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Sterically hindered silyl perchlorates: synthetic and mechanistic studies

Christopher Raymond Tully
Iowa State University

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SYNTHETIC AND MECHANISTIC STUDIES.

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Sterically hindered silyl perchlorates:
Synthetic and mechanistic studies

by

Christopher Raymond Tully

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry

Major: Organic Chemistry

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In Charge of Major Work

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Iowa State University
Ames, Iowa

1977

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ABSTRACT

Sterically hindered silyl perchlorates were initially examined in hopes of finding evidence of a trivalent cationic silicon species or silylenium ion. Although our studies failed to uncover solid evidence of ionization, it was discovered that these compounds had unique synthetic potential as silylating agents. All silyl perchlorates examined to date have been found to be highly reactive, relative to their halogenide counterparts, toward nucleophilic agents.

t-Butyldimethylsilyl perchlorate offers a significant improvement over the widely used t-butyldimethylsilyl chloride in that it reacts readily with tertiary alcohols. The di-t-butylmethylsilyl moiety, a heretofore unknown alcohol blocking group, was also examined and found to be dramatically more resistant to acidic and basic solvolysis than the t-butyldimethylsilyl group. The route to prepare the tri-t-butylsilyl-perchlorate, although successful, was found to be too arduous for the group to be of any synthetic utility in the protection of alcohols.

Silyl perchlorates were found to react readily with carbanions. Di-t-butylfluorenyl silane prepared in this manner was used as a precursor to a sterically and electronically stabilized silene; however, attempts to effect the conversion failed. The reaction of silyl perchlorates with carbanions is of limited utility in the synthesis of sterically hindered

organosilanes since it was found that reaction of di-t-butylsilyl perchlorate with a carbanion containing hydrogens beta to the anionic center, such as t-butyllithium resulted in reduction of the perchlorate group rather than alkylation at silicon.

All silyl perchlorates examined, save the tri-t-butyl, were found to be readily available through a hydride exchange reaction between the silyl hydride and trityl perchlorate. The kinetics of this and other similar hydride exchange reactions involving trityl fluoroborate and hexafluoroantimonate were examined and the reaction was found to be second order overall, first order in silane and first order in trityl cation. The reaction was demonstrated to be anion independent with these ionic trityl salts, thus suggesting that the reaction may proceed through a silylenium ion. Rather anomalous results were obtained with trityl bromide suggesting that perhaps a free radical chain reaction mechanism may be involved.

INTRODUCTION

It was perhaps inevitable that someone would eventually study sterically hindered silyl perchlorates, though initial work on silyl perchlorates was somewhat misleading. In preparing silicon compounds by nucleophilic attack of some functional group on silicon, silyl halides are generally reactive enough toward nucleophilic agents to provide the desired results; however, when building sterically hindered systems normal methods often prove unsatisfactory due to decreased reactivity of the hindered silyl halide. A natural solution to the problem would be to place a better leaving group on silicon and since covalent organic perchlorates are rare one might have expected perchlorate to be at the least an excellent leaving group for silicon. It is this solution to a long-standing problem which is examined in this thesis; however, initial interest in silyl perchlorates was not in this direction, but in hopes of generating a trivalent, cationic silicon species or silylenium ion.

The search for silylenium ions is also a long-standing problem and as yet no direct evidence for the existence of a trivalent cationic silicon species in solution has been published. This has puzzled chemists for many years because the greater electropositive nature of silicon suggests that silylenium ions should be more thermodynamically stable than

the corresponding carbenium ions. The historical section will provide a brief review of the classic works on this subject.

This work is intended to be only an introduction to the chemistry and synthetic applications of silyl perchlorates and it is hoped that other possible uses for this interesting class of compounds will be investigated.

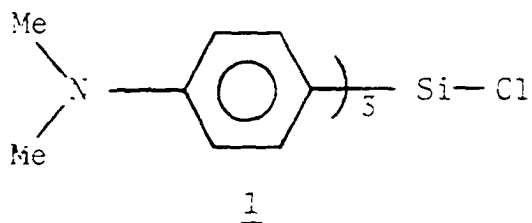
HISTORICAL

The initial thrust of this work was a quest for the long sought after silylenium R_3Si^{\oplus} ion¹. While in organic chemistry carbenium ions are quite commonly encountered as intermediates and many stable salts thereof have been isolated, to date there exists no direct evidence for the existence of a trivalent cationic silicon species, either as an isolable salt or even as an intermediate in solution. This fact has puzzled chemists for years because the greater electropositive nature of silicon relative to carbon suggests that silylenium ions should be more thermodynamically stable than corresponding carbenium ions. Since a complete review of the literature on this subject is not within the scope of this work (such reviews are already in print (1,2)), only a few of the classic works most pertinent to this dissertation will be mentioned to bring the reader at least somewhat up to date.

A number of early workers attempted to observe silylenium ions by imitating the structures, reactions, and physiochemical methods of observation which had been used to establish the presence of carbenium ions (1). An example of this type of work is that of Wannagat and Brandmair (3,4).

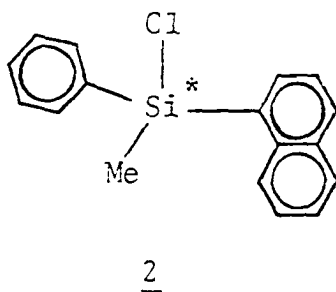
¹Although the cation R_3Si^{\oplus} is often referred to as a silicenium ion, if a protonated carbene is to be called a carbenium ion a protonated silylene, R_3Si^+ , should be named a silylenium ion.

They prepared the silicon analogue (1) of the highly stable carbocation, "crystal violet", but found that it behaved

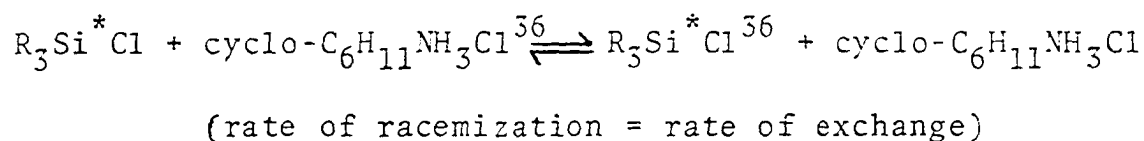


as a covalent compound (conductivity, IR spectra, X-ray diffraction, chemical behavior, etc.). Also, Wannagat and Liehr (5) were the first to prepare silyl perchlorates but were disappointed to find them to be covalent perchloric esters (this work will be scrutinized more closely in the results and discussion section).

After early failures to directly observe stable silylenium ions, investigators began taking more subtle approaches to the problem by trying to find evidence that silylenium ions did at least have a fleeting existence as reaction intermediates. Without a doubt the most extensively studied reaction which might involve a silylenium cation is the racemization of optically active halosilanes. Sommer (6) has shown that when optically active α -NpMePhSiCl (2) is



dissolved in solvents such as benzene or chloroform, there is no change in optical activity, but in solvents of high dielectric constant such as acetonitrile or nitrobenzene there is immediate loss of optical activity. This result was interpreted by invoking an ionization to an intimate or solvent-separated ion pair. Another observation (7) which was explained by an ionization step was that racemization of 2 in chloroform was promoted by addition of halide salt and that racemization occurred at the same rate as $\text{Cl} \rightleftharpoons \text{Cl}^{36}$ exchange. This, of course, is half of what would be expected



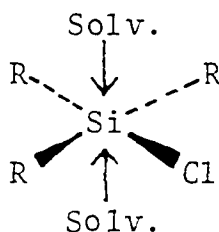
by a $\text{S}_{\text{N}}2$ type process. It was also observed that the rate of this salt-induced racemization was relatively insensitive to variation in the halide ion component of the salt. Sommer et al. (7) concluded that the data suggested an ionization or $\text{S}_{\text{N}}1$ -Si mechanism involving salt-promoted formation of silylenium ion pairs in the rate-controlling step and the rapid exchange reaction takes place equally fast by retention or inversion reactions of the silylenium ion pairs.

Further investigation showed that the conclusions of Sommer et al. (7) were premature and incorrect. Grant and Prince (8,9) found that the initial observation of equality of exchange and racemization rates was a unique case - a

misleading coincidence. In acetone-dioxane the racemization rate is double that of exchange (8) and in benzene the exchange rate is 40-80 times the racemization rate (9).

These results can be explained by two competing exchange processes, one with retention, the other with inversion, where changing the solvent drastically affects that competition.

Corriu et al. (10) discovered that the solvent-induced racemization reported by Sommer et al. (7) was second order with respect to the racemizing solvents and that the key factor in racemization was the nucleophilic power of the solvent and not the dielectric constant. The best racemizing solvents were HMPA, DMF, and DMSO, but relatively low polarity solvents such as ethers and esters were also generally able to cause racemization. This is best explained by solvent interaction to form the symmetrical complex shown below from which racemization is already established. A

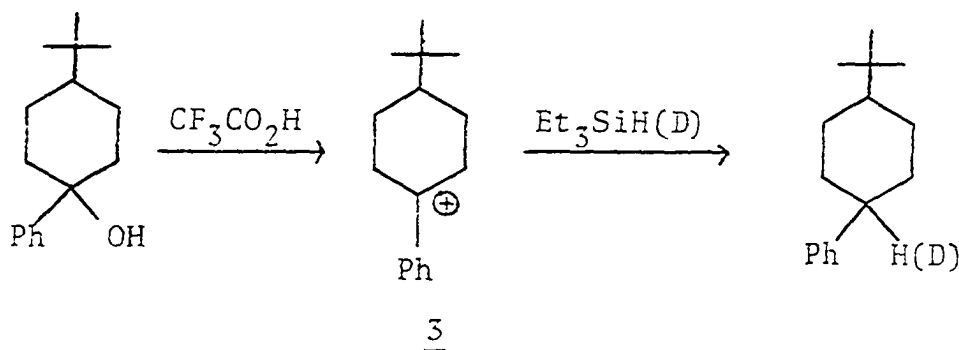


number of complexes of this type involving halosilanes are known (11). Carre et al. (12) examined the reaction with a series of compounds and found the racemization was slowed

by increasing steric bulk which is opposite to the effect observed in carbenium ion formation.

Eventually, Sommer et al. (13) also provided evidence against the S_N1 -Si mechanism by showing that replacing the phenyl on 2 with perfluorophenyl produced an increase in the rate of racemization which is consistent with the work of Corriu et al. (10) and their explanation of the reaction but not with an S_N1 -Si mechanism.

Another reaction which might involve a silylenium ion involves silyl hydrides which undergo one typical reaction of their carbon analogs, and that is hydride abstraction by a carbocation. Carey and Tremper (14) have extensively investigated this reaction using trifluoroacetic acid to generate carbenium ions from alcohols and olefins. For example, 4-t-butyl-1-phenyl cyclohexyl cation (3) in the presence of triethylsilane produces good yields of the corresponding hydrocarbon. Hydride abstraction from silicon

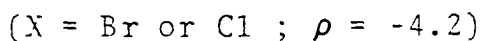
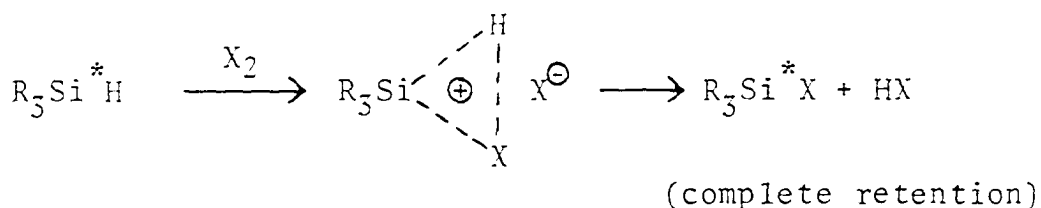
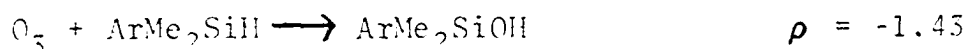
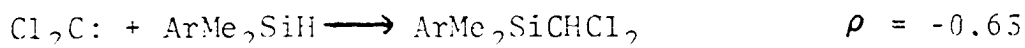


was proven by using deuterated silane which yielded deuterated hydrocarbon.

Carey and Hsu (15) examined the kinetics of this reaction using a series of substituted triarylsilanes and substituted aryldimethylsilanes to find ρ values of -1.87 and -1.01, respectively. By way of comparison, the ρ value for the insertion of dichlorocarbene into aryldimethylsilanes (16)

$$\rho(\text{Ar}_3\text{SiH}) = -1.87 \qquad \rho(\text{ArMe}_2\text{SiH}) = -1.01$$

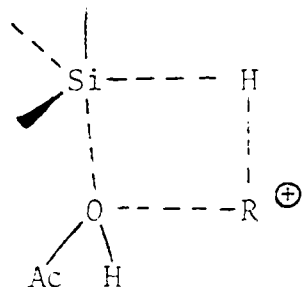
is -0.63, while ρ for the ozonolysis of aryldimethylsilanes has been reported as -1.43 (17). For the bromination and chlorination of trialkylsilanes (18) the ρ value is -4.2.



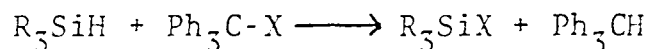
Since complete retention of stereochemistry (19) is observed, it is unlikely that a silylenium ion is involved even though the reaction has a relatively large negative ρ value.

Thus Carey and Hsu (15) believed that their observed ρ values were too small to be consistent with the formation of a silylenium ion. They favored a four-centered

intermediate of the type which had been proposed earlier by Corey and West (20).

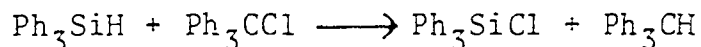


Corey and West (20) had examined another very interesting exchange reaction. They discovered that triphenylmethyl (trityl) halides and silyl hydrides undergo halogen-hydride exchange when dissolved in a variety of solvents.



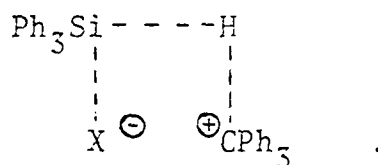
They found that the reaction is fast in good ionizing solvents such as nitrobenzene and methylene chloride and slow in benzene. It might be surprising to see methylene chloride referred to as a good ionizing solvent, but Evans et al. (21) have found that partially chlorinated ethanes promote the dissociation of trityl halides much better than would be expected on the basis of their dielectric constants.

Corey and West (20) examined the kinetics of the reaction of triphenylsilane and trityl chloride in benzene and found first order dependence on both trityl halide and silyl hydride. The reaction was monitored by following the

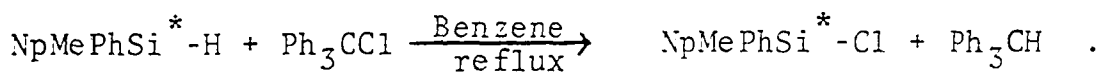


$$\begin{aligned} \text{rate} &= k_2 [\text{Ph}_3\text{SiH}] [\text{Ph}_3\text{CCl}] \\ \text{(in benzene)} \end{aligned} \quad k_2 = 2.3 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1} @ 25^\circ$$

infrared absorption bands of Si-H at 2150 cm^{-1} and of C-Cl at 900 cm^{-1} . They proposed a mechanism involving a four-centered transition state:



Strong support for this mechanistic picture was given by Austin and Eaborn (22) when they reported the high stereospecificity observed when the reaction is carried out with α -NpMePhSi-H:



(at least 95% retention)

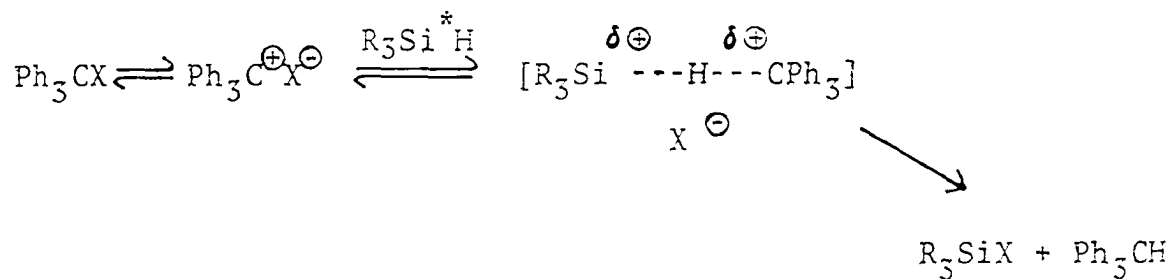
Sommer and Bauman (23) examined the stereochemistry of this reaction and that of trityl bromide in greater detail. They followed the rate of racemization polarimetrically and the rate of destruction of silyl hydride by infrared. The results of their studies are shown below:



$$\text{rate} = k_2[\text{R}_3\text{SiH}][\text{Ph}_3\text{CX}]$$

X	Solvent	$k_2\text{M}^{-1}\text{sec}^{-1}$	Stereochemistry(%)
Br	HCCl_3	1.6×10^{-4}	23 inv., 77 rac.
Cl	HCCl_3	5.4×10^{-5}	38 inv., 62 rac.
Br	PhH	---	11 ret., 89 rac.
Br	H_2CCl_2	5.5×10^{-4}	100 rac.
Cl	H_2CCl_2	1.3×10^{-4}	100 rac.

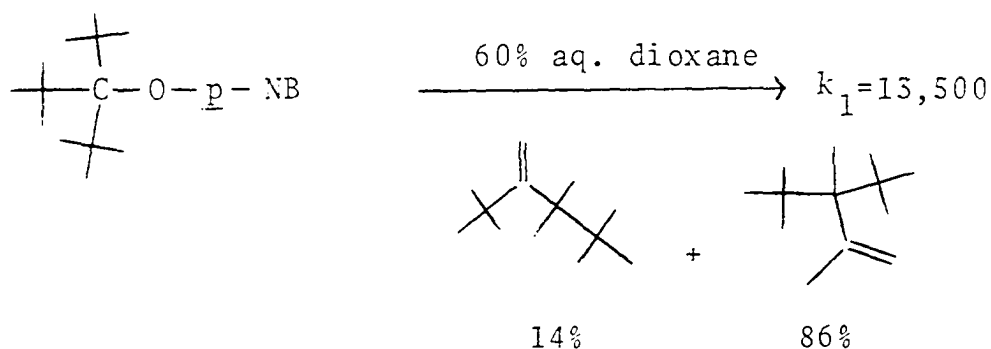
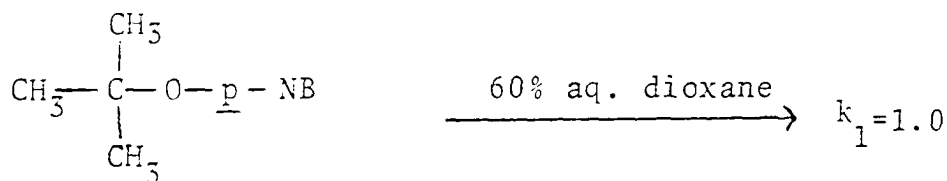
They were surprised to find that the stereochemistry of this reaction is extremely solvent dependent and that indeed both chloride and bromide gave complete racemization in methylene chloride. But presumably since the reaction rates were not anion independent, Sommer and Bauman (23) did not propose a completely formed silylenium ion intermediate. Another factor which likely caused them to be cautious was that earlier claims (6,7) of such an intermediate were refuted rather forcefully (8-10,12). Sommer and Bauman (23) proposed an intermediate where silicon-hydride bond breakage was almost complete before silicon-halide bond formation began, thus allowing attack from either the rear or front of silicon to provide racemization.



This is how the situation for this reaction stood for several years until the recent work of Corey (24) and Corey, Gust and Mislow (25). Their work is so intimately involved with this dissertation that it will be described in the results and discussion section.

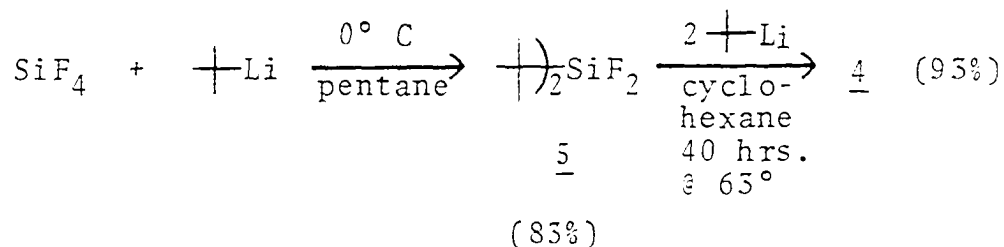
RESULTS AND DISCUSSION

This work began in an examination of tri-t-butylsilyl perchlorate. We were interested in the tri-t-butylsilyl system because we felt it offered an excellent opportunity for another attempt to observe the elusive silylenium ion. Bartlett and Tidwell (26) had examined the analogous tri-t-butyl carbon system and observed a tremendous steric acceleration of ionization in the solvolysis of the p-nitrobenzoate esters of t-butanol and tri-t-butylcarbinol. We felt that if tri-t-butylsilyl perchlorate could be prepared it might exhibit some rather interesting chemical behavior.



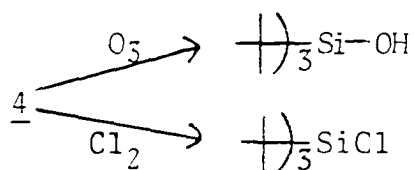
The parent compound tri-t-butylsilane (4) or any derivative thereof had eluded silicon chemists for years until recently when three groups independently developed methods

simply bubbling silicon tetrafluoride gas through the commercially available solutions of t-butyllithium in pentane to give clean, high yields of 5. t-Butyllithium in pentane is then added to a solution of 5 in cyclohexane and the



pentane is removed by distillation until the vapor temperature is 63° and then the mixture is refluxed for 40 hours to give 4 in high yield.

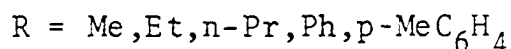
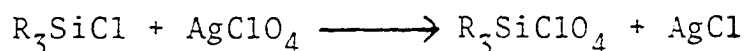
They then studied the reactivity of 4 under a variety of conditions finding that it was readily ozonized and chlorinated. They found that hydrolysis of 4 in alkaline,



aqueous ethanol was slow relative to triethylsilane, but the magnitude of the steric effect was in line with that of previously observed systems. In contrast to the observed facile chlorination of 4, fluorination with standard fluorinating agents failed. The silane was inert toward HF in polar and non-polar solvents, as well as toward PF₅. Antimony

pentafluoride, a reagent which normally causes violent decomposition of organosilicon compounds, fluorinated 4 smoothly and quantitatively at room temperature when dissolved in hexafluorobenzene. Tri-t-butylsilyl fluoride was found to be unreactive toward LAH in ether at 25°C, but reduction back to 4 was complete and quantitative within 20 hours in refluxing THF.

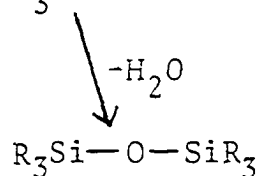
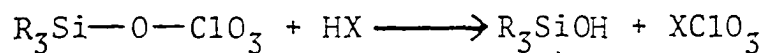
Silyl perchlorates were first prepared some twenty years ago by Wannagat and Liehr (5) by the reaction of silyl chloride with silver perchlorate. They were also searching



for a silylenium ion and they felt that they could differentiate between a covalent or ionic silyl perchlorate by examining the products of solvolysis. If the perchlorate was



or

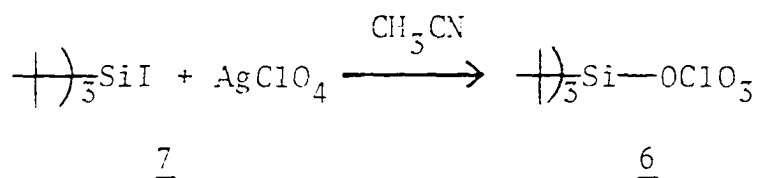


ionic then they expected the product with the attacking

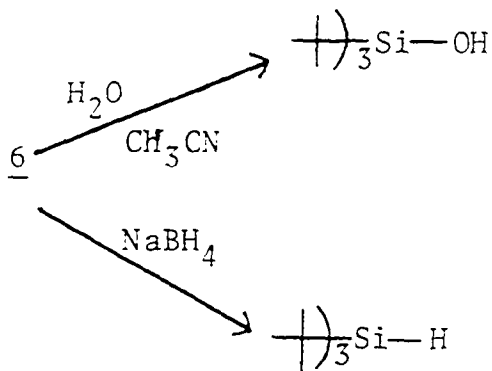
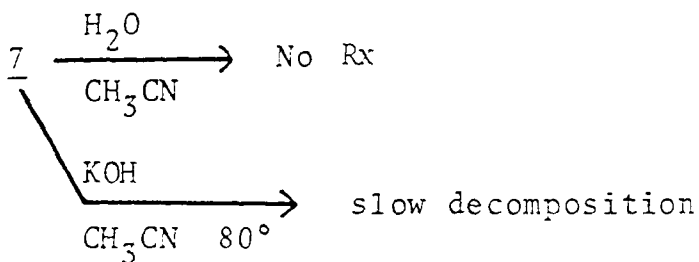
nucleophile bound to silicon, if covalent, then the product should be silanol or siloxane.

When reactions were run in benzene on the triarylsilyl-perchlorates with water, methanol, or ammonia, only disiloxanes were obtained and no methoxysilanes or aminosilanes were found. Thus their reasoning led them to believe that silyl perchlorates were covalent esters.

We found that indeed we were able to prepare tri-t-butylsilyl perchlorate (6) from the iodide 7 and silver perchlorate. Perchlorate 6 was found to be a white, sublimable



solid which decomposed at approximately 150°. The iodide (7) itself was rather interesting in that it was totally inert toward water while all previously prepared silyl iodides are instantly hydrolyzed by water. In fact it decomposed only slowly in hot, concentrated KOH in acetonitrile. In dramatic contrast the perchlorate (6) is instantly hydrolyzed by water. In addition, while halo- and alkoxysilanes are resistant to borohydride reduction (30), 6 is instantly reduced to 4 by NaBH₄ in diglyme and this was not consistent with earlier work on silyl perchlorates. Wannagat and Liehr (5) would have expected tri-t-butylsilanol or



4

disiloxane as the reduction product. Another interesting observation was that perchlorate 6 was much more soluble in the highly polar solvent acetonitrile than in hexane - exactly opposite to the solubility behavior of iodide 7.

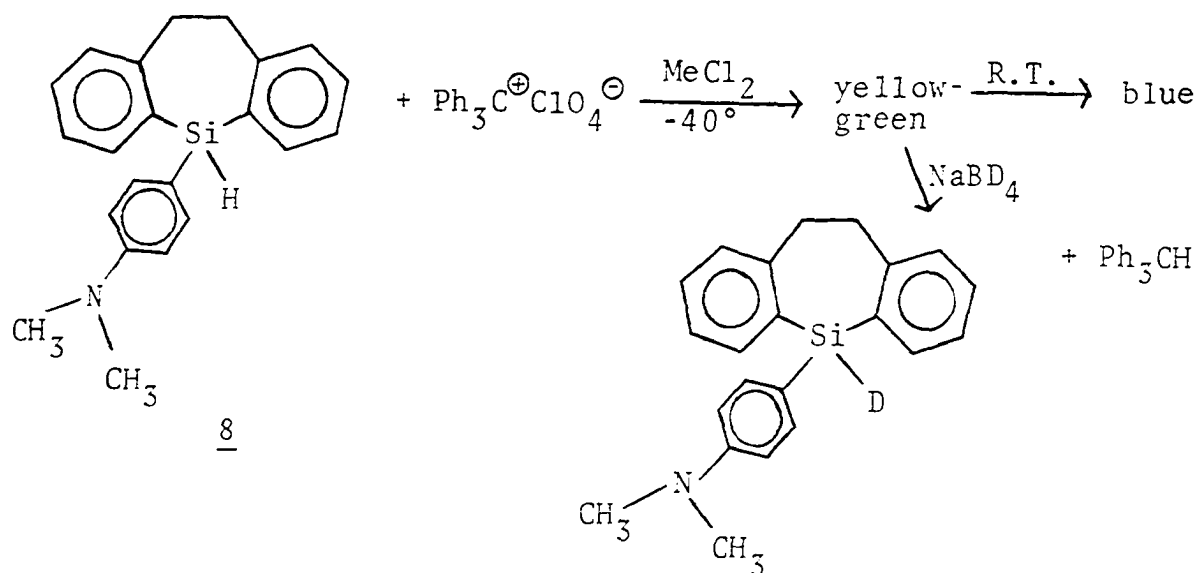
We then attempted to find spectroscopic evidence that we were dealing with an ionic silyl perchlorate and had prepared the first silylenium ion. The results of carbon-13 and silicon-29 nmr spectroscopy are shown below.

$\overset{+}{\text{Si}}\text{I}$	$\overset{+}{\text{Si}}-\text{OCIO}_3$	$\text{Et}_3\text{Si}-\text{OCIO}_3$
<u>7</u>	<u>6</u>	---
<u>C-13</u> : (CDCl_3) 24.5	(CD_3CN) 23.2	---
<u>Si-29</u> : (CDCl_3) 47.9	29.33	45.6

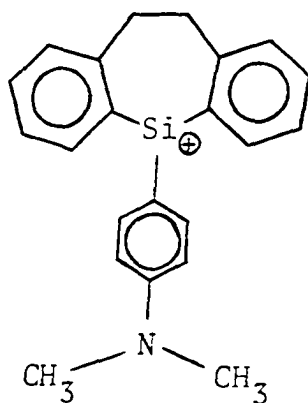
(All chemical shifts relative to TMS)

For carbon bound to silicon, the carbon-13 chemical shift of 7 is downfield from that of 6. This is exactly opposite to what might be expected if 6 were ionized, for presence of a cationic center causes downfield shifts in the nmr spectra of organic compounds. Likewise, the silicon-20 chemical shift of triethylsilyl perchlorate, a compound we have to reason to believe ionic, is well downfield of 6. Again exactly opposite to what might be expected if 6 existed as a silylenium ion. Thus the spectroscopic evidence indicated 6 to be a covalent material, although it does not rule out the possibility of an equilibrium process.

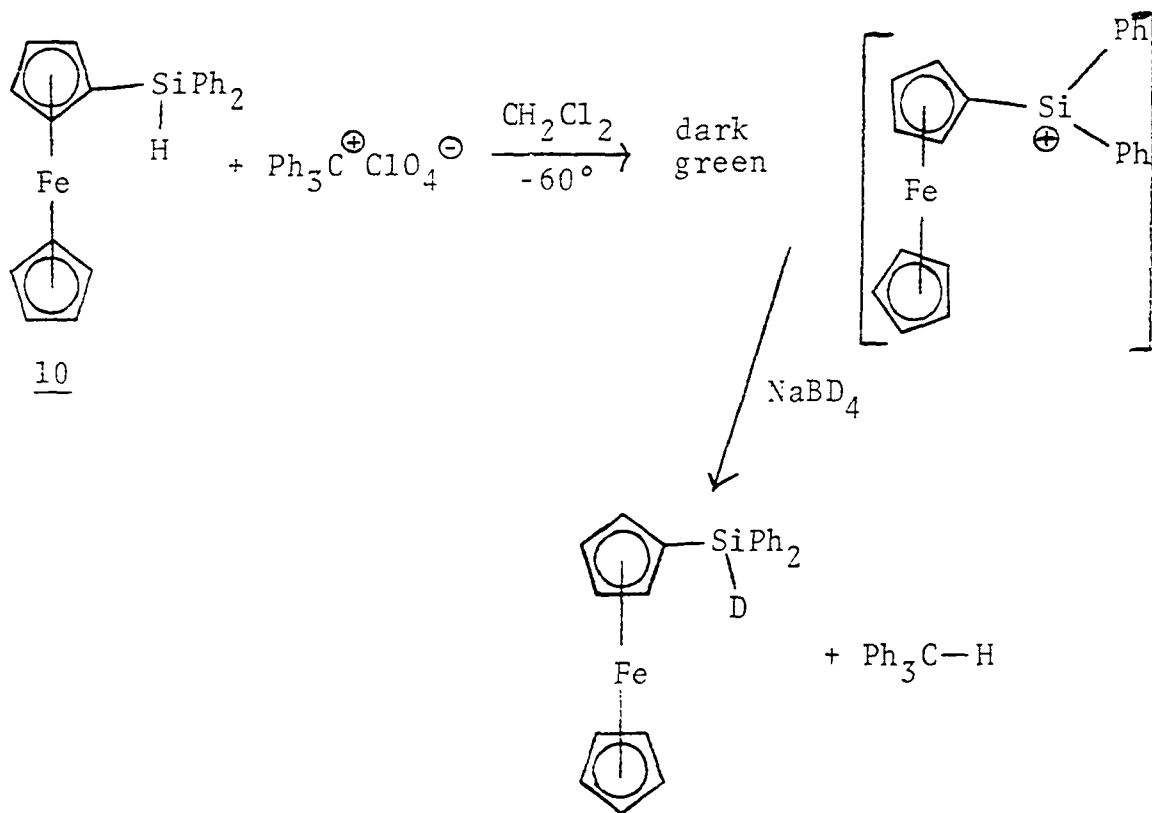
During the progress of this work, two reports (24,25) had appeared involving silyl perchlorates in which the authors claimed to "provide prima facie evidence for the generation of a silicenium ion in methylene chloride at low temperatures". Corey (24) examined silane 8, whose carbon analog is known to produce an extremely stable cation, and found that when



treated with trityl perchlorate in methylene chloride at low temperatures, a yellow-green solution was produced, which upon warming turned a brilliant blue-green solution from which no identifiable organo silicon products could be isolated. When the cold, yellow-green solution was quenched with sodium borodeuteride, work-up afforded high yields of deuterated silane and non-deuterated triphenylmethane. Corey (24) claimed that these experiments indicated that the cold, yellow-green solution contained cation 9.

