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LETTERS TO THE EDITORS

The Reaction of Vinyl Halide–Palladium(II) Chloride Complexes with Nucleophiles: Catalytic Vinylation

Previously, we reported the production of vinyl compounds in reactions of olefins with nucleophiles and $PdCl_2$ in which the palladium salt was reduced to metal (*1*). We now wish to report the *catalytic* participation of $PdCl_2$ in the reaction of vinyl halides with nucleophiles in nonaqueous media to produce vinyl esters, ethers, and amines. While other transformations of vinyl compounds in which $PdCl_2$ functions as a catalyst have been described, these are either saponification (*2*) or decomposition reactions (*3*) in which the double bond is lost or transesterification reactions (*2*) which are also catalyzed readily by other means (*4*).

In contrast to the difficulties normally encountered in displacing vinylic halides, reactions in this case proceeded smoothly under mild conditions. Vinyl chloride, when shaken with $PdCl_2$ (0.02 mole) and disodium hydrogen phosphate (0.08 mole) in isooctane (50 ml) containing acetic acid (0.06 mole), at room temperature and about 2 atm pressure, was converted to 26.6 mole % (based on $PdCl_2$) vinyl acetate after 48 hr [Eq. (1)].

$$CH_2 = CHCl + CH_3COOH \rightarrow CH_2 = CHOCOCH_3 + HCl \quad (1)$$

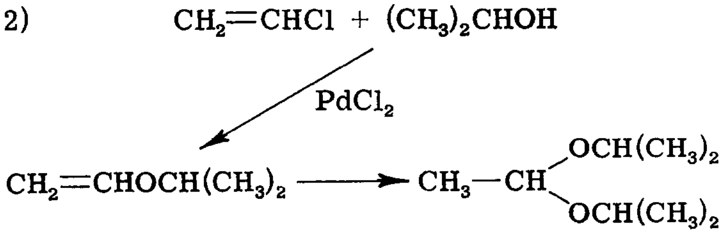
No ethylidene diacetate was formed. Acetaldehyde and acetic anhydride were also absent, indicating that vinyl acetate decomposition is not catalyzed by $PdCl_2$ under the conditions of our reaction in contrast to results reported by other workers (*3*).

Under similar conditions, vinyl chloride reacted with isopropyl alcohol to yield 37.5 mole % isopropyl acetal.

This reaction occurs via formation of vinyl isopropyl ether followed by the addition of a second mole of alcohol [Eq. (2)]. Indeed, a vinyl chloride-ethanol mixture, when passed over supported $PdCl_2$ at 190° formed vinyl ethyl ether.

$$1)\quad CH_2{=}CHCl + CH_3COOH \xrightarrow{PdCl_2} CH_2{=}CHOCOCH_3 + HCl$$

2)



$$CH_2{=}CHCl + (CH_3)_2CHOH \xrightarrow{PdCl_2} CH_2{=}CHOCH(CH_3)_2 \longrightarrow CH_3{-}CH(OCH(CH_3)_2)_2$$

Reaction of vinyl chloride with *n*-butylamine in tetrahydrofuran, in the presence of $PdCl_2$ and Na_2HPO_4, at room temperature for 168 hr, followed by hydrogenation of the product mixture led to the formation of ethylbutylamine. This is in agreement with similar reactions of ethylene in which isolation of unsaturated products was complicated by formation of stable $PdCl_2$ complexes (*1*).

In all of the above reactions involving vinyl chloride, no reduction of $PdCl_2$ was noted.

A detailed mechanism is not suggested at this time. However, the overall reaction may be viewed as involving formation of a vinyl halide — $PdCl_2$ complex followed either by displacement of the vinylic halogen by a nucleophile from solution or exchange with a nucleophilic ligand. Neither of these processes would result in a net change in the oxidation state of Pd(II). The ease with which these normally difficult reactions occur must be a consequence of the bonding between vinyl halides and $PdCl_2$. A simple view is that the complex structure is similar to that accepted for ethylene-$PdCl_2$ (*5*). Back-donation of electrons from metal to the olefin pi system could then facilitate a displacement by increasing the electron density on the carbon holding the halide.

We are grateful to Professor Harry B. Gray for helpful discussions concerning possible complex structures.

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The Initiation of the Free Radical Thermal Decomposition of Saturated Hydrocarbons by Mercury Perchlorate

Recently Fejes and Emmett (*1*) made use of a mercury perchlorate trap to remove olefins (*2*) from the gas mixture resulting from the cracking of propane, isobutane, and *n*-butane over a silica-alumina cracking catalyst in a circulating system. They concluded that by removing the olefins formed, the surface of the catalyst became covered with methyl carbonium ions. The cracking of these hydrocarbons in the presence of the mercury perchlorate trap resulted in a predominance of methane in the final products and a considerable acceleration in the rate of cracking after a period of 20–30 min.

In an attempt to duplicate these results using a flow reactor we have found that the mercury perchlorate is not inert toward the saturated hydrocarbons. In fact, it reacts with saturated hydrocarbons at room temperature to form volatile species which, upon reaching the reactor furnace (at 470°), are initiators for the homogeneous, thermal decomposition reaction. It has also been found that a mercury perchlorate-hydrocarbon species decomposes explosively if exposed to oxygen.

No acceleration of the cracking rate was observed, nor was the production of methane enhanced by varying the flow rate, the