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THE PALLADIUM (II) CATALYZED VINYL INTERCHANGE REACTION—I

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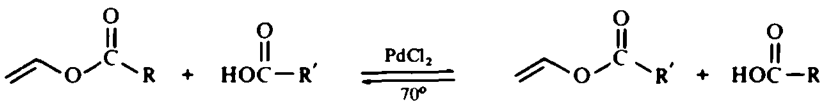
Abstract—The vinyl interchange reaction between vinyl ethers and alcohols is catalyzed by palladium (II) salts. The reaction is stereospecific and proceeds with inversion of configuration. A mechanism for the reaction is proposed.

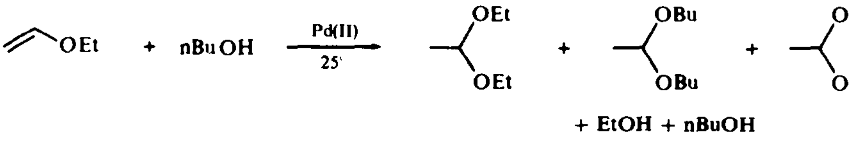
Vinyl interchange reactions between vinyl esters and carboxylic acids and vinyl ethers and alcohols using mercuric ion catalysts have been known for some time.[1] In addition to a mercuric salt, a strong acid co-catalyst is required, a factor which has limited the synthetic utility of such reactions and which appears to have complicated the study of the mechanisms of catalyst action.

Some time ago Smidt[2] *et al.* discovered that vinyl interchange between vinyl esters and carboxylic acids was rapid and efficient in the presence of small amounts of simple salts of Pd (II).



We have also studied the interchange of vinyl esters and ethers with nucleophiles of the type HA (e.g., carboxylic acids, alcohols, amides etc) in the presence of Pd catalysts. We have been able to develop a useful synthetic process for interchange of the vinyl group between vinyl ethers and alcohols. In addition, we have been able to establish with reasonable certainty the mechanism of catalyst activity.

When butanol is added to a solution of bis(benzonitrile) dichloropalladium (II) in vinyl ethyl ether at room temperature, a rapid exothermic reaction takes place accompanied by the appearance of metallic Pd. At the end of the reaction no vinyl ethers can be detected in the reaction mixture, which now consists of an apparent equilibrium mixture of alcohols and acetals.

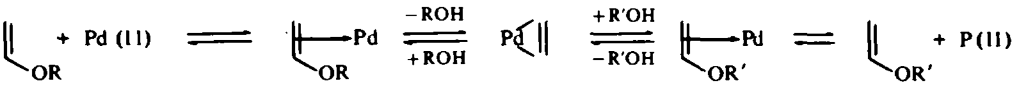


A similar reaction, in which n-butanol (0·5 mole) precooled to −40° was added to a solution of dichloro-bis(benzonitrile) palladium (II) (0·015 mole) in vinyl ethyl ether (0·5 mole) at −40°, proceeded smoothly to give an equilibrium mixture of vinyl ethers: no other products were formed.

The reaction proceeds at a detectable rate at −65°, but catalyst solubility is a problem at these low temperatures. The rate increases rapidly above −40° but when the temperature exceeds about −25° (the exact temperature is somewhat dependent on reactant ratios and the nature of the vinyl ether) acetal formation occurs. At temperatures near −20° acetal formation may exhibit an appreciable induction period. In fact, reactions may sometimes be run to completion at −10° or higher before acetal formation begins. Once acetals appear, the vinyl ethers are converted rapidly and completely to a mixture of acetals. Initiation of acetal formation is associated with reduction of at least part of the Pd catalyst to palladium metal. The reducing agent is the vinyl ether or a common contaminant of the vinyl ethers such as acetaldehyde.

The vinyl interchange reaction provides a convenient method for the preparation of a large variety of vinyl ethers. The general method can be illustrated by the following example. Propanol (2 m) was added to a solution of $(PhCN)_2 PdCl_2$ (4×10^{-3} m) in vinyl butyl ether (2 m) at −30°. After stirring for 3 hr an equilibrium mixture of ethers, vinyl propyl ether: vinyl butyl ether (45:55 by weight, $K_{equil} = 0{\cdot}98$) resulted. Addition of further propanol (2 m) then resulted in a new equilibrium mixture, vinyl propyl ether: vinyl butyl ether (71:38 by weight, $K_{equil} = 0{\cdot}95$). Addition of pyridine and distillation of the reaction mixture then gave vinyl propyl ether (1·27 m). Similarly the reaction between allyl alcohol and vinyl ethyl ether at −40° gave vinyl allyl ether, and the reaction between ethylene chlorohydrin and vinyl butyl ether at −40° gave 2-chloroethyl vinyl ether.

