Journal of Organometallic Chemistry, 358 (1988) C1–C5
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Pentacoordinate silicon intermediates in relay substitution reactions of organosilanes: successive nucleophilic attack at silicon and its adjacent carbon

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(Received March 31st, 1988)

Abstract

Chloromethylsilyl chlorides of the type, $ClCH_2R_2SiCl$, have been shown to undergo kinetically controlled nucleophilic attack at silicon, with either phenols or amines (PhEH, with E = O or NMe), to yield products of the type, $PhESiR_2CH_2Cl$. Subsequent treatment of the latter products with KF in acetonitrile causes the nucleophile to be shifted from silicon to carbon with the formation of $FSiR_2CH_2EPh$. Alternatively, treatment of $ClCH_2R_2SiCl$ simultaneously with PhEH and KF yields the same thermodynamically controlled product directly, $FSiR_2CH_2EPh$. This possibility of directing nucleophilic attack toward silicon or its adjacent carbon has great importance in the synthesis of substituted organosilanes.The mechanism of these so-called relay nucleophilic substitutions is proposed as involving pentacoordinate silicon intermediates. This concept of initial nucleophilic attack at silicon and the subsequent relaying of the nucleophile from the pentacoordinate silicon to the adjacent carbon is also shown to be applicable to the unusual reactions of α,β-epoxyalkylsilanes.

Chloromethyl(dimethyl)silyl chloride (I) is a versatile intermediate in synthesis, because both the silicon and the methylene carbon centers are sensitive to nucleophilic attack. For example, this type of reactivity has been employed for the synthesis of sila-substituted nitrogen heterocycles from 2-mercaptoimidazoles [1]. Since the silicon–chlorine bond, however, is much more reactive to nucleophilic attack than the carbon–chlorine bond, substitution at silicon can be effected very selectively to form II in high yield (eq. 1) [2]:

$$\underset{(I)}{ClSiMe_2CH_2Cl} + RMgX \rightarrow \underset{(II)}{RSiMe_2CH_2Cl} + MgClX \qquad (1)$$

In a dinstinctly separate process, compounds of type II, where R = aryl, alkyl, benzyl and similar organic groups, can be caused to undergo a subsequent 1,2-shift

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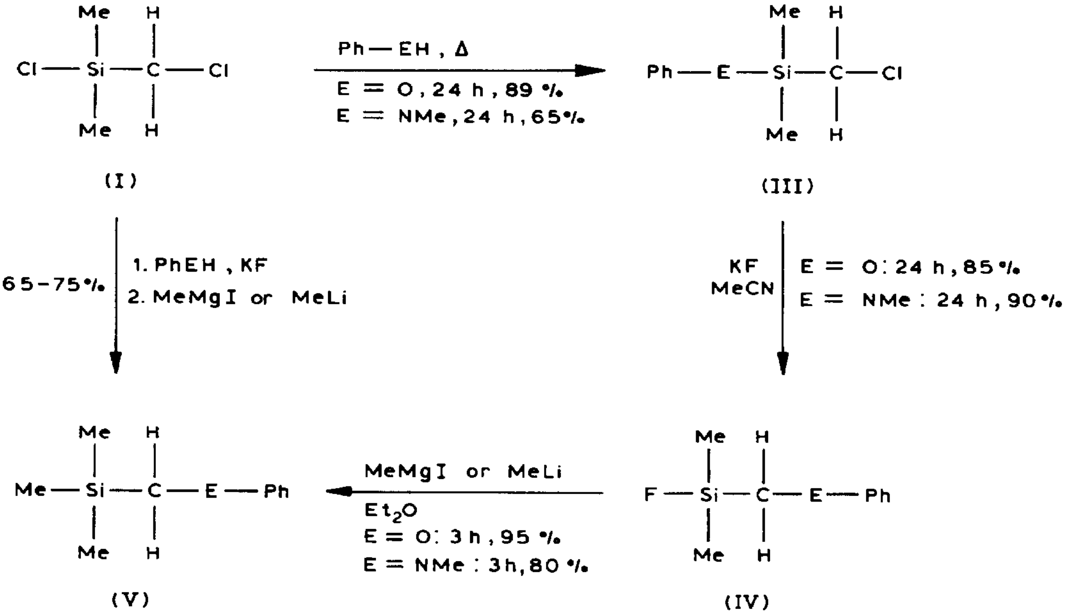

Scheme 1

of the R group from silicon to the adjacent carbon by agency of nucleophiles, such as F^- and RO^- (eq. 2) [3–5]:

$$RSiMe_2CH_2Cl + D^- \rightarrow DSiMe_2CH_2R \qquad (2)$$

In the course of a study of nucleophilic suhstitutions of phenols and amines on I, we have observed striking examples of what can be termed relay substitution processes: initial, kinetically controlled nucleophilic substitution at silicon with PhEH (E = O or NMe) to form III, followed by fluoride ion-induced relaying of the nucleophile from silicon to its adjacent carbon in a thermodynamically determined process (IV in Scheme 1) *.

