

Solvent-free Sonogashira coupling reaction *via* high speed ball milling

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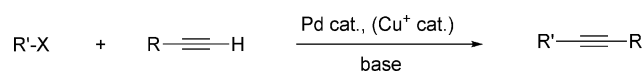
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Herein, we report on the solvent-free Sonogashira reaction utilizing high speed ball milling. Sonogashira coupling of a variety of *para* substituted aryl halides were performed with trimethylsilylacetylene or phenylacetylene. We observed that iodo and bromo substituted aromatics successfully undergo Sonogashira coupling. However, chloro and fluoro substituted aryl compounds were unreactive. Conducting the coupling reaction in the absence of copper iodide led to low yields. Alternately, if the reaction is conducted with a copper ball in a copper vial in lieu of copper iodide, the coupling product is observed in high yields. This demonstrates the first report on the use of the vial and ball material as a catalyst in a ball milled chemical reaction.

Introduction

Recently, the scientific community has taken a proactive approach to environmental pollution.^{1,2} Within the area of organic synthesis, solvent-free reactions have gained widespread attention for their ability to significantly reduce solvent waste.³⁻¹⁰ High-speed ball milling (HSBM) under solvent-free conditions is a method that has been shown to be a viable alternative to solution based chemistry. HSBM is a technique that works on the same principles as a mortar and pestle; specifically, it uses mechanical energy to convert reactants to products during the course of the reaction.¹¹⁻¹⁴ Many reports in the literature have shown that HSBM is effective for various organic transformations and for the development of environmentally benign reactions.¹⁵⁻²³ Herein, we report our results on the Sonogashira reaction under solvent-free high-speed ball milling conditions.

The Sonogashira reaction (which is an adaptation to the Castro–Stephens protocol)^{24,25} is the coupling between a terminal alkyne and an aryl halide or aryl triflate through the use of a palladium catalyst (scheme 1).²⁶⁻²⁹ This reaction is important in the synthesis of various molecules critical to the development of natural products, pharmaceuticals and organic materials.³⁰



Scheme 1 Sonogashira reaction.

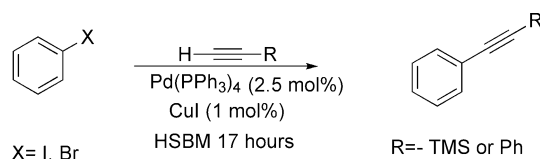
Due to the importance of the Sonogashira reaction there has been a tremendous amount of research investigating various types of metal catalysts, solvents, reaction times and temperatures. Additionally, a fair amount of research has been geared towards making this important reaction more environmentally benign. There has been research conducting the reaction under aqueous conditions,³¹⁻³⁶ microwave conditions³⁷⁻⁴¹ and using

ionic liquids.⁴²⁻⁴⁵ There have been reports of solvent-free Sonogashira reactions, but several of these procedures are run for long reaction times under high temperature conditions.⁴⁶⁻⁴⁸ Other drawbacks are that these solvent-less methods only react with aryl iodides⁴⁹ or strongly electron withdrawing groups on the aryl ring.⁴⁸ To this end, we wanted to investigate the Sonogashira coupling reaction under HSBM conditions.

Results and discussion

Sonogashira coupling reaction under solvent-free aerobic high speed ball milling conditions

Initially, we chose to investigate the coupling of iodobenzene with both phenyl acetylene and trimethyl silyl acetylene under HSBM conditions. To a custom-made 1/2" × 2" stainless steel vial, we added iodobenzene, catalytic copper iodide, potassium carbonate and tetrakis(triphenyl)phosphine palladium catalyst (Scheme 2). These reactions were carried out under aerobic conditions in the absence of a solvent; typically, Sonogashira reactions are carried out under inert atmosphere using dry solvents.



Scheme 2 Solvent-free Sonogashira reaction *via* high speed ball milling conditions.

After successfully conducting the Sonogashira reaction under ball milling conditions, we next turned our attention to optimizing the catalytic loading, the base, type of palladium catalyst and versatility of other aryl halides.

