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MECHANISM OF NUCLEOPHILIC SUBSTITUTION AT SILICON: KINETIC EVIDENCE ON THE SLOW FORMATION OF A PENTA-COORDINATE SILICON INTERMEDIATE

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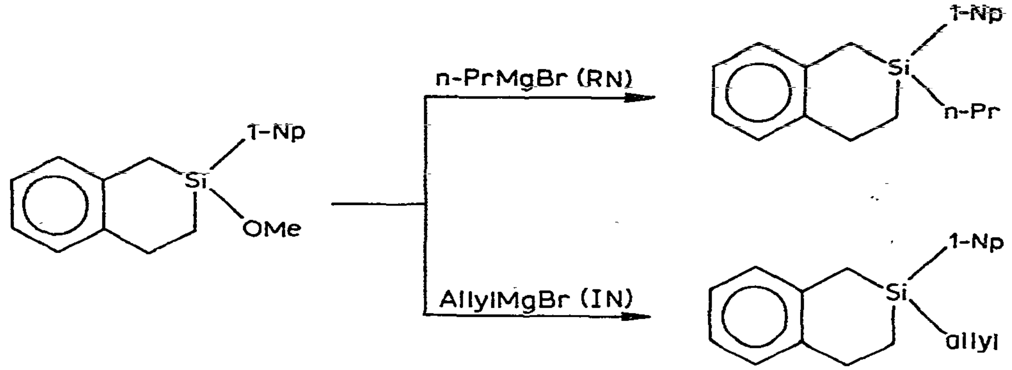
Summary

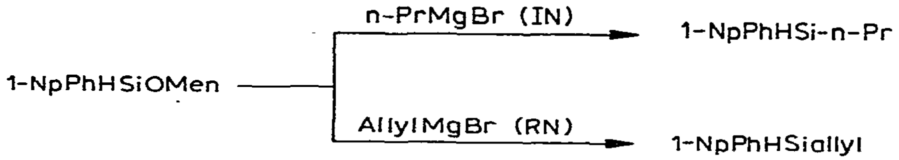
Kinetic studies of various coupling reactions between silicon derivatives (Si—F, Si—Cl, Si—OMe, Si—H) and organometallic reagents (RMgX, RLi) were performed for systems involving retention and inversion of configuration. The results show that for both stereochemical courses, the rupture of the Si—X bond is not the rate determining step. Results are in good agreement with the rate determining formation of a pentacoordinate silicon intermediate.

A stereochemical study of substitution reactions of mono-functional organosilanes R_3SiX (X = F, Cl, OMe, H) with carbon nucleophiles (RMgX, RLi) has shown the reactions to be stereospecific [1-4]. The principal factors influencing the reaction stereochemistry are: (1) The electronic structure of the organometallic reagent. (2) The type of leaving group. (3) The organosilane structure.

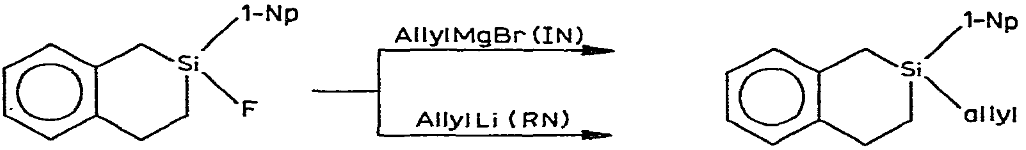
We observed in general that "hard" reactants react with retention while "soft" compounds give inversion at the silicon atom. The idea of soft and hard reactants [5] was used by Anh et al. to explain 1,2 or 1,4 addition of organometallic reagents to α,β unsaturated carbonyl derivatives [6]. They showed that the hard reactants add 1,2 and the soft add 1,4. Carbon nucleophiles are useful for this type of study because the electronic structure can be widely varied while keeping the same atom as reaction center.

