

Synthesis of Aromatic Vinyl Esters by Exchange Reaction Catalyzed with Pd(II)

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Abstract: Pd(II) catalyzed the exchange reaction of vinyl acetate with aromatic acids to produce the corresponding vinyl esters in good yields.

Keywords: Palladium, exchange reactions, vinyl acetate, aromatic acids, aromatic vinyl esters.

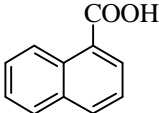
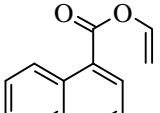
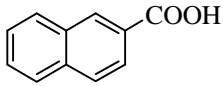
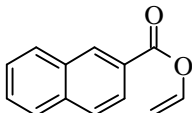
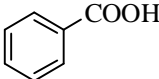
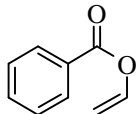
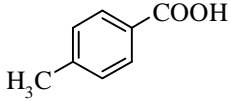
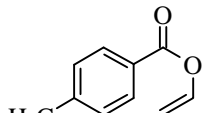
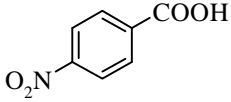
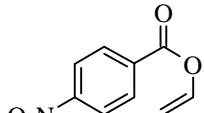
Introduction

Palladium catalyzed oxidation of organic compounds is an expanding area of organopalladium chemistry with many application in industrial processes [1]. Today there is an increasing need for mild aerobic catalytic processes for energy saving and environment reasons. Most Pd(II) reactions with an organic substrate are oxidative in nature [2,3] resulting in reduction of Pd(II) to Pd(0) and giving oxidized organic products [4,5]. However, there are some Pd(II) reactions in which the oxidation state of the Pd(II) remains unchanged, and are thus truly catalytic [6]. One class of these non-oxidative reaction is the Pd(II)-catalyzed exchange reactions [7-10]. These reactions can be used industrially to prepare vinyl esters from vinyl acetate, and are also suitable for laboratory preparations. Vinyl esters of a few aliphatic carboxylic acids are produced by the exchange reaction of cheaply available vinyl acetate with acids [11-13]. We wish to report the use of the aromatic acid as the exchange component with vinyl acetate for preparation of the various vinyl aromatic esters.

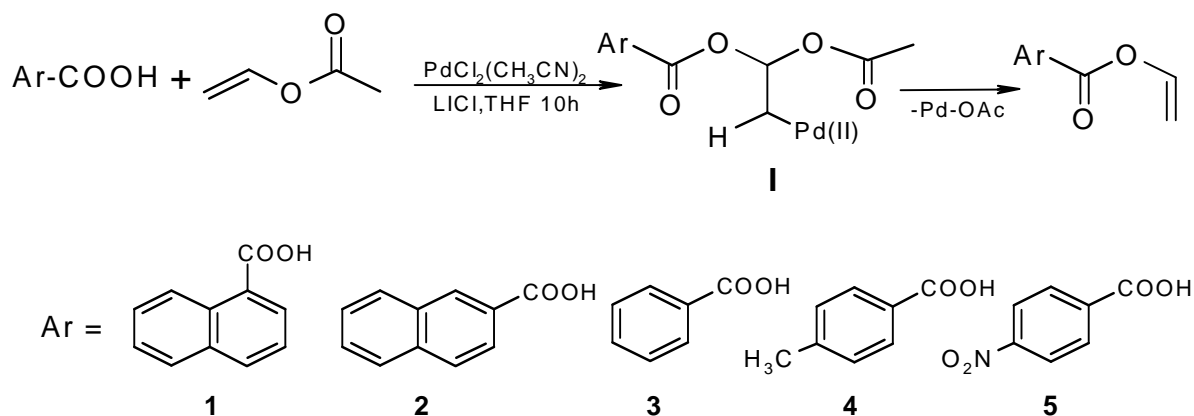
Results and Discussion

The Pd(II)-catalyzed exchange reaction is operationally simple, the reaction conditions are mild, the reaction displays the specificity typical for PdCl₂(CH₃CN)₂ complexes and is also convenient, i.e., no moisture-free and oxygen-free manipulations are required. In the process of investigating the Pd(II)-catalyzed esterification we observed that a) a much faster reaction is achieved in the presence of LiCl than with NaCl or LiBr, b) the solvent could be omitted, however this resulted in a considerably slow reaction, c) a much faster reaction was achieved in 20% THF or other ethers, d) addition of a base such as Li₂CO₃ suppressed the formation of product completely resulting in the formation of other adducts in the presence of base, e) elevated temperatures more than 60.8°C give an unsatisfactory product distribution and a somewhat slower conversion (Table 1).

Table 1. The structure and yields of aromatic vinyl esters produced by palladium catalyzed reactions of aromatic acids and vinyl acetate.

Aromatic acid	Product	Yield
		53%
		51%
		43%
		47%
		39%

The formation of vinyl esters can be envisaged as shown in Scheme 1. Coordination of vinyl acetate to PdCl_2 followed by oxypalladation gives the s-bond intermediate, where the oxygen nucleophile has attacked the more electron deficient carbon of vinyl acetate. Evidence for this type of intermediate comes from the effect of substitution on the aromatic ring which affects the reaction rate. Electron withdrawing groups decrease the reaction rate which is consistent with a positively charged transition state leading to the intermediate (I).



