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TERTIARY ALCOHOLYSIS OF CHLOROSILANES VIA TETRACOORDINATE SILYLATED QUATERNARY AMMONIUM INTERMEDIATES *

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Summary

The rate-enhancing effects of tertiary amine-HCl acceptors on the alcoholysis of Ph_2SiCl_2 and $Ph_2Si(OR)Cl$ with ROH ($R = ViMe_2C$) have been studied. Relative rates greater than 10^6 for Ph_2SiCl_2 and 10^4 for $Ph_2Si(OR)Cl$ have been observed. These profoundly enhanced rates bear no relationship whatsoever to the amine basicity differences, but correlate with the nucleophilic propensities of the amines; however, this is true only if the additional assumption is made that the slow and rate-determining steps involve ionic quaternary ammonium chloride intermediates in which the nitrogen bears a tetracoordinate silicon substituent. The proposed tetracoordinate-silylated quaternary ammonium intermediates derive further credibility from a number of stable species reported previously and reviewed herein.

Introduction

Solvolytic reactions of silicon chlorides are important because of their practical use in the conversion of industrially produced chlorosilanes to commercially useful alkoxy- and acyloxy-silanes as well as the important siloxane derivatives (better known as silicones). Numerous studies during the past four decades have attempted to deduce mechanistic details of these reactions from a consideration of structure/reactivity correlations, solvent effects, and dynamic stereochemical behavior. The first such efforts were by Allen and Modena [1] who studied the hydrolysis and alcoholysis of hindered chlorosilanes such as $i\text{-}Pr_3SiCl$ in various solvents. They concluded that such reactions proceed by an S_N2 type mechanism of the following

* Dedicated to Prof. Makoto Kumada in recognition of his outstanding contribution to organosilicon chemistry.

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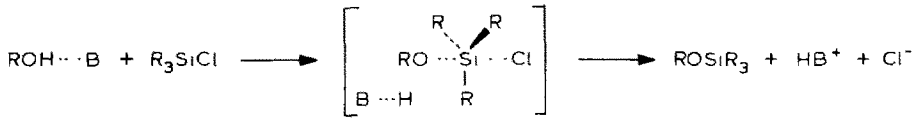
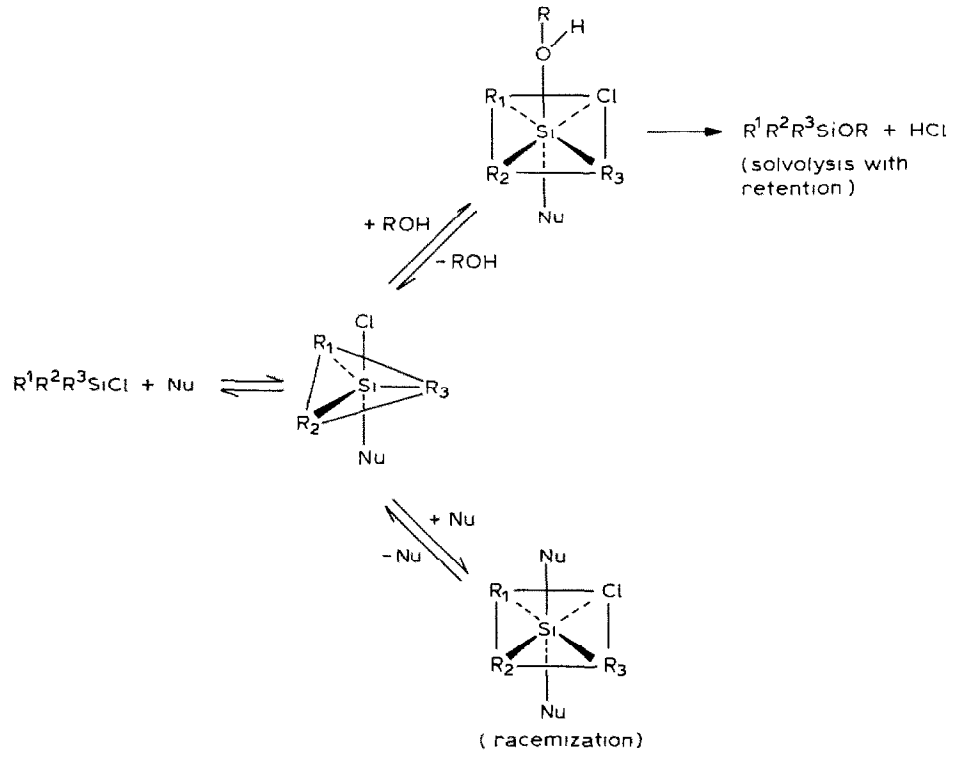
type where B can be any base such as ROH, H_2O, halide ion, etc.:

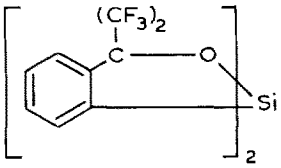


With the advent of optically active substrates, Sommer et al. [2] were able to demonstrate inversion as the overwhelmingly preferred stereochemical consequence of chloride displacement from silicon centers, unless such pathways were absolutely precluded as at bridgehead sites. There were very few exceptions reported for the preferentially invertive chloride displacement until Corriu [3,4] found that the presence of certain nucleophilic agents (e.g., DMF, HMPT, DMSO) not only afforded substantial enhancement of the solvolysis rates, but also dramatically reversed the stereochemical pathway to one of ostensible retention. He also observed enhanced rates of racemization [4], and proposed the following mechanism to account for the 1st and 2nd order relationships of the nucleophilic agents to the respective solvolysis and racemization rates:



In an attempt to differentiate between the above route for nucleophile-assisted racemization and a similar route involving ionic pentacoordinate siliconium chloride intermediates, Cartledge et al. [5] studied the kinetics of isomerization and halide exchange reactions of sila-cyclobutyl and -cyclopentyl compounds. They interpreted

their data as evidence for a mechanism involving pseudo-rotation of a pentacoordinate intermediate. However, Chojnowski et al. [6] then reported the formation of 1/1 adducts of Me_3SiBr and Me_3SiI with HMPT which they have formulated as salts involving tetracoordinate silicon centers. They suggested that Corriu's and Cartledge's data might also be rationalized in terms of repeated invertive diplacement upon tetracoordinate silicon species. This view recently received additional support from Bassindale and Stout's NMR studies [7] of the apparently ionic DMF adducts of various Me_3SiX species which were also ascribed tetracoordinate silicon structures when X was Br, I, or O_3SCF_3. Even more recently, in his recent review [8] of "frozen" transition states, Martin has suggested pseudorotation of a pentacoordinate silicon species to rationalize his observations regarding the racemization of the novel spirocyclic, compound I in the presence of added nucleophiles. It is in this



(I)

context of conflicting mechanistic views that we report our brief study of the tertiary alcoholysis of chlorosilanes.

Having had occasion to prepare $(Ph)_2Si(OCMe_2Vi)_2$, we attempted to do so via the alcoholysis of Ph_2SiCl_2 using a tertiary amine acceptor. Although some colleagues had encountered no difficulty with pyridine, we were completely unsuccessful in our presumedly parallel efforts with Et_3N as the acceptor. Even after prolonged refluxing in toluene solution, we were unable to drive the reaction beyond the monosubstituted derivative, i.e.:

$$Ph_2SiCl_2 + ROH \xrightarrow[\Delta]{\text{Toluene},Et_3N} Ph_2Si(OR)Cl + Et_3NHCl$$

$$Ph_2Si(OR)Cl_2 + ROH \xrightarrow[\Delta]{\text{Toluene},Et_3N} \text{No reaction}$$