Through our analysis, we discovered that using 2.5% of the catalyst was the lowest we could use that gave high yields of coupling product after 17 hours of milling. We substituted tetrakis(triphenyl)phosphine palladium with *trans*-dichlorobis(triphenyl)phosphine palladium and observed

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similar catalytic activity; hence, each catalyst under these conditions afforded very high yields of coupling product. It has been shown that the activated palladium(0) catalyst can be prepared from cheaper more readily available palladium catalysts such as palladium chloride and palladium acetate with the addition of free ligand.⁵⁰⁻⁵⁶ When we used palladium acetate as the catalyst and free triphenylphosphine, the reaction did not give the coupling product even after extended milling times.

The size and ball material has often affected the results of these ball milled reactions. We examined 1/8" and 1/4" stainless steel, brass, bronze, aluminium, tungsten carbide and aluminium oxide balls in this reaction. Our best yield in the shortest reaction time occurred when a 1/4" tungsten carbide ball was used. We were able to couple the reagents in high yields in a reaction time of approximately 17 hours. Many of the reactions could be completed in shorter time durations, however, for the sake of comparison each reaction was carried out for a 17 hour time period.

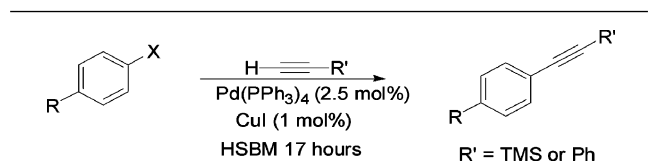
After completing the optimization of the iodobenzene system, we went on to study the Sonogashira of a variety of haloaromatics using trimethylsilyl acetylene and phenylacetylene as coupling partners (Table 1). Our investigation found that a wide variety of iodo and bromo aryl compounds could be coupled to both trimethylsilylacetylene and phenyl acetylene, as indicated in Table 1. Various functional groups were tolerated; however, benzyl alcohols and phenols did not provide the coupling product. In most cases there was little difference in yield coupling to either trimethylsilyl or phenyl acetylene, which suggests that the Sonogashira coupling under HSBM conditions should tolerate a wide range of alkynes. Consistent with the reaction in

solution, iodosubstituted aryl groups were more reactive than the bromosubstituted analogs. Unfortunately, we did not have success coupling chloro or fluoro aryl compounds, but typically these halogens are sluggish coupling partners. We next examined how dihaloaromatics performed under HSBM conditions. Coupling 1,4-bromoiodobenzene or 1,4-chloroiodobenzene with trimethylsilylacetylene or phenylacetylene, we observed selective coupling to the iodo- group to give only a mono coupling product at the iodo position in very high yields. However, even when a large excess of the acetylene is used, only the mono addition product is observed. Furthermore, reacting 1,4-dibromobenzene or 1,4-bromochlorobenzene with the acetylene derivatives gives selective coupling to the bromo substituted carbon but the yield dramatically decreases, and again using excess acetylene does not provide high yields of the disubstituted coupled product. We are currently in the process of trying to optimize these conditions for dihalogenated aryl systems to improve the yields of the disubstituted product.

Copper-free Sonogashira

One area of Sonogashira reactions that has been the focus of extensive research has been the use of copper-free reaction conditions. Copper iodide is needed to activate the alkyne to increase the rate of coupling. One major drawback to the use of this co-catalyst is that it increases the amount of alkyne-alkyne coupling (*i.e.* Glaser coupling). We wanted to determine if Sonogashira coupling reactions would be successful under ball milling conditions without the addition of copper iodide. When copper iodide was omitted as the co-catalyst, the yield of the Sonogashira coupling was significantly lower than when copper iodide is used as the co-catalyst for all examples, except for the very reactive iodobenzene (Table 2). Although we had success under copper-free conditions, typically the yields were lower than when copper iodide was used. It has been previously reported that there are trace amounts of copper inside commercial sources of palladium catalyst.⁵⁷ Therefore, it is very possible that these "copper-free" reactions aren't truly copper-free and the low yield could be attributed to the minute traces of copper in the tetrakis(triphenylphosphine) palladium we used in the reaction.

