THE PALLADIUM(II) CLEAVAGE OF ALLYLSILANES

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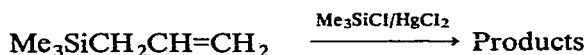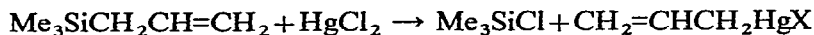
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SUMMARY

Lithium tetrachloropalladate(II), lithium dichlorodiacetatopalladate(II); and palladium(II) acetate cleave allylsilanes in hydroxylic solvents to give allyl–palladium complexes and organic cleavage products. The overall reaction is not catalytic in palladium. A mechanism is proposed in which a rapid, stoichiometric metal-ion cleavage produces an allyl–metal complex and chlorosilane. The latter then reacts further with any hydroxylic moiety that is present to give siloxanes and disiloxanes. The HCl produced from this reaction of chlorosilanes then catalyzes the further decomposition of allylsilane.

INTRODUCTION

In a recent paper, Roberts described the kinetics of the mercuric salt-catalyzed cleavage of trimethylallylsilane[1]. In that case, the products were trimethylchlorosilane, an allylmercuric chloride and "products";

$$Me_3SiCH_2CH=CH_2 + HgCl_2 \rightarrow Me_3SiCl + CH_2=CHCH_2HgX$$

$$Me_3SiCH_2CH=CH_2 \xrightarrow{Me_3SiCl/HgCl_2} Products$$

The "products" were not identified.

At about the same time, Poist and Kraihanzel[2] reported that platinum(II) halides catalyze the cleavage of trimethylalkynylsilanes in ethanol at 40° to give ethoxytrimethylsilane, a platinum residue that contained alkyne bonds (via IR) and gaseous products. In addition, trimethylallylsilane also reacted with platinum(II) halides but the organic products were not completely identified.
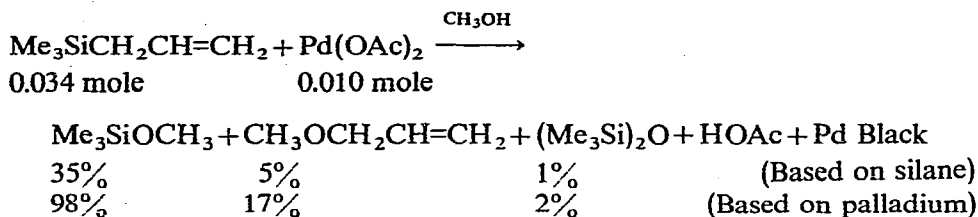
RESULTS

We have found that palladium(II) salts cleave allylsilanes in an extremely rapid reaction*. The products, in hydroxylic or moist solvents, are palladium com-

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* Attempts to follow the reaction by UV spectroscopy gave the known spectrum of π-allylpalladium chloride in a matter of seconds at −20°.
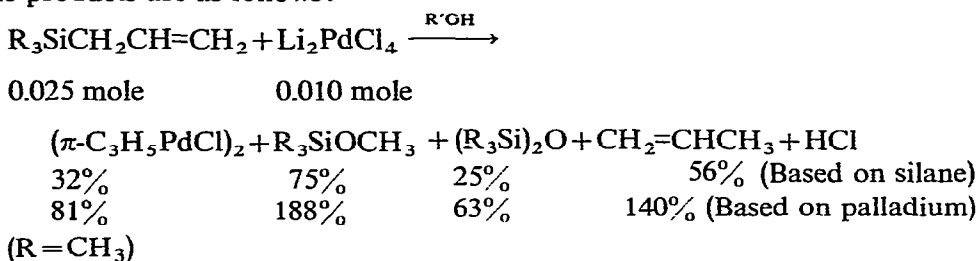
plexes (if stable) and various organic products, the yields of which depend on the anion of the original palladium salt.

For example, excess trimethylallylsilane and palladium(II) acetate react in methyl alcohol as follows:

$$Me_3SiCH_2CH=CH_2 + Pd(OAc)_2 \xrightarrow{CH_3OH}$$
0.034 mole   0.010 mole

$$Me_3SiOCH_3 + CH_3OCH_2CH=CH_2 + (Me_3Si)_2O + HOAc + Pd\ Black$$

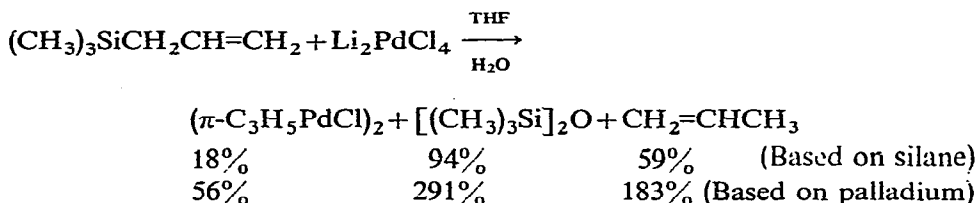| 35% | 5% | 1% | (Based on silane) |
| 98% | 17% | 2% | (Based on palladium) |

In the above reaction, 63% of the allylsilane remains unreacted.