9

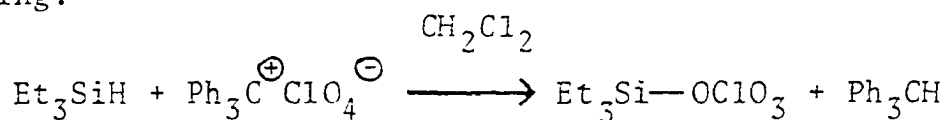
Shortly after this a similar report appeared by Corey, Gust and Mislow (25) concerning the ferrocenyl silane 10. Again treatment of the silane with trityl perchlorate in methylene chloride at low temperatures produced a highly colored solution. Quenching this cold, dark green solution



with borodeuteride afforded deuterated silane and non-deuterated triphenylmethane. This work was claimed to be another generation of a silylenium cation in solution.

We were skeptical of these claims for several reasons and felt that there were other explanations for the observed

phenomena. First, several exchange reactions involving silyl hydrides have been previously investigated and the generation of silylenium ions was not demanded (see historical section). We felt that it was likely that this new exchange reaction of silyl hydrides was a general reaction of silanes and indeed we have found that all silyl hydrides attempted to date, save the most highly hindered for which the reaction is slower, react with trityl perchlorate in methylene chloride to instantaneously decolorize the solution and afford triphenylmethane and the silyl perchlorate. For example, triethylsilane reacts with trityl perchlorate to produce triphenylmethane and triethylsilyl perchlorate, both in essentially quantitative yield. Thus the observation that both 8 and 10 react with trityl perchlorate is hardly surprising.

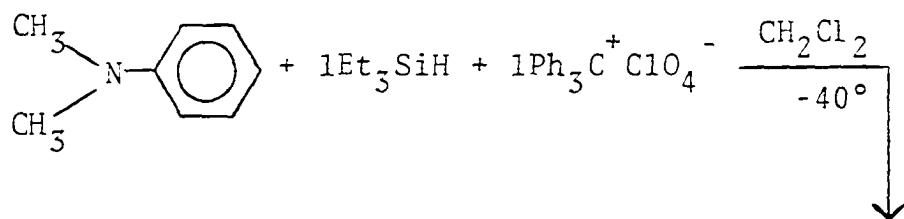


Secondly, since we found 6 to be reduced readily by borohydride, yet spectroscopic evidence indicated the material to be covalent, we felt that reduction of silyl perchlorates by borohydride might also be a general reaction. Indeed we have found that triethylsilyl perchlorate reacts immediately and quantitatively with sodium borohydride to afford triethylsilane, under similar conditions to those reported in references 24 and 25. Therefore formation of deuterated

silanes from reduction of any silyl perchlorate, whether ionic or covalent, by sodium borodeuteride is to be expected.

Lastly we had to deal with the colors generated by the reactions of trityl perchlorate with 8 and 10 in methylene chloride solution. Since in all cases investigated by us, including triphenylsilane, the reaction of silyl hydride and trityl perchlorate produced no color whatsoever, we suspected the dimethyl amino function of 8 to be the culprit in that case. Indeed it was discovered (31) that N,N-dimethylaniline produces a deep green color when mixed with trityl perchlorate in methylene chloride. Further addition of trityl perchlorate turns this solution a deep blue. The aromatic ring is not necessarily involved in this reaction as triethylamine produces a deep violet solution with trityl perchlorate in methylene chloride. The reaction, or lack thereof, between trityl salts and tertiary amines has been a subject of some controversy (32). We did not attempt to resolve this question, but we do feel that this amine-trityl interaction could account for the colors reported in reference 24. Perhaps the color reported in reference 25 can be explained by an electron transfer to trityl ion as it was discovered (31) that addition of trityl perchlorate to a methylene chloride solution of ferrocene itself instantly yields a deep green solution which presumably involves the green ferrocenyl cation (33).

Since one can mimic the color-producing reactions (24,25) without the presence of silyl perchlorate, the crucial question is then can silyl perchlorates be prepared independently from, but in the presence of the colored species. This question was dealt with (31) by reacting trityl perchlorate with a methylene chloride solution containing one equivalent of both triethyl silane and N,N-dimethylaniline to find that the color-forming reaction did not interfere appreciably with consumption of triethyl silane by trityl perchlorate. It is important to note that all the colors observed in these

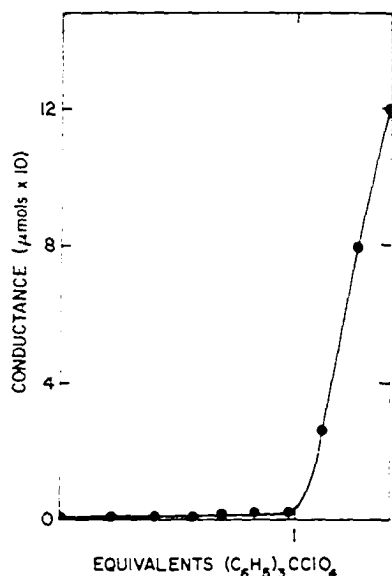


blue-green color, but
 Et_3SiH was consumed
 (monitored by ir)

systems are instantly dissipated by addition of sodium borohydride.

In summary, while it is still possible that silanes 8 and 10 do form silylenium ions, all of the evidence thus far presented (24,25) can be reproduced with systems for which there is no particular reason to presume silylenium ion involvement.

Well after this work was submitted for publication (34), it was learned that Lambert and Sun (35) and Bickart et al. (36) had each independently arrived at similar conclusions. The work of Lambert and Sun (35) was particularly interesting because of their choice of substrates for the trityl exchange reaction. It was their opinion that if one were attempting to stabilize a silylenium ion, carbon substituents might not be the best choice because "carbon is more electronegative (2.55) than silicon (1.90), so that a carbon substituent automatically destabilizes a silicenium ion inductively". They expected inductive effects to be dominant since "p -p overlap between carbon and silicon is considerably poorer than between carbon and carbon because of the differences in orbital dimensions". They felt that silyl substituents would be better at stabilizing silylenium ions. They examined the series R_3SiH , R_3SiR_2SiH , and $(R_3Si)_3SiH$ in the trityl perchlorate-hydride exchange reaction. All silanes examined were found to behave similarly under the hydride exchange conditions, all gave deuterated silanes when quenched with borodeuteride, and no spectroscopic (nmr) evidence for silylenium ion formation was observed. Conductance studies were undertaken and the results are reproduced below.

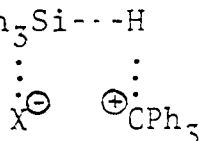


The conductance of a solution of tris(trimethylsilyl)silane in CH_2Cl_2 at $-20^\circ C$. as a function of added triphenylmethyl perchlorate.

Thus conductance showed no hint of ionization for silyl perchlorate and Lambert and Sun (35) concluded that the previous reports (24,25) of the formation of silylenium ions were based on insufficient evidence.

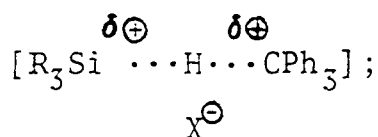
We decided to examine the kinetics of this trityl perchlorate-silyl hydride exchange reaction. Corey and West (20), in work described in the historical section, had examined the trityl halide-silyl hydride reaction and found it to proceed most readily in moderate ionizing solvents such as methylene chloride. Qualitative observations also indicated that the reaction rate increased for the series of halides: $Ph_3CCl < Ph_3CBr < Ph_3CI$. They concluded that their evidence

was "...consistent with the hypothesis that carbonium ions are intermediates in the reaction". Corey and West (20) proposed that a trityl ion pair attacked silicon via a four-centered transition state:



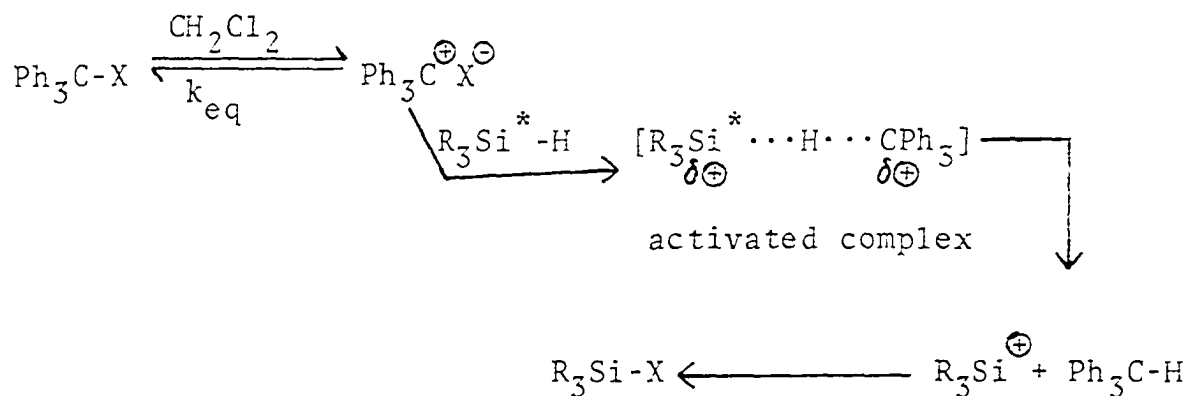
Strong support for this mechanistic picture was provided by Austin and Eaborn (22) when they reported that the reaction of α -NpMePhSiH proceeded with retention of configuration in benzene.

Sommer and Bauman (23), as described in the historical section, had examined the stereochemistry of the reaction and observed total racemization in the formation of the silyl halide using both Ph_3CCl and Ph_3CBr in methylene chloride. They proposed a similar transition state:



and in their words, "In this situation, Si-H bond breakage might be somewhat complete before the Si-X bond begins to form, allowing attack from the front or from the rear of silicon to occur with about equal probability". There is some speculation as to the reasons for this remarkable equivocation in the historical, but it is possible that through some coincidental interplay of steric and electronic factors that collapse of such a transition state could occur by front or

backside attack with equal probability in the case of one halide ion; however, in changing to a different halide ion we consider it highly improbable that a new and different coincidental interplay of steric and electronic factors would develop. We felt that the published evidence is consistent with and more plausibly explained by the following mechanistic picture:



An assumption which is basic to such a picture is that the difference in rates of reaction for different trityl halides is accounted for by increasing amounts of ionization (increasing $k_{\text{eq}}\text{'s}$) in going from Ph_3CCl to Ph_3CBr to Ph_3CI . The novelty of this picture is that the halide ion is not involved in the transition state and the silylenium ion is formed. It would seem that this is the most plausible explanation for the stereochemical results observed in methylene chloride (23).

One test of this picture would be to find the respective $k_{\text{eq}}\text{'s}$ for Ph_3CCl and Ph_3CBr and determine if the difference

in rates observed for the chloride and bromide (23) is superficial:

$$\text{observed rate} = k_2' [\text{Ph}_3\text{C-X}] [\text{R}_3\text{Si-H}];$$

but if the ion pair (i.p.) is the reactive species,

$$\text{rate} = k_2^{\text{i.p.}} [\text{Ph}_3\text{C}^{\oplus} - \text{X}^{\ominus}] [\text{R}_3\text{Si-H}],$$

and since

$$K_{\text{eq}} = \frac{[\text{Ph}_3\text{C}^{\oplus} - \text{X}^{\ominus}]}{[\text{Ph}_3\text{C-X}]}$$

$$[\text{Ph}_3\text{C}^{\oplus} - \text{X}^{\ominus}] = K_{\text{eq}} [\text{Ph}_3\text{C-X}]$$

$$\therefore \text{observed rate} = k_2 K_{\text{eq}} [\text{Ph}_3\text{C-X}] [\text{R}_3\text{Si-H}]$$

$$\text{and the observed } k_2' = k_2^{\text{i.p.}} K_{\text{eq}}$$

$$k_2^{\text{i.p.}} = \frac{k_2'}{K_{\text{eq}}}$$

The hydride exchange itself could be said to be anion independent if dividing k_2' by K_{eq} for the chloride gave the same number as for the bromide ($k_2^{\text{i.p.}}$ chloride = $k_2^{\text{i.p.}}$ bromide); however, this experiment might fail to show anion independence if the reactivity of the ion pair is significantly affected by the particular halide ion. If the free trityl ion were the reactive species, then the experiment would certainly prove the involvement or non-involvement of the anion in the transition state, but Evans et al. (21) have shown that trityl chloride does not form free ions

in halogenated ethanes, so it is most likely that ion pairs are the reactive species for the chloride, at least. The bromide may, however, form some free ions and this might further complicate the picture.

We felt that a kinetic study of the reaction with totally ionic trityl salts, such as trityl perchlorate, would answer the question of anion involvement in the transition state more directly since it should minimize the pre-transition state effects of the anion. We first examined the reactions of chloromethyldimethylsilane which was found to react at a pace more amenable to kinetic studies than the relatively fast triethylsilane. The reactions with trityl perchlorate, hexafluoroantimonate, and fluoroborate were run in methylene chloride and were followed by U.V., looking at the 430 nm peak of the trityl cation. A numerical and graphical treatment of the data are provided in the next pages.

The numeric treatment was accomplished using a computer program which assumed second-order behavior and provided a linear least-squares fit of $\ln[\text{SiH}/\text{Tr}^{\oplus}]$ versus time and a standard deviation for the calculated second-order rate constant, k_2 . The same function, $\ln[\text{SiH}/\text{Tr}^{\oplus}]$ versus time, was plotted to check the assumption of linearity. The program also had a provision for adjusting the data to fit the assumption that the reaction began at the first data point and recalculating the rate constant and standard deviation

accordingly. It was felt that this adjusted treatment should minimize aberrations in the reaction rate due to concentration gradients present during the mixing of reactants or because the reaction mixture had not reached thermal equilibrium. In some cases this adjusted treatment provided lower standard deviations. In others it did not.

Two mixing techniques were used: one, whereby equal volumes of methylene chloride solutions of both the reactants were mixed; and the other, whereby a sample of pure silane was injected into a methylene chloride solution of the trityl salt and then shaken vigorously. For some reactions duplicate runs were made and these results are also included (see pages 34-42).

All three trityl salts showed second-order kinetics with chloromethyldimethylsilane and the rate constants are summarized below:

$\frac{\text{ClCH}_2\text{SiMe}_2\text{H}}{\text{Rate} = k_2 [\text{Tr}^{\oplus}] [\text{SiH}]}$	k_2 in liters mole ⁻¹ sec ⁻¹ @25°		
$\text{Tr}^{\oplus}\text{ClO}_4^{\ominus}$	$\text{Tr}^{\oplus}\text{BF}_4^{\ominus}$	$\text{Tr}^{\oplus}\text{SbF}_6^{\ominus}$	
1.16	1.06	1.09	
1.09	1.19 (neat addn.)		

Trityl Perchlorate and Chloromethyldimethylsilane Run#1
 initial concentration Si-H: .001204
 initial concentration Tr: .00054

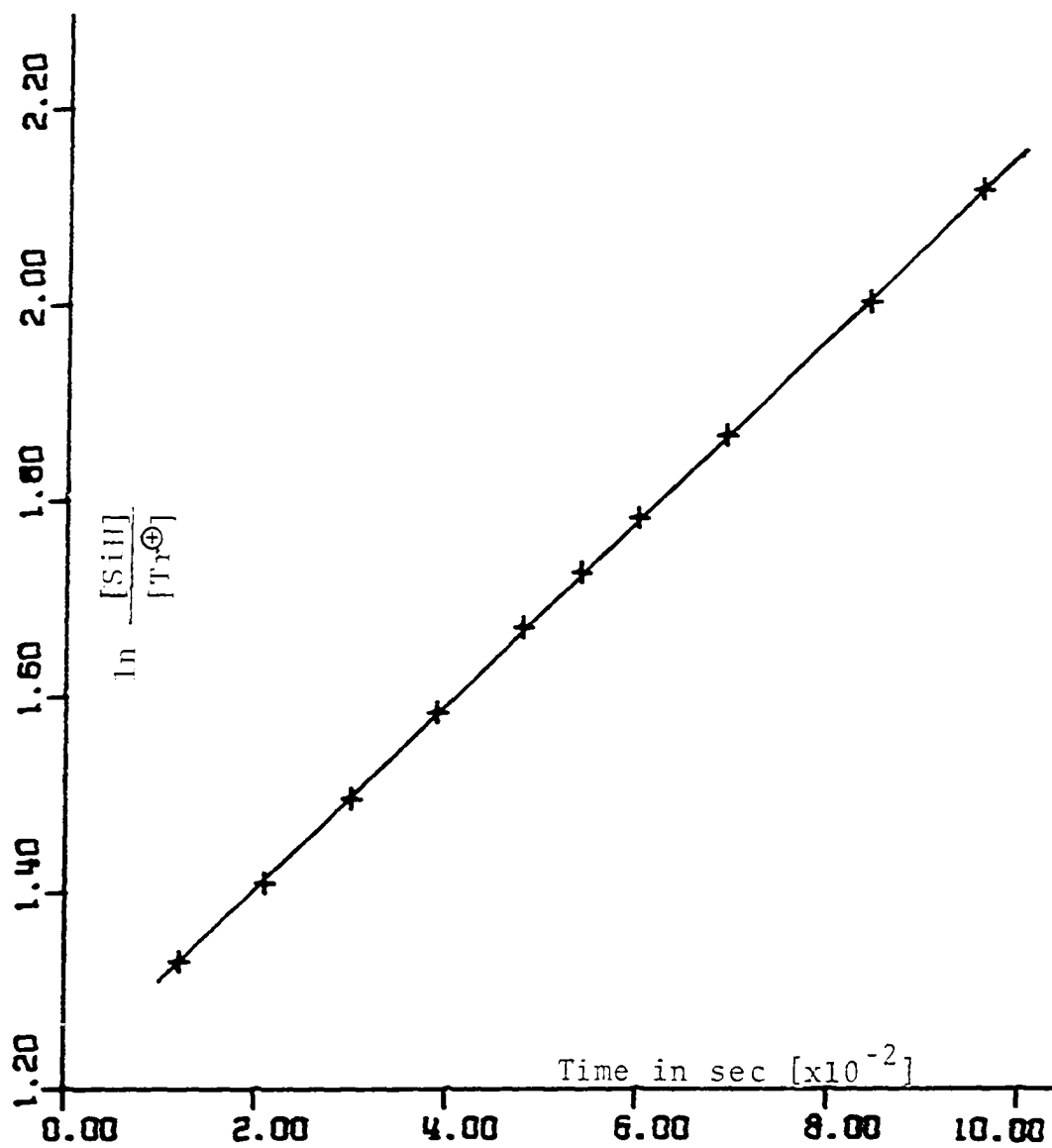
THE SECOND-ORDER RATE CONSTANT IS
 1.1595580377359 +OR- .004284019064152 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
120.0	1.175	1.104	1.538
210.0	1.050	0.980	1.422
300.0	0.935	0.873	1.511
390.0	0.833	0.780	1.603
480.0	0.740	0.699	1.698
540.0	0.691	0.650	1.755
600.0	0.645	0.605	1.812
690.0	0.580	0.544	1.901
840.0	0.485	0.458	2.056
960.0	0.422	0.400	2.178

Trityl Perchlorate and Chloromethyldimethylsilane Run#1a
 initial concentration Si-H: .0011713074927697
 initial concentration Tr: .00030730749276968
 Tzero and initial conc. are adjusted to 120 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 1.1641360086208 +OR- .004125472878775 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
30.0	1.050	1.041	1.422
180.0	0.935	0.926	1.511
270.0	0.833	0.826	1.603
360.0	0.740	0.738	1.698
420.0	0.691	0.686	1.755
480.0	0.645	0.638	1.812
570.0	0.580	0.573	1.901
720.0	0.485	0.481	2.056
840.0	0.422	0.420	2.178



Reaction 1. Trityl perchlorate and chloromethyldimethylsilane (Run #1).

Trityl Perchlorate and Chloromethyldimethylsilane Run#2
 initial concentration Si-H: .001204
 initial concentration Tr: .00054

THE SECOND-ORDER RATE CONSTANT IS
 1.0868202082474 +OR- .003060948872892 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
120.0	1.187	1.115	1.531
210.0	1.065	0.997	1.411
300.0	0.952	0.894	1.497
390.0	0.853	0.804	1.584
480.0	0.766	0.725	1.670
540.0	0.715	0.677	1.726
600.0	0.668	0.633	1.783
690.0	0.604	0.573	1.867
840.0	0.515	0.486	2.003
950.0	0.452	0.428	2.117

Trityl Perchlorate and Chloromethyldimethylsilane Run#2a
 initial concentration Si-H: .0011744459762573
 initial concentration Tr: .00031044597625732
 Tzero and initial conc. are adjusted to 120 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 1.0874133533583 +OR- .0037842727562637 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
90.0	1.065	1.060	1.411
180.0	0.952	0.949	1.497
270.0	0.853	0.852	1.584
360.0	0.766	0.767	1.670
420.0	0.715	0.716	1.726
480.0	0.668	0.669	1.783
570.0	0.604	0.605	1.867
720.0	0.515	0.513	2.003
840.0	0.452	0.451	2.117

Trityl BF₄ and Chloromethyldimethylsilane Run#1
 initial concentration Si-H: .001204
 initial concentration Tr: .000392

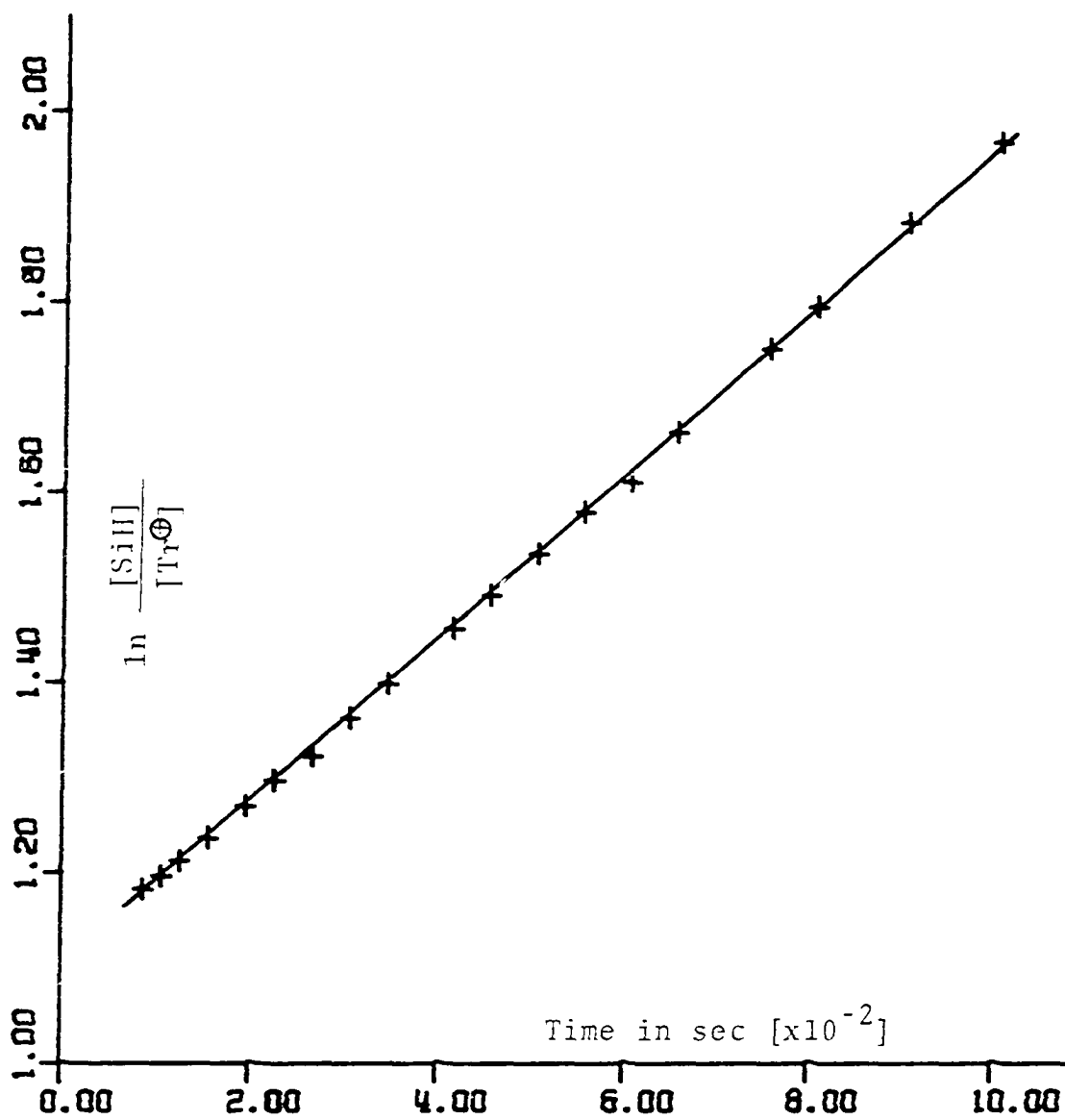
THE SECOND-ORDER RATE CONSTANT IS
 1.0534869300106 +OR- .0039303868417942 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

87.0	1.373	1.346	1.183
107.0	1.345	1.313	1.197
127.0	1.316	1.282	1.212
157.0	1.271	1.236	1.237
197.0	1.214	1.179	1.270
227.0	1.170	1.138	1.296
267.0	1.128	1.087	1.323
307.0	1.068	1.038	1.363
347.0	1.019	0.992	1.399
417.0	0.944	0.917	1.457
457.0	0.903	0.878	1.491
507.0	0.854	0.831	1.534
557.0	0.807	0.787	1.579
607.0	0.775	0.746	1.611
657.0	0.727	0.708	1.663
757.0	0.653	0.638	1.751
807.0	0.620	0.606	1.794
907.0	0.558	0.548	1.882
1007.0	0.506	0.496	1.966

Trityl BF₄ and Chloromethyldimethylsilane Run#1a
 initial concentration Si-H: .0011708104553223
 initial concentration Tr: .0003588104553227
 Tzero and init. conc. are adjusted to 87 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 1.0558204810162 +OR- .0038161065639559 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
20.0	1.345	1.340	1.197
40.0	1.316	1.307	1.212
70.0	1.271	1.261	1.237
110.0	1.214	1.202	1.270
140.0	1.170	1.160	1.296
180.0	1.128	1.107	1.323
220.0	1.068	1.057	1.363
260.0	1.019	1.010	1.399
330.0	0.944	0.933	1.457
370.0	0.903	0.893	1.491
420.0	0.854	0.845	1.534
470.0	0.807	0.800	1.579
520.0	0.775	0.759	1.611
570.0	0.727	0.719	1.663
670.0	0.653	0.648	1.751
720.0	0.620	0.615	1.794
820.0	0.558	0.556	1.882
920.0	0.506	0.503	1.966



Reaction 2. Trityl fluoroborate and chloromethyldimethylsilane (Run #2).

Trityl BF₄ and Chloromethyldimethylsilane(neat addn.) Run#1
 initial concentration Si-H: .00115
 initial concentration Tr: .000392

THE SECOND-ORDER RATE CONSTANT IS
 1.1398229455055 +OR- .0073592858064668 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
100.0	1.541	1.511	1.160
140.0	1.274	1.244	1.196
200.0	1.182	1.151	1.249
260.0	1.091	1.068	1.307
320.0	1.022	0.991	1.355
400.0	0.928	0.900	1.427
450.0	0.875	0.848	1.472
500.0	0.820	0.800	1.525
550.0	0.770	0.755	1.572
600.0	0.750	0.715	1.615
700.0	0.649	0.657	1.710

Trityl BF₄ and Chloromethyldimethylsilane(neat addn.) Run#1a
 initial concentration Si-H: .0011184478963216
 initial concentration Tr: .00035044789632161
 Tzero and init. conc. are adjusted to 100 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 1.1957239041604 +OR- .0084118071351662 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
40.0	1.274	1.272	1.196
100.0	1.182	1.176	1.249
160.0	1.091	1.090	1.307
220.0	1.022	1.012	1.355
300.0	0.928	0.918	1.427
350.0	0.875	0.865	1.472
400.0	0.820	0.815	1.525
450.0	0.770	0.769	1.572
500.0	0.750	0.726	1.615
600.0	0.649	0.648	1.710

Trityl SbF₆ and Chloromethyldimethylsilane Run#1
 initial concentration Si-H: .001204
 initial concentration Tr: .000356

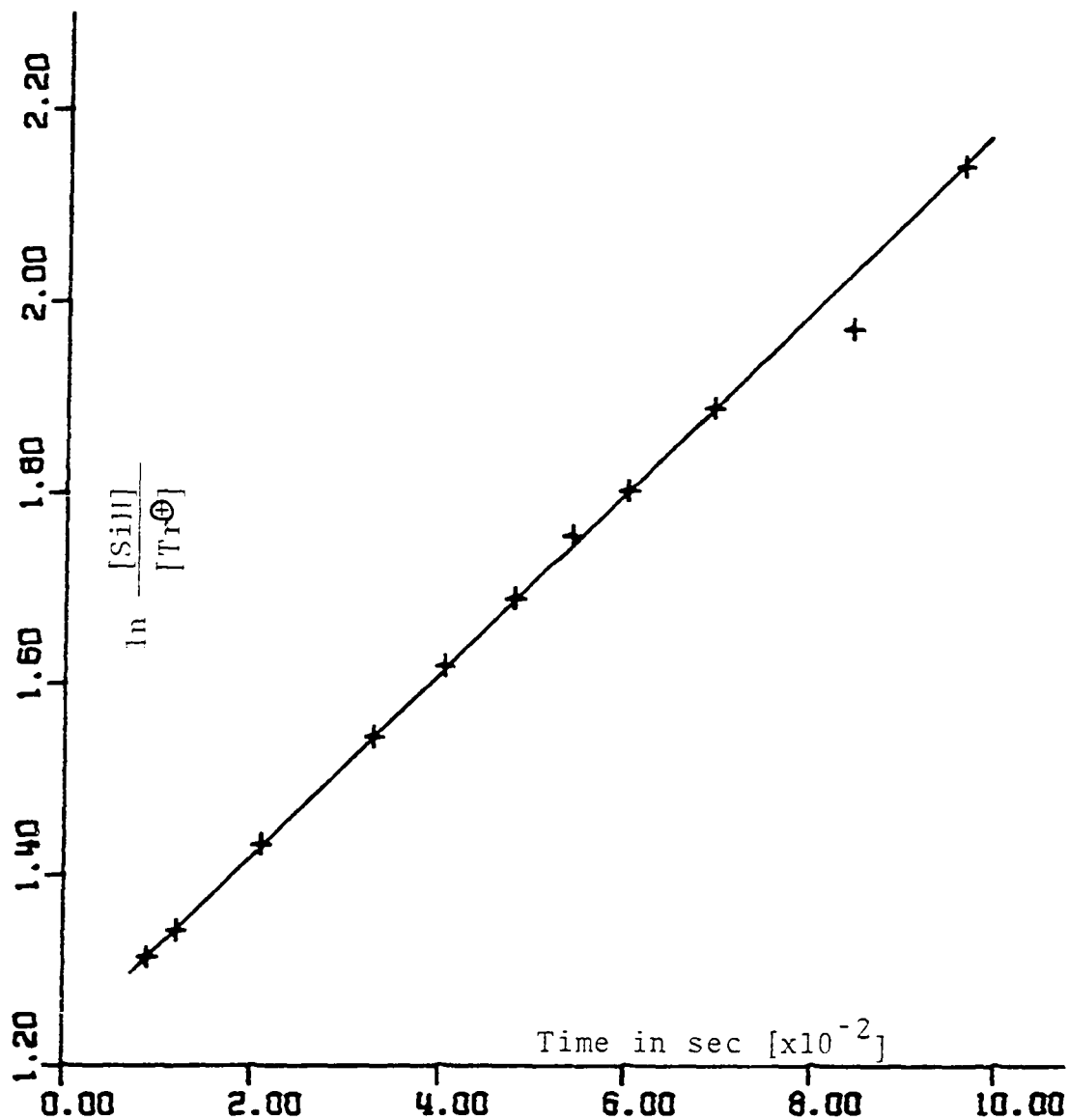
THE SECOND-ORDER RATE CONSTANT IS
 1.0914595074504 +OR- .023242402148918 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
90.0	1.190	1.212	1.515
120.0	1.148	1.167	1.542
210.0	1.018	1.044	1.452
330.0	0.880	0.904	1.545
405.0	0.802	0.828	1.618
480.0	0.755	0.759	1.689
540.0	0.679	0.709	1.754
600.0	0.640	0.663	1.803
690.0	0.579	0.600	1.888
840.0	0.525	0.510	1.971
960.0	0.432	0.449	2.141

Trityl SbF₆ and Chloromethyldimethylsilane Run#1a
 initial concentration Si-H: .0011590424747551
 initial concentration Tr: .0005110424747551
 Tzero and init. conc. are adjusted to 90 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 1.0852640730277 +OR- .027376798456755 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

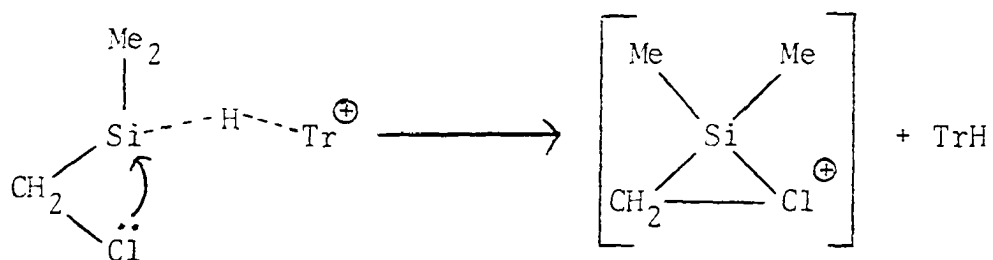
Time(SEC)	D-Obsd	D-Calcd	ln B/A
90.0	1.148	1.146	1.542
120.0	1.018	1.026	1.432
240.0	0.880	0.889	1.545
315.0	0.802	0.815	1.618
390.0	0.755	0.748	1.689
450.0	0.679	0.699	1.754
510.0	0.640	0.654	1.803
600.0	0.579	0.592	1.888
750.0	0.525	0.504	1.971
870.0	0.452	0.444	2.141



Reaction 3. Trityl hexafluoroantimonate and chloromethyl-
dimethylsilane (Run #1).

