Tetrahedron Letters,Vol.25,No.11,pp 1163-1166,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

TRANSITION-METAL CATALYZED SILYLMETALATION OF ALLENES

Yoshitomi Morizawa, Hiroji Oda, Koichiro Oshima*, and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606, Japan

Abstract: Addition of $PhMe_2SiMgMe$, $(PhMe_2Si)_2Zn$, or $PhMe_2SiAlEt_2$ to allenes proceeds in the presence of various transition-metal catalysts. Whereas copper catalyzed silylmagnesation of 1,2-cyclononadiene gives 1-dimethylphenylsilyl-1-cyclononene exclusively, palladium catalyzed silylalumination affords 3-dimethylphenylsilyl-1-cyclononene preferentially with high degrees of regioselectivity.

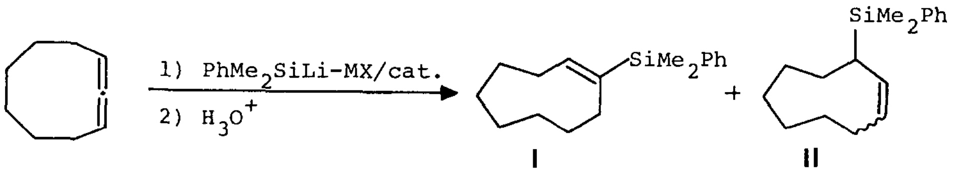
The recently reported silylmetalation of terminal acetylenes proceeds in the presence of various transition-metal catalysts with high regio- and stereoselectivity.[1] Further extension of this reaction to allenes as substrates[2] has provided a novel synthesis of vinylsilanes and allylsilanes,[3] respectively, under good control of the regioselectivity.

Silylmagnesation of 1,2-cyclononadiene in the presence of CuI catalyst, followed by aqueous quenching, produces exclusively 1-dimethylphenylsilyl-1-cyclononene (**I**) in which the $PhMe_2Si$ group is attached to the central carbon of the allene. Among many combinations examined, a part of which has been given in Table 1, the $PhMe_2SiAlEt_2$-$PdCl_2(P(\underline{o}\text{-}MeC_6H_4)_3)_2$ system was found to afford the isomeric 3-dimethylphenylsilyl-1-cyclononene (**II**) predominantly.[4] Ligands of palladium catalysts play an important role to control the product distributions. The reaction of 1,2-cyclononadiene with $PhMe_2SiAlEt_2$ in the presence of $Pd(PPh_3)_4$ gave a mixture of **I** and **II** in a 55:45 ratio.

Some electrophiles smoothly reacted with the allylic Grignard intermediates derived from CuI catalyzed silylmagnesation of 1,2-cyclononadiene (Table 2) and 1,2-propadiene (Table 3). Thus, methyl iodide, allyl bromide, trialkylchlorosilanes, and aldehydes gave the corresponding silylalkenes carrying the electrophilic partners E.

An ethereal solution of methylmagnesium iodide (1.3 $\underline{M}$, 9.8 ml, 13.0 mmol) was added to a THF solution of dimethylphenylsilyllithium (0.82 $\underline{M}$, 15.9 ml, 13.0 mmol) at 0°C under an argon atmosphere. After stirring for 15 min, CuI (95 mg, 5 mol%) was added and the resulting solution was stirred for an additional 5 min. A solution of 1,2-cyclononadiene (1.22 g, 10.0 mmol) in THF (7 ml) was added and the whole was stirred for 10 min at 0°C.

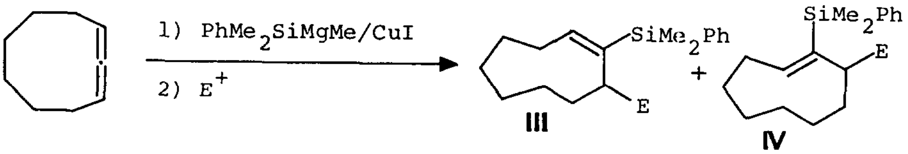
Table 1. Transition-metal catalyzed silylmetalation[a]



Entry	Reagent	Catalyst	Conditions Temp(°C)	Time(h)	Yield (%)	Ratio of I/II I	II
1	$PhMe_2SiMgMe$	CuI	0	0.2	74	>95	<5
2	$(PhMe_2Si)_2Zn$[b]	$PdCl_2(PBu_3)_2$	0	2	70	50	50
3	$(PhMe_2Si)_2Zn$[b]	$PdCl_2(P(\underline{o}\text{-}MeC_6H_4)_3)_2$	0	1.5	40	30	70
4	$PhMe_2SiAlEt_2$	$Pd(PPh_3)_4$	80	4	41	55	45
5	$PhMe_2SiAlEt_2$	$PdCl_2(P(\underline{o}\text{-}MeC_6H_4)_3)_2$	25	15	36	10	90

[a] Two mol of $PhMe_2Si$-Mtl reagent, one mol of 1,2-cyclononadiene, and 5 mol% of catalyst were employed. [b] A reagent was produced by mixing the silyllithium with $ZnBr_2$ in a 2:1 ratio.

