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# CONVERSION OF DISILANES TO FUNCTIONAL MONOSILANES

## III*. PREPARATION OF ALLYLMETHYLSILANES BY TETRAKIS(TRIPHENYLPHOSPHINE)-PALLADIUM(0)-CATALYZED REACTIONS OF METHYLCHLORODISILANES WITH ALLYLIC HALIDES.

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## Summary

Various allylmethylsilanes were prepared by the reactions of methylchlorodisilanes with allylic halides catalyzed by tetrakis(triphenylphosphine)-palladium(0).

## Introduction

The synthesis of allylsilanes by means of the transition metal complex-catalyzed cleavage of disilanes with allyl chloride was first described in a patent literature [2] and hexachlorodisilane, sym-dimethyltetrachlorodisilane and sym-tetramethyldichlorodisilane were reported to be converted to the corresponding allylsilanes in the presence of phosphine complexes of Pd(II) and Ni(II). In view of our recent findings on the cleavage of disilanes with aryl halides in the presence of tetrakis(triphenylphosphine)palladium(0) [1,3], we have undertaken an investigation of the cleavage reactions of a systematic series of methylchlorodisilanes ($Me_nSi_2Cl_{6-n}$, where n = 2-6) by some typical allylic halides in the presence of the Pd(0) complex. This paper describes several features of these reactions.

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* For part II of this series see ref. 1

## Results and Discussion

Most of the cleavage reactions were conducted in a stainless steel bomb and selected examples are listed in Table 1. In the first example, allyl chloride (slight excess) and 1,2-dimethyl-1,1,2,2-tetrachlorodisilane were sealed in the reaction vessel with the Pd(0) complex (0.1 mol% based on the disilane charged) and the mixture was heated at 150°C for 2 h. Subsequent GLC analysis showed the presence of a 1:1 mixture of allylmethyldichlorosilane (87% yield) and methyltrichlorosilane, together with the excess of allyl chloride. Catalyst removal and distillation gave the allylsilane in 75% isolated yield. 1,1,2,2-Tetramethyl-1,2-dichlorodisilane and hexamethyldisilane reacted similarly with allyl chloride under somewhat more vigorous conditions to give the corresponding allylsilanes in excellent yields.

$$Cl_2MeSiSiMeCl_2 + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{(87\%)}{CH_2{=}CHCH_2SiMeCl_2} + MeSiCl_3 \qquad (1)$$

$$ClMe_2SiSiMe_2Cl + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{(89\%)}{CH_2{=}CHCH_2SiMe_2Cl} + Me_2SiCl_2 \qquad (2)$$

$$Me_3SiSiMe_3 + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{(93\%)}{CH_2{=}CHCH_2SiMe_3} + Me_3SiCl \qquad (3)$$

Although these allylsilanes have been prepared previously by other methods [4-7], reactions 1-3 obviously provide a quick and direct method for preparing them from readily available disilanes [8-10].

It is of considerable interest to see whether or not selective cleavage could occur when unsymmetrical methylchlorodisilanes are employed. It was found that the reaction pentamethylchlorodisilane with allyl chloride gave a 97:3 mixture of allyldimethylchlorosilane and allyltrimethylsilane, respectively (92% combined yield). Likewise, the reaction of 1,1,2-trimethyl-1,2,2-trichlorodisilane with allyl chloride produced a 98:2 mixture of allylmethyldichlorosilane and allyldimethylchlorosilane. Apparently, the silicon atom in the allylsilane which is the prediminant product originates from the more

Table 1.

REACTIONS OF METHYLCHLORODISILANES WITH ALLYLIC HALIDES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)-PALLADIUM(0).[a]

| Run | Disilane | Halide | Conditions | Allylsilane | Yield,%[b] |
|---|---|---|---|---|---|
| 1 | $Cl_2MeSiSiMeCl_2$[c] | $CH_2$=$CHCH_2Cl$ | 150°C, 2 h | $CH_2$=$CHCH_2SiMeCl_2$ | 87 (75) |
| 2 | $Cl_2MeSiSiMe_2Cl$[d] | $CH_2$=$CHCH_2Cl$ | 150°C, 2 h | $CH_2$=$CHCH_2SiMeCl_2$ (98) | 86 (72) |
| | | | | $CH_2$=$CHCH_2SiMe_2Cl$ ( 2) | |
| 3 | $ClMe_2SiSiMe_2Cl$[d] | $CH_2$=$CHCH_2Cl$ | 170°C, 5 h | $CH_2$=$CHCH_2SiMe_2Cl$ | 89 (77) |
| 4 | $ClMe_2SiSiMe_3$[e] | $CH_2$=$CHCH_2Cl$ | 170°C, 6 h | $CH_2$=$CHCH_2SiMe_2Cl$ (97) | 92 |
| | | | | $CH_2$=$CHCH_2SiMe_3$ ( 3) | |
| 5 | $Me_3SiSiMe_3$[e] | $CH_2$=$CHCH_2Cl$ | 170°C, 8 h | $CH_2$=$CHCH_2SiMe_3$ | 93 (78) |
| 6 | $Cl_2MeSiSiMeCl_2$[e] | $CH_2$=$CMeCH_2Cl$ | reflux, 8 h | $CH_2$=$CMeCH_2SiMeCl_2$ | 79 (72) |
| 7 | $Me_3SiSiMe_3$[c] | $CH_2$=$CHCH_2Br$ | 120°C, 3 h | $CH_2$=$CHCH_2SiMe_3$ | 52 |

