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Palladium-Catalyzed Decarboxylative *sp*-*sp*^{2} Cross-Coupling Reactions of Aryl and Vinyl Halides and Triflates with α,β-Ynoic Acids using Silver Oxide

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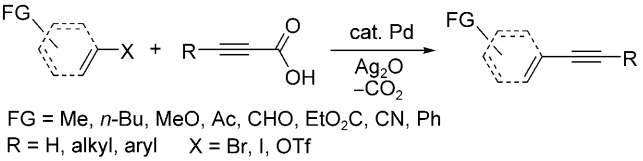
Abstract: Palladium-catalyzed decarboxylative *sp*-*sp*^{2} cross-coupling reactions of aryl and vinyl halides and triflates with α,β-ynoic acids using silver oxide have been developed. A variety of α,β-ynoic acids were readily decarboxylated in the presence of silver oxide and then, generated *in situ*, silver acetylides were coupled with electrophiles in the presence of a palladium(0) catalyst under neutral conditions, producing either symmetrical or unsymmetrical diarylacetylenes, arylalkylacetylenes and arylvinylacetylenes in good to excellent yields.

Keywords: cross-coupling reaction; decarboxylation; silver salts; Sonogashira reaction

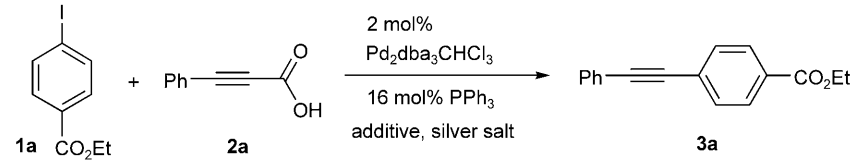
Transition metal-catalyzed cross-coupling reactions represent an extremely versatile tool in organic synthesis.[1] In particular, the Sonogashira reaction of terminal alkynes with aryl and alkenyl (pseudo)halides is the most straightforward method for the preparation of acetylene derivatives, which are highly useful building blocks in organic synthesis.[2] The Sonogashira reactions are most frequently carried out by palladium catalysts together with a copper co-catalyst using an amine as solvent. Although alkynes are generally obtained in good to excellent yields, diynes are frequently produced as contaminants owing to copper-catalyzed Glaser-type oxidative coupling. Sometimes, amines such as piperidine, diethylamine and triethylamine that are required in most Sonogashira reactions add to the environmental burden.[3] Therefore, several modifications of the original Sonogashira protocol have been revealed, such as new homo- and heterogeneous catalysts,[4] bimetallic systems,[5] copper-free,[6] amine-free,[3,7] aqueous media[8] or solvent-free reaction conditions.[9] Also, the development of new surrogates replacing the terminal alkyne has been examined.[10] Recently, transition metal-catalyzed decarboxylative cross-coupling reactions continue to attract a great deal of attention because they allow the use of readily available carboxylic acids or esters under neutral conditions.[11] Although the synthetic method for diarylacetylenes with propiolic acid was reported, this method has some limitations due to the excessive use (2–6 equiv.) of tetrabutylammonium fluoride (TBAF) (1.0 M solution in THF), low functional group tolerance, long reaction time (12 h at 25 °C and then 12 h at 90 °C) in *N*-methylpyrrolidine (NMP).[12] Along with this line, efficient and mild decarboxylative Sonogashira reactions with a variety of α,β-ynoic acids are of high interesting. Herein, we report the efficient Pd-catalyzed decarboxylative *sp*-*sp*^{2} cross-coupling reactions of aryl and vinyl halides and triflates with α,β-ynoic acids with silver oxide under neutral conditions (Scheme 1).

Our initial study focused on Pd-catalyzed cross-coupling reactions of ethyl 4-iodobenzoate (**1a**) with phenylpropiolic acid (**2a**) in the presence of a variety of silver salts (Table 1). The use of $AgNO_3$, Ag_2CO_3, AgCl and AgBr did not produce the desired product even at 140 °C in DMSO (entries 1–4). The decarboxylative coupling product **3a** was not obtained in NMP and DMF despite liberation of carbon dioxide from the pre-mixture of **2a** and Ag_2O (entries 6 and 7).