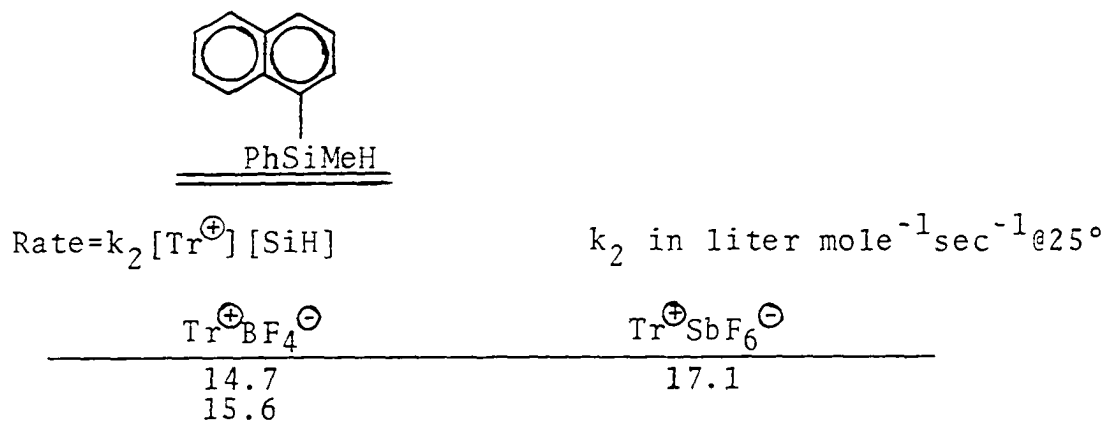
It is apparent that there is no appreciable difference in rate for the three trityl salts and thus it is unlikely that the anion is involved in the transition state.

Upon further consideration we realized that perhaps this anion independence could be explained by internal trapping by the chlorine atom:



We then examined the reaction with α -naphthylmethylphenylsilane, the silane examined by Sommer and Bauman (23) (see pages 44 - 56).

We were surprised to find that the reaction with trityl perchlorate did not plot second-order; however, both the fluoroborate and hexafluoroantimonate were reasonable well behaved:



Trityl Perchlorate and 1-NpMePhsilane Run#1
 initial concentration Si-H: .000307
 initial concentration Tr: .0000395

THE SECOND-ORDER RATE CONSTANT IS
 23.182407858487 +OR- .65630124808841 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
110.0	1.027	0.681	2.354
130.0	0.946	0.597	2.429
140.0	0.900	0.559	2.474
150.0	0.860	0.525	2.516
160.0	0.820	0.490	2.560
170.0	0.780	0.459	2.606
180.0	0.740	0.431	2.655
190.0	0.700	0.404	2.707
200.0	0.665	0.378	2.755
210.0	0.630	0.355	2.805
220.0	0.594	0.335	2.861
240.0	0.550	0.295	2.969
260.0	0.468	0.258	3.087
280.0	0.410	0.227	3.214
300.0	0.356	0.200	3.343
320.0	0.306	0.176	3.496
340.0	0.260	0.155	3.654
360.0	0.220	0.137	3.817
380.0	0.185	0.121	3.998
400.0	0.155	0.107	4.174

Trityl Perchlorate and 1-NpMePhsilane Run#1a

initial concentration Si-H: .00029557368803189

initial concentration Tr: .000028073688031895

Tzero and init. conc. are adjusted to 110 sec from actual

THE SECOND-ORDER RATE CONSTANT IS

25.623600891966 +OR- .64198508426335 M-1 SEC-1

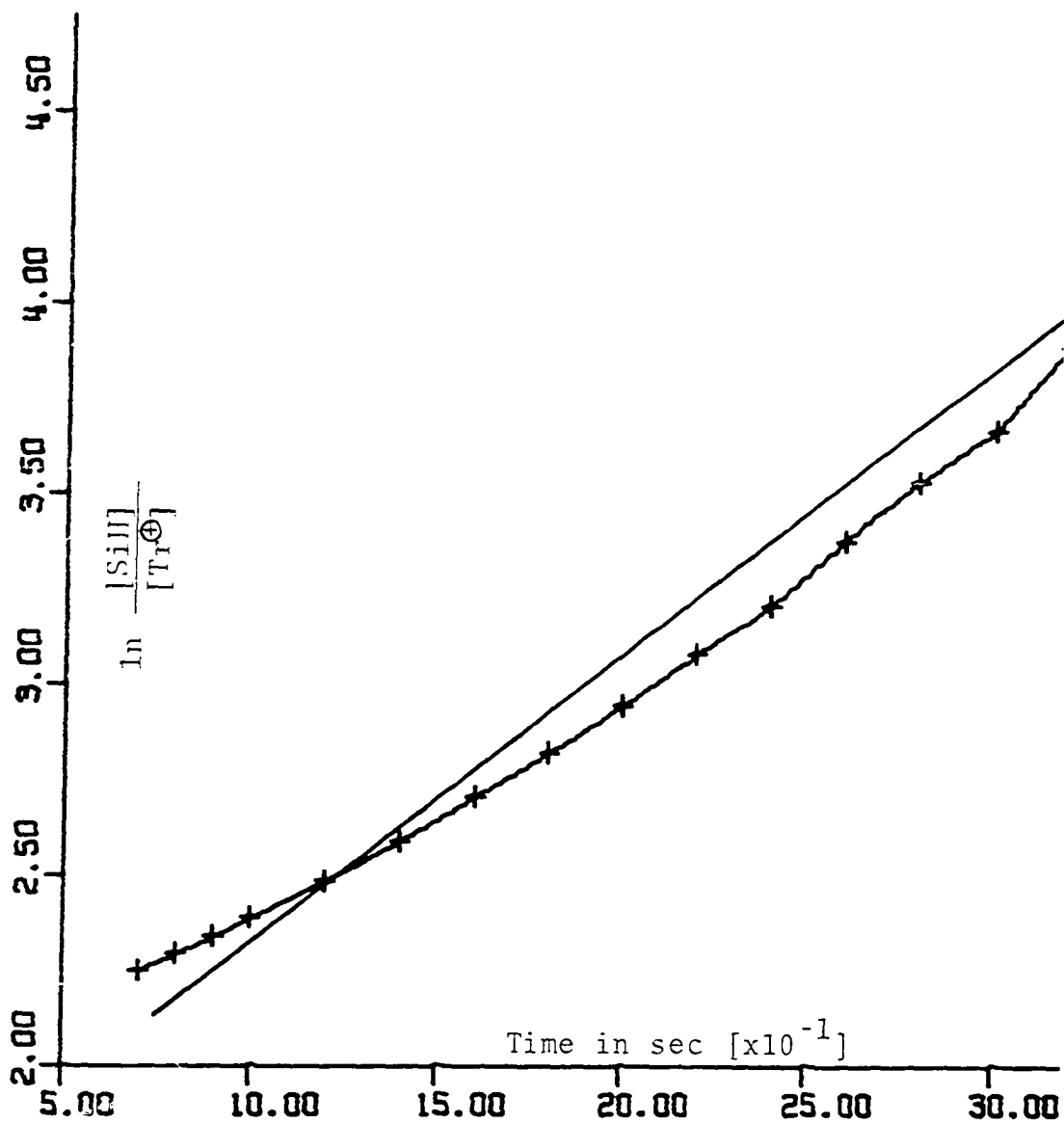
Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
20.0	0.946	0.894	2.429
30.0	0.900	0.834	2.474
40.0	0.860	0.779	2.516
50.0	0.820	0.728	2.560
60.0	0.780	0.680	2.605
70.0	0.740	0.636	2.655
80.0	0.700	0.595	2.707
90.0	0.665	0.556	2.755
100.0	0.630	0.520	2.805
110.0	0.594	0.487	2.861
130.0	0.550	0.426	2.969
150.0	0.488	0.374	3.087
170.0	0.410	0.328	3.214
190.0	0.356	0.288	3.349
210.0	0.306	0.253	3.496
230.0	0.260	0.222	3.654
250.0	0.220	0.195	3.817
270.0	0.185	0.172	3.998
290.0	0.155	0.151	4.174

Trityl Perchlorate and 1-NpMePhsilane Run#2
 initial concentration Si-H: .000307
 initial concentration Tr: .0000378

THE SECOND-ORDER RATE CONSTANT IS
 26.452457829705 +OR- .92133034503721 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
70.0	1.215	0.832	2.248
80.0	1.154	0.770	2.294
90.0	1.096	0.714	2.341
100.0	1.040	0.662	2.388
120.0	0.935	0.569	2.485
140.0	0.835	0.490	2.530
160.0	0.738	0.422	2.704
180.0	0.654	0.364	2.818
200.0	0.572	0.314	2.944
220.0	0.496	0.271	3.080
240.0	0.436	0.235	3.203
260.0	0.384	0.203	3.377
280.0	0.340	0.175	3.532
300.0	0.270	0.152	3.666
320.0	0.216	0.131	3.885
340.0	0.178	0.114	4.074
360.0	0.145	0.099	4.276
400.0	0.093	0.074	4.715



Reaction 4. Trityl perchlorate and α -naphthylmethyl-phenylsilane (Run #2).

Trityl Perchlorate and 1-NpMePhsilane Run#2a
 initial concentration Si-H: .0003003833700477
 initial concentration Tr: .000031783370047705
 Tzero and init. conc. are adjusted to 70 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 26.914681944901 +OR- .95467511872562 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
10.0	1.154	1.121	2.294
20.0	1.096	1.055	2.541
30.0	1.040	0.956	2.588
30.0	0.935	0.816	2.485
70.0	0.835	0.699	2.590
90.0	0.738	0.599	2.704
110.0	0.654	0.514	2.818
130.0	0.572	0.442	2.944
150.0	0.496	0.380	3.080
170.0	0.430	0.327	3.203
190.0	0.364	0.282	3.377
210.0	0.310	0.243	3.532
230.0	0.270	0.209	3.666
250.0	0.216	0.181	3.885
270.0	0.178	0.156	4.074
290.0	0.145	0.135	4.276
330.0	0.093	0.100	4.715

Trityl BF₄ and i-NpMePhsilane Run#1
 initial concentration Si-H: .000307
 initial concentration Tr: .0000337

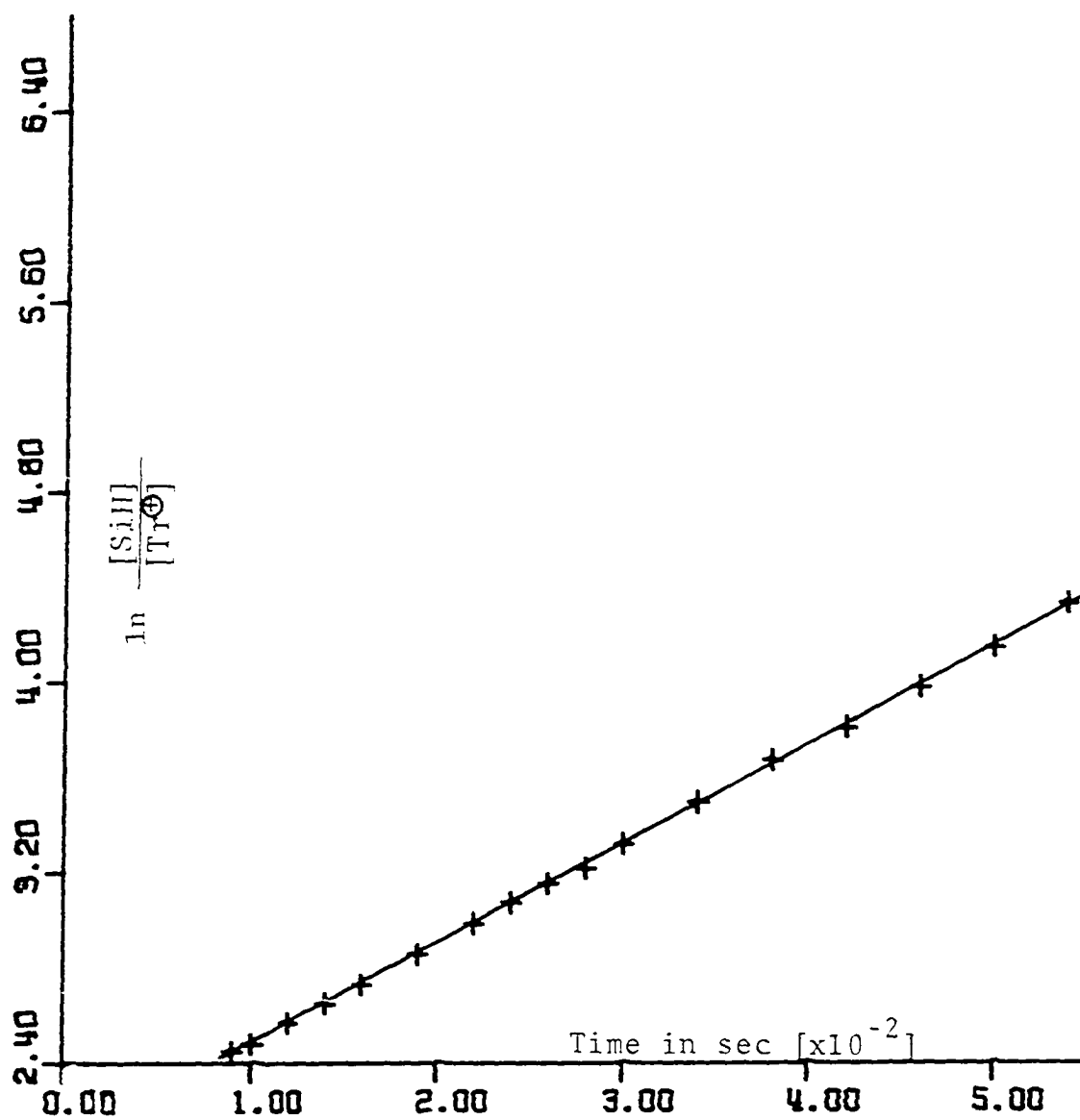
THE SECOND-ORDER RATE CONSTANT IS
 15.573526290427 +OR- .094257957757022 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

30.0	0.390	0.846	2.448
100.0	0.953	0.808	2.483
120.0	0.872	0.738	2.565
140.0	0.799	0.674	2.646
160.0	0.729	0.615	2.731
190.0	0.639	0.538	2.855
220.0	0.558	0.470	2.983
240.0	0.510	0.431	3.069
260.0	0.468	0.394	3.151
280.0	0.436	0.361	3.219
300.0	0.391	0.330	3.323
340.0	0.326	0.277	3.499
380.0	0.272	0.233	3.675
420.0	0.237	0.196	3.810
460.0	0.200	0.165	3.976
500.0	0.168	0.139	4.147
540.0	0.140	0.117	4.327
600.0	0.106	0.090	4.602
720.0	0.060	0.054	5.167

Trityl BF₄ and 1-NpMePhsilane Run#1a
 initial concentration Si-H: .0002991627893897
 initial concentration Tr: .000025862789389699
 Tzero and init. conc. are adjusted to 90 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 15.604270816317 +OR- .098913651017464 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
10.0	0.953	0.945	2.483
30.0	0.872	0.861	2.565
50.0	0.799	0.786	2.646
70.0	0.729	0.717	2.731
100.0	0.639	0.626	2.855
130.0	0.558	0.547	2.983
150.0	0.510	0.500	3.069
170.0	0.468	0.457	3.151
190.0	0.436	0.418	3.219
210.0	0.391	0.383	3.323
250.0	0.326	0.321	3.499
290.0	0.272	0.269	3.675
330.0	0.237	0.226	3.810
370.0	0.200	0.190	3.976
410.0	0.168	0.160	4.147
450.0	0.140	0.134	4.327
510.0	0.106	0.104	4.602
630.0	0.060	0.062	5.167



Reaction 5. Trityl fluoroborate and α -naphthylmethyl-phenylsilane (Run #1).

Trityl BF₄ and i-NpMePhsilane Run#2
 initial concentration Si-H: .000307
 initial concentration Tr: .0000337

THE SECOND-ORDER RATE CONSTANT IS
 14.663796083254 +OR- .11920255411987 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
104.0	0.980	0.816	2.457
114.0	0.948	0.782	2.483
134.0	0.879	0.717	2.557
154.0	0.815	0.659	2.627
174.0	0.755	0.605	2.698
194.0	0.704	0.556	2.764
214.0	0.650	0.511	2.839
234.0	0.599	0.470	2.916
254.0	0.552	0.432	2.993
294.0	0.469	0.366	3.149
314.0	0.430	0.337	3.232
334.0	0.395	0.310	3.314
374.0	0.333	0.263	3.479
394.0	0.305	0.242	3.564
414.0	0.281	0.225	3.644
454.0	0.236	0.190	3.814
494.0	0.200	0.161	3.976
514.0	0.184	0.148	4.058
594.0	0.130	0.107	4.400
654.0	0.100	0.084	4.660

Trityl BF₄ and 1-NpMePhsilane Run#2a

initial concentration Si-H: .00029890154932876

initial concentration Tr: .00002560154932376

Tzero and init. conc. are adjusted to 104 sec from actual

THE SECOND-ORDER RATE CONSTANT IS

14.744228499276 +OR- .11319207048527 M-1 SEC-1

Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
10.0	0.948	0.938	2.488
30.0	0.879	0.859	2.557
50.0	0.815	0.788	2.627
70.0	0.755	0.725	2.698
90.0	0.704	0.663	2.764
110.0	0.650	0.609	2.839
130.0	0.599	0.559	2.916
150.0	0.552	0.514	2.993
190.0	0.469	0.434	3.149
210.0	0.430	0.399	3.232
230.0	0.395	0.367	3.314
270.0	0.335	0.311	3.479
290.0	0.305	0.286	3.564
310.0	0.281	0.265	3.644
350.0	0.236	0.223	3.814
390.0	0.200	0.190	3.976
410.0	0.184	0.175	4.058
490.0	0.130	0.126	4.400
550.0	0.100	0.099	4.660

Trityl SbF6 and 1-NpMePhsilane Run#1
 initial concentration Si-H: .000307
 initial concentration Tr: .0000387

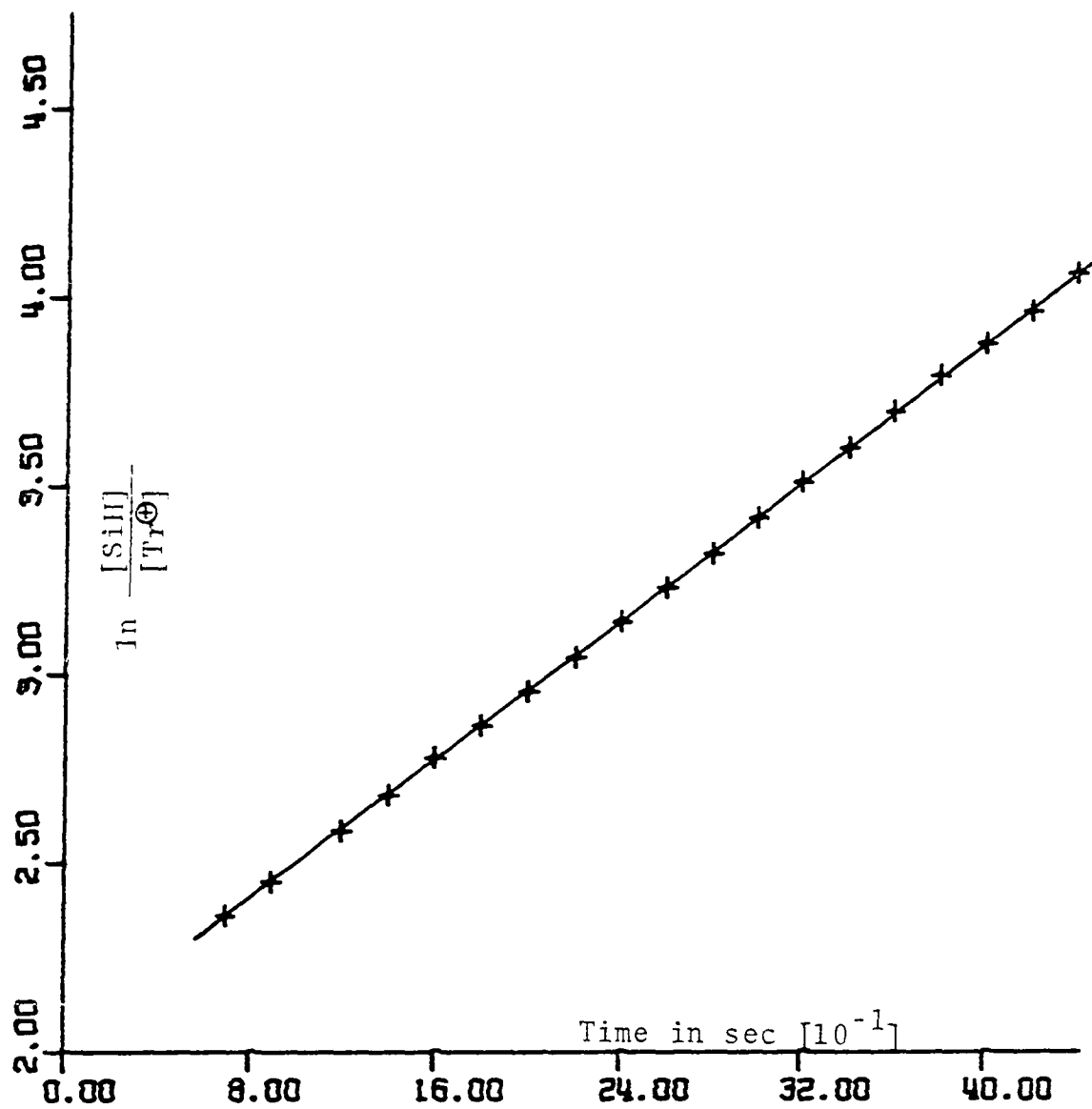
THE SECOND-ORDER RATE CONSTANT IS
 17.092921917538 +OR- .028574322310008 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

70.0	1.070	1.033	2.360
90.0	0.969	0.934	2.450
120.0	0.835	0.804	2.587
140.0	0.755	0.729	2.680
160.0	0.680	0.661	2.778
180.0	0.620	0.600	2.865
200.0	0.564	0.544	2.955
220.0	0.513	0.494	3.045
240.0	0.465	0.449	3.138
260.0	0.423	0.408	3.229
280.0	0.384	0.371	3.322
300.0	0.348	0.338	3.417
320.0	0.316	0.307	3.511
340.0	0.288	0.279	3.601
360.0	0.262	0.254	3.693
380.0	0.237	0.232	3.791
400.0	0.218	0.211	3.873
420.0	0.199	0.192	3.962
440.0	0.180	0.175	4.060
500.0	0.138	0.132	4.322

Trityl SbF₆ and 1-NpMePhsilane Run#1a
 initial concentration Si-H: .00029627904607412
 initial concentration Tr: .00002797904607412
 Tzero and init. conc. are adjusted to 70 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 17.091991290924 +OR- .031599045903439 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
20.0	0.360	0.967	2.450
50.0	0.835	0.853	2.587
70.0	0.755	0.755	2.680
90.0	0.680	0.684	2.778
110.0	0.620	0.620	2.865
130.0	0.564	0.565	2.955
150.0	0.515	0.511	3.045
170.0	0.465	0.464	3.138
190.0	0.425	0.422	3.229
210.0	0.384	0.384	3.322
230.0	0.348	0.349	3.417
250.0	0.316	0.317	3.511
270.0	0.288	0.289	3.601
290.0	0.262	0.265	3.693
310.0	0.237	0.239	3.791
330.0	0.218	0.218	3.875
350.0	0.199	0.198	3.962
370.0	0.180	0.181	4.060
430.0	0.138	0.157	4.522



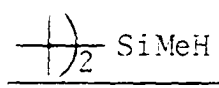
Reaction 6. Trityl hexafluoroantimonate and -naphthyl-methylphenylsilane (Run #1).

At the present we have no explanation for the seemingly anomalous behavior of the perchlorate reaction; however, all the reactions of α -NpMePhSiH put considerable strain on our experimental technique because they were so rapid that errors resulting from concentration gradients occurring during mixing should be more significant and more importantly, impurities introduced in the preparation and handling of the reactant solutions were likely more significant because the concentrations of cation employed were one-tenth those for the chloromethyldimethylsilane experiments.

We then decided to examine a silane which reacted at a more leisurely pace for which we could return to higher concentrations and which did not have the added variable of the aromatic rings: $\text{---})_2\text{SiMeH}$. This silane happened to be one which we were interested in for other reasons which will be developed later.

Di-t-butylmethylsilane was found to react in a well behaved, second-order manner with all three trityl salts (see pages 59-67).

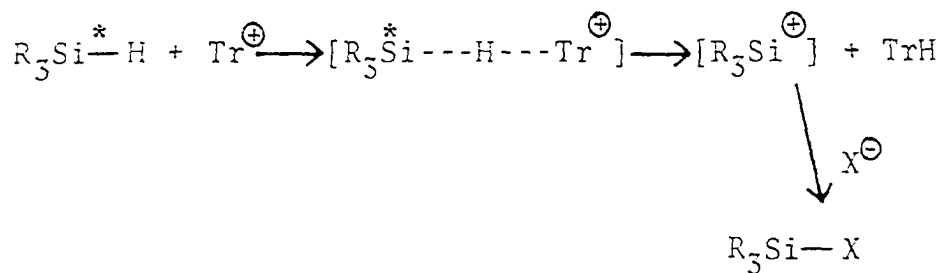
The direct injections of pure silane into the methylene chloride solution of trityl salts was used in all three experiments and the results are summarized below:



$$\text{Rate} = k_2 [\text{Tr}^{\oplus}] [\text{SiH}] \quad k_2 \text{ in liter mole}^{-1} \text{sec}^{-1}$$

$\text{Tr}^{\oplus} \text{ClO}_4^{\ominus}$	$\text{Tr}^{\oplus} \text{BF}_4^{\ominus}$	$\text{Tr}^{\oplus} \text{SbF}_6^{\ominus}$
0.085	0.084	0.092

Again it is apparent that there is no appreciable difference in rate for the three trityl salts and again it is indicative that the anion is not involved in the transition state. If we can generalize the stereochemistry results of Sommer and Bauman (23) with the reaction of trityl chloride and bromide with α -NpPhMeSiH to cover the reactions of the trityl salts studied then we are directed to an obvious answer. If racemization does not occur before the transition state is reached then it is likely that some symmetrical intermediate is involved after the transition state, that is, the silylenium cation:



Trityl Perchlorate and Di-t-butylmethylsilane(neat addn.)
 initial concentration Si-H: .00451
 initial concentration Tr: .000407

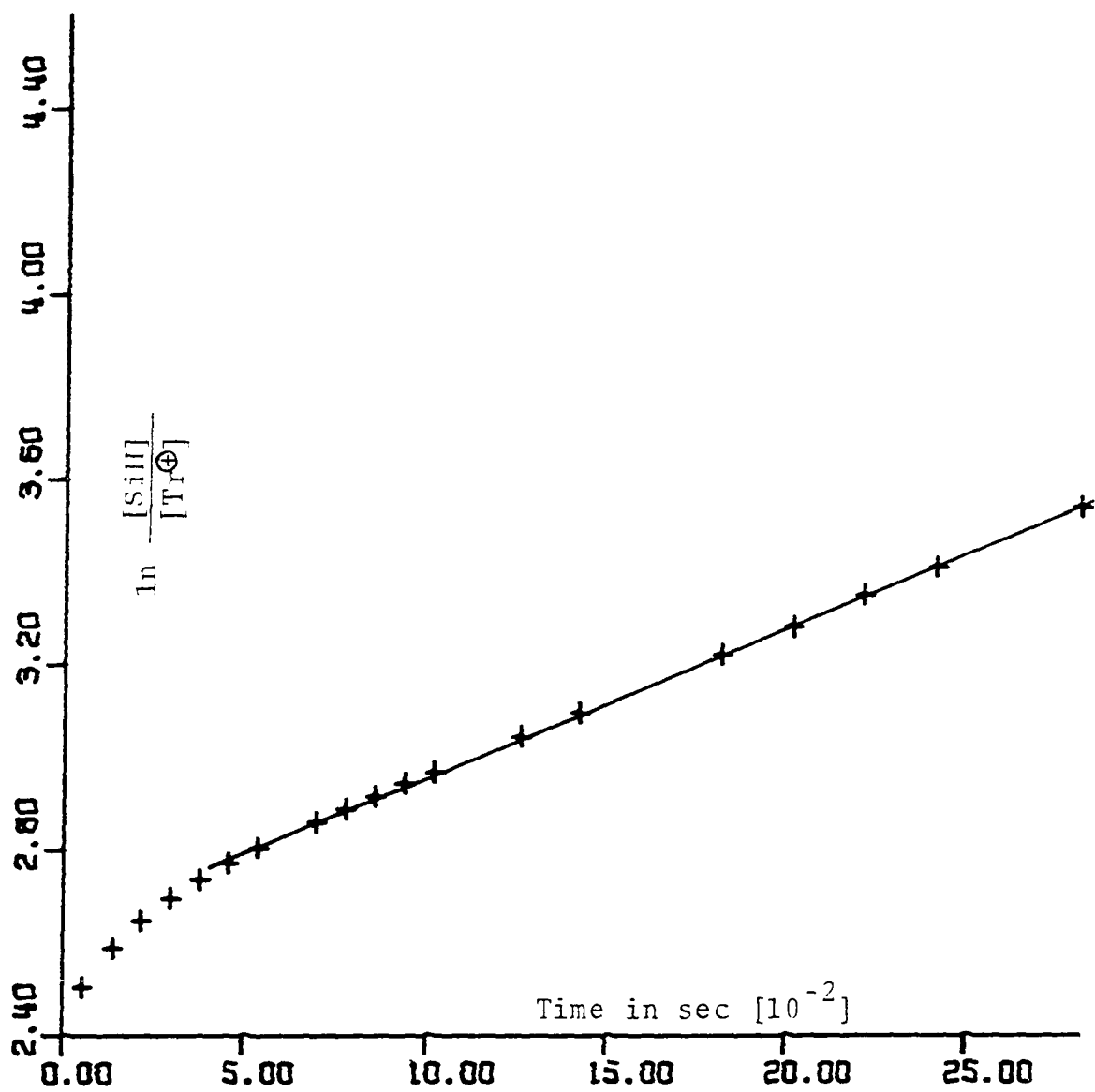
THE SECOND-ORDER RATE CONSTANT IS
 .087526420311957 +OR- .0020954724554457 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
50.0	1.529	1.525	2.505
140.0	1.212	1.478	2.590
220.0	1.158	1.455	2.648
300.0	1.082	1.392	2.695
380.0	1.057	1.352	2.735
460.0	0.998	1.312	2.771
540.0	0.964	1.274	2.805
700.0	0.908	1.201	2.860
780.0	0.881	1.166	2.888
860.0	0.856	1.132	2.915
940.0	0.850	1.099	2.944
1020.0	0.809	1.068	2.960
1260.0	0.748	0.978	3.045
1420.0	0.708	0.925	3.096
1820.0	0.622	0.799	3.220
2020.0	0.585	0.744	3.282
2220.0	0.545	0.695	3.347
2420.0	0.511	0.645	3.409
2820.0	0.448	0.560	3.557
3620.0	0.345	0.422	3.797

Trityl Perchlorate and Di-t-butylmethylsilane(neat addn.)a
 initial concentration Si-H: .0042501776654793
 initial concentration Tr: .00054717766547926
 Tzero and init. conc. are adjusted to 60 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 .0855785825643 +OR- .0014078871814653 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
80.0	1.212	1.291	2.590
160.0	1.138	1.254	2.648
240.0	1.082	1.219	2.695
320.0	1.037	1.184	2.735
400.0	0.998	1.150	2.771
480.0	0.964	1.118	2.803
640.0	0.908	1.056	2.860
720.0	0.881	1.026	2.888
800.0	0.856	0.997	2.915
880.0	0.830	0.969	2.944
960.0	0.809	0.942	2.969
1200.0	0.748	0.866	3.043
1360.0	0.708	0.818	3.096
1760.0	0.622	0.711	3.220
1960.0	0.585	0.665	3.282
2160.0	0.545	0.619	3.347
2360.0	0.511	0.577	3.409
2760.0	0.448	0.505	3.557
3560.0	0.343	0.382	3.797



Reaction 7. Trityl perchlorate and di-t-butylmethylsilane.

