Microwave-Assisted Copper-Catalyzed Sonogashira Reaction in PEG Solvent

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Abstract: A catalytic system composed of copper salt, potassium carbonate and appropriate poly(ethylene glycol) (PEG; liquid or solid, various molecular weight: 300< MW <3400) was developed to perform a Sonogashira arylation under microwave activation. In the presence of copper(I) iodide, various substituted diphenylacetylenes could be synthesized.

Key words: Sonogashira coupling, microwave, arylation, copper, poly(ethylene glycol)

Discovered in the early 1970s, the Sonogashira reaction[1] has become one of the most powerful synthetic method for the carbon–carbon bond formation.[2,3] Since then, it has found tremendous developments in synthetic chemistry for the high-throughput preparation of small organic molecules, which can be screened for their biological activity,[4,5] for the synthesis of organic materials,[6,7] or the preparation of complex organic molecules. The Sonogashira reaction is associated with palladium catalysis and as such has also promoted the use of palladium as a catalyst in several organic transformations especially in cascade reactions.[8]

Despite its efficiency, palladium is an expensive metal, rendering commercial processes based on Pd less attractive unless extremely active and/or recyclable catalysts are available. It has been calculated that 1 mol% of Pd catalyst for a 200 dalton product adds 112 euros to the cost.[9] For this reason, the search for other metallic catalytic systems that could substitute or complement the palladium catalysts tool box, is a valuable task. One cheaper metal which has proved to be useful in coupling reactions is copper.[10,11]

Copper catalysis has been mostly applied to the so-called Ullmann coupling for the formation of carbon–nitrogen bonds. Surprisingly, only few publications report on the use of copper[12–17] as the only catalyst for the Sonogashira reaction that is traditionally a bismetallic-mediated process (palladium and copper required). Copper can take part in cross-coupling chemistry in a way strikingly similar to palladium, but it is more versatile and productive since it exits in four oxidation states from 0 to +3, while palladium has at its disposal only two stable oxidation states 0 and +2. As an ongoing project related to the use of poly(ethylene glycol)s (PEGs) as organic solvents,[18–22] we have already explored the use of copper catalyst in the Heck reaction[22] under microwave activation in these solvents.

We report herein an alternative catalytic system, phosphine- and palladium-free, for C–C coupling in Sonogashira conditions, made of a catalytic amount of copper(I) iodide (CuI), potassium carbonate and poly(ethylene)glycol (of various molecular weight), as organic solvent, under microwave activation.

PEGs are homopolymers that can substitute volatile organic solvents. They present some interesting characteristics, including high polarity and high boiling points, special properties arising from its cation complexation ability and have been used to a certain extent in substitution, oxidation, reduction and organometallic reactions.[23] Furthermore they present low toxicity and they have been used for biomedical applications, especially in the field of drug discovery[24] and as soluble polymeric support in organic synthesis.[25] PEGs with low molecular weight (less than 800 dalton) are liquid at room temperature while high molecular weight PEGs (more than 800 dalton) are solids, that melt at a moderate temperature and can therefore be used as solvent.[18–22,26]

Initially, we employed the CuI-catalyzed coupling reaction of iodobenzene (**1a**, R = H) with phenylacetylene (**2**), mixed together with PEG_{3400} and potassium carbonate, as a model for testing reaction conditions (Scheme 1). The reaction mixture was heated for 30 minutes under microwave,[27–30] which is known as a practical heating technique to reduce reaction times. Then, the mixture was cooled, dissolved in a small amount of CH_2Cl_2, precipitated in diethyl ether and filtered. The expected product was obtained from the filtrate after evaporation of the solvent and analyzed by ^1H NMR using CH_2Br_2 as an internal standard. The precipitate, after filtration, contained a mixture of copper salt, the solvent, the inorganic base, and inorganic by-products.

