

# Quantitative substituent effects in the Grignard reaction with silanes

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## Abstract

Kinetics of reactions of ethyl- and phenylmagnesium chlorides with chlorosilanes,  $\text{RMeSiCl}_2$ , were investigated in diethyl ether under pseudo-first order conditions with a great excess of the Grignard reagent. Rate constants for alkyl substituted silanes correlate well with  $E_s(\text{Si})$  steric parameters. A good linear correlation of rate data for substituted phenyl derivatives with  $\sigma^0$  inductive constants together with correlations of the literature data rule out the resonance effect of substituents at least in nucleophilic displacement reactions at the silicon center. An attempt to calculate the steric constants for polar substituents was made. It appeared that the inductive constants  $\sigma^*$  derived from the carbon chemistry are not applicable to the silicon chemistry. New scales of parameters for description of polar and steric effects in the organosilicon chemistry need to be created.

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## 1. Introduction

Grignard chemistry is a versatile method for the production of organosilanes [1]. However, quantitative aspects of the reaction have been little investigated. A small number of kinetic studies of the Grignard reaction with silanes have been published [2–10] and no attempts to ascertain the structure-reactivity relationships for the reaction were made until our recent work [10].

We have launched an investigation into quantitative aspects of the reactivity in the Grignard reaction with silanes [6–10]. The main attention is focused on the structure-reactivity relationships for the reaction. In parallel to this we set out to revise the current approach to reactivity problems of organosilicon compounds [11]. We confine ourselves to nucleophilic substitutions at silicon. This is an area of both commercial and academic interest. The commercial interest

lies largely in the hydrolysis reactions of silicon compounds to produce silicones but not less in the reactions for production of a wide range of monomeric organosilicon compounds.

The Grignard reaction with silanes is a particular instance of nucleophilic displacements at the silicon center since a Grignard reagent is one of the strongest nucleophiles applicable in common coupling reactions. In our recent work [10] the reaction between methylvinyl dichlorosilane and a series of alkylmagnesium chlorides proved to be a good test of applicability for steric constants  $E_s(\text{Si})$  of alkyl substituents [11], further allowing calculation of missing constants.

In this work we exploit the Grignard reaction with chlorosilanes for testing the significance of the resonance effect of substituents, using correlation of kinetic data for substituted phenylsilanes with  $\sigma^0$  constants. Further we assess the applicability of polar substituent constants  $\sigma^*$  derived from reactions at carbon centers [12,13] to silicon chemistry. Available in the literature data for nucleophilic displacement reactions at the silicon center will be involved in the discussion.

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## 2. Experimental

### 2.1. Materials

Commercial reagents were carefully purified. Reagent grade magnesium shavings 99.8% Mg were purchased from Fluka. The reagents and solutions were operated under dry argon, and transferred by use of cannulas or syringes.

Methyltrichlorosilane, dimethyldichlorosilane, methylphenyl-, and methylvinyl-dichloro-silanes were donated by Dow Corning Corp. Methylchloromethyldichlorosilane was purchased from Aldrich. Methylethyl-, methyl-*n*-butyl-, methylisobutyl-, methyl-*sec*-butyl-, and methylisopropyl-dichlorosilanes were prepared from corresponding alkylmagnesium chlorides and methyltrichlorosilane. Methyl-4-methoxy-, methyl-3-methoxy-, methyl-4-chloro-, methyl-3-chloro-, and methyl-4-methylphenyldichlorosilanes were synthesized from corresponding substituted phenylmagnesium bromides and methyltrichlorosilane.

Alkylmagnesium chlorides and substituted phenylmagnesium bromides were prepared in diethyl ether by conventional methods [14] from corresponding commercial halides. Chlorobenzene does not react with magnesium even in boiling diethyl ether, therefore ethereal solutions of phenylmagnesium chloride were prepared according to Gilman and Brown [15] in an autoclave at 130 °C.

