THE BEHAVIOR OF ALKOXIDES WITH ALLYL(CHLOROMETHYL)DIMETHYLSILANES AND
(CHLOROMETHYL)DIMETHYLVINYLSILANE; THE ABILITIES OF ALLYL AND
VINYL GROUPS TO MIGRATE FROM PENTACOORDINATE SILICON

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Abstract: Sodium methoxide in tetrahydrofuran attacks silicon in allyl(chloromethyl)-
dimethylsilane and in (chloromethyl)dimethylvinylsilane with displacement of chloride and
1,2-migration of the allyl and the vinyl groups to give 1-(3-butenyl)methoxydimethylsilane
and allylmethoxydimethylsilane.

Sodium alkoxides in dioxane and in part in alcohols react on silicon in (halomethyl)-
silanes ($\underset{\sim}{1}$) with (1) halide displacement and substituent (Z) migration to give $\underset{\sim}{3}$ (Eq. 1)
and (2) halomethide expulsion ($\underset{\sim}{5}$, Eq. 2).[1a-f] Little is known as yet about the migratory
abilities of substituents (Z) in displacement-rearrangement from pentacoordinate silicon
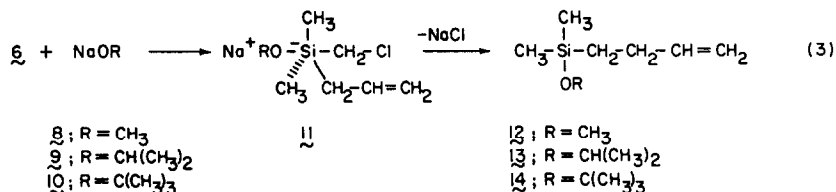($\underset{\sim}{2}$).[2] The phenyl group rearranges 5 times faster than methyl in the reactions of
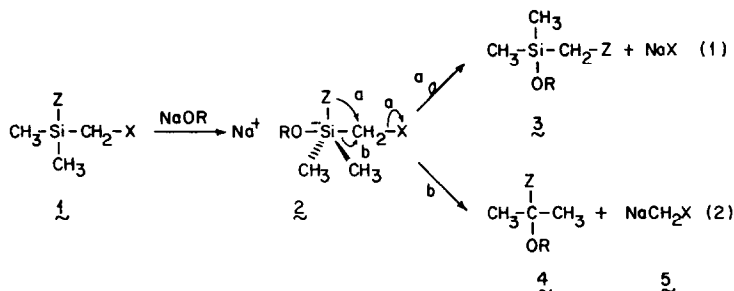
(chloromethyl)dimethylphenylsilane ($\underset{\sim}{1}$; Z = C_6H_5; X=Cl) with sodium methoxide in dioxane at
60°C.[1f] In displacement-rearrangement of (chloromethyl)dimethylsilanes $\underset{\sim}{1}$ (Z = H, $(CH_3)_3$Si,
C_6H_5 and $\underline{p}$-ClC_6H_4; X = Cl) by sodium alkoxides in alcohols, the hydrogen,[1c] trimethyl-
silyl,[1d] phenyl[1b] and $\underline{p}$-chlorophenyl[1b] substituents migrate exclusively. Carbanionic
stabilization in the migrating group is presumed to control the migratory aptitude.[1b,f]

    The behavior of allyl(chloromethyl)dimethylsilane ($\underset{\sim}{6}$), varied substituted-allyl(chlor-
omethyl)dimethylsilanes and (chloromethyl)dimethylvinylsilane ($\underset{\sim}{7}$) with metal alkoxides in
aprotic and alcoholic environments is now reported. The objectives of this study are to
determine the roles which allyl, substituted-allyl and vinyl groups play in reactions of
their (chloromethyl)dimethylsilyl derivatives with alkoxides.
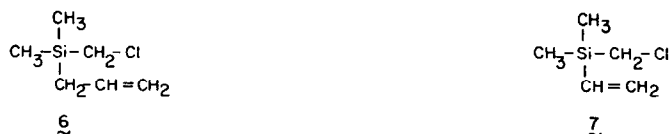
Reaction of $\underset{\sim}{6}$[3a] with sodium methoxide ($\underset{\sim}{8}$) in tetrahydrofuran at 65°C occurs smoothly
on silicon by displacement-rearrangement to give the single silyl product, 1-(3-butenyl)-

methoxydimethylsilane[3b] (12, Eq. 3) in 94% yield. Similarly, the bulkier bases, sodium isopropoxide (9) and sodium t-butoxide (10) react with 6 in tetrahydrofuran (65°C) to yield 1-(3-butenyl)isopropoxydimethylsilane (13, 81%) and 1-(3-butenyl)-t-butoxydimethylsilane (14, > 64%).

