

COPPER CATALYZED SILYLZINCATION OF ACETYLENES

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Abstract: Dialkyl(dimethylphenylsilyl)zinc-lithium adds effectively to internal acetylenes as well as terminal acetylenes in the presence of CuCN catalyst.

Extensive studies have been explored with the reactions of cuprate complexes such as conjugated addition or substitution.¹ In contrast, few examples are known for the synthetic utility of organozinc reagents.² Here we wish to report that silylzinc compounds, $\text{PhMe}_2\text{SiZnR}_2\text{Li}$ derived from PhMe_2SiLi and dialkylzinc, add to triple bonds effectively to give vinylsilanes under good control of the regio- and stereoselectivity.³

A THF solution of PhMe_2SiLi ⁴ (0.59 M, 1.7 ml, 1.0 mmol) was added to an ethereal solution of $^t\text{Bu}_2\text{Zn}$ ⁵ (1.0 M, 1.0 ml, 1.0 mmol) at 0 °C under an argon atmosphere. After stirring for 20 min, the reaction mixture was diluted with THF (2.0 ml). Then a catalytic amount of CuCN (2.0 mg, 0.02 mmol) and a THF solution of 1-dodecyne (85 mg, 0.5 mmol) were added at 0 °C, and the whole was stirred at 0 °C for 30 min and at 25 °C for an additional 50 min. The resulting mixture was poured into sat. NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried, and concentrated in vacuo. Purification of the residual oil by preparative thin layer chromatography on silica-gel gave 2-dimethylphenylsilyl-1-dodecene (0.14 g) in 92% yield.

The experimental results are summarized in Tables 1 and 2, and they indicate the following: (1) The uncatalyzed reaction of silylzinc compounds with acetylenes proceeded very slowly to provide silylated olefins in low yield after prolonged reaction times. For instance, the reaction of $\text{PhMe}_2\text{SiZnEt}_2\text{Li}$ with 1-dodecyne gave a mixture of 1-dimethylphenylsilyl-1-dodecene and the 2-silyl isomer (5:3) in 13% combined yield after stirring at 25 °C for 20 h. CuI, CuCN, $\text{Pd}(\text{PPh}_3)_4$, and $\text{CoCl}_2(\text{PPh}_3)_2$ were effective catalysts for this silylzincation reaction, while $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{PPh}_3)_3$ were not efficient. (2) The regioselectivity of the reaction

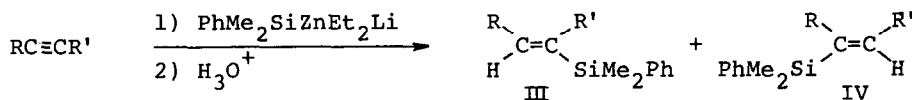
Table 1. Silylzincation of Terminal Acetylenes^a

$$\text{RC}\equiv\text{CH} \xrightarrow[2) \text{H}_3\text{O}^+]{1) \text{PhMe}_2\text{SiZnR}_2\text{Li}} \begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{SiMe}_2\text{Ph} \\ \text{I} \end{array} + \begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{PhMe}_2\text{Si} \quad \text{H} \\ \text{II} \end{array}$$

Entry	Substrate R	Reagent ^b	Catalyst	Yield (%)	Ratio of I/II I : II
1	ⁿ C ₁₀ H ₂₁	Ph ₃ SiZnEt ₂ Li	CuI	90 ^c	100 : 0
2		PhMe ₂ SiZnEt ₂ Li	Pd(PPh ₃) ₄	80	75 : 25
3		PhMe ₂ SiZnEt ₂ Li	CuCN	81	58 : 42
4		PhMe ₂ SiZnEt ₂ Li	CoCl ₂ (PPh ₃) ₂	60	30 : 70
5		PhMe ₂ SiZn ^t Bu ₂ Li	CuCN	92	1 : 99
6	THPOCH ₂ CH ₂	(PhMe ₂ Si) ₃ ZnMgMe ^d	CuCN	97	100 : 0
7		PhMe ₂ SiZnEt ₂ Li	CuCN	80	67 : 33
8		PhMe ₂ SiZn ^t Bu ₂ Li	CuCN	87	1 : 99
9	PhCH ₂ OCH ₂ CH ₂	Ph ₃ SiZnEt ₂ Li	CuI	87 ^c	100 : 0
10		PhMe ₂ SiZnEt ₂ Li	CuCN	78	67 : 33
11		PhMe ₂ SiZn ⁱ Pr ₂ Li	CuCN	91	33 : 67
12		PhMe ₂ SiZn ^t Bu ₂ Li	CuCN	98	5 : 95
13	HOCH ₂	PhMe ₂ SiZnEt ₂ Li ^e	CuCN	82	100 : 0
14	HOCH ₂ CH ₂	PhMe ₂ SiZnEt ₂ Li ^e	CuCN	84	67 : 33

