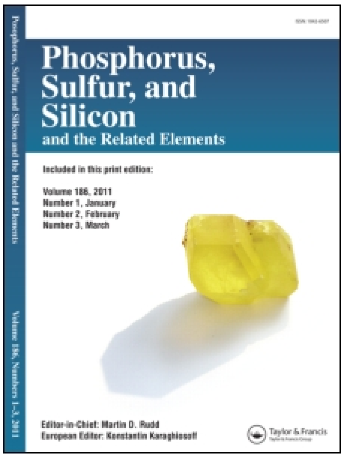
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Steric Effects of Alkylmagnesium Chlorides in the Grignard Reaction with Silanes

Dmitri Panov[a]; Anu Ploom[a]; Ants Tuulmets[a]
[a] Institute of Organic and Bioorganic Chemistry, University of Tartu, Tartu, Estonia

To cite this Article Panov, Dmitri , Ploom, Anu and Tuulmets, Ants(2006) 'Steric Effects of Alkylmagnesium Chlorides in the Grignard Reaction with Silanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 12, 2807 — 2816

To link to this Article: DOI: 10.1080/10426500600864866

URL: http://dx.doi.org/10.1080/10426500600864866

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 181:2807–2816, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600864866

Steric Effects of Alkylmagnesium Chlorides in the Grignard Reaction with Silanes

Dmitri Panov
Anu Ploom
Ants Tuulmets
Institute of Organic and Bioorganic Chemistry, University of Tartu,
Tartu, Estonia

Rate constants for the reactions of methylvinyldichlorosilane and tetraethoxysilane with alkylmagnesium chlorides RMgCl (R = Et, n-*Bu,* i-*Bu,* i-*Pr,* s-*Bu,* t-*Bu) in diethyl ether were determined. Excellent correlations of rate data with steric constants E_S(Si) by Cartledge and* v' *by Charton were found for the reaction of methylvinyldichlorosilane. Linear correlations with break points were obtained for the tetraethoxysilane reaction. It was assumed that this could be referred to a change in the reaction mechanism.*

Keywords Grignard reaction; kinetics; Linear Free Energy (LFE) relationships; silanes

INTRODUCTION

To correlate steric effects with chemical and physical properties, it is necessary to differentiate between steric and electronic effects in relation to a property. In traditional organic chemistry, this issue has a long history and protocols for a quantitative separation of the effects have been developed.[1–4] However, in organometallic chemistry a general and unequivocal approach still needs to be created if such is possible at all.[5,6]

The importance of steric effects in organosilicon chemistry has always been stressed,[7–10] however, attempts of a quantitative description of the effects are not numerous[8,10–15] and have never been done for the Grignard reaction with organosilicon compounds.

Received; accepted.

This work was financially supported by the Dow Corning Corporation (Midland, USA), and the Estonian Science Foundation (grant No 6512).

Address correspondence to Ants Tuulmets, Institute of Organic and Bioorganic Chemistry, University of Tartu, Jakobi 2, Tartu, 51014 Estonia. E-mail: ants.tuulmets@ut.ee

Monomeric organosilicon compounds are important products in a wide range of applications apart from silicone chemistry, which is the largest consumer of silanes. Grignard chemistry is a versatile method for the production of organosilanes.[16] However, only a few investigations deal with quantitative aspects of the reaction. Only a small number of kinetic studies of the Grignard reaction with silanes have been published,[17–23] and no attempts to ascertain the structure-reactivity relationships for the reaction have been made except for our semiquantitative observation that substituents at the silicon center control the rate of the Grignard reaction with chlorosilanes through their inductive and steric effects.[23]

