Pergamon

Tetrahedron Letters 40 (1999) 2075–2078

TETRAHEDRON
LETTERS

Palladium Chloride and Tetraphenylphosphonium Bromide Intercalated Clay as a New Catalyst for the Heck Reaction

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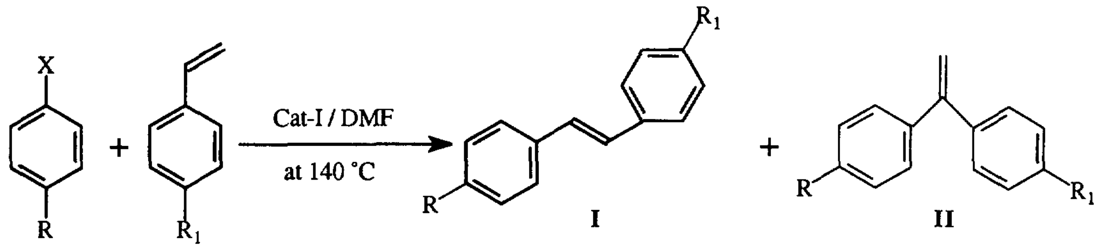
Received 8 December 1998; accepted 8 January 1999

A new modified clay material, prepared by intercalating palladium chloride and tetraphenylphosphonium bromide into montmorillonite K10 clay, catalyzes the Heck reaction and affords *trans*-stilbenes in high yields.

The palladium-catalyzed reaction of aryl halides with olefins is an important C–C bond forming reaction (Heck)[1] in organic chemistry. Over the past decade, the use of additives such as silver (I) or thallium (I) salts, organotrifluoromethanesulfonates and tetraalkylammonium salts have provided marked improvements in Heck-type reactions.[1c] Recently it has been demonstrated that $PdCl_2$ or $Pd(OAc)_2$ in the presence of tetraphenylphosphonium salts,[2a] or palladium complexes of (diisopropylphosphino)-ferrocenes[2b] exhibit high catalytic activity.[2] The palladium salt employed in homogeneous reactions is reduced *in situ* to an active zero valent palladium species. The regenerated Pd^{II} species in such reactions[1c] have strenuous requirements of separation and processing before they can be reused further. In order to improve the catalyst efficiency and its reusability in industrial context, the development of new catalytic materials is desired.[3a] Clays and cation-exchanged montmorillonite K 10 clay, clay-supported reagents and pillared clays[3-9] have found extensive applications in organic synthesis under relatively mild reaction conditions. These modified clay materials, unlike other conventional catalysts, enjoy considerable advantages such as ease of handling, recyclability, low cost, and easier modulation of acidity levels by suitable exchange of cations. Our interest in modified clay materials and their application in organic functional group conversions[9] prompted us to explore the arylation of olefins using new clay-based catalyst system, palladium chloride and tetraphenylphosphonium bromide intercalated clay (Cat-I). Herein, we report our preliminary results using this $PdCl_2/Ph_4PBr$ intercalated clay in the Heck reaction.

In a typical example, an equimolar amount (1 mmol) of aryl halide and styrene is refluxed with mixture of catalyst and sodium acetate in dimethylformamide (**Scheme**) with continuous stirring for a specified time as shown in the table.

