Journal of Organometallic Chemistry, 231 (1982) 291—298
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

INSERTION REACTIONS OF DIMETHYLSILYLENE: RELATIVE REACTIVITY TOWARDS OXYGEN—HYDROGEN, SILICON—HYDROGEN, AND SILICON—ALKOXY BONDS

KENT P. STEELE, DONGJAW TZENG, and WILLIAM P. WEBER *
Department of Chemistry, University of Southern California, Los Angeles, California 90007 (U.S.A.)

(Received September 9th, 1981; in revised form January 4th, 1982)

Summary

Photochemically-generated dimethylsilylene is found in competition experiments to insert preferentially into oxygen—hydrogen bonds of alcohols compared to either silicon—hydrogen bonds of silanes or silicon—oxygen bonds of alkoxysilanes. This selectivity for O—H bonds compared to Si—H bonds is quite high in tetrahydrofuran and in dilute hydrocarbon solutions. However, it decreases in more concentrated hydrocarbon solutions. These effects are discussed in terms of aggregation of alcohols, hydrogen bonding, and solvent-mediated dimethylsilylene reactivity.

The chemistry of silylenes is most frequently studied by determination of the products that are formed by insertion of the silylene into heteronuclear single bonds or by addition of the silylene to multiple bonds [1]. Silicon—hydrogen [2], silicon—oxygen [2], silicon—sulphur [3,4], silicon—halogen [2], oxygen—hydrogen [5], and nitrogen—hydrogen [5] single bonds that have been used to trap silylenes. We have been interested in the relative reactivities of various single bonds toward photochemically-generated silylenes [6—8].

In this paper, we report the relative reactivities of Si—H bonds of silanes and O—H bonds of alcohols towards photochemically-generated dimethylsilylene. Oxygen—hydrogen bonds are more reactive towards dimethylsilylene than Si—H bonds. The relative reactivities are solvent-dependent, and in non-polar solvent, the relative reactivities depend on alcohol concentration.

Results

Dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane (I) [2], inserts into O—H bonds of alcohols to form dimethylalkoxysilanes [5],

0022-328X/82/0000—0000/$02.75

and into Si—H bonds of monosilanes to form disilanes [2,6]. In non-competitive reactions, these bonds are equally effective traps, based on yields of insertion products, for dimethylsilylene [5,9]. In this study, alcohols and silanes competed against each other for photochemically generated dimethylsilylene.

The photolysis of a solution of I, ethanol, and n-butyldimethylsilane in tetrahydrofuran (THF) produced ethoxydimethylsilane (99.4%) [5] from insertion of dimethylsilylene into ethanol, and 1-n-butyl-1,1,2,2-tetramethyldisilane (0.6%) [6] from insertion of dimethylsilylene into the silane. The relative reactivity ratio for O—H/Si—H equals to 186. A similar experiment with t-butanol gave a relative reactivity ratio for O—H/Si—H equal to 175. Due to experimental difficulties in accurately measuring small quantities of 1-n-butyl-1,1,2,2-tetramethyldisilane these numbers may not be significantly different. Nevertheless, the greater reactivity of O—H bonds compared to Si—H bonds is noteworthy since the energy of activation of dimethylsilylene insertion into Si—H bonds has been calculated to be approximately zero [10,11].

The observed relative reactivity of alcohols to silanes is concentration dependent in nonpolar hydrocarbon solvents. The photolysis of a solution of I with equal amounts of ethanol and n-butyldimethylsilane in cyclohexane gave both ethoxydimethylsilane and 1-n-butyl-1,1,2,2-tetramethyldisilane in a 34/1 molar ratio. A similar experiment with t-butanol and n-butyldimethylsilane in n-decane gave t-butoxydimethylsilane and 1-n-butyl-1,1,2,2-tetramethyldisilane in a 14/1 ratio. These results are consistent with previous work in which ethanol was found to be twice as reactive as t-butanol toward dimethylsilylene in cyclohexane solvent [7].

