CHEMISTRY LETTERS, pp. 223-226, 1982. © The Chemical Society of Japan 1982

HIGHLY REGIOSELECTIVE SYNTHESIS OF (1-METHYL-2-PROPENYL)TRIMETHYLSILANE USING THE "CROTYL" GRIGNARD REAGENT AND TRIMETHYLCHLOROSILANE[1)]

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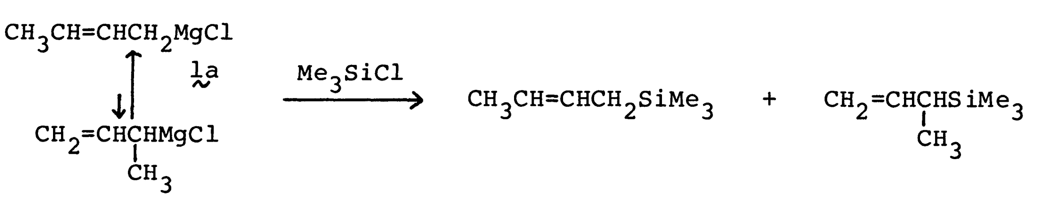
Factors influencing the regioselectivity of the reaction of the "crotyl" Grignard reagent(**1**) with trimethylchlorosilane are investigated. The regioselectivity of the reaction is strikingly controlled by changing solvent and reaction temperature and by the addition of cuprous iodide. (1-Methyl-2-propenyl)trimethylsilane is obtained selectively in THF at low temperature in the presence of cuprous iodide.

We have recently described that allylsilanes are useful and convenient reagents for the regiospecific allylation of carbon electrophiles with 1,3-transposition of the allylic group.[2)] However, to date, regioselective synthesis of alkyl-substituted allylsilanes, necessary for this purpose, has not been fully developed except for a few examples.[3)] Previously we have found the regioselective preparation of a regioisomer of methyl-substituted allylsilanes by fluoride ion-promoted isomerization, whose silicon atom is bonded to the less substituted carbon atom of the allylic group.[4)] Further, reactions of methyl-substituted allylic Grignard reagents with trichlorosilane or methyldichlorosilane, which is sterically less hindered around a silicon atom due to a hydrogen substitution, give allylic silanes regioselectively, the silicon atom of which is bonded to the more substituted carbon atom of the allylic group, in striking contrast to the reaction with trimethylchlorosilane or tetrachlorosilane.[5)] We report here that a regioselective synthesis of α-methallyltrimethylsilane(**2b**) can be readily obtained by the reaction of trimethylchlorosilane with the "crotyl" Grignard reagent(**1**)[6)] using THF as a solvent at low temperature by addition of a copper(I) salt in a single step. This is the most simple and convenient synthetic method of **2b** reported hitherto.[3,5)]

It has been well-documented that the reaction of the Grignard reagent(**1**) with trimethylchlorosilane gives usually a mixture of (but-2-enyl)trimethylsilane (**2a**) and (1-methyl-2-propenyl)trimethylsilane(**2b**) in ether or THF.[7)] (eq. 1)



$$\begin{array}{c} CH_3CH{=}CHCH_2MgCl \\ \updownarrow \ \mathbf{1a} \\ CH_2{=}CH\underset{\displaystyle CH_3}{CH}MgCl \end{array} \xrightarrow{Me_3SiCl} CH_3CH{=}CHCH_2SiMe_3 + CH_2{=}CH\underset{\displaystyle CH_3}{CH}SiMe_3 \qquad (1)$$

1b **2a** (E and Z) **2b**

Table 1. Reactions of the "crotyl" Grignard reagent(1) with trimethylchlorosilane in various conditions

Entry	Temp/°C	Solvent	Ratio of Products[a] 2a(E/Z) : 2b	% Yield[b] (2a + 2b)
1	35	Et_2O	45(55/45) : 55	85
2	0	Et_2O	39(48/52) : 61	69
3	-30	Et_2O	22(34/66) : 78	86
4	-78	Et_2O	13(38/62) : 87	43
5	66	THF	33(29/71) : 67	59
6	0	THF	30(22/78) : 70	60
7	-30	THF	24(18/82) : 76	78
8	-78	THF	11(16/84) : 89	78
9	0	Et_2O-Dioxane	27(46/54) : 73	71
10	-78	Et_2O-Dioxane	9(30/70) : 91	35
11	0	THF-HMPA	66(3/97) : 34	36

