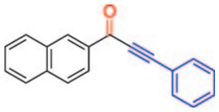
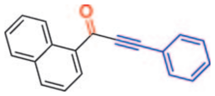
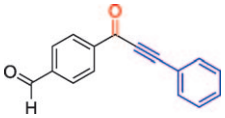
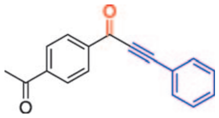
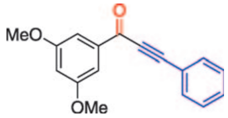
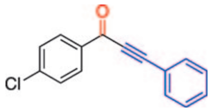
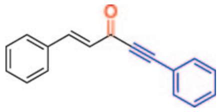
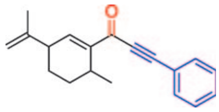
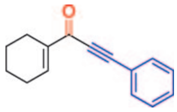
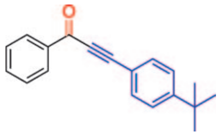
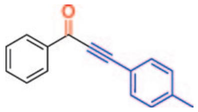
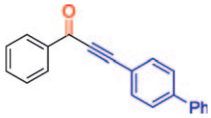
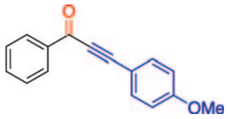
Entry	Product		Yield [%][b]
1		**3a**	81
2		**3b**	80
3		**3c**	78
4		**3d**	74
5		**3e**	50
6		**3f**	72

Table 3. (Continued)

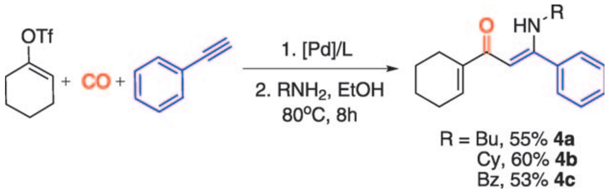
Entry	Product		Yield [%][b]
7		**3g**	68
8		**3h**	64
9		**3i**	72
10		**3j**	60
11		**3k**	80
12		**3l**	76
13		**3m**	79
14		**3n**	69
15		**3o**	83

[a] Aryl triflate (1.0 mmol), alkyne (1.2 mmol), CO (10 bar), [{Pd(cinnamyl)Cl}$_2$] (1 mol %), L = Xantphos (2 mol %), toluene (2 mL), NEt_3 (2 mmol), 110 °C, 20 h. [b] Isolated yield.

stituents in moderate to good isolated yields (50–81 %; Table 3, entries 1–8). At this point, it should be noted that carbonylative Sonogashira reactions of aryl bromides containing electron-withdrawing substituents or sterically hindered aryl substrates are still challenging,[7] However, improved yields can be obtained with the current system (50–72 %).

The straightforward preparation of vinyl triflates from aldehydes or ketones[15] offers an attractive possibility for the synthesis of 1-vinyl-3-arylproynones. Indeed, three different vinyl triflates reacted well under our conditions and gave the corresponding products in 60–80 % yield (Table 3, entries 9–11).[15] Furthermore, different aryl acetylenes were tested and the corresponding 1,3-diarylalkynones were isolated in good yields (Table 3, entries 12–15). However, applying more reactive alkynes with *p*-CN, *p*-NO_2, *p*-CHO, *p*-CH_3CO substituents mainly resulted in the non-carbonylative Sonogashira reaction.

Müller and co-workers,[16] as well as other groups,[17] have elegantly demonstrated the potential of alkynones in various cascade sequences for organic synthesis. Also, under our conditions further modification of the alkynones is possible without purification. As shown in Scheme 1, three different enaminones have been synthesized in a one pot-sequence starting from cyclohexenyl triflate and phenyl acetylene. Following the carbonylation reaction, aliphatic amines, dissolved in ethanol, were added to the reaction mixture. After heating at 80 °C, the corresponding enaminones were obtained in 53–60 % isolated yield.



Scheme 1. The cascade sequence for the synthesis of enaminones.

In conclusion, the first general, chemoselective protocol for the carbonylative Sonogashira coupling reaction of aryl triflates has been developed. Both electron-rich and electron-poor aryl triflates are smoothly coupled with aryl acetylenes under low pressures of CO. The use of easily available vinyl triflates allows for an interesting extension of the substrate scope. The obtained products represent useful building blocks for the synthesis of biologically active compounds. As an example, the straightforward one-pot preparation of 1-cyclohexenyl-3-phenylenaminones was demonstrated.

Experimental Section

General procedure for carbonylative Sonogashira reactions: [{Pd(cinnamyl)Cl}$_2$] (1 mol %) and Xantphos (2 mol %) were transferred into a vial (4 mL reaction volume) sealed with a septum, a small cannula and a stirring bar. After the vial was purged with argon, aryl triflate (1.0 mmol), phenyl acetylene (1.2 mmol), toluene (2 mL), and NEt_3 (2 mmol) were injected into the vial by syringe. Then, the vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments, under an argon atmosphere. After flushing the autoclave three times with CO, the pressure was adjusted to 10 bar and the reaction was performed for 20 h at 110 °C. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Water (6 mL) was added to the reaction mixture and the solution was extracted with ethyl acetate (3–5 × 2–3 mL). The extracts were evaporated in the presence of a small amount of silica gel and the crude product was purified by column chromatography on silica gel by using *n*-heptane and *n*-heptane/AcOEt (50:1) as the eluent. The product was obtained as a yellow oil.

General procedure for enaminone synthesis: After the carbonylative Sonogashira reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Ethanol (1 mL) and amine (1.5 equiv) were added to the reaction mixture, the vial was closed again and heated at 80 °C for 8 h. After cooling it to room temperature, water (6 mL) was added to the reaction mixture and the solution was extracted with ethyl acetate (3–5 × 2–3 mL). The extracts were evaporated in the presence of a small amount of silica gel and the crude product was purified by column chromatography on silica gel by using *n*-heptane and *n*-heptane/AcOEt (10:1) as the eluent.

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Keywords: alkynones · aryl triflates · carbonylation · palladium · Sonogashira reaction

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