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A NOVEL METHOD FOR THE CONVERSION OF THE ALCOHOL TO THE ALDEHYDE VIA 1,5-SILICON REARRANGEMENT

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Abstract : A conceptually novel method for the conversion of alcohols to aldehydes is reported. The 1,5 - silicon rearrangement is involved as the key element of the reaction.

During the recent study for the utilization of silicon rearrangement[1-3] in organic synthesis, we have found a novel method for the conversion of alcohols to aldehydes which involves the 1,5-silicon rearrangement.[4] We wish to report the preliminary results of the selective formation of the aldehydes under the basic conditions.

Treatment of alkyllithiums with o-(trimethylsilyl)methyl benzyl alcohol derivatives in the various solvents produced o-(trimethylsilyl)methyl benzaldehyde derivatives with some recovery of the starting materials (Eq. 1).

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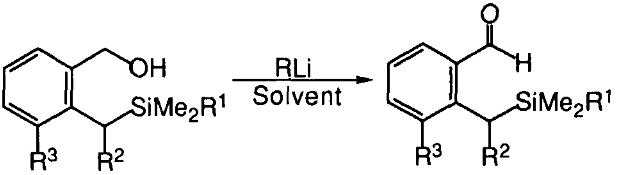
Table 1. Formation of aldehydes under basic conditions

Entry	Alcohol	RLi(eq.)	Solvent	Conc.[a]	Yield[b]	Recovery[c]	%Conversion[d]
1	R^1=Me,R^2=H,R^3=H	R= *n*-Bu(1.2)	Hex.-THF[e](1:5)	0.02	51%	43%	92%
2				0.04	49%	40%	89%
3				0.07	54%	45%	96%
4				0.09	52%	42%	90%
5				0.2	49%	47%	89%
6		R = *n*-Bu(3)		0.04	50%	45%	94%
7		R = *n*-Bu(6)		0.04	51%	43%	93%
8		R = *sec*-Bu(1.2)		0.04	51%	43%	92%
9		R = *tert*-Bu(1.2)		0.04	53%	44%	95%
10		R = *n*-Bu(1.2)	Benzene	0.09	56%	41%	96%

Table 1. continued

Entry	Alcohol	RLi(eq.)	Solvent	Conc.[a]	Yield[b]	Recovery[c]	%Conversion[d]
11	R^1=Me,R^2=H,R^3=H	R= *n*-Bu(1.2)	Benzene-THF(1:5)	0.09	48%	51%	96%
12			Benzene-Ether(1:5)	0.09	55%	40%	91%
13			Hex.-CH_2Cl_2(1:5)	0.09	43%	45%	91%
14			THF	0.09	51%	44%	95%
15			Diethyl Ether	0.09	50%	43%	94%
16	R^1=Me,R^2=$SiMe_3$,R^3=H		Hex.-THF(1:5)	0.13	40%	50%	83%
17	R^1=Me,R^2=H,R^3=Me			0.18	44%	52%	91%
18	R^1=Me,R^2=H,R^3=F			0.03	31%	58%	74%
19	R^1=Me,R^2=$SiMe_3$,R^3=F			0.12	13%	82%	80%
20	R^1=Ph,R^2=H,R^3=H			0.17	45%	50%	84%
21	R^1=Ph,R^2=$SiMe_2Ph$,R^3=H			0.09	40%	50%	80%

a) Concentration in M. b) Isolated yield. c) Recovery of the starting material. d) Based on the recovered starting material. e) The mixed solvent of hexane and tetrahydrofuran.