[a] Reactions were carried out using a 1/1-1.4 mixture of a disilane and an allylic halide. [b] Yields (via GLC) are based on the disilane charged. In the parentheses are given isolated yields. Conversion of the disilane charged was complete. [c] The catalyst concentration was 0.1 mol% based on the disilane charged. [d] The catalyst concentration was 0.2 mol%. [e] The catalyst concentration was 0.3 mol%.

highly chlorinated silicon moiety in the starting disilanes.

$$ClMe_2SiSiMe_3 + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{97}{CH_2{=}CHCH_2SiMe_2Cl} \; + \; \underset{3}{CH_2{=}CHCH_2SiMe_3} \qquad (4)$$

$$Cl_2MeSiSiMe_2Cl + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{98}{CH_2{=}CHCH_2SiMeCl_2} \; + \; \underset{2}{CH_2{=}CHCH_2SiMe_2Cl} \qquad (5)$$

This observation led us to investigate relative rates of reaction of different sym-methylchlorodisilanes toward allyl chloride by the competitive experiments in which two disilanes were allowed to react with a deficiency of allyl chloride. The relative reactivities of the disilanes were found to fall in the order $Cl_2MeSiSiMeCl_2$ (97) $>$ $ClMe_2SiSiMe_2Cl$ (18) $>$ $Me_3SiSiMe_3$ (1). Thus, successive substitution of a chlorine atom for methyl group in hexamethyldisilane substantially increases the rate of the cleavage. The observed trend is in accord with that of intramolecular competition and also parallels the reported reactivity order of fluoromethyldisilanes in disilane methathesis induced by a Pd(II) complex [11].

The reaction of 2-methylallyl chloride with 1,2-dimethyl-1,1,2,2-tetrachlorodisilane could be carried out under reflux conditions to give 2-methylallylmethyldichlorosilane in 72% isolated yield.

$$Cl_2MeSiSiMeCl_2 + CH_2{=}CMeCH_2Cl \xrightarrow[reflux]{Pd(0)} \underset{(72\%\ isolated\ yield)}{CH_2{=}CMeCH_2SiMeCl_2} \qquad (6)$$

A Comparison of the reactivity of hexamethyldisilane toward allyl bromide and allyl chloride was made and it was found that the reaction of allyl bromide was faster than that of allyl chloride (compare entries 5 and 7 in Table 1). However, the yield of allyltrimethylsilane was only 52% starting from the bromide, compared with 93% starting from the chloride. The lower yield in the bromide case might reflect the fast coupling reaction between allyltrimethylsilane and allyl bromide. In a preliminary experiment, these two compounds were found to react with each other in the presence of the Pd(0) complex (0.5 mol%)

to give 1,5-hexadiene (22% yield) and trimethylbromosilane (100% yield) upon heating at 160°C for 24 h.

In these reactions, the initial step will be oxidative addition of allylic halide to the Pd(0) complex. In order to test this, chloro(2-methylallyl)bis-(triphenylphosphine)palladium(II) was prepared. This Pd(II) complex then was conceived as the actual catalyst, and that this is the case is supported by the fact that the reaction between sym-dimethyltetrachlorodisilane and 2-methylallyl chloride was effectively initiated upon heating under reflux in the presence of 0.3 mol% of the Pd(II) complex. Rate enhancement can be clearly seen in Figure 1.

Finally, catalyst efficiency was tested briefly with other common Group VIII metal-phosphine complexes using the reaction of sym-dimethyltetrachlorodisilane with allyl chloride as a standard. For example, dichlorobis(triphenylphosphine)-palladium(II) also was found to initiate the cleavage reaction but the reaction gave only a 25% yield of allylmethyldichlorosilane after heating at 150°C for 3 h. Further, chlorotris(triphenylphosphine)rhodium(I) and tetrakis(triphenylphosphine)-platinum(0), the first of which is known to interact with allyl chloride under mild conditions [12], were tested as potential catalysts for the reaction but these complexes failed to effect the expected reaction to any appreciable extent under comparable conditions.

