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## Potential of metal nanoparticles in organic reactions

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**Abstract.** Palladium(0) nanoparticle has been used as efficient catalyst for (a) the stereoselective synthesis of (*E*)- and (*Z*)-2-alkene-4-ynoates and –nitriles by a simple reaction of *vic*-diiodo-(*E*)-alkenes with acrylic esters and nitriles and (b) for the allylation of active methylene compounds by allylacetate and its derivatives. Copper(0) nanoparticle catalyzes aryl-sulfur bond formation very efficiently. All these reactions are ligand-free.

### 1. Introduction

In recent times, interest in nanoparticle-catalysis has increased considerably because of its improved efficiency under mild and environmentally benign conditions in the context of Green Chemistry [1]. Palladium nanoparticles have been found to be active species in various C-C bond formation, namely Heck, Sonogashira, Suzuki coupling reactions and thus showed great promise for further applications [2]. We report here novel applications of palladium and copper nanoparticles as efficient catalysts for carbon-carbon and carbon-heteroatom bond formation.

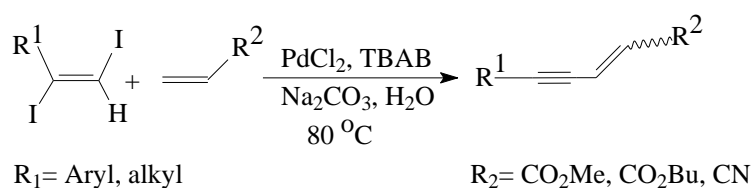
### 2. Results and Discussion

#### (a) A new route to the synthesis of (*E*)- and (*Z*)-2-alkene-4-yn-oates and nitriles from vicinal-diiodo-(*E*)-alkenes catalyzed by Pd(0) nanoparticles in water

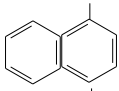
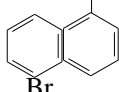
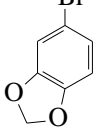
The 1,3-enyne unit is of considerable interest in organic synthesis as these moieties are present in many naturally occurring and biologically active compounds such as terbinafine, a potent drug for superficial fungal infections, calicheamicin  $\gamma_1$ , an effective antitumour antibiotic. The enynoates are also very useful synthetic intermediates.

We now report a new route involving a simple reaction of *vic*-diiodoalkenes with an activated alkene catalyzed by Pd(0) nanoparticles in water (Scheme 1). A simple reaction of *vic*-diiodo alkene and conjugated alkene in presence of PdCl<sub>2</sub>/TBAB/Na<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O system provided the product. The palladium(0) nanoparticles (2-6 nm by TEM) were produced *in situ* from this reagent system. Several structurally diverse *vic*-diiodoalkenes underwent reactions with conjugated alkenes such as acrylic ester and nitriles catalyzed by *in situ* prepared Pd(0) nanoparticles in water to produce the corresponding 1,3-enyne esters and nitriles in good yields. The results are summarized in Table 1.

**Scheme 1.**



**Table 1.** Cross-coupling reaction of various diiodo compounds with activated alkenes.

Entry	R <sub>1</sub>	R <sub>2</sub>	Time (h)	Yield (%) <sup>[a]</sup>	E:Z
1	C <sub>6</sub> H <sub>5</sub>	CO <sub>2</sub> Me	6.5	82	100:00
2	C <sub>6</sub> H <sub>5</sub>	CO <sub>2</sub> Bu	7	78	100:00
3	C <sub>6</sub> H <sub>5</sub>	CN	6.5	72	10:90
4	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Me	6	78	100:00
5	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	CN	6	72	20:80
6	<i>p</i> -Cl-C <sub>6</sub> H <sub>5</sub>	CO <sub>2</sub> Me	6.5	72	100:00
7	<i>p</i> -Cl-C <sub>6</sub> H <sub>5</sub>	CN	7	70	5:95
8	<i>m</i> -Br-C <sub>6</sub> H <sub>5</sub>	CO <sub>2</sub> Me	12	68 <sup>[b]</sup>	100:00
9	<i>m</i> -OMe-C <sub>6</sub> H <sub>5</sub>	CO <sub>2</sub> Me	6.5	80	100:00
10		CO <sub>2</sub> Me	6.5	78	100:00
11		CO <sub>2</sub> Bu	7	74	100:00
12		CO <sub>2</sub> Me	9.5	65 <sup>[b]</sup>	100:00
13	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CO <sub>2</sub> Me	26	78	100:00
14	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CO <sub>2</sub> Bu	24	72	100:00

[a] Yield refer to those of pure isolated product characterized by IR, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopic data.

[b] Reaction was carried out in sonication at room temperature.