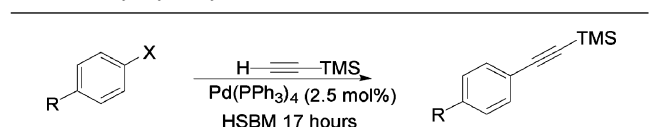
Table 1 Sonogashira reactions of *p*-substituted benzene with trimethylsilylacetylene and phenylacetylene



X	R	Percent Yield ^a R' = Ph	Percent Yield ^a R' = TMS
I	OMe	86	84
I	Me	84	40
I	H	95	93
I	Br	88	76
I	Cl	87	74
I	I	trace ^b	20 ^c
I	I ^d	39 ^e	30 ^f
Br	OMe	trace	trace
Br	Me	33	26
Br	H	93	90
Br	Cl	7	4
Br	CHO	89	87
Br	CHO	90	89
Br	NO ₂	85	66
Br	Br	9 ^g	5 ^h
Br	Br ⁱ	8 ^h	3 ^h

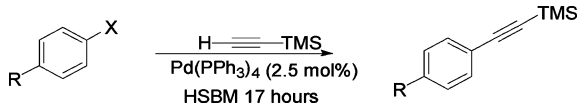
^a Reported as isolated yields. ^b 1,2 substituted. ^c Isolated 43% disubstituted product. ^d Isolated 8% disubstituted product. ^e Isolated 63% disubstituted product. ^f Isolated 31% of disubstituted product. ^g Isolated 48% disubstituted product. ^h No disubstituted product was observed. ⁱ 1,2 substituted.

Table 2 "Copper-free" Sonogashira reactions of *p*-substituted benzene with trimethylsilylacetylene



X	R	Percent Yield ^a w/CuI	Percent Yield ^a "copper-free"
I	H	95	39
I	Me	84	17
I	Br	88	43
I	Cl	87	37
I	OMe	84	58
Br	CHO	87	44
Br	CHO ^b	89	46

^a Reported as isolated yields. ^b 1,2 disubstituted.

Table 3 Sonogashira reactions of *p*-substituted benzene with trimethylsilylacetylene using a 3/32" copper ball in a stainless steel vial


X	R	Percent Yield ^a w/CuI	Percent Yield ^a w/Cu ball
I	H	95	87
I	Me	84	46
I	Br	88	31
I	Cl	87	52
I	OMe	84	40
Br	CHO	87	85
Br	CHO ^b	89	88

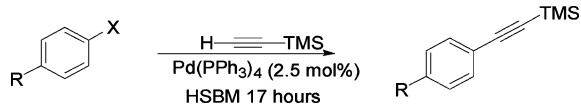
^a Reported as isolated yields. ^b 1,2 disubstituted.

Using the ball and vial as a source of copper

Although "copper-free" conditions were successful under HSBM conditions, the yields were low. Therefore, the use of a copper co-catalyst is an important aspect of the reaction under ball milling conditions. We decided to use a copper ball as the ball bearing used in the reaction. The copper ball not only can be used to break down the crystal lattice, but also as the reacting catalyst. Metal leaching in ball milling reactions is not uncommon;^{58,59} therefore, if small amounts of copper were introduced into the reaction environment, it should increase the product yields. Furthermore, the recovery of the catalyst, in this case the copper ball, would be as simple as removing the copper ball from the reaction media. Using a 3/32" copper ball bearing with a stainless steel vial, we repeated the Sonogashira reaction on various substrates. Using the copper ball as the catalyst resulted in low yields, similar to the reaction conducted in an absence of copper iodide (Table 3). It has been calculated that using the Spex 8000 M mill there are approximately 142 impacts per second.⁶⁰ This led us to believe that there weren't enough contacts between the copper ball and the alkyne. Thus, we decided to machine a copper vial which would give more surface area for the copper and presumably be better at activating the alkyne to successfully undergo the Sonogashira coupling reaction.