Scheme 1. Decarboxylative cross-coupling reaction mediated by silver oxide.

Table 1. Opimization of decarboxylative coupling reaction.



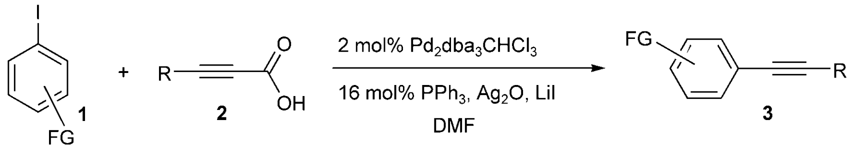
Entry	Silver salt	Additive (equiv.)	Solvent	T [°C]	t [h]	Yield [%]
1	$AgNO_3$		DMSO	140	3	0
2	Ag_2CO_3		DMSO	140	3	0
3	AgCl		DMSO	140	12	0
4	AgBr		DMSO	140	12	0
5	Ag_2O		DMSO	140	3	30 (50)[a]
6	Ag_2O		NMP	140	12	0 (38)[a](42)[b]
7	Ag_2O		DMF	100	4	0 (44)[a] (40)[b]
8	Ag_2O		THF	70	4	20 (26)[a] (32)[b]
9	Ag_2O	LiCl (3)	DMSO	140	2	66
10	Ag_2O	LiBr (3)	DMSO	140	2	72
11	Ag_2O	LiI (3)	DMSO	140	2	82
12	Ag_2O	LiI (3)	DMF	100	1	92
13	Ag_2O	LiI (3)	THF	70	8	78 (10)[b]
14	Ag_2O	LiI (1)	DMF	100	2	26 (48)[a]
15	Ag_2O	LiI (3)	DMF	100	2	38[c]

[a] 1,4-Diphenylbutadiyne.
[b] **1a**.
[c] 0.5 equiv. of Ag_2O was used.

However, the use of DMSO and THF produced **3a** in 30% and 20% yields, respectively, together with 1,4-diphenylbutadiyne (entries 5 and 8). With this result in hand, we examined a variety of additives (LiCl, LiBr and LiI) and solvents (DMF, THF, DMSO and NMP) in the presence of Ag_2O. Of the catalytic systems examined, the best results were obtained with 2 mol% $Pd_2dba_3CHCl_3$ and 16 mol% Ph_3P in the presence of 1 equivalent of Ag_2O and 3 equivalents of LiI in DMF at 100 °C for 1 h, affording selectively **3a** in 92% yield without contamination by homo-coupling products (entry 12). Under the optimum reaction conditions, the use of a catalytic amount of Ag_2O (0.5 equiv.) was not effective for the reaction of **1a** with **2a** (entry 15). Although the role of LiI is not completely established at present, the use of LiI as an additive is essential for satisfactory results.

To demonstrate the efficiency and scope of the present method, we applied these catalytic decarboxylative conditions to the reaction of a variety of electrophilic coupling partners with α,β-ynoic acids (Table 2). Reaction of 1-iodonaphthalene (**1b**) with **2a** gave 1-naphthylphenylacetylene (**3b**) in 64% yield in DMF at 100 °C for 90 min (entry 1). 2-Iodobiphenyl was treated with **2a** in the presence of 2 equivalents of Ag_2O to produce alkyne **3c** in 82% yield (entry 2). For a vast number of aryl iodides, the presence of various substituents, such as methyl, *n*-butyl, methoxy, aldehyde, ketone and ethoxycarbonyl on the aromatic ring, showed little effect on the efficiency of the reactions (entries 3–12). Under the optimum reaction conditions, 3-iodotoluene and 4-*n*-butyliodobenzene gave the corresponding alkynes **3d** and **3e** in 83% and 70% yields, respectively (entries 3 and 4). In the case of methoxy groups, the desired acetylenes were obtained in good yields (entries 5 and 6). It is noted that **1h**, **1i** and **1j** possessing a nucleophile-labile formyl or acetyl group provided **3h**, **3i** and **3j** in good to excellent

Table 2. Pd-catalyzed decarboxylative cross-coupling reactions of aryl iodides with α,β-ynoic acids.[a]

