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METAL CATALYZED CROSS-COUPLING REACTIONS OF CARBANIONS α TO SILAFUNCTIONAL GROUPS. NEW α-HYDROXYALKYL ANION EQUIVALENTS[1]

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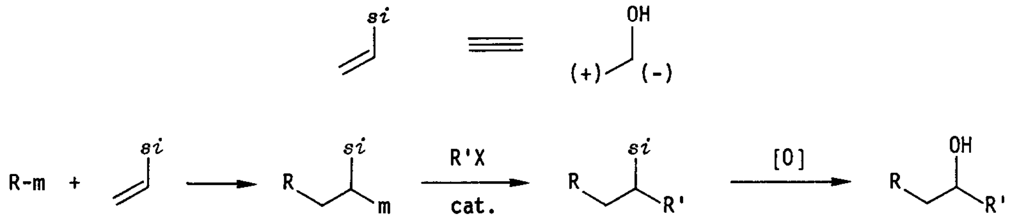
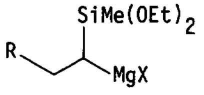
Summary: Carbanions α to (alkoxy)silyl or (amino)silyl groups act as nucleophilic α-hydroxyalkylating agents for organic halides and epoxides via the metal catalyzed coupling reaction and the subsequent oxidative cleavage of the carbon-silicon bond.

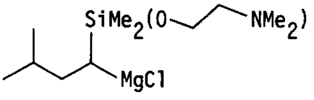
In the previous paper,[1] we have described the formation of carbanions α to (alkoxy)silyl or (amino)silyl groups. This paper is concerned with the metal catalyzed coupling reactions of such a species[2] with organic halides and epoxides and the subsequent oxidative cleavage of the carbon-silicon bond to form the corresponding alcohols. The overall transformation is illustrated in Scheme 1, where a silafunctional vinylsilane acts as a new two-carbon building block and in turn the α-silyl carbonion as an α-hydroxyalkyl anion equivalent. Throughout this paper, *si* represents a functional silyl group. The α-silyl carbanions 1-8 employed in this study are listed below.



Scheme 1



1 R = *i*-Pr; X = Cl or Br
2 R = cyclo-C_6H_{11}; X = Br



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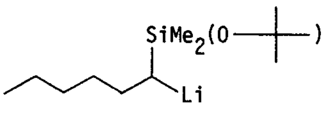

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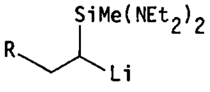
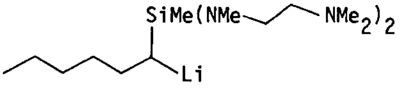


5 R = *n*-Bu
6 R = *sec*-Bu
7 R = *t*-Bu



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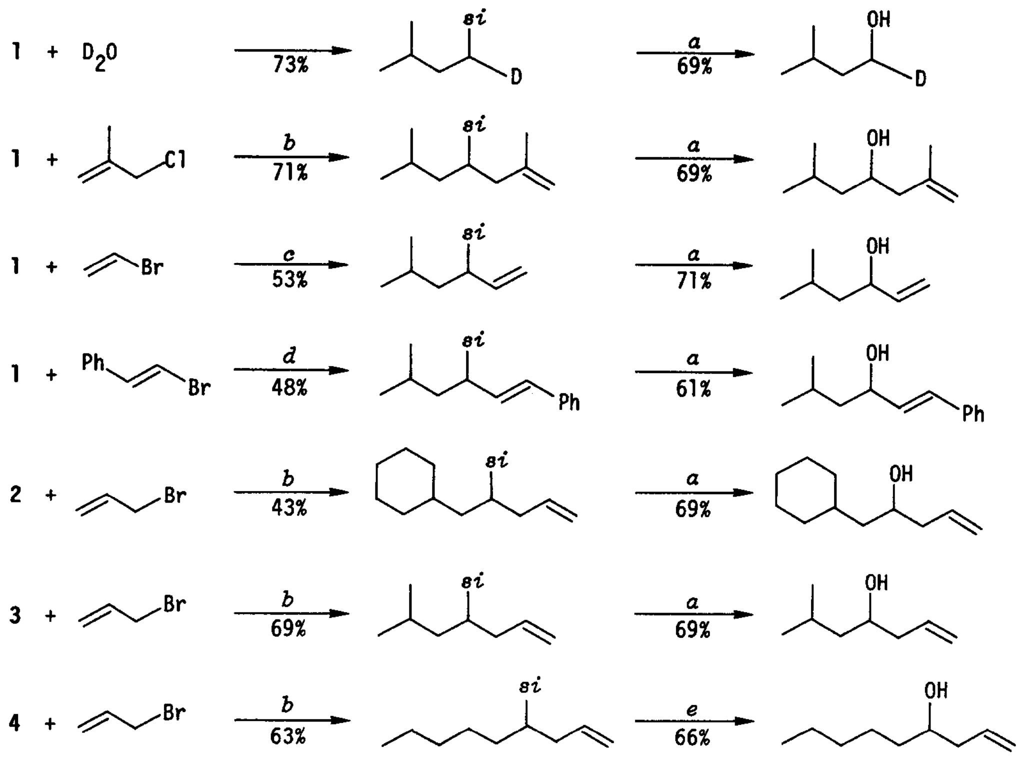
In a series of the alkoxysilyl derivatives 1–4 the hydrolysis or coupling products were isolated[3] and then subjected to the MCPBA-oxidation.[4] Several representative results are given in eqs. (1)-(7). Yields of the first step are based on the vinylsilane.



