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Preliminary communication

The Addition Rates of Dichloro- and Trichlorosilane to 2-Pentene and 1-Octene

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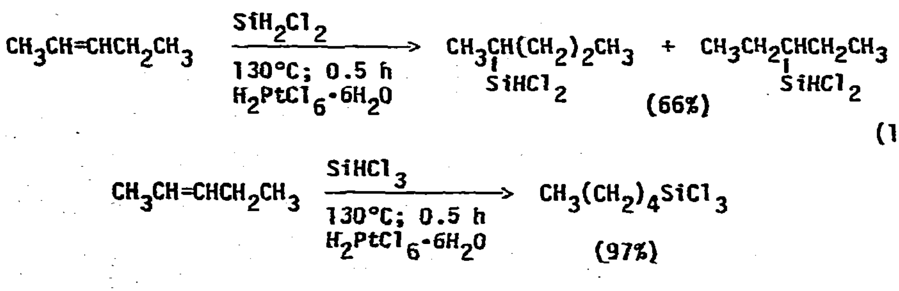
Summary

When mixtures of dichloro- and trichlorosilane were added to 2-pentene and 1-octene in the presence of a solution of chloroplatinic acid, dichlorosilane added much more rapidly than trichlorosilane. But when each silane was added separately under identical conditions, trichlorosilane added much more rapidly than dichlorosilane to the same olefins.

During the course of our investigation [2,3] of the addition of dichlorosilane to olefinic double bonds, some relative rate studies were carried out using 2-pentene and 1-octene as the olefin substrates and both dichloro- and trichlorosilane. Chloroplatinic acid was used as the catalyst in every case.

When the reactions were carried out individually, with no admixing of the two chlorosilanes, the addition of trichlorosilane was always faster than the dichlorosilane (Table 2). This was true even though both bond migration and addition were occurring [4] in the case of 2-pentene and trichlorosilane (eq 1).



$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[\substack{130°C;\ 0.5\ h \\ H_2PtCl_6\cdot 6H_2O}]{SiH_2Cl_2} CH_3\underset{SiHCl_2}{CH}(CH_2)_2CH_3 + CH_3CH_2\underset{SiHCl_2}{CH}CH_2CH_3 \quad (66\%) \qquad (1)$$

$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[\substack{130°C;\ 0.5\ h \\ H_2PtCl_6\cdot 6H_2O}]{SiHCl_3} CH_3(CH_2)_4SiCl_3 \quad (97\%)$$

When the two reactions in eq. 1 were run at 130° for only 0.25 h, the same yield of n-pentyltrichlorosilane (97%) was obtained, but only a 50% total yield of the dichloro adducts was realized.

Similar results were obtained when 1-octene was used as the substrate. This olefin was chosen to determine the effect of a terminal double bond (eq. 2).

$$\begin{array}{ll} CH_3(CH_2)_5CH{=}CH_2 \xrightarrow[\substack{64°C;\ 1\ h \\ H_2PtCl_6\cdot 6H_2O}]{SiH_2Cl_2} CH_3(CH_2)_7SiHCl_2 & \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad (3\%) & (2) \\ CH_3(CH_2)_5CH{=}CH_2 \xrightarrow[\substack{64°C;\ 1\ h \\ H_2PtCl_6\cdot 6H_2O}]{SiHCl_3} CH_3(CH_2)_7SiCl_3 & \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad (86\%) & \end{array}$$

In this case, trichlorosilane reacted much faster than dichlorosilane, probably because a relatively low temperature was used. In our experience, dichlorosilane requires temperatures in excess of 100°C to react with most olefins at any convenient rate.

As indicated in Table 2 (entry 2), a mixture of 2- and 3- pentyldichlorosilane did not react with 2-pentene under conditions in which dichlorosilane yielded 66% of addition products with 2-pentene. The difference here might well be the result of steric factors, wherein the internal chlorosilane olefin adducts were too bulky to add to another olefin at any appreciable rate. Further experiments will be needed to establish this point.

In Table 1 are shown the results of competitions of various chlorosilanes for 1-octene and 2-pentene. In these experiments, a solution of chloroplatinic acid was again used as catalyst and the competitions were carried out in the same container. The dichlorosilane was contaminated with as much as 5% monochlorosilane. We gleaned some information about the reactivity of this chlorosilane along with the others. It became clear from the data in Table 1 that, in contrast to the results of Table 2, dichlorosilane reacted faster than trichlorosilane. Also, while the evidence is more sparse, monochlorosilane reacted the fastest of all. Competitive data of this sort have been studied rather extensively [5-12] in other systems, but we believe this is the first instance in which attention has been focused solely on dichloro- and trichlorosilane with a catalyst of chloroplatinic acid.