We machined a 1/2" × 2" screw-capped copper vial to be used in conjunction with a 3/32" copper ball bearing. Using various haloaromatics, we were able to perform ball milled Sonogashira reactions. Implementing the same conditions and examining the same substrates, we were able to undergo the coupling in very high yields (Table 4); yields which equal the results with copper iodide as co-catalyst under these conditions. To the best of our knowledge, this represents the first report of ball milling which uses the ball and vial material as a catalyst for conducting chemical reactions.⁶¹ At the conclusion of each reaction, the vials and ball bearing were weighed and we noticed no significant change in mass of either the ball bearing or the vial. After each use, the copper vial was washed with a small amount of acetone to ensure a clean reaction surface for the next reaction. After continual use of the copper vial to conduct Sonogashira reactions, we observed no depreciation in the yield of the reactions after using it for more than a month.

All the Sonogashira reactions we investigated were conducted in either a stainless steel or a copper vial. We wanted to further

Table 4 Sonogashira reactions of *p*-substituted benzene with trimethylsilylacetylene using a 3/32" copper ball in a copper vial


X	R	Percent Yield ^a w/CuI	Percent Yield ^a w/Cu ball and Cu vial
I	H	95	88
I	Me	84	83
I	Br	88	89
I	Cl	87	86
I	OMe	84	42
Br	CHO	87	84
Br	CHO ^b	89	90

^a Reported as isolated yields. ^b 1,2 disubstituted.

show that the copper vial was responsible for the increased reactivity. We machined a 1/2" × 2" Teflon vial and conducted the "copper-free" Sonogashira reaction. Under these conditions, the reaction gave low yields similar to the reaction without the inclusion of copper iodide. This further demonstrates that the copper vial is the source of the copper co-catalyst in the reaction. We are currently investigating the surface of the copper vial to determine the catalytic species.

Conclusions

In conclusion, we have shown the first Sonogashira coupling reaction under solvent-free ball milling conditions. Under these conditions, iodo and bromo aromatics make very good coupling partners but we had little success with chloro or fluoro aryl compounds. We investigated the reaction under aerobic conditions, where traditionally an inert atmosphere is used for these reactions. Conducting the reaction in the absence of copper iodide led to moderate yields of the coupling product. However, substituting the copper iodide and conducting the reaction using a copper ball and a copper vial allows yields similar to the use of copper iodide. This demonstrates a novel use of the vial material as a catalyst for the reaction. Ball milling is a powerful method that can allow for the formation of environmentally benign reactions. Further understanding of the chemistry in this process can lead to a paradigm shift in the way chemists conduct organic reactions.

Experimental

General

¹H NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Deuterated chloroform was obtained from Cambridge Isotope Laboratories, Inc., Andover, MA., and used without further purification. GC-MS data was obtained using a Hewlett-Packard 6890 series GC-MS with a Zebtron ZB-5, 15 mm × 0.25 mm × 0.25 mm column. All aryl halide reagents and terminal alkynes were purchased from Acros Organics and used without further purification. Copper iodide, palladium(II)chloride, palladium(II)acetate, trans-dichlorobis(triphenylphosphine)palladium(II), and

tetrakis(triphenylphosphine)palladium(0) were purchased from Strem Chemicals, Inc. and used without further purification. Potassium carbonate was purchased from Acros Organics. Tungsten carbide ball-bearings were purchased from Small Parts Inc. and copper ball-bearings were purchased from McMaster-Carr Supply. Simriz 486 Perfluoroelastomer O-rings (6/16" ID × 7/16" OD × 3/32" width) were purchased from Small Parts Inc. The copper rods used to make copper vials were purchased from McMaster-Carr Supply. The Teflon rods used to make Teflon vials were purchased from McMaster-Carr Supply. The stainless steel rods used to make stainless steel vials were purchased from McMaster-Carr Supply. All measurements for the vials refer to the inner diameter and the measurements for the ball bearings refer to its outer diameter. Ball-milling was carried out in an 8000M SpexCertiprep Mixer/Mill purchased from Spex certiprep.