### 2.2. Kinetic measurements

Kinetic experiments were carried out in a 100 ml two-necked flask equipped with a thermostat, sealed with septa, capped with an inert gas balloon, and equipped with a magnetic stirrer and a thermometer. A 0.5 M solution of the Grignard reagent (usually 50 mL) was transferred into the flask and when the temperature of system was equilibrated at 20 °C a calculated amount of the silane (providing a 15–20-fold molar excess of the Grignard reagent) was added.

At appropriate time points 1 mL aliquots were taken from the homogeneous solution through a septum with a syringe and quenched with a cool dry ethanol/pyridine mixture. The solution was analyzed for the alkoxy-silanes formed in quenching, using a Varian 3700 gas chromatograph with a flame ionization detector.

The first order rate constants were calculated using the peak areas for the initial and product silanes corrected for the difference in sensitivity of the flame detector. The reaction was usually monitored during the first or two half-lives. The coupling followed excellent first order kinetics. Virtually only primary products were detected by the end of the monitoring time. Experiments were carried out in duplicate or triplicate, the rate constants were reproducible within an accuracy of  $\pm 5\%$  or better.

The fast reactions were investigated in a thermostatic flask equipped with a stirrer and a thermistor. The thermistor was connected through a bridge circuit to a PC. A 15 mL sample of the Grignard reagent was transferred into

the flask and when the system was equilibrated at 20 °C a calculated amount of the silane (about 0.05 mL, providing about 20-fold excess of the Grignard reagent) was injected into the flask. The temperature change of the reaction solution was recorded as a plot of temperature vs. time. Use of a differential method for calculation of rate constants [8] eliminated the minor contribution of heat exchange with the reaction vessel. The measurements were carried out in duplicate or triplicate the rate constants being reproducible within an accuracy better than  $\pm 5\%$ .

## 3. Results and discussion

### 3.1. Rate constants

Kinetics of reactions of ethyl- and phenylmagnesium chlorides with chlorosilanes were investigated under pseudo-first order conditions with a great excess of Grignard reagent. The rate measurements were carried out with 0.5 M solutions of Grignard reagents in diethyl ether at 20 °C. The first order rate constants are collected in Table 1.

Phenylmagnesium chloride reacts faster under these conditions, in line with its nucleophilicity superior to ethylmagnesium chloride. A noticeable rate accelerating effect of polar substituents in silanes is also obvious. Steric effects of alkyl substituents will be discussed in the next section.

### 3.2. Steric effects of alkyl substituents

In our previous paper [11] available in the literature quantitative data concerning the reactivity of organosilicon compounds were collected and the rate data for

Table 1

First order rate constants for Grignard reactions with chlorosilanes, and corresponding substituent constants. Concentration of Grignard reagents 0.5 M

R in RMeSiCl <sub>2</sub>	$k \times 10^4 \text{ s}^{-1}$		$E_s(\text{Si})^a$	$\sigma^0$ [13]	$\sigma^*$ [13] <sup>b</sup>
	EtMgCl	PhMgCl			
Me	2.00	10.33	0	–	0
Et	–	7.58	–0.149	–	0
<i>n</i> Bu	0.618	–	–0.225	–	0
<i>i</i> Bu	0.467	5.72	–0.405	–	0
<i>i</i> Pr	0.157	4.17	–0.556	–	0
<i>s</i> Bu	0.123	–	–0.67	–	0
Vinyl	8.83 <sup>c</sup>	7.00 <sup>c</sup>	–	–	0.40
ClCH <sub>2</sub>	18.3 <sup>c</sup>	41.7 <sup>c</sup>	–	–	1.05
Cl	–	61.6 <sup>c</sup>	–	–	2.9
Ph	4.50	4.25	–	0	0.60
4-MePh	–	3.40	–	–0.15	–
4-MeOPh	–	3.50	–	–0.16	–
3-MeOPh	–	6.00	–	0.06	–
4-ClPh	–	11.3	–	0.27	–
3-ClPh	–	13.5	–	0.37	0

<sup>a</sup> Steric constants by Cartledge [11,16].