$$6 + NaOR \longrightarrow Na^+ RO-\underset{\underset{CH_2-CH=CH_2}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_2-Cl \xrightarrow{-NaCl} CH_3-\underset{\underset{OR}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_2-CH_2-CH=CH_2 \qquad (3)$$

8 ; R = CH_3   11   12 ; R = CH_3
9 ; R = CH(CH_3)_2   13 ; R = CH(CH_3)_2
10; R = C(CH_3)_3   14 ; R = C(CH_3)_3

Silanes 12, 13 and 14 are thus formed by attack of the alkoxides on silicon in 6 with allyl migration and chloride loss (Eq. 3)[2]. Of note is that products of (1) displacement-rearrangement with methyl migration, (2) chloromethide loss (as in Eq. 2), (3) bimolecular nucleophilic substitution on chloromethyl carbon and (4) allyl displacement are not obtained from reactions of 6 with the sodium alkoxides.

The principal feature of the behavior of alkoxides (8-10) with 6 is coordinative attack on silicon with chloride displacement and facile allyl migration. The mechanistic path by which the allyl group moves, be it a 1,2-rearrangement process in which the location of the double bond is preserved or a cyclic Claisen-like rearrangement in which the double bond is shifted, is not clear, however. The mechanism of allyl migration was thus investigated from unsymmetrically-substituted allyl(chloromethyl)dimethylsilanes and sodium methoxide as follows.

Reaction of chloro(chloromethyl)dimethylsilane (15) with the Grignard reagent (16, Eq. 4) from 3-chloro-1-butene gives a product mixture of 52% 3-(1-butenyl)chloromethyldimethyl-silane (17) and 48% (Z)- and (E)-1-(2-butenyl)chloromethyldimethylsilanes (18 and 19). Exhaustive gas chromatography resulted in isolation and identification of (Z)- and (E)-butenylsilanes 18 and 19 as a mixture. Silane 17 could not be totally freed of 18 and
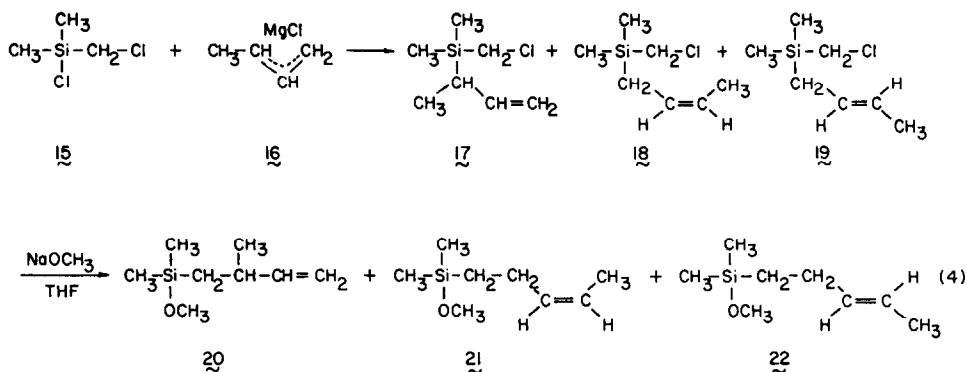
19. The ^{1}H NMR of 17 at 1.09 δ, however, allows accurate integrative determination of its percentage in 18 and 19. Extensive preparative gas chromatography led to enrichment of the initial mixture of 17-19 to 73% 17 and 27% 18 and 19.

