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Pd(II) And Hg(II)-Catalyzed Acetalization Reaction

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ABSTRACT

Pd(II) and Hg(II) catalyzed the acetalization of vinyl acetate with aryl alcohols to produce the corresponding acetal. Insights into the conformation of these compounds come from the analysis of ¹H-NMR spectra. © 2007 Trade Science Inc. -INDIA

INTRODUCTION

Acetals and ketals are among the most important protecting group and perfume materials and industrial materials of organic synthesis. There are now many methods to synthesize them^[1-12]. In the same way synthesis of dioxepines has received considerable attention^[13-15]. The most efficient approach to the dioxepine has been the nucleophilic substitution of dihalides with compounds bearing two OH groups such as 1,1'-binaphthyl-2,2'-diol or biphenyl-2,2'-diol. Acetalizations of terminal olefins bearing electron-withdrawing groups upon treatment with optically active 1,3-diols in the presence of a Pd(II) catalyst^[16-18] prompt us to report a new approach to some derivatives of acetals and dioxepine.

Treatment of 1,1'-binaphthyl and biphenyl-2,2'-diol with catalytic amount of PdCl₂(CH₃CN)₂ in vinyl acetate produce the corresponding acetals. a

and b, respectively. In the same way reaction of p-cresol, p-bromophenol, and phenol with Hg(OAc)₂ in vinyl acetate produce the corresponding acetals. c-e respectively figure 1 and TABLE

These reactions proceed under mild conditions. The oxygen nucleophile has attacked the more electron deficient carbon of metal π-complex of vinyl acetate. The acetyl part of vinyl acetate can be exchanged with OH group via dealkoxy metalation. This is a reaction in which the oxidation state of the Pd(II) and Hg(II) remains unchanged and thus truly catalytic. Exchange reaction gives vinyl ether, which undergoes cyclization or another addition of aryl alcohol to give the acetal. In the last step acetal formation can be catalyzed by Pd(II), Hg(II) or H⁺ that generated in reaction figure 2.

Insight of the acetals a-e comes from the analysis of their ¹H-NMR spectra. The chemical shifts of the hydrogen atom on the acetal carbon and the methyl

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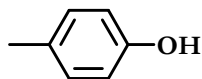


Figure 1

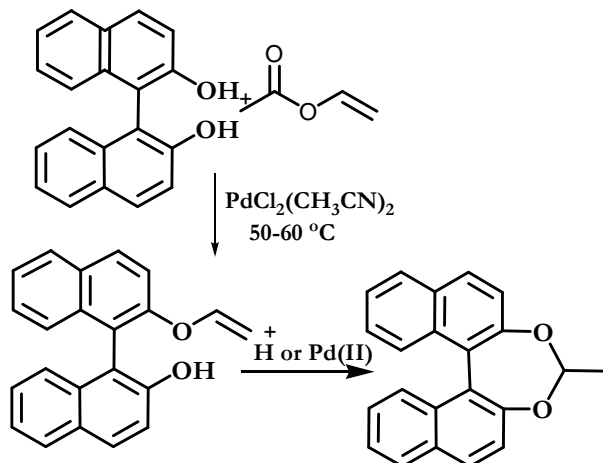


Figure 2

groups of these compounds are nearly the same.

EXPERIMENTAL

The $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and 1,1'-binaphthyl-2,2'-diol were prepared according to the literature methods^[7],

TABLE

Ar = Reactant	Product	
		a
		b
		c
		d
		e

other compounds were purchased from Merck and were used as received. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ chemical shifts are given relative to TMS in CDCl_3 .

Typical procedure

Dichloro bis(acetonitrile)palladium(II) (1.5 mmol) was charged together with the 50ml vinylacetate and 10ml THF in a 100 ml tube. The mixture was stirred until a clear orange solution was obtained (20min.) where upon the biaryl diol (4.5mmol) and lithium chloride (0.02mol) was added and the tube closed heating with stirring at 50-60°C for 8-16 hours. The reaction mixture was cooled down and 20ml of 10% sodium carbonate was added. After extraction of the aqueous phase and evaporation of the combined organic layers, the residual oil was subjected to flash chromatography on silica gel using hexane/ethylacetate (90:10) as eluent.

Typical procedure for c-e

Aryl alcohol (0.05 mol) and $\text{Hg}(\text{OAc})_2$ (1mmol) was charged together with the 0.1 mol vinylacetate and 25 ml CH_2Cl_2 . The mixture was heating with stirring at reflux teperature for 24 hours. After extraction of the aqueous phase and evaporation of the combined organic layers, the residual oil was subjected to flash chromatography on silica gel using petroleum ether/ethylacetate (90:10) as eluent.

a: $^1\text{H-NMR}$ δ : 1.6(d, $J=4.8$ Hz, 3H), 6.0(q, $J=4.8$ Hz, 1H), 7.4 (m, 8H), 7.9(m, 4H). $^{13}\text{C-NMR}$ δ : 20.9, 111.1, 121.7, 123.9, 125.5, 125.6, 126.6, 126.7, 126.9, 127.6, 127.7, 127.9, 128.9, 129.0, 130.0, 130.8, 132.2, 132.4, 132.9, 133.0, 149.7, 152.8. MS m/z (%): 312(M^+ , 22), 268(10), 239(100).

b: $^1\text{H-NMR}$: 1.7(d, $J=5.6$ Hz, 3H), 5.9(q, $J=5.6$ Hz, 1H), 7.3(m, 4H), 7.6(m, 2H). $^{13}\text{C-NMR}$ δ : 21.2, 108.1, 122.3, 125.2, 129.0, 129.2, 131.3, 154.1. MS m/z (%): 212(M^+ , 10), 211(80), 168 (42), 43(100).

c: $^1\text{H-NMR}$ δ : 1.7(d, $J=5.2$ Hz, 3H), 2.3(s, 6H) 5.9 (q, $J=5.2$ Hz, 1H), 6.9(4H), 7.1(m, 4H). $^{13}\text{C-NMR}$ δ : 20.9, 21.0, 99.0, 118.1, 130.4, 132.1, 154.2. MS m/z (%): 242(M^+ , 10), 135(100), 91(63).

d: $^1\text{H-NMR}$: 1.6(d, $J=5.2$ Hz, 3H), 5.9(q, $J=5.2$ Hz, 1H), 6.9(4H), 7.4(m, 4H). $^{13}\text{C-NMR}$ δ : 20.5, 98.8, 115.0, 120.0, 132.9, 155.2. MS m/z (%): 372(M^+ , 5), 199(100), 120(70).

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e: $^1\text{H-NMR}$ δ : 1.8(d, $J=5.1$ Hz, 3H), 6.1(q, $J=5.1$ Hz, 1H), 7.14(6H), 7.4(4H). $^{13}\text{C-NMR}$ δ : 20.9, 98.6, 118.1, 122.9, 130.0, 156.4. MS m/z (%): 214(M^+ , 10), 121(100), 93(20).

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