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PROTECTION OF ALCOHOLS AND ACIDS WITH ALLYLSILANES CATALYZED BY IODINE OR IODOTRIMETHYLSILANE IN CHLORINATED HYDROCARBON[1]

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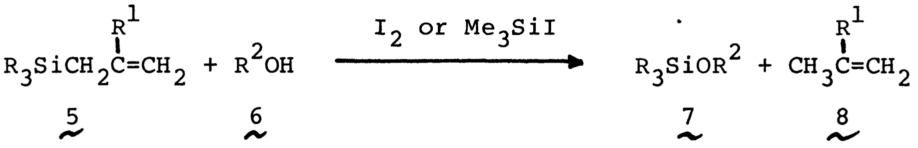
Many triorganosilyl ethers and esters were prepared by the reaction of allylsilanes with alcohols catalyzed by iodine or iodotrimethylsilane in excellent yields. Bromine and bromotrimethylsilane were also effective catalysts.

Triorganosilyl ethers and esters have been used extensively in organic chemistry as protected alcohols and carboxylic acids.[2] Chlorosilane-base, silylamines including silazane and silylimidazole and silylamides have been used generally for the conversion of hydroxy functions with a silyl group. Recently it has been reported that hexamethyldisiloxane is also effective.[3] More recently, Morita et al. have shown that allylsilanes can be employed for the silylation of hydroxy groups catalyzed by p-toluenesulfonic acid and that acetonitrile is the most suitable solvent.[4] This report prompts us to communicate our own results on the new silylation reactions by using allylsilanes. We have previously described that allylsilanes (1), with highly nucleophilic double bond due to σ(Si-C)-π conjugation,[5] are useful and convenient reagents for the regiospecific allylation reactions of a variety of electrophiles.[6] A general pattern of the reaction can be expressed by eq. 1, in which E and N denote electrophilic and nucleophilic moieties of the reagent, respectively. Furthermore, we have recently reported some new reactions of *in situ* generated iodotrimethylsilane.[7] In an extention of these studies, we have found that allylsilanes are effective reagents for the protection of hydroxy functions and carboxylic acids in chlorinated hydrocarbon (CH_2Cl_2, $CHCl_3$ and CCl_4) or under neat condition catalyzed by iodotrimethylsilane or iodine. (eq. 2)

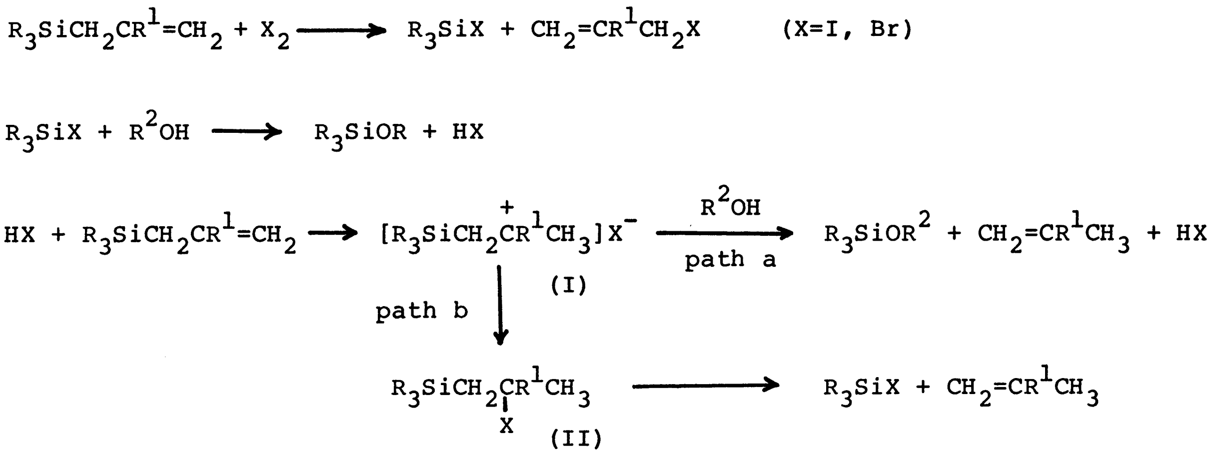
$$\underset{\mathbf{1}}{R_3SiCR^1R^2CR^3{=}CR^4R^5} + \underset{\mathbf{2}}{E\text{-}N} \longrightarrow \underset{\mathbf{3}}{R^1R^2C{=}CR^3CR^4R^5\text{-}E} + \underset{\mathbf{4}}{R_3SiN} \qquad (1)$$