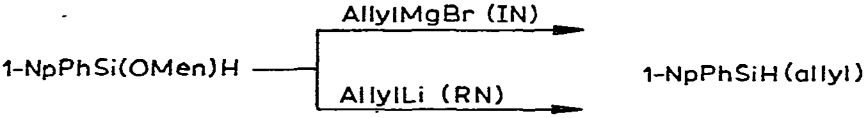
The electronic structure of the nucleophile varies with the organic group, the metal, and the nature of the solvent. The influence of the organic group is illustrated by the different stereochemistries observed for n-propylmagnesium bromide and allylmagnesium bromide. The harder of the two (n-PrMgBr) reacts with retention (RN) while the softer (allylMgBr) reacts with inversion (IN) [3a,3b,4c].



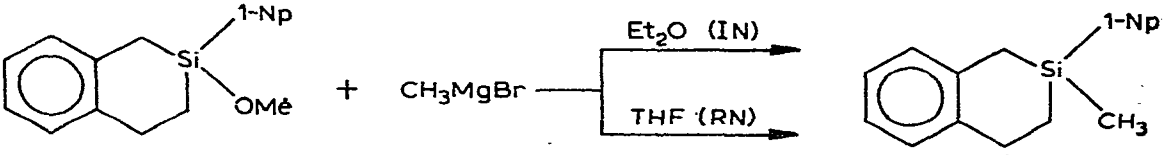


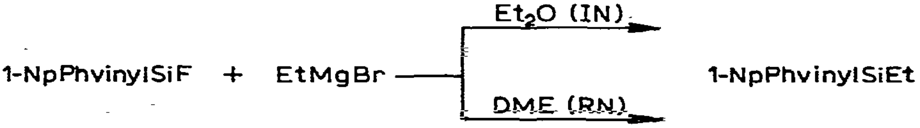
Replacement of magnesium by the harder metal lithium gives a greater degree of retention in the reaction; for example:





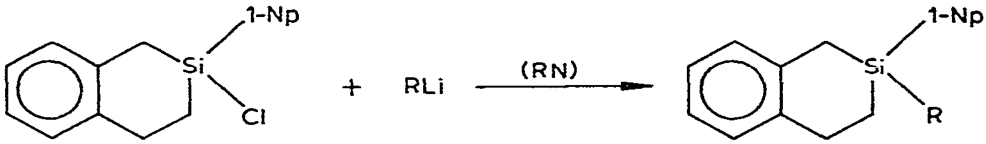
The reaction stereochemistry can be changed to retention by using a solvent more basic than ether, such as THF or DME. The hardness of the nucleophile is then increased by solvation of the metal. This is illustrated in the following examples:





The structure of the organosilicon compound also influences the stereochemistry; thus a cyclic structure changes the stereochemistry to retention of configuration, e.g.:

$$\text{1-NpPhMeSiCl} + \text{RLi} \xrightarrow{\text{(IN)}} \text{1-NpPhMeSiR} \qquad [8]$$



[4b]

(R = saturated aliphatic group)

The tendency for retention is accentuated further with 1-phenyl-1-chlorosilaacenaphtene. Thus retention is found in basic hydrolysis to give the silanol and in the $LiAlH_4$ reduction to give the silane [9].

The nature of the group replaced is also important. Good leaving groups (Br, Cl, F, SR) are replaced with inversion and bad leaving groups (OMe, H) with retention of configuration [1,10]. This result cannot be correlated with any physical properties of the group such as the polarisability of the Si—X bond [11] or the p*K*a of the conjugate acid [12]. It is however possible to give an empirical order for the ease of substitution: $Br > Cl \geqslant F > OMe > H$. This order applies only for carbon nucleophiles, and other types of nucleophile probably give different orders.

Stereochemical studies of nucleophilic substitution at the silicon atom allows determination of the factors influencing the reaction mechanism. In this paper, which follows two preliminary communications [13,14], we outline the mechanism and show that the reaction proceeds through an intermediate.

A priori, one can conceive a number of energy diagrams for the substitution reactions (see Fig. 1A-C).