## Experimental

Boiling points are uncorrected. IR spectra were recorded on a Hitachi EPI-3G spectrophotometer. NMR spectra were recorded with a Varian A-60D instrument. GLC analyses were carried out with an Ohkura Model 802T gas chromatograph, using Teflon columns (100-150 X 0.4 cm) packed with 10% Silicone KF-96, 15% DCQF-1 and 10% XF-1105 on 60-80 mesh Celite 545. Corrections were made for thermal conductivity of the various components.

Reagent grade allyl chloride, 2-methylallyl chloride and allyl bromide were used without further purification. 1,2-Dimethyl-1,1,2,2-tetrachlorodisilane [8], 1,1,2-trimethyl-1,2,2-trichlorodisilane [9], 1,1,2,2-tetramethyl-1,2-dichlorodisilane [9], pentamethylchlorodisilane [10] and hexamethyldisilane [10] were prepared according to literature procedures. Tetrakis-triphenylphosphine)palladium(0) [13], tetrakis(triphenylphosphine)platinum(0) [14], chlorotris(triphenylphosphine)rhodium(I) [15], chlorobis(triphenylphosphine)palladium(II) [16] and chloro(2-methylallyl)bis(triphenylphosphine)-palladium(II) [17] were prepared according to literature directions.

Preparation of allylmethyldichlorosilane from 1,2-dimethyl-1,1,2,2-tetrachlorodisilane and allyl chloride.

The disilane (114g, 502 mmol), allyl chloride (51.6g, 674 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.557g, 0.55 mmol) were placed in a stainless steel reaction vessel. The vessel was flushed with nitrogen, sealed and heated at 150°C for 2 h. GLC analysis of the resulting yellow-brown solution showed that allylmethyldichlorosilane had been produced in 87% yield based on the disilane charged. The mixture then was diluted with petroleum ether (30-60°C) to precipitate the catalyst which was removed by filtration. Evaporation and subsequent distillation of the residue gave 58.1g (75% yield) of allylmethyldichlorosilane, b.p. 119-120°C [lit. [6] b.p. 120°C]. The IR and NMR spectra of this product showed the patterns expected for the structure assigned.

Preparation of allyldimethylchlorosilane and allyltrimethylsilane from the corresponding disilanes and allyl chloride.

Essentially the same procedure as above employing 1,1,2,2-tetramethyl-1,2-dichlorodisilane and hexamethyldisilane gave allyldimethylchlorosilane (71% isolated yield), b.p. 110-112°C [lit. [4] b.p. 111-113°C] and allyltrimethylsilane (78% isolated yield), b.p. 83.5-85.0°C [lit. [5] b.p. 84.9°C], respectively. The identity of these compounds was established by their IR and NMR spectra.

Reactions of unsymmetrical disilanes with allyl chloride.

1,1,2-Trimethyl-1,2,2-trichlorodisilane (51.9g, 250 mmol) was allowed to react with allyl chloride (23.4g, 300 mmol) in essentially the same manner as above. Work-up of the resulting mixture gave 31.8g (72% isolated yield) of a liquid boiling at 115-119°C. The liquid was shown by GLC analysis to consist of 98% allylmethyldichlorosilane and 2% allyldimethylchlorosilane. A similar reaction of pentamethylchlorodisilane (3.30g, 20.3 mmol) with the chloride

(1.68g, 23 mmol) was found by GLC analysis to give a mixture containing 97% allyldimethylchlorosilane and 3% allyltrimethylsilane in 92% combined yield. Structural assignment for these allylsilanes was based on a comparison of their IR spectra and GLC retention times with those of authetic samples after isolation by GLC.

Preparation of 2-methylallylmethyldichlorosilane from 1,2-dimethyl-1,1,2,2-tetrachlorodisilane and 2-methylallyl chloride.

The disilane (114g, 500 mmol), 2-methylallyl chloride (50g, 550 mmol) and the Pd(0) complex (1.58g, 1.5 mmol) were relfuxed under nitrogen for 8 h. Work-up gave 61g (72% yield) of 2-methylallylmethyldichlorosilane, b.p. 140°C [lit. [18] b.p. 139°C). The identity of this compound was established by its IR and NMR spectra.

Concentration-time profiles of the reaction of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane with 2-methylallyl chloride.

A mixture of 4.75g (20.1 mmol) of the disilane, 2.10g (23.4 mmol) of the chloride, 5 ml of benzene and 0.064g (0.06 mmol) of tetrakis(triphenylphosphine)palladium(0) or 0.037g (0.06 mmol) of chloro(2-methylallyl)bis-(triphenylphosphine)palladium(II) was heated under reflux under an atmosphere of nitrogen. The course of the reaction was monitored by GLC. The results are shown in Figure 1.

