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CHEMISTRY OF ORGANOSILICON COMPOUNDS 113
CHEMOSELECTIVE ALLYLATION OF CARBONYL COMPOUNDS WITH ALLYLSILANES PROMOTED BY TETRA-n-BUTYLAMMONIUM FLUORIDE. A NEW SYNTHESIS OF HOMOALLYL ALCOHOLS

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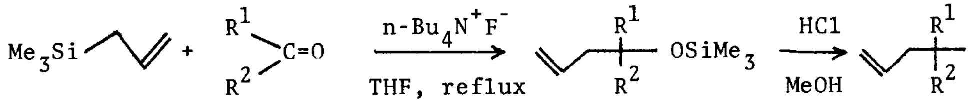
Fluoride ion displays nucleophilic affinity specifically to a silicon atom in an organosilicon compound[1-4] due to the high silicon-fluorine bond energy,[5] and allows to produce a functionalized carbanion when the pK_a value of the conjugate acid is relatively small.[6-8] We now report that an allyl-silicon bond of allylsilanes[9] is readily cleaved in the presence of tetra-n-butylammonium fluoride (TBAF)[10] to give a new allylic anion species, which chemoselectively adds to a carbonyl compound to afford a homoallyl silyl ether. The latter gives a homoallyl alcohol after hydrolysis generally in high yield.

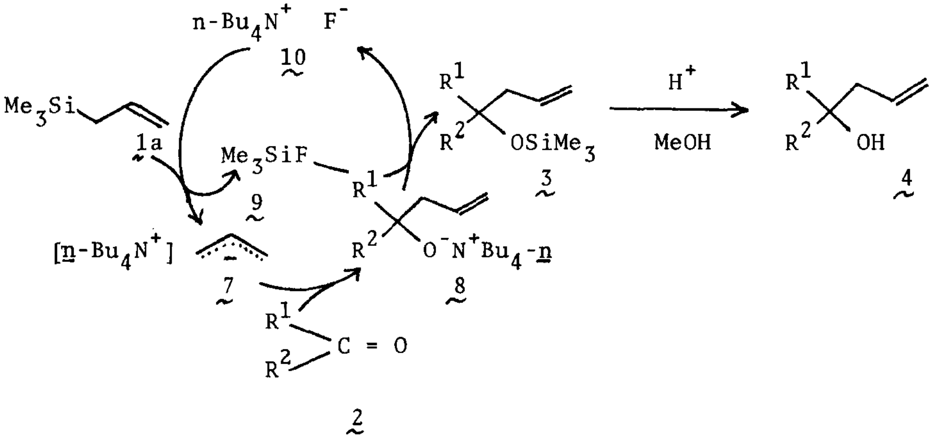


1a 2 3 4 (1)

A variety of aldehydes and ketones are effective to this new allylation reaction, although aldehydes are more reactive than ketones. (eq. 1) On the contrary, nitriles, epoxides and esters do not react with this reagent even by heating for a prolonged time. Therefore, methyl levulinate (5), for example, can be allylated chemoselectively only at the keto group but not at the ester group to give a lactone 6 in 71 % yield. (Table 1, entry 9)

This new allylating system, allylsilane-TBAF, has several strikingly different features in the reaction from other carbanionic allylic reagents of alkali or alkaline earth metals.[11] Thus, with alkyl-substituted allylsilanes, the allylation of the carbonyl group occurs favorably at the less substituted carbon end of the allylic group. (entry 11-13) Indeed, the allylation takes place exclusively at the primary site of the allylic part in the reaction of γ,γ-dimethylallyltrimethylsilane (1d) with benzophenone.[12] (entry 13) With α,β-enones as an electrophile, conjugate addition takes place simultaneously along with 1,2-addition to carbonyl group. (entry 10) A catalytic amount of TBAF is sufficient to drive the reaction, while potassium fluoride is ineffective as a catalyst even in the presence of 18-crown-6.

The mechanistic rationale illustrated in Scheme 1, therefore, is reasonable to the present reaction. The nucleophilic attack of a fluoride ion to a silicon atom of **1** forms trimethylfluorosilane (**9**),[13] and new allylic anion species **7**, the counter cation being tetra-*n*-butylammonium. The reaction of **7** with a carbonyl compound forms an allylated alkoxide **8** which reacts with **9** to afford a silyl ether **3**. The fluoride ion **10** is thereby regenerated to complete the catalytic cycle. Indeed, without methanolysis of the reaction mixture, a silyl ether **3** can be isolated in good yield, along with a small amount of homoallyl alcohol. (entry 4)



Scheme 1. A catalytic cycle of the allylation

The first step of the reaction, which formally resembles to the metal-metal exchange reaction, provides a novel preparative method of allylic anions. The allylation method presented in this communication can be carried out under very mild and neutral conditions and therefore is quite complementary to the recently reported allylations via allylsilane-Lewis acid in acidic media.[14]

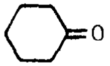
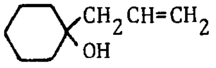
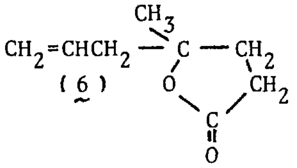
Preparation of 6-phenylhex-1-ene-4-ol illustrates the standard procedure: To a mixture of TBAF (26 mg, 0.1 mmol), 4A molecular sieves (50 mg), and 5 ml of dry tetrahydrofuran (THF) was added a solution of 3-phenylpropanal (264 mg, 2.0 mmol) and **1a** (229 mg, 2.0 mmol) in 5 ml of THF at room temperature with stirring under argon. The resulting pale yellow mixture was heated to reflux for 4 h. After methanolysis of the reaction mixture with MeOH-HCl, the solvent was evaporated and the residue was purified by tlc affording 303 mg (86 %) of 6-phenylhex-1-ene-4-ol.[15]

Related works are in progress.

