# MARKED MEDIUM EFFECTS ON THE SUBSTITUTION AND THE ADDITION–REARRANGEMENT–EJECTION REACTIONS OF (HALOMETHYL)SILANES WITH METHOXIDES

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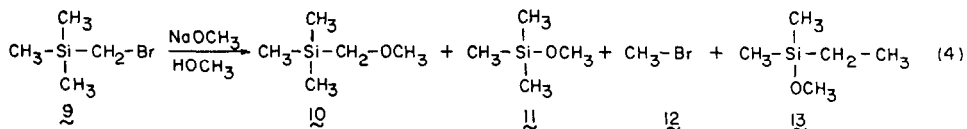Chemistry Department, The Ohio State University, Columbus, Ohio 43210

Abstract: Reactions of methoxides with (halomethyl)silanes at silicon are facilitated by aprotic solvents and cation separation.

(Chloromethyl)dimethylphenylsilane (1) reacts with sodium ethoxide in ethanol to give (1) (ethoxymethyl)dimethylphenylsilane (3, Eq 1) by displacement of chloride ion from chloro-methyl-carbon and (2) ethoxydimethylphenylsilane (6, Eq 2) and chloromethide ion (7) by attack on silicon (5;a) with cleavage.[1a] Of particular interest is that benzylethoxydimethylsilane (8) is formed by a process (Eq 3) presumed to involve attack on silicon (5;b) with phenyl migration to chloromethylcarbon and chloride ion ejection.[1a] Also, sodium methoxide in methanol reacts with (chloromethyl)dimethylsilanes, $Z-(CH_3)_2Si-CH_2-Cl$ [Z=H, $(CH_3)_3Si$ and
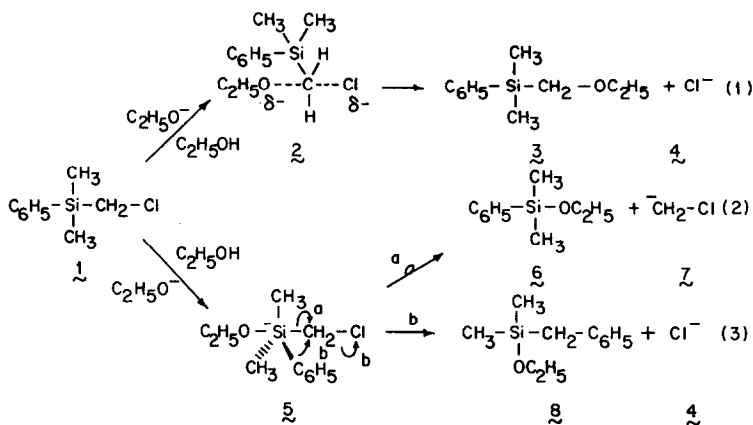
p-ClC_6H_4], possibly via the addition-rearrangement-ejection mechanism of Eq 3, to give products [$CH_3O-Si(CH_3)_2-CH_2-Z$; Z=H, $(CH_3)_3Si$ and p-ClC_6H_4] derived exclusively from migration of the hydrogen, trimethylsilyl and p-chlorophenyl groups.[1b,c] Investigation has now been made of the behavior of (bromomethyl)trimethylsilane (9, Eq 4) and 1 with methoxides under various conditions. The studies (1) reveal significant differences in the effects of solvents, metallic cations and temperature on the competitive reactions of 9 and 1 with methoxides and (2) establish that the addition-rearrangement-ejection processes postulated (Eq 3) do indeed involve initial attack of methoxide on silicon in 9.

The behavior of 9 with sodium methoxide (1.2 equiv) in various solvents (Eq 4, Table 1) at reflux temperatures was investigated first. With sodium methoxide in methanol, 9 is converted essentially totally to (methoxymethyl)trimethylsilane (10, 98%). As dioxane is substituted for methanol, the reactions of 9 with methoxide change dramatically in that methoxytrimethylsilane (11), methyl bromide (12) and the rearrangement product,

$$CH_3-Si-CH_2-Br \xrightarrow[\text{HOCH}_3]{\text{NaOCH}_3} CH_3-Si-CH_2-OCH_3 + CH_3-Si-OCH_3 + CH_3-Br + CH_3-Si-CH_2-CH_3 \quad (4)$$

with silicon groups CH_3 on each structure:
9, **10**, **11**, **12**, **13**

Table 1: Products (% Yields) from 9 and Sodium Methoxide (Eq 4).