Eq. 1

Experimental results are summerized in Table 1. To observe the effect of concentration in this reaction, experiments were done varing the concentration of strarting material from 0.02M to 0.2M (entries 1-5). But we could not see any notable change in the yield and the reaction rate. This result indicates that the reaction may be an intramolecular reaction. Several attempts with lithium bases such as *n*-butyllithium, *sec*-butyllithum, and *tert*-butyllithium did not change the course of the reaction under hexane-THF (1:5) system (entries 7-9). A brief survey of solvent effects indicated little dependence of the reaction on solvent (entries 10-15). However, in the case of the polar aprotic solvents such as HMPA or DMSO, the aldehyde product was not observed. When the reactants bear two silyl groups (R^2 = trimethylsilyl or dimethylphenylsilyl), the corresponding aldehydes were also obtained but the reaction rate was slower than that of the reactants with mono silyl group (entries 16, 19, and 21). To extend the scope of the reaction, we carried out the reactions using 3-methyl-2-(trimethylsilyl)methyl benzyl alcohol and 3-fluoro-2-(trimethylsilyl)methyl benzyl alcohol (entries 17 and 18) as the starting materials. Both reactants gave the corresponding silylated aldehydes under the standard conditions. We have investigated the possibility of the air oxidation and found that the reaction was not effected by the presence or absence of air.

To understand the mechanism of the reaction in details, we carried out the experiments under the standard conditions using *o*-methyl benzyl alcohol

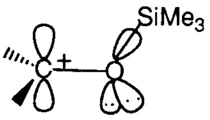
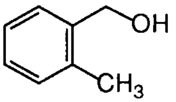
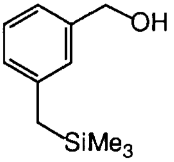


Fig. 1 Vertical stabilization of the trimethylsilyl group

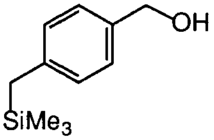
(1), *m*-(trimethylsilyl)methyl benzyl alcohol (2), and *p*-(trimethylsilyl)methyl benzyl alcohol (3) as the starting materials. No reaction was occured with *o*-methyl benzyl alcohol (1) and the starting material was completely recovered. In the case of *m*-(trimethylsilyl)methyl benzyl alcohol (2) and *p*-(trimethylsilyl)methyl benzyl alcohol (3), both reactants gave trace amount (less than 5%) of the corresponding aldehydes. These results indicate that the critical importance of the silyl group for the reaction and the spatial arrangement between the silyl group and the hydroxyl group.



1



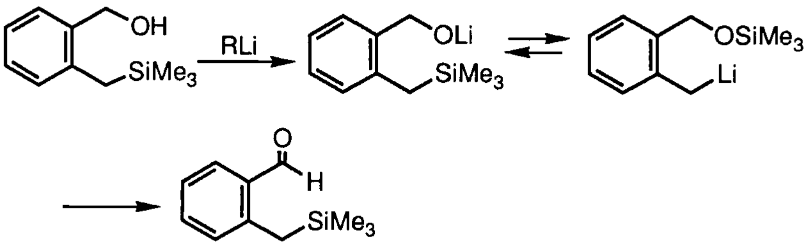
2



3

Jung[5] reported a method for the oxidation of trimethylsilyl ether via hydride abstraction. He also recognized the essential role of the silyl group for the success of the oxidation. He suggested that the trimethylsilyl group provided additional stabilization of the intermediate carbonium ion by a mechanism of vertical stabilization such as in Fig. 1.

We propose a plausible reaction mechanism involving the 1,5-silicon rearrangement in Eq. 2.



Eq. 2

The deprotonated alkoxide compound undergoes the intramolecular 1,5-silicon rearrangement from carbon to oxygen. This kind of rearrangement is known as an equilibrium process.[6] The resulting benzyl silyl ether is converted to the corresponding aldehyde by a hydride transfer and the return of silyl group to the carbanionic center. Further studies will be needed to elucidate the mechanistic details.

In summary, we have found a conceptually novel method for the conversion of the alcohol to the aldehyde via 1,5-silicon rearrangement. The resulting silylated aldehydes[7] are useful for the natural product synthesis.

EXPERIMENTAL

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-300 MHz FT-NMR spectrometer and are reported in parts per million (δ). The IR spectra were obtained with BOMEN model FT-IR M100-C15 and are reported in cm^{-1}. The mass spectra were obtained using Kratos-25-RFA instrument. Column chromatography was performed on Merk silica gel 60 (particle size 230-400 mesh).