Typical procedure for the coupling of aryl halides with trimethylsilyl acetylene

In all cases, the aryl halide was used as the limiting reagent. Iodobenzene (0.200 g, 0.98 mmol), trimethylsilyl acetylene (0.103 g, 1.05 mmol), potassium carbonate (0.137 g, 0.99 mmol), copper iodide (0.002 g, 0.01 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.028 g, 0.025 mmol) were added to a custom-made 2.0 × 0.5 inch screw capped stainless steel vial inserted with a perfluoroelastomer O-ring, along with a 0.250 inch tungsten carbide ball bearing. After placement of the vial in a Spex Certiprep 8000M mixer/mill, the reagents were ball milled for 17 hours. The resulting mixture was removed from the vial and the organic layer was extracted with ethyl acetate using a separatory funnel and dried over anhydrous magnesium sulfate. The organic layer was removed under reduced pressure to give trimethylsilylphenylacetylene in 95% yield (0.162 g, 0.093 moles).

Typical procedure for the copper-free coupling of aryl halides with trimethylsilyl acetylene

Iodobenzene (0.200 g, 0.98 mmol), trimethylsilyl acetylene (0.103 g, 1.05 mmol), potassium carbonate (0.137 g, 0.99 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.028 g, 0.025 mmol) were added to a custom-made 2.0 × 0.5 inch screw capped stainless steel vial with an inserted perfluoroelastomer O-ring, along with a 0.250 inch tungsten carbide ball bearing. After placement of the vial in a Spex Certiprep 8000D mixer/mill, the reagents were ball milled for 17 hours. The resulting mixture was removed from the vial and the organic layer was extracted with ethyl acetate using a separatory funnel and dried over anhydrous magnesium sulfate. The organic layer was removed under reduced pressure to the crude product. The crude product was purified by column chromatography using a cyclohexane/ethyl acetate eluent to afford trimethylsilylphenylacetylene in 39% yield (0.066 g, 0.038 moles).

Typical procedure for copper ball catalyzed coupling of aryl halides with trimethylsilyl acetylene

Iodobenzene (0.200 g, 0.98 mmol), trimethylsilyl acetylene (0.103 g, 1.05 mmol), potassium carbonate (0.137 g,

0.99 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.028 g, 0.025 mmol) were added to a custom-made 2.0 × 0.5 inch screw capped stainless steel vial with inserted perfluoroelastomer O-ring, along with a 3/32" inch copper ball bearing. After placement of the vial in a Spex Certiprep 8000D mixer/mill, the reagents were ball milled for 17 hours. The resulting mixture was removed from the vial and the organic layer was extracted with ethyl acetate using a separatory funnel and dried over anhydrous magnesium sulfate. The organic layer was removed under reduced pressure to the crude product. The crude product was purified by column chromatography using a cyclohexane/ethyl acetate eluent to afford trimethylsilylphenylacetylene in 87% yield (0.148 g, 0.085 moles).

Typical procedure for copper ball catalyzed coupling of aryl halides with trimethylsilyl acetylene

Iodobenzene (0.200 g, 0.98 mmol), trimethylsilyl acetylene (0.103 g, 1.05 mmol), potassium carbonate (0.137 g, 0.99 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.028 g, 0.025 mmol) were added to a custom-made 2.0 × 0.5 inch screw capped copper vial with inserted perfluoroelastomer O-ring, along with a 3/32" inch copper ball bearing. After placement of the vial in a Spex Certiprep 8000D mixer/mill, the reagents were ball milled for 17 hours. The resulting mixture was removed from the vial and the organic layer was extracted with ethyl acetate using a separatory funnel and dried over anhydrous magnesium sulfate. The organic layer was removed under reduced pressure to the crude product. The crude product was purified by column chromatography using a cyclohexane/ethyl acetate eluent to afford trimethylsilylphenylacetylene in 88% yield (0.150 g, 0.086 moles).

Acknowledgements

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