Solvent	Time, hr	10	11	13
CH_3OH	19	98	0.5	0
50% CH_3OH, $C_4H_8O_2$	21	96	1.2	0.3
5% CH_3OH, $C_4H_8O_2$	18	24	9	60
$C_4H_8O_2$	7	1	6	>80

ethylmethoxydimethylsilane (13), are formed along with 10. Of further significance is that 13 is by far the major product (60%) of reaction of 9 with <u>sodium methoxide in 5% methanol/-dioxane</u> or even more (>80%) in <u>pure dioxane</u>. Excess sodium methoxide, less solvent, shorter reaction times or prolonged heating cause no change in the distribution of the products from 9 and <u>sodium methoxide in dioxane</u> and 10 is stable to sodium methoxide for long periods.

The facts that <u>sodium methoxide</u> reacts with 9 <u>in limited methanol</u> or <u>in dioxane</u> to give rearrangement product 13 essentially exclusively are interpretable on the basis of preferential attack on silicon in the aprotic environments via pentacovalent complex 14, methyl migration and bromide ejection analogous to 5 in Eq 3. Alternate routes to 13 as well as 10 however involve trimethylsilylcarbene (16) as generated by proton abstraction from 9 by methoxide to form 15 followed by (or with) loss of bromide ion. Carbene 16 could then capture methanol to give 10 or undergo methyl migration to 2-methyl-2-sila-2-butene (17) or methyl-C-H insertion to 1,1-dimethyl-1-silacyclopropane (18).[1d-f] Reaction of 17 and/or 18 with methanol would thus yield 13.[1d-g] Indeed (chloromethyl)trimethylsilane is converted by lithium 2,2,6,6-tetramethylpiperidide to 16 (or its carbenoid) capturable by electron-rich olefins[1h]. Further, photolysis and thermolysis of trimethylsilyldiazomethane [$(CH_3)_3SiCH=N_2$] give discrete 16, isomerization of which results in 17 and 18.[1d-f] Reactions of methanol to give 13 are known for 17[1d-f] and expected for 18.[1g]

$CH_3O-Si-CH_2-Br$ with CH_3 groups

14, **15**, **16**, **17**, **18**
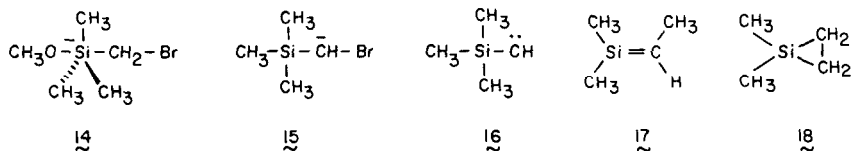
Possible <u>alpha-elimination</u> of 9 with rearrangement and/or C-H insertion was then studied with <u>sodium methoxide in dioxane containing methanol-O-D(~5%)</u>. If 16-18 were captured by the labelled solvent, 10 and 13 would be formed containing deuterium. Further, if reversible deprotonation of 9 by methoxide were to occur, some deuterium should be in the 9 recovered. Analyses of 9 and 16-18 from many such experiments revealed however that deuterium had not been incorporated, thus eliminating 15-18 as reaction intermediates.

The present study thus reveals that <u>sodium methoxide in dioxane</u> attacks 9 preferentially on silicon presumably via 14[11] with methyl migration and bromide ejection or with bromomethide ($^-CH_2Br$) expulsion, whereas <u>in methanol</u> displacement occurs essentially exclusively on

bromomethylcarbon. Since <u>dioxane</u> solvates cations well and anions poorly, it is presumed that "naked" <u>methoxide ion</u> reacts preferably with 9 at silicon, making use of the vacant 3d orbitals and the strength of the developing silicon-oxygen bond. Reaction is then completed by rearrangement-ejection to 13 and bromide ion or collapse to 11 and bromomethide ion. <u>Methoxide ion in methanol</u> is apparently highly hydrogen-bonded and thus reaction on silicon in 9 would require stripping of the solvent from the oxyanion. Attack of the solvated methoxide nucleophile then occurs by displacement on relatively-sterically available carbon in 9 to give 10.[1j]

