ONE-STEP REGIOSPECIFIC SYNTHESIS OF ALLYLIC SILANES - EXTENSION TO BENZYLSILANES

Marcel LEFORT<sup>\*</sup> and Christian SIMMONET<sup>\*</sup> Marc BIROT<sup>\*\*</sup>, Gérard DELERIS<sup>\*\*</sup>, Jacques DUNOGUES<sup>\*\*</sup> and Raymond CALAS<sup>\*\*</sup>

★ : Société Rhône-Poulenc, Centre de Recherches des Carrières 69190 SAINT-FONS (France).

\*\*: Laboratoire de Chimie des Composés Organiques du Silicium et de l'Etain associé au CNRS Université de Bordeaux I 33405 TALENCE (France).

Allyltrichlorosilanes are prepared according to a one-step regiospecific process based on the reaction of allyl chlorides with SiCl<sub>4</sub> and NiCp<sub>2</sub>/HMPA (catalyst), in the presence of industrial methylchlorodisilane fraction. Benzyltrihalosilanes are similarly obtained.

Allylic trialkylsilanes have become increasingly more useful as versatile synthons. Reactions involving such species<sup>1,2</sup> demonstrate a high regioselectivity, most notably in the cases of acylation<sup>3</sup>, sulfonation<sup>4</sup> or addition<sup>5</sup> reactions. Allyltrichlorosilanes are other species whose interest extends over areas :

- 1) potential applications for industrial purposes (fibreglass adhesives, ...)
- 2) basic synthetic purposes as organic reagents (dienophiles, enophiles)
- 3) as a source for the corresponding allyltrimethylsilanes by methylation (notably with MeCl/Zn in N-methyl 2-pyrrolidone $^{6}$ ).

Presently known syntheses of these intermediates generally result in products silylated at both possible allylic sites and Z/E isomerism often is observed in applicable cases.

We thus propose a new method of access to the allyltrichlorosilanes. The process involves the use of the "disilane fraction<sup>\*</sup>" (the common residue in the industrial synthesis of methylchlorosilanes) as a chlorine trapping agent in the reaction of allylchlorides with SiCl<sub>4</sub> and NiCp<sub>2</sub>/HMPA acting as the catalyst :

 $R-C1 + SiC1_4 + C1_2 MeSiSiMeC1_2$   $RSiC1_3 + 2MeSiC1_3$ 

$$\begin{array}{ll} (and/or & (and/or \\ Cl_2MeSiSiMe_2Cl) & Me_2SiCl_2 + MeSiCl_3) \end{array}$$

Results are summarized in Table 1.

If  $SiCl_4$  is not used, the reaction proceeds with greater difficulty. This can be seen in the case of allyl chloride and the results are then comparable to those of Atwell and Bokerman<sup>7</sup>:

<sup>\* :</sup> Major constituents : Cl<sub>2</sub>MeSiSiMeCl<sub>2</sub> - Cl<sub>2</sub>MeSiSiMe<sub>2</sub>Cl : 60 % - 30 %.

## TABLE 1

	RC1	Reaction time and (temperature)	R'SiCl <sub>3</sub>	Yield (%) isolated product)
A	A-CL	15 h (90°) (autoclave)	SiCl <sub>3</sub> 1	35
В	<i>p</i> -ci	3,5 h (reflux)	SiCla 2	80
с	∕∕× <sup>CL</sup>	20 h (reflux)	X-SiCla 2	50
D	La	15 h (reflux)	Sich <sub>3</sub> 3	100
Е	∕~~cı	15 h (reflux)	SiCla 4	72
F	ACL	20 h (reflux)	SiCl3 4	30
G	L CL	100 h (reflux)	Sicl <sub>3</sub>	85

Silylation always appears to be regiospecific 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.<sup>8</sup> posed more difficulties in execution but also resulted in a mixture of *cis* and *trans* crotyltrimethylsilanes (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)	Yield (%) R'SiCl <sub>3</sub> (isolated product
Н	QCL	24 h (reflux)	0
I	() <sup>Br</sup>	24 h (reflux)	$ \underbrace{\bigcirc}_{\mathbf{s}} \overset{\text{SiCl}_3}{\mathbf{s}} + \underbrace{\bigcirc}_{\mathbf{z}} \overset{\text{SiCl}_2 Br}{\mathbf{s}} \overset{90}{\mathbf{s}} \\ \underbrace{\mathbf{s}}_{\mathbf{z}} \overset{\mathbf{s}}{\mathbf{s}} \underbrace{\mathbf{s}}_{\mathbf{z}} \underbrace{\mathbf{s}} \mathbf{s$
J	Onci	24 h (reflux)	
к	OC CL	6 h (reflux)	SiCla 50
L		15 h (reflux)	$ \begin{array}{c c} SiCl_{3} & SiCl_{3} \\ \hline O & O & 100 \\ CL & SiCl_{3} \\ \underline{10} & \underline{11} & \underline{10/11} = 70/30 \\ \end{array} $

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 (NiCl<sub>2</sub>, 2 HMPA)<sup>9</sup> in which HMPA, bonded through its oxygen atom, behaves as a very strong ligand<sup>10</sup>.

-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<sub>2</sub>/HMPA during the same reaction time).

-4- Disilanes easily reduce NiCl<sub>2</sub> to Ni<sup>0 11</sup>.

-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

- 1 T.H. CHAN and I. FLEMING, Synthesis, (1979), 761.
- 2 E.W. COLVIN, Chem.Soc.Rev. (1978), 7, 15.
- 3 J-P. PILLOT, G. DELERIS, J. DUNOGUES and R. CALAS, <u>J.Org.Chem.</u> (1979) <u>44</u> 3397 and ref. cited therein.
- 4 J-P. PILLOT, G. DELERIS, J. DUNCGUES and R. CALAS, to be published.
- 5 G. DELERIS, J. DUNOGUES and R. CALAS, <u>J.Organometal.Chem.</u> (1975), <u>93</u>, 43; (1976), <u>116</u>, C 45.
- 6 RHÔNE-POULENC, French Patent(1969), 2051903.
- 7 W.H. ATWELL and G.N. BOKERMAN (DOW CORNING), German Pat. (1973), 2 260 282; (1975), 2 430 950.
- 8 D. SEYFERTH, Th. F. JULA, H. DERTOUZOS and M. PEREYRE, <u>J.Organometal.Chem.</u> (1968), <u>11</u>, 63.

D. SEYFERTH and Th. F. JULA, ibid, (1974), 66, 195.

9 - J.T. DONOGHUE, Diss.Abstr., (1964), 24, 3535.

- 10 M.W.G. DE BOLSTER and W.L. GROENEVELD, Rec. Trav. Chim. Pays-Bas (1971), 90, 477.
- 11 R. CALAS, E. FRAINNET and Y. DENTONE, C.R.Acad.Sci. Paris, (1964), 259, 3777.
- 12 All products gave IR and NMR spectra in good agreement with proposed structures.

(Received in France 4 February 1980)