When a palladium(II) halide salt is used, the allylsilane is totally consumed and the products are as follows:

$$R_3SiCH_2CH=CH_2 + Li_2PdCl_4 \xrightarrow{R'OH}$$
0.025 mole   0.010 mole

$$(\pi\text{-}C_3H_5PdCl)_2 + R_3SiOCH_3 + (R_3Si)_2O + CH_2=CHCH_3 + HCl$$

| 32% | 75% | 25% | 56% (Based on silane) |
| 81% | 188% | 63% | 140% (Based on palladium) |

$(R = CH_3)$

If the solvent is not an alcohol, but contains some water the reaction proceeds just as smoothly:

$$(CH_3)_3SiCH_2CH=CH_2 + Li_2PdCl_4 \xrightarrow[H_2O]{THF}$$

$$(\pi\text{-}C_3H_5PdCl)_2 + [(CH_3)_3Si]_2O + CH_2=CHCH_3$$

| 18% | 94% | 59% | (Based on silane) |
| 56% | 291% | 183% | (Based on palladium) |

We do not believe that this apparent difference in catalytic activity is due to the palladium. More likely, it is a function of the anion of the acidic product of the reaction. In the Li_2PdCl_4 reaction, the acid produced is a strong one, strong enough to cleave the allyl–silicon linkage of $Me_3SiCH_2CH=CH_2$*. Thus, the HCl produced then can take part in a secondary reaction, i.e., cleavage of the allylsilane (as well as condensation of any alkoxysilanes to disiloxanes). This reaction of HCl was, in fact, observed. Support for the postulate that the initial reaction gives the π-allyl complex and trimethylchlorosilane (which reacts rapidly with solvent or water to give siloxanes) and that HCl derived from siloxane formation results in further decomposition of the allylsilane to propylene and more trimethylsilyl derivatives is based on the following: (1) these reaction mixtures are acidic even after distillation; i.e., the reaction

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* The HCl cleavage of trimethylallylsilanes is known and gives trimethylchlorosilane and propylene[3].

continues after removal from the metal ion; and (2) the π-allyl complex does not catalyze the reaction even though it is instantaneously formed.

The reaction of $Pd(OAc)_2$ with trimethylallylsilane is different in that the acid formed is acetic acid, a weak acid, which does not cleave allylsilanes (under these conditions of time and temperature), nor apparently does it cause the condensation to the disiloxane. Thus, in this case, the reaction stops directly upon cleavage to the trimethylsilyl acetate and π-allylpalladium acetate. The silyl acetate reacts with the alcohol solvent to give the observed products while the allylpalladium derivative decomposes to metallic palladium or reacts partially with the alcohol to give the observed allyl methyl ether. This is not unreasonable since it is known that certain types of π-allylplatinum and -palladium complexes react with alcohols to give allyl ethers[4].
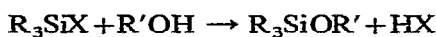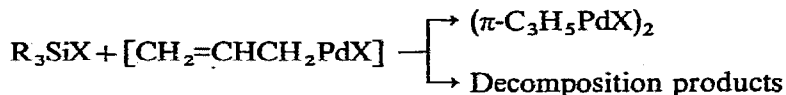
The experimental results of these and other reactions carried out in this study are given in Table 1 and the Experimental Section.
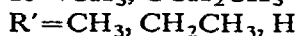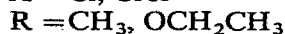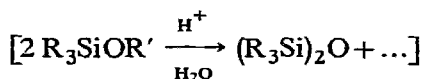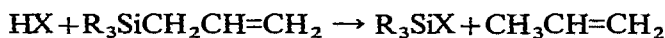
TABLE 1