It was speculated initially that removal of the second chlorine might require electrophilic assistance by the protonated tertiary ammonium ion, and that the conjugate acid of pyridine should be a much more effective electrophilic agent than the Et_3N^+H. However, the addition of Et_3N to the pyridine runs did relatively little to reduce the pyridine's effectiveness; i.e., even though the excess Et_3N (because of its greater basicity) precludes the presence of Pyr^+H, the reaction rate of the second alkoxylation was not greatly diminished and did in fact appear to be directly dependent upon the free pyridine base level. This system appeared not only to offer an excellent opportunity to evaluate the relative importance of basicity, nucleophilicity and steric effects on chlorosilane solvolysis with less complicated and hopefully less ambiguous reagents than those hitherto employed, but also possibly to permit a clear-cut choice between the conflicting mechanistic conclusions previously described.

Results

Conditions were selected for independently studying the two alkoxylation steps of Ph_2SiCl_2 with 2-methyl-3-buten-2-ol (vinyldimethylcarbinol) with various tertiary amines present as reactants and/or HCl-acceptors. Table 1 lists the relative rates for the first step; i.e.:

$$Ph_2SiCl_2 + ROH \xrightarrow[R_3N]{\text{Toluene}} Ph_2Si(OR)Cl + R_3N^+ \; HCl^-$$

Under these conditions (toluene solution, slight excesses of ROH and amine, 25°C) it is evident that the reaction rates are dominated by the nucleophilicities of the amine, and that steric effects are important only in so far as they determine the ease with which the amine can interact nucleophilically with the silicon center of the Ph_2SiCl_2 substrate; e.g., the large steric requirements of Et_3N obviously preclude effective coordination with Ph_2SiCl_2. This amine is functioning solely as an HCl acceptor as evidenced by the relative insensitivity of rate to Et_3N levels. Basicity is obviously unimportant as evidenced by the nearly equivalent rates with pyridine and quinuclidine despite their large difference in basicity.

The rate enhancement relative to pyridine afforded by 3,5-lutidine is presumably a consequence of increased nucleophilicity and/or basicity relating to the inductive effects of the methyl substituents, while the retardation noted with 2,6-lutidine is clearly steric in origin. These effects closely parallel those described by Brown, McDaniel and Hafliger for dissociation constants of trimethylboron with various amine Lewis bases [9]. The very large rate increase produced by the "super nucleophile" [10], 4-dimethylaminopyrine (DMAP) presumably reflects the ability of the 4-dimethylamino moiety to mesomerically delocalize the positive charge produced when the pyridyl nitrogen datively bonds to the silicon center.

TABLE 1

RELATIVE RATES FOR TERTIARY ALCOHOLYSIS [a] OF Ph_2SiCl_2

Amine	pK_B	k_1 [b]	k_2 [c,d]
Et_3N	3.36	0.06 [h]	< 0.25 [h]
Quinuclidine	3.42	90	1
4-Dimethylaminopyridine	4.3	190,000 [g]	13,300 [g]
2,6-Lutidine	7.2	9	4
3,5-Lutidine	7.8	300	100
Pyridine	8.8	100 [e]	100 [f]
N,N-Dimethylaniline	9.6	0.8	0.5
Tetramethylethylenediamine		1	< 0.5
Tetramethylguanidine		> 1000	1
HMPT		1000 [g]	100 [g]

[a] $R^tOH = ViMe_2COH$. [b] $Ph_2SiCl_2 + R^tOH \xrightarrow{k_1} Ph_2Si(Cl)OR^t + R_3NHCl$; Conditions: 5.0 g toluene, 2.2 meq. R_3N, 3.0 meq. R^tOH, 1.0 meq. Ph_2SiCl_2; room temperature. [c] $Ph_2Si(Cl)OR^t + R^tOH \xrightarrow{k_2} Ph_2Si(OR^t)_2 + R_3NHCl$; Conditions: 50 meq. R^tOH, 2.7 meq. R_3N, 1.0 meq. Ph_2SiCl_2; room temperature. [d] NOTE: k_2 values should not be compared to k_1 values because of the grossly differenct conditions employed for the 1st and 2nd alkoxylations. [e] t (50% conversion) = 20 min. [f] t (50% conversion) = 5 h. [g] Inferred from comparisons of rates obtained in presence of Et_3N with pyridine rates also in presence of Et_3N. [h] Variations in Et_3N levels had no effect on rates.