**(b) Solvent controlled highly selective bis- and mono-allylation of active methylene compounds by allyl acetate using palladium(0) nanoparticle**

We report another novel ligand-free protocol for allylic substitution of active methylene compounds by allyl acetate and its derivatives (Tsuji-Trost reaction), catalyzed by palladium(0) nanoparticles. The reaction in THF leads to bis-allylation in one stroke, whereas highly selective monoallylation by allyl acetate takes place in H<sub>2</sub>O.

Several structurally diverse active methylene compounds underwent allylation by allyl acetate or its derivatives by in situ generated palladium(0) nanoparticles in THF to produce the corresponding allylated products in high yields. The results are summarized in Table 2. As evident from the results all the substrates produced bis-allylated products under these conditions. The participating active methylene compounds were acyclic and cyclic 1,3-diketones, 1,3-keto esters, 1,3-diester, and allylic agents used were allyl acetate, crotyl acetate, cinnamyl acetate and its derivatives.

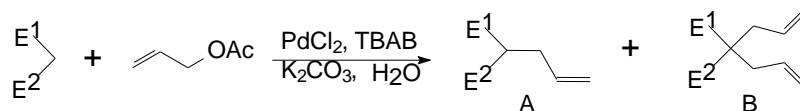
Interestingly, when the reaction was carried out in H<sub>2</sub>O monoallylation took place selectively. The results are reported in Table 3. However, this reaction was not very general. The reaction proceeded successfully only with allyl acetate; cinnamyl acetate and crotyl acetate failed to produce any allylated product.

**Table 2.** Allylation of active methylene compounds by allyl acetate catalyzed by Pd(0) nanoparticle in THF

		$\begin{array}{c} E^1 \\ \diagdown \\ \text{---} \\ \diagup \\ E^2 \end{array} + R\text{-CH=CH-CH}_2\text{-OAc} \xrightarrow[\text{K}_2\text{CO}_3, \text{THF}]{\text{PdCl}_2, \text{TBAB}} \begin{array}{c} E^1 \\ \diagdown \\ \text{---} \\ \diagup \\ E^2 \end{array} \text{-CH}_2\text{-CH=CH-R}$							
Entry	E <sup>1</sup> , E <sup>2</sup>	R	Time (h)	Yield (%) <sup>[a]</sup>	Entry	E <sup>1</sup> , E <sup>2</sup>	R	Time (h)	Yield (%) <sup>[a]</sup>
1	COMe, COMe	H	6	82	8		H	6.5	85
2	COMe, CO <sub>2</sub> Et	H	7	88	9		H	5	70
3	CO <sub>2</sub> Et, CO <sub>2</sub> Et	H	12	75	10	COMe, COMe	Me	9	75
4		H	1.5	85	11	COMe, CO <sub>2</sub> Me	Me	9.5	72
5		H	1.5	90	12	COMe, COMe	Ph	10	85
6		H	7	87	13	COMe, CO <sub>2</sub> Et	Ph	11	81
7		H	6	88	14		Ph	9	76
					15	COMe, COMe		11	72
					16			7	78

<sup>[a]</sup> Yields refer to those of purified products characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data.

**Table 3.** Allylation of active methylene compounds by allyl acetate catalyzed by Pd (0) nanoparticle in H<sub>2</sub>O



Entry	E <sup>1</sup> & E <sup>2</sup>	Time (h)	A : B	Yield (%) <sup>[a]</sup>
1	COMe, COMe	9	100 : 00	72
2	COMe, CO <sub>2</sub> Et	8	80 : 20	86
3	CO <sub>2</sub> Et, CO <sub>2</sub> Et	12	100 : 00	75
4		7	100 : 00	70