Silane (moles)	Solvent	Palladium compound (moles)	Product	Yield (%)
$(CH_3)SiCH_2CH=CH_2$ (0.025)	CH_3OH	Li_2PdCl_4 (0.01)	$(\pi\text{-}C_3H_5PdCl)_2$ $[(CH_3)_3Si]_2O$ $(CH_3)_3SiOCH_3$ $CH_2=CHCH_3$	32^a, 81^b 25^c, 83^d 75^c, 12^d 56^c
$(CH_3)_3SiCH_2CH=CH_2$ (0.039)	CH_3CH_2OH	Li_2PdCl_4 (0.01)	$(\pi\text{-}C_3H_5PdCl)_2$	65^b
$(EtO)_3SiCH_2CH=CH_2$ (0.021)	CH_3OH	Li_2PdCl_4 (0.01)	$(\pi\text{-}C_3H_5PdCl)_2$	45^b
$(CH_3)_3SiCH_2CH=CH_2$ (0.031)	THF (Moist)	Li_2PdCl_4 (0.01)	$(\pi\text{-}C_3H_5PdCl)_2$ $[(CH_3)_3Si]_2O$ $CH_2=CHCH_3$	18^a, 56^b 94^c 59^a
$(CH_3)_3SiCH_2CH=CH_2$ (0.030)	CH_3OH	$Li_2Pd(OAc)_2$ (0.01)	$(CH_3)_3SiOCH_3$ $[(CH_3)_3Si]_2O$ Pd mirror + Pd black Unreacted silane	22^a, 66^b 6^a, 17^b 72
$(CH_3)_3SiCH_2CH=CH_2$ (0.034)	CH_3OH	$Pd(OAc)_2$ (0.01)	$(CH_3)_3SiOCH_3$ $CH_3OCH_2CH=CH_2$ $[(CH_3)_3Si]_2O$ Pd mirror + Pd black Unreacted silane	35^a, 98^b 5 2^a, 1^b 63
$(CH_3)_3SiCH_2CH=CH_2$ (0.032)	CH_3OH	Conc. HCl (0.01)	$[(CH_3)_3Si]_2O$ $(CH_3)_3SiOCH_3$ $CH_2=CHCH_3$	58 39 32^c
$(CH_3)_3SiCH_2CH=CH_2$	CH_3OH	$(\pi\text{-}C_3H_5PdCl)_2$	No reaction	
$(CH_3)_3SiCH_2CH=CH_2$	CH_3OH	LiCl	No reaction	
$(CH_3)_3SiCH_2CH=CH_2$	CH_3OH	CH_3CO_2H	No reaction observed	

[a] Based on starting silane. [b] Based on palladium. [c] Immediately after reaction product mixture distilled. [d] After three weeks. [e] Losses occurred during distillation due to our inability to completely trap this material during vacuum distillation.

Based upon the above considerations, we offer the following reaction course which we feel not only explains our data, but also sheds some light on the reactions and observations previously noted[1,2].

$$R_3SiCH_2CH{=}CH_2 + PdX_2 \rightarrow$$

$$R_3SiX + [CH_2{=}CHCH_2PdX] \longrightarrow \begin{cases} (\pi\text{-}C_3H_5PdX)_2 \\ \text{Decomposition products} \end{cases}$$

$$R_3SiX + R'OH \rightarrow R_3SiOR' + HX$$

if $X = Cl$, then

$$HX + R_3SiCH_2CH{=}CH_2 \rightarrow R_3SiX + CH_3CH{=}CH_2$$

$$[2\,R_3SiOR' \xrightarrow[H_2O]{H^+} (R_3Si)_2O + ...]$$

$X = Cl, OAc$
$R = CH_3, OCH_2CH_3$
$R' = CH_3, CH_2CH_3, H$

EXPERIMENTAL

General

All chemicals were reagent grade and were not purified or dried prior to use. Gas–liquid-phase chromatographic separations were carried out on an Aerograph Model A-90-P3, with a 16' combination Carbowax 20M and Apiezon M column at 95° and 60 ml per min helium flow rate. Mass spectra were recorded on an AIC MS-9 spectrometer.

Reactions

(A). In a typical reaction, 0.02 mole of LiCl and 0.01 mole of $PdCl_2$ were mixed in 15 ml of the reactant solvent (methyl or ethyl alcohol or moist THF) and the mixture was heated to reflux under a condenser with magnetic stirring. No attempt was made either to exclude oxygen or atmospheric water. After solution occurred (purple color), the condenser was connected to a Dry Ice trap and the silane was added by syringe through a septum to the reaction flask. The solution immediately turned yellow and refluxing (~50°) was continued for 1–2 h. The mixture was then distilled at reduced pressure into the Dry Ice trap. Identification of the volatile components was made by GLC and mass spectrometry.

The solid that remained after the above distillation was taken up in cold methyl alcohol and filtered, m.p. 123–124°. Its mixed melting point with authentic π-allyl-palladium chloride was undepressed, and it had superimposable IR and NMR spectra with authentic π-allylpalladium chloride.

(B). In a different type of experiment with the Li_2PdCl_4, the reaction mixture was distilled immediately after addition of the silane. A comparable yield of the π-allylpalladium complex was obtained, however, the distillate contained a considerable

amount of unconverted silane (GLC). The distillate was acidic and was heated to reflux in a distillation flask under a Dry Ice condenser for 2 h. At the end of this time, almost all of the allylsilane had reacted to give essentially the same organic products as before (by GLC, mass spectroscopy).

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4 J. M. KLIEGMAN, PhD thesis, The University of Chicago, 1963.