<sup>b</sup> The  $\sigma^*$ -values for alkyl groups are taken to be zero [11,17,18].

<sup>c</sup> Thermographic method (See Section 2).

compounds with alkyl substituents were subjected to a correlation analysis. Four sets of steric constants for alkyl substituents of silicon compounds were considered. Some missing values were calculated and several corrections were made. It appeared that the improved sets of parameters were practically equivalent. Chronologically, the first among them was the  $E_s(\text{Si})$  scale by Cartledge [16] and subsequently we use this scale of parameters. Results of our analysis corroborated former suppositions that alkyl substituents contribute to the reactivity of silicon compounds exclusively with their steric effects, and that steric effects in silicon compounds are additive. The kinetic data of this work (Table 1) were allowed to a correlation analysis with the reduced Taft equation matched for silicon compounds (Eq. (1))

$$\log k = \log k_o + \delta E_s(\text{Si}), \quad (1)$$

where  $\delta$  is the susceptibility factor for steric effects.

From Fig. 1 it can be seen that rate constants for reactions of ethylmagnesium and phenylmagnesium chlorides with alkyl substituted chlorosilanes correlate well with  $E_s(\text{Si})$  parameters. The regression coefficients are  $1.81 \pm 0.18$  and  $0.64 \pm 0.11$ , respectively with corresponding correlation coefficients 0.985 and 0.970. So far only one reaction series can be brought for comparison, viz. the reaction between alkylmagnesium chlorides and methylvinylchlorosilane [10] with  $\delta = 1.04 \pm 0.03$  ( $R = 0.998$ ).

The observed large dissimilarity of steric requirements between the reaction series of present work is somewhat unexpected. Although, conformations of a transition state sterically favorable for the planar phenyl moiety may be conceivable, such a great difference hardly can be explained merely by structural diversities between ethyl and phenyl groups. Provisionally, we tend to assign the extremely small steric effect in the reaction with phenylmagnesium chloride to a rather early transition state of the reaction. This assumption is consistent with the considerable nucleophilicity of the reagent and does not contradict a remark-

able charge development in the transition state manifested by strong substituent effects of polar groups (cf. the data in Table 1). As a whole, these few susceptibility parameters found from Grignard reactions fit the range of available  $\delta$  values for the reactions of organosilicon compounds [11].

### 3.3. The resonance effect of substituents

To correlate structural effects with chemical or physical properties it is necessary to differentiate between steric and electronic (polar) effects in relation to a property. According to current principles [19] the polar effect can be decomposed into inductive and resonance components.

While in traditional organic chemistry this issue has a long history and protocols for quantitative separation of the effects are available [12,13], the participation of d-orbitals in the structure formation of silicon compounds has been a subject of continuing debates [20–22]. Theoretical studies of the  $S_N2(\text{Si})$  reaction and pentacoordinate silicon intermediates or transition states show that d-orbitals are unlikely to have any significant involvement in the bonding in such species [21,22]. Streitwieser et al. [23] found that bonds between Si and H, C, O and F are extensively polarized with significant charge transfer. As a result Si–O and Si–F bonds are dominated by ionic interactions, and Si–H and Si–C bonds have an important ionic character. Thus a resonance interaction requiring an overlap of p- and/or d-orbitals should be considerably hindered. As an unambiguous experimental test of the theoretical considerations, correlation of kinetic data for substituted phenylsilanes with  $\sigma^0$  constants was implicated by Chvalovský et al. [24]. By definition [13] the  $\sigma^0$  constants measure the inductive effect of substituted phenyl groups at the reaction center. A linear correlation with  $\sigma^0$  constants thus rules out the conjugation of substituents with the reaction center.