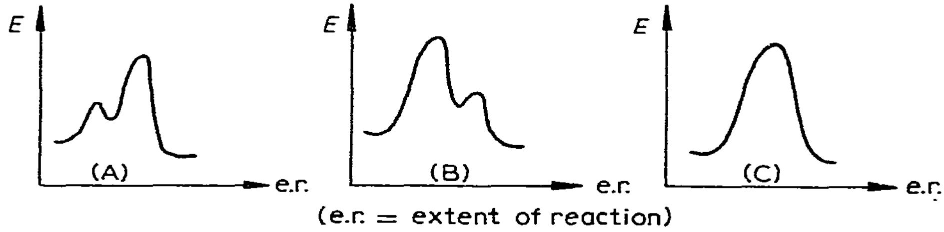


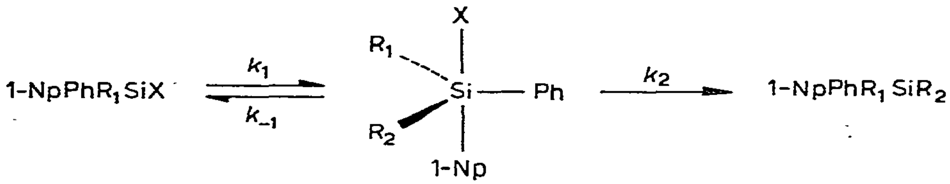
Fig. 1. Energy diagrams.

A: Rapid formation of an intermediate complex followed by slow cleavage of the Si—X bond to give the products.

B: Formation of an intermediate in a slow step, then rapid breakdown to the products.

C: Synchronous bond forming and bond-breaking, involving a single transition state.

The possibility A, presented in the equation below, can be eliminated.

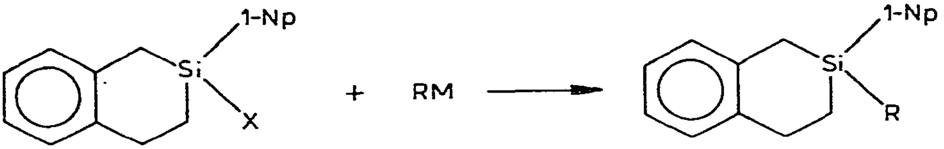


This is because in such a process the intermediate would return to the reactants (k_{-1}) by rupture of a Si—C bond. Thus, one would expect a mixture of products since Si—R^1, Si—R^2, Si—Ph or Si—1-Np could be cleaved. The only product observed is that of normal substitution, and so the mechanism does not involve a rapid pre-equilibrium.

In order to determine the reaction energy profile we studied the rate of reactions between various organometallic reagents and organosilanes which give either retention or inversion of configuration at the silicon atom. We compared the rates for two organosilanes with the same organometallic reagent, which was taken in large excess to give pseudo first order conditions. The progress of reaction was followed by GLC.

The results for reactions giving retention are summarised in Tables 1 and 2, and those for inversion in Tables 3-5. We observe two types of behaviour, rate constants being related by a factor of one or a factor $>10^3$. The former are in the majority and apply to both retention and inversion while the latter are only found for F and OMe, in reactions giving inversion of configuration. Factors approximating to 1 show that the slow step does not involve Si—X bond cleavage. Thus the energy scheme C (Fig. 1) involving a single transition state can be eliminated. In fact this mechanism involves a stretching of the Si—X bond and one should observe an influence of the substituent on the reaction rate. This is not found. In contrast the small influence of the leaving group agrees with the

TABLE 1



(X = OMe, F)

RM	Solvent	k_F/k_{OMe}
EtMgBr	Et_2O	1.5-2.5
PhMgBr	Et_2O	2-3
MeMgBr	THF	1-1.5
AllylLi	Et_2O	4-5
PhMgBr	Et_2O	k_F/k_{Cl} 20-40

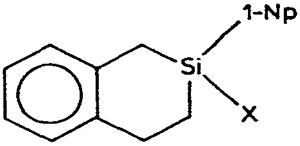
TABLE 2

1-NpPhEtSiX

X		RM	Solvent	k_α/k_β
α	β			
OMe	H	PhLi[a]	Et_2O	1.5-2
OMe	H	n-BuLi	Et_2O	5-6
H	D	PhLi[a]	Et_2O	1.3
H	D	n-BuLi	Et_2O	1
F	OMe	n-BuLi	Et_2O	50

[a] We assume that PhLi and *p*-MePhLi give the same stereochemistry.