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00149-5



R = H, CHO; R_1 = H, Cl, Me, OMe; X = I, Br

Scheme

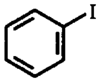
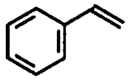
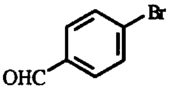
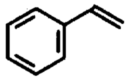
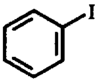
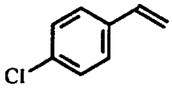
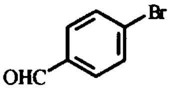
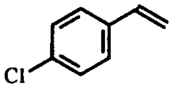
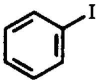
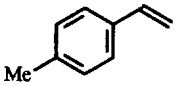
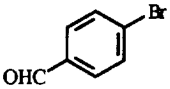
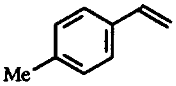
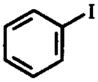
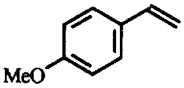
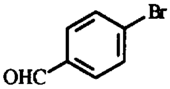
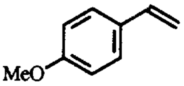
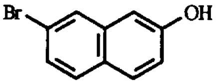
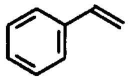
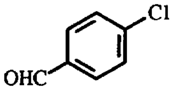
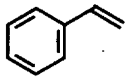
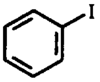
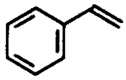
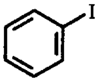
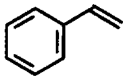
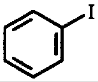
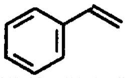
Our results for the formation of a variety of stilbenes are summarized in the Table and are exemplified by a variety of substrates. Styrene bearing an electron withdrawing substituent undergo faster reactions when compared to styrenes bearing electron releasing group appended. The reaction rate using this heterogeneous catalyst is much faster, even at these low concentrations, when compared to the corresponding homogeneous reaction conditions. In the case of *p*-chlorobenzaldehyde (entry 10), only the formation of stilbene is observed that is devoid of aldehyde functionality. In general, the reaction with chloro compounds did not work as well. We have also explored this reaction in aqueous media using ultrasound activation (entry 11) and observed the formation of stilbenes in good yields.

In conclusion, this method is superior to the reactions in the homogeneous medium because of the organized assembly of aluminosilicate layers which leads to the formation of quantitative yield of products in a short time. The manipulative ease and the separation of the catalysts by simple filtration are some of the salient features of the reactions described here. The subsequent reuse of the catalyst (entries 12 and 13) without loss in activity makes this an ideal protocol, useful and attractive alternative to the currently available methods.

The catalyst was prepared by refluxing 6 g of sodium-exchanged clay[9a,10] with the solution of 300 mg of $PdCl_2$ and 1.5 g of tetraphenylphosphonium bromide in 50 ml of water for 48 h. The clay material was then filtered, washed thoroughly with water and dried overnight in an oven at 100-110 °C.

General protocol for the preparation of stilbenes:- In a typical experiment, the clay catalyst (20 mg) and sodium acetate (164 mg, 2 mmol) were intimately mixed using a pestle and mortar and then transferred to a round bottomed flask. To this, equimolar amounts (1 mmol) of starting materials (styrene and aryl halide) were added followed by dimethylformamide (2.0 ml) and the contents refluxed with continuous stirring for the time specified in the Table. After completion of the reaction, monitored by TLC examination, the mixture was quenched with water and the products extracted into ethyl acetate. The organic layer was washed with excess of water to remove any residual dimethylformamide. The products, after removal of the solvent, were analyzed by GC-MS analysis (Hewlett-Packard model 5890 gas chromatograph with a mass spectrometer). The identity of the products were confirmed on the basis of their spectral data. The clay material was collected from the aqueous layer, washed with organic solvent and dried overnight in an oven and reused (entries 12 and 13) in reactions without any loss in activity.

Table: Product distribution in Heck reaction catalyzed by palladium chloride and tetraphenylphosphonium bromide intercalated clay[a]

Entry	Starting Materials		Reaction Conditions (h)	Products[b]	
				I	II
1			2	95	05
2			3	98	02
3			1	98	02
4			1.5	99	01
5			2	97	03
6			3	99	01
7			15	80	05
8			25	98	02
9			3	97	03
10			36[c]	61	02
11			3[d]	95	05
12			2[e]	95	05
13			2[f]	93	07

[a] The relative amounts of product formation are determined by GC-MS analysis. [b] The products exhibited physical and spectral properties in accord with the assigned structures. [c] Refers to the formation of products I and II which is avoid of aldehyde functionality. [d] Result refers to the use of ultrasound activation in aqueous media. [e,f] Results obtained using recycled clay catalyst once and twice, respectively.

ACKNOWLEDGMENT: We thank Prof. T. J. Pinnavaia for help in the preliminary characterization of the intercalated clay materials. We are grateful for financial support to the Texas Research Institute for Environmental Studies (TRIES).

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