Table 2. Transition-metal catalyzed silylmetalation of 1,2-cyclononadiene followed by reaction with electrophiles

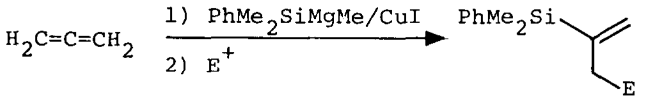


Entry	Electrophile	Conditions Temp(°C)	Time(h)	Yield (%)	Ratio[a] of III/IV III	IV
1	MeI	0	0.1	88	100	0
2	$CH_2=CHCH_2Br$	0	0.1	94	100	0
3	$PhMe_2SiCl$	0	0.2	91	15	85
4	Me_3SiCl	0	0.2	84	0	100
5	PhCHO	-78	0.2	56	23	77
6	CH_3CHO	-78	0.5	67	100	0
7	$CH_2=CHCHO$	-78	0.5	71	-[b]	
8	$CH_3CH=CHCHO$	-78	1.0	91	-[b]	

[a] The ratios were determined by the examination of ^1H-NMR spectra of the mixtures according to the reported data. See ref. 2. [b] Major products were III. Exact isomeric ratio could not be determined because of the complexity of ^1H-NMR spectra. 1,2-Adduct was obtained exclusively.

The mixture was cooled at -78°C and treated with a solution of crotonaldehyde (1.05 g, 15.0 mmol) in THF (4 ml). Purification by silica gel column chromatography gave 3-(1-hydroxy-2-butenyl)-2-dimethylphenylsilyl-1-cyclononene[5] (3.0 g) in 91% yield.

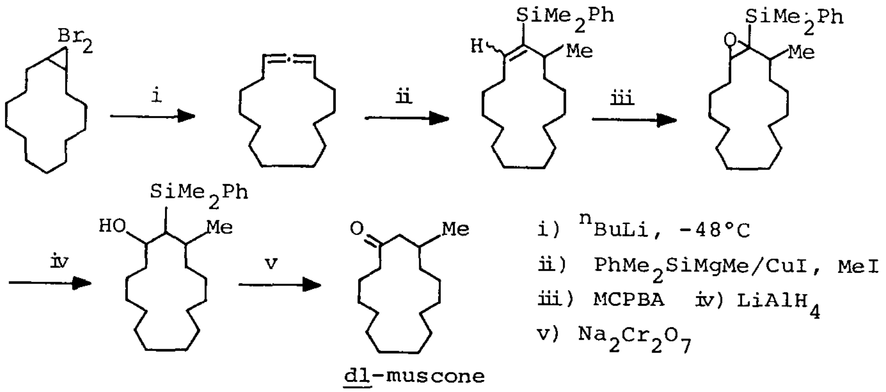
Table 3. Transition-metal catalyzed silylmetalation of 1,2-propadiene followed by reaction with electrophiles[a]



Entry	Electrophile	Yield[b](%)
1	H_2O	60
2	$CH_2{=}CHCH_2Br$	30
3	PhCHO	62
4	$CH_3CH{=}CHCHO$	48
5	Me_3SiCl	47

[a] One mol of $PhMe_2SiMgMe$ reagent, excess of 1,2-propadiene, and 5 mol% of catalyst were employed. [b] Based on the reagent, $PhMe_2SiMgMe$.