Trityl BF₄ and Di-t-butylmethylsilane(neat addn.)
 initial concentration Si-H: .004256
 initial concentration Tr: .000358

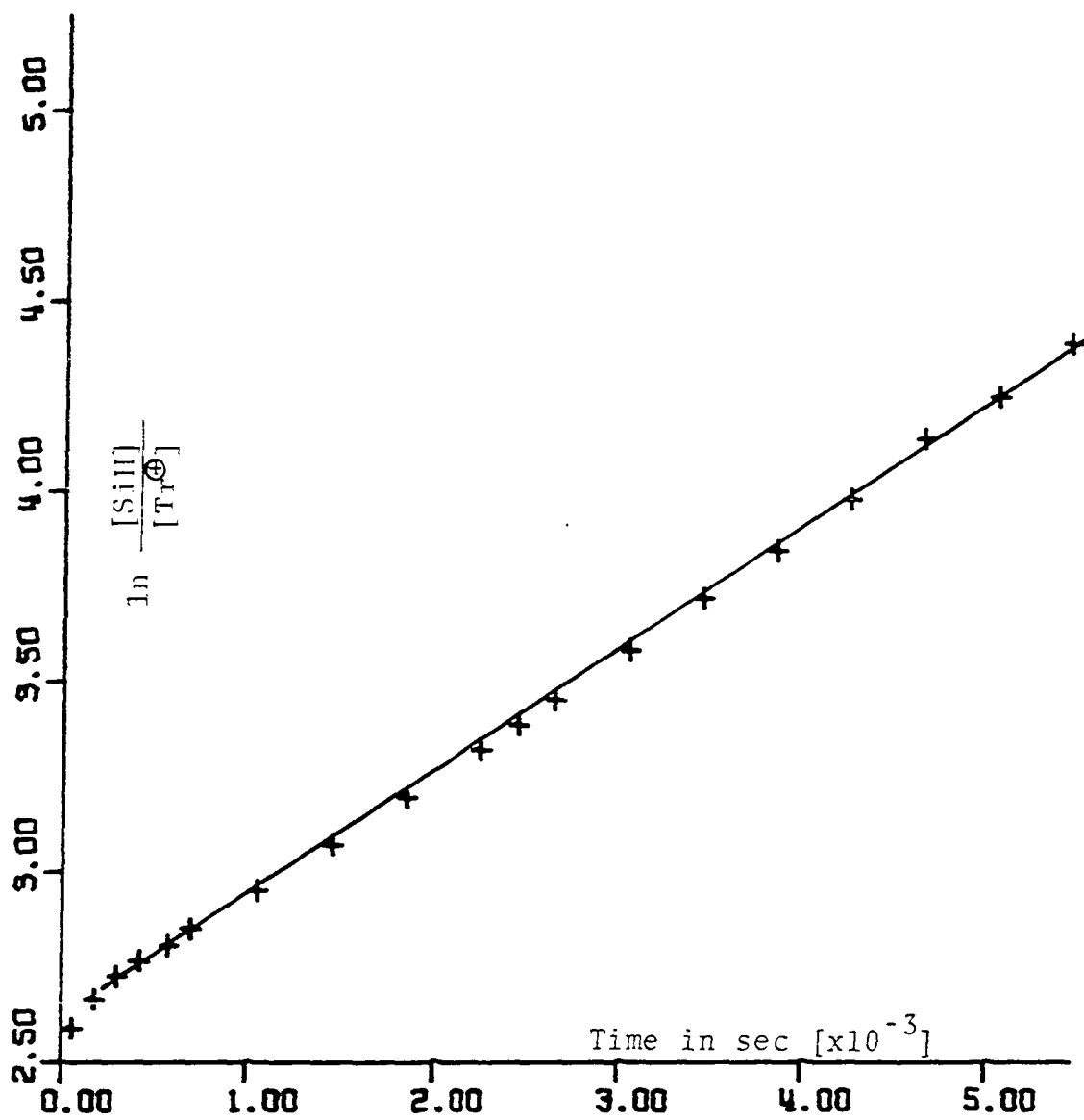
THE SECOND-ORDER RATE CONSTANT IS
 .084006682051952 +OR- .0008132580969525 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
60.0	1.208	1.540	2.591
180.0	1.116	1.284	2.664
300.0	1.047	1.230	2.724
420.0	1.002	1.179	2.765
580.0	0.961	1.114	2.804
700.0	0.915	1.068	2.850
1060.0	0.824	0.942	2.949
1460.0	0.724	0.820	3.072
1860.0	0.656	0.715	3.196
2260.0	0.558	0.623	3.322
2460.0	0.522	0.582	3.386
2660.0	0.488	0.544	3.451
3060.0	0.427	0.475	3.581
3460.0	0.373	0.415	3.713
3860.0	0.328	0.363	3.838
4260.0	0.286	0.317	3.973
4660.0	0.248	0.278	4.113
5060.0	0.217	0.245	4.244
5460.0	0.188	0.215	4.386
6060.0	0.142	0.174	4.663

Trityl BF₄ and Di-t-butylmethylsilane(neat addn.)a
 initial concentration Si-H: .004215897534066
 initial concentration Tr: .000515897534066
 Tzero and init. conc. are adjusted to 60 sec from actual

THE SECOND-ORDER RATE CONSTANT IS
 .085755426918656 +OR- .00084828966150827 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
120.0	1.110	1.158	2.664
240.0	1.047	1.110	2.724
360.0	1.002	1.065	2.765
520.0	0.961	1.007	2.804
640.0	0.915	0.966	2.850
1000.0	0.824	0.852	2.949
1400.0	0.724	0.745	3.072
1600.0	0.656	0.648	3.196
2200.0	0.558	0.566	3.322
2400.0	0.522	0.529	3.386
2600.0	0.488	0.494	3.451
3000.0	0.427	0.432	3.581
3400.0	0.375	0.373	3.713
3800.0	0.323	0.330	3.838
4200.0	0.286	0.289	3.973
4600.0	0.248	0.255	4.113
5000.0	0.217	0.222	4.244
5400.0	0.188	0.194	4.386
6000.0	0.142	0.159	4.663



Reaction 8. Trityl fluoroborate and di-t-butylmethylsilane.

Trityl SbF6 and Di-t-butylmethylsilane(neat addn.)
 INITIAL CONCENTRATION Si-H: .0042
 initial concentration Tr: .000349

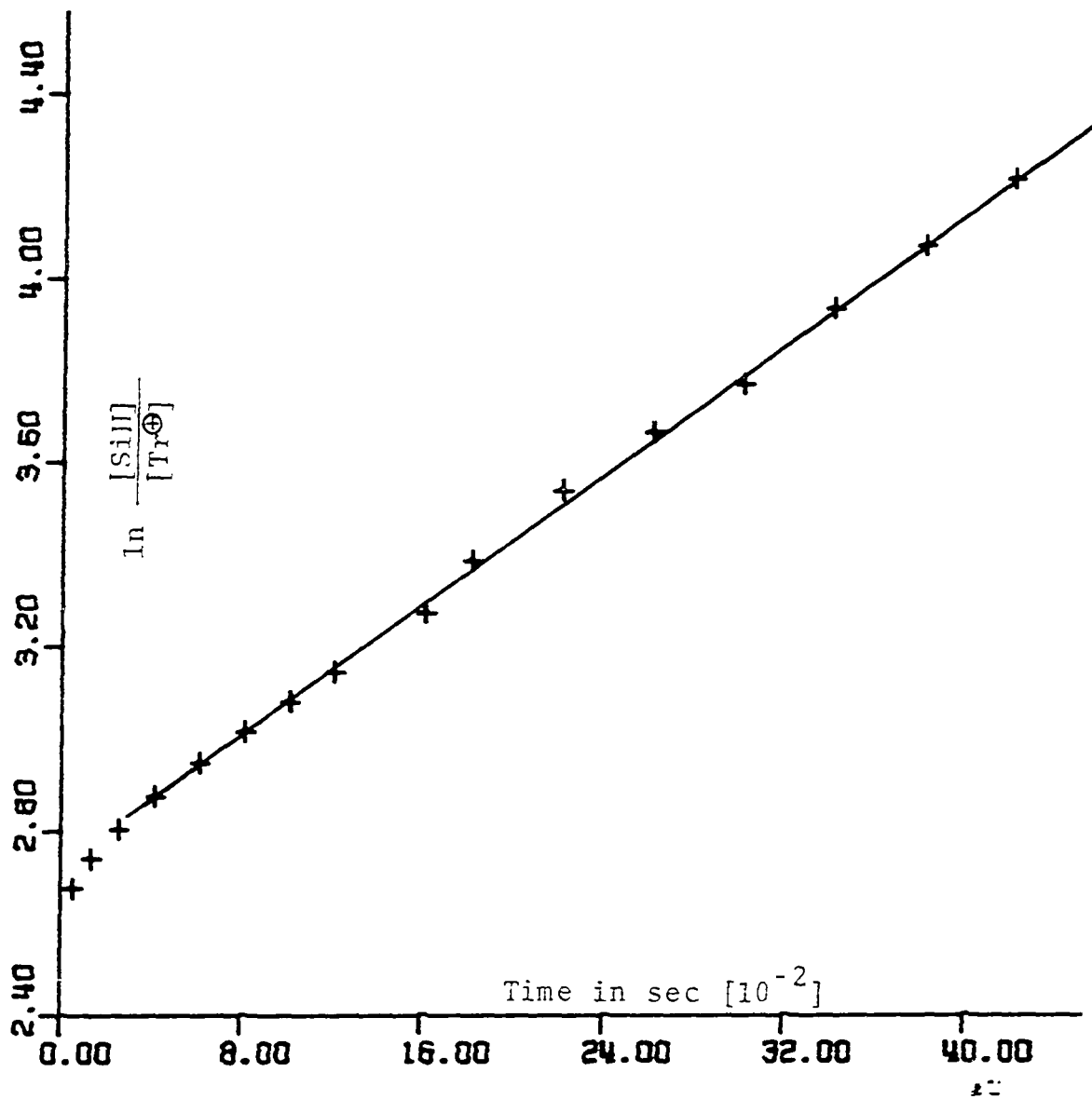
THE SECOND-ORDER RATE CONSTANT IS
 .095195487656032 +OR- .001099368662071 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

60.0	1.091	1.505	2.675
140.0	1.018	1.265	2.740
260.0	0.948	1.207	2.806
420.0	0.881	1.135	2.875
620.0	0.817	1.050	2.947
820.0	0.759	0.973	3.017
1020.0	0.710	0.901	3.080
1220.0	0.663	0.835	3.146
1620.0	0.580	0.718	3.274
1820.0	0.517	0.666	3.385
2220.0	0.442	0.574	3.537
2620.0	0.387	0.494	3.666
3020.0	0.348	0.426	3.770
3420.0	0.295	0.368	3.931
3820.0	0.257	0.318	4.067
4220.0	0.222	0.274	4.211

Trityl SbF6 and Di-t-butylmethylsilane(neat addn.)a
 initial concentration Si-H: .0041359931478606
 initial concentration Tr: .00028490314786059
 Tzero and init. conc. are adjusted to 60 sec from actual

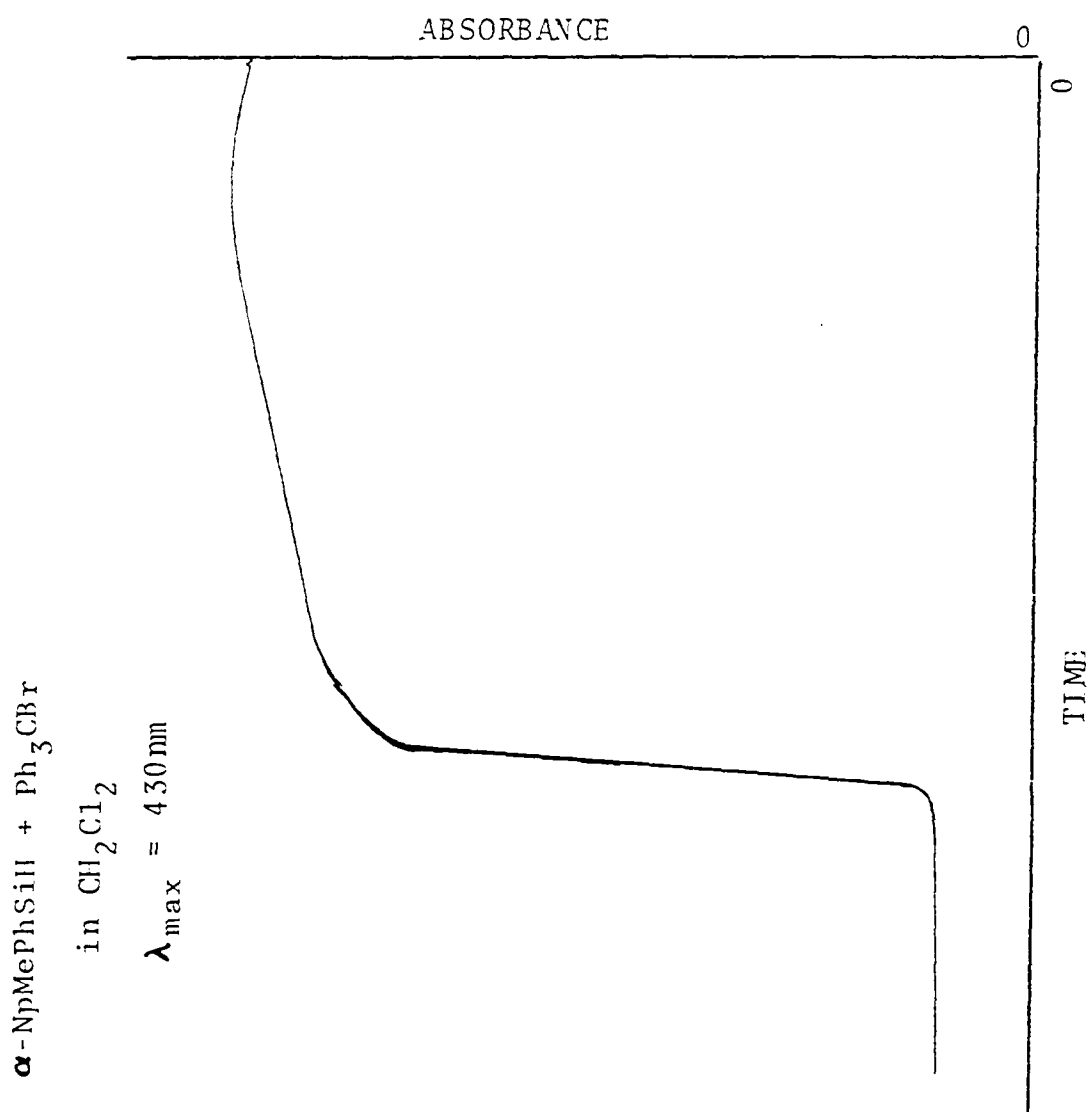
THE SECOND-ORDER RATE CONSTANT IS
 .092213563887292 +OR- .00085846366878611 M-1 SEC-1
 Time(SEC) D-Obsd D-Calcd ln B/A

Time(SEC)	D-Obsd	D-Calcd	ln B/A
80.0	1.018	1.058	2.740
200.0	0.948	1.011	2.806
360.0	0.881	0.952	2.875
560.0	0.817	0.882	2.947
760.0	0.759	0.819	3.017
960.0	0.710	0.760	3.080
1160.0	0.665	0.705	3.146
1360.0	0.620	0.608	3.274
1760.0	0.517	0.565	3.385
2160.0	0.442	0.487	3.537
2560.0	0.387	0.421	3.666
2960.0	0.348	0.364	3.770
3360.0	0.295	0.315	3.931
3760.0	0.257	0.272	4.067
4160.0	0.222	0.236	4.211



Reaction 9. Trityl hexafluoroantimonate and di-t-butylmethylsilane.

At this point we felt it was necessary to attempt to follow the reaction of trityl bromide with α -NpMePhSiH by monitoring the absorption of the trityl cation at 430 nm. A condensation of the UV trace of this reaction is provided below:



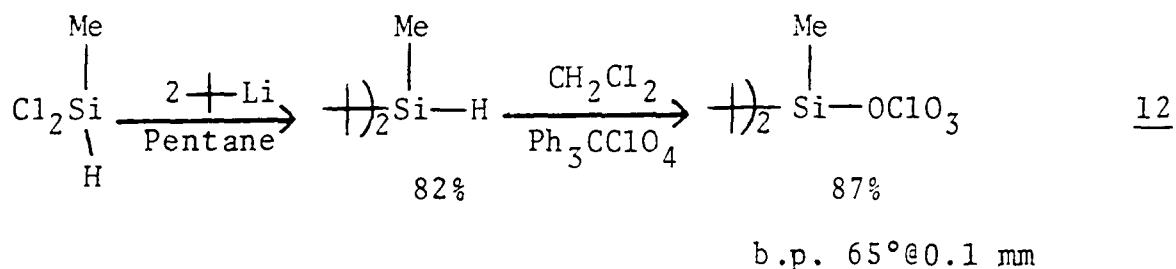
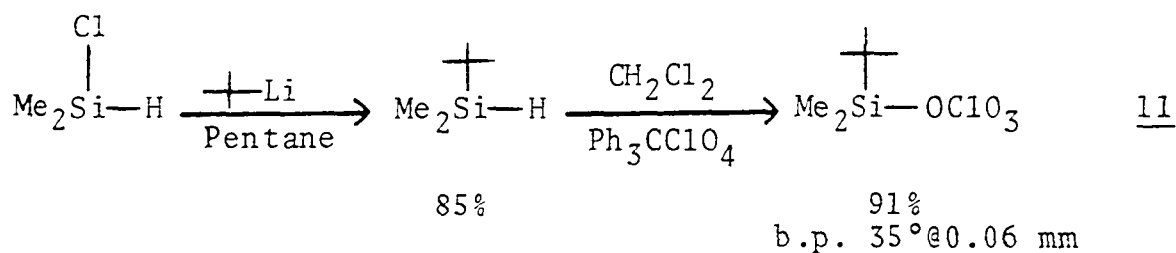
This result proved not to be a fluke as observation of the reaction with triethylsilane showed it to exhibit the same general behavior, although it progressed more rapidly.

At this preliminary stage there is little concrete to say about this reaction except that it is certainly not second-order as reported by Corey and West (20) and Sommer and Bauman (23), though they followed the reaction by ir (20,23) and polarimetrically (23). It is apparent that the reaction of trityl bromide proceeds by a different mechanism than the ionic trityl salts and the stereochemistry of the reaction with the trityl salts must now be determined.

Sakurai and Mochida (37) have recently examined the reaction of triethylgermane and trityl chloride and found that heating mixtures of the two in benzene generated strong ESR signals that were assigned to the trityl radical; however, in methylene chloride they saw no ESR signals for the reaction, which proceeded rapidly even at room temperature. Their findings could have some bearing on our work since we observed a long period of very slow reaction after which the rate increased rapidly until completion was achieved. This could be explained by a free radical chain reaction with a long inhibition period. Presently this very interesting development in the reactions of trityl halides with silyl hydrides is being vigorously pursued by another member of our research group.

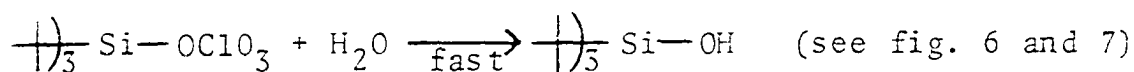
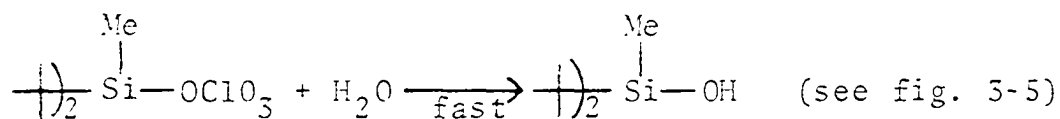
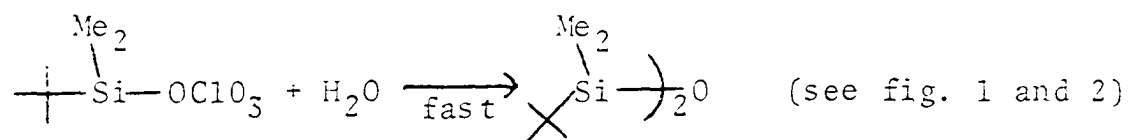
There is another reaction in which we have investigated the possibility of intermediate silylenium ions and this is the solvolysis of silyl perchlorates. In our initial investigation of tri-t-butylsilyl perchlorate (6) we were quite amazed at its reactivity relative to the iodide and hoped that it might be due to ionization. Though we found no spectroscopic evidence for any degree of ionization we still had hopes of proving it reacted through an S_N1 process. Attempts to observe the kinetics of reaction of 6 with water failed as it was too rapid to measure (instantaneous at 25°), so we next attempted to observe a steric acceleration in rate as Bartlett and Tidwell (26) had done.

We prepared a series of silyl perchlorates, t-butyldimethyl (11), di-t-butylmethyl (12), and tri-t-butylsilyl perchlorate (60) and studied their relative reactivities.



It is possible to prepare 6 by the reaction of tri-t-butylsilane with trityl perchlorate but the reaction is very slow and the product is difficult to separate from triphenylmethane. The previously mentioned preparation using the silyl iodide and silver perchlorate is the preferred method.

All three perchlorates were found to react extremely rapidly with water, so in hopes of slowing the reaction



down to obtain rate data, t-butanol was chosen as the nucleophile. Since a by-product of the solvolysis reaction is perchloric acid it was considered desirable to have a buffer present. Our first choice was pyridine, but we found that all three perchlorates reacted quite rapidly with pyridine to form some type of pyridinium complex as evidenced by changes in the NMR spectrum in the region of the silyl perchlorate and the region of pyridine (Figures 8-14). For comparative purposes a sample of pyridine was treated with concentrated perchloric acid and the changes in the

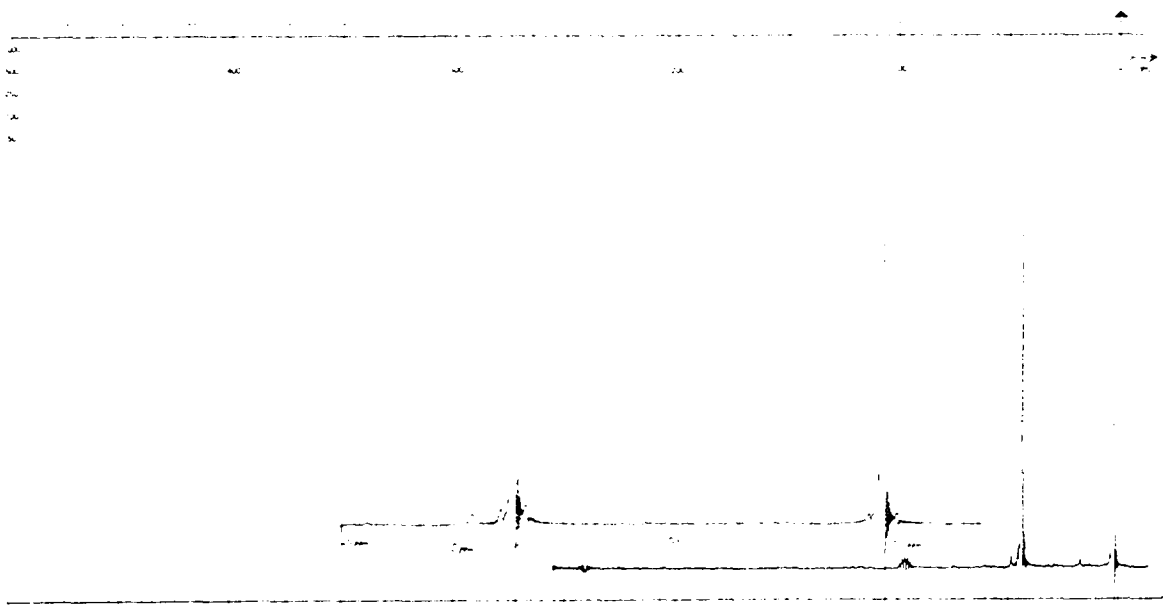


Figure 1. $\begin{array}{c} + \\ | \\ \text{Si}-\text{OClO}_3 \\ | \\ \text{Me}_2 \end{array} + 1/2 \text{H}_2\text{O}, t=50 \text{ sec.}$

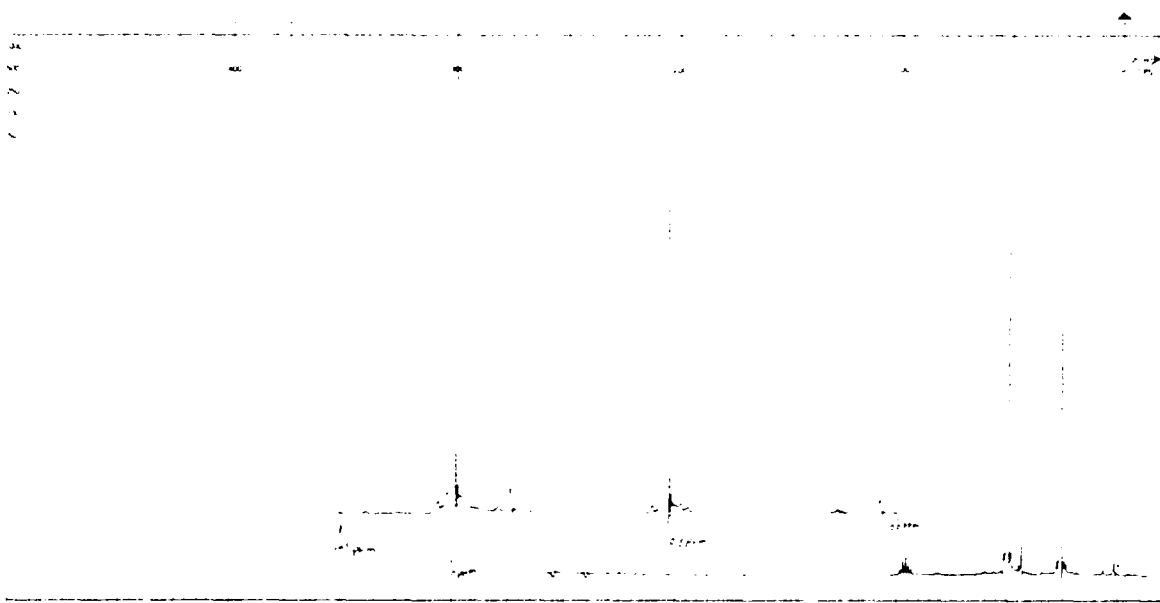
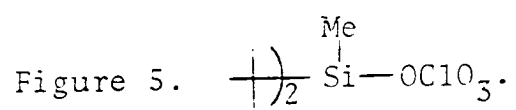
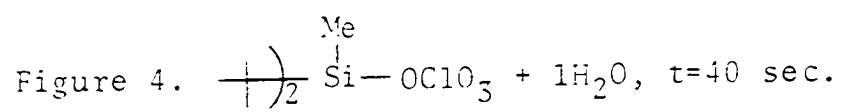
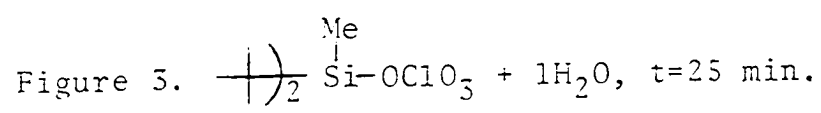
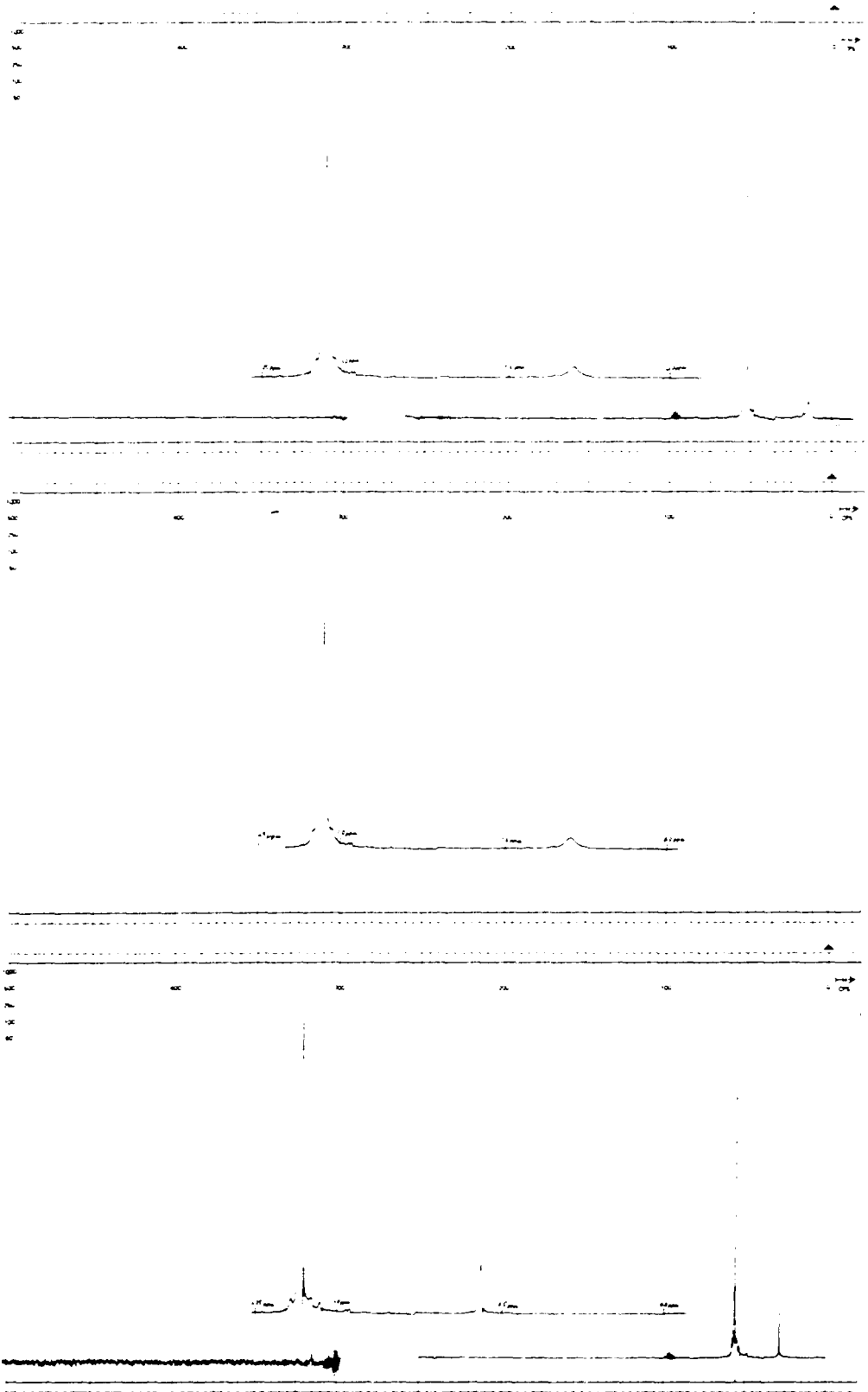


Figure 2. $\begin{array}{c} + \\ | \\ \text{Si}-\text{OClO}_3 \\ | \\ \text{Me}_2 \end{array}$





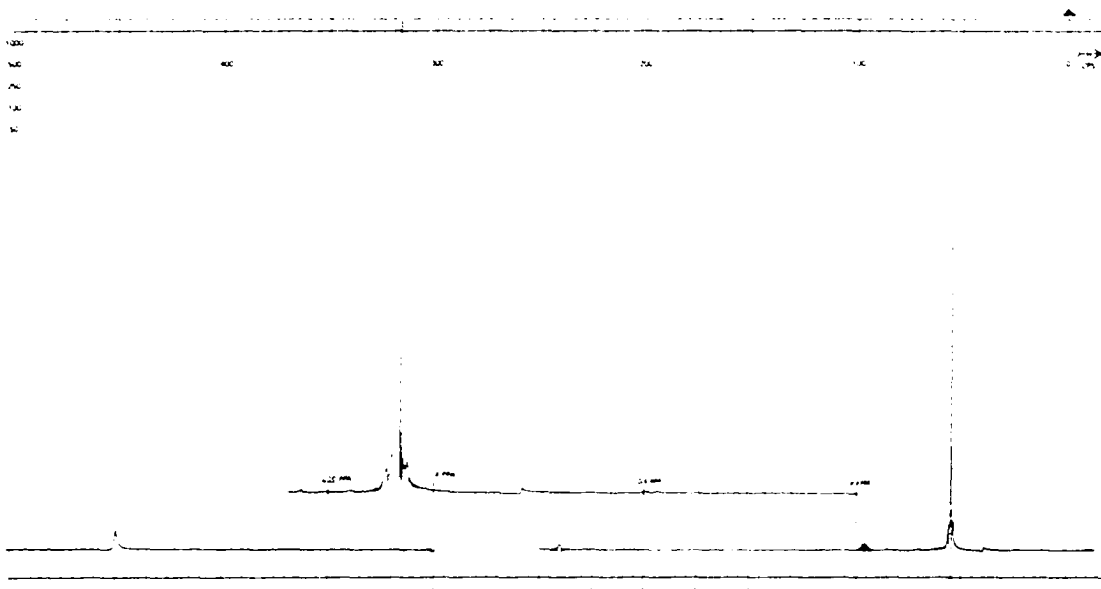


Figure 6. $\frac{1}{3} \text{Si-OC10}_3 + 1\text{H}_2\text{O}$, $t=40$ sec.

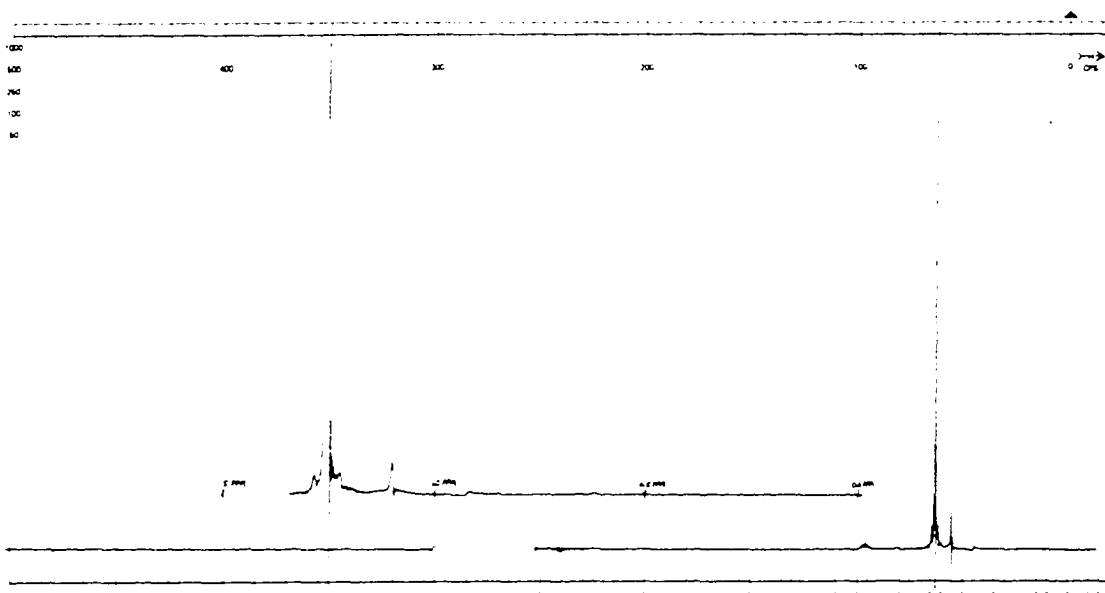


Figure 7. $\frac{1}{3} \text{Si-OC10}_3$.