The Pd catalyzed vinyl interchange reaction has thus been shown to be a facile reaction, and since it readily gives equilibrium mixtures of vinyl ethers at low temperatures in very high efficiency, and since the reaction is not complicated by the need of a strong acid co-catalyst as is the case in the mercury catalyzed reactions, it appeared to be an ideal model for studies on the mechanism of the catalytic activity.



One possible mechanism for the Pd catalyzed reaction is similar to that originally proposed by Adelman for the mercury catalyzed reaction, and involves an intermediate of a Pd–acetylene complex. It was readily proved that this type of mechanism was not involved in the interchange reaction. The reaction of vinyl butyl ether with anhydrous deuteroethanol (98% C_2H_5OD) in the presence of $(PhCN)_2PdCl_2$ at −40° gave normal vinyl ethyl ether, neither the NMR nor mass spectrum of this material indicated any deuterium incorporation. The mechanism illustrated above would require the incorporation of deuterium, since one stage involves the addition of the alcohol to a Pd–acetylene complex, and therefore cannot be used to describe the interchange reaction.

In order to gain further insight into the mechanism, the stereochemistry of the vinyl interchange reaction using *cis*- and *trans*-ethyl propenyl ethers was studied. Propanol (0·037 mole) was added to a solution of *trans*-ethyl propenyl ether (0·018 mole) and $(PhCN)_2PdCl_2$ (7×10^{-4} mole) in 1.2-dimethoxyethane at −30° and the reaction was followed by GLC. The sole initial product was found to be *cis*-propyl propenyl ether and even at conversions* as high as 36% the product was predominately the *cis* isomer. This reaction is illustrated in Table 1.† Similarly. the reaction of *cis*-ethyl propenyl ether with propanol at −30° gave *trans*-propyl propenyl ether as the sole product at low conversions.‡ At higher conversions. however. a significant amount of the *cis*-isomer was also produced. undoubtedly by the interchange of the *trans*-isomer with excess propanol. This reaction is illustrated in Table 2.

TABLE 1. THE REACTION OF TRANS-ETHYL PROPENYL ETHER WITH PROPANOL AT −30°

Time (Min)	% Conversion	% Composition			
		Ethyl propenyl ether		Propyl propenyl ether	
		cis	trans	cos	trans
5	1·8	0	100	100	0
10	2·7	0	100	100	0
25	5·1	0	100	100	0
40	9·7	1	99	100	0
65	12·0	2	98	100	0
90	15·3	2	98	99	1
180	23·0	3	97	95	5
270	31·0	4	96	95	5
420	36·0	7	93	94	6

Thus it was demonstrated that the Pd catalyzed interchange reaction of vinyl ethers is stereospecific and proceeds with inversion of configuration. These facts are consistent with the following mechanism. which involves the insertion of the vinyl ether into a Pd–oxygen bond.

The addition of a Pd-propoxide species across the double bond of the vinyl ether results in a σ-Pd-alkyl complex. Rotation about the C—C bond followed by the elimination of a Pd-ethoxide species then results in product. Elimination without rotation would regenerate starting material. Since the overall reaction proceeds with inversion of configuration. the stereochemistry of the addition step and elimination step must be the same. probably *cis* addition-*cis* elimination. Also since the overall reaction is stereospecific. both steps must be concerted.