We have launched an investigation into quantitative aspects of the reactivity of the Grignard reaction with silanes.[20–23] The main attention will be focused on the structure-reactivity relationships for the reaction. The Grignard reaction with silanes is a particular example of nucleophilic displacements at a silicon atom. Some of these have been subjected to correlation analysis (see, e.g.,[8,10,15]) by the use of the Taft equation[1] or other Linear Free Energy (LFE) relationships. Only in few instances the structural effects in the nucleophiles have been quantitatively analyzed; e.g., the rates of dehydrocondensation of a silane with a series of alcohols were correlated with the parameters of the Taft equation.[24,25] However, the conclusions of these investigations as well as of a number of studies dealing with the structural effects of alkyl groups in silanes obviously should be revised according to the current understanding of the nature of Taft's σ^* constants for alkyl substituents.[2,3,26] A need for revision also emerges from contradictory conclusions concerning the applicability of Taft–type steric parameters to the reactions at a silicon center.[5,11–15]

In this context our present contribution offers a distinct choice between the sets of steric parameters for alkyl groups in reactions at a silicon center, thus providing a benchmark for further extension of the research.

In this study kinetic experiments were carried out under pseudo-first-order conditions with a great excess of the Grignard reagent over the silane. Solutions of alkylmagnesium chlorides in diethyl ether with a fixed concentration of 0.5 M were used because of the definitely dimeric structure of all Grignard reagents under investigation in the range of this concentration.[27] Six Grignard reagents were involved to cover primary, secondary, and tertiary alkyl groups. Methylvinyldichlorosilane and tetraethoxysilane were chosen for model silanes considering the compatibility of their reaction rates with our experimental facilities. The rate data were analyzed using linear free energy relationship (LFER) methods.

EXPERIMENTAL

Materials

Tetraethoxysilane (98% GC) was purchased from Aldrich, and methylvinyldichlorosilane (99.0%) was donated by Dow Corning Corp. Reagent-grade magnesium shavings 99.8% purity were purchased from Fluka. Commercial chloroalkanes and diethyl ether were carefully dried and purified. Grignard reagents were prepared by conventional methods.[28] The reagents and solutions were operated under dry argon and transferred by the use of cannulas or syringes.

Kinetic Measurements

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

At appropriate time points, 1 mL of aliquots was taken through a septum with a syringe and quenched with ice water in the case of ethoxysilane or with a cool dry ethanol/pyridine mixture in the case of chlorosilane. The organic layer was separated, dried, and analyzed for the alkoxysilanes contained in the sample or formed during 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 one or two half-lives. The coupling followed excellent first-order kinetics. Practically no products of the consecutive couplings were detected by the end of the monitoring time. Experiments were carried out in duplicate or triplicate, and rate constants were reproducible within an accuracy of ±5% or better.

RESULTS

Pseudo-first-order rate constants for the coupling reaction of methylvinyldichloro-silane and tetraethoxysilane with 6 alkylmagnesium chlorides at fixed 0.5 M concentration in diethyl ether (see the Introduction) were determined and are presented in Table I.

TABLE I Rate Constants (k × 10^5, s^{-1}) for the Coupling Reaction of Silanes with Alkylmagnesium Chlorides, RMgCl, in Diethyl Ether at 20°C

R	$MeViSiCl_2$	$Si(OEt)_4$
Et	9.17	1700[a]
n-Bu	8.00	200
i-Bu	4.92	4.67
i-Pr	4.00	2.55
s-Bu	2.72	0.85
t-Bu	0.40	0.0147

[a] A rough estimation from previous data.[19]

For both silanes, the sequence of the reaction rates Et > *n*-Bu > *i*-Bu > *i*-Pr > *s*-Bu > *t*-Bu is in line with generally accepted steric characteristics of the groups[1–3] except for *i*-Pr and *i*-Bu. However, susceptibility to steric effects of the reaction with tetraethoxysilane is incomparably greater than that with methylvinyldichlorosilane. To some extent, this could be referred to greater steric requirements of the substituents in the alkoxysilane in comparison with the chlorosilane. This is also in line with the remarkable susceptibility of the Grignard reaction with alkoxysilanes to steric requirements of the silane molecule found in one of our recent investigations.[20]

In Figure 1 a preliminary LFE analysis of the data is presented. It is obvious that no linearity between logarithms of the rate constants exists. In general, this is considered evidence of diverse reaction mechanisms.[4] Indeed, we have shown recently that the Grignard reaction with alkoxysilanes consists of a replacement of a donor molecule at the magnesium center by the silane followed by the subsequent rearrangement of the complex to products through a four-center transition state, while chlorosilanes react differently without solvent molecule replacement.[21,22]

A correlation analysis of the data is presented in the next section.