(Continued on p. C7)

Table 1

Competition Studies Involving Olefins and Chlorosilanes

Olefins (mol)	Chlorosilanes (mol)	Temp °C (time, h)[a]	Products (% Distribution)	Bp °C (mm)	Yield (%)
2-pentene (0.1)	$ClSiH_3$ (0.015)[b]		2-+3-$C_5H_{11}SiH_2Cl$ (14)	128-36 (740)	100
	Cl_2SiH_2 (0.2)	130 (8)	2-+3-$C_5H_{11}SiHCl_2$ (86)		85
	Cl_3SiH (0.2)				
1-octene (0.1)	$ClSiH_3$ (0.005)[b]		1-$C_8H_{17}SiH_2Cl$ (1)		100
	Cl_2SiH_2 (0.2)	60 (8)	1-$C_8H_{17}SiHCl_2$ (98)	74-6 (3.6)[c]	65
	Cl_3SiH (0.2)		1-$C_8H_{17}SiCl_3$ (1)		<1
2-pentene (0.058)	Cl_2SiH_2(0.116)	130 (8)	2- + 3-$C_5H_{11}SiHCl_2$ (100)[e]		67
	2-+3-$C_5H_{11}SiHCl_2$ (0.116)[d]			67-72 (57)	67

[a] In all cases, the olefins and chlorosilane mixtures were heated together in the same bomb.

[b] The Cl_2SiH_2 contained up to 5% of $ClSiH_3$ as a contaminant. [c] The pressure was lowered to 0.5 mm to complete the distillation. [d] By NMR analysis, contained 76% 2-$C_5H_{11}SiCl_2H$ and 24% 3-$C_5H_{11}SiCl_2H$; [e] Distillation pot taken to dryness; no evidence of a dipentyl adduct.

Table 2

Relative Rates of Addition of Chlorosilanes to 2-Pentene and 1-Octene

Olefins (mol)	Chlorosilanes (mol)[a]	Temp °C (time h)	Products (% Distribution)	Bp °C (mm)	Yield (%)
2-pentene (0.1)	SiH_2Cl_2 (0.2)	130 (0.5)	2-+3-$C_5H_{11}SiHCl_2$	66-73 (56)	66
2-pentene (0.1)	$SiHCl_3$ (0.2)		1-$C_5H_{11}SiCl_3$ (100)	168-9 (750)	97
2-pentene (0.055)	2-+3-$C_5H_{11}SiHCl_2$ (0.11)	130 (0.5)	2-+3-$C_5H_{11}SiHCl_2$ (97% recovery)		∿0
2-pentene (0.055)	SiH_2Cl_2 (0.11)		2-+3-$C_5H_{11}SiCl_2H$	68-72 (56)	66
1-octene (0.1)	SiH_2Cl_2 (0.2)	64 (1)	1-$C_8H_{17}SiCl_2H$	- (0.7 g)	3
1-octene (0.1)	$SiHCl_3$ (0.2)		1-$C_8H_{17}SiCl_3$ (100)	74-5 (1.9)	86

[a] Each of the chlorosilanes was allowed to react separately with the olefin indicated.

To summarize: in individual experiments, trichlorosilane is more reactive than dichlorosilane with both internal and terminal olefins (Speier's catalyst). When the chlorosilanes are allowed to compete for the same olefin in the same container, the order of reactivity is reversed such that $ClSiH_3 > Cl_2SiH_2 > Cl_3SiH$.

The reason for these results is not clear and additional experiments are underway to unravel the cause. The phenomena has significance, since hydrosilylations which fail or exhibit long induction periods may do so because of small impurities of a more "reactive" silane [3]. In still other cases, it may not be necessary to purify certain silane mixtures prior to their use in olefin hydrosilylations since one of the silanes in the mixture may be unreactive under the circumstances.

Experimental

2-Pentene and 1-octene were purchased from the Phillips Petroleum Company. 2-Pentene was a pure mixture of cis- and trans- isomers. 1-Octene was isomerically pure. The dichlorosilane (Union Carbide) was contaminated with 1-5% by weight of monochlorosilane.

Competition Studies; General Procedure. (Table 1).

A 150 mL stainless steel bomb (Hoke DOT-3E-1800) was connected to a calibrated tube through which both dichlorosilane and dry nitrogen could flow. The bomb was also open to the atmosphere via a drying tube. After it was flushed well with nitrogen, it was charged with olefin, 50 µL of catalyst solution (1.0 g of $H_2PtCl_6 \cdot 6H_2O$ in 20 mL of isopropyl alcohol) and a magnetic stirring bar. It was then cooled to -78°C. Dichlorosilane was condensed into the calibrated tube at -78°C and then slowly distilled into the cold bomb under dry nitrogen. Another chlorosilane was then added to the cooled bomb (-78°C). The latter was allowed to warm to about 0°C while stirring was continued. It was then immersed in an oil bath at a specified temperature and for a fixed period of time. The workup was similar to that described previously [2].

Relative Rate Studies; General Procedure. (Table 2).

Two identical bombs were used in this study. One was filled with 0.10 mol of the olefin, 50 µL of chloroplatinic acid solution and 0.2 mol of dichlorosilane as described above in the Competition Studies. The other bomb was filled with

0.10 mol of the same olefin along with 50 μL of chloroplatinic acid solution. This was cooled to -78°C and then the other chlorosilane was added. Both bombs were maintained at -78°C for about 0.5 h to insure thermal equilibrium. To maintain a fairly constant oil bath temperature, both bombs (at -78°C) were simultaneously placed in a large volume of water at rt for about 5 min and then immersed in the oil bath at the specified temperature for a fixed period of time. The reactions were quenched by cooling to -78°C. The workup was the same as that described previously [2].

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