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INTRAMOLECULAR CYCLIZATION OF o-SILYLBENZYL ALCOHOLS WITH ELIMINATION OF HYDROCARBON VIA HYPERVALENT SILICON INTERMEDIATES: EFFECT OF STRUCTURE ON THE SELECTIVITY FOR ELIMINATION

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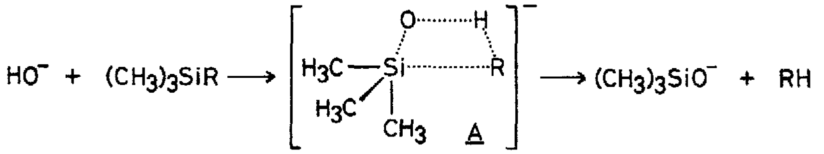
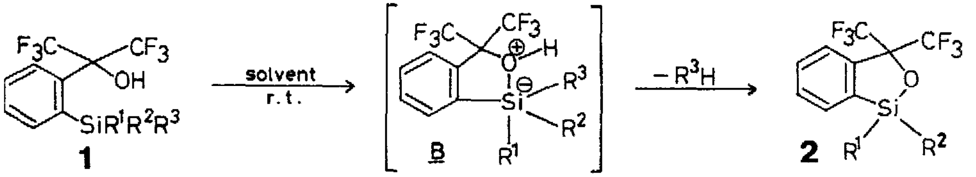
Abstract: o-Silylbenzyl alcohols (**1a**-**1e**) cyclized with elimination of hydrocarbon to give cyclic silanes (**2**) in quantitative yield. The cyclization took place only in aprotic polar solvents such as acetonitrile, indicating that the intermediate of the cyclization was 10-Si-5 zwitterion B. The selectivity for the elimination of substituents was found as the following order, i.e., Ph>Me>t-Bu, and structure of zwitterions was found to play a key role to determine the selectivity.

Synthesis, reaction and application of hypervalent siliconates have been attracting increasing interest,[1] and several reactions via intermediate siliconates have also been reported.[2] DePuy reported a gas-phase reaction of substituted trimethylsilanes (Me_3SiR) with hydroxide ion (OH^-) to form hydrocarbon (RH or MeH) and the corresponding siloxide ion (eq 1), and found that the relative formation rates of hydrocarbons (RH vs MeH) were correlated with the gas-phase acidities of these products.[3] The discussion was supported by a recent calculation on Me_4SiOH^- and $H_3MeSiOH^-$ by Davis.[4] It suggested a concerted four-membered intramolecular transition state such as A in which the substituent being removed was almost completely dissociated to the anion before the proton transfer took place.



(eq 1)

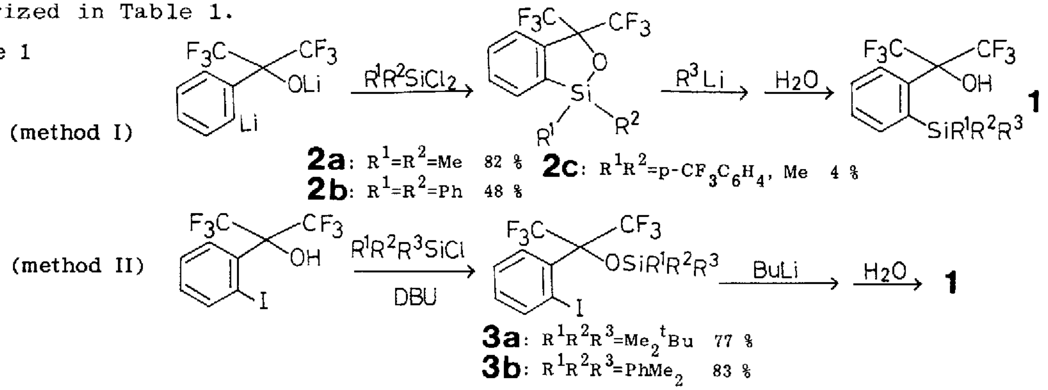
Here we report an intramolecular cyclization of a series of o-silylbenzyl alcohols (**1**) to form cyclic silanes (**2**) and the selectivity for the elimination of hydrocarbon in relation to the structure of intermediate (B) (eq 2).