DISCUSSION

Parameters for the Correlation Analysis

Effects of aliphatic substituents on the reactivity of organosilicon compounds have been described since long with the Taft equation (Eq. (1)),[8,10] in which the two last terms express the independent contributions from polar (inductive) and steric effects to the reactivity, respectively.[1,3]

$$\log \mathrm{k} = \log \mathrm{k_O} + \rho^*\sigma^* + \delta \mathrm{E_S} \qquad (1)$$

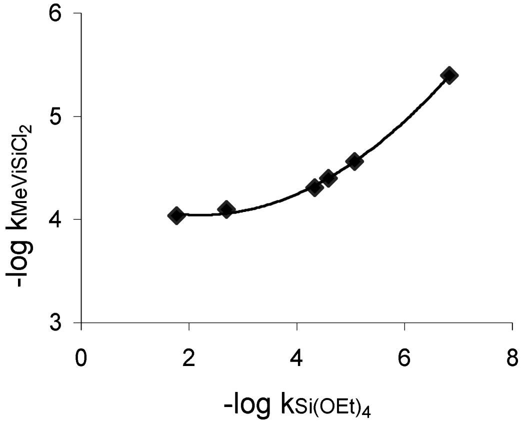


FIGURE 1 A LFE analysis of the reaction of alkylmagnesium chlorides with tetraethoxysilane and methylvinyldichlorosilane.

The σ^*-values measure the polar effects of substituents. However, there have been numerous contributions[2,3,26,29] casting doubt on the status of σ^*-values for alkyl groups. As the main conclusion, it has been stressed that alkyl groups do not exert any inductive effect, and the σ^*-values of alkyl groups are an artifact.

Also the Taft E_S scale of steric parameters has been a matter of criticism from different viewpoints. Several authors have maintained that the Taft E_S parameters do not represent a complete separation of steric and polar effects and have attempted to improve the scale in various ways. Thus Hancock et al.[30] and Palm[31] concluded that E_S contains a contribution due to hyperconjugation, which has to be removed in order to obtain true steric constants. They proposed scales of corrected steric constants, E_S^C and E_S^O (Eq. (2)), respectively.

$$E_S^O = E_S + 0.33(n_H - 3) - 0.13n_C \qquad (2)$$

In Eq. (2), n_H and n_C are the numbers of α-hydrogens and α-carbons, respectively. When only alkyl groups are considered, Eq. (2) reduces to Eq. (3).

$$E_S^O = E_S + 0.20(n_H - 3) \qquad (3)$$

MacPhee et al.[32] have criticized the basic assumptions used in obtaining the Taft E_S scale and have proposed a revised and extended scale, $E_S{}'$, based on a single defining reaction.

Silicon chemists in general use correlations for which the substituent constants have been defined in organic reactions.[5,8,10] However, the steric parameters derived from reactions of organic carbonyl compounds have been moderately successful in describing steric effects in reactions taking place at Si atoms. Considering the greater length of C—Si as compared to C—C bonds, some incompatibility of Taft–type scales with reactions at the Si center could be expected.

Cartledge[11] defined a set of $E_S(Si)$ parameters for 8 alkyl groups and for H from rates of acid-catalyzed hydrolysis of SiH compounds. For 8 reaction series, the correlation with $E_S(Si)$ was better or comparable with that where E_S^O or ${E_S}'^{\,O}$ constants were involved. The Cartledge scale of $E_S(Si)$ constants appeared to be in a good correlation ($R^2 = 0.992$) with v' parameters derived by Charton[33] for the correlation of the nucleophilic substitution at four-coordinate carbon.