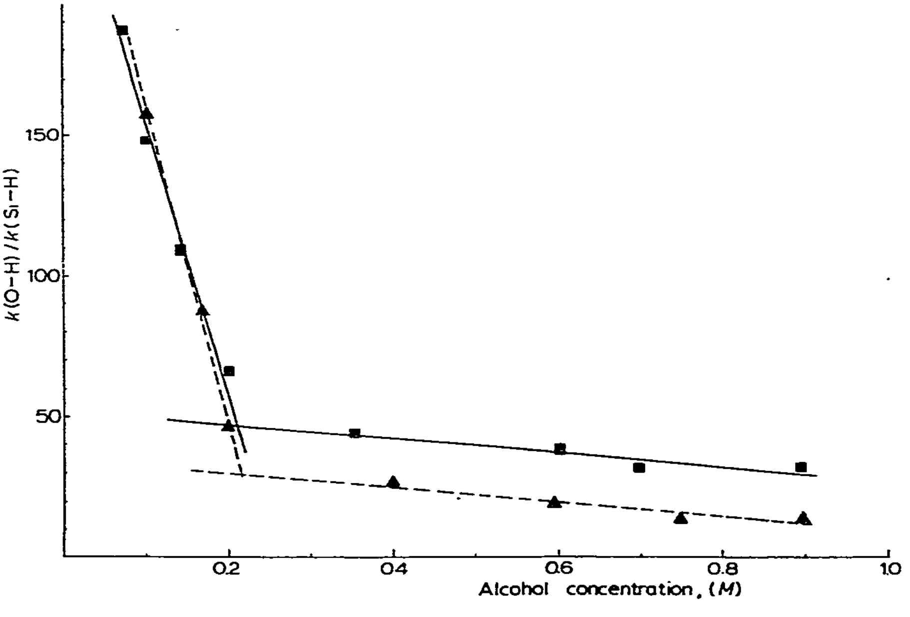


Fig. 1. Variation of relative rates of dimethylsilylene insertion into oxygen—hydrogen and silicon—hydrogen bonds with alcohol concentration. ■, ethyl alcohol/n-butyldimethylsilane; ▲, t-butyl alcohol/n-butyldimethylsilane.

TABLE 1

INSERTION PRODUCT RATIOS FOR COMPETITION EXPERIMENTS BETWEEN ALCOHOLS AND SILANES

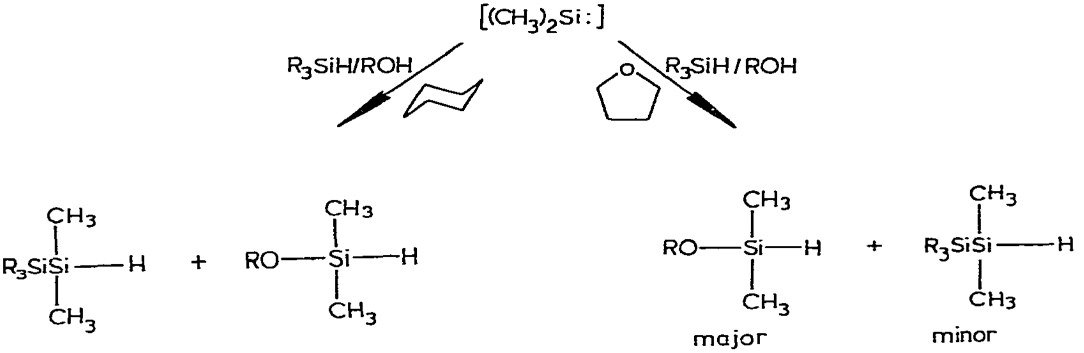
Reagents	Ratio of reagents in mmol	Solvent	Rel. reactivity $\dfrac{\underset{CH_3}{\overset{CH_3}{ROSiH}}}{\underset{CH_3CH_3}{\overset{CH_3CH_3}{HSi{-}SiR}}}$	Alcohol conc. [*M*]
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.026/0.18/0.737	Cyclohexane	185	0.095
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.021/0.24/2.24	Cyclohexane	148	0.10
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.026/0.33/2.15	Cyclohexane	110	0.14
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.039/0.48/1.64	Cyclohexane	66	0.20
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.052/0.84/2.25	Cyclohexane	44	0.35
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.052/1.44/2.24	Cyclohexane	40	0.60
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.045/1.68/2.14	Cyclohexane	32	0.70
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.050/2.16/2.12	Cyclohexane	34	0.90
I/EtOH/HSi(CH$_3$)$_2$-n-Bu	0.057/1.99/2.48	THF	186	0.83
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.018/0.24/2.10	n-Decane	156	0.10
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.034/0.38/2.33	n-Decane	87	0.16
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.030/0.48/1.71	n-Decane	43	0.20
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.054/0.96/2.32	n-Decane	25	0.40
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.037/1.44/1.80	n-Decane	18	0.60
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.054/1.80/2.48	n-Decane	13	0.95
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.064/2.16/1.74	n-Decane	14	0.90
I/t-BuOH/HSi(CH$_3$)$_2$-n-Bu	0.080/2.04/2.31	THF	175	0.85