Table 2. Reactions of the "crotyl" Grignard reagent(1) with trimethylchlorosilane in the presence of cuprous iodide

Entry	mol% of CuI	Temp/°C	Solvent	Ratio of Products[a] 2a(E/Z) : 2b	% Yield[b] (2a + 2b)
1	10	0	Et_2O	26(46/54) : 74	58
2	10	0	THF	12(28/72) : 88	69
3	50	0	Et_2O	16(42/78) : 84	53
4	50	0	THF	12(27/73) : 88	50
5	10	-30	Et_2O	12(35/65) : 88	92
6	10	-30	THF	8(35/65) : 92	81
7	50	-30	THF	7(22/78) : 93	48
8	10	-78	THF	3(24/76) : 97	50

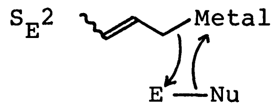
Captions to Tables (common)

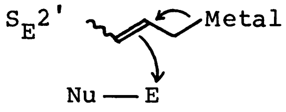
[a] Determined by GLC packed with 30% $AgNO_3$-$PhCH_2CN$ on Celite 545.

[b] Determined by GLC packed with 20% SE30 on Celite 545.

However, we found that the selectivity was dramatically dependent on variations of solvent and reaction temperature, and of the addition of cuprous iodide. Thus, the effect of temperature shown in Table 1 indicates that the relative yield of **2b** to **2a** increases with decreasing reaction temperature; e.g., the ratio of **2a**:**2b**, that is 45:55 at 35° in diethyl ether and 33:67 at 66° in THF, changes to 13:87 and 11:89, respectively, at -78°. The effect of solvent was more remarkable. The selectivity of **2b** over **2a** was better in THF than in ether at any temperature examined. Moreover, the considerable preference of **2b** over **2a** was disclosed by the addition of dioxane to ether solution of **1**, the ratio of **2a**:**2b** resulting in 9:91 at -78°, while the addition of hexamethylphosphoric triamide(HMPA) produced a contrary result. Namely, **2a** was obtained predominantly over **2b**, the ratio being 66:34. Interestingly, cuprous iodide(CuI) reveals great influence on the selectivity; e.g., the ratio of **2b** to **2a** was 12:88 at 0° in the presence of 10 mol% CuI and **2b** could be obtained almost selectively at -78° in THF.8) This is the first example of the regioselective synthesis of **2b** from the readily available reagent(**1**) and trimethylchlorosilane by controlling solvent, temperature and the additive. The results are listed in Table 2.

The effect of temperature, solvent and addition of CuI are summerized as follows. The ratio of **2a**:**2b** is decreasing with decreasing reaction temperature, by changing a solvent in the order of Et_2O-dioxane > THF > Et_2O > THF-HMPA, and by addition of CuI. Although the mechanism of the reaction has not been elucidated fully yet, all features of the reaction can be reasonably explained in terms of the increasing covalent character of the C-Mg bond of organomagnesium species (R_2Mg + RMgX) existing in the Schlenk equilibrium, where the population of R_2Mg species increases at lower temperature and decreases in the order of solvents shown above.9,10) Since the primary isomer(**1a**) is the overwhelmingly predominant species in the reagent,6) both **2a** and **2b** should be formed by the reaction with **1a** by either S_E2 or S_E2' process.11) The more the ionic character of the carbon-metal bond of the reagent increases, the more S_E2 process becomes dominantly. Conversely, less ionic and covalent metal-allyl compounds should give the product by the S_E2' process with concomitant rearrangement of the allylic group.





The facts that ionic butenyllithium12) gave only **2a** exclusively in the reaction with trimethylchlorosilane,13) while covalent allylsilanes2) and -stannanes14) undergo allyl transfer with a variety of electrophiles accompanied by transposition of the allyl group via S_E2' reaction, support strongly that the regiochemistry of allylic organometallics can be controlled by the covalent character of the C-Metal bond.

Acknowledgement: We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

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(Received December 24, 1981)