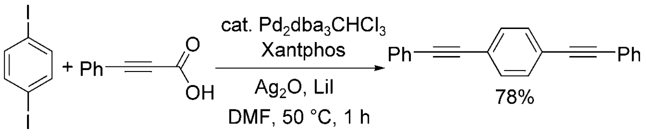


Entry	Aryl iodide		R		T [°C]	t [h]	Alkyne Yield [%]	
1	1-Naph-I	**1b**	Ph	**2a**	100	1.5	**3b**	64
2	2-Ph-C_6H_4-I	**1c**	Ph		100	1	**3c**	82[b]
3	3-Me-C_6H_4-I	**1d**	Ph		100	0.5	**3d**	83
4	4-*n*-Bu-C_6H_4-I	**1e**	Ph		70	2	**3e**	70[c]
5	3-MeO-C_6H_4-I	**1f**	Ph		70	2	**3f**	86
6	4-MeO-C_6H_4-I	**1g**	Ph		50	1.5	**3g**	74[b]
7	4-OHC-C_6H_4-I	**1h**	Ph		70	1	**3h**	85[c]
8	2-Ac-C_6H_4-I	**1i**	Ph		70	1	**3i**	84
9	4-Ac-C_6H_4-I	**1j**	Ph		70	1	**3j**	94
10	2-EtO_2C-C_6H_4-I	**1k**	Ph		70	6	**3k**	72[d]
11	3-EtO_2C-C_6H_4-I	**1l**	Ph		70	2	**3l**	97
12	4-EtO_2C-C_6H_4-I	**1a**	Ph		100	1	**3a**	92
13	2-Py-I	**1m**	Ph		100	1	**3m**	96
14	2-Thieny-I	**1n**	Ph		70	1	**3n**	77[c]
15	3-MeO-C_6H_4-I	**1f**	3-Me-C_6H_4	**2b**	100	1	**3o**	70
16	4-EtO_2C-C_6H_4-I	**1a**	3-MeO-C_6H_4	**2c**	100	3	**3p**	72
17	4-EtO_2C-C_6H_4-I	**1a**	3-Me-C_6H_4	**2b**	100	2	**3q**	94
18	3-EtO_2C-C_6H_4-I	**1l**	4-MeO-C_6H_4	**2d**	100	1	**3r**	64
19	3-Me-C_6H_4-I	**1d**	*n*-Pent	**2e**	70	3	**3s**	78
20	4-Ac-C_6H_4-I	**1j**	*n*-Pent		100	2	**3t**	83
21	4-EtO_2C-C_6H_4-I	**1a**	*n*-Pent		70	2.5	**3u**	73
22	2-Py-I	**1m**	*n*-Pent		100	2	**3v**	70

[a] 1 equiv. of Ag_2O, 1 equiv. of **2** and 3 equiv. of LiI were used.
[b] 2 equiv. of Ag_2O, 2 equiv. of phenylpropiolic acid and 6 equiv. of LiI were used.
[c] 8 mol% Xantphos were used as a ligand.
[d] 1.5 equiv. of Ag_2O and phenylpropiolic acid were used.

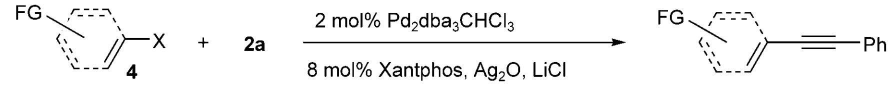
yields (entries 7–9). Although ethyl 3- and 4-iodobenzoate (**1l** and **1a**) gave the desired alkynes **3l** and **3a** in 97% and 92% yields, respectively (entries 11 and 12), ethyl 2-iodobenzoate (**1k**) afforded **3k** in 72% yield presumably due to steric hindrance (entry 10). This result is compatible with the decrease (10% lowering) of yield of 2-iodoacetophenone compared to that of 4-iodoacetophenone (entries 8 and 9). 2-Iodopyridine (**1m**) and 2-iodothiophene (**1n**) turned out to be compatible with the employed reaction conditions, producing **3m** and **3n** in 96% and 77% yields, respectively (entries 13 and 14).