These reactivity ratios were determined for solutions that were 0.75 to 0.9 molar in alcohol. (See Table 1) At lower concentrations of ethanol or t-butanol their apparent relative reactivity increases. Table 1 and Fig. 1 present data for the change of the observed reactivity ratio with change in alcohol concentration.

Competition of ethoxytrimethylsilane and ethanol for dimethylsilylene resulted in a similar relative reactivity of the O—H bond versus Si—O bond as for the O—H bonds versus Si—H bonds. Analysis after photolysis of a solution of I in an ethanol, cyclohexane, and ethoxytrimethylsilane solvent mixture showed that 47.5 times more ethoxydimethylsilane was formed than ethoxypentamethyldisilane [12]. In a similar experiment run in THF in place of cyclohexane, gave ethoxydimethylsilane and ethoxypentamethyldisilane in a ratio of 174/1. An experiment run with a solution of I in t-butanol, THF and ethoxytrimethylsilane gave a product ratio of t-butoxydimethylsilane to ethoxypentamethyldisilane of 151/1. This is expected since we have previously found that the Si—O of alkoxysilanes is approximately equal in reactivity to the Si—H of silanes toward insertion of dimethylsilylene [6].

Discussion

Two factors contribute to the changes in the apparent relative reactivities of O—H bonds of alcohols to Si—H bonds of silanes. Dimethylsilylene has been shown to be a more selective species in THF than in cyclohexane in competition reactions between pairs of alcohols and pairs of silanes [7]. In competition between alcohols and silanes in THF, dimethylsilylene usually selects the O—H bond in preference to the Si—H bond. In cyclohexane, at high concentration O—H and Si—H bonds are more nearly equally reactive traps in the presence of the other. The reaction medium modifies the reactivity of dimethylsilylene [7] and therefore, the observed relative reactivities differ in the different mediums.



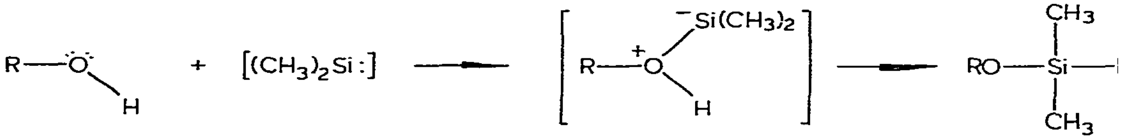
The other factor that contributes to the apparent changes in the relative reactivities is the self-association of alcohols in nonpolar solvents [13]. Most studies, for example IR and NMR, of alcohol self-association have been conducted in carbon tetrachloride solvent [14—18]. The dielectric constants and dipole moments of carbon tetrachloride, cyclohexane, and n-decane are essentially the same [19]. Therefore, we assume that self-association of the trapping alcohols should be similar in these solvents.

Numerous studies have addressed the nature of such associated species [14—18,20]. Regardless whether the species is a cyclic dimer, linear tetramer, or a combination of many aggregates, the effective concentration of "free" alcohol in solution is reduced from the concentration calculated from the mass of alcohol placed in the solution. On the other hand, THF has a much larger dielectric constant and dipole moment [19], and therefore, self-association by alcohols in THF should be much less significant. In place of self-association, hydrogen bonding to solvent becomes important in THF solutions of alcohols [21]. In THF solutions, the effective concentration of alcohol should be closer to the calculated concentration than the effective concentration is to the calculated concentration of alcohol in cyclohexane solutions.

