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Organic Iodide Aided Carbonylation of Terminal Acetylenes with Palladium Catalyst

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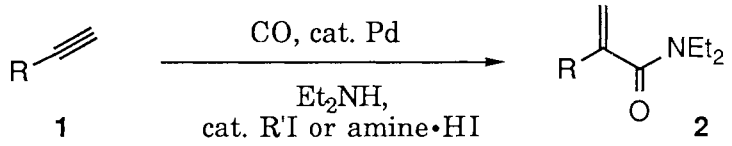
Carbonylation of various terminal acetylenes in the presence of a catalytic amount of organic iodides or amine•HI salt and palladium complexes was found to produce 2-substituted acrylamides in good yields under mild conditions (5 atm, 120 °C, 6 h).

Carbonylation with carbon monoxide is deemed to be a powerful tool for the preparation of carbonyl compounds such as ketones, carboxylic acids, and their derivatives.[1] Among the carbonylations of a variety of functionalities investigated, the conversion of acetylenes to acrylic acid derivatives is of practical importance. Usually, palladium catalysts carbonylate terminal acetylenes to acetylene ketones or carboxylic acids,[2] while presence of additives such as aqueous hydriodic acid enables the transformation of terminal acetylenes to acrylic acid derivatives such as esters and amides.[3] However, the reaction medium is strongly acidic. In the context of our studies on the carbonylation,[4] we examined several organic iodides as a co-catalyst under neutral or weakly basic conditions. Employment of iodomethane and trialkylammonium hydrogen iodide in amine was found to aid the envisioned transformation giving rise to 2-substituted acrylamides in good yields.

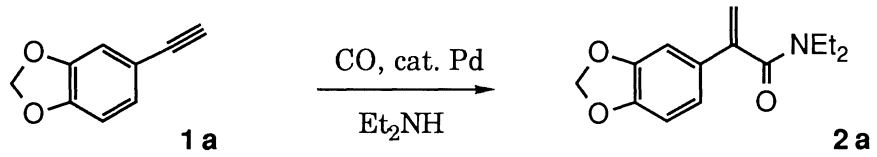


1 2

The results of the carbonylation of **1** under various conditions are listed in Table 1. The carbonylation was found to be assisted by alkyl iodides as well as aryl iodides, among which iodomethane was revealed to be of choice (Entry 2). Simple ammonium salts such as ammonium iodide (Entry 4) and pyridinium *p*-toluenesulfonate (PPTS) (Entry 5) also behaved as co-catalysts. The pressure of carbon monoxide at 5 atm was enough to attain a high yield (Entry 6), although the reaction proceeded at even 1 atm (Entry 7). The yield of the product was not affected by the kind of palladium catalysts as can be seen in Entries 8-10. Bis(triphenylphosphine)palladium(II) chloride with addition of triphenylphosphine (5 mol%) gave the best result (Entry 8). Palladium(II) with a bidentate ligand, dppb (Entry 9) and the combination of palladium acetate and 4 equiv. of triphenylphosphine (Entry 10) proved

effective. To complete the reaction in 6 h, heating at 120 °C and less than 10 mol% of iodides were required.

Table 1. Carbonylation of Terminal Acetylene [a)]



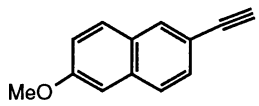
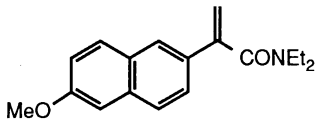
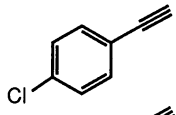
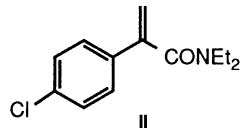
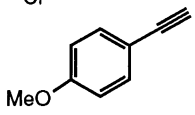
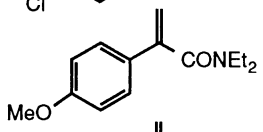
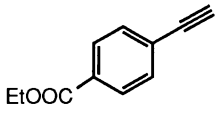
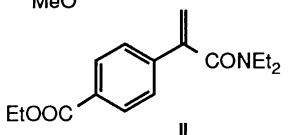
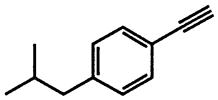
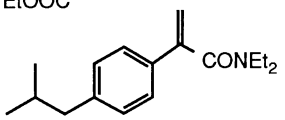
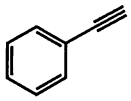
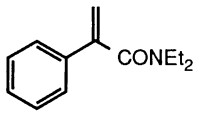
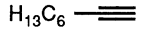
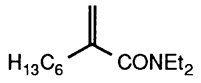
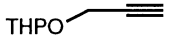
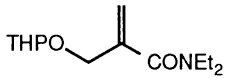
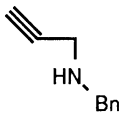
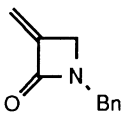
1a **2a**

Entry	R'I	Catalyst	Pressure atm	Products/% **2a**	**1a**
1	PhI	$Cl_2Pd(PPh_3)_2$	20	65	20
2	MeI	"	"	66	23
3	EtI	"	"	53	13
4	NH_4I	"	"	62	15
5	PPTS	"	"	10	22
6	MeI	"	5	81	4
7	"	"	1	77	11
8	"	" - PPh_3 [b)]	5	92	-
9	"	$Cl_2Pd(dppb)$	5	89	-
10	"	$Pd(OAc)_2$ - PPh_3 [c)]	5	91	-

a) Carried out using catalyst (5 mol%), R'I (10 mol%) in Et_2NH (3 ml) at 120 °C for 6 h. b) 5 mol% of PPh_3 was added. c) Pd/ligand = 1/4.