$$\underset{\mathbf{5}}{R_3SiCH_2\overset{R^1}{\overset{|}{C}}{=}CH_2} + \underset{\mathbf{6}}{R^2OH} \xrightarrow{I_2 \text{ or } Me_3SiI} \underset{\mathbf{7}}{R_3SiOR^2} + \underset{\mathbf{8}}{CH_3\overset{R^1}{\overset{|}{C}}{=}CH_2} \qquad (2)$$

From the results of the conversion of a series of alcohols into the corresponding silyl ethers by the present reaction shown in Table 1, several interesting facts can be pointed out. First, while primary and secondary alcohols can be converted into the corresponding silyl ethers in almost quantitative yields, the reaction can not be applied to tertiary alcohols. Since tertiary alcohols may be converted to the corresponding iodides by the iodosilane, the catalytic cycle may be retarded. Second, iodotrimethylsilane itself catalyzes the reaction. Therefore, it appears reasonable that *in situ* generated iodotrimethylsilane from the allylsilane and iodine may be an operative silylating reagent. Bromine and bromotrimethylsilane, instead of iodine and iodosilane, are also effective catalysts for the conversion, although a higher reaction temperature was required for completion of the reaction. Third, the reaction can be applied for carboxylic acids. For example, trimethylsilyl capronate was obtained from caproic acid in 87% yield. Finally, chloroform and dichloromethane are most suitable among various solvents examined for the conversion. Carbon tetrachloride, tetrahydrofuran and benzene are also effective, although the rate of the reaction is considerably slow. The reaction proceeds very smoothly even without solvent.

The Scheme 1 illustrates the mechanistic rationale for the present reaction.



$$R_3SiCH_2CR^1{=}CH_2 + X_2 \longrightarrow R_3SiX + CH_2{=}CR^1CH_2X \qquad (X{=}I,\ Br)$$

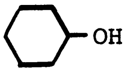
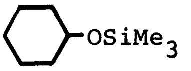
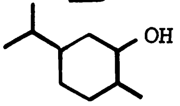
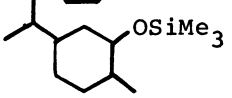
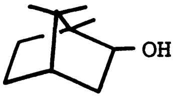
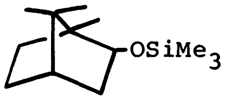
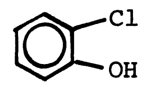
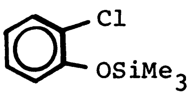
$$R_3SiX + R^2OH \longrightarrow R_3SiOR + HX$$

$$\begin{tikzcd} HX + R_3SiCH_2CR^1{=}CH_2 \arrow[r] & \underset{(I)}{[R_3SiCH_2\overset{+}{C}R^1CH_3]X^-} \arrow[r, "R^2OH", "\text{path a}"'] \arrow[d, "\text{path b}"'] & R_3SiOR^2 + CH_2{=}CR^1CH_3 + HX \\ & \underset{(II)}{R_3SiCH_2\underset{X}{C}R^1CH_3} \arrow[r] & R_3SiX + CH_2{=}CR^1CH_3 \end{tikzcd}$$

Scheme 1. A catalytic cycle for the silylation.

An allylsilane reacts with halogen(I_2 or Br_2) to afford the corresponding halosilane[8)] in the initiation step. The reaction of the halosilane with an alcohol forms a silyl ether and hydrogen halide. Possibly the silylation reaction proceeds by a bimolecular mechanism between alcohol and a carbenium ion intermediate of the type (I) (path a),[9,10)] although the adduct of hydrogen halide to the allylsilane (II) may be formed first and then the halosilane may be regenerated by a thermal decomposition[10)] to complete the catalytic cycle (path b). Propene, evolved during the reaction, was trapped by passing through a solution of bromine in dichloromethane to yield 1,2-dibromopropane.