The reactions of 1 with <u>sodium methoxide in methanol</u> were then investigated. At 65 °C the major product is (methoxymethyl)dimethylphenylsilane (19, Eq 5; 79%, Table 2) as formed by displacement of chloride ion from chloromethylcarbon of 1. Methoxydimethylphenylsilane
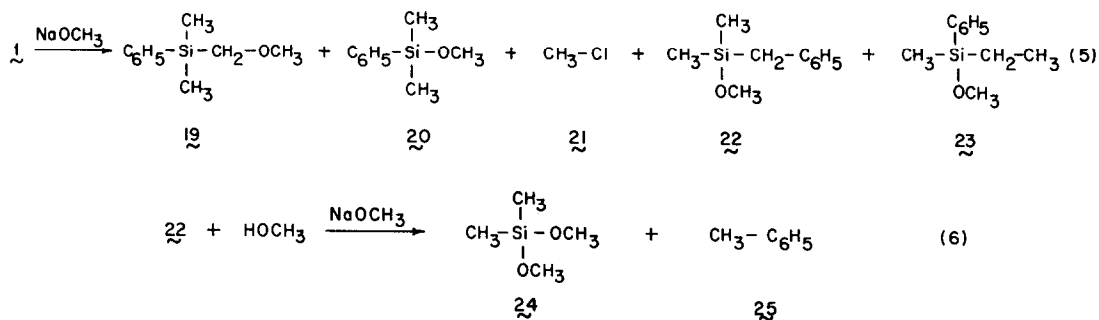
$$\underset{\sim}{1} \xrightarrow{\text{NaOCH}_3} \underset{\underset{19}{\sim}}{C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_2-OCH_3} + \underset{\underset{20}{\sim}}{C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-OCH_3} + \underset{\underset{21}{\sim}}{CH_3-Cl} + \underset{\underset{22}{\sim}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{OCH_3}{|}}{Si}}-CH_2-C_6H_5} + \underset{\underset{23}{\sim}}{CH_3-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{OCH_3}{|}}{Si}}-CH_2-CH_3} \quad (5)$$

$$\underset{\sim}{22} + \text{HOCH}_3 \xrightarrow{\text{NaOCH}_3} \underset{\underset{24}{\sim}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{OCH_3}{|}}{Si}}-OCH_3} + \underset{\underset{25}{\sim}}{CH_3-C_6H_5} \quad (6)$$

Table 2: Products (% Yields) from 1 and Methoxides (Eq 5 and 6).

Methoxide	Solvent	Temp., °C	Time, hr	19	20	22	23	24
NaOCH$_3$	CH$_3$OH	65	12	79	5	---	---	6
NaOCH$_3$	CH$_3$OH, 18-Crown-6	65	18	60	11	---	---	26
KOCH$_3$	CH$_3$OH	65	12	28	14	---	---	46
CsOCH$_3$	CH$_3$OH	65	2	8	20	---	---	66
NaOCH$_3$	C$_4$H$_8$O$_2$	30	168	---	3	76	14	3
NaOCH$_3$	C$_4$H$_8$O$_2$	60	108	---	6	51	26	16
NaOCH$_3$	C$_4$H$_8$O$_2$	100	12	---	12	---	32	44
NaOCH$_3$	C$_4$H$_8$O$_2$, 18-Crown-6	30	18	---	10	---	14	76

