Hydromagnesiation of 3-Trimethylsilylprop-2-yn-1-ol. A Simple Route to (*E*)-3-Trimethylsilylalk-2-en-1-ols

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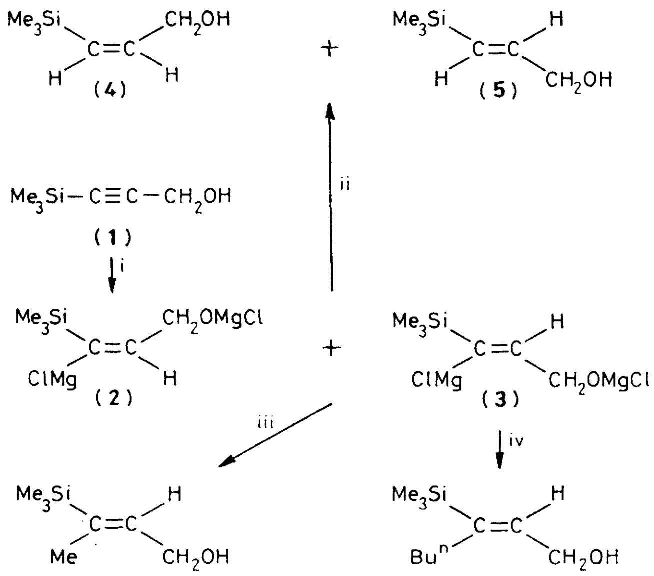
Hydromagnesiation of 3-trimethylsilylprop-2-yn-1-ol affords the alkenylmagnesium halide (**3**) exclusively, which is valuable as a precursor of various (*E*)-3-trimethylsilylalk-2-en-1-ols.

We recently reported that disubstituted acetylenes are readily hydromagnesiated by isobutylmagnesium halides in the presence of a catalytic amount of $(\eta^5\text{-}C_5H_5)_2TiCl_2$. The reaction proceeds *via* a *syn*-pathway and a high regioselectivity is

Table 1. Hydromagnesiation of (**1**).

Reaction time/ min	Hydrolysis products (**4**)	: (**5**)^a	Total yield,%^{b}
10	60	: 40	25
20	50	: 50	30
30	30	: 70	40
60	20	: 80	50
300	5	: 95	98
360	0	: ≈100	≈100

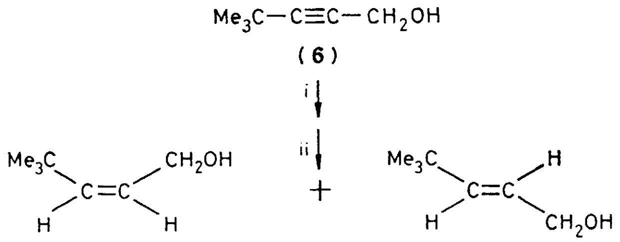
^{a} Determined by ^{1}H n.m.r. spectroscopy. ^{b} Determined by g.l.c.



Scheme 1. *Reagents:* i, 2 Bu^iMgCl, $(\eta^5\text{-}C_5H_5)_2TiCl_2$; ii, $HCl\text{-}H_2O$; iii, MeI; iv, Bu^nI, CuI.

attained for silylacetylenes[1] and prop-2-ynylic alcohols.[2] These results strongly suggested that hydromagnesiation of 3-trimethylsilylprop-2-yn-1-ol (**1**) would afford the alkenylmagnesium halide (**2**). However, we have found that the reaction provides its stereoisomer (**3**) exclusively.†

A mixture of (**1**), isobutylmagnesium chloride, and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (mole ratio 1:2.4:0.08) was stirred in ether at 25 °C. Aliquots were removed periodically, decomposed with dilute hydrochloric acid, and analysed for (*Z*)-3-trimethylsilylprop-2-en-1-ol (**4**), (*E*)-3-trimethylsilylprop-2-en-1-ol (**5**), and unreacted (**1**) by ^{1}H n.m.r. spectroscopy and g.l.c. (Table 1, Scheme 1). It can be seen from Table 1 that the concentration of (**5**) increased continuously and reached almost 100% of the total after 6 h, whilst the concentration of (**4**), which had been predominant at the early stage of the reaction, decreased. The regiochemistry of the Grignard reagent (**3**) has been established by its conversion into (*E*)-3-trimethylsilyl-3-deuterioprop-2-en-1-ol by deuteriolysis; no detectable amounts of the regio-isomer were found by ^{1}H n.m.r. spectroscopy.



Scheme 2. *Reagents:* i, 2 Bu^iMgCl, $(\eta^5\text{-}C_5H_5)_2TiCl_2$; ii, $HCl\text{-}H_2O$.

These results suggest that the hydromagnesiation of (**1**) follows the *syn*-pathway, usually observed with disubstituted acetylenes, to yield (**2**), which is rapidly converted into (**3**) under the reaction conditions. It is interesting to note that no such isomerization occurs in the case of the Grignard reagents obtained by the hydromagnesiation of unsubstituted alk-2-ynylic alcohols.‡

The steric bulk of the trimethylsilyl substituent seemed to explain the facile isomerization of (**2**). Therefore, we have investigated the hydromagnesiation of 4,4-dimethylpent-2-yn-1-ol (**6**). The rate of hydromagnesiation of (**6**) was much lower than that of (**1**) presumably owing to the increase in steric hindrance; however, the *syn*-addition product was predominant. Thus, hydromagnesiation of (**6**) at 25 °C for 12 h in ether gave a 60% yield of 4,4-dimethylpent-2-en-1-ol, (*Z*) >93% and (*E*) <7% (Scheme 2).

While a satisfactory explanation of the facile isomerization of (**2**) into (**3**) must await further study, it should be noted that the hydromagnesiation reaction of (**1**) promises to provide a novel, specific, and operationally simple route to various (*E*)-3-trimethylsilylalk-2-en-1-ols, owing to the high reactivity of the Grignard reagent. For example, hydromagnesiation of (**1**) followed by treatment with methyl iodide in tetrahydrofuran afforded (*E*)-3-trimethylsilylbut-2-en-1-ol in 88% isolated yield, the halide of which acts as an alkylative equivalent of methyl vinyl ketone[3] (see Scheme 1). In the same way, the reagent (**3**) reacted with butyl iodide in the presence of copper iodide (10 mol%) in tetrahydrofuran[4] to give an 89% yield of (*E*)-3-trimethylsilyl-hept-2-en-1-ol with 95% purity.

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References

1 F. Sato, H. Ishikawa, and M. Sato, *Tetrahedron Lett.*, 1981, **22**, 85.
2 F. Sato, H. Ishikawa, H. Watanabe, T. Miyake, and M. Sato, *J. Chem. Soc., Chem. Commun.*, 1981, 1140.
3 G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, 1974, **96**, 3682; G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *ibid.*, p. 3684.
4 C. Huynh and G. Linstrumelle, *Tetrahedron Lett.*, 1979, 1073.

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† Parts of this report were communicated orally at the 45th Annual Meeting of the Japan Chemical Society, April 1982, Tokyo. Similar results were also reported (E. Nakamura, K. Fukuzaki, and I. Kuwajima).

‡ No isomerization was observed even when the reaction mixture from the hydromagnesiation of hept-2-yn-1-ol in ether was heated under reflux for 5 h.