Alkoxylation of the second chlorine moiety, i.e.,

$$Ph_2Si(OR)Cl + ROH \xrightarrow{R_3N} Ph_3Si(OR)_2 + R_2N^+ HCl^-$$

is markedly slower because of the increased steric hindrance arising from the bulky presence of the first tertiary alkoxy substituent, hence the reaction conditions had to be altered to achieve suitable rates. This was readily accomplished by eliminating the hydrocarbon diluent and using the tertiary alcohol as the solvent, thus the resulting data are pseudo second order (i.e., dependent only upon amine and chlorosilane concentrations).

Under this second set of conditions, the first step is complete almost immediately after mixing for the more reactive amines, but requires about 20 minutes for 2,6-lutidine and about two and four days for dimethylaniline and triethylamine, respectively. As shown by the relative rate data in the last column of Table 1, the greatly increased steric requirements of the second alkoxylation step have placed an even higher premium upon "slenderness" in the promoting nucleophiles. Whereas quinuclidine was very similar to pyridine in the first step, it is now at least 200 times slower in the second step. The 3,5-lutidine has now lost its three-fold advantage over pyridine, and 2,6-lutidine is now fifty times slower than either pyridine or 3,5-lutidine. Thus we see the same pattern, whereby nucleophilicity is all-important, repeated in the second step, but with steric factors being even more stringent than in the first alkoxylation. The importance of charge delocalization is again underscored by the more than 100-fold rate enhancement of DMAP relative to pyridine itself.

While we have noted earlier that the addition of Et_3N to the pyridine solvolyses did "relatively little to reduce the pyridine's effectiveness", there was, however, some effect. Once it was determined that the Et_3N was functioning only as an HCl acceptor, and not as a nucleophilic promotor, we studied more carefully its effect upon the rates in the presence of pyridine. By preventing HCl consumption of the pyridine, one might have expected the addition of Et_3N to produce a modest enhancement of the solvolysis rate. Instead, however, we observed a modest retardation, i.e., instead of perhaps doubling the rate observed in the presence of pyridine, the added presence of Et_3N reduced the rate by approximately 50%. We are inclined to interpret this as evidence for the presence of some minor electrophilic assistance by pyridinium ion, the loss of which (by Et_3N neutralization thereof) off-sets the rate enhancement otherwise to be expected from maintaining the level of pyridine in its nucleophilic state. However, we are unwilling to draw any firm conclusions from such modest rate differences in systems such as these where the ionic strength is not rigorously defined and controlled. By the same token we did not even attempt to determine common ion effects on the rates, although our mechanism (presented in the Discussion section) implies rate retardation by increased chloride ion levels. We felt this would be very difficult if not futile since, in these relatively non-polar media, the chloride ion levels rapidly reach steady values governed by the tertiary ammonium chloride solubility and/or restricted ion-pair dissociation phenomena within such media. Hence our caveat regarding any attempts to interpret modest rate differences such as those just mentioned.

An additional caveat concerns the use of nucleophilic solvents such as HMPT, DMSO, DMF, etc. Unless something like Et_3N is used as an HCl acceptor, such "solvents" often result in the conversion of chlorosilanes to siloxanes, accompanied

by chlorine containing degradation products of the solvent. Since much of Corriu's work utilized HMPT as the nucleophilic promoter, we also included this solvent in our study. Under comparable conditions, and relative to pyridine, HMPT produces about an order of magnitude rate enhancement in the first alkoxylation and little or none in the second step, both comparisons having been made with Et_3N present to avoid HMPT degradation.