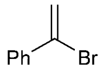
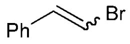
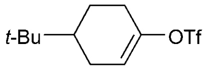
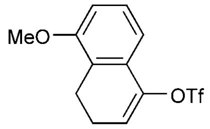
Next, a variety of α,β-ynoic acids (**2b**, **2c** and **2d**) as coupling partners were examined (entries 15–18). Combination of electron-withdrawing and donating group on the aromatic ring of aryl iodide and arylpropiolic acid showed little effect on efficiency of the reactions. However, the reaction of ethyl 3-iodobenzoate (**1l**) with 4-methoxyphenylpropiolic acid (**2d**) afforded the acetylene **3r** in 64% yield (entry 18). Finally, 2-octynoic acid (**2e**) was applied to the silver-mediated decarboxylative cross-coupling reactions (entries 19–22). Subjecting **1d** to **2e** and Ag$_2$O in the presence of LiI in DMF provided **3s** in 78% yield (entry 19). We were pleased to obtain 4-(1-heptynyl)-acetophenone (**3t**) and ethyl 4-(1-heptynyl)benzoate (**3u**) in 83% and 73% yields, respectively, from the reactions of aryl iodides **1j** and **1a** with **2e** liberating carbon dioxide (entries 20 and 21). The reaction also worked equally well with 2-iodopyridine (**1m**) and **2e**, producing 2-(2-pentylethynyl)pyridiene (**3v**) in 70% yield (entry 22). Exposure of 1,4-diiodobenzene to 2 equivalents of phenylpropiolic acid and Ag$_2$O in the presence of 2 mol% of Pd$_2$dba$_3$·CHCl$_3$, 8 mol% of Xantphos and 6 equivalents of LiI in DMF at 50 °C for 1 h led to the formation of 1,4-di(phenylethynyl)-benzene in 78% yield through double decarboxylative cross-coupling reactions.



With these results in hand, the Pd-catalyzed decarboxylative cross-coupling reactions of aryl and vinyl bromides and triflates were examined (Table 3). Treatment of 3-bromoanisole (**4a**) with **2a** and silver

Table 3. Pd-catalyzed decarboxylative cross-coupling reactions of aryl and vinyl bromides and triflates.[a]



Entry	4		T [°C]	t [h]	Yield [%]	
1	3-MeO-C$_6$H$_4$-Br	**4a**	70	3	**3f**	83
2	2-OHC-C$_6$H$_4$-Br	**4b**	70	2	**5a**	97
3	3-Ac-C$_6$H$_4$-Br	**4c**	70	2	**5b**	92
4	4-EtO$_2$C-C$_6$H$_4$-Br	**4d**	70	2	**3a**	96 (73)[b]
5	4-NC-C$_6$H$_4$-Br	**4e**	80	3	**5c**	86[c]
6	2-Ac-C$_4$H$_2$S-Br	**4f**	80	3	**5d**	76
7		**4g**	80	2	**5e**	89
8[d]		**4h**	80	2	**5f**	92[e]
9	2-EtO$_2$C-C$_6$H$_4$-OTf	**4i**	70	2	**3k**	72[c]
10		**4j**	70	2	**5g**	86
11		**4k**	70	2	**5h**	92

[a] 1.2 equiv. of Ag$_2$O, 1,2 equiv. of **2a** and 3 equiv. of LiCl were used in DMF.

[b] 1 equiv. of Ag$_2$O, 1 equiv. of **2a** and 3 equiv. of LiCl were used.

[c] 3 equiv. of LiI were used.

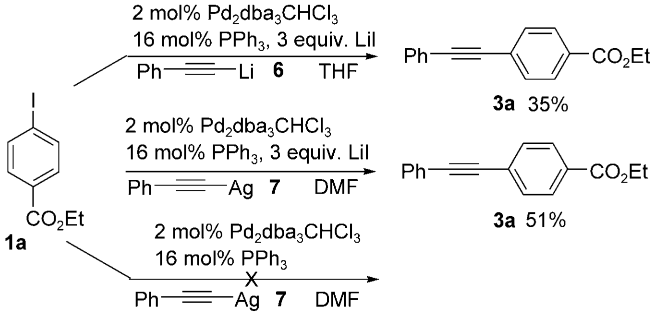
[d] Diastereomeric ratio of α-bromostyrene = 1:5.

