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Montmorillonite–palladium–copper catalyzed cross-coupling of methyl acrylate with aryl amines

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Abstract

Heck vinylation reactions of different anilines were performed with vinylacetate by using palladium chloride and copper nitrate intercalated montmorillonite K10 clay as catalyst. The substituted methylcinnamates were obtained in good yields without simultaneous side reaction to stilbenes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: arylation; heck reactions; aryl amines; montmorillonite; palladium; copper.

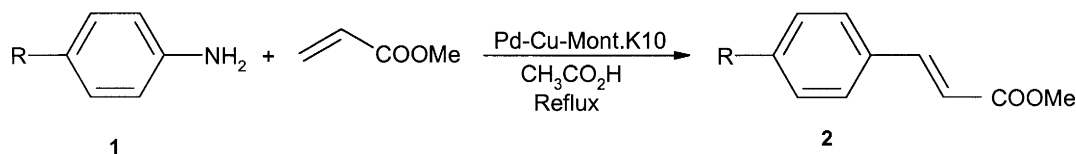
Heck vinylation of substituted aromatics is one of the most frequently studied reactions in organic synthesis. The reaction is generally performed with aryl halides using homogeneous catalysts.^{1–7} Recently, several publications have appeared on the development of heterogeneous catalysts^{8–10} such as modified montmorillonite K10 clay^{11,12} in order to perform Heck vinylation in a simple and inexpensive way. By comparison with palladium diacetate and triphenylphosphine, palladium intercalated montmorillonite K10 is less expensive for the synthesis of methyl substituted cinnamates from aryl halides (X=r, I).^{13,14}

From an industrial point of view, aryl halides have no considerable commercial interest because of further reactions leading to stilbenes^{3,7,11,12} and the expensive cost of catalysts or halides used (X=Br, I). For these reasons, many studies on the amination of aryl halides^{15–17} and on the vinylation of substituted anilines with inexpensive simple salts were realized.^{18–21} In this framework, two different mechanisms have been suggested: the first one is a C–N bond cleavage of aryl amines when treated with palladium salts and acetic acid to give Ar–Pd–N species.¹⁸ When the vinylation is performed in the presence of nitrites,^{19,21} oxidative addition of aryldiazoniums to palladium occurred, yielding Ar–Pd species.²²

To the best of our knowledge, no direct synthesis of methyl cinnamates from anilines by using Pd–Cu exchanged montmorillonite K10 clay^{23–25} (Pd–Cu–Mont.K10) as heterogeneous catalyst has been described. We thus investigate the use of this catalyst for the arylation of methyl acrylate with aryl amines (Scheme 1) and the influence of *tert*-butyl nitrite on this reaction. Our results are summarized in Table 1.

By using the modified K10 clay as catalyst, good yields in methyl cinnamates were obtained from aromatic amines and no stilbenes by-products were formed.²⁷ This vinylation is selective and no side

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Scheme 1.

Table 1

Pd-Cu-Mont.K10 catalyzed synthesis of methyl cinnamates from substituted anilines²⁶

Entry	Substrate	Product	Time (h)	Yield (%)
1			5	66 ^a [11] ^c
2			4	68 ^a [37] ^c
3			7	76 ^a
4			7	72 ^a
5			5	63 ^a
6			4	75 ^a [13] ^c 70 ^b

^aYields were determined by ¹H NMR or GC. ^bRecrystallized yield. ^cLiterature yields obtained when palladium diacetate in AcOH-dioxane was used. ^{14,18}

reaction from a halogen (entries 3 and 4) was observed. Interestingly, the addition of an equimolar amount of *tert*-butyl nitrite to the heterogeneous catalyst hindered the reaction. Thus, this arylation can be favorably compared to other modified Heck reactions performed with aromatic amines and simple palladium catalysts.¹⁸

This work allowed us to synthesize a monomer (Table 1, entry 6) in an inexpensive way.^{28,29} Polymerization of this compound yields electron transfer polymer¹⁴ which can be used as a cheap reagent to remove dissolved oxygen from organic solvents.³⁰

Conclusively, we have described a new variation of Heck reactions giving good yields of cinnamates starting from anilines, without the formation of by-products.

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26. General procedure for the arylation of methyl acrylate (Table 1, entry 6): A solution of methyl acrylate (8.0 g, 93.5 mmol) in dichloromethane (10 mL) was slowly added to a mixture of 2,5-dimethoxy-1-(4'-aminobenzyl)benzene (11.3 g, 46.7 mmol), Pd–Cu–Mont.K10 clay (1.1 g) in acetic acid (50 mL) and dichloromethane (15 mL). The suspension was refluxed with stirring until the starting material was completely consumed as judged by HPLC analysis. The catalyst was collected²⁹ and the cooled reaction mixture was stirred with 100 mL of water. The aqueous layer was extracted with dichloromethane (50 mL), and the organic phases were dried over CaCl₂ and concentrated under vacuum. The brown solid was recrystallized from petroleum ether/diethyl ether giving the monomer **2** (10.2 g, 70%) as a white solid, mp 83°C; IR (KBr): 2995, 2835, 1710, 1600, 1500, 1430, 1320, 1230, 1170, 1020 cm⁻¹; ¹H NMR (CDCl₃): δ 3.72 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 3.95 (s, 2H), 6.38 (d, J=16.1 Hz, 1H), 6.66 (d, J=3.0 Hz, 1H), 6.72 (dd, J=8.8 Hz, J=3.0 Hz, 1H), 6.79 (d, J=8.8 Hz, 1H), 7.22 (d, J=8.1 Hz, 2H), 7.42 (d, J=8.1 Hz, 2H), 7.66 (d, J=16.1 Hz, 1H); ¹³C NMR (CDCl₃): δ 36.1, 51.7, 55.7, 56.0, 111.5, 116.9, 128.2, 128.4, 130.2, 132.1, 143.7, 144.9, 151.7, 153.6, 167.7; *m/z* 312 (M⁺, 100). Anal. calcd for C₁₉H₂₀O₄: C, 73.06; H, 6.45. Found: C, 72.92; H, 6.29.
27. At the end of the reaction, only final product and a small amount of polymers are observed in the reaction mixture.
28. Accordingly, the preparation of the catalyst,^{23,25} only 0.0029 g of Pd were necessary to synthesize methyl cinnamates starting from 100 g of substituted aryl amines.
29. The catalyst from the reaction mixture was recovered by simple filtration and was successfully reused once without losing its activity in the vinylation of 2,5-dimethoxy-1-(4'-aminobenzyl)benzene (Table 1, entry 6). Ramchandani reused this catalyst three times in vinylation of aryl iodides.²⁵
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