Tetrahedron. Vol. 28, pp. 233 to 238. Pergamon Press 1972. Printed in Great Britain

THE PALLADIUM (II) CATALYZED VINYL INTERCHANGE REACTION—II

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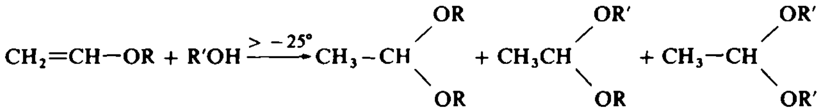
(*Received in USA* 4 *June* 1971; *Received in the UK for publication* 9 *June* 1971)

Abstract—Acetals formed when the vinyl ether interchange reaction catalyzed by $(PhCN)_2PdCl_2$ is run at temperatures above −25° are formed by a reaction catalyzed by HCl, which results from decomposition of the catalyst. New catalysts, the *cis*-complexes of palladium acetate with bidentate ligands, have been prepared. With these new catalysts the ether-interchange reaction can now be run at ambient temperatures without acetal formation or catalyst-decomposition. These complexes are also very efficient catalysts for the vinyl ester interchange reaction.

IN A previous paper,[1] a general method for the preparation of vinyl ethers by a palladium(II) catalyzed vinyl interchange reaction was described. It was found that, while palladium(II) salts of strong acids for example $PdCl_2$, were efficient catalysts for this reaction at temperatures below −25°, at higher temperatures acetal formation also occurred along with reduction of the catalyst to palladium metal.

$$CH_2{=}CH{-}OR + R'OH \rightleftharpoons CH_2{=}CH{-}OR' + ROH$$



$$CH_2{=}CH{-}OR + R'OH \xrightarrow{> -25^\circ} CH_3{-}CH\begin{matrix}OR\\OR\end{matrix} + CH_3CH\begin{matrix}OR'\\OR\end{matrix} + CH_3{-}CH\begin{matrix}OR'\\OR'\end{matrix}$$

We have now found that this acetal-forming reaction is not catalyzed by Pd(II) but is catalyzed by acid formed by reduction of the catalyst. When precautions are taken to eliminate the formation of acid, the vinyl interchange reaction can be conveniently and efficiently run at ambient temperatures.

Since the acetal-forming reaction and the catalyst decomposition were coincident at temperatures above −25°, it appeared that these two reactions were related. The palladium salts of strong acids were stable under the reaction conditions at temperatures below −25°, but with Pd salts of weak acids, for example $Pd(OCOCH_3)_2$, reduction to Pd metal was appreciable even at −40°. However, when these weak acid salts were reduced, no acetals were formed even if the reaction was run at room-temperature. It thus appeared that the acetal-forming reaction was catalyzed by HCl, formed by reduction of $(PhCN)_2PdCl_2$, rather than by Pd(II) or Pd(O). This conclusion was readily confirmed, since the reaction of ethylene glycol and vinyl ethyl ether gave a quantitative yield of 2-methyl-1,3-dioxolane when treated with either $(PhCN)_2PdCl_2$ or an equivalent amount of dry HCl at 0°.

The effect of adding alkaline buffers to the $PdCl_2$ catalyzed vinyl-interchange reaction provided additional evidence that the acetal forming reaction was acid catalyzed. When $(PhCN)_2PdCl_2$ was added to a solution of vinyl butyl ether and ethanol in 1,2-dimethoxyethane at room temperature, there was a fast reaction to form acetals. However, when the reaction was repeated in the presence of sodium dihydrogen phosphate, an equilibrium mixture of vinyl ethyl ether and vinyl butyl ether was formed in 3½ minutes and no acetals were formed. The addition of a buffer, therefore, suppressed acetal formation, but it did not, however, stabilize the catalyst, since Pd metal was precipitated throughout the course of the reaction. It is of interest that in the related $PdCl_2$ catalyzed vinyl-ester-interchange reaction,[2] reduction of the catalyst also occurs, although at a much slower rate than in the ether interchange reaction.

$$CH_2{=}CH{-}OCOR + R'CO_2H \xrightleftharpoons{PdCl_2} CH_2{=}CH{-}OCOR' + RCO_2H$$

The use of a buffer did, however, allow the vinyl-interchange reaction between a vinyl ester and an alcohol to be demonstrated.