Encouraging results were obtained in the presence of 0.5 equivalent of copper(I) iodide (150 °C, 64% yield), and only one equivalent of phenylacetylene (**2**). Since the reaction was performed under microwave in a sealed tube, volatile phenylacetylene (**2**) vaporized and, probably, less than an equimolar amount of **2** was effectively present in the reaction mixture. We decided to increase the amount of alkyne from one to two equivalents with respect to phenyl iodide.[22] The yields dropped drastically by reducing the quantity of catalyst to 0.1 equivalent, or lowering

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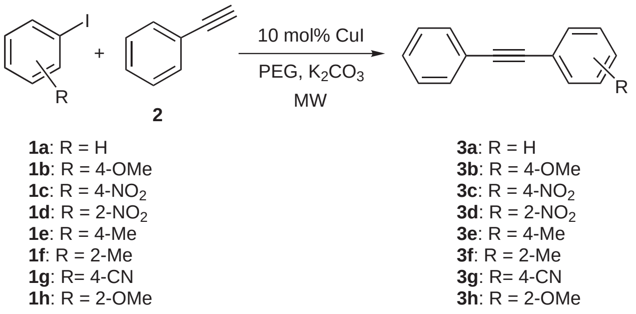

Scheme 1

the temperature. We also tried to prepare and heat the copper salt, base and PEG mixture prior to the addition of the two starting materials together, or one after the other,[31,32] but the results did not improve.

With the aim of studying the recyclability of the system, the reaction was performed in a second cycle by using the precipitate obtained from the first experiment in the presence of the base and starting materials. Although satisfying results were obtained (66% yield), the catalytic system needed some induction period to be fully effective.[33] All the reactions have been performed under no special conditions, moisture playing probably a significant role in the catalytic reaction by improving the base solubility that otherwise would remain mostly undissolved. Moreover, the ability of PEG to complex with large alkali metal ions leading to solubilization of the base is well known.[34]

We expanded our initial study of the activity of PEG–CuI catalytic system to the Sonogashira coupling of 4-iodoanisole (**1b**) in the presence of two equivalents of phenylacetylene, to study the effects of other bases, temperature, solvent and additives on the yield. The results are summarized in Table 1.

Poor yields were obtained at 150 °C, and no improvements were observed on doubling the reaction time (entry 1).

Table 1 Reaction Conditions for the Copper-Catalyzed Sonogashira Reaction for 4-Iodoanisole (**1b**, R = OMe) in Different PEGs

Entry	Base	Solvent	CuI (equiv)	Temp (°C)	Time (min)	Yield (%)[a]
1	K_2CO_3	HO-PEG$_{3400}$-OH	0.1	150	60	14
2	K_2CO_3	HO-PEG$_{3400}$-OH	0.1	220	30	69
3	K_2CO_3	HO-PEG$_{3400}$-OH	0.1	220	60	89
4	K_2CO_3	HO-PEG$_{3400}$-OH	–	220	30	0
5	$(n\text{-}C_8H_{18})_3N$	HO-PEG$_{3400}$-OH	0.1	220	30	0
6	Cs_2CO_3	HO-PEG$_{3400}$-OH	0.1	220	30	40
7	CsOAc	HO-PEG$_{3400}$-OH	0.1	220	30	23
8	Bu_4NOAc	HO-PEG$_{3400}$-OH	0.1	220	30	2
9	K_2CO_3	HO-PEG$_{3400}$-OH–DMF	0.1	220	30	64
10	K_2CO_3	HO-PEG$_{3400}$-OH[b]	0.1	220	30	66
11	K_2CO_3	HO-PEG$_{3400}$-OH–DMF[b]	0.1	220	30	89
12	K_2CO_3	HO-PEG$_{3400}$-OH	0.1	220	30	58
13	K_2CO_3	HO-PEG$_{3400}$-OH	cycle 2	220	30	63
14	K_2CO_3	HO-PEG$_{300}$-OH	0.1	220	30	78
15	K_2CO_3	HO-PEG$_{550}$-OMe	0.1	220	30	94
16	K_2CO_3	HO-PEG$_{550}$-OMe	0.1	180	60	2
17	K_2CO_3	HO-PEG$_{550}$-OMe	0.1	180	90	92
18	K_2CO_3	HO-PEG$_{550}$-OMe	0.1	200	60	100
19	K_2CO_3	–	cycle 2	200	60	44
20	K_2CO_3	MeO-PEG$_{250}$-OMe	0.1	220	30	62
21	K_2CO_3	MeO-PEG$_{250}$-OMe–H_2O	0.1	220	30	10

[a] Yields were calculated by ^{1}H NMR using CH_2Br_2 as an internal standard.