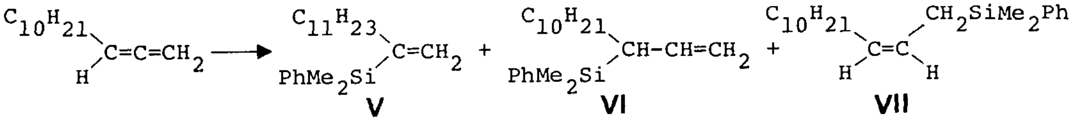
This new method has provided us with a simple route to dl-muscone.[6] Silylmagnesation of 1,2-cyclopentadecadiene followed by quenching with MeI gave 3-methyl-2-dimethylphenylsilyl-1-cyclopentadecene[7] in 77% yield. Epoxidation (97%) and oxirane ring opening[8] (47%) gave hydroxysilane. Final oxidation of the hydroxysilane produced dl-muscone (96%).[9]



i) ^nBuLi, -48°C
ii) $PhMe_2SiMgMe/CuI$, MeI
iii) MCPBA iv) $LiAlH_4$
v) $Na_2Cr_2O_7$

References and Notes

1. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, J. Am. Chem. Soc., **105**, 4491 (1983). Other examples of silylmetalation: G. Altnau, L. Rösch, F. Bohlman, and M. Lonitz, Tetrahedron Lett., **21**, 4069 (1980); G. Altnau and L. Rösch, ibid, **24**, 45 (1983); K. Tamao, M. Akita, R. Kanatani, N. Ishida, and M. Kumada, J. Organomet. Chem., **226**, C9 (1982).
2. M. Laguerre, J. Dunoguès, and R. Calas, Tetrahedron Lett., **1978**, 57.
3. E. W. Colvin, "Silicon in Organic Synthesis," Chap. 7 and 9, Butterworths, 1981, London; W. P. Weber, "Silicon reagents for Organic Synthesis," Chap 7 and 11, Springer-Verlag, 1983, Berlin; T. H. Chan and I. Fleming, Synthesis, **1979**, 761; I. Fleming, Chem. Soc. Rev., **10**, 83 (1981); B. M. Trost, J. Yoshida, and M. Lautens, J. Am. Chem. Soc., **105**, 4495 (1983).
4. Acyclic allene gave the similar results as cyclic ones. For instance, CuI catalyzed silylmagnesation of 1,2-tridecadiene provided 2-dimethylphenylsilyl-1-tridecene (V) exclusively (68%). In contrast, $PdCl_2(PPh_3)_2$ promoted silylalumination gave an isomeric mixture (V:VI:VII = 40:35:25, 55%) and silylzincation in the presence of $PdCl_2(PPh_3)_2$ afforded the mixture (V:VI:VII = 30:22:48, 81%).



5. ^{1}H-NMR (CCl_4) δ 0.31 (s, 1.4H), 0.37 (s, 2.6H), 0.40 (s, 2.0H), 1.0-1.8 (m + d (δ 1.58, J = 4.8 Hz, 2.0H, one of diastereomers) + d (δ 1.66, J = 4.8 Hz, 1.0H, one of diastereomers), totally 14H), 2.0-2.9 (m, 3H), 3.6-3.9 (m, 1H), 5.2-5.5 (m, 2H), 5.91 (t, J = 9.3 Hz, 0.65H), 6.05 (t, J = 8.7 Hz, 0.35H), 7.1-7.6 (m, 5H); IR (neat) 3450, 1255, 1105 cm^{-1}.
6. Some references for the synthesis of dl-muscone. H. Taguchi, H. Yamamoto, and H, Nozaki, Tetrahedron Lett., **1972**, 4661; T. Hiyama,T. Mishima, K. Kitatani, and H. Nozaki, ibid., **1974**, 3297; K. Utimoto, M. Tanaka, M. Kitai, and H. Nozaki, ibid., **1978**, 2301; J. Tsuji, T. Yamada, M. Kaito, and T. Mandai., ibid., **1979**, 2257.
7. bp 150-155°C (bath temp, 1 Torr); ^{1}H-NMR ($CDCl_3$) δ 0.25 (s, 1.5H), 0.35 (s, 1.5 H), 0.38 (s, 3H), 0.7-1.6 (m + d (δ 0.88, J = 4.8 Hz, 1.5H) + d (δ 0.96, J = 4.8 Hz, 1.5H), totally 25H), 1.6-2.8 (m, 3H), 5.67 (dd, J = 5.7, 7.6 Hz, 0.5H), 5.95 (t, J = 6.0 Hz, 0.5H), 7.1-7.5 (m, 5H); IR (neat) 1255, 1110 cm^{-1}; MS (%) 356 (M^+, 3), 341 (2), 135 (100). Found: C, 80.84, H, 11.25%. Calcd for $C_{24}H_{40}Si$: C, 80.82; H; 11.30%.
8. J. J. Eisch and J. T. Trainor, J. Org. Chem., **28**, 2870 (1963).
9. W. E. Fristad, T. R. Bailey, and L. A. Paquette, ibid., **45**, 3028 (1980).

(Received in Japan 15 December 1983)