In Fig. 2 the correlation of rate data for the reaction between phenylmagnesium chloride and substituted methylphenyldichlorosilanes (from Table 1) with  $\sigma^0$  constants

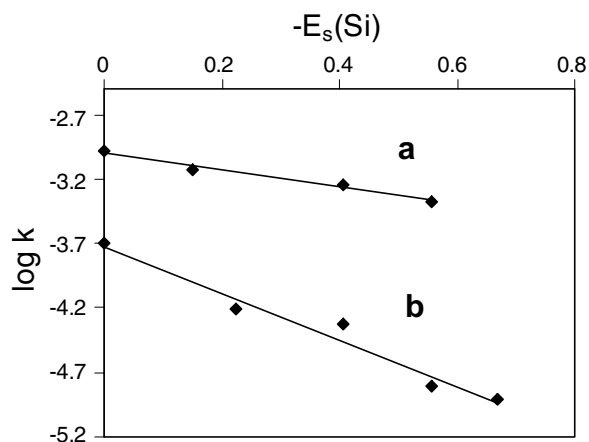


Fig. 1. Correlation of rate data for the reactions between Grignard reagents and alkylmethylchlorosilanes with steric constants  $E_s(\text{Si})$ . (a) phenylmagnesium chloride and (b) ethylmagnesium chloride.

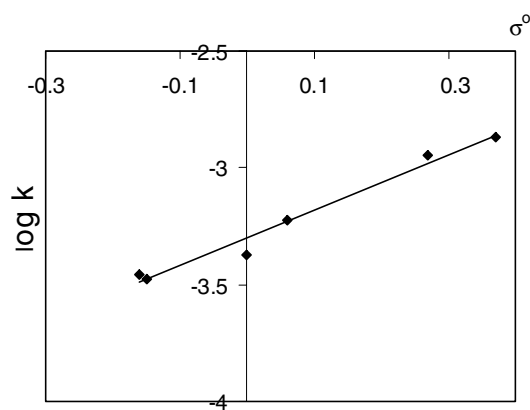


Fig. 2. Correlation of rate data for the reaction between phenylmagnesium chloride and methylphenyldichlorosilanes substituted in phenyl group with inductive  $\sigma^0$  constants.

is shown. The regression coefficient  $\rho^0 = 1.12 \pm 0.10$  ( $R = 0.985$ ) was found. The good linear correlation indicates that the resonance effect of substituents is insignificant in the reaction if present at all. Also correlation data for a variety of reactions in Table 2 provide a good evidence of insignificance of the resonance effect at least in nucleophilic displacement reactions at the silicon center. Because of scarcity of kinetic data we included in Table 2 also correlations consisting of just three compounds, however, the correlations were good to excellent.

### 3.4. Calculation of steric constants for polar substituents

Effects of aliphatic substituents on the reactivity of organosilicon compounds have been described with the Taft equation (Eq. (2)) [20,30], where the two last terms express the independent contributions from inductive and steric effects, respectively [12,13].

$$\log k = \log k_0 + \rho^* \sigma^* + \delta E_s. \quad (2)$$

The substituent constants in Eq. (2) have been defined in organic reactions. At present it is understood that the steric parameters derived from reactions of organic carbonyl compounds are not suitable for description of steric effects in reactions taking place at Si atoms [10,11,16,25]. For alkyl substituents appropriate scales of parameters, e.g. that of  $E_s(\text{Si})$  constants, have been developed [11,16]. However, the scales of steric constants still need to be expanded to cover also polar substituents.

If one accepts the  $\sigma^*$  constants by Taft [12,13] for polar substituents, and the  $\sigma^0$  constants for substituted phenyl groups, a simple procedure can be envisaged. Within a reaction series susceptibility to the steric effect can be determined from a variety of alkyl substituents. A correlation for substituted phenyl groups with  $\sigma^0$  constants will give  $\rho^0$  parameter which can be applied for  $\rho^*$  in Eq. (2) provided  $\sigma^*$  values for phenyl substituents are calculated as

$$\sigma^*(\text{XC}_6\text{H}_4-) = \sigma^0(\text{XC}_6\text{H}_4-) + \sigma^*(\text{C}_6\text{H}_5-).$$

Then, according to Eq. (2), novel steric substituent constants can be calculated from Eq. (3).