[b] PPh_3 (0.2 equiv) was added.

When the temperature was increased to 220 °C, better results were obtained (entry 2) and improved by extending the reaction time to one hour (entry 3). In the absence of CuI (entry 4), no reaction occurred under microwave irradiation. Further studies were carried out to study the influence of the base and the reaction temperature for assessing the catalyst performance. The use of other group 1 metal carbonates, or acetates gave lower conversion with respect to K_2CO_3 (entries 5–8). The best results were obtained with K_2CO_3 that became the base of choice for this project. This result can be rationalized considering that PEG can form a loose complex with large alkali metal ions such as K^+, leaving the basic anion as a free ion in the medium and increasing the base solubility and strength. This hypothesis can explain the low yield obtained in presence of Bu_4NOAc, dissolved in PEG: the concentration of AcO^- in the solution is low due to the ion pair formed with Bu_4N^+, diminishing the overall catalyst efficiency. Different solvent–additive–base combinations were also tested: DMF as a co-solvent (entry 9), or PPh_3 as an additive (entry 10) gave comparable results and no improvements in the yields. However 89% yield was achieved through their synergistic effect (entry 11). The investigation was completed by recycling the catalytic system (entries 12 and 13) and good yields were obtained in a second run.

Low-molecular-weight liquid PEGs can be regarded as protic solvents with aprotic binding sites constituted by the ethylene oxide units. Several organic substrates are soluble in low-molecular-weight liquid PEG.[23]

Different factors affect the phase catalytic activity, such as PEG molecular weight, chain end effects, and nature of the associated cations and anions. For these reasons we also explored the Sonogashira coupling with liquid PEG_{300} (entry 14), PEG_{550} monomethylether (entries 15–19) and PEG_{250} dimethylether (entry 20). Yield was increased from 69% (entry 2) to 78% (entry 14) on replacing PEG_{3400} with PEG_{300}, probably due to a better solubility of the substrates in PEG_{300}. Monomethyl PEG gave better results than dimethyl PEG or PEG. Most probably, chelation of cations by the polymer is optimum when one hydroxyl group is present. One OH group allows at one end of the polymer, together with the neighboring ethylene oxides, stabilization of a cation (K^+ or Cu^+) involved in the reaction.[35] If two OH groups are present both ends may stabilize the cations, provoking repulsive interactions resulting in PEG uncoiling and poor results.[36] Dimethoxy PEGs are unable to generate the same synergistic hydroxyl–ethylene oxide stabilizing effect, as in the case of monomethoxy PEG.[37] We also tried to recycle the catalytic system CuI–PEG_{550} monomethyl ether; *n*-hexane was added to the reaction vessel containing the crude from the first cycle. The upper layer, containing **3b** was separated and the catalytic system was used in a second run (entries 18 and 19). The recycling was not efficient in this case. No improvement was obtained when PEG_{3400} was replaced by PEG_{250} dimethylether (entry 20).