Hydrogen bonding, either as self-association or to solvent, is much less significant for silanes. NMR has been used to estimate the magnitude of self-association and hydrogen bonding to solvent of Si—H bonds of silanes in solution [22]. This support the interpretation that for silanes, change of solvent in the primary effect on silylene reactivity [7].

A combination of solvent-modified silylene reactivity and self-association of the alcohol may be responsible for the large changes in the apparent reactivity ratios observed in this study. In THF, the alcohol is hydrogen bonded to solvent. Under these conditions, the alcohol consumes most of the silylene. The Si—H bonds are not effective competitors for the silylene compared to such O—H bonds.

Mechanistically, the relative reactivity ratios observed in this study support previously advanced mechanisms for silylene insertions. The electrophilic silylene has been proposed to attack the alcohol oxygen's lone pairs to form a zwitterionic intermediate which rearranges to form the alkoxydimethylsilane [23].



The rate of this process may be enhanced by the hydrogen bonding between the alcohol and THF. The O—H bond is weakened by hydrogen bonding to solvent [21], and insertion into the weakened bond should be easier.

The hydrosilanes have no comparable site of electron density as the lone pairs of the alcohol oxygen. Furthermore, because the hydrosilane is not hydrogen-bonded to the solvent, no rate enhancement is possible.

Alkoxysilanes would appear to have the same available electron density as the alcohols. However, alkoxysilanes and disiloxanes are known to be less basic, due to decreased electron density at oxygen, than ethers [24—27]. This effect may be manifested by the observed relative reactivities of alcohols and alkoxysilanes towards dimethylsilylene.

At high concentration in nonpolar solvents, insertion of silylenes into Si—H bonds appears to become much more favorable in comparison to O—H bonds. Silylenes are more reactive and less selective toward pairs of silanes in hydrocarbon solvents [7]. In addition, the self-association of the alcohols not only decreases the effective concentration of the alcohol, but it also decreases the availability of the oxygen lone pairs of the self-associated species. The Si—H bond is able to compete more effectively with one or more of the self-associated species than it is able to compete with the "free" alcohol. With the available data, it is difficult to determine whether the concentration of free alcohol is decreased and the self-associated species are not reacting at all, or whether the silylene actually inserts into one or more of the self-associated species at a slower rate than it inserts into the "free" alcohol.

The graphic representation (Fig. 1) of the relative rates of dimethylsilylene insertion in cyclohexane shows two distinct linear relationships between the relative insertion rate and alcohol concentration for both the ethanol/n-butyldimethylsilane system and the t-butanol/n-butyldimethylsilane system.

One interpretation of this data is that at alcohol concentrations of about 0.2 *M*, there is a change in the predominant aggregate species. The species that dominates at lower concentrations is a better trap for dimethylsilylene than the predominant species at higher concentrations. Certainly, more information on the nature of alcohol aggregates at different concentrations and their reactivity towards silylenes will be needed to quantitatively describe this system in nonpolar solvents.

Finally, dimethylsilylene exhibits little selectivity for various alcohols compared to n-butyldimethylsilane at the higher alcohol concentrations. This observation supports the views the dimethylsilylene is non-selective towards different alcohols in non-polar solvents [7], and that low molecular weight alcohols aggregate to a similar extent in nonpolar solvents [28,29].

In conclusion, this study has shown that the O—H bond of alcohols in THF and dilute hydrocarbon solvents is a much more effective trap for silylenes than Si—H bonds.

Experimental

All starting materials and products were known compounds. Products were identified by comparison of GLC retention time with authentic samples and by NMR spectroscopy. Product mixtures were analysed either on a Hewlett—Packard F & M 700, or a Gow-Mac 550 Gas Chromatograph equipped with a thermal conductivity detector, and on a Hewlett—Packard 5710A Gas Chromatograph equipped with a flame ionization detector. Eight to fourteen feet columns packed with Chromosorb W 60/80 mesh coated with 20% SE-30 were used. NMR spectra were obtained on a Varian XL-100-15 NMR spectrometer operated in the FT mode. Samples were 1% in deuterochloroform with chloroform as internal standard.