Similarly, Shimizu et al.[12] have proposed a quantitative scale for the structural effect on reactivity toward nucleophilic displacement at silicon using the rates of solvolysis for triorganochlorosilanes. The steric constants E_S^{Si} by Shimizu et al.[12] for alkyl groups correlate with Cartledge $E_S(Si)$ constants ($R^2 = 0.920$) as well as with v′ parameters by Charton ($R^2 = 0.974$). On the contrary, Rühlmann et al.[13–15] apply the Taft steric constants in their original form or a modified Taft scale fitted for silane reactions. The steric constants by Käppler et al.[15] for alkyl groups also correlate with Cartledge $E_S(Si)$ constants ($R^2 = 0.949$).

The major difference in the parameters derived from silicon compounds and those derived from carbonyl compounds is a greater effect of branching in the α-position to the reaction center than that of branching in the β-position. The steric effects appeared to be additive.[11] Charton[33] has concluded that steric effects are more sensitive to the reaction type than to the identity of the atom under attack and that a reaction involving an expansion of coordination from four to five will show a different sensitivity to α and β branching than a reaction involving a change of coordination from three to four.

The Reaction with Methylvinyldichlorosilane

Kinetic data (Table I) was allowed to LFE analysis with a reduced Taft equation (Eq. (4)). Different sets of steric constants (Table II) were used for E in Eq. (4).

$$\log k = a_O + \delta E \qquad (4)$$

As is seen in Table III and Figure 2, data for the reaction with methylvinyldichlorosilane correlates well with parameters $E_S(Si)$ and v′. This excellent correlation enabled us to calculate the steric parameters for the s-Bu group $E_S(Si) = 0.67$ and $v' = 0.71$.

This result excludes any contribution of other structural effects provided the steric parameters adequately describe the steric requirements

TABLE II Steric Parameters Used in the Correlation Analysis

R	$-E_S{}'^{a}$	$-E_S{}^{O,b}$	$-E_S(Si)^c$	v'^d
Et	0.08	0.28	0.149	0.38
n-Bu	0.31	0.51	0.225	0.42
i-Bu	0.93	1.13	0.405	0.55
i-Pr	0.48	0.88	0.556	0.62
s-Bu	1.00	1.40	$(0.67)^e$	$(0.71)^e$
t-Bu	1.43	2.03	1.46	1.23

[a] Taft steric parameters revised by MacPhee et al.[32]

[b] Steric parameters by Dubois corrected for hyperconjugation according Palm[31] (Eq. 3).

[c] Steric parameters by Cartledge.[11]

[d] Steric parameters by Charton.[33]

[e] Calculated from our experimental data using Eq. (4).

of the alkyl groups. However, the nucleophilicity of Grignard reagents in the reaction may be related in some way to the alkyl groups. Although not exerting any polar effect, the groups differ considerably with regard to their polarizability. It appears that the polarizability constants σ_α by Taft and Topsom[34] for alkyl groups are closely correlated with the steric parameters $E_S{}'^{O}$ ($R^2 = 0.939$) and v' ($R^2 = 0.894$). Thus, the separation of steric and polarizability effects for alkyl groups hardly can be realized. However, experimentally observed remarkable exothermicity indicates an early transition state of the reaction. Accordingly, a little developed charge separation can be assumed for the transition state. On the other hand, a detailed analysis of substituent electronic effects by Taft and Topsom[34] leads to a conclusion that polarizability effects are significant only in the gas phase for a full charge transfer processes. Consequently, one can conclude that rates of the reactions of alkylmagnesium compounds with chlorosilanes are determined exclusively by steric effects of the alkyl groups.