TABLE 3



X	RMgX	Solvent	k_F/k_{Cl}
F, Cl	CH_3MgBr	Et_2O	1
F, Cl	AllylMgBr	Et_2O	0.9
F, Cl	CrotylMgBr	Et_2O	1
F, Cl	$PhCH_2MgCl$	Et_2O	1.6
X	RMgX	Solvent	k_F/k_{OMe}
F, OMe	AllylMgBr	Et_2O	$>10^5$
F, OMe	$PhCH_2MgCl$	Et_2O	$2 \times 10^3 < k_F/k_{OMe} < 5 \times 10^3$

TABLE 4

1-NpPhvinylSiX

X	RMgX	Solvent	k_F/k_{Cl}
F, Cl	CH_3MgBr	Et_2O	0.32
F, Cl	AllylMgBr	Et_2O	0.5
F, Cl	$PhCH_2MgCl$	Et_2O	0.7
F, Cl	CrotylMgBr	Et_2O	0.5
F, Cl	n-PropylMgBr	Et_2O	1.7

TABLE 5

1-NpPhEtSiX

X	RMgX	Solvent	k_F/k_{OMe}
F, OMe	AllylLi	Et_2O	$>10^3$

slow formation of a pentacoordinated intermediate. The very small deuterium isotope effect confirms this proposal.

The factor $k_F/k_{OMe} > 1000$ applies only to configurational inversion, and the two groups react at similar speeds when replaced with retention, even using α-unsaturated organometallic reagents such as allyllithium (see Table 1). One can explain these results by assuming the inversion of configuration to be under "frontier control" [14,15]; there is an orbital interaction in the transition state between the carbanion and the silicon d_z2 orbital. This interaction is much more important for a good leaving group. Thus configurational inversion for the poor leaving group Si—OR is difficult because the reactant is susceptible to charge effects but not to orbital interactions; it is therefore not surprising to find a slower rate compared to the fluorosilanes.

We conclude that nucleophilic substitution by carbon nucleophiles at a silicon atom occurs with formation of a pentacoordinated intermediate in a slow step.

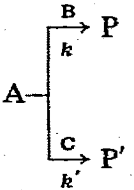
Experimental

The preparation of reactants and the analytical method have been previously described [16]. Allyllithium was prepared by cleavage of phenylallylether [17] and the concentration of all the organometallic reagents was measured by iodometric titration as described by Jolibois [18].

The derivatives of 1-NpPhEtSiH [19] and 1-NpPhEtSiD [20] were available in our laboratory.

In certain cases instead of employing an internal standard we based analyses on the peak width × peak height values. Such values are used in place of the usual integrated areas in the case of sharp, symmetrical peaks [21]. This method is particularly useful when a peak, either of reactant or product, is very small in relation to the other, as is the case both for the slow and fast reactions.

For concurrent reactions the following equations can be written:



$$V = k|A|^n \times |B|^m$$

$$V' = k'|A|^{n'} \times |C|^{m'}$$

If the reaction order for the reactant is the same ($n = n'$) and if the order for B and C equals 1 ($m = m' = 1$) then the relationship between the rate constants is given by the following equation:

$$\frac{k}{k'} = \frac{\log \dfrac{b}{b-y}}{\log \dfrac{c}{c-z}}$$

The factor k/k' should be independent of time and of the initial concentrations of B and C. We verified this by determining the relationship k/k' for three different initial concentrations.

We have carried out concurrent reactions for the leaving groups F and OMe and also two kinetic studies under identical conditions for the pairs SiH, SiD and SiF, SiCl.