Relative reactivities were calculated using the equation of Doering and Henderson [30]. Control experiments demonstrated that the products were stable under the reaction conditions. Thus product ratios are identical to dimethylsilylene trapping ratios. Mole fractions of insertion products were determined by comparison of peak areas corrected for the difference in sensitivity of the FID to the various compounds. Molarities were calculated as moles of alcohol in total volume of reaction mixture. Reaction mixtures were photolyzed in 5 mm quartz NMR tubes with a medium-pressure Hanovia Hg lamp in an ice-water bath at 5°C.

THF was distilled from the sodium ketyl of benzophenone immediately prior to use. Cyclohexane was distilled from sodium before use. n-Decane, Aldrich Gold Label, was used without further purification.

Absolute ethanol was used without further purification. Isopropanol was distilled from calcium oxide before use, and t-butanol was distilled from sodium.

n-Butyldimethylsilane was prepared by the reaction of dimethylchlorosilane with n-butyl lithium in ether [31]. Ethoxytrimethylsilane [32] was prepared by treatment of absolute ethyl alcohol in pyridine with trimethylchlorosilane.

Dodecamethylcyclohexasilane was prepared by the reaction of dimethyldichlorosilane with excess lithium in THF [33].

Competitions experiments

Photolysis of I with ethanol and n-butyldimethylsilane in THF. A solution of I (19.8 mg, 0.57 mmol), ethanol (92 mg, 1.99 mmol) n-butyldimethylsilane (288 mg, 2.48 mmol), and THF (2.2 ml) in a 5 mm quartz NMR tube was photolyzed at 5°C for 90 min with a 450 W medium-pressure Hanovia Hg lamp. Analysis of the colorless solution by FID-GLC indicated formation of ethoxydimethylsilane and 1-n-butyl-1,1,2,2-tetramethyldisilane [6] in a molar ratio of 186/1. Addition of toluene as an internal standard and reanalysis indicated that ethoxydimethylsilane was formed in a 90% yield based on two moles of dimethylsilylene per mole of I [2].

Photolysis of I with ethanol and n-butyldimethylsilane in cyclohexane. A solution of I (17.4 mg, 0.05 mmol), ethanol (9 mg, 2.16 mmol), n-butyldimethylsilane (246 mg, 2.12 mmol), and cyclohexane (2.2 ml) was photolyzed as above. Analysis indicated formation of ethoxydimethylsilane and 1-n-butyl-1,1,2,2-tetramethyldisilane in a molar ratio of 34/1.

Photolysis of I with t-butanol and n-butyldimethylsilane in n-decane. A solution of I (22.4 mg, 0.064 mmol), t-butanol (160 mg, 2.16 mmol), n-butyldimethylsilane (202 mg, 1.74 mmol), and n-decane (2.06 g, 14.5 mmol) was photolyzed as above. Analysis of the solution showed formation of t-butoxydimethylsilane [5] and 1-n-butyl-1,1,2,2-tetramethyldisilane in a molar ratio of 17.4/1 which gives $k(\text{O—H})/k(\text{Si—H}) = 14$.

Photolysis of I with ethanol and ethoxytrimethylsilane in cyclohexane. A solution of I (38 mg, 0.11 mmol), ethanol (63 mg, 1.37 mmol), ethoxytrimethylsilane (124 mg, 1.05 mmol), and cyclohexane (2.3 ml) was photolyzed as above. GLC analysis indicated formation of ethoxydimethylsilane and ethoxypentamethyldisilane [12] in a molar ratio of 61.9/1 which gives $k(\text{O—H})/k(\text{Si—O}) = 47.5$.

Photolysis of I with ethanol and ethoxytrimethylsilane in THF. A solution of I (5.3 mg, 0.015 mmol), ethanol (22.1 mg, 0.48 mmol), ethoxytrimethylsilane (179 mg, 1.52 mmol), and THF (1.7 ml) was photolysed as above. GLC analysis indicated formation of ethoxydimethylsilane and ethoxypentamethyldisilane in a molar ratio of 54.9/1 which gives $k(\text{O—H})/k(\text{Si—O}) = 174$.

Photolysis of I with t-butanol and ethoxytrimethylsilane in THF. A solution of I (9.1 mg, 0.026 mmol), t-butanol (35.5 mg, 0.48 mmol), ethoxytrimethylsilane (204 mg, 1.73 mmol), and THF (1.7 ml) was photolysed as above. Analysis showed formation of t-butoxydimethylsilane and ethoxypentamethyldisilane in a molar ratio of 41.9/1 which gives $k(\text{O—H})/k(\text{Si—O}) = 151$.