TABLE III The Correlation of the Rate Data for the Reaction With Methylvinyldichlorosilane with Steric Parameters

E^a	a_o	δ	R^2	s
$E_S(Si)$	-3.86 ± 0.02	1.04 ± 0.03	0.997	0.032
v'	-3.42 ± 0.01	-1.60 ± 0.02	0.999	0.012
$E_S{}'$	-3.85 ± 0.19	0.87 ± 0.23	0.780	0.260
$E_S{}'^{O}$	-3.70 ± 0.16	0.74 ± 0.13	0.887	0.186

[a] For specification, see footnotes to Table II.

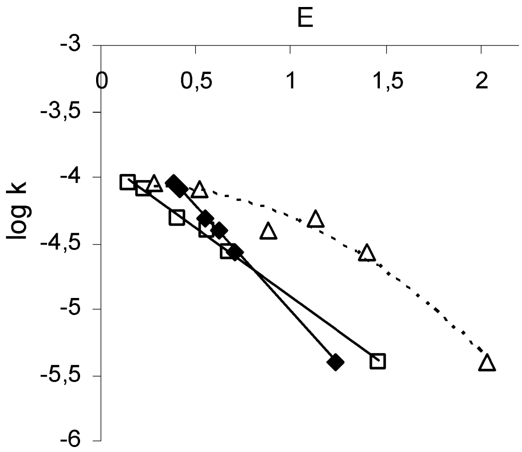


FIGURE 2 The correlation of the rate data for the reaction with methylvinyldichlorosilane with steric parameters: $-E_S(Si)$ (□), v′(◆), $-E_S'^{O}$(△).

The Reaction with Tetraethoxysilane

A correlation of the rate data for the reaction with tetraethoxysilane, which involves novel parameters for the *s*-Bu group (see the previous section), is represented in Figure 3. The data does not correlate as a whole; however, the points lay well on two intersecting lines.

As a rule, a change in the mechanism of a reaction is indicated by a nonlinear free-energy correlation.[4] Typical curves with break points in Figure 3 can be referred to a reaction changing its mechanism for a sterically less-demanding pathway when groups of higher steric

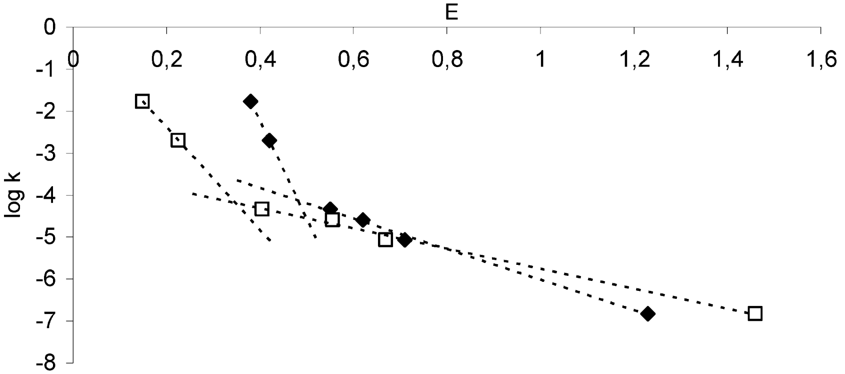


FIGURE 3 The correlation of the rate data for the reaction with tetraethoxysilane with steric parameters: $-E_S(Si)$ (□), v′ (◆).

requirements are involved. The validity of this conclusion as well as details of the mechanism can only be elucidated by independent experiments. A relevant investigation is in progress.

REFERENCES

[1] R. W. Taft, Jr., In M. Newman (Ed.), *Steric Effects in Organic Chemistry*, Chapter 13 (Wiley, New York, 1956).

[2] N. B. Chapman and J. Shorter (Eds.), *Advances in Linear Free Energy Relationships* (Plenum Press, London, 1972).

[3] J. Shorter, *Correlation Analysis in Organic Chemistry* (Clarendon Press, Oxford, 1973).

[4] A. Williams, *Free Energy Relationships in Organic and Bio-organic Chemistry* (RSC, Cambridge, 2003).

[5] V. I. Galkin, R. D. Sayakhov, and R. A. Tcherkasov, *Usp. Khim.*, **60,** 1617 (1991).