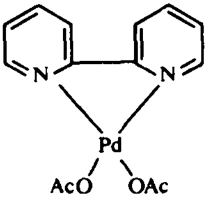
$$CH_2{=}CH{-}OCOCH_3 + C_2H_5OH \xrightleftharpoons[NaH_2PO_4]{PdCl_2} CH_2{=}CH_2{-}OC_2H_5 + CH_3CO_2H$$

When $(PhCN)_2PdCl_2$ was added to a mixture of vinyl acetate and ethanol at room temperature, there was a rapid reaction to form 1,1-diethoxyethane (at temperatures below 0° there was no reaction) but if the reaction was repeated with sodium dihydrogen phosphate present, the reaction product was vinyl ethyl ether.

It therefore appeared that the acetal forming reaction was catalyzed by HCl formed during the course of the interchange reaction. This HCl could be formed by solvolytic displacement of chloride from a $PdCl_2$ species, but more likely results from the reduction of $PdCl_2$ or one of its complexes formed during the course of the reaction. Therefore, since the inability to run the ether-interchange reaction at ambient temperatures, and the formation of undesirable side products, were apparently due to the instability of the Pd(II) salts used as catalysts, attempts were made to develop more stable catalytic complexes.

Catalysts based on Pd(II) acetate or salts of acids of similar strength cannot give rise to acetal formation, since strong acids cannot be formed by decomposition of these salts. Unfortunately palladium acetate and similar compounds are generally too unstable toward reduction to Pd metal to be useful catalysts near ambient temperatures. We, therefore, undertook to stabilize Pd salts of weak acids, while retaining catalytic activity. Complexes of these salts with monodentate strong sigma donor ligands (e.g. pyridine, triethylphosphine, triphenylphosphine, etc.) were prepared and were found to exhibit excellent stability, but unfortunately they were also found to be essentially inert as catalysts for the vinyl-interchange reaction. In these complexes, the strong sigma donor ligands occupy mutually trans positions in the substitution plane of the metal,[3] leaving only two non-adjacent coordination sites for participation in the interchange reaction. The loss of catalytic activity in these complexes, therefore, suggested that two available adjacent coordination sites were essential for the complex to function as a catalyst, and that cis complexes of Pd salts should be much more effective catalysts. In these complexes, two cis coordination sites would be available and additionally these should be very substitution labile sites since both are now trans to a strong donor (strong trans effect) ligand. Several cis complexes of Pd salts of weak acids were therefore prepared.

The two most readily available complexes, diacetato(2,2′-bipyridyl)palladium(II) (1)[4] and diacetato(1,10-phenanthroline)palladium(II) (11) were found to be very efficient catalysts for the vinyl ether interchange reaction, and were stable in the reaction mixtures at temperatures as high as 80°. Other complexes such as diacetato-(N,N,N′,N′-tetramethylethylenediamine)palladium(II) and diacetato(P,P,P′, P′-tetraphenyl-1,2-diphosphinoethane)palladium(II) were also found to be effective catalysts.



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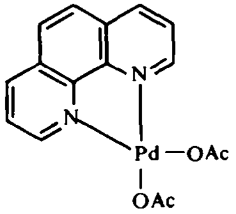


II

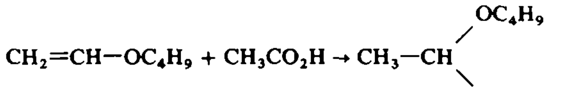
In the presence of I or II, vinyl butyl ether reacted with ethanol and ethylene chlorohydrin at room temperature to give vinyl ethyl ether and 2-chloroethyl vinyl ether. No other products such as acetals could be detected. On large-scale runs catalyst was readily removed during work-up by precipitation on the addition of pyridine or by adsorption on activated charcoal. It has been found that these complexes adsorbed on charcoal also will function as catalysts in these reactions. It has previously been shown that the vinyl ether interchange reaction catalyzed by $(PhCN)_2PdCl_2$ at temperatures below −25° is stereospecific and proceeds with inversion of configuration. The interchange reaction catalyzed by complexes I and II likewise was found to be stereospecific, proceeding with inversion. Thus the reaction of *trans*-ethyl propenyl ether with propanol at 60° gave *cis*-propyl propenyl ether as the initial product. This reaction using II as the catalyst is illustrated in the table below. It therefore appears likely that the interchange reaction catalyzed by I and II proceeds by the same mechanism[1] as the reaction catalyzed by $(PhCN)_2PdCl_2$. It is noteworthy that in these ether interchange reactions catalyzed by these complexes no acetals were ever formed and no reduction of the catalyst occurred.