(1)

(2)

(3)

(4)

(5)

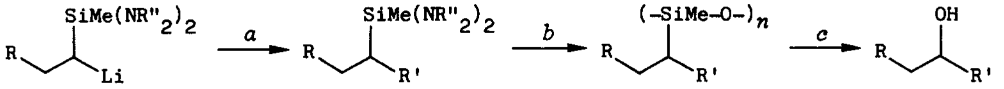
(6)

(7)

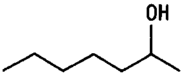
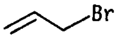
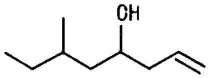
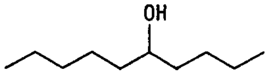
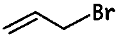
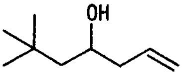
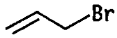
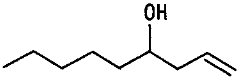
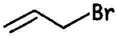
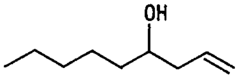
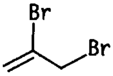
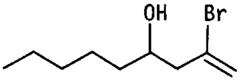
[a] MCPBA (2-2.2 eq), KF (2.2 eq), DMF, rt, 3-5 h. [b] CuI (10 mol%),[5] THF, rt, 1.5-7 h. [c] $NiCl_2$(dppp) (1 mol%),[6] 0°C, 1.5 h. [d] $PdCl_2$(dppf) (1 mol%),[7] rt, 4 h. [e] MCPBA (8 eq), KF (2.2 eq), DMF, 60°C, 53 h.

With the aminosilyl carbanions 5–8, the lithium reagents were converted to their magnesium analogs by treatment with $MgBr_2$ prior to the coupling reactions. The coupling products were not isolated, but decomposed by acid hydrolysis to the corresponding siloxanes which were oxidized by 90% H_2O_2 or MCPBA,[8] as shown by eq. 8 and by several data listed in the accompanying table. Overall isolated yields based on the vinylsilanes are given.

Epoxides also reacted with organolithium reagent 5 in the presence of CuI[9] to form the corresponding 1,3-diols after work-ups similar to those given in eq. 8 (eqs. 9 and 10). In the reaction of isoprene monoepoxide,[9b] the transmetallated magnesium reagent, 5(+$MgBr_2$), afforded a 1,5-diol arising from an S_N' type reaction, under otherwise the same conditions (eq. 11).



(8)

carbanion	R'X	alcohol	yield (%)[d]	carbanion	R'X	alcohol	yield (%)
5	MeI		67 (45)	6			51
5			48 (74)	7			67
5			67 (72)	8			54
5			63				

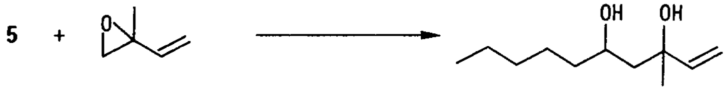
[a] (1) $MgBr_2$, ether. (2) R'X (2 eq), CuI (10 mol%), THF, rt, 3 h.

[b] (1) 6N HCl. (2) Ether extraction, drying (Na_2SO_4), and evaporation.

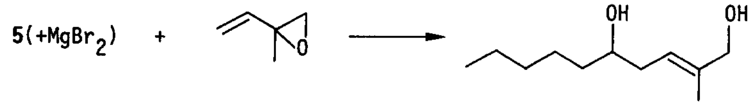
[c] 90% H_2O_2 (10 eq), KHF_2 (3 eq), DMF, 60°C, 16-18 h.

