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REACTIONS OF VINYL SILANES WITH PALLADIUM SALTS - VINYL HECK REACTIONS

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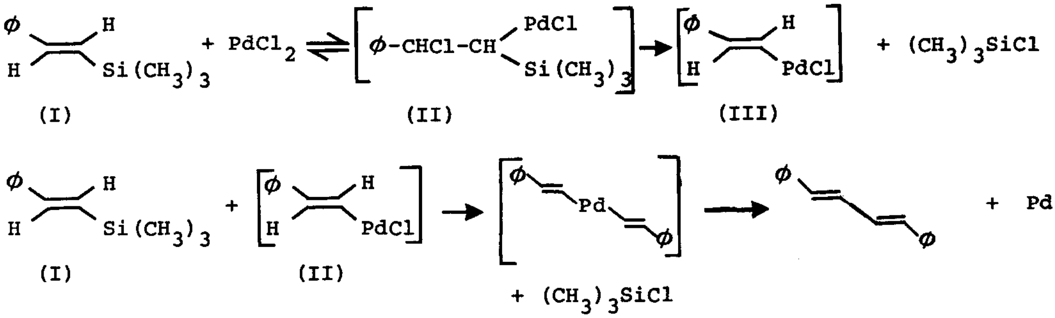
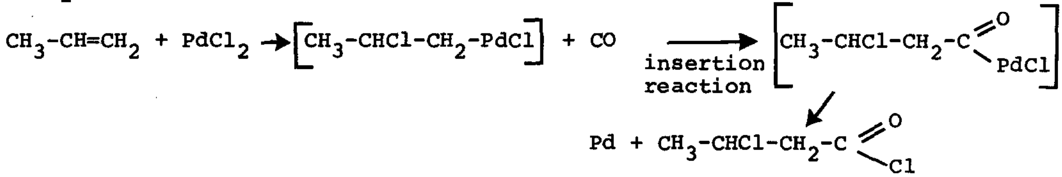
Aryl palladium species formed by metal exchange reactions between aryl mercurial compounds and palladium salts have been shown by Heck to be most versatile synthetic intermediates.[1,2] We find that the products of reaction of vinyl silanes with palladium salts can be interpreted in terms of the chemistry expected of vinyl palladium intermediates.

The reaction of β-trimethylsilyl styrene[3] (I) with $PdCl_2$ in methanol leads to formation of trans,trans-1,4-diphenyl-1,3-butadiene[4] in reasonably high yield. A possible mechanism for this reaction involves the following steps. Addition of $PdCl_2$ across the carbon-carbon double bond of I yields II in which the trimethylsilyl group and a chlorine are beta to one another. Elimination of trimethylchlorosilane from II leads to formation of a β-styryl palladium chloride intermediate (III). A similar sequence of addition of palladium chloride of III across the double bond of another molecule of I followed by elimination of trimethylchlorosilane leads to formation of bis-β-styryl palladium. Oxidative coupling of the two styryl groups with concurrent reductive elimination of Pd(0) is the product forming step.



Evidence to support this mechanism follows: A particularly unambiguous example of the addition of $PdCl_2$ to olefins has been reported by Tsuji, who showed that terminal olefins yield β-chloro acid chlorides in the presence of

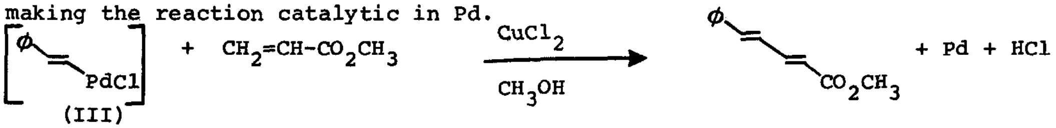
$PdCl_2$ and carbon monoxide.[5,6]



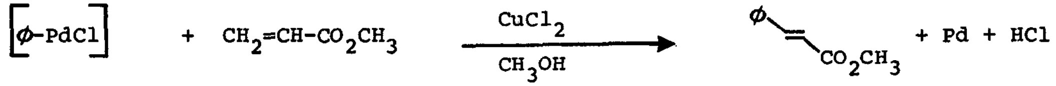
$$CH_3\text{-}CH{=}CH_2 + PdCl_2 \rightarrow [CH_3\text{-}CHCl\text{-}CH_2\text{-}PdCl] + CO \xrightarrow[\text{reaction}]{\text{insertion}} [CH_3\text{-}CHCl\text{-}CH_2\text{-}C(=O)PdCl] \rightarrow Pd + CH_3\text{-}CHCl\text{-}CH_2\text{-}C(=O)Cl$$

The solvolytic fragmentation of β-chloroethyl-trimethylsilane in ionizing solvents to yield trimethylchlorosilane and ethylene is well known.[7,8] The decomposition of diaryl palladium species to yield biphenyls and palladium, analogous to our product forming step,has been observed.[9,10]

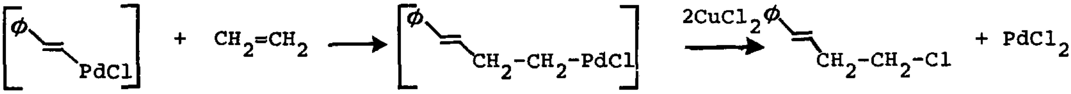
Finally, if our reaction involves β-styryl palladium chloride (III) as an intermediate, III should be capable of undergoing other reactions similar to those of aryl palladium chloride intermediates. To test this hypothesis we reacted I with $PdCl_2$ in the presence of methyl acrylate. The product obtained in 35% yield was 1-phenyl-4-carbomethoxy-1,3-butadiene.[11] In analogy to this, the reaction of phenyl palladium chloride with methyl acrylate yields methyl cinnamate in comparable yields.[12] $CuCl_2$ was used to reoxidize Pd (0) to $PdCl_2$, making the reaction catalytic in Pd.