All other photolyses were run and analyzed as described above.

Acknowledgement

This work was supported by the Air Force Office of Scientific Research Grant Number 80-0006. We thank Prof. M.A. Ring for helpful discussions.

References

1 For a review of silylene chemistry, see P.P. Gaspar in M. Jones and R.A. Moss, (Eds.), Reactive intermediates, Vol. I, Wiley-Interscience, New York, 1978, p. 229—277.
2 M. Ishikawa, and M. Kumada, J. Organometal. Chem., 42 (1972) 325.
3 A. Chihi, and W.P. Weber, J. Organometal. Chem., 210 (1981) 163.
4 H.S.D. Soysa, I.N. Jung, and W.P. Weber, J. Organometal. Chem., 171 (1979) 177.
5 T.Y. Gu, and W.P. Weber, J. Organometal. Chem., 184 (1980) 7.
6 T.Y. Gu, and W.P. Weber, J. Am. Chem. Soc., 102 (1980) 6095.
7 K.P. Steele, and W.P. Weber, J. Am. Chem. Soc., 102 (1980) 6095.
8 H. Okinoshima, and W.P. Weber, J. Organometal. Chem., 150 (1978) C25.
9 M. Ishikawa, T. Takaoka, and M. Kumada, J. Organometal. Chem., 42 (1972) 333.
10 I.M.T. Davidson, F.T. Lawrence, and N.A. Ostoh, J. Chem. Soc. Chem. Commun., (1980) 859.
11 I.M.T. Davidson, and N.A. Ostah, J. Organometal. Chem., 206 (1981) 149.
12 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, and K. Shiina, J. Org. Chem., 21 (1956) 1264.
13 S.N. Vinogradov, and R.H. Linnell, "Hydrogen Bonding", Van Nostrand Reinhold Co., New York, 1971, p. 125—128.

14 A.N. Fletcher, and C.A. Heller, J. Phys. Chem., 72 (1968) 1837.
15 M. Saunders, and J.B. Hyne, J. Chem. Phys., 29 (1958) 1319.
16 U. Liddel, and F.D. Becker, Spectrochim. Acta., 10 (1968) 70.
17 D.A. Ibbitson, and L.F. Moore, J. Chem. Soc. B, (1967) 76.
18 W. Masschelein, Spectrochim. Acta., 18 (1962) 1557.
19 J.A. Riddick, and W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, 1970, p. 536—550.
20 E.E. Tucker, and F.D. Becker, J. Phys. Chem., 77 (1973) 1783.
21 Ref. 17, p. 12.
22 C.M. Huggins, and D.R. Carpenter, J. Phys. Chem., 63 (1959) 238.
23 K.P. Steele, and W.P. Weber, Inorg. Chem., 20 (1981) 1302.
24 R. West, L.S. Wilson, and D.L. Powell, J. Organometal. Chem., 178 (1979) 5.
25 R. West, L.S. Whatley, and K.J. Lake, J. Am. Chem. Soc., 83 (1961) 761.
26 E.A.V. Ebsworth, in A.G. MacDiarmid, (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 1, Marcel Dekker, New York, 1968, p. 61—65.
27 W. Adcock, G.L. Aldous, and W. Kitching, Tetrahedron Lett., (1978) 3387.
28 R. West, D.L. Powell, M.K.T. Lee, and L.S. Whatley, J. Am. Chem. Soc., 86 (1964) 3227.
29 E.F. Tucker, and E. Lippert, in P. Schuster, G. Zundel, and C. Sandorfy, (Eds.), The Hydrogen Bond, Vol. II, North-Holland, Amsterdam, 1976, p. 790—830.
30 W.v.E. Doering, and W.A. Henderson Jr., J. Am. Chem. Soc., 80 (1958) 5274.
31 I.N. Jung, and W.P. Weber, J. Org. Chem., 41 (1976) 946.
32 A.G. Sharkey Jr., R.A. Friedel, and S.H. Langer, Anal. Chem., 29 (1957) 770.
33 A. Languerre, J. Dunogues, and R. Calas, J. Chem. Soc. Chem. Commun., (1978) 272.