TABLE 1. THE REACTION OF TRANS-ETHYL PROPENYL ETHER WITH PROPANOL CATALYZED BY DIACETATO (1,10-PHENANTHROLINE) PALLADIUM (II) AT 60°

Time (mins)	% Conversion	% Composition			
		Ethyl propenyl ether		Propyl propenyl ether	
		cis	*trans*	*cis*	*trans*
60	6·8	6	94	100	0
120	7·8	6	94	98	2
240	8·2	8	92	95	5
360	8·7	13	87	96	4
480	10·8	12	88	94	6

The *cis* palladium acetate complexes were also found to be excellent catalysts for the interchange reaction between a vinyl ester and a carboxylic acid. Thus the reaction of vinyl acetate with propionic acid and lauric acid gave vinyl propionate and vinyl laurate respectively. The efficiencies of these reactions were essentially quantitative and the catalysts were extremely stable and could be used repeatedly. These catalysts are, therefore, markedly superior to $PdCl_2$, which under the same conditions was slowly reduced to palladium metal.[5]

These *cis* complexes also catalyzed the addition of carboxylic acids to vinyl ethers to give 1-acyloxy-1-alkoxyethanes. Thus the addition of acetic acid to vinyl butyl ether gave a quantitative yield of 1-acetoxy-1-butoxy ethane.



$$CH_2{=}CH{-}OC_4H_9 + CH_3CO_2H \rightarrow CH_3{-}CH\begin{matrix} \diagup OC_4H_9 \\ \diagdown OCOCH_3 \end{matrix}$$

Finally under more vigorous conditions these complexes would also catalyze the interchange reaction between a vinyl ester and an alcohol to give a vinyl ether.

To summarize, the use of the *cis* complexes of palladium acetate with bidentate ligands as catalysts in the vinyl ether and vinyl ester interchange reactions, has now made these reactions important synthetic routes to a large variety of vinyl ethers and esters. The ready availability of these complexes and their stability under the reaction conditions, plus, in the case of the ether reaction, the lack of acetal formation, make them by far the catalysts of choice.

EXPERIMENTAL

The reaction of vinyl ether with ethylene glycol

(1) *In the presence of* $(PhCN)_2PdCl_2$. Ethylene glycol (31·0 g) was added to a soln of $(PhCN)_2PdCl_2$ (0·77 g) in vinyl ethyl ether (54 g) at 0°. After stirring for 30 mins the mixture was flash-distilled (24°/0·3 mm), and the product was fractionally distilled to give 2-methyl-1,3-dioxolane (35·2 g, 95% yield, b.p. 80–82°).

(2) *In the presence of dry* HCl. Ethylene glycol (1·24 g) and vinyl ethyl ether (1·44 g) precooled to 0° were added to a soln of dry HCl (0·001 mole) in 1,2-dimethoxyethane (25 ml) at 0°. VPC analysis showed that there was a quantitative conversion to 2-methyl-1,3-dioxolane in less than 10 mins.

The vinyl-interchange reaction between vinyl butyl ether and ethanol in the presence of a buffer

Anhyd sodium dihydrogen phosphate (0·84 g) and bis(benzonitrile)palladium chloride (0·27 g) were added to 1,2-dimethoxyethane (25 ml). A soln of vinyl butyl ether (2·0 g) and EtOH (2·70 g) in 1,2-dimethoxyethane (5 ml) was added and the mixture was stirred at room temp and followed by VPC analysis.

An equilibrium state, vinyl ethyl ether (70%) and vinyl butyl ether (30%) was reached after 3½ mins and no other products were formed.

The reaction between vinyl acetate and ethanol to form vinyl ethyl ether

Bis(benzonitrile)palladium chloride (0·27 g) and sodium dihydrogen phosphate (0·84 g) were added to vinyl acetate (25 ml). A soln of EtOH (4·3 g) and cyclohexane (1.0 g) in vinyl acetate (5 ml) were added, the mixture was stirred at room temp and followed by VPC analysis.

After 8 mins there was a 31% conversion to vinyl ethyl ether (based on ethyl alcohol charged) and no acetals were formed.

Preparation of diacetato-(1,10-phenanthroline)palladium(II)

A soln of 1,10-phenanthroline (5·4 g) in benzene (250 ml) was added dropwise with stirring to a soln of palladium acetate (6·42 g) in benzene (200 ml). The mixture was filtered and the ppt was washed with light petroleum (b.p. 40–60°) and air-dried to give a pale yellow solid (11·1 g). Recrystallization from

CH_2Cl_2 gave diacetato-(1,10-phenanthroline)palladium(II) (5.6 g, m.p. 234°). (Found- C, 47·76%; H, 3·4; N, 7·03; Pd, 26·56. $C_{16}H_{14}N_2O_4Pd$ requires: C, 47·5; H, 3·48; N, 7·03; and Pd 26·30%).