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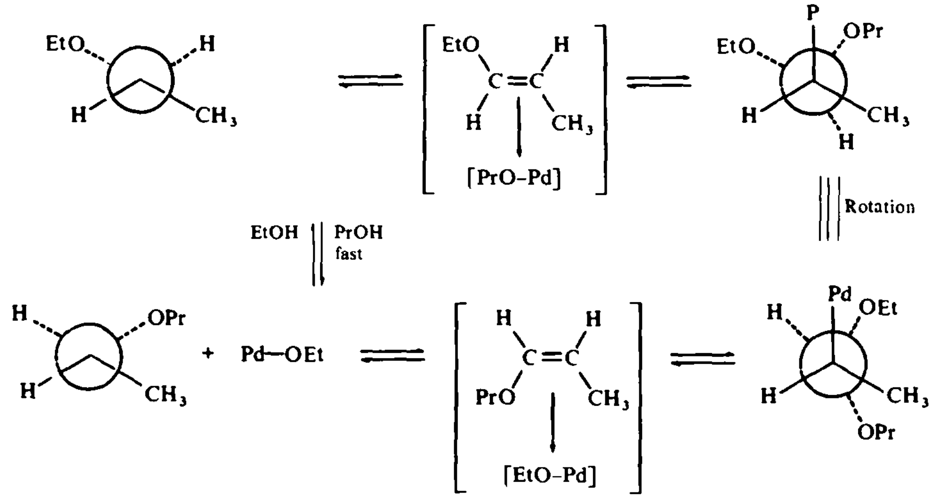
* Even though this is an equilibrium reaction. it is convenient to use the term "conversion" as a measure of the progress of the reaction in its initial stages.

$$\text{"\% conversion"} = \frac{(\text{moles of products})}{(\text{moles of products}) + (\text{moles of starting material})} \times 100$$

† The rate of reaction of propenyl ethers is markedly slower than that of vinyl ethers under similar conditions.

‡ Sodium dihydrogen phosphate was added as a buffer in this reaction. Without the addition of this salt the stereochemical course of the reaction was the same; however. some low boiling products were also formed. The use of buffers in these reactions will be discussed in a later paper.



During the preparation of this paper, a similar mechanism for the Pd (II) catalyzed vinyl ester interchange reaction has been proposed by Sabel, Smidt, Jira and Prigge[3] based on their interpretation of isomer mixtures resulting from ester interchange. A similar mechanism was also among several suggested for the reaction of vinyl chloride with acetate.[4]

Table 2. The reaction of cis-ethyl propenyl ether with propanol at −30°

Time (Min)	% Conversion	% Composition			
		Ethyl propenyl ether		Propyl propenyl ether	
		cis	trans	cis	trans
10	0·33	100	0	0	100
20	0·80	100	0	0	100
30	1·21	100	0	0	100
40	2·9	100	0	4	96
50	3·3	100	0	6	94
60	4·0	100	0	5	95
70	4·3	100	0	6	94
80	4·8	100	0	6	94
90	5·8	100	0	8	92
100	6·3	100	0	8	92
140	10·0	100	0	12	88

EXPERIMENTAL

The reaction of vinyl ethyl ether and n-*butanol*

A soln of bis(benzonitrile)palladium chloride (5·76 g; 0·015 mole) in vinyl ethyl ether (36 g: 0·5 mole) was cooled to −40°. n-BuOH (42 g; 0·5 mole), precooled to −40°, was added and the mixture was stirred at −40° for 1 hr. Pyridine (15 g) was added, the mixture was warmed to room temp, washed with a large excess of water, and dried (Na_2CO_3). Distillation, using a 36" spinning-band column, gave vinyl ethyl ether (12·6 g, b.p. 34–35°) and vinyl butyl ether (27·8 g, b.p. 92–93°).

The reaction of vinyl butyl ether and n-*propanol*

Vinyl butyl ether (200 g) was added to a soln of $(PhCN)_2PdCl_2$ (1·54 g) in n-PrOH (120 g). After stirring for 3 hr at −30°, an equilibrium mixture of ethers (vinyl propyl ether: vinyl butyl ether, 45:55 by weight) was formed. PrOH (120 g) was added and the mixture was stirred for another hr. At this time a new equilibrium mixture of ethers (vinyl propyl ether: vinyl butyl ether. 71:38 by weight) had formed. Pyridine (100 ml) was added. the reaction mixture was flash-distilled (75°/5 mm) and the resulting distillate was fractionally distilled to give vinyl propyl ether (109·6 g. b.p. 61–62°) and vinyl butyl ether (65 g. b.p. 92–93°).

The reaction of ethylene chlorohydrin and vinyl butyl ether

$(PhCN)_2PdCl_2$ (0·27 g). sodium dihydrogen phosphate (4·2 g) and vinyl butyl ether (2·0 g) were dissolved in 1,2-dimethoxyethane (20 ml). After cooling to −40°, a precooled soln of ethylene chlorohydrin (6·4 g) in 1.2-dimethoxyethane (5 ml) was added. After stirring at −40° for 2 hr. GLC analysis (15′ × ¼″. 20% Carbowax 20 M on Chromosorb P) indicated that an equilibrium mixture of 2-chloroethyl vinyl ether (43%) and vinyl butyl ether (57%) had been formed. 2-Chloroethyl vinyl ether was identified by comparison of its GLC retention time and the mass spectrum of a GLC collection sample with that of an authentic sample.