$$E_s(\text{Si}) = \frac{\log k - \log k_0 - \rho^* \sigma^*}{\delta}. \quad (3)$$

In Table 3 results of the calculations are collected. The values obtained for  $E_s(\text{Si})$  parameters are unreasonable to senseless. If one does not discard promptly the calculation procedure, one can surmise the incompatibility of Taft's induction constants derived from carbon chemistry with polar effects in silicon compounds. Indeed, a serious doubt has been cast on the  $\sigma^*$  values for phenyl and vinyl groups [24,31]. The authors have estimated for phenyl group  $\sigma^* = 0.06$  from the bromination reaction of organosilicon hydrides instead of  $\sigma^* = 0.60$  for carbon compounds, and suggest that the inductive effect of vinyl group is comparable to or less than that of phenyl group.

Some steric constants  $E_s(\text{Si})$  calculated using different  $\sigma^*$  values are presented in Table 4. Reactions IV, V, and X seem to be the most compatible with each other issuing comparable and seemingly reasonable  $E_s(\text{Si})$  values at  $\sigma^* \leq 0.06$ . For chloromethyl group  $\sigma^* = 0.65$  was estimated iteratively assuming that steric requirements of the group should not much differ from those of ethyl group. Similarly, from reaction X the tabulated value  $\sigma^* = 0.40$  for vinyl group leads to an evidently overvalued  $E_s(\text{Si}) = -0.68$  while  $\sigma^*$  value 0.06 suggested in the literature [24,31] gives a  $E_s(\text{Si})$  value  $-0.09$  which is sufficiently concordant with imaginable dimensions of the vinyl group.

As an inevitable inference from the reasonings above we must admit that the scale of  $\sigma^*$  inductive constants by Taft cannot be applied to silicon chemistry. However, the situation seems to be even more complicated. Examination of Table 3 suggests a conclusion that the data cannot be described by means of a two-parameter equation like Eq. (2). Apparently one more variable needs to be involved to unravel the structure-reactivity relationships in this particular field. An additional evidence of this can be the total failure of correlation of the data for reaction of

Table 2  
Correlation data for nucleophilic displacement reactions at the silicon center

Reaction, Solvent	Induction effect			Steric effect		
	$n^a$	$\rho^0$	$R^b$	$n^a$	$\delta$	$R^b$
I. $\text{RMe}_2\text{SiCl} + \text{Me}_3\text{SiOLi}$ , $\text{Et}_2\text{O}$ [25]	3	$0.73 \pm 0.02$	0.999	7	$1.59 \pm 0.29$	0.924
II. $\text{RMe}_2\text{SiCl} + \text{PhMe}_2\text{SiOLi}$ , $\text{Et}_2\text{O}$ [25]	5	$0.74 \pm 0.09$	0.976	6	$1.31 \pm 0.16$	0.971
III. $\text{RMe}_2\text{SiCl} + \text{Me}_2\text{CHOLi}$ , $\text{Et}_2\text{O}$ [25]	3	$1.11 \pm 0.08$	0.997	7	$1.62 \pm 0.11$	0.988
IV. $\text{RMe}_2\text{SiCl} + \text{H}_2\text{O}$ , diox [26]	3	$1.20 \pm 0.11$	0.996	8	$2.30 \pm 0.11$	0.993
V. $\text{RSiCl}_3 + \text{tBuOLi}$ , $\text{Et}_2\text{O}$ [27]	5	$1.02 \pm 0.08$	0.990	7	$1.61 \pm 0.09$	0.992
VI. $\text{RSiCl}_3$ acetolysis, $\text{Ac}_2\text{O}$ [28]	6	$1.85 \pm 0.16$	0.989	6	$1.59 \pm 0.19$	0.973
VII. $\text{RMe}_2\text{SiCl} + \text{tBuOLi}$ , $\text{Et}_2\text{O}$ [27]	5	$0.83 \pm 0.08$	0.987	–	–	–
VIII. $\text{RMe}_2\text{SiH}$ acidic solvolysis [29]	3	$0.35 \pm 0.04$	0.994	–	–	–
IX. $\text{RMe}_2\text{SiH}$ alkaline solvolysis [24]	6	$2.41 \pm 0.06$	0.999	–	–	–
X. $\text{RMeSiCl}_2 + \text{PhMgCl}$ , $\text{Et}_2\text{O}^c$	6	$1.12 \pm 0.10$	0.985	4	$0.64 \pm 0.11$	0.970

<sup>a</sup> Number of compounds in the correlation.