[6] D. White and N. J. Coville, *Adv. Organomet. Chem.*, **36,** 95 (1994).

[7] C. Eaborn, *Organosilicon Compounds* (Butterworths, London, 1960).

[8] L. H. Sommer, *Stereochemistry, Mechanism, and Silicon* (McGraw-Hill, New York, 1965).

[9] J. R. Hwu, S. C. Tsay, and B. L. Cheng, In Z. Rappoport and Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds, Vol. 2*, pp. 431–494 (Wiley, Chichester, 1998).

[10] V. P. Mileshkevich and N. F. Novikova, *Usp. Khim.*, **50,** 85 (1981).

[11] F. K. Cartledge, *Organometallics*, **2,** 425 (1983).

[12] N. Shimizu, N. Takesuke, A. Yamamoto, T. Tsutsumi, S. Yasuhara, and Y. Tsuno, *Chem. Lett.*, 1263 (1992).

[13] U. Scheim, H. Grosse-Ruyken, K. Rühlmann, and A. Porzel, *J. Organomet. Chem.*, **293,** 29 (1985).

[14] K. Käppler, U. Scheim, K. Rühlmann, and A. Porzel, *J. Organomet. Chem.*, **441,** 15 (1992).

[15] K. Käppler, U. Scheim, and K. Rühlmann, *Phosphorus, Sulfur, and Silicon*, **106,** 203 (1995).

[16] B. Arkles, In G. S. Silverman and P. E. Rakita (Eds.), *Handbook of Grignard Reagents*, Chapter 32 (Marcel Dekker, New York, 1996).

[17] A. F. Reid and C. J. Wilkins, *J. Chem. Soc.*, 4029 (1955).

[18] R. J. P. Corriu and B. Henner, *J. Organomet. Chem.*, **102,** 407 (1975).

[19] A. Tuulmets, M. Hõrak, T. Kõopere, and J. Ruotsi, *Org. Reactivity* (Tartu), **19,** 102 (1982).

[20] M. Sassian, D. Panov, and A. Tuulmets, *Appl. Organomet. Chem.*, **16,** 525 (2002).

[21] A. Tuulmets, D. Panov, and M. Sassian, *Tetrahedron Lett.*, **44,** 3943 (2003).

[22] A. Tuulmets, B. T. Nguyen, D. Panov, M. Sassian, and J. Järv, *J. Org. Chem.*, **68,** 9933 (2003).

[23] A. Tuulmets, B. T. Nguyen, and D. Panov, *J. Org. Chem.*, **69,** 5071 (2004).

[24] K. A. Andrianov, L. M. Tartakovskaya, V. M. Kopylov, and Zh. N. Sementsova, *Zh. Obshch. Khim.*, **45,** 112 (1975).

[25] E. Lukevics and M. Dzintara, *Zh. Obshch. Khim.*, **51,** 2043 (1981).

[26] D. F. DeTar, *J. Org. Chem.*, **45,** 5166 (1980).

[27] F. W. Walker and E. C. Ashby, *J. Am. Chem. Soc.*, **91,** 3845 (1969).

[28] B. J. Wakefield, *Organomagnesium Methods in Organic Synthesis* (Academic Press, New York, 1995).

[29] M. Charton, *J. Am. Chem. Soc.*, **97,** 3691 (1975).

[30] C. K. Hancock, E. A. Meyers, and B. Y. Yager, *J. Am. Chem. Soc.*, **83,** 4211 (1961).

[31] V. A. Palm, In *Fundamentals of the Quantitative Theory of Organic Reactions* (Khimiya, Leningrad, 1967).

[32] J. A. MacPhee, A. Panaye, and J.-E. Dubois, *Tetrahedron*, **34,** 3553 (1978).

[33] M. Charton, *J. Am. Chem. Soc.*, **97,** 3694 (1975).

[34] R. W. Taft and R. D. Topsom, *Progr. Phys. Org. Chem.*, **16,** 1 (1987).