The reaction of allyl alcohol and vinyl ethyl ether

Bis(benzonitrile)palladium chloride (5·4 g) was dissolved in a mixture of vinyl ethyl ether (18 g) and cyclohexane (4·5 g)—added as an internal standard for GLC analysis. This soln was cooled to −40°. precooled allyl alcohol (29 g) was added. and the mixture was stirred at −40°. After 3 hr. precooled allyl alcohol (29 g) was added and the mixture was stirred for a further 90 min. GLC analysis (18′ × ⅛″. 20% Carbowax 20 M on Chromosorb P) indicated that an equilibrium mixture of vinyl allyl ether (70%) and vinyl ethyl ether (30%) had been formed. Pyridine (20 ml) was added. the mixture was warmed to room temp. washed with water and dried ($MgSO_4$). Vinyl allyl ether was separated from this mixture by GLC and identified by comparison of its NMR and IR spectra with that of an authentic sample.

The reaction of vinyl butyl ether and deuteroethanol

Deuteroethanol (98% C_2H_5OD. Volk Radiochemical Company) (29 g) precooled to −40° was added to a soln of bis(benzonitrile)palladium chloride (1·54 g) in vinyl butyl ether (63 g) at −40°. After stirring for 9 hr at −40°. bis(benzonitrile)palladium chloride (1·54 g) and vinyl butyl ether (23 g) was added. and the mixture was stirred for a further 5 hr at −35°.

The mixture was flash-distilled (−40°/0·25 mm) and a fraction of vinyl ethyl ether (12 g) collected. This distillate was further purified by preparative GLC (20′ × ⅜″. 20% Carbowax 20 M on Chromosorb P). The NMR spectrum of this material was identical to that of normal vinyl ethyl ether. Neither the NMR or mass spectrum indicated any deuterium incorporation.

The separation of cis *and* trans-*ethyl propenyl ethers*

A mixture (66% *cis* and 33% *trans*) of ethyl propenyl ethers. obtained by the vapor-phase cracking of 1.1-diethoxypropane. was separated into pure *cis*- and pure *trans*-ethyl propenyl ethers by fractional distillation using a 7′ × 2″ column packed with ⅛″ glass helices. followed by preparative scale GLC using a 10′ × ⅜″. 20% Hallcomid on Chromosorb W column at 70°.

The two isomers were identified by their NMR spectra. In the *cis* isomer the coupling constant of the vicinal olefinic protons was 6·5 cps and in the *trans* isomer it was 12·7 c/s. The rest of both spectra were consistent with the proposed structures.

The reaction of trans-*ethyl propenyl ether with propanol*

Bis(benzonitrile)palladium chloride (0·27 g) and cyclohexane (0·5 g) (added as an internal standard for GLC analysis) were dissolved in 1,2-dimethoxyethane (25 ml) and the soln was cooled to −30° in a constant temp bath. Freshly distilled *trans*-ethyl propenyl ether (1·1 g) in 1.2-dimethoxyethane (2 ml) precooled to −30° was added. followed by a soln of n-PrOH (2·25 g) in 1.2-dimethoxyethane (3 ml) precooled to −30°. The soln was stirred at −30° under N_2 and samples were removed in a pipette (previously cooled in dry ice) at regular time intervals and immediately added to an excess of cold (−30°) pyridine. These samples were then analyzed by GLC using a 15′ × ¼″. 20% Carbowax 20 M on Chromosorb P column at 70 .

The products. *cis* and *trans*-propyl propenyl ethers were collected by preparative GLC and identified by NMR. In the *cis* isomer the coupling constant of the two vicinal olefinic protons was 6·3 c/s and in the *trans* isomer it was 12·8 c/s. The remainder of both spectra was consistent with the proposed structures.

The reaction of cis-*ethyl propenyl ether with propanol*

This reaction was run as for the *trans*-isomer above, except *cis*-ethyl propenyl ether (1·1 g) and sodium dihydrogen phosphate (0·42 g) were added instead of the *trans*-ethyl propenyl ether.

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