Tetrahedron Letters, Vol.22, No.31, pp 2985 - 2986, 1981
Printed in Great Britain

0040-4039/81/312985-02$02.00/0

THE USE OF Si-C BOND IN SYNTHESIS : PREPARATION OF FUNCTIONALISED VINYLSILANES FROM THE ALLYLTRIMETHYLSILYL ANION AND SOME ASPECTS OF THEIR REACTIVITY

R.J.P. CORRIU, C. GUERIN and J. M'BOULA

Université des Sciences et Techniques du Languedoc - Laboratoire des Organométalliques
Equipe de recherche associée au C.N.R.S. N°554 - Place Eugène Bataillon - 34060 Montpellier-cedex (France)

Summary : A general preparation of functionalised vinylsilanes is reported through the allyltrimethylsilylanion. Their reactivity is studied.

Vinylsilanes are valuable synthetic intermediates in organic synthesis (1,2,3,4,5,6) and a number of synthetic pathways to such compounds has been developped (7,8,9,10,11,12).

In this paper, we wish to report a general synthetic approach to vinylsilanes. Our interest is specially to attain functionalised vinylsilanes.

Treatment of allyltrimethylsilane with n-butyllithium in ether containing tetramethylethylene diamine (1.0 eq.) at 0° gives solutions of **1** (13). The trimethylsilylallyl copper reagent **2** ,

$$\mathbf{1} = [(CH_3)_3Si - CH = CH - CH_2^{\ominus}\ Li^+ \quad , \quad \mathbf{2} = [(CH_3)_3Si - CH = CH - CH_2^{\ominus}]Cu(CN)Li^+$$

is prepared by mixing one equivalent of **1** with one equivalent of copper(I) cyanide at -78°C, and reacted with a wide range of electrophiles (Table I).

It may be noted that **2** gives selective substitution reactions with the alkyl- , and acyl halides ,and highly selective conjugate addition reactions to α,β-ethylenic esters and ketones. In contrast, α,β-ethylenic aldehydes lead only to 1,2-addition. At last, **2** reacts to give regioselectively the γ product.

In order to test the synthetic possibilities of such functionalised vinylsilanes, we have studied some electrophilic reactions as shown in Table II.

The functionalised silanes (runs 3,5)have been also efficiently converted to the corresponding α,β - epoxysilanes which are precursors of carbonyl compounds under acidic conditions (14).

Efforts are now underway to improve the use of the trimethylsilylallylanion as precursor of functionalised vinyl- and allylsilanes.

References

1 - T.H. Chan and I. Fleming, Synthesis, 763 (1979).
2 - I. Fleming and A. Pearce, J.C.S. Chem. Comm., 633 (1975).
3 - T.H. Chan, W. Mychajlowskij, B.S. Ong and D.N. Harpp, J. Organometal. Chem., 107 C1 (1976) ; ibid., J. Org. Chem., 43, 1526 (1978).
4 - J.P. Pillot, J. Dunogès, R. Calas, C.R. Acad. Sci. Ser. C, 278, 789 (1974) ; ibid., Bull. Soc. Chim. Fr., 2143(1975) ; ibid., Synthesis, 469 (1977).
5 - J.O. Yoshida, K. Tamao, M. Takahashi, M. Kumada, Tetrahedron Lett., 2161 (1978).
6 - W.E. Fristad, T.R. Bailey and L. A. Paquette, J. Org. Chem., 45, 3028 (1980).
7 - (a) F.A. Carey and J.R. Toler, J. Org. Chem., 41, 1966 (1976) ; (b) A.D. Petrov and S.I. Sadykh-Zade, Dokl. Chem. (Engl. Transl.), 129, 1033 (1959).

8 - G. Stork, M.E. Jung, E. Colvin and Y. Noel, J. Amer. Chem. Soc., 96, 3684 (1974).

9 - L.H. Sommer, D.M. Bailey and F. Whitmore, J.Amer. Chem. Soc., 76, 1613 (1954) ; H. Sakuraï, K. Nishiwaki and M. Kira, Tetrahedron Lett., 4193 (1973).

10 - K. Uchida, K. Utimoto and M. Nozaki, J. Org. Chem., 41, 2941 (1976) ; ibid., 41, 2215 (1976) ; J.J.Eisch and G.A. Damasevitz, J. Org. Chem., 41, 2214 (1976).