To determine the scope of the Sonogashira cross-coupling reaction in different PEGs (solid or liquid), we performed the reaction with other substrates, at 150 °C for 2.5 hours.[38]

As summarized in Table 2, we found that electron-deficient (**1c**,**d**,**g**) or electron-rich aryl iodides (**1b**,**e**,**f**,**h**) reacted with phenylacetylene (**2**) to give the corresponding substituted diphenylacetylenes **3b**–**h** with moderate to

Table 2 Yield of Copper-Catalyzed Sonogashira Reaction with Different Aryl Iodides in Different PEGs[a]

	Aryl iodide	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
Entry	Physical state of **1**	l	s	s	s	s	l	s	s
1	MeO-PEG_{250}-Me (liquid)	–	13	27	15	19	83	–	10
2	HO-PEG_{300}-OH (liquid)	50	49	9	1	35	88	18	42
3	HO-PEG_{550}-OMe (liquid)	70	87	5	3	50	80	41	15
4		–	74[b]	–	–	–	–	100[c]	–
5		–	–	–	–	–	–	99[d]	–
6	MeO-PEG_{2000}-OMe (solid)	52	24	47	4	36	55	–	48
7	HO-PEG_{3400}-OH (solid)	56	50	57	2	36	92	5.1	24
8		–	–	–	5[d]	15[d]	–	80[d]	–
9		–	–	–	2[e]	–	–	–	–
10	HO-PEG_{2000}-OMe (solid)	67	20	58	6	53	69	11	34

[a] Yields were calculated by ^1H NMR using CH_2Br_2 as an internal standard; '–' indicates reaction not performed.
[b] Yield is given for a second cycle.
[c] Reaction was carried out at 200 °C for 60 min.
[d] Reaction was carried out at 220 °C for 30 min.
[e] Reaction was carried out at 220 °C for 60 min.

good yields depending on the physical states of both the PEG and the substrates, that seem to play a key role.

When liquid phenyl iodide (**1a**) was used, all conditions yielded good results: small or large PEGs afforded average yields of diphenylethyne (**3a**).

PEG_{550} monomethylether (entries 3–5) or PEG_{3400} (entry 8) were the best solvents for the synthesis of 1-(4-cyanophenyl)-2-phenylethyne (**3g**), with yields ranging from 41% (entry 3) up to 99% at 200 °C (entry 4) or at 220 °C (entry 5) for shorter reaction times. The coupling product 1-(4-nitrophenyl)-2-phenylethyne (**3c**) was obtained in 47–58% yields in solid PEGs (entries 6, 7 and 10). Poor yields and extensive degradation was observed in liquid PEGs (entries 1–3). When 2-nitroiodobenzene (**1d**) was the substrate, very poor yields of 1-(2-nitrophenyl)-2-phenylethyne (**3d**) were obtained in any PEG (entries 1–3 and 6–10). Probably, the nitro group in *ortho* position to the alkyne moiety is not tolerated under these conditions.[16,39] Moderate yields of 1-(4-methylphenyl)-2-phenylethyne (**3e**) could be obtained only in PEG_{550} (entry 3) or PEG_{2000} (entry 10) monomethylether, and higher temperatures with shorter reaction time afforded even lower conversion of the starting materials. The isomeric 1-(2-methylphenyl)-2-phenylethyne (**3f**) could be obtained with good yields in every type of PEG (entries 1–3, 6, 7 and 10). However the reaction did not proceed in the absence of PEG, clearly showing that the PEGs play a key role in the catalytic system. Very poor yields were obtained in DMF (9%). In the case of 4-iodoanisole (**1b**), 1-(4-methoxyphenyl)-2-phenylethyne (**3b**) could be obtained in moderate yields in DMF (44%) or PEG_{3400} (entry 7). Better results were obtained in PEG_{550} monomethylether and recycling was also possible (entries 3 and 4). On the contrary, the yield of the isomeric cross-coupling product 1-(2-methoxyphenyl)-2-phenylethyne (**3h**)[40] under our standard conditions was compromised by a competitive reaction affording 2-phenylbenzo[*b*]furan.[41] Only PEG_{2000} dimethylether afforded **3h** in a moderate yield (entry 6).