(III)



1-Chloro-4-phenyl-3-butene (95:5 trans:cis)[13] is obtained in 30% yield from the reaction of (I) with $PdCl_2$ and $CuCl_2$ in the presence of ethylene in methanol solvent. The mechanism of formation of this product may involve addition of (III) to ethylene to form a primary alkyl palladium species which is oxidized by $CuCl_2$ to yield the product and regenerate $PdCl_2$ before elimination of HPdCl can occur. Heck has observed a similar reaction in which phenyl palladium chloride formed in the presence of ethylene and a high concentration of $CuCl_2$ yields β-chloroethylbenzene.[14]



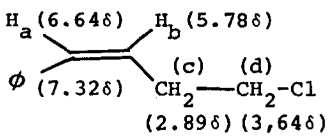
$$[\phi\text{-}PdCl] + CH_2{=}CH_2 \longrightarrow [\phi\text{-}CH_2\text{-}CH_2\text{-}PdCl] \xrightarrow{2CuCl_2} \phi\text{-}CH_2\text{-}CH_2\text{-}Cl + PdCl_2$$

There are two synthetic advantages to our system. Vinyl silanes are less toxic than organomercurial reagents, and trimethylchlorosilane or trimethylmethoxysilane (formed in methanol) are more easily removed than colloidal mercury in work-up.

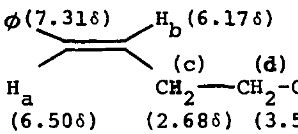
HCl produced by the reaction of trimethylchlorosilane with methanol constitutes, however, a problem because vinyl silanes react with acids.[15] A related reaction, the proton desilylation of aryltrimethylsilanes is well known.[16] Hence to minimize side reactions of the vinyl silane, one equivalent of a sterically hindered tertiary amine must be added to remove HCl. The reaction under these conditions is stoichiometric in $PdCl_2$ rather than catalytic since $CuCl_2$ is ineffective in reoxidizing Pd(0). In dipolar aprotic solvents such as acetonitrile, no HCl is produced and therefore no amine is necessary. In this case, anhydrous $CuCl_2$ can be used as a reoxidant for Pd (0), making the reaction catalytic in palladium.

Similar reactions have been carried out using trimethylvinylsilane. The scope of this vinylation reaction, which may in certain ways compliment the HECK arylation,[1,2] is under active investigation.

Typical experimental conditions used to prepare 1-chloro-4-phenyl-3-butene: In a dry 250ml round bottom flask equipped with a magnetic stirring bar was placed 1.0 g of I (95:5, trans:cis), 50mg of $PdCl_2$, 200mg of LiCl, 1.5g of anhydrous $CuCl_2$, and 20 ml of dry acetonitrile(freshly distilled from P_2O_5), under an atmosphere of CP grade ethylene. The reaction mixture was stirred vigorously to saturate the liquid phase with ethylene. After 18 hours, 150ml of ether was added. The reaction was then filtered to remove solid material - largely CuCl. The solvent was removed by evaporation under reduced pressure. The residue was analyzed by gas chromatography on a 1/4" X 3 meter 20% Versamid column at 200°. In addition to a very small amount of starting material, a 30% yield of 1-chloro-4-phenyl-3-butene (95:5, trans:cis) was obtained. The spectral properties of the trans compound are in complete accord with literature values.[13] The cis compound is unknown. nmr data:



J_{ab} = 11.5 Hz
J_{bc} = 7.0 Hz
J_{cd} = 7.0 Hz
J_{ac} = 1.5 Hz



J_{ab}= 15.5Hz
J_{bc}= 7.0Hz
J_{cd}= 7.0Hz
J_{ac}=0.5Hz

Mass spectral data and ir are consistent.

Typical experimental conditions for preparation of trans,trans-1,4-diphenyl-1,3-butadiene: In a 100 ml round bottom flask was placed 4.5 g of I, 200mg of $PdCl_2$, 1.0 g of LiCl, 10.2 g of $CuCl_2 \cdot 2H_2O$, and 50ml of methanol. The mixture was stirred for 22 hours. 150ml of ether was then added, and the solids, mostly CuCl, removed by filtration. The ether layer was then washed with three 50ml portions of water, dried over anhydrous $MgSO_4$, filtered, and the solvents removed under reduced pressure. The residue was recrystallized from 95% ethanol -yield 1.4g (52% based on I, 700% based on Pd) trans,trans-1,4-diphenyl-1,3-butadiene mp 150-151°. The reaction can be done stoichiometrically in $PdCl_2$ under anhydrous conditions in the presence of 1 equivalent of dicyclohexylethylamine. In this case work-up is by dilution with ether followed by washing with 10% HCl. The yield in this case is 79% based on both I and $PdCl_2$.

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