(20, 5%) results from reaction of methoxide on silicon of 1 (as in Eq 3) with loss of 7. Dimethoxydimethylsilane (24, 6%) and toluene (25) are produced by methanolysis of benzylmethoxydimethylsilane (22) as derived by attack of methoxide on silicon of 1 with phenyl migration and chloride loss (as in Eq 3). Addition however of <u>18-crown-6 ether</u> in trace amounts to 1 and <u>sodium methoxide in methanol</u> or substituting <u>potassium methoxide</u> or <u>cesium methoxide</u> for <u>sodium methoxide</u> causes a dramatic shift in the product distribution (Table 2) from Eq 5 and 6. Upon making the reactant changes progressively, 19 decreases from 79 to 8% while 20 and 24 increase from 11 to 86% and thus there is a shift from predominant methoxide attack on carbon to that on silicon. Also, all of the products from 1 and <u>sodium methoxide in dioxane</u> result from attack of methoxide on silicon and (2) the reactions of 1 with <u>sodium methoxide</u>

are much faster in dioxane than in methanol. Further, 1 in dioxane does not react detectably with lithium methoxide, lithium methoxide containing 12-crown-4 ether, magnesium methoxide or calcium methoxide for long periods at 100 °C.

The differences in the presently observed behavior of 1 obviously stem from the effects of cations, solvation and covalency on methoxide ion as a reactant.[1k] 18-Crown-6 ether complexes sodium ion and, upon addition to sodium methoxide in methanol, leads to methoxide ion more effectively separated from its counter cation. The sizes and the ionic stabilities of cesium, potassium and sodium ions are Cs > K > Na and thus the reaction paths of the various alkali-metal methoxides with 1 in methanol (Table 2) reflect the dissociation of the metallic ions in that the more separated methoxides react preferentially on silicon. That sodium methoxide in dioxane reacts with 1 with rapidity and essentially exclusively on silicon emphasizes again the differences in behavior of halomethylsilanes with methoxide in ether and in hydrogen-bonding environments. The lack of reactivity of lithium methoxide and alkaline-earth methoxides with 1 in dioxane illustrates clearly that covalency to methoxide represses nucleophilicity with respect to 1.

Of further interest is that methoxide attack on silicon in 1 in dioxane results in methyl migration and chloride ion ejection to give ethylmethoxymethylphenylsilane (23, Eq 5, Table 2) along with 20-22, 24 and 25. Conversion of 1 to 23 by methoxide in dioxane increases with temperature and is the first example of an alkyl group (methyl) migrating competitively with a phenyl group in rearrangement from anionic pentavalent silicon (at 60 °C the relative migratory ability of phenyl to methyl as statistically corrected is 5:1). The fact that phenyl migrates in preference to methyl in the present systems is consistent with the supposition[1a] that the transition states for rearrangement-ejection are close in structure to 5 and thus the group that rearranges preferentially is that which can better support its electron pair (inductively) on departure from silicon.[1a,1]

References and Notes

1. (a) C. Eaborn and J. C. Jeffrey, J. Chem. Soc., 137 (1957). (b) L. H. Sommer, W. P. Barie, Jr. and D. R. Weyenberg, J. Am. Chem. Soc., 81, 251 (1959). (c) M. Kumada, M. Ishikawa and K. Tamao, J. Organomet. Chem., 5, 226 (1966). (d) R. L. Kreeger and H. Shechter, Tetrahedron Lett., 2061 (1975). (e) R. L. Kreeger, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1976. (f) M. R. Chedekel, M. Skoglund, R. L. Kreeger and H. Shechter, J. Am. Chem. Soc., 98, 7846 (1976). (g) D. Seyferth, R. L. Lambert and D. C. Annarelli, J. Organomet. Chem., 122(3), 311 (1976). (h) R. A Olafson, D. H. Hoskins and K. D. Lotts, Tetrahedron Lett., 1677 (1978). (i) It is not yet definitive whether 5 and 14 are discrete negatively-charged intermediates or whether they are by-passed as transition states upon attack of methoxide. (j) An additional effect may be that 9 is more highly solvated and thus blocked at silicon by methanol than by dioxane; see R. W. Bort, C. Eaborn and B. M. Rushton, J. Organomet. Chem., 3, 455 (1965). (k) P. F. Hudrlik and R. Feasley, Tetrahedron Lett., 1781 (1972) have found that acetoxy-t-butyldimethylsilane is cleaved by the following 1-butoxides in glyme by attack on silicon or carbonyl in the indicated mole ratios: Li, 0.0363; Na, 0.351; K, 1.777. (1) It is not yet clear whether pi-electron participation of the phenyl group to chloro-