Procedure for the generation of *o*-(trimethylsilyl)methyl benzaldehyde.

n-Butyllithium (1.6 N in Hexane, 1.3 ml, 1.22 mmole) was added slowly to a stirred solution of *o*-(trimethylsilyl)methyl benzyl alcohol (200 mg, 1.03 mmole) in dry hexane (1 ml) at -78 ^{0}C. The solution was stirred for 30min and then dry THF (5 ml) was added dropwise to the reation mixture at -78 ^{0}C. After warming up gradually to room temperature, the mixture was stirred for 48 hours. The reation mixture was filtered and concentrated. This crude product was purified with silica gel column chromatography with a 10% ether-hexane mixture to afford yellow oil of *o*-(trimethylsilyl)methyl benzaldehyde (100 mg, 53%).

^{1}H NMR ($CDCl_3$) ; δ 10.1 (1H, s, CHO), 7.65 (1H , dd , J = 7.7 Hz , J = 1.5 Hz , aromatic-H), 7.44 - 7.21 (2H , m , aromatic - H), 7.07 (1H , dd, J = 8 Hz , J = 1.4 Hz , aromatic -H), 2.69 (2H , s , CH_2), -0.02 (9H, s , $SiMe_3$)

IR (neat) ; 2730 (CHO), 1694 (C=O), 849 cm^{-1}

^{13}C NMR ($CDCl_3$) ; δ 192.9, 144.4, 133.3, 132.8, 130.7 (2), 124.5, 23.9, -1.6

mass (m/e) ; 192 (M^+), 177, 165, 149, 104, 97, 73, 69, 57

3 - Methyl - 2 - [(trimethylsilyl) methyl]benzaldehyde

^{1}H NMR ($CDCl_3$) ; δ 10.1 (1H, s, CHO), 7.60 - 7.13 (3H , m , aromatic - H), 2.74 (2H, s, CH_2), 2.28 (3H , s , CH_3), 0.00 (9H, s, $SiMe_3$)

IR (neat) ; 2724 (CHO), 1691(C=O), 848 cm^{-1}

^{13}C NMR($CDCl_3$) ; δ 193.2, 143.2, 136.5, 135.5, 133.0, 131.2, 124.0, 20.4, 19.4, -0.4

mass (m/e) ; 206 (M^+), 191, 163, 147, 133 (C_9H_9), 73 ($SiMe_3$)

o - [(Dimethylphenylsilyl)methyl] benzaldehyde

^{1}H NMR ($CDCl_3$) ; δ 9.99 (1H, s, CHO), 7.69 (1H, dd , J = 7.0 Hz , J = 1.3 Hz , aromatic -H), 7.43 (7H , m , aromatic -H), 6.97 (1H , dd, J = 7.7 Hz , J = 1.5 Hz , aromatic -H), 2.88 (2H, s, CH_2), 0.23 (6H, s, $SiMe_2Ph$)

IR (neat) ; 2730 (CHO), 1694 (C=O), 827 cm^{-1}

^{13}C NMR ($CDCl_3$) ; δ 192.5, 143.5, 139.0, 137.6, 133.7, 133.2, 132.8, 130.7, 129.2, 127.8, 124.7, 23.4, -3.5

mass (m/e) ; 254 (M^+), 239, 178, 136, 135, 105, 91, 75 , 43

o - [Bis (dimethylphenylsilyl)methyl]benzaldehyde

^{1}H NMR ($CDCl_3$) ; δ 9.90 (1H, s, CHO), 7.53 (1H, dd , J = 7.7 Hz , J= 1.5 Hz, aromatic -H), 7.37 - 7.15 (12H, m , aromatic- H), 7.05 (1H, dd, J = 7.9 Hz , J = 1.4 Hz , aromatic -H), 4.06 (1H, s, CH), 0.19 (6H , s, $SiMe_2Ph$), 0.10 (6H, s, $SiMe_2Ph$)

IR (neat) ; 2730 (CHO), 1694 (C=O), 827 cm^{-1}

^{13}C NMR ($CDCl_3$) ; δ 193.7, 146.5, 138.6, 135.1, 133.7, 132.5, 130.6, 128.9, 127.5, 123.6, 22.2, -1.5, -1.7

mass (m/e) ; 388 (M^+), 209, 178, 135, 107, 75, 43

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