Table 1. Conversion of alcohols phenols, and carboxylic acids into silyl derivatives with allylsilanes catalyzed by iodine.[a]

Entry	Starting compound	Allylsilane	Conditions Temp/°C(time/h)	Silyl ether[b]	Yield(%)
1	$ClCH_2CH_2OH$	$Me_3SiCH_2CH{=}CH_2$ (1a)	60 (0.5)	$ClCH_2CH_2OSiMe_3$	93
2	$n\text{-}C_4H_9OH$	$t\text{-}BuMe_2SiCH_2CH{=}CH_2$	70 (1)[c]	$n\text{-}C_4H_9OSiMe_2\text{-}t\text{-}Bu$	90
3	$i\text{-}C_4H_9OH$	$Et_3SiCH_2CH{=}CH_2$ (1b)	60 (0.5)[c]	$i\text{-}C_4H_9OSiEt_3$	93
4	$HO(CH_2)_4OH$	1a	60 (2)[d]	$Me_3SiO(CH_2)_4OSiMe_3$	83
5	$n\text{-}C_8H_{17}OH$ (6a)	1a	40 (1)	$n\text{-}C_8H_{17}OSiMe_3$ (7a)	95
6	6a	1a	40 (1)[e]	7a	94
7	6a	1a	70 (4)[f]	7a	93
8	6a	1a	70 (4)[g]	7a	89
9	6a	1a[h]	60 (1)	7a	93
10	6a	$Me_3SiCH_2C(CH_3){=}CH_2$	40 (1)[e]	7a	90
11	$sec\text{-}C_8H_{17}OH$ (6b)	1a	60 (2)	$sec\text{-}C_8H_{17}OSiMe_3$ (7b)	90
12	6b	1a[i]	80 (4)[c]	7b	93
13	6b	1a[j]	80 (4)[c]	7b	90
14		1a	30 (1)		93
15		1a	60 (1)		93
16		1a	60 (1)		94
17	$PhCH_2OH$	1a	40 (2)[e]	$PhCH_2OSiMe_3$	92
18		1a	60 (0.5)		95
19	$n\text{-}C_5H_{11}CO_2H$	1a	60 (0.5)[c]	$n\text{-}C_5H_{11}CO_2SiMe_3$	87
20	6b	$Et_2MeSiCH{=}CH_2$	80 (3)[c]	$sec\text{-}C_8H_{17}OSiMeEt_2$	44

a) All reactions were catalyzed by iodine in $CHCl_3$ or $CDCl_3$ unless otherwise noted. b) Isolation by GLC, TLC, CLC or distillation. c) In neat solution. d) In THF. e) In CH_2Cl_2. f) In CCl_4. g) In C_6H_6. h) Catalyzed by Me_3SiI. i) Catalyzed by Br_2. j) Catalyzed by Me_3SiBr.

In contrast to the results of the reaction of alcohols and iodotrimethylsilane by Jung and Orstein, leading to the corresponding iodides,11) the present conversion of alcohols to silyl ethers is attributed to the high reactivity of allylsilanes toward the electrophile, that is, proton of hydrogen halides.

Instead of allylsilanes, vinylsilanes may be used as a precursor to halosilanes,12,13) but the results were less satisfactory. (Entry 20)

As a general procedure, a mixture of an allylsilane (1.5-2 mmol) and an alcohol (1 mmol) in chloroform (1 ml) was stirred in the presence of iodine (0.05-0.1 mmol) under a given condition in the Table. Propene was immediately evolved which could be trapped by bromine in dichloromethane. After the complete formation of the product that was best monitored by GLC, a drop of pyridine was added. The mixture was passed through a short column(silica gel), yielding a silyl ether after the solvent was evaporated. The product was mostly pure and was characterized by GLC, NMR, IR, and low- and high-resolution mass spectra.

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References and Notes

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