The results of the carbonylation with a variety of terminal acetylenes are summarized in Table 2. The carbonylation was carried out by heating a mixture of terminal acetylene **1** (1 mmol), organic iodides (0.1 mmol), bis(triphenylphosphine)palladium(II) chloride (0.05 mmol), and triphenylphosphine (0.05 mmol) in diethylamine (3 ml) under carbon monoxide (5 atm) at 120 °C for 6 h in a stainless autoclave. Various aryl acetylenes gave the desired products in high yields. However, the reaction of 1-octyne resulted in a low yield (Entry 8) in spite of a good result on the carbonylation of propargyl alcohol derivative (Entry 9). The branched amides **2** always predominate over the linear amides. Both acid labile and base sensitive groups such as ester and THP could tolerate the weakly basic conditions. Formation of ammonium salts formulated as $R_3N \cdot HI$ or $R_2NH \cdot HI$ from alkyl iodides and diethylamine is supposed to be an essential step, while the carbonylation of iodobenzene in diethylamine generates HI forming diethylammonium salt together with diethyl benzamide. Hence, the corresponding ammonium salt, $Et_2MeN \cdot HI$, was prepared and was found to act as a successful co-catalyst as well (Entry 7). The usefulness of this method is exemplified by the formation of β-lactam (Entry 10).

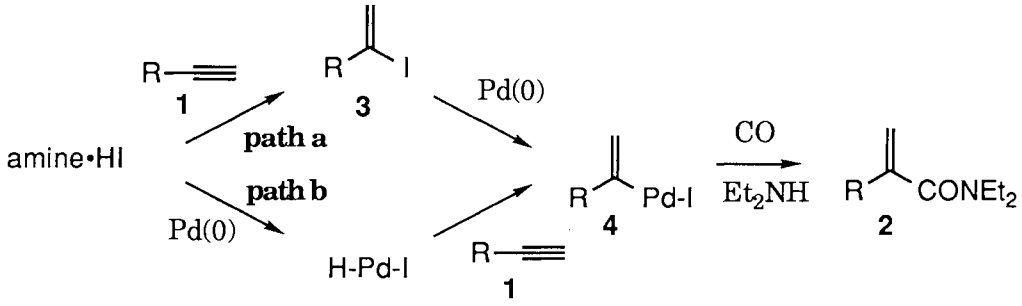
Table 2. Carbonylation of Acetylenes [a)]

Entry	1	2	Yield/%
1			78
2			57 [b)]
3			93
4			61 [c)]
5			98 [b,d)]
6			81 [b)]
7			92 [e)]
8			37 [b)]
9			78 [b)]
10			46 [f)]

a) General conditions : MeI (10 mol%), $Cl_2Pd(PPh_3)_2$ (5 mol%), PPh_3 (5 mol%) in Et_2NH (3 ml) at 5 atm of CO at 120 °C for 6 h. b) Contaminated with less than 5% of linear amide. c) Contaminated with ca. 25% of *N,N*-diethyl *p*-ethoxycarbonyl-cinnamamide. d) for 10 h by adding 10 mol% of PPh_3. e) Carried out with Et_2MeN•HI (10 mol%) instead of MeI. f) Carried out with Et_2MeN•HI (10 mol%) instead of MeI in $^iPr_2NH$ (3 ml).

Two reaction paths illustrated in Scheme 1 are conceivable. At first, alkylammonium salt is formed by either the reaction of alkyl iodides and diethylamine or the carbonylation of iodobenzene. **Path a** is an addition of HI to acetylene affording vinyl iodide **3**[5)] followed by oxidative addition giving **4**. Another route is an insertion of acetylene to palladium hydride stemming from Pd(0) and HI (**path b**). Further reaction of **4** to the product **2** is well established.[1,2)] At present, we suppose that the **path b** is more plausible due to the following

results. The reaction without palladium catalyst and carbon monoxide did not produce **3** but **1** was recovered, even though stoichiometric amount of iodomethane was subjected. The carbonylation of internal acetylenes did not take place, although the addition of HI to acetylenes is well known wherein internal acetylenes more readily react.[6] Another salt of proton acid, PPTS, also promoted the carbonylation as shown in Table 1, Entry 5.[7]



Scheme 1. Possible reaction paths.

Every HI-assisted reaction including carbonylation catalyzed by transition metals is carried out in acidic conditions, wherein the starting materials are initially converted to organic iodides reactive to the catalysts.[1] However, our reaction comprises completely different feature. Thus, a practically useful method to convert terminal acetylenes to 2-substituted acrylamides has been exploited.

SC-NMR Laboratory of Okayama University is appreciated for high resolution NMR.

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7) For other reactions considered to proceed via a formation of hydridopalladium from protonic acid and palladium, see: J. Tsuji, K. Ohno, and T. Kajimoto, *Tetrahedron Lett.*, **1965**, 4565; A. Kasahara, T. Izumi, and A. Suzuki, *Bull. Chem. Soc. Jpn.*, **50**, 1639 (1977); J. F. Knifton, *J. Mol. Catal.*, **2**, 293 (1977); B. M. Trost, M. Lautens, C. Chan, D. J. Jebaratnam, and T. Mueller, *J. Am. Chem. Soc.*, **113**, 636 (1991). and the literatures therein.

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