<sup>b</sup> Correlation coefficient.

<sup>c</sup> This work.



Table 3  
Calculated steric constants  $E_s(\text{Si})$  for polar substituents. Numeration of reaction series as in Table 2

Substituent	I	II	III	IV	V	VI	X
Ph	−0.301	−0.356	−0.557	−0.683	−0.952	−1.45	−1.46
X-C <sub>6</sub> H <sub>4</sub> <sup>a</sup>	−0.322	−0.368	−0.542	−0.658	−0.967	−1.39	−1.29
ClCH <sub>2</sub> −	0.038	−0.028	−0.288	−0.313	−0.394	−	−0.64
Cl <sub>2</sub> CH−	0.023	−0.003	−	−0.623	−0.724	−	−
BrCH <sub>2</sub> −	−0.031	−0.105	−0.205	−	−	−	−
PhCH <sub>2</sub> −	−0.538	−0.750	−0.489	−0.356	−0.293	−	−

<sup>a</sup> Average value for substituted phenyl groups.

Table 4  
Steric constants  $E_s(\text{Si})$  calculated using different  $\sigma^*$  values

Reaction series	Phenyl group			Chloromethyl group	
	0.60	0.06	0.00	1.05	0.65
III	−0.56	−0.19	−0.15	−0.29	−0.014
IV	−0.68	−0.40	−0.37	−0.31	−0.10
V	−0.95	−0.61	−0.57	−0.39	−0.14
VI	−1.45	−0.82	−0.75	−	−
X	−1.46	−0.43	−0.32	−0.64	−0.061

ethylmagnesium chloride (Table 1) with novel  $E_s(\text{Si})$  and  $\sigma^*$  values estimated above as well as with the tabulated values.

It cannot be excluded that our observations may be related to the complex character of the inductive effect discovered only recently [32,33]. The principle is that a simple inductive effect can be observed only on the interaction with a charged group. When both interacting groups are less polar, the effect must be expressed by two terms. The second term is small, it depends only on the first atom of the substituent and decreases with the distance more steeply. Its physical meaning is still unclear. Note that the novel conception of the inductive effect stems from the carbon chemistry. If applicable to the silicon chemistry, the proportions between the components of the effect need not remain the same.

Despite scarce kinetic data for organosilicon reactions, we hope to be able to cast light on these challenging problems through an extensive statistical treatment of all available data.

#### 4. Conclusions

Rate constants for reactions of ethyl- and phenylmagnesium chlorides with alkyl substituted chlorosilanes correlated well with  $E_s(\text{Si})$  steric parameters thus proving recurrently applicability of these constants in silicon chemistry.

Rate constants for the reactions with substituted phenylsilanes, involving also the literature data, were correlated with  $\sigma^0$  inductive constants. The obtained good linear correlations ruled out the conjugation of substituents with the reaction center well in line with the results of quantum chemical calculations.

It was concluded that only steric and inductive effects are operating. Next an attempt was made to calculate from

kinetic data the steric constants for polar substituents involving the inductive constants  $\sigma^*$  by Taft. It appeared that the  $\sigma^*$  constants derived from the carbon chemistry are not applicable to the silicon chemistry. As the main conclusion, new scales of parameters for description of polar and steric effects in the organosilicon chemistry need to be created.