11 - See, for example : I.M. Grerdtsiteli and L.V. Baramidze, J. Gen. Chem. USSR, 38, 1547 (1968) ; ibid., L.V. Sovbsch. Akad. Nauk Gruz. SSR, 83, 50 (1968) ; A.J. Chalk and J.D. Harrod, J. Amer. Chem. Soc., 89, 1640 (1967).

12 - L.A. Paquette, W.E. Fristad, D.S. Dime and T.R. Bailey, J. Org. Chem., 45, 3017 (1980).

13 - For references to allyltrimethylsilylanion see : R. Corriu and J. Massé, J. Organometal. Chem., 57, C5 (1973) ; R. Corriu, J. Massé and D. Samaté, J. Organometal. Chem., 93, 71 (1975) ; R. Corriu, G. Lanneau and D. Samaté, J. Organometal. Chem., 127, 2881 (1977); A.C. Chass, E. Ehlinger and P. Magnus, J.C.S. Chem. Comm., 772 (1977) ; P.W.K. Lau and T.H. Chan, Tetrahedron Lett., 2383 (1978).

14 - (a) J.J. Eisch and J.T. Trainor, J. Org. Chem., 28, 2870 (1963); (b) G. Stork and E. Colvin, J. Amer. Chem. Soc., 93, 2080 (1971).

Table I

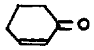
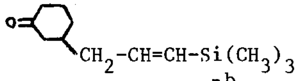
Electrophile	Runs	Conditions	Products (Yield %)^{a}
CH_3CHO	1	- 78°C, 2h	$(CH_3)_3SiCH{=}CH\text{-}CH_2\underset{\displaystyle OH}{CH}\text{-}CH_3$ (75)
$CH_3CO\text{-}Cl$	2	- 78°C, 15 mn	$(CH_3)_3SiCH{=}CH\text{-}CH_2CO\text{-}CH_3$ + (45) $(CH_3)_3SiCH_2CH{=}CH\text{-}CO\text{-}CH_3$ (15)
CH_3OCH_2Cl	3	- 78°C, 2h	$(CH_3)_3SiCH{=}CH\text{-}CH_2\text{-}CH_2\text{-}OCH_3$ (70)
$R\text{-}CH{=}CH\text{-}CHO$ ($R = CH_3$, C_6H_5)	4	- 78°C, 2h	$(CH_3)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle OH}{CH}\text{-}CH{=}CH\text{-}R$ (75)
$R\text{-}CH{=}CH\text{-}CO_2C_2H_5$ ($R = CH_3$, C_6H_5)	5	- 78°C, 3h	$(CH_3)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle R}{CH}\text{-}CH_2\text{-}CO_2C_2H_5$ (75-80)
	6	- 78°C, 3h	 (65)
——		- 78°C → r.t.	$[(CH_3)_3SiCH{=}CH\text{-}CH_2\text{-}]_2^{b}$ (70)

Table II

Vinylsilane	Electrophile	Conditions	Products (Yield %)^{a}
$[(CH_3)_3SiCH{=}CH\text{-}CH_2\text{-}]_2$	Br_2/CH_2Cl_2	- 8°C, 4h	$[Br\text{-}CH{=}CH\text{-}CH_2\text{-}]_2$ (50)
$[(CH_3)_3SiCH{=}CH\text{-}CH_2\text{-}]_2$	$(CH_3)_2C{=}CH\text{-}COCl/AlCl_3$	-78°C→ 20°C 4h	$[(CH_3)_2C{=}CH\text{-}CO\text{-}CH{=}CH\text{-}CH_2\text{-}]_2$ (45)
$(CH_3)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle C_2H_5\text{-}O_2C\text{-}CH_2}{CH}\text{-}C_6H_5$	Br_2/CH_2Cl_2	-80°C, 4h	$Br\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle CH_2CO_2C_2H_5}{CH}\text{-}C_6H_5$ (60)
$(CH_3)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle C_2H_5\text{-}O_2C\text{-}CH_2}{CH}\text{-}C_6H_5$	$RCOCl/AlCl_3$ ^{c}	-78°C→ 20°C 4h	$RCO\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle CH_2CO_2C_2H_5}{CH}\text{-}C_6H_5$ (75-80)

a - Yield after isolation by chromatography on SiO_2, unless otherwise stated ; b - Product isolation by distillation ; c - $R = CH_3$, $CH_3\text{-}CH{=}CH\text{-}$, $(CH_3)_2C{=}CH\text{-}$.

(Received in France 31 March 1981)