The reaction of vinyl butyl ether with ethanol catalyzed by diacetato(2,2′-bipyridyl)palladium(II)

Vinyl butyl ether (2·0 g) was added to a soln of diacetato(2,2′-bipyridyl)palladium(II) (0·0007 mole) in EtOH (25 ml). The mixture was stirred at room temp and after 430 min there was a 93% conversion to vinyl ethyl ether. No other products could be detected.

The reaction of vinyl butyl ether with ethanol catalyzed by diacetato-(1,10-phenanthroline)palladium(II)

The above reaction was repeated using diacetato(1,10-phenanthroline)palladium(II) (0·007 mole) as catalyst instead of diacetato(2,2′-bipyridyl)palladium(II). After stirring at room temp for 240 min there was a 91% conversion to vinyl ethyl ether. No other products could be detected.

The preparation of 2-chloroethyl vinyl ether

Vinyl butyl ether (2·0 g) and $NaHCO_3$ (0·5 g) were added to a soln of diacetato(1,10-phenanthroline)-palladium(II) (0·15 g) in ethylene chlorohydrin (25 ml) and the mixture was stirred at room temp. The reaction was followed by VPC using a 15′ × ¼″, 6% Versamid 900 on Chromasorb G column at 135°.

The reaction proceeded as shown below:

Time (mins)	% Conversion to 2-Chloroethyl vinyl ether
50	14·5
135	25·0
180	29·1
240	33·0
300	35·5
360	38·1

The reaction of trans-*ethyl propenyl ether with propanol catalyzed by diacetato*(1,10-*phenanthroline*)*palladium*(II)

trans-Ethyl propenyl ether (2·0 g) was added to a soln of diacetato(1,10-phenanthroline)palladium(II) (0·28 g) in propanol (25 ml). (Cyclohexane (1·05 g) was also added as an internal standard for VPC analysis.) The mixture was heated to 60° and samples were removed at regular time intervals and analyzed by VPC.

Preparation of vinyl propionate

Vinyl acetate (10·32 g) and cyclohexane (3·0 g) were added to a soln of diacetato(1,10-phenanthroline)-palladium(II) (0·28 g) in propionic acid (100 ml). The mixture was heated to 50° and followed by VPC analysis. The reaction proceeded as shown below:

Time (mins)	% Conversion (to vinyl propionate)
60	26
120	46
180	57
240	68

The mixture was then concentrated to 40 ml by removal of the volatile products on a Buchi Roto-vapor (50/20 mm). The residue was diluted to 100 ml by the addition of propionic acid, and vinyl acetate (10·32 g) and cyclohexane (3 g) was added. The mixture was heated to 50° and followed as before.

Time (mins)	% Conversion (to vinyl propionate)
60	18
120	40
180	53
240	62
300	74

Reaction to form vinyl laurate

Diacetato(2,2′-bipyridylpalladium(II) (0·28 g) was dissolved in a soln of lauric acid (20·0 g) in chloroform (50 ml). Vinyl acetate (2·15 g) and cyclohexane (0·5 g) were added and the mixture was stirred at 50°. The reaction was followed by VPC analysis and proceeded as follows:

Time (hr)	% Vinyl acetate used
1	28
2	45
3	62

The only products formed in the reaction were acetic acid and vinyl laurate. The latter was isolated and identified by comparison of its NMR and IR spectra with those of an authentic sample.

The addition of acetic acid to vinyl butyl ether

Diacetato(1,10-phenanthroline)palladium(II) (0·25 g) vinyl butyl ether (12·0 g) and cyclohexane (3 g) (added as an internal standard for VPC analysis) were dissolved in AcOH (100 ml). VPC analysis showed a quantative conversion to 1-acetoxy-1-butoxyethane (retention time identical to that of an authentic sample) after stirring at room temp for 30 min.

The reaction of vinyl acetate and ethanol catalyzed by diacetato(1,10-phenanthroline)palladium(II)

Diacetato(1,10-phenanthroline)palladium(II) (0·5 g), vinyl acetate (2·0 g) and cyclohexane (1 g) were dissolved in EtOH (15 ml). The mixture was heated at 100° in a sealed tube for 1 hr. VPC analysis of the resultant product showed that there was an 11% conversion to vinyl ethyl ether.

The experiment was repeated, and after heating at 100° for 2 hr a 20% conversion to vinyl ethyl ether resulted.

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