Intermediate IV can be subsequently alkylated with an organometallic reagent, RM, to give the carbon-substituted organosilane, V. Alternatively, in a single step I can be converted into IV by the simultaneous reaction with PhEH and KF. Therefore, one is now in a position to introduce the nucleophile selectively onto silicon or its adjacent carbon in I.

The mechanism of the fluoride ion-induced relay of the PhE group from silicon to carbon cannot be established unambiguously at this time. But such 1,2-group shifts most probably involve pentacoordinate silicon anionic intermediates. In a series of pioneering studies Corriu and co-workers have demonstrated that pentacoordinate intermediates formed with fluoride ion activate the silicon to attack by strong nucleophiles. Such heightened reactivity is ascribed to the greater electroposi-

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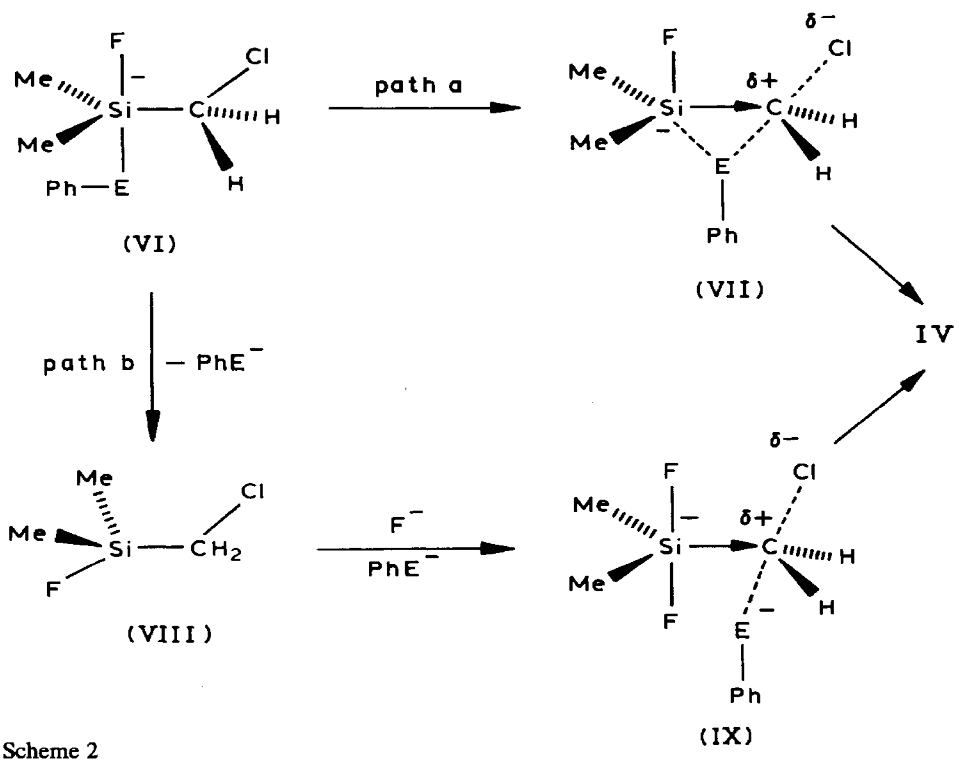
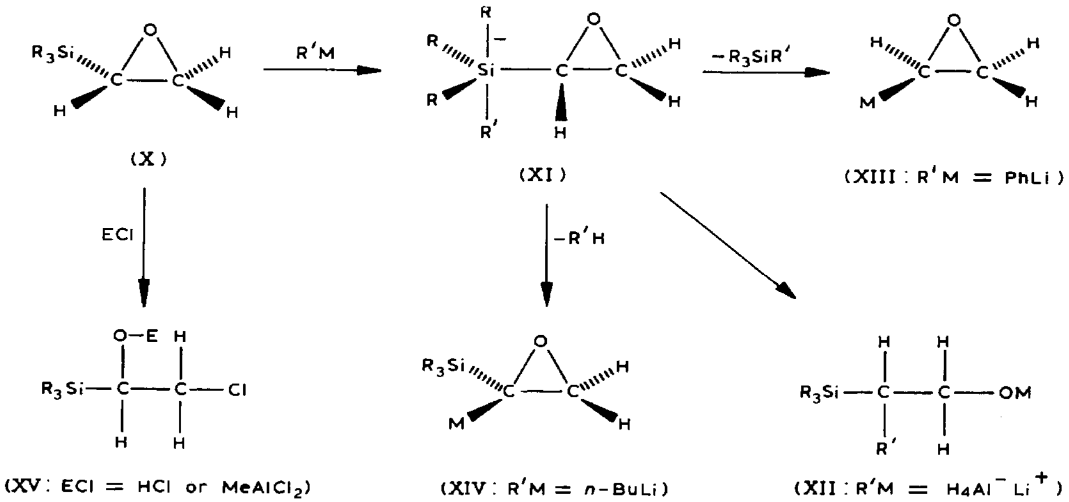
* All intermediates and products were fully characterized by ^1H NMR, IR, and MS data. ^1H NMR ($CDCl_3$) of Me_3SiCH_2OPh: 0.00 (s, 9H), 3.39 (s, 2H), 6.72–7.35 (m, 5H); ^1H NMR ($CDCl_3$) of Me_3SiCH_2NMePh: 0.00 (s, 9H), 2.93 (s, 2H), 3.01 (s, 3H), 6.40–7.30 (m, 5H). The conversion of I into III was conducted by heating I and PhEH at reflux without solvent. The conversion of III into IV was then performed in removing refluxing acetonitrile. Finally, the conversion of IV into V was carried out by the acetonitrile from IV in vacuo and then adding the ethereal MeMgI. The yields of the intermediate steps have not been maximized through systematic experimental variations.