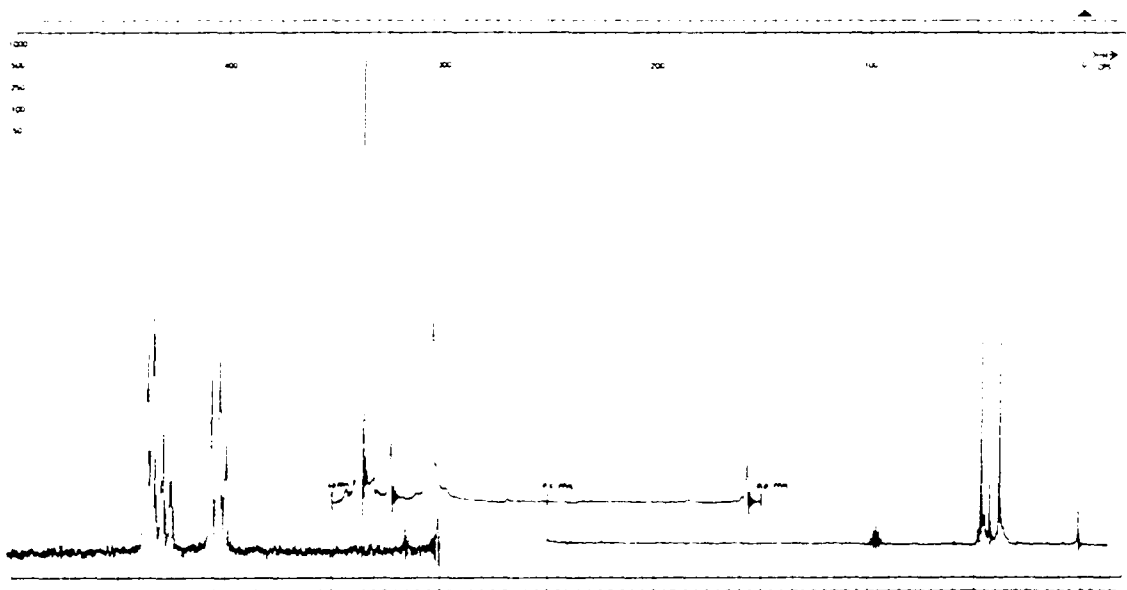


Figure 8. $\text{---Si---OC10}_3 + \text{C}_6\text{H}_5$
 Me_2

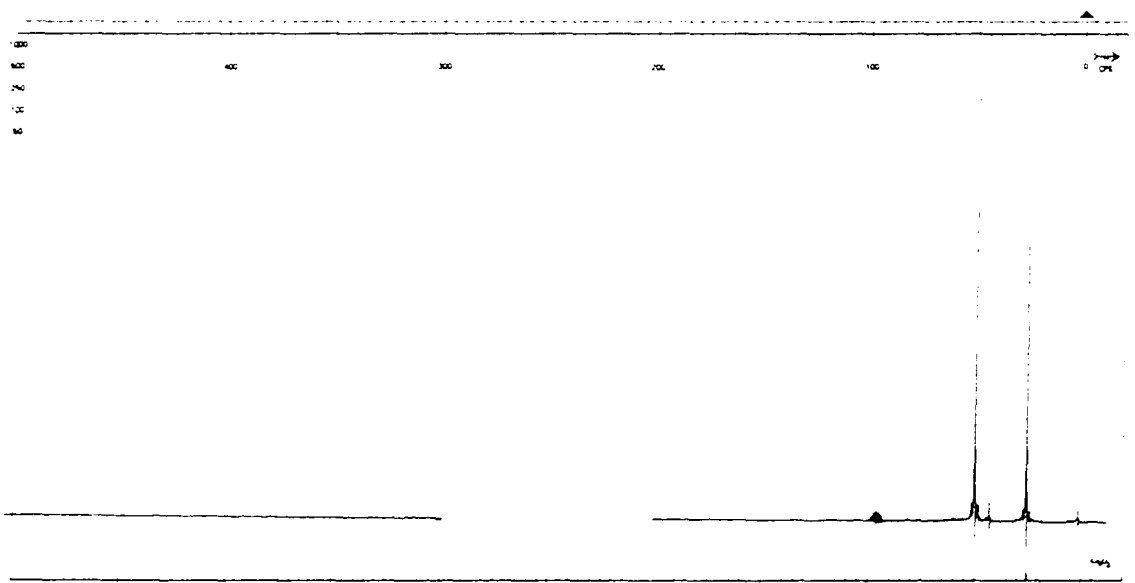


Figure 9. ---Si---OC10_3
 Me_2

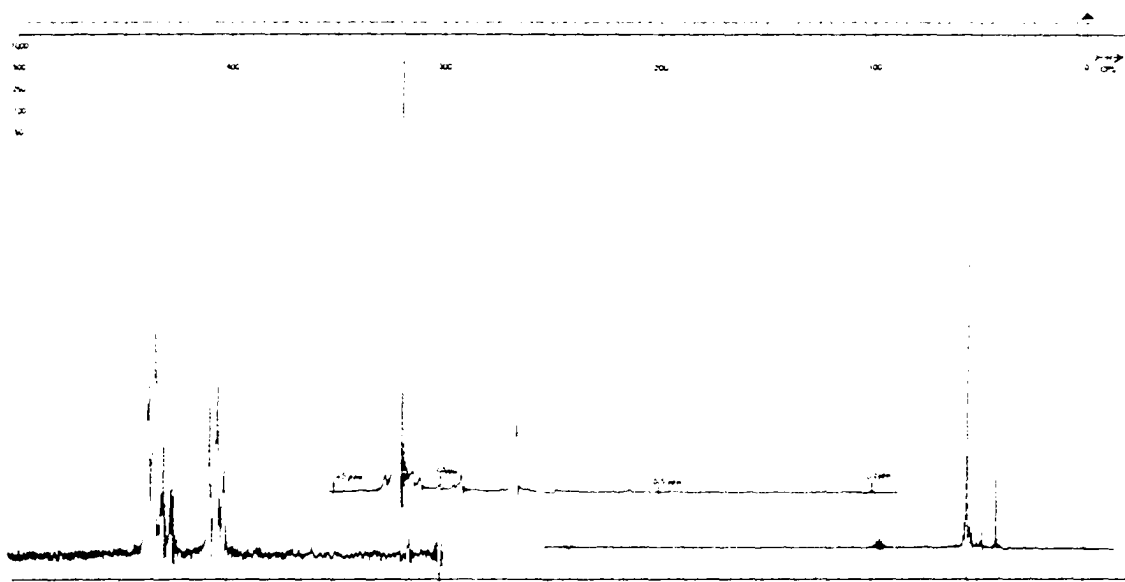


Figure 10. $\text{Me}_2\text{Si}-\text{OC}_6\text{H}_5 + \text{C}_6\text{H}_5$.

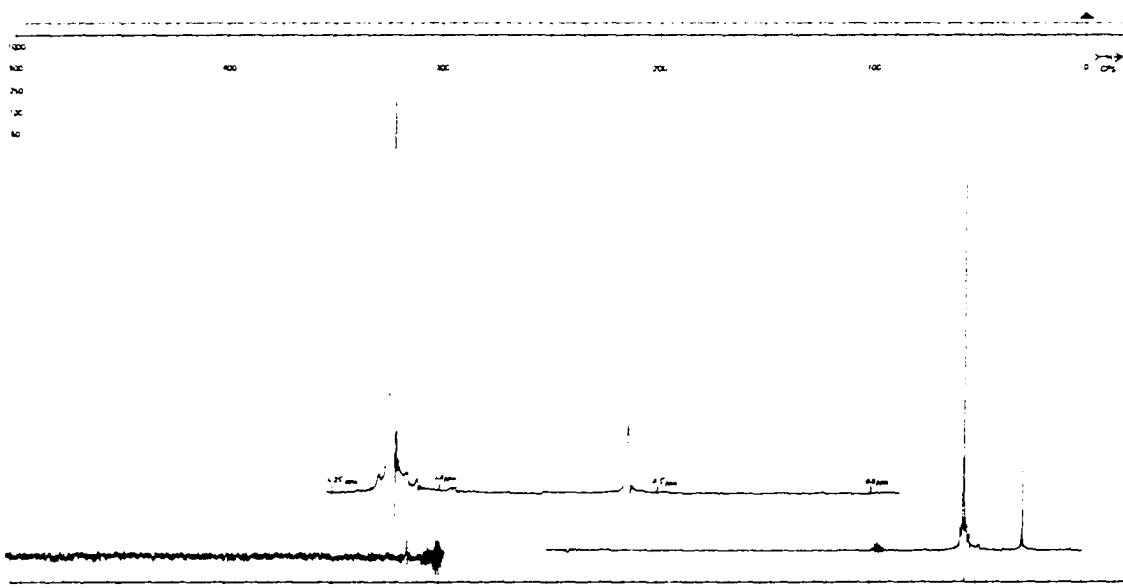
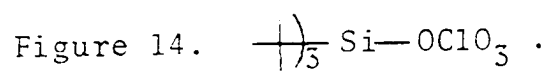
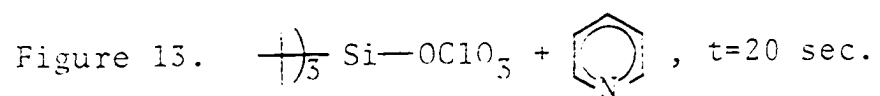
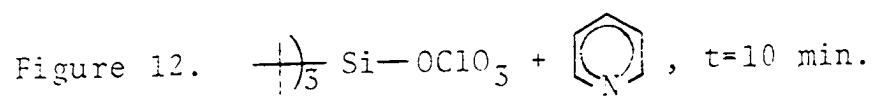
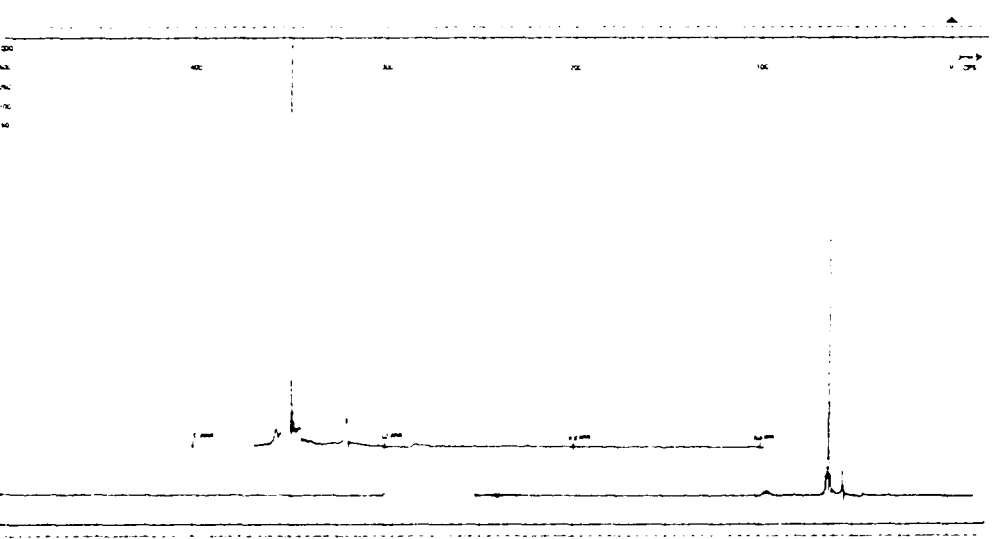
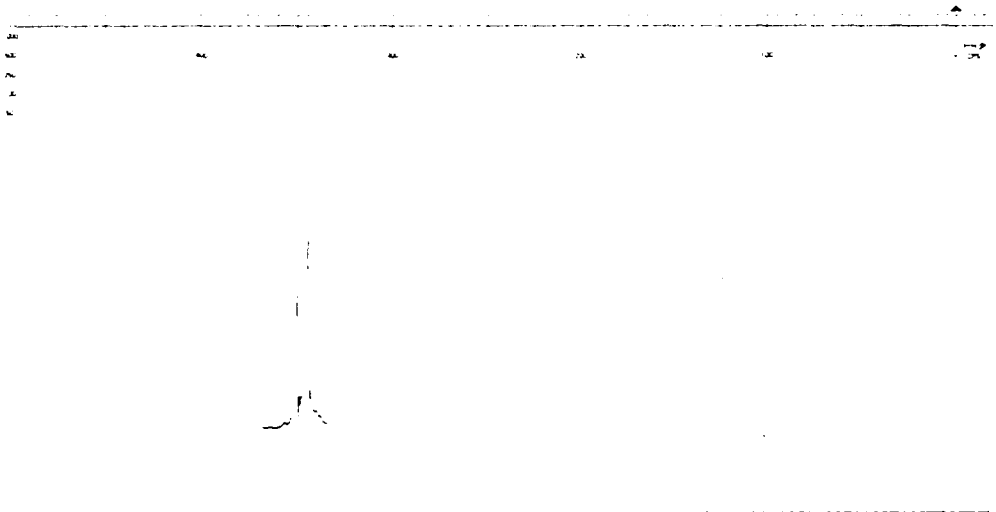
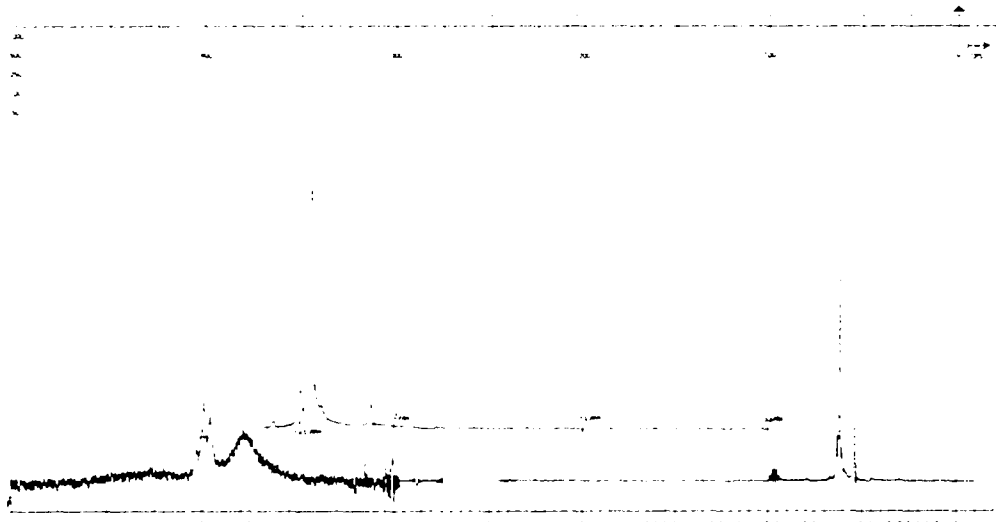


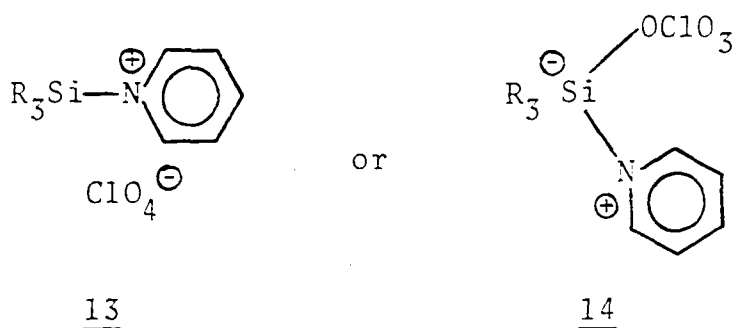
Figure 11. $\text{Me}_2\text{Si}-\text{OC}_6\text{H}_5$.



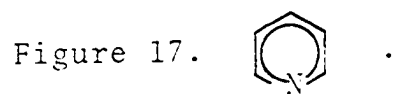


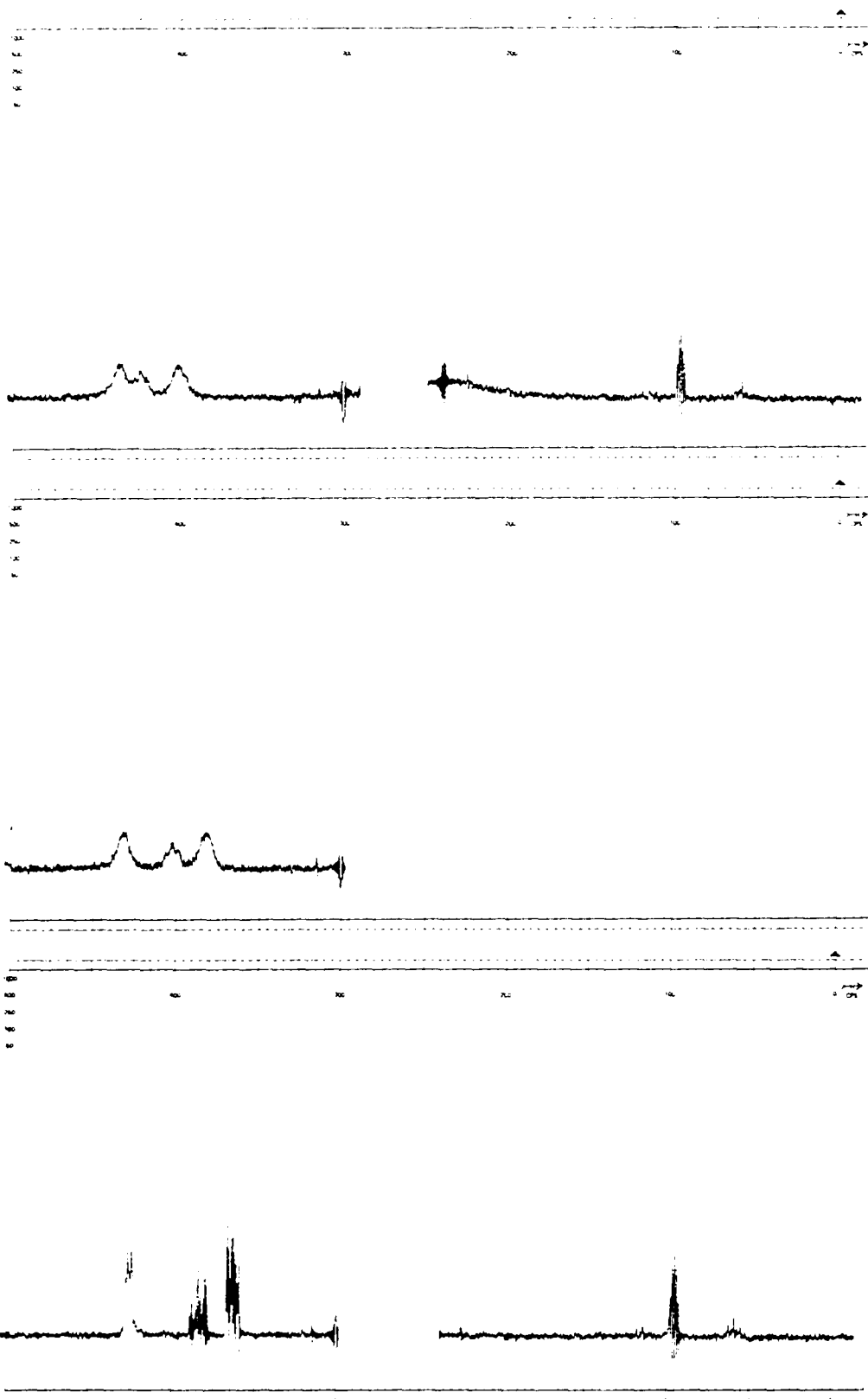
nmr spectrum were recorded (Figures 15-17). Similarities in the chemical shifts of the aromatic protons in figures 8,10 and 15 are apparent, though in figures 15 and 16 considerable broadening was observed.

Two possibilities come to mind for the structures of these pyridinium compounds:



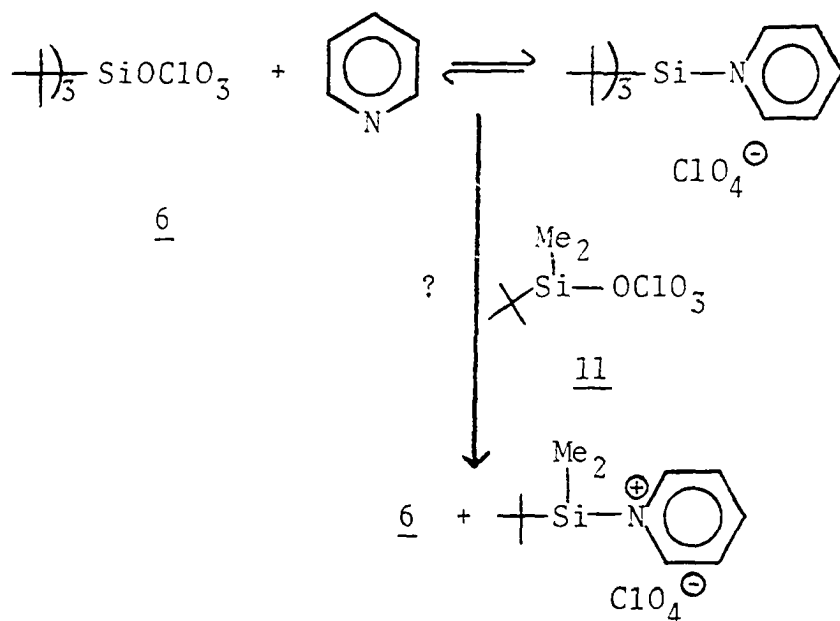
Both structures could account for the shift of the aromatic protons but structure 13 most easily accounts for the downfield shifts of approximately 0.25 ppm observed for methyl on silicon in 11 and 12 since presence of an adjacent positive charge results in downfield shifts for carbon compounds. Structure 14 might be expected to cause an upfield shift since a negative charge is present on silicon, but depending on the conformation of the methyl group relative to the aromatic ring, either diamagnetic or paramagnetic anisotropy might result. A conductance experiment could,





in principle, differentiate between these two possibilities because 13 is an ionized species while 14 is merely a polar one.

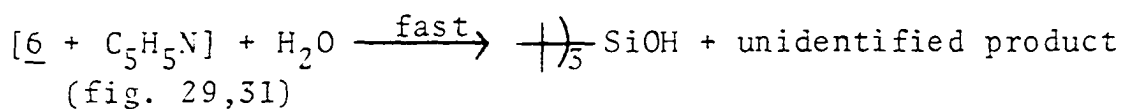
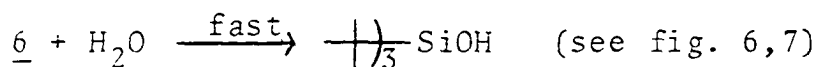
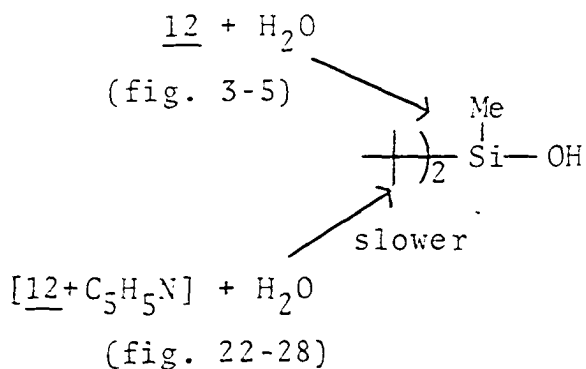
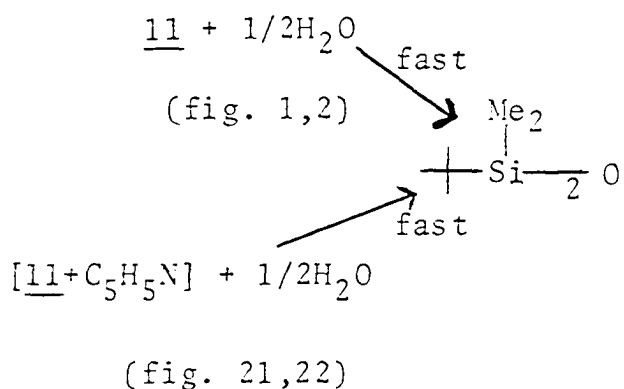
While 11 and 12 exhibited similar behavior (figures 8 and 10) with regard to the formation of a pyridinium complex, 6 was quite different with regard to the chemical shift and sharpness of the pyridine region (see figure 12) reminiscent of the addition of half an equivalent of perchloric acid to pyridine (figure 16)-- that is, the peaks were broad and their chemical shifts were somewhere in between those of pyridine and pyridinium. One explanation which came to mind was an equilibrium between pyridine and pyridinium:



It occurred to us that perhaps such an equilibrium could be disturbed by the addition of t-butyldimethylsilyl

perchlorate (11) to the system. Indeed, when a slight excess of 11 was added to the system, the aromatic region became identical to that observed in the reaction of 11 alone with pyridine (figures 8,9,18,19).

When the pyridinium complexes were quenched with water we observed some rather interesting differences between them and the perchlorates themselves:



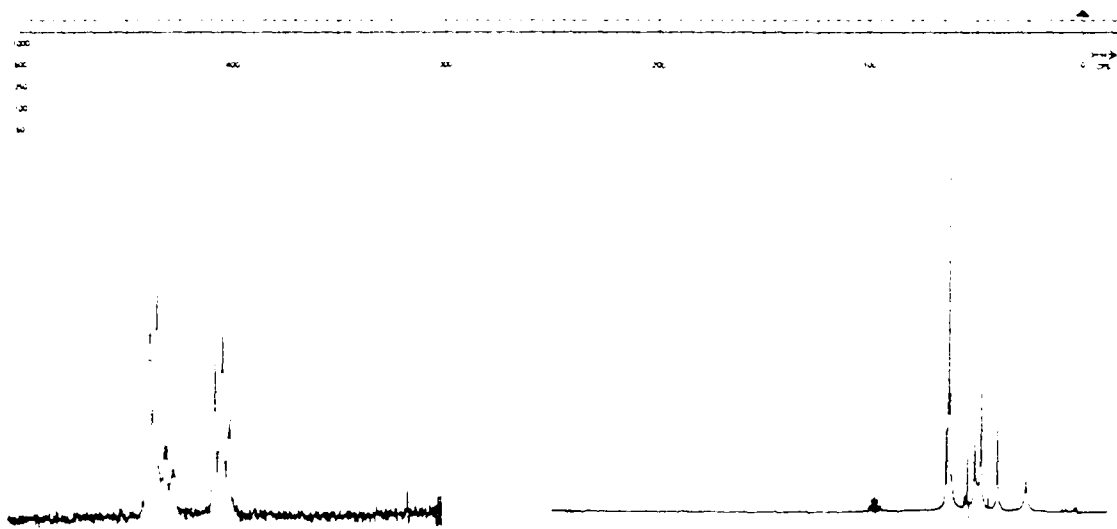


Figure 18. $[\text{---} \text{Si} - \text{OCIO}_3 + \text{C}_6\text{H}_5\text{N}, t=12 \text{ hrs}] +$
 $\text{---} \text{Si} - \text{OCIO}_3, t=1 \text{ min.}$
 Me_2

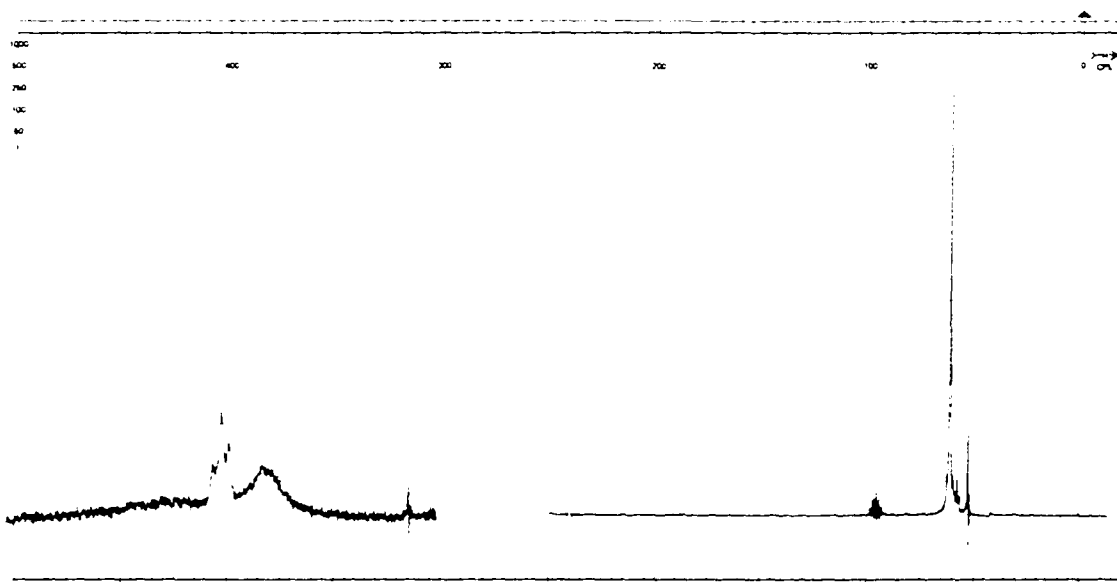


Figure 19. $\text{---} \text{Si} - \text{OCIO}_3 + \text{C}_6\text{H}_5\text{N}, t=12 \text{ hrs.}$

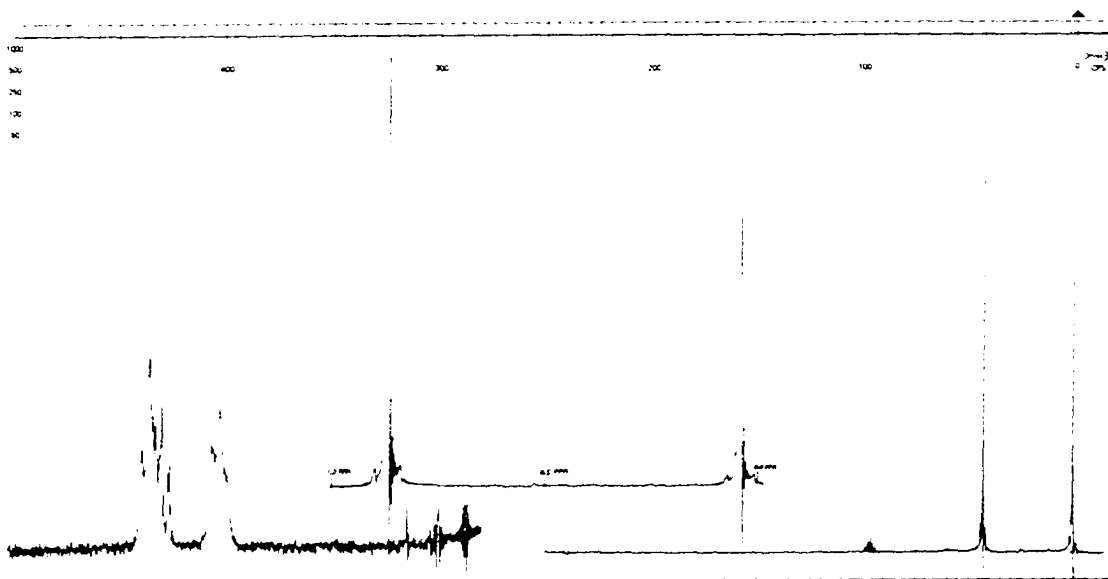


Figure 20. $\left[\begin{array}{c} + \text{Si} - \text{OCIO}_5 \\ | \\ \text{Me}_2 \end{array} + \text{C}_6\text{H}_5\text{N} \right] + 1/2 \text{H}_2\text{O}, t=3 \text{ min.}$