In conclusion, a palladium- and phosphine-free reaction condition for Sonogashira-type coupling was developed that used PEG–CuI–K_2CO_3 as the catalyst system under microwave activation. This reaction was applicable to a range of aryl iodides. In spite of the fact that higher temperatures were required than with palladium-based catalyst systems,[1,42,43] the catalyst system had the advantage of using available and less expensive reagents that were easily removable (by simple precipitation). The reaction we have set up is operationally simple and cross-coupling products could be obtained in good yields, depending on the physical state of the aryl iodide–PEG combination. In general, liquid substrates afforded cleaner reactions and better yields. The pivot role of PEG for this catalytic system has been widely demonstrated and no homocoupling products were detected in the crude. Since the recovery of the PEG-based catalytic system is based on a precipitation step, this system is a very practical alternative to the other catalytic system for the Sonogashira reaction.

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(38) **Copper-Catalyzed Sonogashira Reaction of 4-Iodoanisole (1g) with Phenylacetylene (2)**: Microwave-assisted reactions were performed with a Biotage Initiator 60 EXP® instrument. Temperature was measured with an IR sensor on the outer surface of the reaction vial. In a typical experiment, to a mixture of CuI (0.0043 g, 0.023 mmol, 0.1 equiv), finely powdered K_2CO_3 (0.047 g, 0.34 mmol, 1.5 equiv) and PEG_{3400}-OH (0.25 g) were added 4-iodoanisole (**1b**; 0.053 g, 0.23 mmol, 1.0 equiv) and phenylacetylene (**2**; 0.046 g, 0.46 mmol, 2.0 equiv). The resulting mixture was heated by microwave irradiation at 220 °C (initial power 400 W) for 30 min. After cooling, the reaction mixture was solubilized in CH_2Cl_2 and precipitated in Et_2O. Filtration and evaporation afforded 1-(4-methoxyphenyl)-2-phenylethyne (**3b**) in 58% yield (measured by ^1H NMR using CH_2Br_2 as an internal standard). HPLC analysis did not detect the presence of by-products. The precipitate was reused in a similar reaction with finely powdered K_2CO_3 (0.047 g, 0.34 mmol, 1.5 equiv), 4-iodoanisole (0.053 g, 0.23 mmol, 1.0 equiv) and phenylacetylene (0.046 g, 0.46 mmol, 2.0 equiv) to give 1-(4-methoxyphenyl)-2-phenylethyne (**3b**) in 88% yield (measured by ^1H NMR using CH_2Br_2 as internal standard). When PEG_{550}-monomethylether was the solvent of choice, the workup was achieved by adding cyclohexane (0.5 mL) to the reactor containing the crude, and the supernatant was recovered and evaporated, affording 1-(4-methoxyphenyl)-2-phenylethyne (**3g**) in 44% yield (measured by ^1H NMR using CH_2Br_2 as an internal standard). The lower phase was reused in a similar reaction with finely powdered K_2CO_3 (0.047 g, 0.34 mmol, 1.5 equiv), 4-iodoanisole (0.053 g, 0.23 mmol, 1.0 equiv) and phenylacetylene (0.046 g, 0.46 mmol, 2.0 equiv) to give 1-(4-methoxyphenyl)-2-phenylethyne (**3b**) in 100% yield (measured by ^1H NMR using CH_2Br_2 as an internal standard); TLC [cyclohexane–Et_2O (50:50), λ = 254 nm]: $R_f = 0.66$; mp 58–61 °C; HPLC (λ = 214 nm): t_R = 14.253 min. IR (CCl_4): 2210 (w), 1500 (s), 1435 (m), 1242 (s), 1168 (m), 1030 (s), 825 (s) cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ = 7.46–7.53 (m, 4 H), 7.32–7.34 (m, 3 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 159.61, 113.06, 131.46, 128.32, 127.94, 123.59, 115.37, 114.00, 89.36, 88.06, 55.32. MS (ESI+): *m/z* = 435 $[(2 \times M + H_2O) + H]^+$, 417 $[2 \times M + H]^+$, 209 $[M + H]^+$. HRMS: *m/z* calcd for $C_{15}H_{12}O$: 208.0888; found: 208.0882.

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