[d] Yields in parentheses were obtained with the MCPBA oxidation (cf., footnote *a* of eq. 1).

71% (9)



45% (10)



56% (11)

E/Z = 92/8[10]

Several general comments should be made. (1) The α-monodeuterio primary alcohol obtained in eq. 1 is unique in that the deuterium arises from deuterium oxide, in contrast to the conventional standard method via reduction of aldehydes by deuteride reagents. (2) All the α-silyl carbanions examined readily underwent the copper catalyzed coupling reaction with allylic halides and methyl iodide: coupling with *n*-butyl iodide being rather sluggish (cf., data in eq. 8). (3) In the nickel or palladium catalyzed coupling reactions with alkenyl halides (e.g., eqs. 3 and 4), concomitant ß-hydride elimination of the carbanions occurred to give the corresponding vinylsilane RCH=CH-*si* in substantial amounts. This side reaction is responsible for the somewhat low yields of the coupling products.

The present development has opened up a new method for nucleophilic α-hydroxyalkylation[11,12] of organic halides and epoxides. Refinement of the present procedure and further applications of α-silyl carbanions are now in progress.[13]

REFERENCES AND NOTES

(1) Silafunctional Compounds in Organic Synthesis. 23. For part 22 see, K. Tamao, R. Kanatani, and M. Kumada, *Tetrahedron Lett.*, preceding paper.

(2) It has been reported, in the attempted Peterson olefination, that α-silyl carbanion 1 does not add to a carbonyl group but reduce it to an alcohol as a result of the β-hydride elimination. T. H. Chan and E. Chang, *J. Org. Chem.*, **39**, 3264 (1974).

(3) The coupling reaction affords a new efficient method for the preparation of secondary alkyl organosilicon compounds containing alkoxy group(s) on the silicon atom. Secondary alkyl silicon compounds are hardly accessible: Cf., (a) R. A. Benkeser and W. C. Muench, *J. Am. Chem. Soc.*, 95, 285 (1973). (b) R. A. Benkeser, E. C. Mozden, W. C. Muench, R. T. Roche, and M. P. Silcolosi, *J. Org. Chem.*, **44**, 1370 (1979).

(4) K. Tamao, T. Kakui, M. Akita, T. Iwahara, R. Kanatani, and M. Kumada, *Tetrahedron*, **39**, 983 (1983). The oxidation should be achieved also by hydrogen peroxide: K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, *Organometallics*, 2, 1694 (1983).

(5) Copper catalyzed coupling reactions: F. Derguini-Boumechal and G. Linstrumelle, *Tetrahedron Lett.*, 3225 (1976).

(6) dppp = $Ph_2P(CH_2)_3PPh_2$. Cf., K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Jpn.*, 49, 1958 (1979).

(7) dppf = 1,1'-bis(diphenylphosphino)ferrocene. Cf., T. Hayashi, M. Konishi, and M. Kumada, *Tetrahedron Lett.*, 1871 (1979).

(8) Oxidative cleavage of the carbon-silicon bond in polysiloxanes can also be carried out by peracetic acid or 30% H_2O_2 with somewhat less efficiency.

(9) (a) C. Huynh, R. Derguini-Boumechal, and G. Linstrumelle, *Tetrahedron Lett.*, 1503 (1979). (b) C. Cahiez, A. Alexakis, and J. F. Normant, *Synthesis*, 528 (1978).

(10) Determined by ^1H NMR chemical shifts, δ 1.64 (*E*) and 1.78 (*Z*), of the methyl protons $=C(CH_3)CH_2OH$. Cf., K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, 33, 3382 (1968).

(11) Nucleophilic α-hydroxyalkylating agents: (a) W. C. Still, *J. Am. Chem. Soc.*, **100**, 1481 (1978). (b) W. C. Still and C. Sreekumar, *ibid.*, 102, 1201 (1980). (c) T. Cohen and J. R. Matz, *ibid.*, 102, 6900 (1980). (d) H. Nishiyama, S. Narimatsu, and K. Itoh, *Tetrahedron Lett.*, 5289 (1981). See also references cited therein.

(12) We have recently developed a new nucleophilic hydroxymethylating agent based on the same concept: K. Tamao, N. Ishida, and M. Kumada, *J. Org. Chem.*, 48, 2120 (1983).

(13) We thank Shin-etsu Chemical Industrial Co., Ltd. for support of this work and for a gift of vinylsilanes, and Mitsubishi Gas-Chemical Industrial Co., Ltd., for a gift of 90% H_2O_2.

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