Results for reactions giving retention of configuration

(I) 2-α-NAPHTYL-2-SILA-1,3,4-TRIHYDRONAPHTALENE

X = F, OMe; EtMgBr/Et_2O; T = 25°C; V_t = 60 ml
[EtMgBr] = 1.1 mol l^{-1}; [F] + [OMe] = 0.11 mol l^{-1}
[F] = [OMe]: k_F/k_{OMe} = 2.0-3.0
[F] = 2[OMe]: k_F/k_{OMe} = 1.5-2.5
2[F] = [OMe]: k_F/k_{OMe} = 1.5-2.5

X = F, OMe; PhMgBr/Et_2O; T = 25°C; V_t = 48 ml
[PhMgBr] = 0.6 mol l^{-1}; [F] + [OMe] = 0.06 mol l^{-1}
[F] = [OMe]: k_F/k_{OMe} = 1.8-2.2
2[F] = [OMe]: k_F/k_{OMe} = 1.8-2.0
[F] = 2[OMe]: k_F/k_{OMe} = 2.0-2.6

X = F, OMe; CH_3MgBr/THF; T = 25°C; V_t = 48 ml
[CH_3MgBr] = 0.6 mol l^{-1}; [F] + [OMe] = 0.06 mol l^{-1}
[F] = [OMe]: k_F/k_{OMe} = 1.0-1.1
[F] = 2[OMe]: k_F/k_{OMe} = 1.2-1.5
2[F] = [OMe]: k_F/k_{OMe} = 1.0-1.2

X = F, OMe; allylLi/Et_2O; T = —15°C

We carried out the reactions for each compound and then compared the rate constants. We confirmed the results by competitive rate measurements.

[allylLi] = 4 × 10^{-2} mol l^{-1}; [Si—X] = 4 × 10^{-3} mol l^{-1}; V_t = 50 ml

$$\left.\begin{array}{l}\text{X = F: very rapid reaction, 1 aliquot after 30 sec, } k = 2.2\ \text{min}^{-1}\\ \text{X = OMe: rapid reaction, 1 aliquot 1 min, } k = 0.55\ \text{min}^{-1}\end{array}\right\} k_F/k_{OMe} = 4$$

Concurrent kinetics

[allylLi] = 4 × 10^{-2} mol l^{-1}; [Si—F] = [Si—OMe] = 2 × 10^{-3} mol l^{-1}; V_t = 100 ml.

1 aliquot 30 sec: k_F/k_{OMe} = 3.8

X = F, Cl; PhMgBr/Et_2O; T = 25°C, V_t = 50 ml
[PhMgBr] = 0.4 mol l^{-1}; [Si—X] = 2 × 10^{-2} mol l^{-1}

$$\left.\begin{array}{l}\text{X = F, } k = 2.4 \times 10^{-3}\ \text{min}^{-1}\\ \text{X = Cl, } k = 6.1 \times 10^{-5}\ \text{min}^{-1}\end{array}\right\} k_F/k_{Cl} = 37$$

(II) 1-NAPHTYL PHENYLETHYLSILANE

X = OMe, F; n-BuLi/Et$_2$*O; T = —15°C; V*$_t$ *= 80 ml*
[n-BuLi] = 2.5 × 10^{-2} mol l^{-1}; [Si—F] = 1.6 × 10^{-3} mol l^{-1}; [Si—OMe] = 8.75 × 10^{-4} mol l^{-1}.
$k_F/k_{OMe} = 46$

X = OMe, H; n-BuLi/Et$_2$*O; T = 0°C; V*$_t$ *= 120 ml*
[n-BuLi] = 5.3 × 10^{-2} mol l^{-1}; [Si—OMe] = [Si—H] = 2.6 × 10^{-3} mol l^{-1}
$k_{OMe}/k_H = 5\text{-}6$

X = H, D; n-BuLi/Et$_2$*O; T = 0°C; V*$_t$ *= 108 ml*
[n-BuLi] = 5 × 10^{-2} mol l^{-1}; [Si—X] = 5 × 10^{-3} mol l^{-1}.