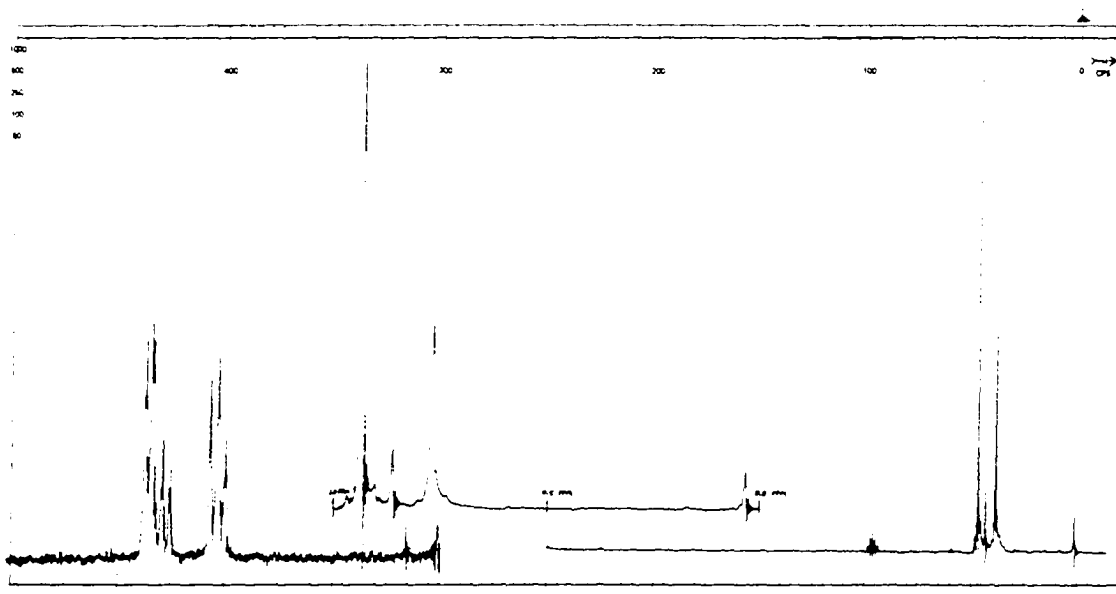
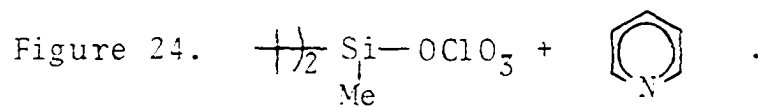
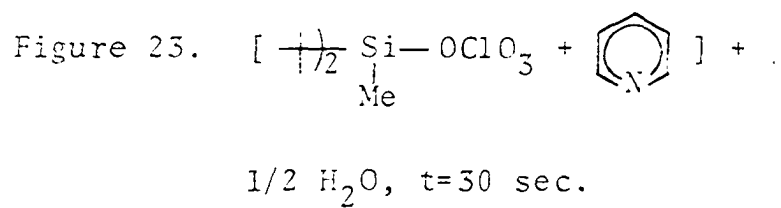
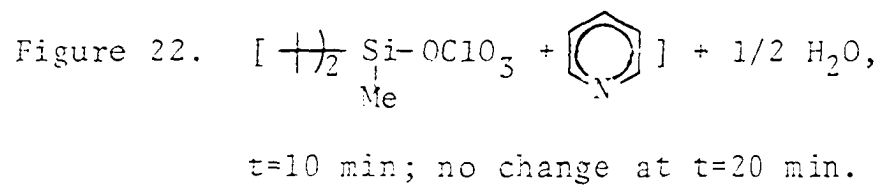
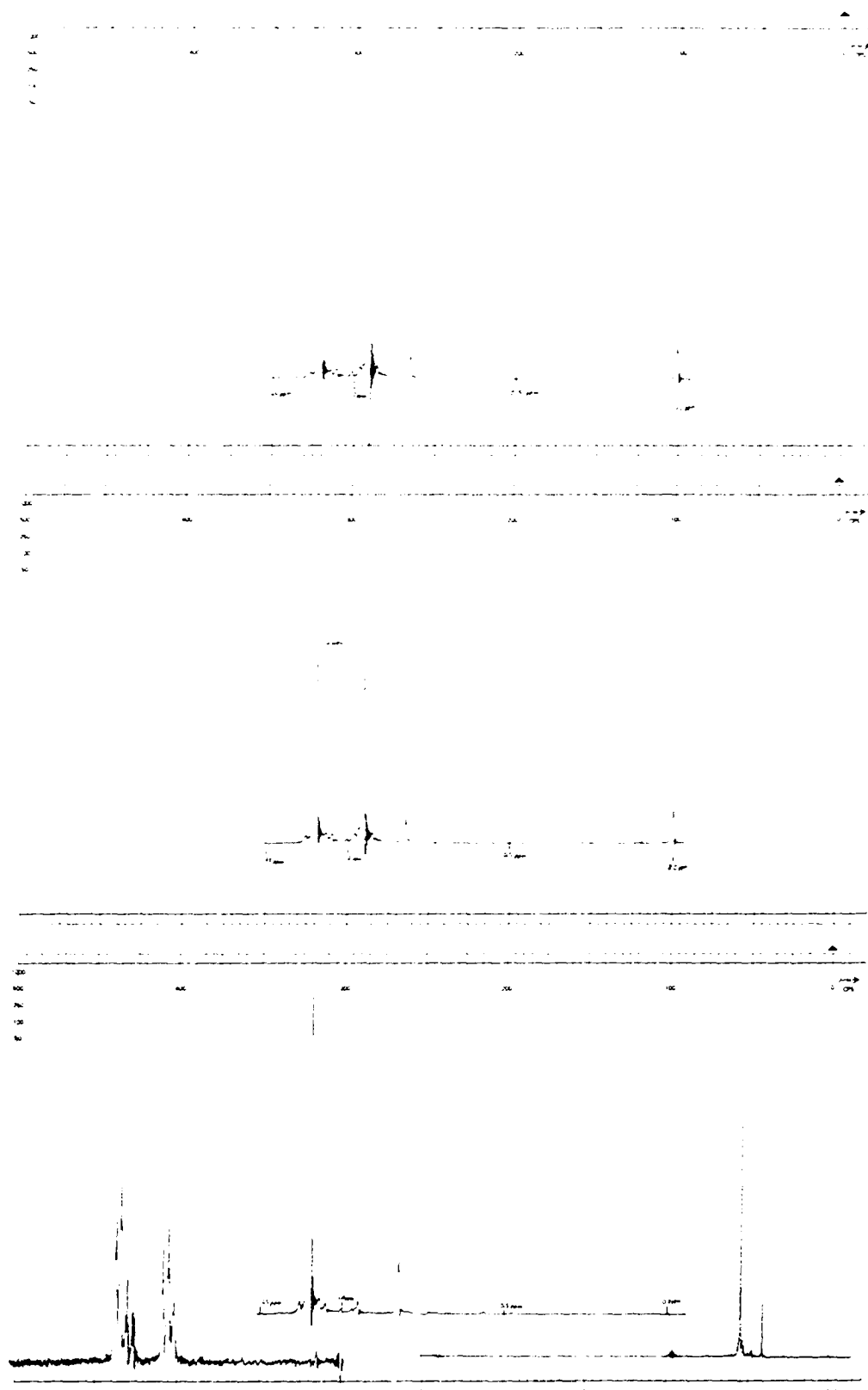


Figure 21. $\begin{array}{c} + \text{Si} - \text{OCIO}_3 \\ | \\ \text{Me}_2 \end{array} + \text{C}_6\text{H}_5\text{N} .$





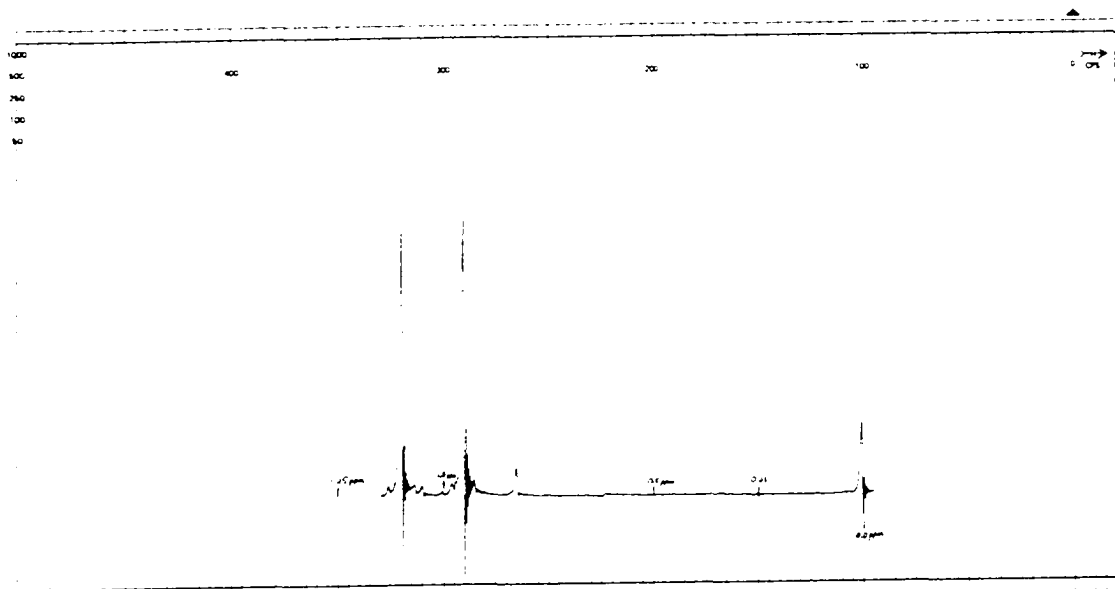


Figure 25. $\left[\begin{array}{c} + \\ | \\ \text{Si} - \text{OCIO}_3 \\ | \\ \text{Me} \end{array} \right]_2 + \text{C}_6\text{H}_5\text{N}] + 1 \text{ H}_2\text{O}, t=50 \text{ sec.}$

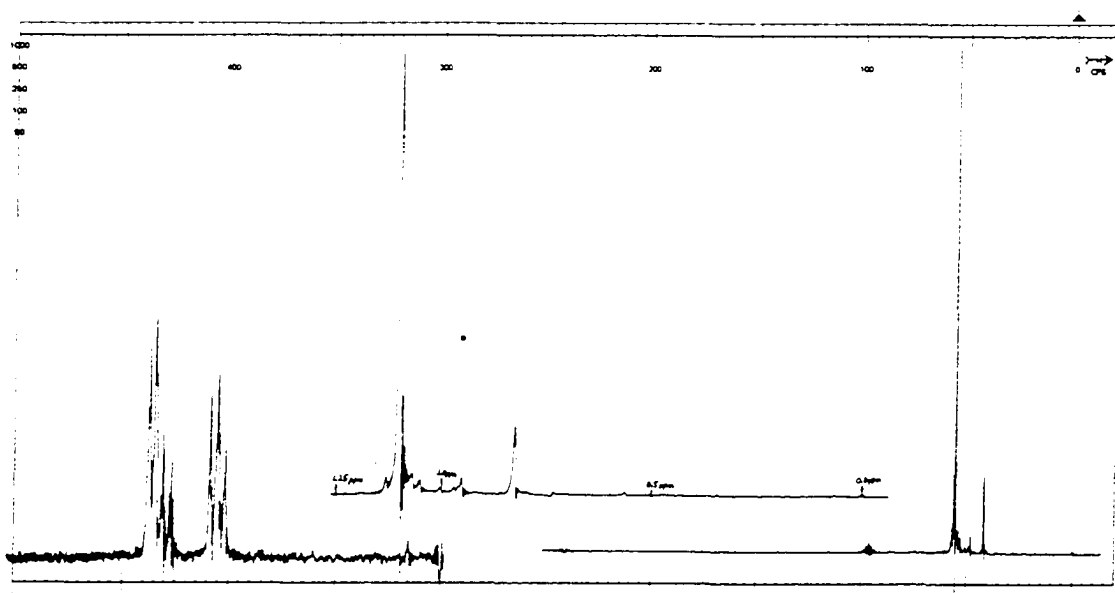


Figure 26. $\begin{array}{c} + \\ | \\ \text{Si} - \text{OCIO}_3 \\ | \\ \text{Me} \end{array} + \text{C}_6\text{H}_5\text{N} .$

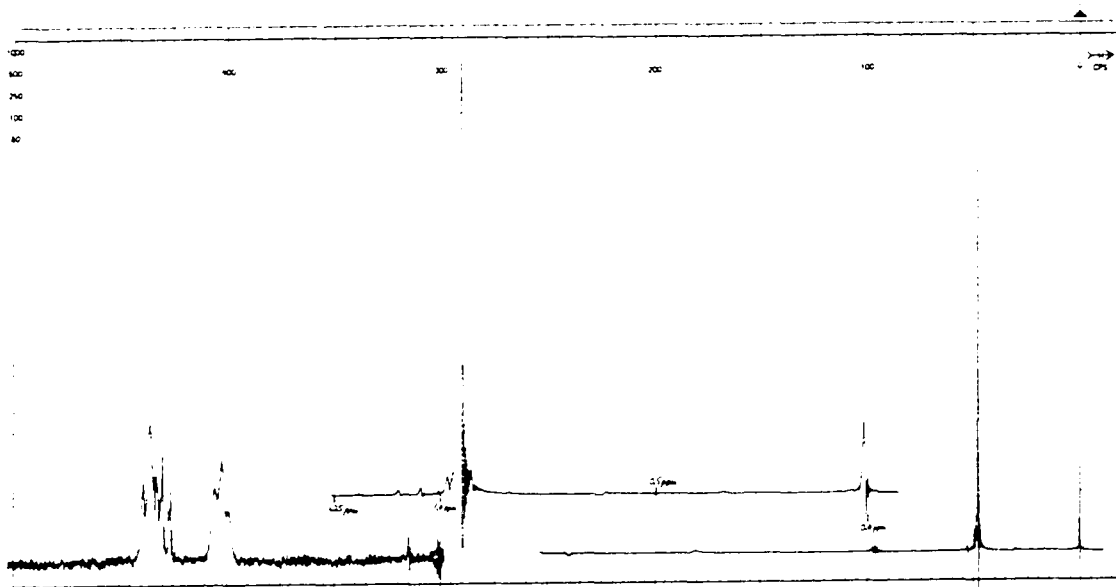


Figure 27. $\left[\begin{array}{c} \text{---} \\ | \\ \text{---} \end{array} \right]_2 \text{Si} - \text{OClo}_3 + \text{C}_5\text{H}_5\text{N}] + 1 \text{H}_2\text{O}, t=25 \text{ min.}$

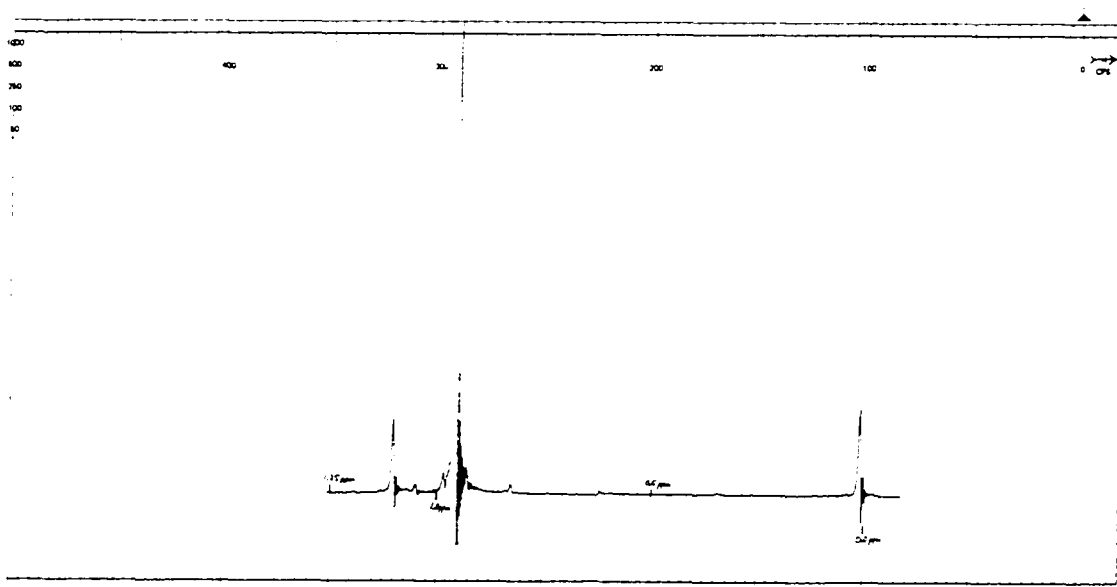
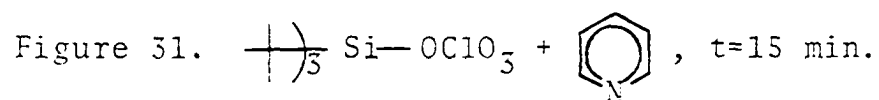
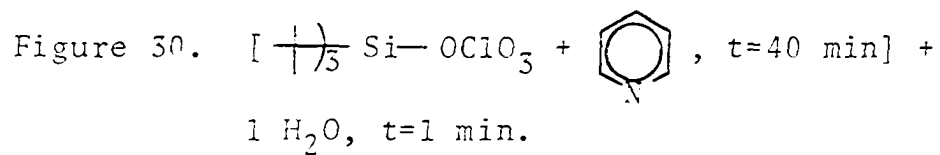
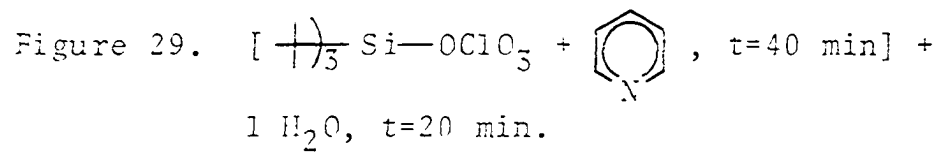
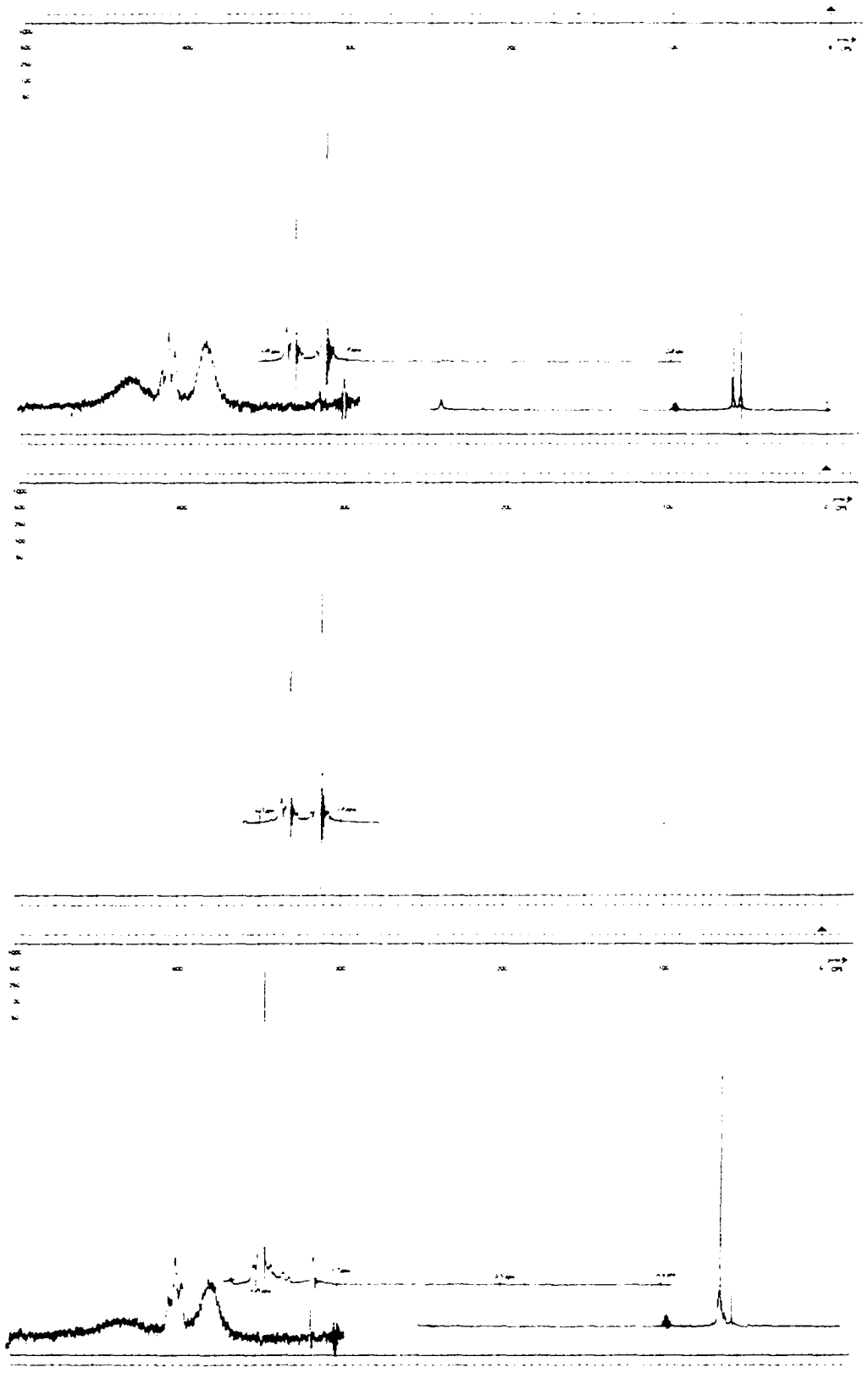


Figure 28. $\left[\begin{array}{c} \text{---} \\ | \\ \text{---} \end{array} \right]_2 \text{Si} - \text{OClo}_3 + \text{C}_5\text{H}_5\text{N}] + 1 \text{H}_2\text{O}, t=5 \text{ min.}$





At this point it was apparent that if the reactions of the perchlorates themselves were to be observed, then a less nucleophilic base would be required. We felt that a 2,6-di-t-butylpyridine offered the best hope for a non-nucleophilic base in our sterically crowded systems. We chose 2,6-di-t-butyl-4-methylpyridine (15) as a convenient preparation had recently appeared (38) by which it could be obtained in good yield and high purity.

It was quite surprising to find that all three perchlorates reacted with 15, indeed it appeared that perhaps the reactivity order of the series was 11 < 12 < 6 (see figures 32-38). Another very interesting observation was that in the reaction of 6 it appeared that an intermediate species increased in concentration for the early part of the reaction then disappeared rather rapidly (see figure 37). It also appeared that, at least for 12, quenching of the rather complicated reaction mixture with methanol led to a single product (see figures 39 and 40).

These preliminary results were extremely exciting and consequently we decided to study the kinetics of these reactions more carefully. It seemed that FTNMR was the ideal method to monitor the reactions. Using FTNMR, the areas of various peaks as functions of time are readily available.

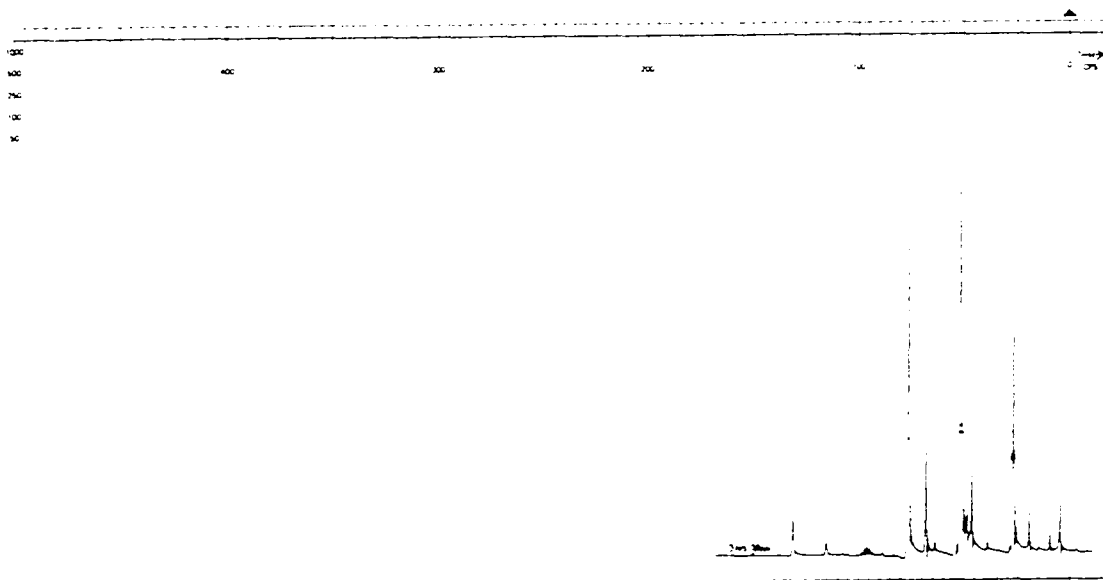
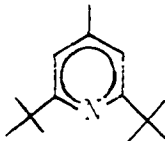


Figure 32. $\text{---Si}(\text{Me}_2)\text{---OCIO}_3 +$  , t=210 min.

15

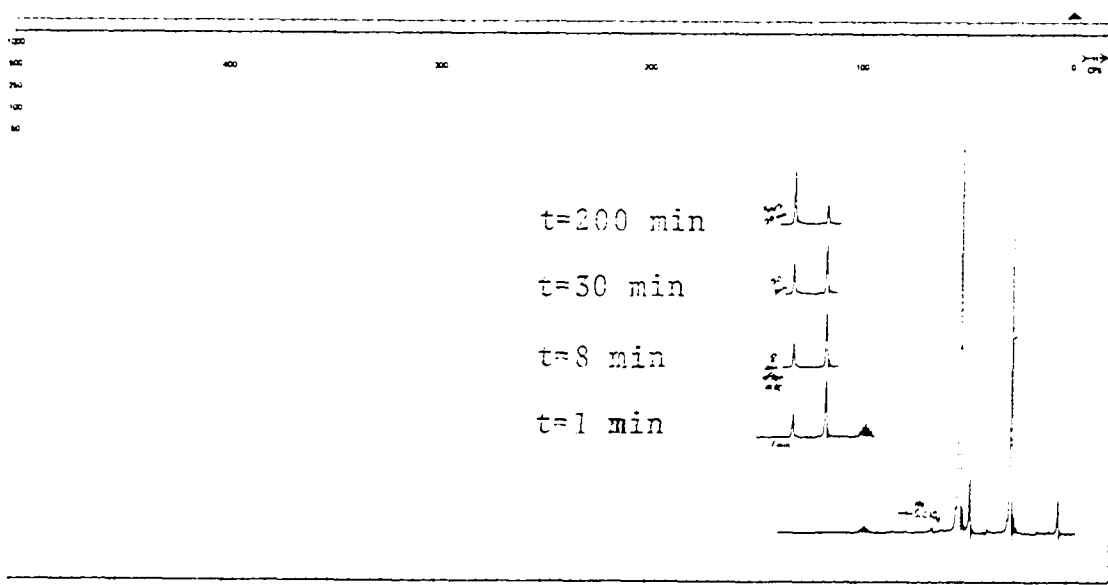


Figure 33. $\text{---Si}(\text{Me}_2)\text{---OCIO}_3 +$ 15.

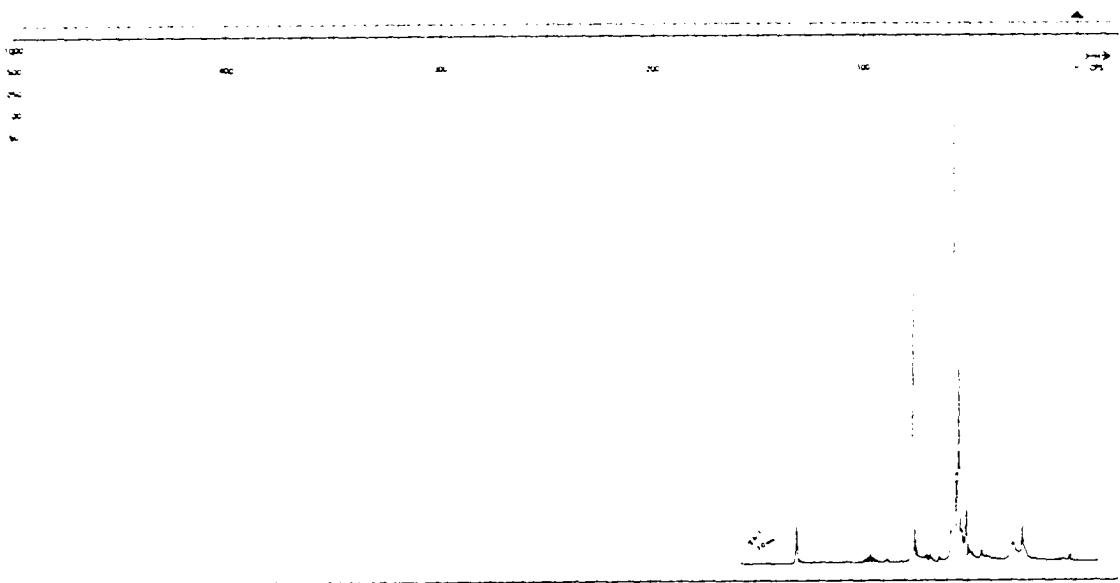


Figure 34. $\left(\frac{1}{2}\right)_2 \text{Si}-\text{OClO}_3 + \underline{15}$, $t=200$ min.
Me

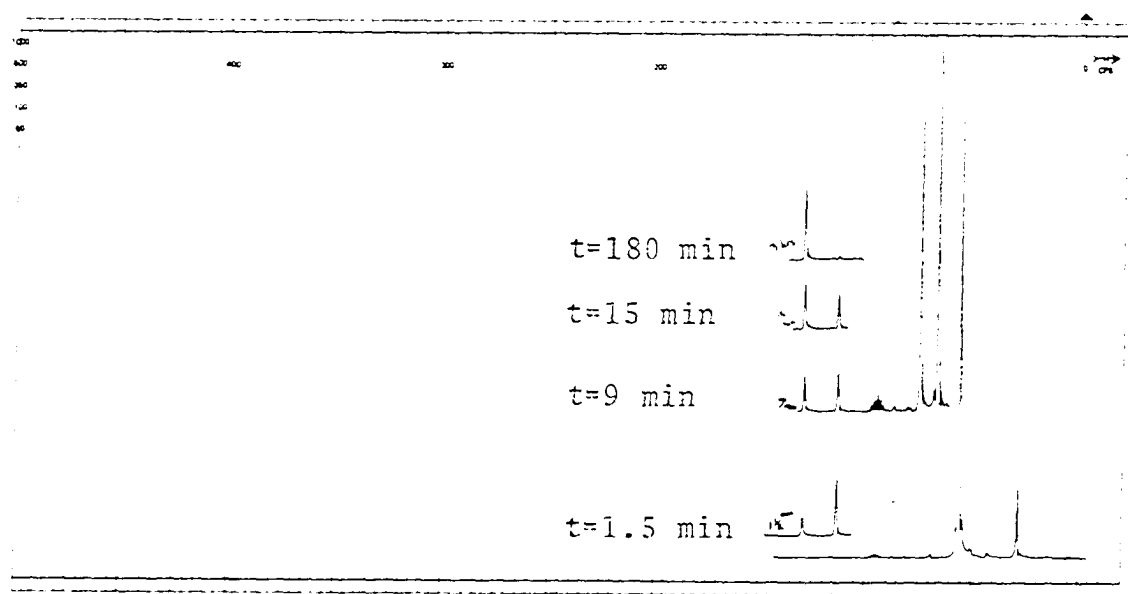
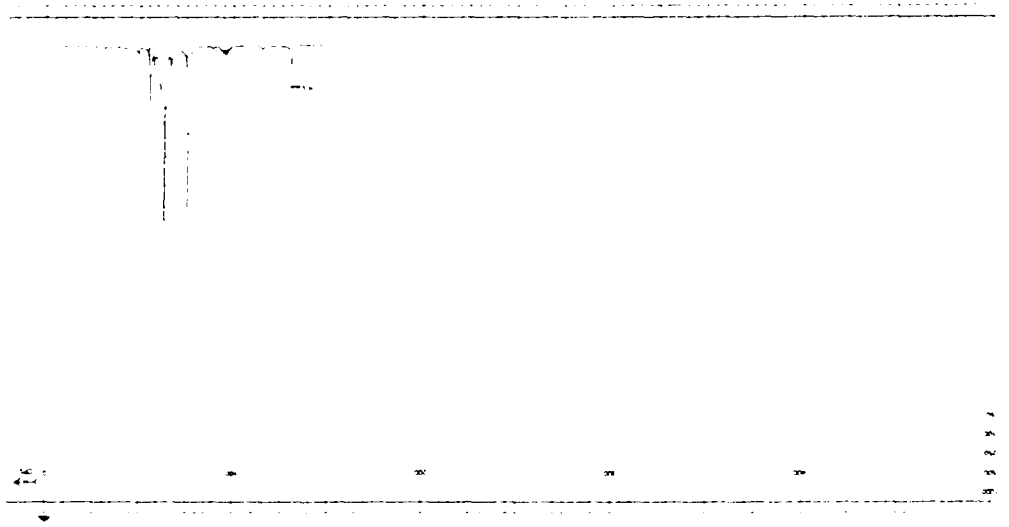
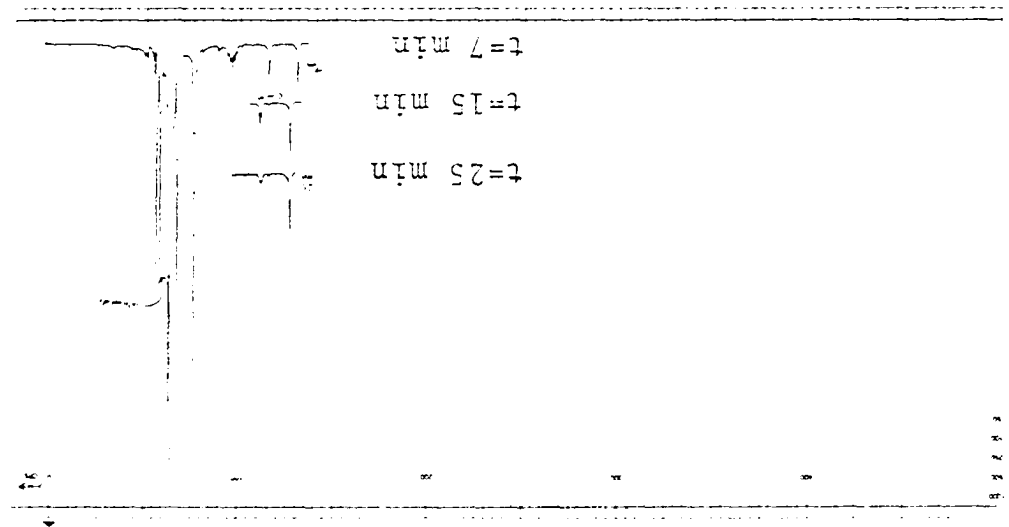
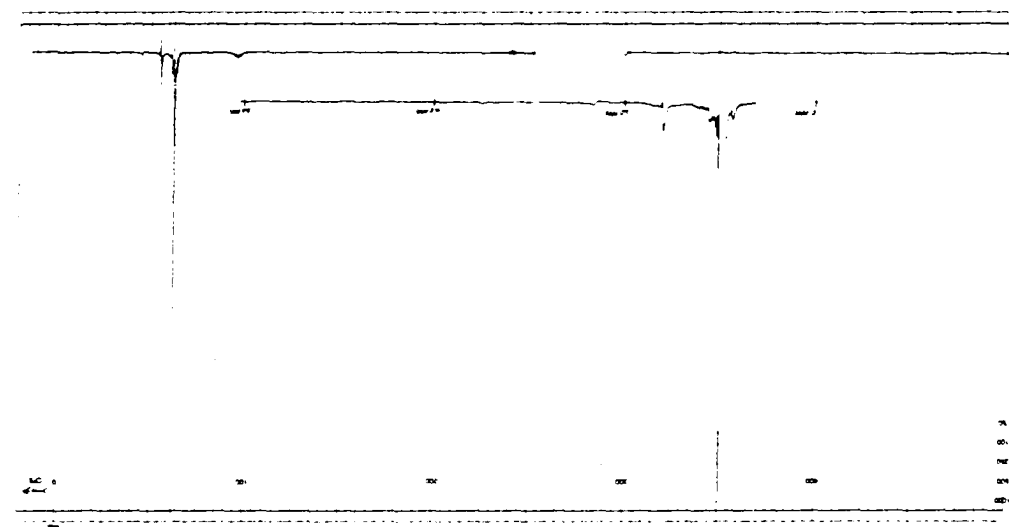


Figure 35. $\left(\frac{1}{2}\right)_2 \text{Si}-\text{OClO}_3 + \underline{15}$.
Me

Figure 36. $\frac{+)}{3} \text{Si-OC10}_3 + \underline{15}$, $t=43$ min.