Acknowledgment

We thank Toshiba Silicon Co., Ltd., for gifts of chlorosilanes.

Table 1. Reaction of allylsilanes with carbonyl compounds catalyzed by tetra-n-butylammonium fluoride in THF at reflux

Entry	Allylsilane	Carbonyl compound	Reaction time	Products	(% yield)^a
1	$Me_3SiCH_2CH=CH_2$ (1a)	$CH_3(CH_2)_2CHO$	15	$CH_3(CH_2)_2\underset{OH}{C}HCH_2CH=CH_2$	(83)
2	1a	$CH_3(CH_2)_3CHO$	15	$CH_3(CH_2)_3\underset{OH}{C}HCH_2CH=CH_2$	(92)
3	1a	$CH_3(CH_2)_4CHO$	15	$CH_3(CH_2)_4\underset{OH}{C}HCH_2CH=CH_2$	(87)
4	1a	PhCHO	30	$Ph\underset{OH}{C}HCH_2CH=CH_2$	(93)
5^b	1a	PhCHO	36	$Ph\underset{OSiMe_3}{C}HCH_2CH=CH_2$ $Ph\underset{OH}{C}HCH_2CH=CH_2$	(72) (28)
6	1a	$PhCH_2CH_2CHO$	4	$PhCH_2CH_2\underset{OH}{C}HCH_2CH=CH_2$	(86)
7	1a		16		(60)
8	1a	$PhCOCH_3$	16	$Ph\underset{OH}{C}(CH_3)CH_2CH=CH_2$	(60)
9	1a	$CH_3COCH_2CH_2CO_2CH_3$ (5)		 (6)	(71)
10^b	1a	$PhCH=CHCOCH_3$	5	$CH_3COCH_2CH(Ph)CH_2CH=CH_2$ $PhCH=CH\underset{OSiMe_3}{C}(CH_3)CH_2CH=CH_2$ $PhCH=CH\underset{OH}{C}(CH_3)CH_2CH=CH_2$	(24) (22) (28)
11	$Me_3SiCH_2CH=CHCH_3$ (1b)	$CH_3(CH_2)_2CHO$	24	$CH_3(CH_2)_2\underset{OH}{C}HCH_2CH=CHCH_3$ 12a $CH_3(CH_2)_2\underset{OH}{C}HCH(CH_3)CH=CH_2$ (12b)	(37) (23)
12	$Me_3SiCH(CH_3)CH=CH_2$ (1c)	$CH_3(CH_2)_2CHO$	24	(12a) (12b)	(41) (30)
13	1d	PhCOPh	48	$Ph_2\underset{OH}{C}CH_2CH=C(CH_3)_2$	(87)^c

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[a] Isolated yields are shown unless otherwise noted. Yields are not always optimized. [b] Products without methanolysis. [c] Determined by nmr.

References and Notes

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9. The pK_a value of propene, a conjugate acid of allyl anion, is 36.5.
10. Organohydrosilanes, R_nSiHMe_{3-n} ($R=PhCH_2$, $CH_2=CHCH_2$; n=1,2) react with alcohols by stepwise replacement of R and H with alkoxide in the presence of tetramethylammonium fluoride. See, K. A. Andrianov, L. M. Tartakovskaya, V. M. Kopylov, and M. L. Sarafavova, Izv. Akad. Nauk, SSSR, Ser. Khim., 1443 (1975): Chem. Abstr., 83 147538d (1975).
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12. By the Girgnard reaction with benzophenone, we found that the allylation occurred only at the tertiary site of the allylic part to give 3,3-dimethyl-4,4-diphenyl-but-1-ene-4-ol in 98 % yield.
13. It was found that the first step in this allylation was reversible (Scheme 1), and, therefore, that a sterically less hindered allylsilane around the silicon atom was obtained at the end of the reaction, when a mixture of regioisomers of alkyl-substituted allylsilanes was heated with stirring in the presence of TBAF in THF.
14. We have recently reported that allylsilanes are versatile synthetic intermediates in the presence of Lewis acid as an activator. In this case, however the Lewis acid works as an activator of carbonyl compounds or acetals rather than allylsilanes. See a) A. Hosomi and H. Sakurai, J. Am. Chem. Soc., 99, 1673 (1977); b) idem, Tetrahedron Lett., 1295 (1976); c) A. Hosomi, H. Hashimoto, and H. Sakurai, J. Org. Chem., 43, in press (1978).
15. All products gave satisfactory spectral data and correct. elemental analysis.

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