$$\left.\begin{array}{l} X = H\text{: } k = 0.015\ \text{min}^{-1} \\ X = D\text{: } k = 0.014\ \text{min}^{-1} \end{array}\right\} \rightarrow k_H/k_D = 1$$

X = H, D; PhLi/Et$_2$*O; T = 0°C; V*$_t$ *= 120 ml*
[PhLi] = 5 × 10^{-2} mol l^{-1}; [Si—X] = 5 × 10^{-3} mol l^{-1}

$$\left.\begin{array}{l} X = H\text{: } k = 0.111\ \text{min}^{-1} \\ X = D\text{: } k = 0.086\ \text{min}^{-1} \end{array}\right\} \rightarrow k_H/k_D = 1.3$$

X = OMe, H; PhLi/Et$_2$*O; T = 0°C; V*$_t$ *= 40 ml*
[PhLi] = 5.25 × 10^{-2} mol l^{-1}; [OMe] + [H] = 5.25 × 10^{-3} mol l^{-1}
[H] = [OMe]: $k_{OMe}/k_H = 1.5\text{-}2$
[OMe] = 2[H]: $k_{OMe}/k_H = 1.5\text{-}2$

Results for reactions giving inversion of configuration

(I) 2-α-NAPHTYL-2-SILA-1,3,4-TRIHYDRONAPHTALENE

CH$_3$*MgBr/Et*$_2$*O; T = 25°C; V*$_t$ *= 50 ml*
(a) [CH$_3$MgBr] = 0.4 mol l^{-1}; [Si—X] = 2.0 × 10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{: } k = 3.4 \times 10^{-2}\ \text{min}^{-1} \\ X = Cl\text{: } k = 3.8 \times 10^{-2}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.9$$

(b) [CH$_3$MgBr] = 0.4 mol l^{-1}; [Si—X] = 1 × 10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{: } k = 3.7 \times 10^{-2}\ \text{min}^{-1} \\ X = Cl\text{: } k = 3.5 \times 10^{-2}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 1$$

AllylMgBr/Et$_2$*O; T = 25°C; V*$_t$ *= 50 ml*
(a) [allylMgBr] = 0.1 mol l^{-1}; [Si—X] = 1.0 × 10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{: } k = 0.46\ \text{min}^{-1} \\ X = Cl\text{: } k = 0.53\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.9$$

(b) [allylMgBr] = 0.1 mol l^{-1}; [Si—X] = 5.0 × 10^{-3} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{: } k = 0.43\ \text{min}^{-1} \\ X = Cl\text{: } k = 0.46\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.9$$

(c) [allylMgBr] = 0.1 mol l^{-1}; [Si—OMe] = 1.0 × 10^{-2} mol l^{-1}
No reaction after 14 h 30 min. 1% of Si—allyl product is found by the analysis used. Assuming 1% reaction gives: $k = 5.0 \times 10^{-6}\ \text{min}^{-1} \rightarrow k_F/k_{OMe} \geqslant 10^5$

CrotylMgBr/Et$_2$O; $T = 25$°C; $V_t = 50$ ml

(a) [crotylMgBr] = 0.2 mol l^{-1}; [Si—X] = 2.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 3.3 \times 10^{-2}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 3.1 \times 10^{-2}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 1$$

(b) [crotylMgBr] = 0.2 mol l^{-1}; [Si—X] = 1.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 2.4 \times 10^{-2}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 2.5 \times 10^{-2}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 1$$

PhCH$_2$MgCl/Et$_2$O: $T = 25$°C; $V_t = 50$ ml

(a) [PhCH$_2$MgCl] = 0.4 mol l^{-1}; [Si—X] = 2.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 5.4 \times 10^{-3}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 3.2 \times 10^{-3}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 1.7$$

X = OMe: very slow reaction, $k = 1\text{-}2 \times 10^{-6}$ min^{-1} → $2 \times 10^3 \leqslant k_F/k_{OMe} \leqslant 5 \times 10^3$

(b) [PhCH$_2$MgCl] = 0.4 mol l^{-1}; [Si—X] = 1.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 5.0 \times 10^{-3}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 3.2 \times 10^{-3}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 1.6$$