a) The reactions were performed at 25°C in THF. Reagent (2.0 mmol), acetylene (1.0 mmol), and catalyst (2 mol%) were employed. b) Prepared from PhMe₂SiLi and the corresponding dialkylzinc (1:1). c) The corresponding triphenylvinylsilane was obtained. d) Prepared from PhMe₂SiMgMe (3.0 mmol) and ZnBr₂ (1.0 mmol). e) Reagent (3.0 mmol) and acetylene (1.0 mmol) were employed.

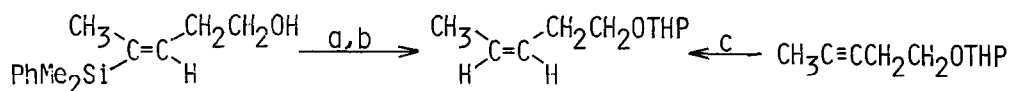
heavily depends on the nature of the dialkylzinc employed. The use of bulky alkyl group favours the formation of 2-silyl-1-alkenes (II). In the case of PhMe₂SiZn^tBu₂Li, high regioselectivity (>95%) was achieved for all examined substrates. (3) The opposite regio-isomers, 1-silyl-1-alkenes (I) were obtained selectively with Ph₃SiZnEt₂Li or (PhMe₂Si)₃ZnMgMe.⁶ (4) In contrast to the previously reported silylmetal reagents such as PhMe₂SiMgMe, PhMe₂SiAlEt₂, and (PhMe₂Si)₂Zn, silylzinc compounds, PhMe₂SiZnR₂Li are much more reactive and add easily to internal acetylenes as well as terminal acetylenes (Table 2). Regioselective silylmetalation was performed for propargylic or homopropargylic alcohols. Thus, 2-butyne-1-ol or 3-pentyn-1-ol gave (E)-3-dimethylphenylsilyl-2-buten-1-ol or (E)-4-dimethylphenylsilyl-3-penten-1-ol exclusively.

Table 2. Silylzincation of Internal Acetylenes in the Presence of CuCN Catalyst^a

Entry	Substrate R	R'	Reagent	Yield (%)	Ratio of III/IV III : IV
1	ⁿ C ₅ H ₁₁	ⁿ C ₅ H ₁₁	PhMe ₂ SiZnEt ₂ Li	90	—
2	CH ₃	CH ₂ OH	PhMe ₂ SiZnEt ₂ Li ^b	85 ^c	0 : 100
3	CH ₃	CH ₂ CH ₂ OH	(PhMe ₂ Si) ₃ ZnLi ^{b,d}	89	0 : 100
4	ⁿ C ₆ H ₁₃	SiMe ₃	(PhMe ₂ Si) ₃ ZnLi	42	0 : 100
5	ⁿ C ₃ H ₇	CH ₂ CH ₂ OTHP	(PhMe ₂ Si) ₃ ZnLi	96 ^e	50 : 50
6	CH ₃	CH ₂ CH ₂ OCH ₂ Ph	PhMe ₂ SiZnEt ₂ Li	78	20 : 80
7	CH ₃	CH ₂ CH ₂ OSiMe ₂ ^t Bu	PhMe ₂ SiZnEt ₂ Li	62	17 : 83

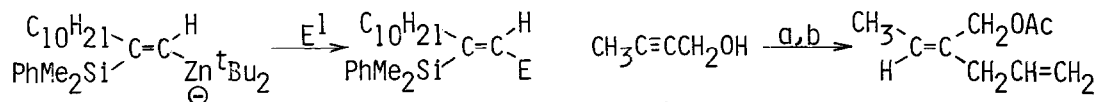
- a) Reagent (2.0 mmol), acetylene (1.0 mmol), and CuCN (2 mol%) were employed.
 b) Three mmol of reagent was used per 1.0 mmol of substrate. c) See ref. 8.
 d) See ref. 9. e) See ref. 10.