Scheme 1.

Experimental

The $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ was prepared according to the literature method [14]; other compounds were purchased from Merck and were used as received. The NMR spectra were recorded on a Bruker AC 80 (80MHz 1H and 20MHz 13C); the 1H-NMR and 13C-NMR chemical shifts are given relative to TMS in CDCl_3 . All reactions were run in a 100 ml heavy-walled sealed Pyrex tube, with magnetic stirring.

Typical procedure: Dichloro bis(acetonitrile) palladium(II) (1.5 mmol) was charged together with 50 ml vinylacetate and 10 ml THF in a 100 ml tube. The mixture was stirred until a clear orange solution was obtained (20 min.) whereupon the aromatic acid (4.5 mmol) and lithium chloride (0.02 mol) were added. The reaction mixture was stirred at 50-60 C for 8-16 hours. The reaction mixture was cooled down to room temperature and 20 ml of 10% sodium carbonate solution was added. After extraction of the aqueous phase and evaporation of the combined organic layer, the residual oil was subjected to flash chromatography on silica gel using hexane/ ethyl acetate (90:10) as eluent.

2: 1H-NMR δ : 4.5 (dd, $J=1.6$ and 6.4 Hz, 1H), 4.9 (dd, $J=1.6$ and 13.6 Hz, 1H), 7.5 (m, 6H), 8.1 (dd, $J=0.8$ and 7.2 Hz, 1H), 8.8 (m, 1H).

13C-NMR δ : 98.6, 124.9, 125.8, 126.3, 127.0, 128.6, 129.2, 131.5, 132.2, 134.4, 134.8, 142.1, 164.6.

3: 1H-NMR δ : 4.5 (dd, $J=1.6$ and 5.6 Hz, 1H), 5.0 (dd, $J=1.6$ and 13.6 Hz, 1H), 7.6 (m, 7H), 8.7 (s,

1H).

^{13}C -NMR δ : 98.6, 125.6, 126.6, 127.2, 128.3, 128.8, 129.0, 129.9, 132.2, 132.9, 136.3, 142.1, 164.1.

4: 1H-NMR δ : 4.6 (dd, $J=1.6$ and 6.4 Hz, 1H), 4.9 (dd, $J=1.6$ and 13.6 Hz, 1H), 7.4 (m, 4H), 8.0 (m, 2H).

^{13}C -NMR δ : 98.8, 129.1, 130.6, 132.1, 134.2, 142.1, 164.2.

5: 1H-NMR δ : 2.3 (s, 3H), 4.6 (dd, $J=1.6$ and 6.4 Hz, 1H), 4.9 (dd, $J=1.6$ and 13.6 Hz, 1H), 7.6 (m, 5H).

^{13}C -NMR δ : 22.1, 96.8, 128.2, 128.7, 130.4, 140.1, 141.7, 164.3.

6: 1H-NMR δ : 4.7 (dd, $J=1.6$ and 5.8 Hz, 1H), 5.0 ($J=1.6$, 13.4 Hz, 1H), 7.5 (dd, $J=5.8$ and 13.4 Hz, 1H), 8.4 (m, 4H).

^{13}C -NMR δ : 97.5, 130.4, 130.8, 131.7, 139.6, 143.4, 164.5.

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References and Notes

1. Tsuji, J. *Synthesis* **1990**, 739-749.
2. Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*, Reidel, Dordrecht, **1980**, 41-84.
3. Tsuji, J. *Palladium Reagents and Catalysts*, Wiley, New York, **1996**, 19-108.
4. Jira, R.; Freiesleben, W. *Organomet. React.* **1972**, *3*, 1-190.
5. Larock, R. C.; Hightower, T. R. *J. Org. Chem.* **1993**, *58*, 5298-5300.
6. Kaneda, K.; Uchiyama, T.; Fujiwara, Y.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1979**, *44*, 55-63.
7. Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabel, A. *Angew. Chem.* **1962**, *74*, 93-102.
8. McKeon, J. E.; Fitton, P. *Tetrahedron* **1972**, *28*, 233-238.
9. Keith, D. D.; Tortora, J. A.; Ineichen, K.; Leimgruber, W. *Tetrahedron* **1975**, *31*, 2633-2636.
10. Divers, G. A.; Berchtold, G. A. *Synth. Commun.* **1977**, *7*, 43-48.
11. Henry, P. M. *Acc. Chem. Res.* **1973**, *6*, 16-24.
12. Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7316-7322.
13. Bjorkquist, D. W.; Bush, R. D.; Ezra, F. S.; Keough, T. *J. Org. Chem.* **1986**, *51*, 3192-3196.
14. Kharasch, M. S.; Seyler, R. C.; Mayo, R. R. *J. Am. Chem. Soc.* **1938**, *60*, 882-884.

Samples Availability: Available from the authors.