(eq 2)

The starting o-silylbenzyl alcohols (**1a**-**1e**) were prepared by method I or method II outlined in scheme 1. The reaction of disubstituted dichlorosilanes with lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide[5] gave cyclic silanes (2a-2c), which reacted with a substituted lithium reagent to afford 1c-1e (method I).[6] Silylation of 1,1,1,3,3,3-hexafluoro-2-(2-iodophenyl)-2-propanol[5] gave silylated adducts (3a,3b), which were treated with n-BuLi to afford rearranged alcohols 1a and 1b (method II). The results were summarized in Table 1.

Scheme 1



2a: $R^1=R^2=Me$ 82 %
2b: $R^1=R^2=Ph$ 48 %
2c: $R^1R^2=p\text{-}CF_3C_6H_4$, Me 4 %
3a: $R^1R^2R^3=Me_2{}^tBu$ 77 %
3b: $R^1R^2R^3=PhMe_2$ 83 %

Table 1. Preparation of o-Silylbenzyl Alcohols (1) by Method I or Method II.

Starting 2 or 3	Method	Product 1	R^1	R^2	R^3	Yield (%)
3a	II	1a	Me	Me	t-Bu	96
3b	II	1b	Ph	Me	Me	94
2a	I	1c	Me	Me	$p\text{-}CF_3C_6H_4$	78
2b	I	1d	Ph	Ph	Me	93
2c	I	1e	Me	$p\text{-}CF_3C_6H_4$	$p\text{-}CF_3C_6H_4$	88

The alcohol 1a cyclized with elimination of methane to give cyclic silane 2d (R^1, R^2=Me,t-Bu) in aprotic polar solvents such as acetonitrile-d_3 and dimethyl sulfoxide-d_6 (in quantitative yield at room temperature for several hours). The cyclization did not take place in methanol-d_4, acetone-d_6, deuteriochloroform and benzene-d_6 (rt 1 d). The result indicated that the intermediate (or transition state) of the cyclization was 10-Si-5 zwitterion B. Intermolecular hydrogen-bonding of the hydroxyl group in 1 with methanol may prevent intramolecular coordination of the group to the central silicon atom, in fact addition of a small amount of water to acetonitrile solution of 1a prevented the cyclization.

Cyclization of alcohols 1a-1e was carried out at room temperature in acetonitrile-d_3 to examine the selectivity for elimination of substituents. The reaction could be easily followed by ^{19}F NMR and the produced cyclic silanes (2) were characterized by spectroscopies and elemental analyses.[7] The results were summarized in Table 2. The ratio of methane to isobutane elimination (-MeH:-t-BuH) from 1a (R^1, R^2, R^3=Me_2t-Bu) was 100:0, and the ratio of benzene to methane elimination (-PhH:-MeH) in 1d (R^1, R^2, R^3=Ph_2Me) was also

100:0. The selectivity order (Ph>Me>t-Bu) was slightly different from but was almost consistent with the gas-phase result by DePuy (Ph≫ t-Bu>Me). But in 1b (R^1, R^2, R^3=$PhMe_2$) the ratio of -PhH:-MeH was 75:25, which was not in good agreement with the above result. Further remarkable inconsistency was observed in the cyclization of 1c (R^1, R^2, R^3=Me_2Ar) and 1e [Ar_2Me(Ar=p-CF_3-C_6H_4)]. ArH was eliminated exclusively from 1e but in contrast methane was eliminated predominantly from 1c (-ArH:-MeH=11:89). These results indicated that the structure of o-silylbenzyl alcohols (1) affected the selectivity for the elimination of substituents dramatically.

Table 2. Selectivity of Substituents for Elimination of Hydrocarbons from o-Silylbenzyl Alcohols (1a-1e).[a),b)]

	Products	Ratio of hydrocarbon elimination		
1(R^1,R^2,R^3)	2(R^1R^2;ratio)	-ArH(-PhH)	-MeH	-t-BuH
1a(Me_2t-Bu)	2d(t-BuMe;100):2a(Me_2; 0)	-	100	0
1b(Me_2Ph)	2a(Me_2; 75):2e(PhMe; 25)	75	25	-
1c(Me_2Ar)[b)]	2c(ArMe; 89):2a(Me_2; 11)	11	89	-
1d(Ph_2Me)	2e(PhMe;100):2b(Ph_2; 0)	100	0	-
1e(Ar_2Me)[b)]	2c(ArMe;100):2f(Ar_2; 0)	100	0	-

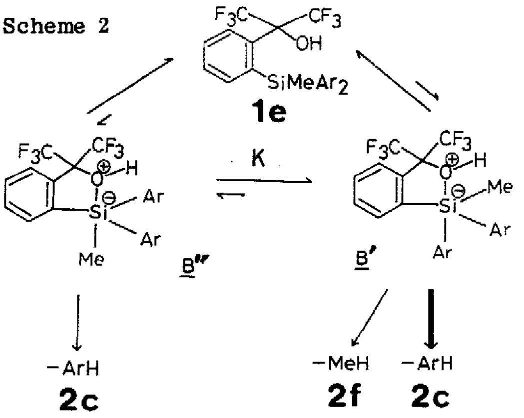
a) in acetonitrile at room temperature. b) Ar=p-$CF_3C_6H_4$.