The *cis* mode of addition was confirmed by the comparison of the tetrahydropyranyl ether of (*Z*)-3-penten-1-ol derived from the silylzincation product of 3-pentyn-1-ol (entry 3 in Table 2) with an authentic sample.¹¹



- a: dihydropyran, TsOH/CH₂Cl₂ b: ⁿBu₄NF/HMPA¹²
 c: H₂/Pd-C, 5% BaSO₄, quinoline

The intermediary vinylzinc compound could be easily trapped by some electrophiles. For instance, treatment of the intermediate derived from CuCN catalyzed silylzincation (PhMe₂SiZn^tBu₂Li) of 1-dodecyne with methyl iodide or benzaldehyde gave the corresponding silylalkene in 92% or 70% yield, respectively. The application of this new method is exemplified by the synthesis of the trisubstituted olefin¹³ depicted below.¹⁴



E¹ = MeI or PhCHO E = Me or PhCH(OH)

- a: 1) (PhMe₂Si)₃ZnLi
 2) CH₂=CHCH₂Br/Pd(O)
 b: 1) Ac₂O, Py 2) ⁿBu₄NF/DMSO

References and Notes

1. Gmelin Handbook of Inorganic Chemistry 8th ed., Springer Berlin, Heidelberg, New York, Tokyo, 1983, "Organocopper Compounds Part 2"
2. M. Isobe, S. Kondo, N. Nagasawa, and T. Goto, *Chem. Lett.*, 1977, 679; D. Seebach and W. Langer, *Helv. Chim. Acta*, **62**, 1701, 1710 (1979).
3. The reagent is also effective for 1,4-addition to α,β -unsaturated carbonyl compounds. For instance, the addition of $\text{PhMe}_2\text{SiZnEt}_2\text{Li}$ to 2-cyclohexenone gave the 1,4-adduct, 3-dimethylphenylsilylcyclohexanone in 80% yield, while PhMe_2SiLi provided 1-dimethylphenylsilyl-2-cyclohexen-1-ol (60% yield) as the main product.
4. H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, **80**, 607 (1958).
5. Prepared according to the following references. $^t\text{Bu}_2\text{Zn}$: M. H. Abraham, *J. Chem. Soc.*, 1960, 4130. $^i\text{Pr}_2\text{Zn}$: M. W. Rathke and H. Yu, *J. Org. Chem.*, **37**, 1732 (1972). ZnCl_2 was used instead of ZnI_2 . We thank Toyo Stauffer Chemical Company for the gift of Et_2Zn .
6. As an alternative method, the selective preparation of 1-dimethylphenylsilyl-1-alkenes has already been achieved by silylmagnesiation with $\text{PhMe}_2\text{SiMgMe}$ in the presence of CuI catalyst.⁷ Thus, we have succeeded to obtain both regioisomers with high selectivity (>95%).
7. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, *J. Amer. Chem. Soc.*, **105**, 4491 (1983).
8. IR (neat) 3330, 3070, 2960, 1425, 1250, 1110, 1010, 815, 700 cm^{-1} ; NMR (CCl_4) δ 0.33 (s, 6H), 1.63 (s, 3H), 2.17 (bm, 1H), 4.17 (d, $J = 6$ Hz, 2H), 5.90 (m, 1H), 7.17-7.58 (m, 5H).
9. Prepared from PhMe_2SiLi (3.0 mmol) and anhydrous ZnBr_2 (1.0 mmol) in THF. The reagent adds to 3-pentyn-1-ol effectively, whereas $\text{PhMe}_2\text{SiZnR}_2\text{Li}$ fails to add.
10. As a mixture of **III** and **IV**: Bp 115-120 $^\circ\text{C}$ (bath temp, 2 Torr); IR (neat) 3070, 2950, 2870, 1615, 1430, 1250, 1120, 1035, 820, 700 cm^{-1} ; NMR (CCl_4) δ 0.32 (s, 3H), 0.33 (s, 3H), 0.92 (t, $J = 7.5$ Hz, 3H), 1.35-1.68 (m, 8H), 1.90-2.55 (m, 4H), 3.20-3.83 (m, 4H), 4.35-4.50 (bm, 0.5H), 4.50-4.63 (bm, 0.5H), 5.87 (t, $J = 6$ Hz, 1H), 7.17-7.60 (m, 5H). Found: C, 72.11; H, 9.81%. Calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Si}$: C, 72.23; H, 9.70%.
11. Silylzincation of terminal acetylenes proceeds in a cis fashion, as it is shown by the examination of ^1H -NMR of the product according to the previous report.⁷
12. H. Oda, M. Sato, Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **24**, 2877 (1983); idem, *Tetrahedron*, submitted for publication.
13. E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226 (1970).
14. Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid for Special Project Research #59104005) is acknowledged.

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