Mixtures of 17, 18 and 19 react with sodium methoxide (8) in tetrahydrofuran at 65°C
to give methoxydimethyl-1-(2-methyl-3-butenyl)silane (20) and (Z)- and (E)-methoxydimethyl-
1-(3-pentenyl)silanes (21 and 22, Eq. 4). The product is separable by gas-chromatography
into 20 and the (Z)/(E) mixture of 21 and 22 in which each component is assignable by IR,
MS and ^{1}H NMR methods. Of significance is that reactions of sodium methoxide in tetrahydro-
furan at 65°C with mixtures containing 73% 17 and 27% 18 and 19 yield 20 along with 21-22
in 73% and 27% proportions. Similarly, reactions of 8 with 17 and 18-19 in 52:48 ratio
give 20 and 21-22 of composition identical to that of the initial chlorides. The results
thus indicate that a single mechanism is likely operational: attack by methoxide on sili-
con and 1,2-rearrangement (non-cyclic) of the 3-(1-butenyl) and the (Z)- and (E)-crotyl
groups with retention of the initial positions of the carbon-carbon double bonds of the
moieties migrating from silicon. The marked ability of allyl to rearrange in 11 presumably
stems from inductive electron attraction of its vinyl group and the capacity of the migrat-
ing allyl group to delocalize during movement.[1b,f]

Investigation then centered on the behavior of (chloromethyl)vinylsilane 7 with alkox-
ides. In dioxane at 100°C, 7 and 8 (Eq. 5-7) give allylmethoxydimethylsilane (24, > 45%),
methoxydimethylvinylsilane (25, > 9%), dimethoxydimethylsilane (28, > 19%) and sodium
chloride. Methoxysilane 24 is converted by 8 (Eq. 7) to 28 and propene (29) and the ratio
of 24 to 28 from 7 and 8 depends on the equivalents of 8 used and the reaction time. The
results of present interest from 7 and 8 are that vinyl migrates rather than methyl in
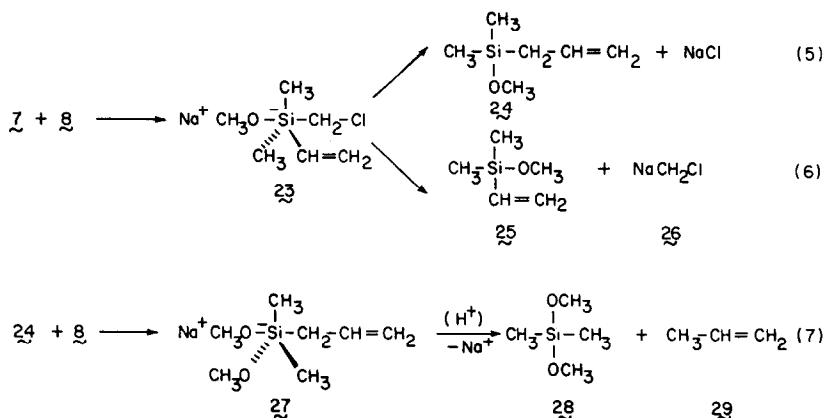
displacement-rearrangement and there is no bimolecular nucleophilic displacement by 8 on
the chloromethyl carbon in 7. That vinyl migrates much better than methyl is consistent
with the supposition that migration from pentavalent silicon is controlled by the ability
of a group to leave (inductively) with an electron pair.[1b,f] There remains for determina-
tion, however, the role of pi-electron donation in facilitating migration of the vinyl
group to partially positive chloromethyl carbon as chloride is expelled.

The reactions of 7 and 8 were then investigated in methanol at 65°C. Indeed, attack
of methoxide/methanol on 7 gives (1) 24 (Eq. 5) and then 28 and 29 (Eq. 7, 12%) and (2) 25
(Eq. 6, 12%). By far, however, the major and revealing new product is (methoxymethyl)-

dimethylvinylsilane ($\underset{\sim}{31}$, 76%) as formed by nucleophilic displacement on chloromethyl carbon of $\underset{\sim}{7}$ by solvated methoxide (Eq. 8). Methoxide becomes less nucleophilic and bulkier when hydrogen-bonded in methanol and presumably loses significantly its ability to make use of the strength of a developing silicon-oxygen bond in reaction with $\underset{\sim}{7}$.[1e,f] Sodium methoxide ($\underset{\sim}{8}$) in methanol is encumbered and/or soft and thus attacks $\underset{\sim}{7}$ on carbon containing chlorine (Eq. 8).