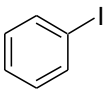
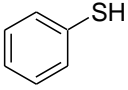
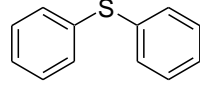
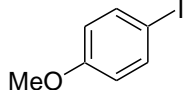
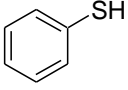
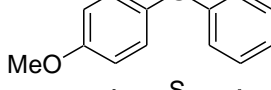
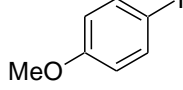
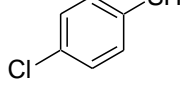
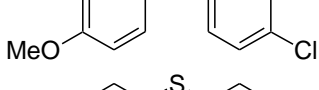
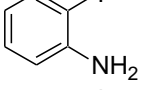
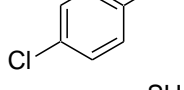
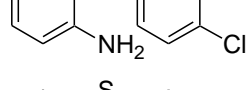
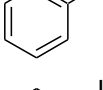
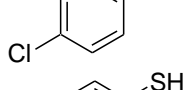
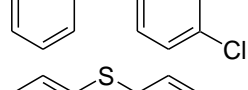
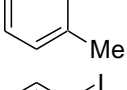
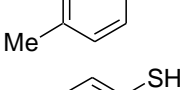
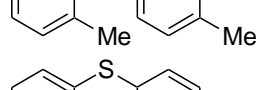
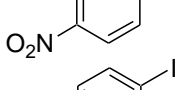
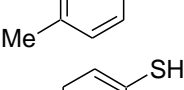
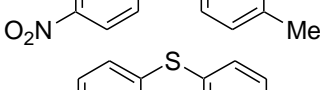
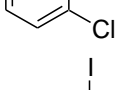
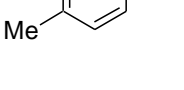
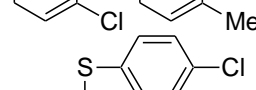
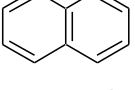
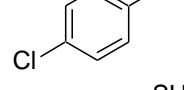
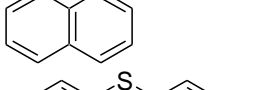
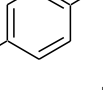
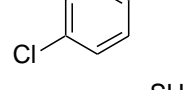
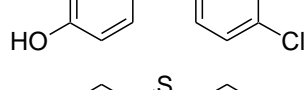
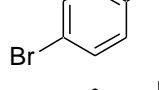
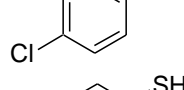
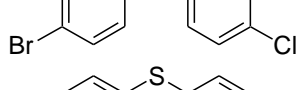
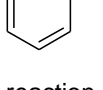
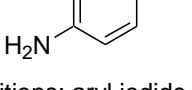
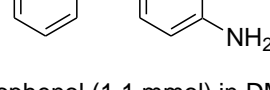
<sup>[a]</sup>Yields refer to those of purified products characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data.

### (c) Microwave Assisted Simple and Efficient Ligand Free Copper Nanoparticle Catalyzed Aryl-Sulfur Bond Formation

The formation of aryl-sulfur bond is of much importance because of the prevalence of this bond in many molecules of pharmaceutical and material interest and the utility of aryl sulfides as useful intermediates in organic synthesis. The classical method for the synthesis of aryl sulfides involved condensation of aryl halides with thiols requiring strongly basic and harsh reaction conditions. Hence, there is a need for improved procedures for this important reaction. We report here a novel ligand-free protocol for the condensation of aryl iodides with thiols using nano copper (20 mol%) under microwave irradiation in presence of a base.

A mixture of an aryl iodide and thiophenol/alkanethiol in DMF was treated under microwave irradiation with K<sub>2</sub>CO<sub>3</sub> and Cu nanoparticles (4-6 nm). Usual work up provided the product. Several diversely substituted aryl iodides underwent reactions with a variety of substituted thiophenols, benzyl mercaptan, butane and dodecane thiols by this procedure to produce the corresponding diaryl/aryl-alkyl sulfides. The results were summarized in Table 4. Both electron-donating and electron withdrawing groups substituted aryl iodides participated in this reaction with similar efficiency. In absence of Cu nanoparticles coupling reaction was not initiated at all. It was found that 20 mol% of Cu nanoparticles provided best results in terms of reaction time and yield. When the reaction was carried out at 120 °C by conventional heating, it required 12-15 h to be completed, whereas under microwave irradiation the reactions were complete by 5-7 minutes..

**Table 4.** Cross coupling reaction of aryl iodide with thiols catalyzed by Cu nanoparticle<sup>[a]</sup>

Entry	Aryl iodide	Thiol	Time (min)	Aryl sulfide	Yield (%)
1			5		98
2			5		94
3			5		93
4			6		97
5			5		95
6			6		92
7			5		87
8			6		91
9			5		95
10			7		72
11			6		81
12			7		88

<sup>[a]</sup> General reaction conditions: aryl iodide (1 mmol) and thiophenol (1.1 mmol) in DMF (0.8 mL) were subjected to microwave irradiation at 120 °C in presence of K<sub>2</sub>CO<sub>3</sub> (2 mmol) and nano Cu (20 mol%, optimized to give best yields).

### 3. Conclusion

The present protocol using *in situ* prepared palladium(0) nanoparticles provides a very convenient and efficient methodology for a one-pot synthesis of conjugated en-yne compounds from *vic*-diiodoalkenes and for allylation of active methylene compounds by allyl acetate. On the other hand, catalysis by copper nanoparticles provides a very efficient and convenient methodology for the coupling of aryl iodides and thiophenols. The significant improvements offered by this procedure are operational simplicity, excellent stereoselectivity, general applicability, high isolated yields of products and reaction in aqueous medium avoiding hazardous organic solvents. To the best of our knowledge this strategy of involvement of metal nanoparticles for these useful reactions are novel and not reported earlier.

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