Scheme 2

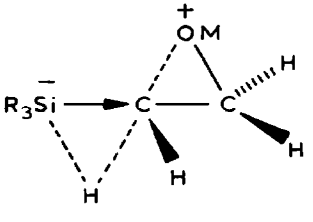
tive character of the pentavalent silicon atom [6]. Applying these concepts to the rearrangement of III into IV, we suggest that III forms a pentacoordinate intermediate with fluoride ion (VI in Scheme 2). The greater electron release of such a silicon center in transition states VII or IX should foster nucleophilic attack by PhE^- at the adjacent carbon, regardless of whether such attack be intramolecular (path a) or intermolecular (path b) (Scheme 2). A choice between path a and path b will be possible, once we have conducted appropriate cross-over experiments now underway. In the absence of such data, however, we tend to favor path a, because it avoids the attack of an anion at a carbon adjacent to a silicon anion (IX).

As an extension of the hypothesis of Corriu, therefore, it appears that pentacoordinate silicon anions not only activate the silicon center to nucleophilic attack, but also the adjacent carbon centers. This realization helps to clarify some unusual reactions of α,β-epoxyalkylsilanes (X). Some 25 years ago, we reported for the first time that nucleophiles, such as $LiAlH_4$ [7], phenyllithium [8] and n-butyllithium [9], brought about unexpected ring-opening and substitution reactions with these epoxides (Scheme 3). The ring opening effected by $LiAlH_4$ (XII) was especially puzzling, since it was directly opposite that induced by electrophiles like HCl [8] and $MeAlCl_2$ [2] (XV). Furthermore, the profound differences in the type of substitution caused by phenyllithium (XIII) or by n-butyllithium (XIV) were difficult to comprehend. But if these unusual reactions are reconsidered in terms of initial nucleophilic attack on the silicon of X, some helpful insight is gained. Because of electron release by the pentacoordinate silicon anion, in the transition state of ring

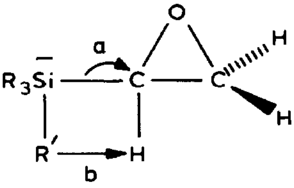


Scheme 3

opening (XVI), intermediate XI ($R' = H$) should aid heterolysis of the epoxide bond as hydride ion shifts from silicon to carbon (XVI).



(XVI)



(XVII)

With organolithium reagents, intermediate XI ($R' = Ph$ or n-Bu) could simply heterolyze at bond a in XVII for the case of phenyllithium or the more basic n-butyl anion could abstract a proton (interaction b). Such a shift of the n-butyl anion from silicon to the epoxide proton is analogous to the shift of the hydride from silicon to the positively polarized carbon in XVI.

From the foregoing findings and the comprehensive investigations of the Corriu group [10], it is evident that pentacoordinate silicon anions are destined to play a major role in mechanistic and synthetic organosilicon chemistry.

Acknowledgments. This research was supported by Grant CHE 8714911 from the National Science Foundation.

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