$$\underset{\sim}{7} \ + \ NaOR \ \longrightarrow \ Na^{+} \ \underset{\delta-}{RO} \text{---} \underset{\underset{H}{|}}{C} \text{---} \underset{\delta-}{Cl} \ \xrightarrow{-\,NaCl} \ CH_3 - \underset{\underset{CH=CH_2}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_2 - OR \qquad (8)$$

with the central structure bearing $H_2C=CH$ and CH_3, CH_3 groups on Si, H.

CH_3OH	$\underset{\sim}{8}$; R = CH_3	$\underset{\sim}{30}$	$\underset{\sim}{31}$; R = CH_3
THF	$\underset{\sim}{9}$; R = $CH(CH_3)_2$		$\underset{\sim}{32}$; R = $CH(CH_3)_2$
THF	$\underset{\sim}{10}$; R = $C(CH_3)_3$		$\underset{\sim}{33}$; R = $C(CH_3)_3$

The effects of bulk and nucleophilicity on the behavior of alkoxides with $\underset{\sim}{7}$ in tetrahydrofuran at $65\,^{\circ}C$ were then investigated. Interestingly, sodium isopropoxide ($\underset{\sim}{9}$) reacts with $\underset{\sim}{7}$ primarily by displacement on chloromethyl carbon to give (isopropoxymethyl)dimethylvinylsilane ($\underset{\sim}{32}$, 50%; Eq. 8). Attack also occurs on silicon (as in Eq. 1 and 2; Z= $CH=CH_2$) to yield allylisopropoxydimethylsilane [$(CH_3)_2CHO-Si(CH_3)_2-CH_2CH=CH_2$, 13%] by displacement-rearrangement and isopropoxydimethylvinylsilane [$(CH_3)_2Si(CH=CH_2)-OCH(CH_3)_2$, 30%] by chloromethide ($\underset{\sim}{26}$) expulsion. Further, sodium t-butoxide ($\underset{\sim}{10}$) effects even greater displacement of chloride from $\underset{\sim}{7}$ to form (t-butoxymethyl)dimethylvinylsilane ($\underset{\sim}{33}$, > 58%; Eq. 8) along with di-t-butoxydimethylsilane {$(CH_3)_2Si[OC(CH_3)_3]_2$, > 20%} as derived by cleavage of displacement-rearrangement product, allyl(t-butoxy)dimethylsilane [$(CH_3)Si(CH_2-CH=CH_2)OC-(CH_3)_3$] by $\underset{\sim}{10}$. Thus as the bulk of the alkoxide is increased (t-BuO$^-$ > i-PrO$^-$ > MeO$^-$), attack on silicon in $\underset{\sim}{1}$ diminishes. Presumably pentavalent silicon processes become more difficult because of steric interference[2] or/and the highly substituted alkoxides are more covalent and thus displacement on carbon becomes preferred.

References and Notes

1. (a) J. L. Speir, J. Am. Chem. Soc., 70, 4142 (1948). (b) C. Eaborn and J. C. Jeffrey, J. Chem. Soc., 137 (1957). (c) L. H. Sommer, W. P. Barie, Jr. and D. R. Weyenberg, J. Am. Chem. Soc., 81, 251 (1959). (d) M. Kumada, M. Ishikawa and K. Tamao, J. Organomet. Chem., 5, 226 (1966). (e) R. L. Kreeger, Diss. Abst. Int., Univ. Microfilms Int., Ann Arbor, Michigan, 37, 3961B (1977). (f) R. L. Kreeger, P. R. Menard, E. A. Sans and H. Shechter, Tetrahedron Lett., in press (1985).

2. It is not yet definitive whether $\underset{\sim}{2}$ and its analogs are discrete negatively-charged pentavalent silicon intermediates or whether they are by-passed as transition states upon direct attack by the alkoxides.

3. (a) Syntheses and the properties of all reactants and products will be described in a full paper based in part on the present communication. (b) All new products give proper analyses and have spectral (IR, ^1H NMR and MS) and GC properties identical with that of authentic samples.