[e] *trans.*

oxide in the presence of 2 mol% of $Pd_2dba_3 \cdot CHCl_3$/16 mol% Ph_3P and LiI produced **3f** in 32% yield. Therefore, we screened again ligands [Ph_3P, $(4\text{-}CF_3\text{-}C_6H_4)_3P$, DPEphos, Xantphos, $(t\text{-}Bu)_3P$, (biphenyl)PCy_2, dppf and IPrHCl] and additives [LiX, NaX and KX (X = F, Cl, Br and I)], obtaining the result that the use of Xantphos and LiCl increased the yield (73%) of **5d** (entry 4). In addition, the use of 1.2 equivalents of silver oxide afforded **3a** in 96% yield. 2-Bromobenzaldehyde (**4b**) and 3-bromoacetophonone (**4c**) turned out to be compatible with the employed reaction conditions, producing **5a** and **5b** in 97% and 92% yields, respectively (entries 2 and 3). In the case of vinyl bromide, the desired products were obtained in good to excellent yields (entries 7 and 8). Reaction of aryl triflate **4i** with **2a** provided phenyl(2-ethoxycarbonylphenyl)acetylene (**3k**) in 72% yield under the optimum reaction conditions (entry 9). The present method worked equally well with vinyl triflates **4j** and **4k**, producing enynes **5g** and **5h** in 86% and 92% yields, respectively (entries 10 and 11).

The Pd-catalyzed cross-coupling reaction of **1a** with lithium phenylacetylide (**6**)[13] in the presence of LiI gave **3a** in 35% yield, while silver phenylacetylide (**7**)[14] derived from phenylpropiolic acid and silver nitrate afforded **3a** in 51% yield. In addition, the use of lithium iodide is critical for a successful reaction (Scheme 2). On the basis of these results, although the mechanism of the decarboxylative cross-coupling reaction is not clear at the moment, we assume that silver phenylacetylide (**7**) might be strongly involved to transmetallation step rather than lithium phenylacetylide (**6**). The elucidation of the detailed reaction mechanism must wait further study.

In summary, efficient Pd-catalyzed decarboxylative *sp-sp*^{2} cross-coupling reactions of aryl and vinyl halides and triflates with α,β-ynoic acids using silver oxide have been developed. A variety of α,β-ynoic acids were readily decarboxylated in the presence of silver oxide and then, the resulting generated *in situ* silver acetylides were coupled with electrophiles under neutral conditions, producing either symmetrical or unsymmetrical diarylalkynes, arylalkylalkynes and arylvinylalkynes in good to excellent yields.



Scheme 2.

Experimental Section

Typical Procedure (Table 2, entry 12)

Phenylpropiolic acid (73.1 mg, 0.5 mmol) and silver oxide (115.8 mg, 0.5 mmol) in DMF (1 mL) were stirred at room temperature for 5 min liberating CO_2. The reaction mixture was added to a solution of $Pd_2dba_3 \cdot CHCl_3$ (10.3 mg, 2 mol%), PPh_3 (21.0 mg, 16 mol%), LiI (200.7 mg, 1.5 mmol) and ethyl 4-iodobenzoate (138.0 mg, 0.5 mmol) in DMF (1.5 mL). The reaction mixture was stirred at 100 °C for 1 h and then, was quenched with water. The aqueous layer was extracted with ether and washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate:hexane = 1:50) to give ethyl 4-phenylethynylbenzoate (**3a**); yield: 115.4 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.56–7.53 (m, 2H), 7.36 (t, $J = 3.2$ Hz, 3H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.40 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.1$, 131.7, 131.4, 129.8, 129.4, 128.7, 128.4, 127.8, 122.7, 92.2, 88.6, 61.1, 14.3; IR (pellet): $\nu = 2987$, 2213, 1707, 1605, 1275, 1105.0, 860, 757 cm^{-1}; mp 78–79 °C; HR-MS $m/z = 250.0991$, calcd. for $C_{17}H_{14}O_2$: 250.0994.

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