(II) 1-NpPhVinylSiX

CH$_3$MgBr/Et$_2$O; $T = 25$°C; $V_t = 50$ ml

(a) [MeMgBr] = 0.4 mol l^{-1}; [Si—X] = 2.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 6.7 \times 10^{-3}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 2.3 \times 10^{-2}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.3$$

(b) [MeMgBr] = 0.4 mol l^{-1}; [Si—X] = 1.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 7.8 \times 10^{-3}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 2.4 \times 10^{-2}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.3$$

AllylMgBr/Et$_2$O; $T = 25$°C; $V_t = 50$ ml

(a) [allylMgBr] = 0.2 mol l^{-1}; [Si—X] = 1.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 0.12\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 0.24\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.5$$

(b) [allylMgBr] = 0.2 mol l^{-1}; [Si—X] = 2.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 0.12\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 0.22\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.5$$

CrotylMgBr/Et$_2$O; $T = 25$°C; $V_t = 50$ ml

(a) [crotylMgBr] = 0.2 mol l^{-1}; [Si—X] = 2.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 4.4 \times 10^{-3}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 9.4 \times 10^{-3}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.5$$

(b) [crotylMgBr] = 0.2 mol l^{-1}; [Si—X] = 1.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 4.1 \times 10^{-3}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 8.8 \times 10^{-3}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.5$$

PhCH$_2$MgCl/Et$_2$O; $T = 25$°C; $V_t = 50$ ml

(a) [PhCH$_2$MgCl] = 0.4 mol l^{-1}; [Si—X] = 2.0×10^{-2} mol l^{-1}

$$\left.\begin{array}{l} X = F\text{:}\ \ k = 5.5 \times 10^{-4}\ \text{min}^{-1} \\ X = Cl\text{:}\ k = 7.4 \times 10^{-4}\ \text{min}^{-1} \end{array}\right\} \rightarrow k_F/k_{Cl} = 0.7$$

(b) $[\mathrm{PhCH_2MgCl}] = 0.4\ \mathrm{mol\ l^{-1}}$; $[\mathrm{Si{-}X}] = 1.0 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$

$$\left.\begin{array}{l}\mathrm{X = F:}\ k = 7.0 \times 10^{-4}\ \mathrm{min^{-1}}\\ \mathrm{X = Cl:}\ k = 9.7 \times 10^{-4}\ \mathrm{min^{-1}}\end{array}\right\} \rightarrow k_\mathrm{F}/k_\mathrm{Cl} = 0.7$$

n-PropylMgBr/Et$_2$O; $T = 25°C$; $V_t = 50$ ml

$[\text{n-propylMgBr}] = 0.4\ \mathrm{mol\ l^{-1}}$; $[\mathrm{Si{-}X}] = 2.0 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$

$$\left.\begin{array}{l}\mathrm{X = F:}\ k = 1.7 \times 10^{-4}\ \mathrm{min^{-1}}\\ \mathrm{X = Cl:}\ k = 1.0 \times 10^{-4}\ \mathrm{min^{-1}}\end{array}\right\} \rightarrow k_\mathrm{F}/k_\mathrm{Cl} = 1.7$$

(III) 1-NpPhEtSiX

AllylLi/Et$_2$O; $T = -15°C$; $V_t = 150$ ml

(a) $[\mathrm{allylLi}] = 3.6 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$; $[\mathrm{Si{-}X}] = 3.6 \times 10^{-3}\ \mathrm{mol\ l^{-1}}$

$$\left.\begin{array}{l}\text{X = F: the reaction is virtually completed in 1 min. By approximation}\\ \text{one assumes 98\% reaction giving: } k = 1.7\ \mathrm{min^{-1}}\\ \mathrm{X = OMe;}\ k = 6.0 \times 10^{-4}\ \mathrm{min^{-1}}\end{array}\right\} \rightarrow k_\mathrm{F}/k_\mathrm{OMe} \geqslant 10^3$$

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