The results can be understood by concerted four-membered elimination of hydrocarbon from hypervalent siliconates B. That is, there are two possible intermediates B' and B'' in the reaction of 1e (scheme 2). Only ArH can be eliminated from B'' *and ArH and MeH can be eliminated competitively from B'.* It is known that pentacoordinate compounds are trigonal bipyramid in general and the more electronegative groups prefer axial positions (apicophilicity), involving rapid positional isomerization among them by Berry pseudorotation.[8] The intermediate B' is, therefore, more stable than B''. It is concluded that elimination of ArH takes place much more easily than that of MeH based on the above result of 1e (ArH≫MeH from B'). The conclusion is reasonable because the aryl anion is more stable than the methyl anion and the strong anionic property of the transition state A was calculated in the reaction of eq 1.[4]

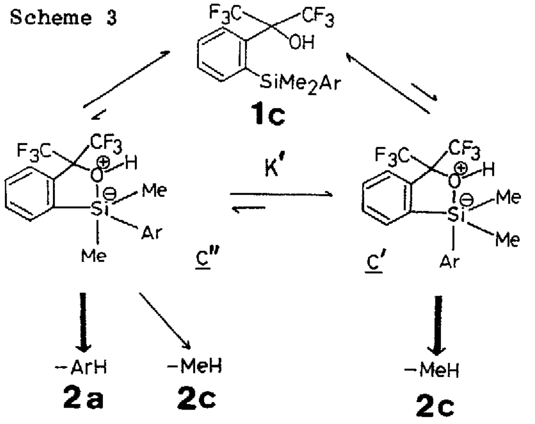
The discussion can be applied to 1c, in which C' and C'' are possible *intermediates and C' is more stable than C'' (scheme 3).* In this case only the methyl group can be eliminated from the predominant C', then MeH elimination from C' can compete with ArH elimination from the minor isomer C''. The ratio of MeH and ArH(or PhH) elimination is determined by the ratio between C' and C'' and the acidity ratio between ArH and MeH. In fact methane was eliminated selectively from 1c and benzene from 1b, which shows explicitly the importance of the ratio between zwitterions.

Effect of structure of the intermediate siliconate A should be reflected in the reaction (eq 1) described by DePuy.[3] The estimation of the gas-phase acidities of hydrocarbons from that reaction, therefore, should be careful on the basis of the present result.

Scheme 2



Scheme 3



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6. 1c: oil. ^{1}H NMR ($CDCl_3$) δ 0.60 (s, 6H), 4.05 (brs, 1H), 7.30-8.00 (m, 8H). ^{19}F NMR ($CDCl_3$) δ -74.7 (s, 6F), -62.5 (s, 3F). Anal Calcd for $C_{18}H_{15}F_9OSi$: C, 48.43; H, 3.39. Found: C, 48.32; H, 3.43. 1e: colorless crystals (mp 107-108 °C (dec)). ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 3H), 3.71 (brs, 1H), 7.23-7.80 (m, 12H). ^{19}F NMR ($CDCl_3$) δ -74.4 (s, 6F), -62.6 (s, 6F). Anal. Calcd for $C_{24}H_{16}F_{12}OSi$: C, 50.01; H, 2.80. Found: C, 49.95; H, 2.76.
7. 2c: oil. ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3H), 7.40-7.80 (m, 8H). ^{19}F NMR ($CDCl_3$) δ -75.9 (q, 3F, J=8Hz), -75.3 (q, 3F, J=8Hz), -63.1 (s, 3F). Anal. Calcd for $C_{17}H_{11}F_9OSi$: C, 47.45; H, 2.58. Found: C, 47.19; H, 2.49. 2a: colorless crystals (sublimed at 50 °C). ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 6H), 7.30-7.70 (m, 4 H). ^{19}F NMR ($CDCl_3$) δ -76.0 (s, 6F). MS m/z 300 (M^+).
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