Figure 37. $\frac{+)}{3} \text{Si-OC10}_3 + \underline{15}$.

Figure 38. $\frac{+)}{3} \text{Si-OC10}_3 \cdot$



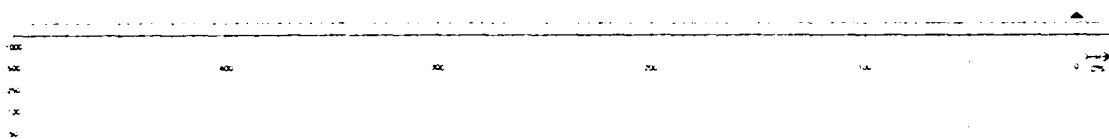


Figure 39. $\left[\begin{array}{c} + \\ 2 \end{array} \right] \text{Si}-\text{OClo}_3 + 2/3 \underline{15}, t=24 \text{ hrs}$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{Me}$

1.5 MeOH, $t=40 \text{ sec.}$

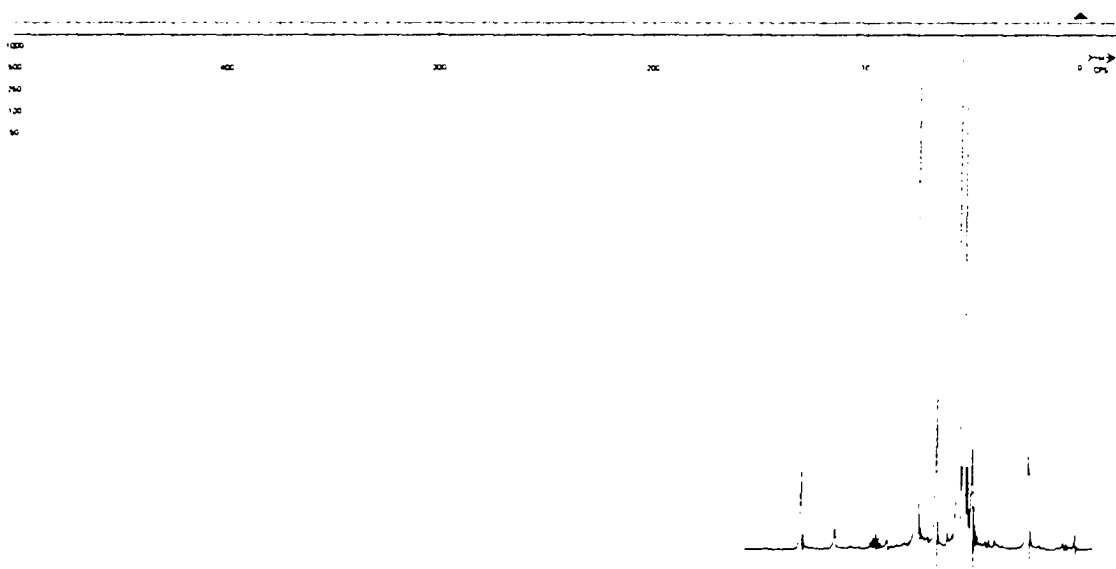
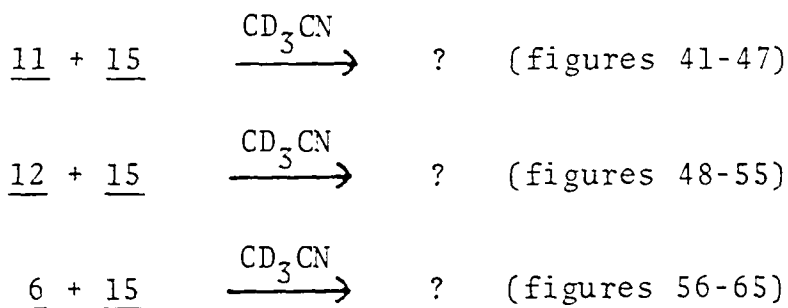


Figure 40. $\left[\begin{array}{c} + \\ 2 \end{array} \right] \text{Si}-\text{OClo}_3 + 2/3 \underline{15}, t=24 \text{ hrs.}$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{Me}$

Computer assistance was used to reduce the data and the salient features of the computer program are mentioned below:

1. Interest centered on the decay of pyridine to pyridinium;
2. All absolute areas within a given block of data acquisition were related to the absolute area of an internal standard to minimize possible fluctuations in the intensities of observed signals;
3. The initial area of a particular pyridine peak was set to one at the beginning of the reaction and all subsequent areas of that peak were normalized to the initial area;
4. A computer plotting routine was used to graph the normalized area of the peak of interest versus time.

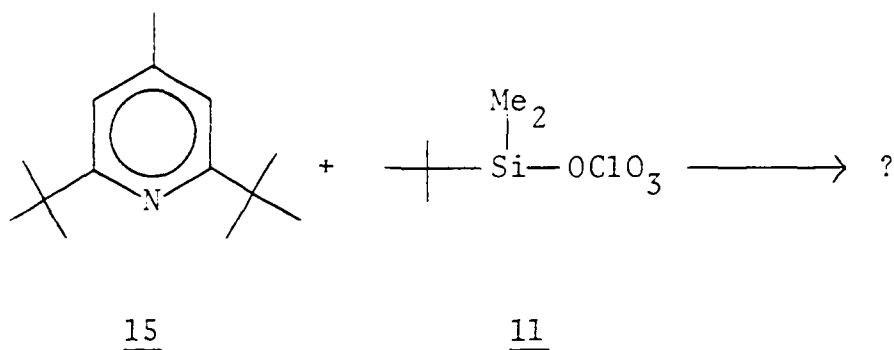
Representative nmr spectra are included with the computer generated plots for all three experiments:



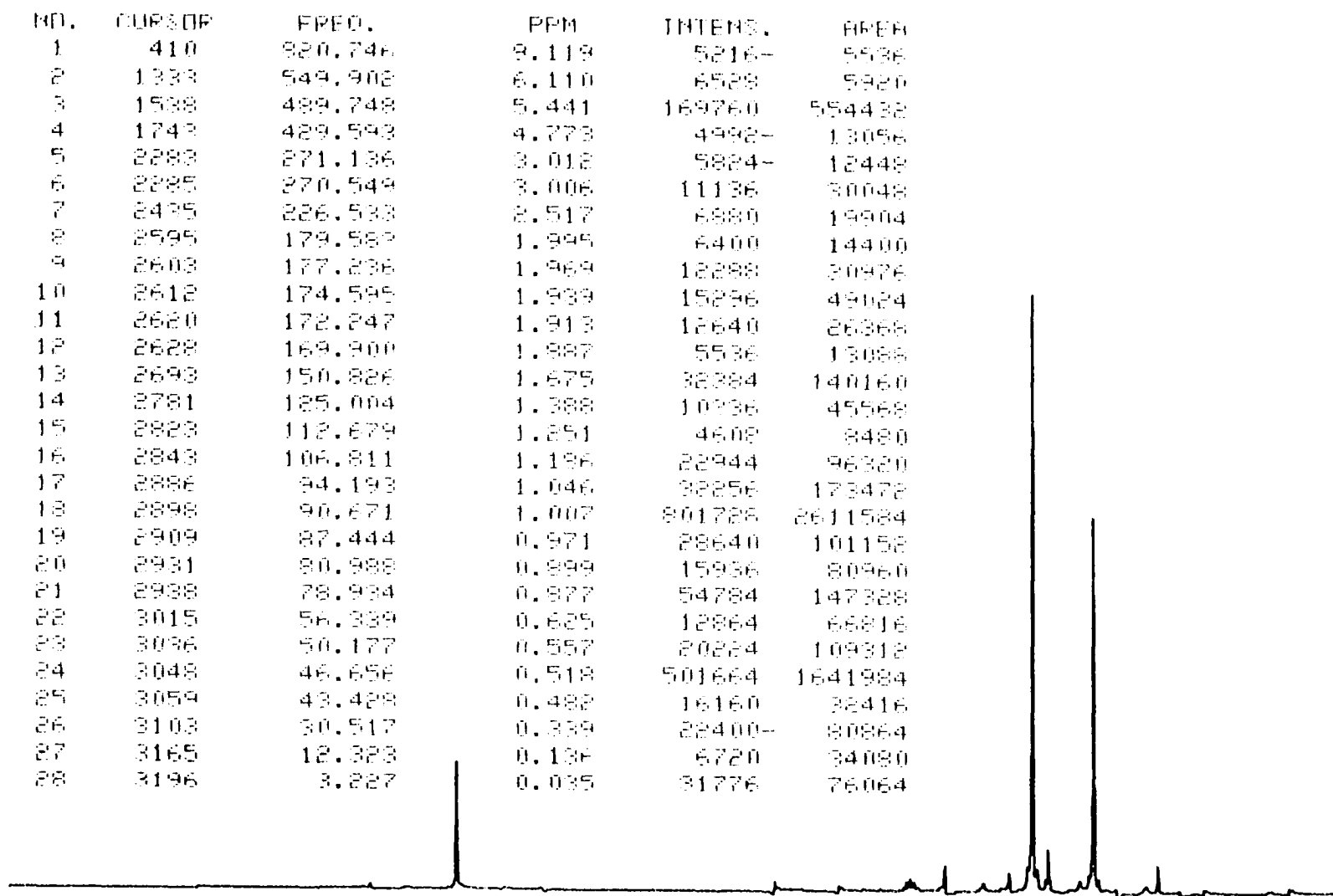
All experiments were run at equal concentrations and 15 was in 10% excess. One might expect this reaction to follow second-order kinetics and therefore the rate of consumption of 15 should slow dramatically as it approaches its final value of 90% conversion; however, examination of

the rate curves for all three perchlorates indicates that the consumption of 15 slows to an ebb long before the theoretical 90% conversion is reached.

On pages 100b-123 the FTNMR data is presented as it was received from Instrumental Services. In some cases the tuning of the instrument seems to vary considerably from one minute to the next as exemplified by the wide variance observed in the intensities of side bands. In general the reactions were much cleaner than the number of peaks observed would indicate. In order to remedy the confusion which these extraneous peaks might generate, an attempt will be made to point out the peaks of interest for each reaction.



internal standard CH ₂ Cl ₂ :		§ 5.44
starting <u>11</u> :	Si —	1.01
	Si — Me	0.52
starting <u>15</u> :	Ar — H	7.02
	Ar — Me	2.29
	Ar —	1.31
product pyridinium:	Ar — H	7.74
	Ar — Me	2.62
	Ar —	1.51



100 b

Figure 41. FTNMR of ---Si---OC10_3 (12).
 Me_2

T-BU DIMETHYLSILYL PERCHLORATE+DI-T-BU METH PYRID

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	832	696.915	7.743	96864	286688
2	1054	631.772	7.019	96256	384128
3	1057	630.891	7.009	100095	222208
4	1539	489.748	5.441	316800	777472
5	2404	235.630	2.618	83456	424064
6	2504	206.386	2.292	221808	1065216
7	2744	135.261	1.509	1015040	3364608
8	2804	118.255	1.313	2463104	7649024
9	2896	91.258	1.013	901120	3101568
10	2906	88.324	0.991	242432	860416
11	2916	84.803	0.942	107392	350208
12	2927	82.162	0.912	41216	252160
13	2938	78.994	0.877	95360	270208
14	3051	45.775	0.508	421632	1756800
15	3100	31.397	0.348	140544	431616
16	3161	13.497	0.149	71168	156544
17	3196	3.227	0.035	48000	125696

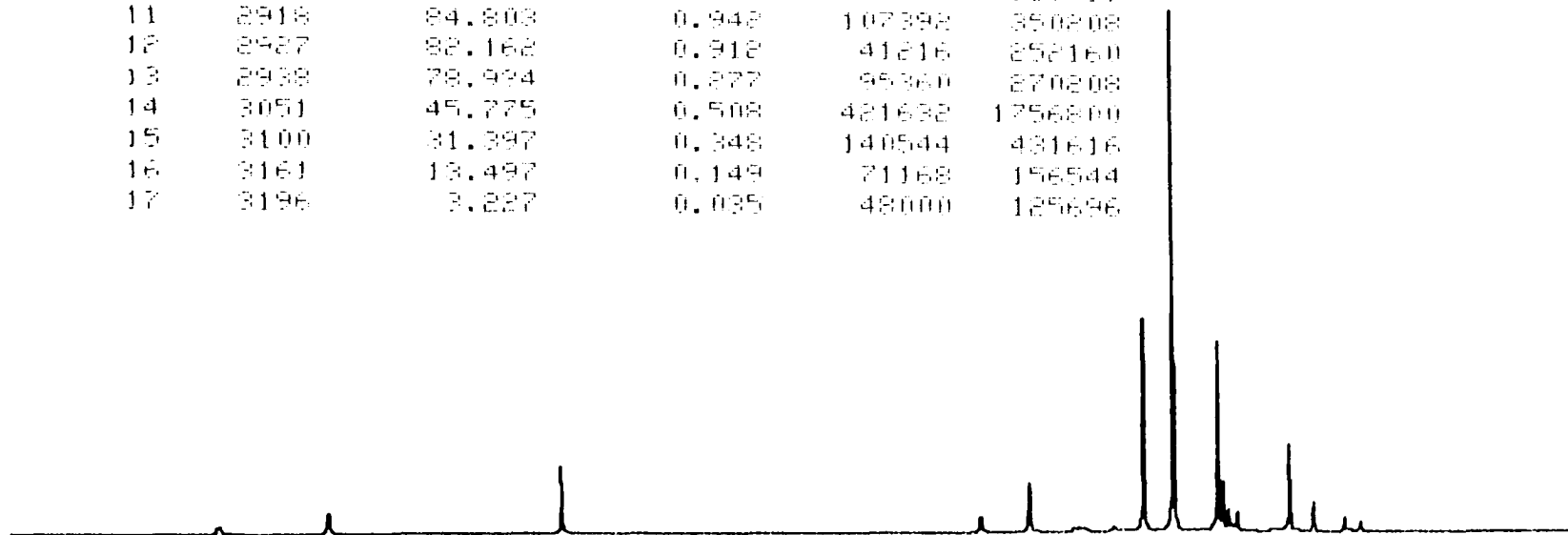


Figure 42. 11 + 15, t=2210 sec.

T-BU DIMETHYLSILYL PERCHLORATE+DI-T-BU METH PYRID					
NO.	CURSOR	FREQ.	PPM	INTERI.	AREA
1	831	697.208	7.746	49024	312192
2	1057	630.891	7.009	92928	536832
3	1538	489.748	5.441	355072	784512
4	2404	235.630	2.618	113792	562688
5	2502	206.873	2.298	120320	333056
6	2504	206.286	2.292	184832	608496
7	2600	178.116	1.979	59128	215552
8	2744	135.861	1.509	1277440	4468224
9	2804	118.255	1.312	1797632	6706252
10	2894	91.845	1.020	620576	2700416
11	2906	89.324	0.991	323584	1220726
12	2919	84.509	0.938	166528	446336
13	2926	82.455	0.916	35268	199552
14	2939	78.934	0.877	110976	244608
15	3054	44.895	0.498	360448	1536284
16	3100	31.397	0.248	248320	623744
17	3162	13.204	0.146	91904	191104
18	3196	3.227	0.035	66944	135168

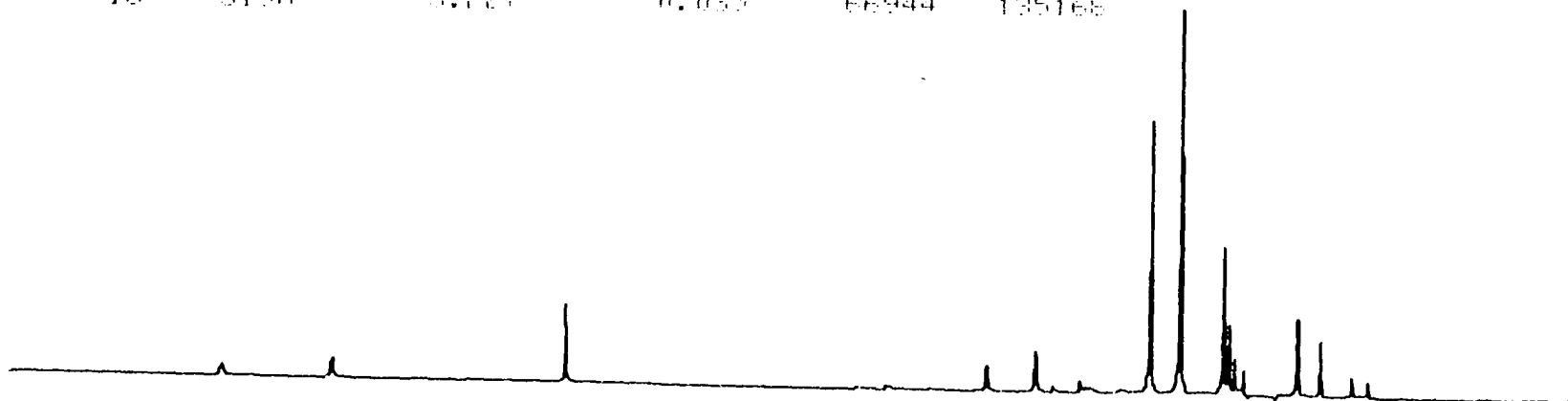


Figure 43. 11 + 15, t=5500 sec.

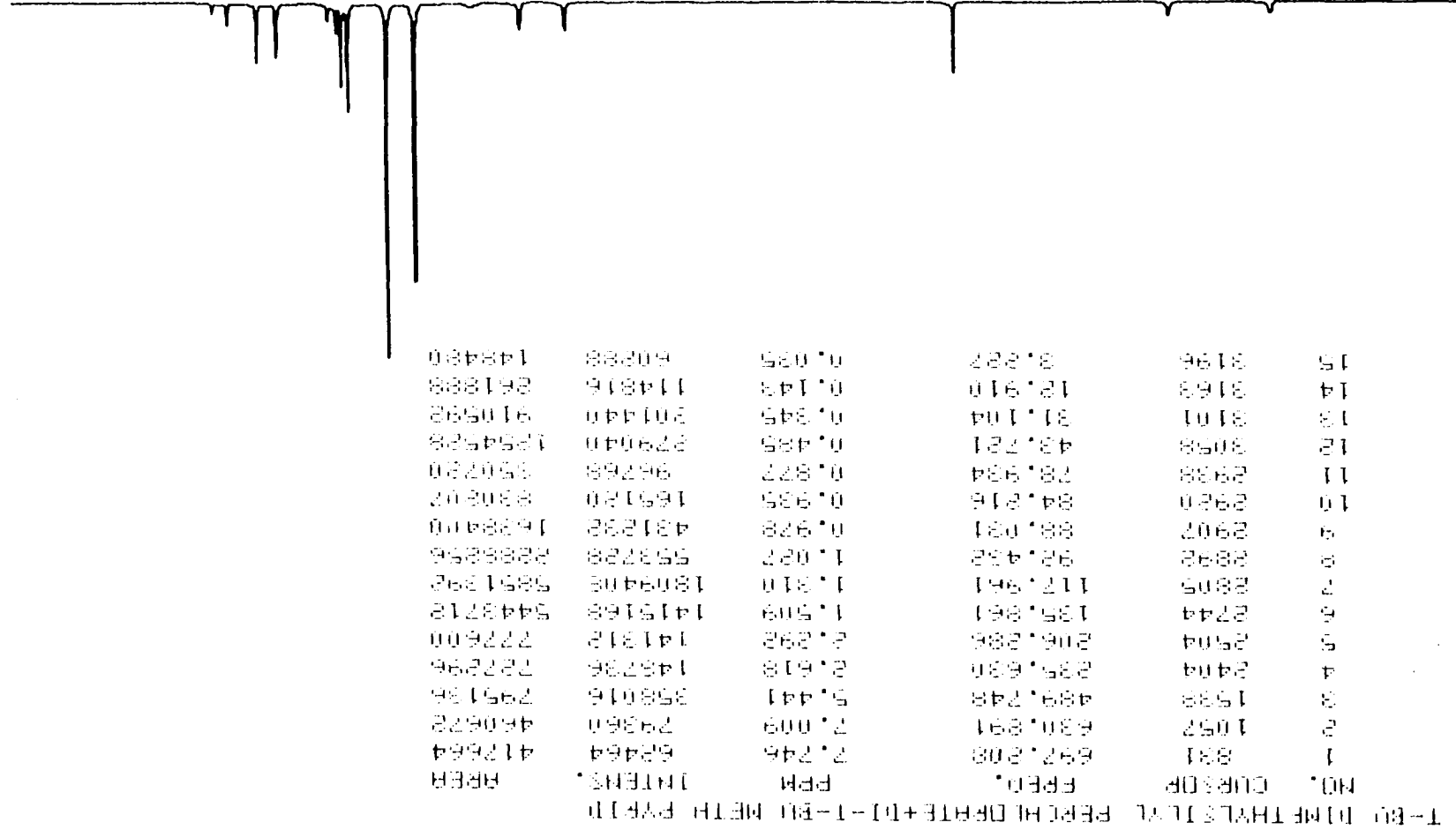


Figure 44. 11 + 15, t=21, 900 sec.

T-BU DIMETHYL PERCHLORATE-D1-1-BU METH EPR10

T-BU DIMETHYLSILYL PERCHLORATE+DI-T-BU METH PYRID

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	833	696.621	7.740	67322	460288
2	1057	630.891	7.009	79972	439936
3	1538	489.748	5.441	343040	628672
4	2404	235.630	2.612	169344	789248
5	2505	205.993	2.229	147072	760576
6	2745	135.568	1.506	1440768	5705216
7	2805	117.961	1.310	1632784	5585152
8	2891	92.726	1.030	499072	2147968
9	2902	87.737	0.974	396672	1697024
10	2920	84.216	0.935	218368	626176
11	2930	81.281	0.903	39926	111616
12	2939	78.641	0.873	117888	382208
13	3059	43.422	0.482	263040	1172096
14	3102	30.310	0.342	293504	977408
15	3163	12.910	0.143	113664	282752
16	3197	2.933	0.032	53376	146688

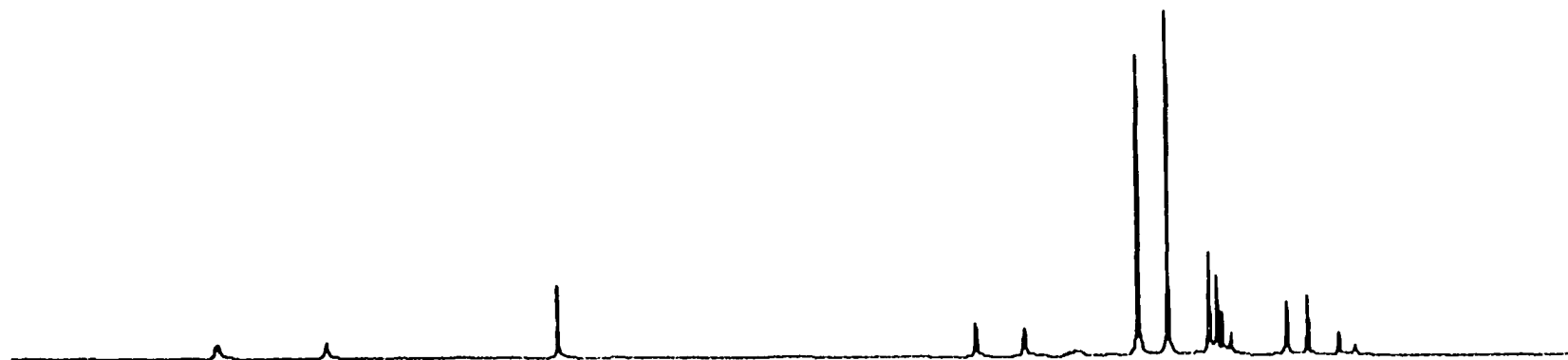


Figure 45. 11 + 15, t=42,500 sec.

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	1539	489.454	5.438	52208	280592
2	2746	135.274	1.503	286176	2106336
3	2806	117.668	1.307	238480	1570640
4	2891	92.726	1.030	61776	653184
5	2909	87.444	0.971	77120	534112
6	3105	29.930	0.332	52704	320864

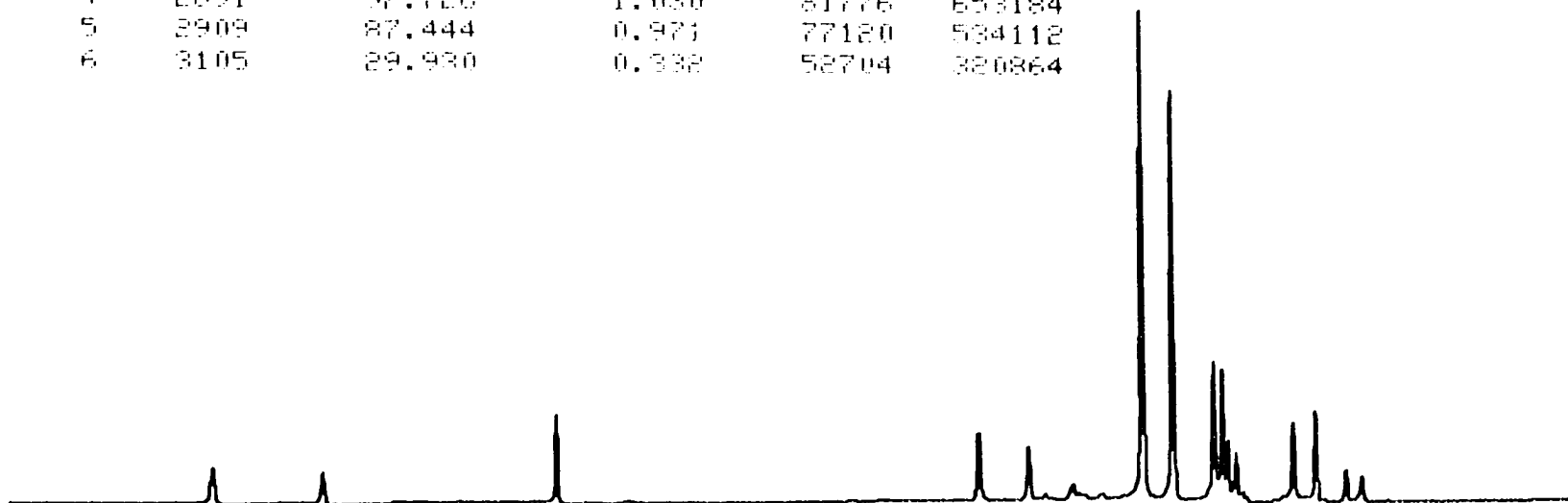


Figure 46. 11 + 15, t=32 hrs.

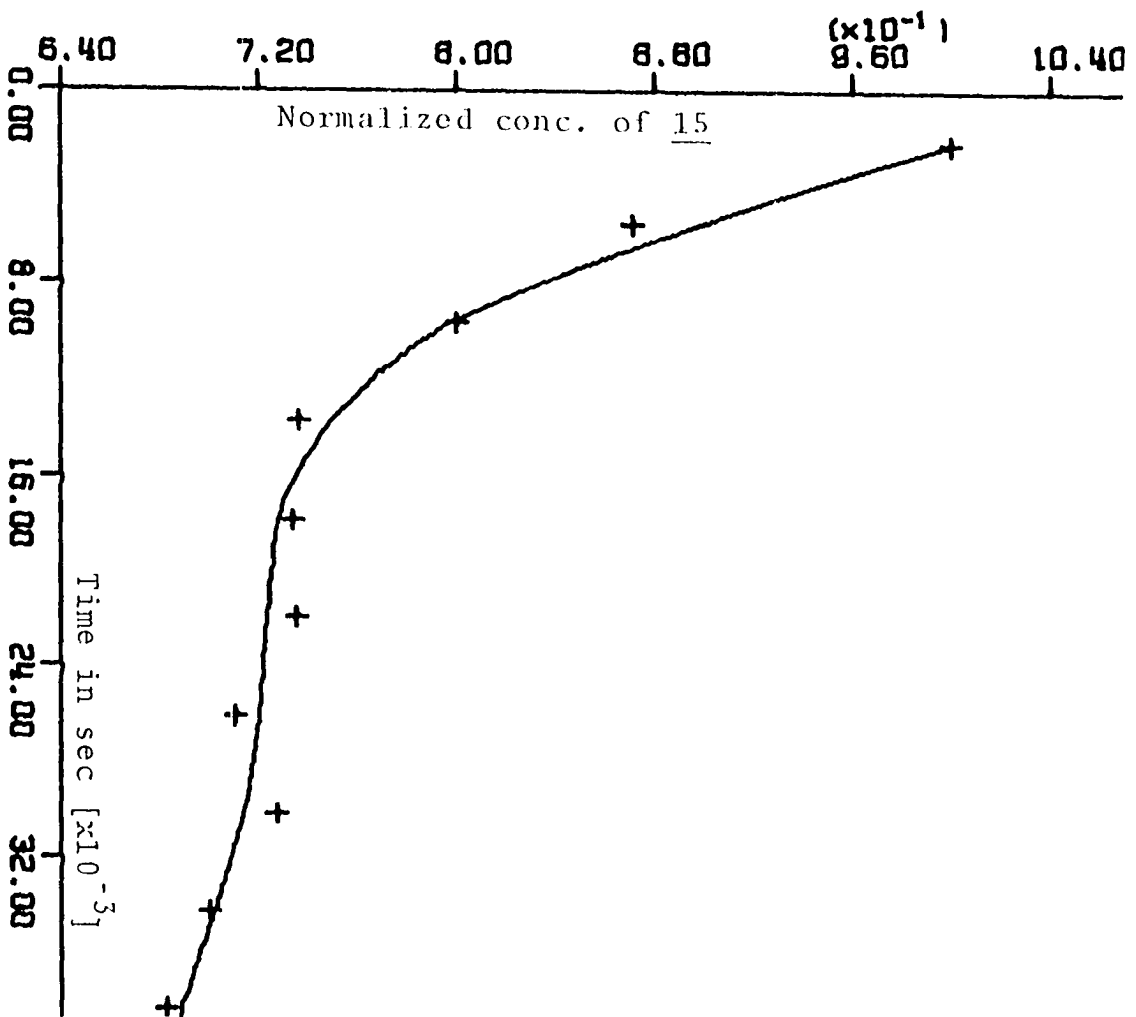
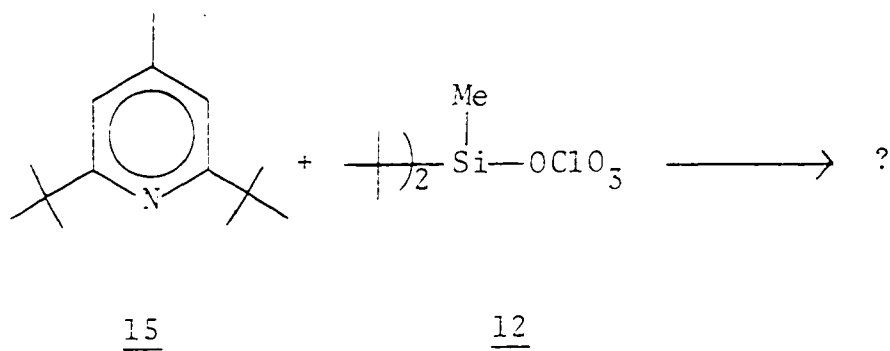
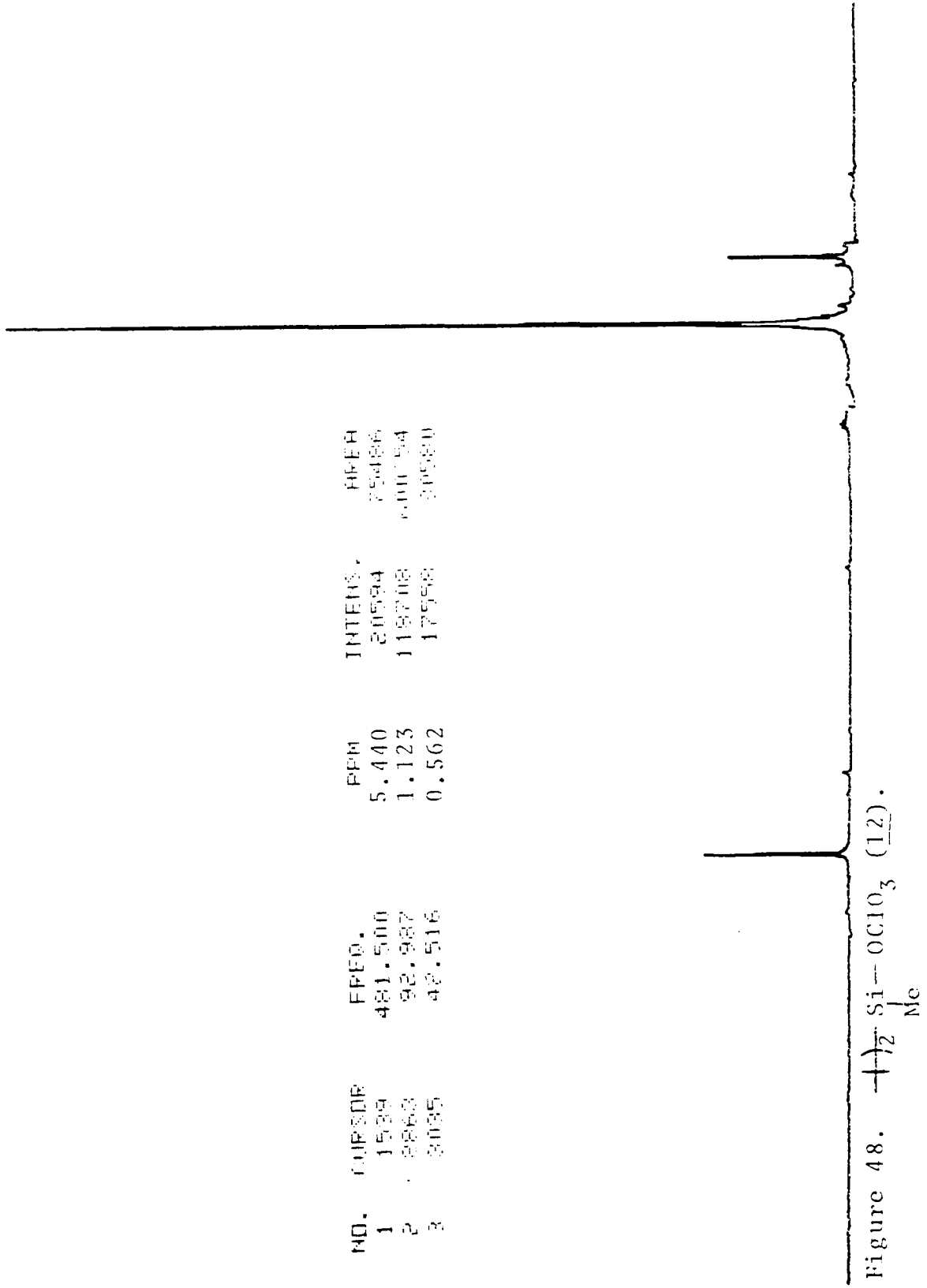


Figure 47. $\text{Me}_2\text{Si-OClO}_3$ (11) + 15.



internal standard CH_2Cl_2 :		δ 5.44
starting <u>12</u> :	Si —	1.12
	Si—Me	0.56
starting <u>15</u> :	Ar—H	7.01
	Ar—Me	2.29
	Ar —	1.31
product pyridinium:	Ar—H	7.74
	Ar—Me	2.62
	Ar —	1.51

Figure 48. $\text{-(CH}_2\text{)}_2\text{-Si(CH}_3\text{)}_2\text{-O-}$ (12).

