
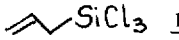







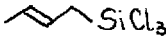
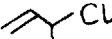
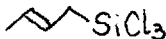

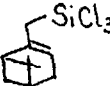










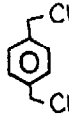
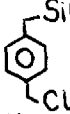
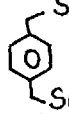
TABLE 1

	RCl	Reaction time and (temperature)	R'SiCl ₃	Yield (%) (isolated product)
A		15 h (90°) (autoclave)	 <u>1</u>	35
B		3,5 h (reflux)	 <u>2</u>	80
C		20 h (reflux)	 <u>2</u>	50
D		15 h (reflux)	 <u>3</u>	100
E		15 h (reflux)	 <u>4</u>	72
F		20 h (reflux)	 <u>4</u>	30
G		100 h (reflux)	 <u>5</u>	85

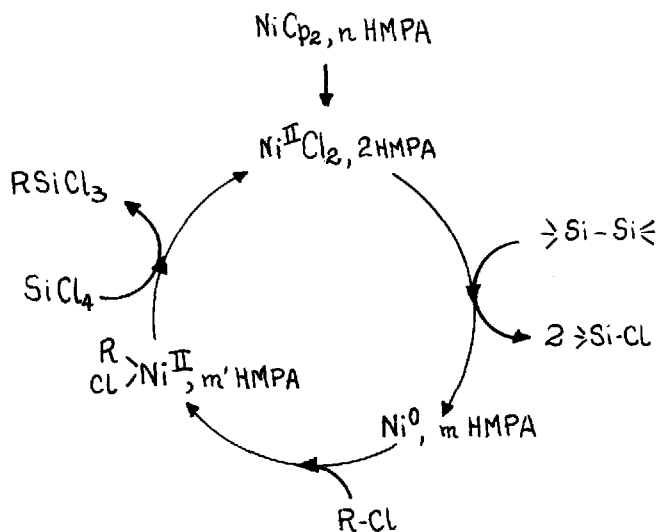
Silylation always appears to be regioselective and yields the thermodynamically stable isomer. Thus, in the case of *trans* crotyl chloride, we obtained *trans* crotyltrichlorosilane 4 (72 %), exclusive of the *cis* and methallyl isomers. The previously proposed route of Seyferth et al.⁸ posed more difficulties in execution but also resulted in a mixture of *cis* and *trans* crotyltrichlorosilanes (40/60, 52 % global yield). With the chlorides C and F we observe a prior rearrangement of the starting halo compounds into prenyl and crotyl chlorides respectively.

Similar behaviour was noted with benzyl chlorides and bromobenzene whereas chlorobenzene remained inert under the same conditions. Results are given in Table 2.

TABLE 2

	RC1	Reaction time and (temperature)	R'SiCl ₃	Yield (%) (isolated product)
H		24 h (reflux)		0
I		24 h (reflux)	 <u>6</u> +  <u>7</u>	90 <u>6/7</u> = 20/80
J		24 h (reflux)	 <u>8</u>	40
K		6 h (reflux)	 <u>9</u>	50
L		15 h (reflux)	 <u>10</u>  <u>11</u>	100 <u>10/11</u> = 70/30

We propose the following catalytic cycle as an aid in the explanation of our results and as a possible mechanism :



This interpretation can be supported by several observations :

- 1- a green solution results from the addition of nickelocene to HMPA.
- 2- the addition of nickel (II) chloride to HMPA yields a blue, tetrahedral complex $(\text{NiCl}_2, 2 \text{HMPA})^9$ in which HMPA, bonded through its oxygen atom, behaves as a very strong ligand¹⁰.
- 3- nickel (II) chloride/HMPA exhibits a catalytic activity in the reaction although less important than that of nickelocene (eg. 5 was obtained in 30 % yield as opposed to 72 % obtained with NiCp_2 /HMPA during the same reaction time).
- 4- Disilanes easily reduce NiCl_2 to Ni^0 ¹¹.
- 5- During the course of the reaction the colour of the medium changes from green to yellow at 70°C (and shows at least a partial inverse colour change).

Further investigations are in progress in an attempt to extend the scope of the reaction, to identify reaction intermediates and to determine catalytic moieties.

References and notes

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- 12 - All products gave IR and NMR spectra in good agreement with proposed structures.

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