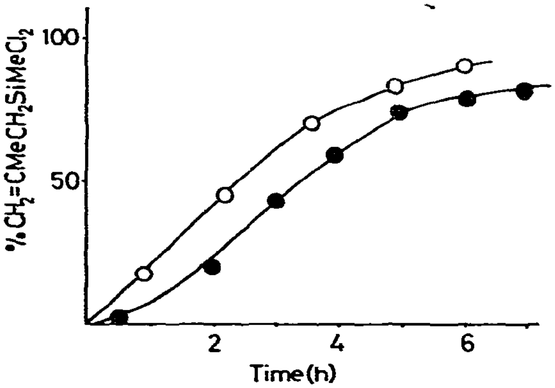

Figure 1. Typical concentration-time profiles for 2-methylallylmethyldichlorosilane in the reaction of $Cl_2MeSiSiMeCl_2$ (20 mmol) with $CH_2=CMeCH_2Cl$ (23 mmol) in the presence of 0.3 mol% of $Pd(PPh_3)_4$ (closed circles) or $PdCl(CH_2CMe=CH_2)(PPh_3)_2$ (open circles). In the reaction 5 ml of benzene was used as a solvent.

### Reaction of hexamethyldisilane with allyl bromide in the presence of $Pd(PPh_3)_4$.

A mixture of 7.32g (50 mmol) of the disilane, 7.86g (65 mmol) of the bromide and 0.55g (0.05 mmol) of the Pd(0) complex was heated in the pressure vessel with stirring at 120°C for 3 h. GLC analysis of the resulting mixture disclosed that the disilane had been completely consumed and that allyltrimethylsilane and trimethylbromosilane had been produced in yields of 52 and 100%, respectively.

### Reaction of allyltrimethylsilane with allyl bromide in the presence of $Pd(PPh_3)_4$.

A mixture of 3.44g (30 mmol) of the allylsilane, 2.42g (20 mmol) of the bromide, 0.11g (0.10 mmol) of the Pd(0) complex and 2 ml of toluene was heated in the pressure vessel at 160°C for 24 h. GLC analysis of the resulting mixture showed 99% consumption of the bromide. However, the coupling product, 1,5-hexadiene, amounted to only 4.4 mmol (22% yield based on the bromide charged), while trimethylbromosilane was produced quantitatively. Structural assignment for these products was based on a comparison of their IR spectra and GLC retention times with those of authetic samples after isolation by GLC.

### Reaction of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane with allyl chloride in the presence of $PdCl_2(PPh_3)_2$, $RhCl(PPh_3)_3$ or $Pt(PPh_3)_4$.

A mixture of 4.56g (20 mmol) of the disilane, 1.68g (22 mmol) of the chloride, 0.042g (0.061 mmol) of the Pd(II) complex was heated in the pressure vessel at 150°C for 3 h. GLC analysis of the resulting mixture showed production of allylmethyldichlorosilane in 25% yield based on the disilane charged.

Similar reactions at 150°C for 3 h with 0.3 mol% of the Rh(I) and Pt(0) complexes were found by GLC analysis to give only traces of allylmethyldichlorosilane.

### Competitive reactions

A mixture of 2.29g (10.1 mmol) of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane, 5.64g (30.1 mmol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 0.354g (4.63 mmol) of allyl chloride and 0.013g (0.012 mmol) of the Pd(0) complex was heated in the pressure vessel at 150°C for 2 h. Quantitative analysis by GLC showed that 0.53 mmol of allylmethyldichlorosilane and 0.12 mmol of allyldimethylchlorosilane had been produced. Relative rates were calculated using the following equation.

$$\frac{k_{(Me_2Si_2Cl_4)}}{k_{(Me_4Si_2Cl_2)}} = \frac{[Me_4Si_2Cl_2]_i}{[Me_2Si_2Cl_4]_i} \times \frac{[CH_2{=}CHCH_2SiMeCl_2]_f}{[CH_2{=}CHCH_2SiMe_2Cl]_f}$$

where $k_{(Me_2Si_2Cl_4)}/k_{(Me_4Si_2Cl_2)}$ is the ratio of the rate constants for $Me_2Si_2Cl_4$ and $Me_4Si_2Cl_2$, $[Me_2Si_2Cl_4]_i$ and $[Me_4Si_2Cl_2]_i$ are the initial concentrations of the disilanes, and $[CH_2{=}CHCH_2SiMeCl_2]_f$ and $[CH_2{=}CHCH_2\text{-}SiMe_2Cl]_f$ are the molar amounts of allylsilanes produced.

A similar competitive experiment between $Me_4Si_2Cl_2$ and $Me_6Si_2$ was conducted at 170°C for 2 h and the results were evaluated in similar fashion.

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