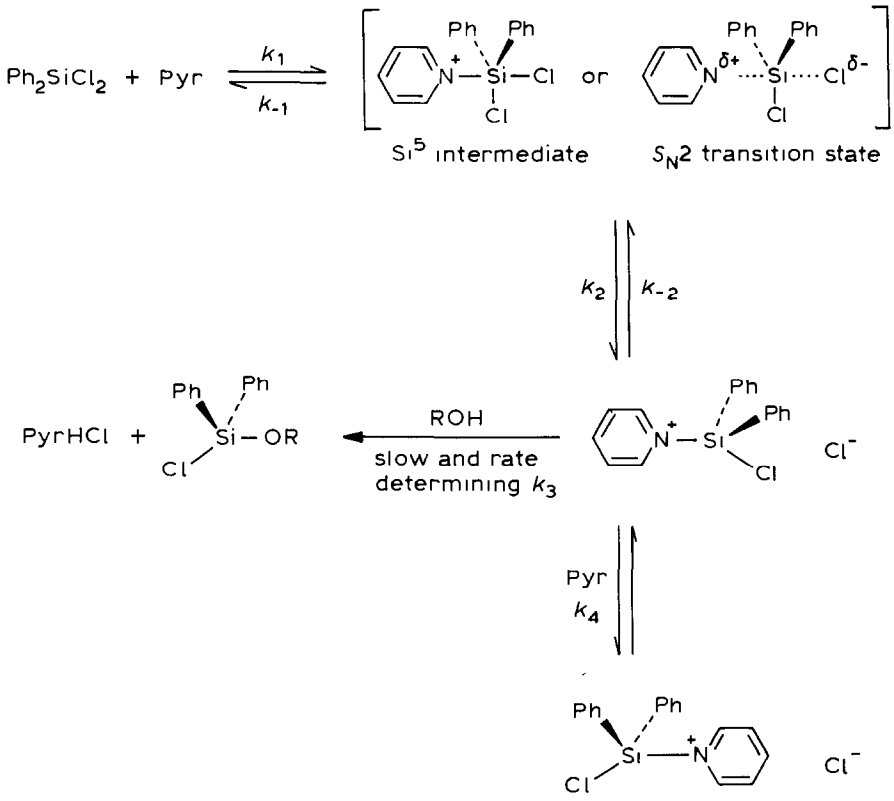
Discussion

It is apparent that the above structure/reactivity pattern is wholly at variance with the type of mechanism described by Allen and Modena [1], since for that mechanism Et_3N would have certainly been expected to be much more effective than the weaker base pyridine. Furthermore, the marked retardation noted for quinuclidine relative to pyridine in the alkoxylation of the second chlorine dramatically underscores our conclusion that an Allen and Modena type mechanism stressing basicity is definitely not involved here. It is also very apparent that sufficiently unencumbered tertiary amines are promoting chlorosilane solvolysis through some sort of nucleophilic attack by the amine on the silicon as postulated by Corriu. In our opinion, however, his conclusions that initially formed pentacoordinate silanes then react with solvolyzing agents via hexacoordinate transition states or intermediates are untenable since they essentially beg the question of the marked rate enhancements; i.e., the silicon center of a penta-coordinate adduct should be markedly less susceptible to attack by a nucleophilic solvolyzing agent than the original tetracoordinate silane for at least two very good reasons: 1. Attack at the silicon will be encumbered by five ligands instead of only four. 2. The extra-coordinate silicon will bear a formal negative charge because of the formation of an essentially dative bond with the nucleophile.

Thus, both of the above considerations would be expected to sharply retard subsequent attack by any other nucleophile. The well-known enhanced solvolytic stability of the alkoxy- and halo-silatranes [11] strongly attests to the validity of this assertion.