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#### References

- [1] B. Arkles, in: G.S. Silverman, P.E. Rakita (Eds.), Handbook of Grignard Reagents, Marcel Dekker, New York, 1996 (Chapter 32).
- [2] A.F. Reid, C.J. Wilkins, J. Chem. Soc. (1955) 4029.
- [3] R.J.P. Corriu, B. Henner, J. Organomet. Chem. 102 (1975) 407.
- [4] A. Tuulmets, M. Hõrak, T. Kõopere, J. Ruotsi, Org. React. (USSR) 19 (1982) 102;  
A. Tuulmets, M. Hõrak, T. Kõopere, J. Ruotsi, Chem. Abstr. 99 (1983) 53836.
- [5] M. Sassian, D. Panov, A. Tuulmets, Appl. Organomet. Chem. 16 (2002) 525.
- [6] A. Tuulmets, D. Panov, M. Sassian, Tetrahedron Lett. 44 (2003) 3943.
- [7] A. Tuulmets, B.T. Nguyen, D. Panov, M. Sassian, J. Järvi, J. Org. Chem. 68 (2003) 9933.
- [8] A. Tuulmets, B.T. Nguyen, D. Panov, J. Org. Chem. 69 (2004) 5071.
- [9] D. Panov, A. Tuulmets, B.T. Nguyen, J. Organomet. Chem. 691 (2006) 4076.
- [10] D. Panov, A. Ploom, A. Tuulmets, Phosphorus, Sulfur, and Silicon 181 (2006) 2807.
- [11] A. Ploom, D. Panov, A. Tuulmets, ARKIVOC (5) (2006) 37.
- [12] R.W. Taft Jr., in: M. Newman (Ed.), Steric Effects in Organic Chemistry, Wiley, New York, 1956 (Chapter 13).
- [13] J. Shorter, Correlation Analysis in Organic Chemistry, Clarendon Press, Oxford, 1973.
- [14] B.J. Wakefield, Organomagnesium Methods in Organic Synthesis, Academic Press, New York, 1995.
- [15] H. Gilman, R.E. Brown, J. Am. Chem. Soc. 52 (1930) 3330.
- [16] F.K. Cartledge, Organometallics 2 (1983) 425.
- [17] M. Charton, J. Am. Chem. Soc. 97 (1975) 3691.
- [18] D.F. DeTar, J. Org. Chem. 45 (1980) 5166.
- [19] C.K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, NY, 1953.
- [20] V.P. Mileshekevich, N.F. Novikova, Usp. Khim. 50 (1981) 85.
- [21] J.Y. Corey, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989 (Chapter 1).

- [22] Y. Apeloig, M. Karni, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, vol. 2, Wiley, New York, 1998 (Chapter 1).
- [23] S. Gronert, R. Glaser, A. Streitwieser, *J. Am. Chem. Soc.* 111 (1989) 3111.
- [24] J. Hetflejš, F. Mareš, V. Chvalovský, *Coll. Czechoslov. Chem. Commun.* 30 (1965) 1643.
- [25] K. Käßler, U. Scheim, K. Rühlmann, A. Porzel, *J. Organomet. Chem.* 441 (1992) 15.
- [26] N. Shimizu, N. Takesuke, A. Yamamoto, T. Tsutsumi, S. Yasuhara, Y. Tsuno, *Chem. Lett.* (1992) 1263.
- [27] K. Käßler, U. Scheim, K. Rühlmann, *Phosphorus, Sulfur, and Silicon* 106 (1995) 203.
- [28] K. Käßler, A. Porzel, U. Scheim, K. Rühlmann, *J. Organomet. Chem.* 402 (1991) 155.
- [29] J.E. Baines, C. Eaborn, *J. Chem. Soc.* (1956) 1436.
- [30] L.H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, 1965.
- [31] J. Hetflejš, F. Mareš, V. Chvalovský, *Coll. Czechoslov. Chem. Commun.* 37 (1972) 1713.
- [32] O. Exner, S. Böhm, *J. Phys. Org.Chem.* 17 (2004) 124.
- [33] O. Exner, S. Böhm, *J. Phys. Org.Chem.* 19 (2006) 393.