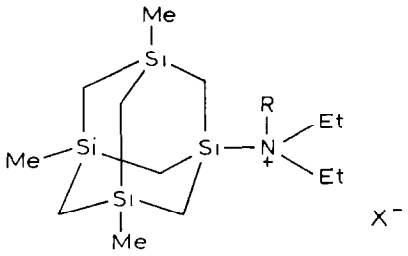
In order to explain both rate enhancement and nucleophilic dependency in the above solvolyses, we are compelled to conclude that tetracoordinate silylated quaternary ammonium chlorides are involved in the rate-determining alkoxylation reactions. The formation of these tetracoordinate silylated quaternary ammonium chloride intermediates may be preceded by the formation of a pentacoordinate silicon intermediate, however the observed kinetics do not require this, and could equally well be accounted for by a conventional S_N2 transition state model. Thus, we suggest the type of kinetic scenario shown in scheme 1 to account for our observations.

As long as k_3 and k_4 are slow relative to k_{-2}, third order kinetics of the type described by Cartledge, Corriu, and in the present work are to be expected for the solvolysis, and isomerization, and racemization reactions studied. Although our search of the halosilane solvolysis literature revealed only a few rather obscure (but highly prescient) explicit suggestions that tetracoordinate silylated onium species might possibly be involved as reaction intermediates [6,7,12], the actual demonstrable existence of several such species has previously been described, as reviewed in the next paragraph.



SCHEME 1

Tetrahedral organosilylated quaternary ammonium halides (I and Br) were first reported in 1966 by the Ebsworth [13] and Beattie groups [22] as the reaction products of halosilanes with tertiary amines. Their compounds were extremely susceptible to solvolysis and are almost immediately hydrolyzed upon exposure to even traces of moisture in the solvents or air. The 2,2′-bipyridine derivative of Ph_3SiI formulated by Corey and West as a pentacoordinate siliconium (sic) iodide [14] may actually have been a tetracoordinate silylated bipyridinium iodide, however the facts there are exceedingly unclear since subsequent crystallographic studies revealed their crystalline composition to have become (or to have been?) a hydrogen bonded 1/1 molecular adduct of Ph_3SiOH with bipyridinium iodide [14]. More recently, Hensen et al. have prepared [16] and crystallographically [17] characterized as tetracoordinate silicon structures a number of halosilane-tertiary amine reaction products, including trimethylsilylpyridinium iodide and bromide. Although they have concluded that Me_3SiCl forms no pyridine complexes, additional studies with DMAP are clearly warranted. Despite the fact that all of the above materials appear to be subject to extremely facile solvolysis, the presence of certain structural features can in some cases afford marked solvolytic stability. The first such solvolytically stable structures to be reported were the tetrasilaadamantane (Ad) derivatives of Frye and Klosowski [18] who were able to prepare hydrochloride and methiodide derivatives of Me_3Ad–NEt_2; i.e.:



(R = H, X = Cl^-, and R = Me, X = I)

The Si–N bond in the hydrochloride salt was sufficiently robust to permit recovery of Me_3Ad–NEt_2 upon neutralization of the acid with NaOH. The methiodide while also solvolytically resistant, underwent thermolysis to regenerate the starting Me_3Ad–NEt_2 and MeI. The bridgehead structural feature is not the only way to achieve solvolytically stable Si–N^+ X^- structures. Sommer and co-workers determined the pK_B values not only for Me_3Ad–NEt_2 [19] but also for t-Bu_3Si–NH_2, –NHMe, and –NMe_2 [20] using the standard method of measuring the pH at the half-neutralization point. More recently Eaborn et al. [21] have demonstrated similar solvolytic stability for $(Me_3Si)_3CSiMe_2\overset{+}{N}H_3$ Cl^-.

The above examples have been adduced to document the evidence for the credibility of our postulate that tetracoordinate silylated onium halides are indeed key, albeit transient, intermediates in the solvolysis of halosilanes. Given our earlier explanation for the solvolytic stability of the halosilatranes, one may still wonder why they do not simply ionize and thereby also undergo facile solvolysis. Although halosilatranes do indeed have a built-in nucleophile datively bound to the silicon, ionization of the halosilicon bond while maintaining the Si–N bond would require the three oxygen atoms to come forward to occupy the remaining three tetrahedral sites about the silicon. Such movement is clearly precluded by their cage structure and this would appear to be yet another reason why the halosilatranes are so solvolytically robust. We strongly suspect that our conclusions have implications for many other solvolytic situations. Therefore we hope that this paper will stimulate a re-assessment of the possible role of ionic tetracoordinate silicon intermediates not only in halosilane solvolysis reactions but in other situations such as, for instance, the novel spirocyclic racemization reported by Martin [8] which we mentioned earlier herein.

Experimental

Reagents. All of the reactants were commercially available (e.g., Aldrich Chemical Co.) and were used with no further purification other than distillation and drying over 4A Molecular Sieves where warranted. As authentic sample of the ultimate reaction product, $Ph_2Si(OCMe_2Vi)_2$, was prepared by the base-catalyzed solvolysis of Ph_2SiH_2 (from Petrarch Systems, Inc.) with $ViMe_2COH$: bp 168 °C (8 mmHg), NMR (60 MHz) (CCl_4) δ (ppm): 1.3 s, 12H, $C(CH_3)_2CH{=}CH_2$); 4.8–6.3 m, ABX pattern, 6H, $C(CH_3)_2CH{=}CH_2$); 7.2–7.8 m, 10H, C_6H_5).

Reaction progress during the chlorosilane solvolyses was monitored by periodic GLC analysis using a Hewlett–Packard Model 5840A Gas Chromatograph fitted with a 25m × 0.20 mm ID fused silica capillary column employing an OV-1

(polydimethylsiloxane) stationary phase, flame ionization detector, and a 18835B capillary inlet system. The Ph_2SiCl_2 and $Ph_2Si(OCMe_2Vi)_2$ peak identities were verified by co-injection with authentic materials, while the $Ph_2Si(Cl)OCMe_2Vi$ intermediate was reasonably assumed to be the only major intervening peak to appear during these studies. A material of identical elution time resulted in high yield from the dibenzoyl peroxide catalyzed reaction of CCl_4 with authentic $Ph_2HSiOCMe_2Vi$, further confirming this peak assignment; i.e.

$$CCl_4 + \underset{\underset{H}{|}}{Ph_2SiOCMe_2Vi} \xrightarrow[R^{\cdot}]{} \underset{\underset{Cl}{|}}{Ph_2SiOCMe_2Vi} + HCCl_3$$

Relative solvolysis rates were derived by simply comparing reaction times required for similar %-conversions (inferred from GLC peak areas) under specified reaction conditions. As indicated below, conditions were selected to permit the individual alkoxylation steps to be studied independently. Conditions for alkoxylation of only one of the Ph_2SiCl_2 chlorines employed toluene as the reaction medium: thus Ph_2SiCl_2 (1.0 mmol) was added to toluene (5.0 g) solutions of the tertiary amine (2.2 mmol) and the vinyldimethylcarbinol (3.0 mmol) in 20 ml septum sealed vials. Under these conditions, only traces of the dialkoxylated derivatives are observed (except in the case of the "super nucleophile", DMAP). Conditions for alkoxylation of the second chloro substitutent employed excess tertiary carbinol in place of the toluene diluent: thus Ph_2SiCl_2 (1.0 mmol) was added to vinyldimethylcarbinol (4.3 g; 50 mmol) solutions of the tertiary amines (2.7 mmol). Under these conditions, the first alkoxylation is almost instantaneous (except for the poorest nucleophiles Et_3N and $PhNMe_2$) but the subsequent progress of the second step is easily monitored, except again in the case of DMAP; it was necessary to use much lower amounts of DMAP to permit measurements of rates for both single (0.03 mmol) and double (0.17 mmol) alkoxylation conditions. In these instances Et_3N (2.2 mmol) was used as HCl acceptor to minimize neutralization of the nucleophile.

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