DI-T-BU Silyl PERCHLORATE+DI-T-BU MET PYRIDINE

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	2	940.469	10.449	916-	1460
2	1057	630.892	7.009	6164	43168
3	1540	489.161	5.435	14256	51728
4	2404	295.630	2.618	1696	9292
5	2506	265.700	2.285	10940	70848
6	2538	196.310	2.181	940	1748
7	2599	178.410	1.982	4760	31940
8	2612	174.595	1.939	1204	2672
9	2621	171.954	1.910	1036	1564
10	2651	163.151	1.812	924	1800
11	2658	161.097	1.789	3444	15796
12	2661	160.217	1.780	1260-	3372
13	2677	155.522	1.728	1268	3920
14	2745	135.568	1.506	12964	69394
15	2805	117.962	1.310	93076	448648
16	2824	112.386	1.248	1188	6004
17	2863	100.942	1.121	73304	382676
18	2883	95.073	1.056	7892	45252
19	2910	87.151	0.968	4364	35244
20	2935	79.815	0.886	2344	13040
21	2994	62.502	0.694	1756	11044
22	3006	58.981	0.655	1648	6456
23	3010	57.807	0.642	3656-	15528
24	3052	51.351	0.570	8228	42056
25	3063	42.255	0.469	2296	11392

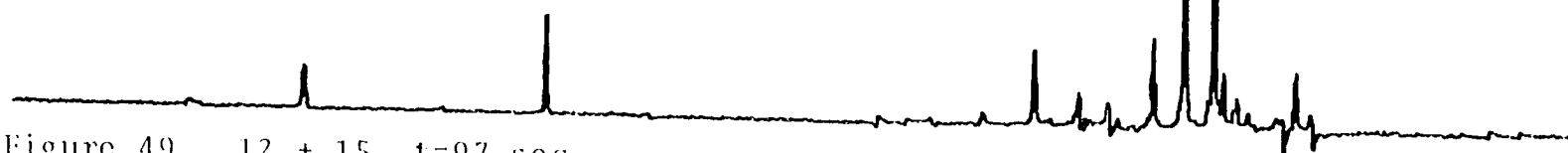


Figure 49. 12 + 15, t=97 sec.

1	832	696.915	7.743	1540	7584
2	1056	631.185	7.013	6116	38644
3	1539	489.455	5.438	17916	51532
4	2404	235.630	2.618	3248	14964
5	2505	205.993	2.288	11008	59016
6	2540	195.723	2.174	1012	1408
7	2600	178.117	1.979	3660	17884
8	2612	174.595	1.939	2208	4720
9	2620	172.248	1.913	1036	2736
10	2658	161.097	1.789	2436	7636
11	2676	155.815	1.731	1236	6168
12	2745	135.568	1.506	24484	123644
13	2805	117.962	1.310	96808	402200
14	2826	111.799	1.242	1060	2808
15	2837	106.572	1.206	976	2856
16	2844	106.518	1.189	1096	2012
17	2863	100.942	1.121	74836	319024
18	2874	97.714	1.085	4908	19012
19	2883	95.073	1.056	17356	83164
20	2898	90.672	1.007	1024	1956
21	2900	90.085	1.000	1028	1812
22	2910	87.151	0.962	4108	26632
23	2935	79.815	0.886	2120	9400
24	2994	62.502	0.694	1340	3260
25	3009	58.100	0.645	1740	3700
26	3032	51.351	0.570	3748	27644
27	3062	42.548	0.472	3544	15360



Figure 50. 12 + 15, t=356 sec.

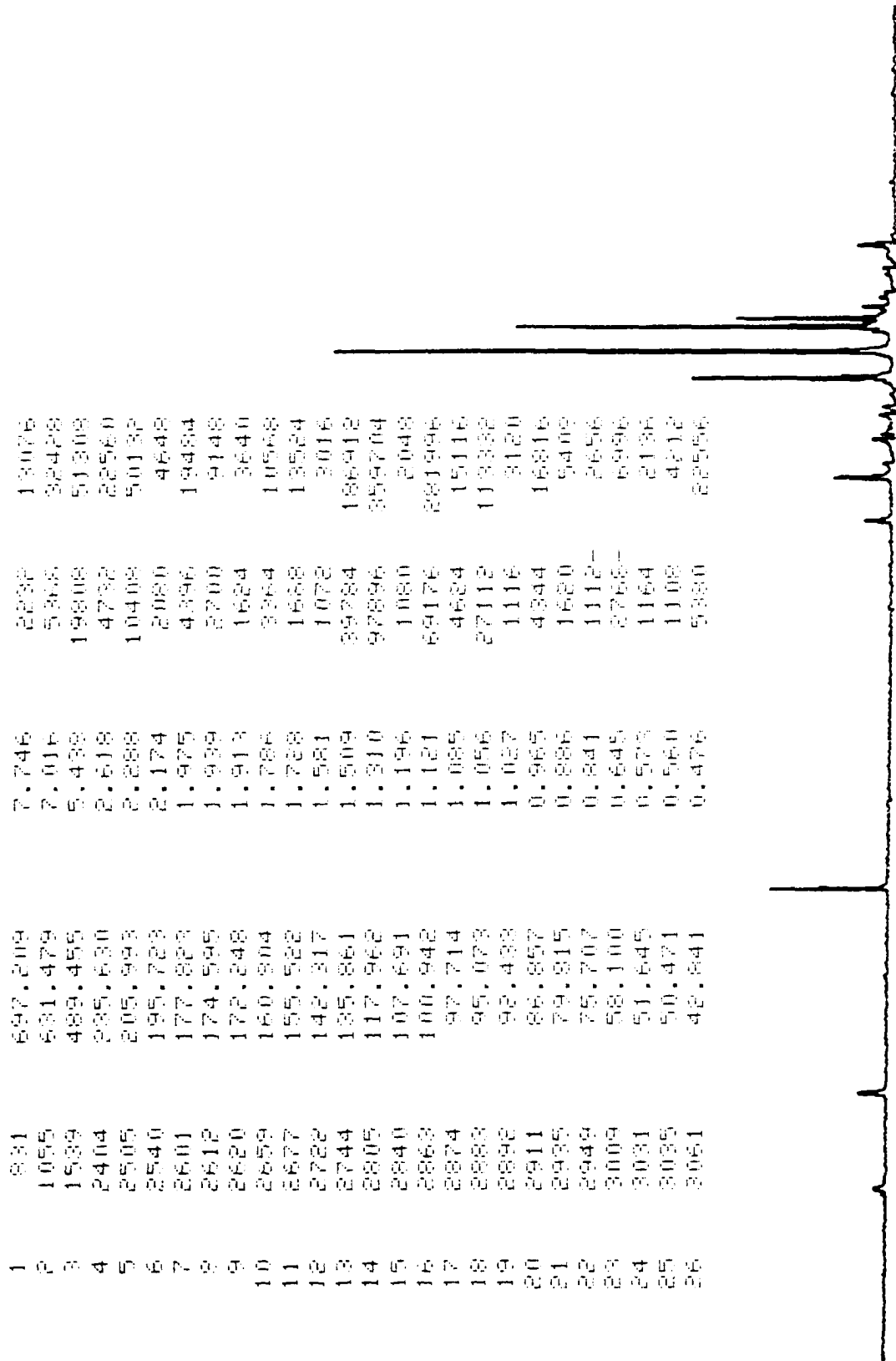
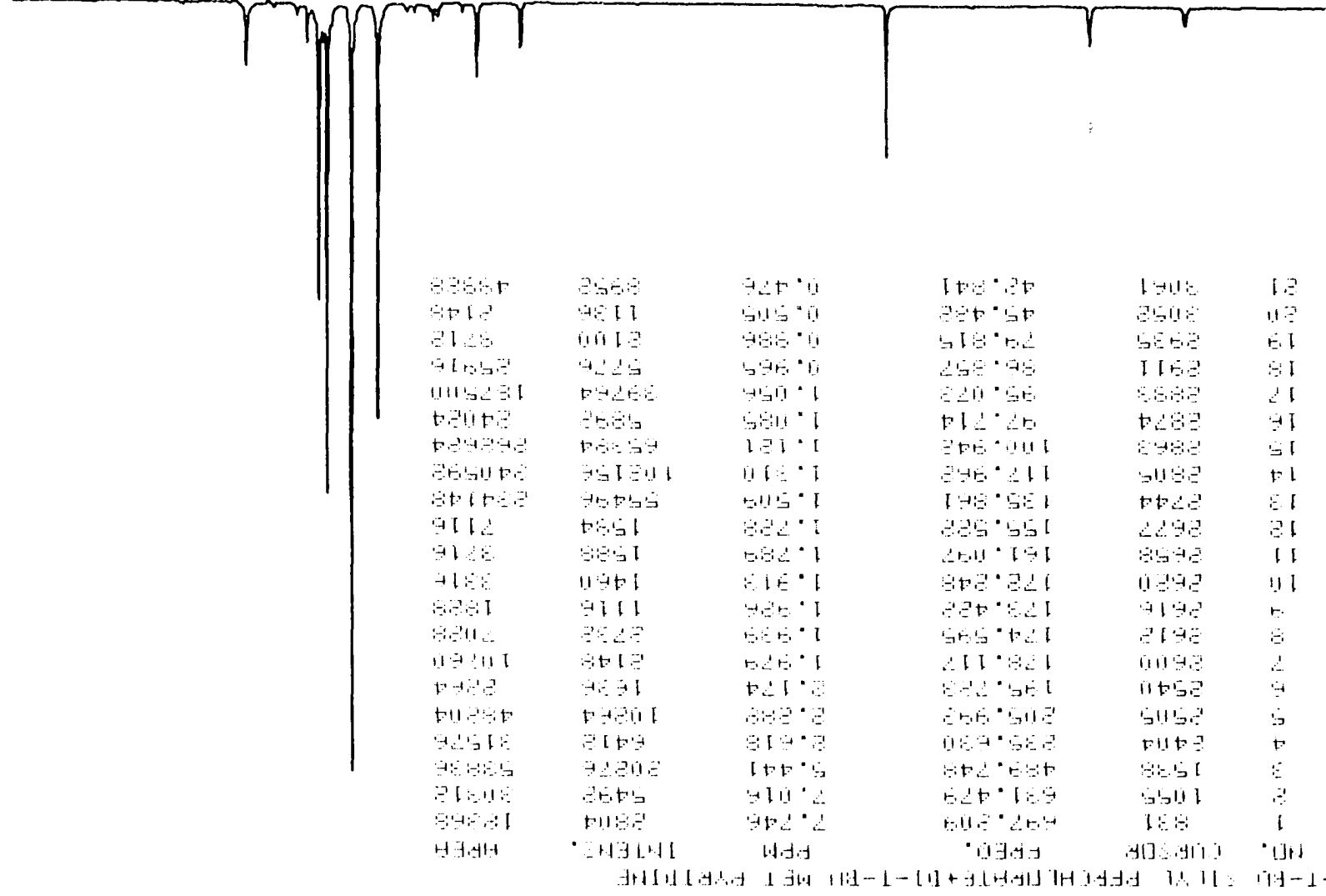


Figure 51. 12 + 15, t=1130 sec.

Figure 52. $\overline{12} + \overline{15}$, $t=3200$ sec.



DI-T-BU SILYL PERCHLORATE+DI-T-BU MET PYRIDINE

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	830	697.502	7.750	25120	162176
2	1055	631.479	7.006	36394	134720
3	1057	630.892	7.009	36736	84480
4	1538	489.748	5.441	195776	431200
5	2403	235.924	2.621	51424	281792
6	2505	205.993	2.288	60512	343552
7	2595	179.584	1.995	9472	16064
8	2599	178.410	1.982	9024	23552
9	2603	177.236	1.969	8672	14976
10	2612	174.595	1.939	17408	35872
11	2620	172.248	1.913	15488	75104
12	2744	135.861	1.509	520832	1991712
13	2805	117.962	1.310	674784	2277344
14	2839	107.985	1.199	7040	27392
15	2862	101.236	1.124	385376	1813856
16	2873	98.008	1.088	39936	174112
17	2883	95.073	1.056	341056	1733216
18	2911	86.857	0.965	47328	230016
19	2925	82.749	0.919	14720	109344
20	2942	77.761	0.864	6752	19040
21	2947	76.293	0.847	12608	42336
22	2983	65.730	0.730	7168	20320
23	3008	58.394	0.648	9512	60032
24	3053	45.189	0.502	7908	12256
25	3063	42.255	0.469	103296	500544

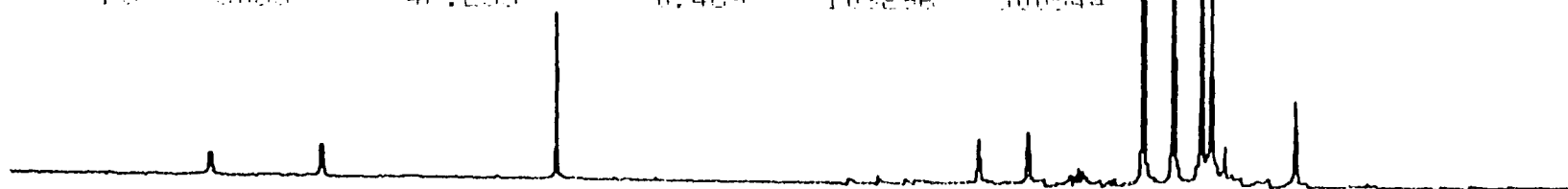


Figure 53. 12 + 15, t=3 hrs.

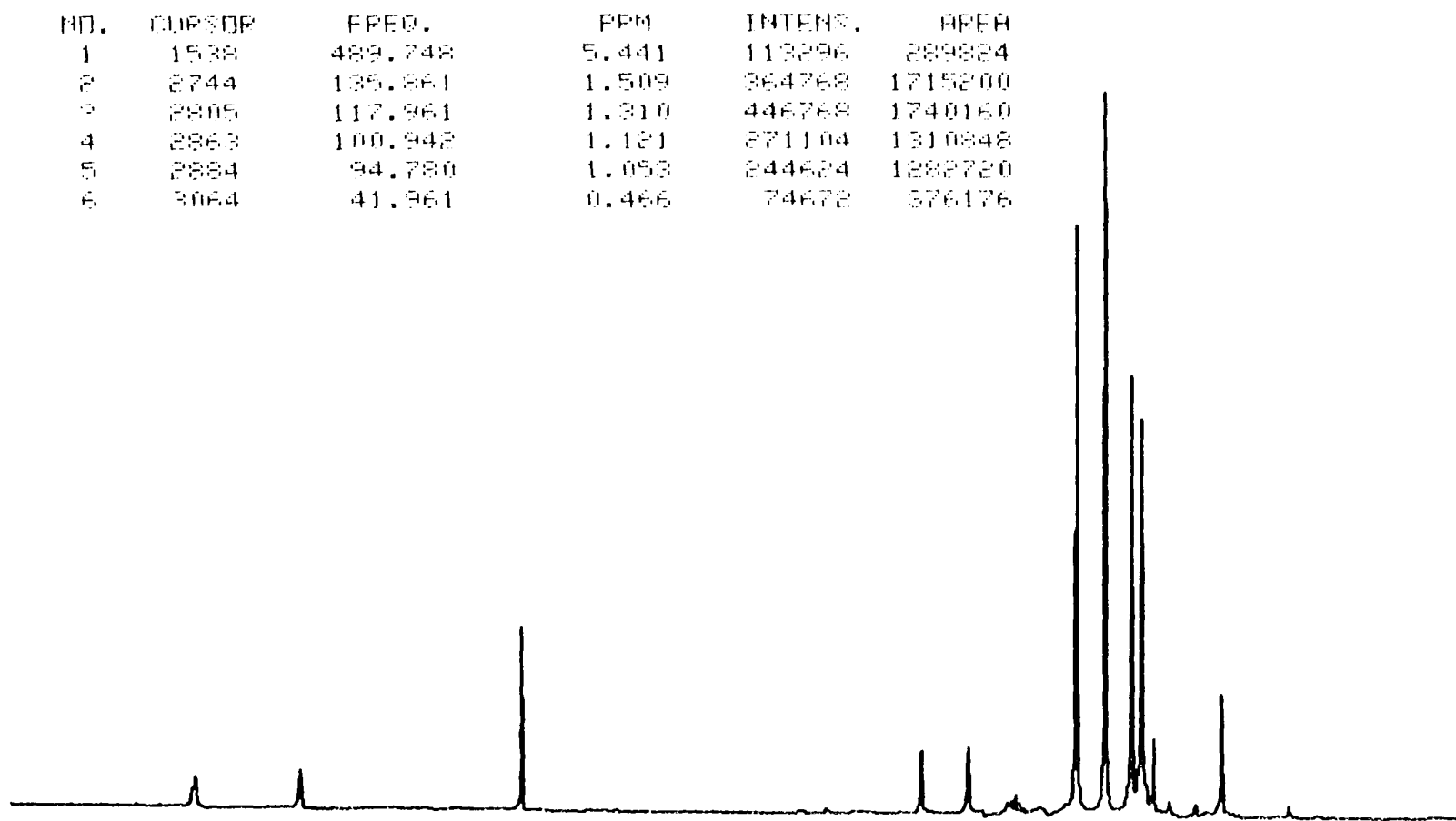
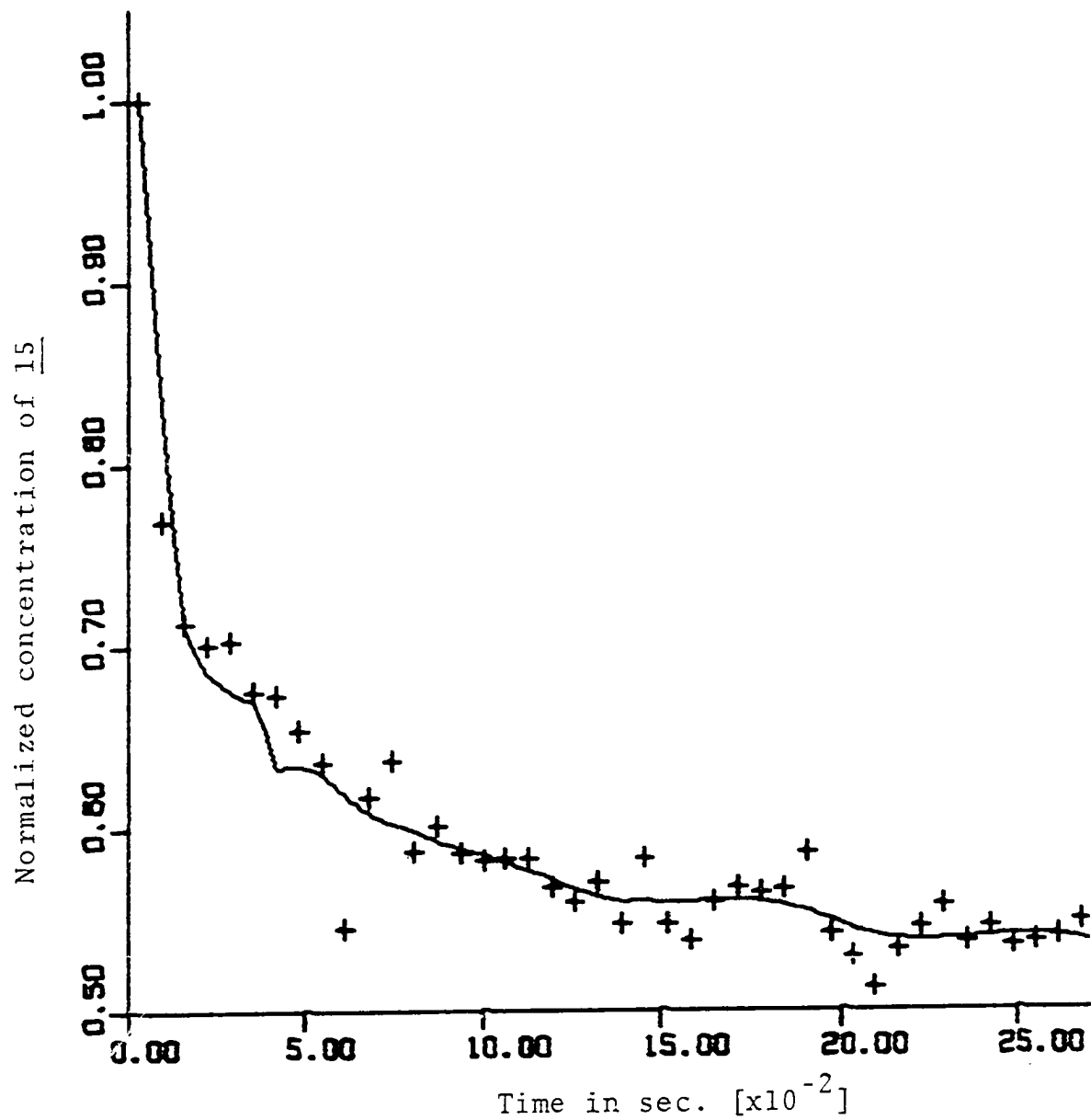
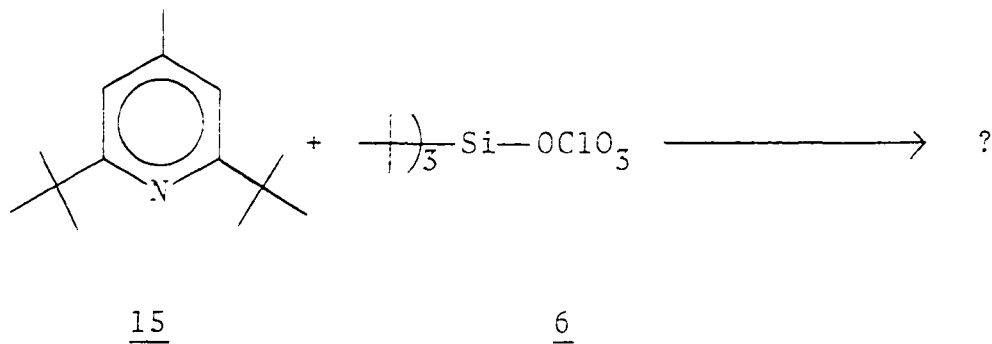


Figure 54. 12 + 15, t=40 hrs.

Figure 55. 12 + 15.



internal standard CH_2Cl_2 :		δ 5.44
starting <u>6</u> :	Si —	1.26
starting <u>15</u> :	Ar—H	7.01
	Ar—Me	2.29
	Ar —	1.31
product pyridinium:	Ar—H	7.74
	Ar—Me	2.62
	Ar —	1.51
unknown intermediate:	Si —	1.13

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	1540	489.748	5.441	66752	269064
2	2822	113.560	1.261	718912	3243712
3	2857	103.289	1.147	52992	254784

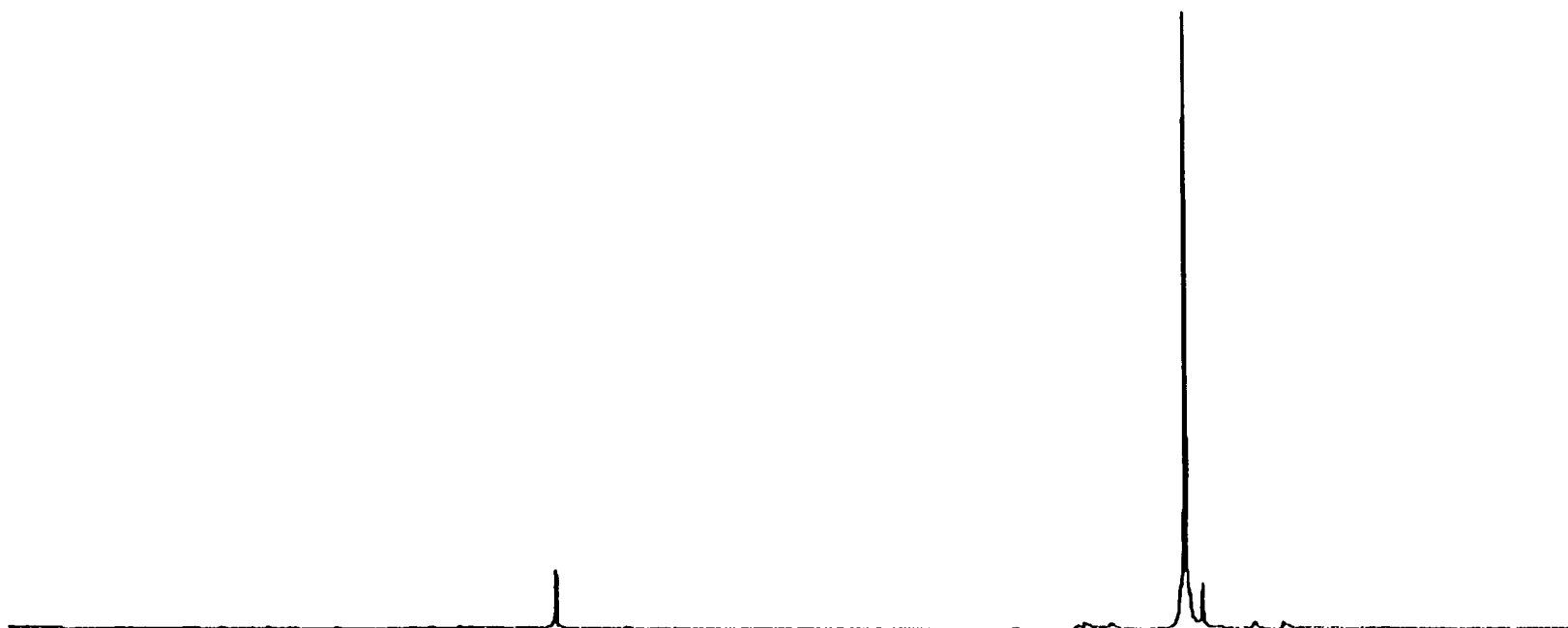
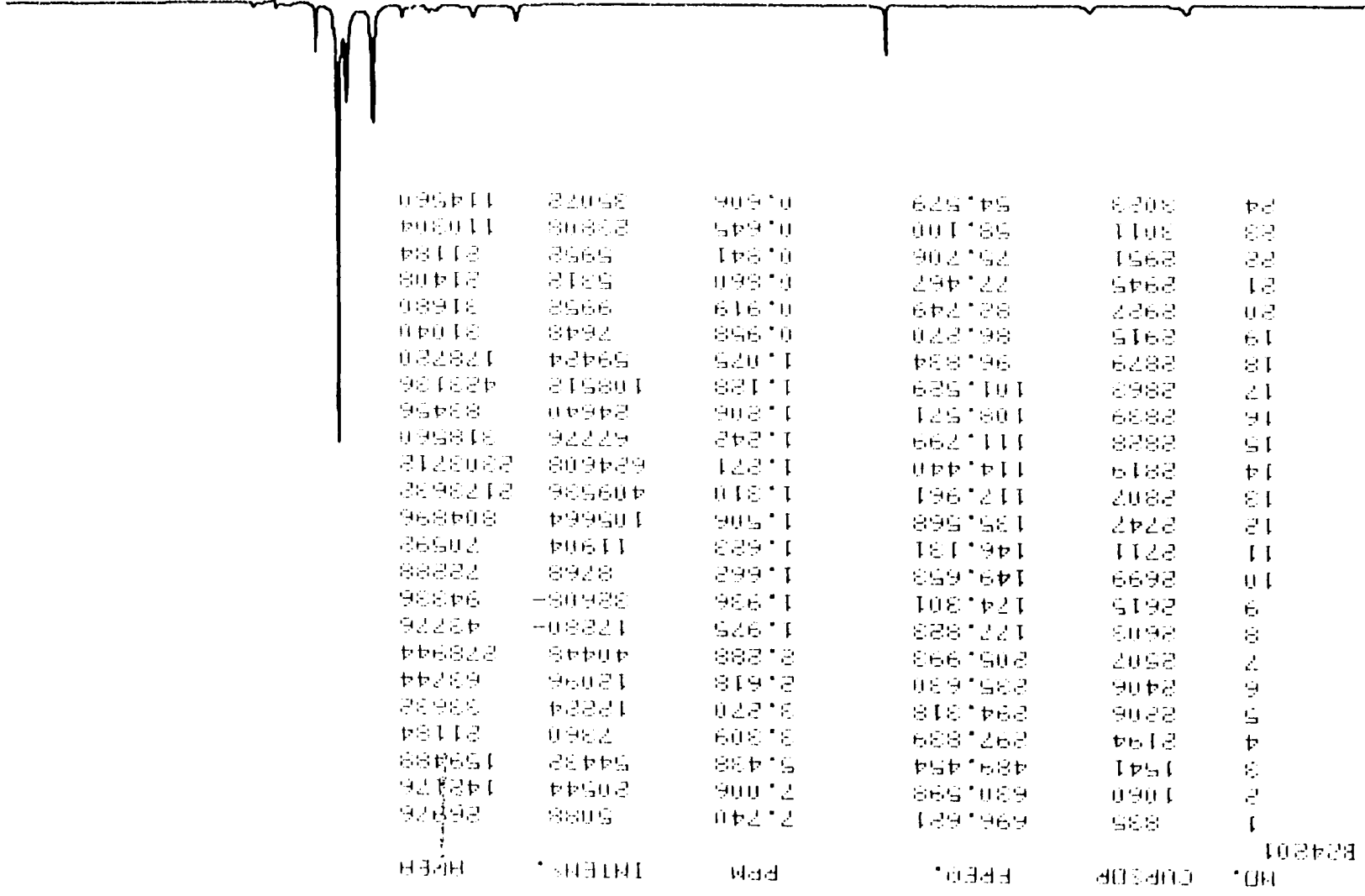


Figure 56. $\left(\text{CH}_3\right)_3\text{Si}-\text{OC10}_3$ (6).

Figure 57. $\bar{6} + \bar{15}$, $t=70$ sec.



1	833	697.208	7.746	14112	96192
2	1058	631.185	7.013	16768	112512
3	1539	490.041	5.444	69312	206176
4	2405	235.923	2.621	29512	193664
5	2505	206.580	2.295	33344	240768
6	2540	196.309	2.181	6656	21696
7	2600	178.703	1.985	11264	118592
8	2612	175.182	1.946	16160	62048
9	2621	172.541	1.917	15040	44928
10	2634	151.120	1.679	7232	42560
11	2714	145.251	1.613	8704	112480
12	2745	136.154	1.512	256064	1524672
13	2806	118.255	1.313	303712	1761536
14	2817	115.027	1.278	274816	1149472
15	2826	112.386	1.248	392184	1883656
16	2836	109.452	1.216	24512	108064
17	2861	102.116	1.134	115360	470336
18	2877	97.421	1.082	66176	194316
19	2918	85.390	0.948	7968	34208
20	2930	81.868	0.909	7456	32256
21	2939	79.227	0.880	9600	52384



Figure 58. 6 + 15, t=760 sec.

1	832	697.502	7.750	13184	102944
2	1057	631.478	7.016	14336	105952
3	1538	490.334	5.448	83168	212384
4	2404	236.217	2.624	28992	205056
5	2505	206.580	2.295	36432	205888
6	2541	196.016	2.177	9696	40192
7	2602	178.116	1.979	12480	74688
8	2612	175.182	1.946	15680	63808
9	2622	172.247	1.913	27712	312320
10	2712	145.838	1.626	14112	350688
11	2745	136.154	1.512	230112	1602048
12	2805	118.548	1.317	255264	1780864
13	2817	115.027	1.278	144384	766528
14	2825	112.679	1.251	502848	2420448
15	2835	109.745	1.219	21568	57600
16	2861	102.116	1.134	35456	112672
17	2877	97.421	1.082	63776	161120
18	2940	78.934	0.877	5920	20384

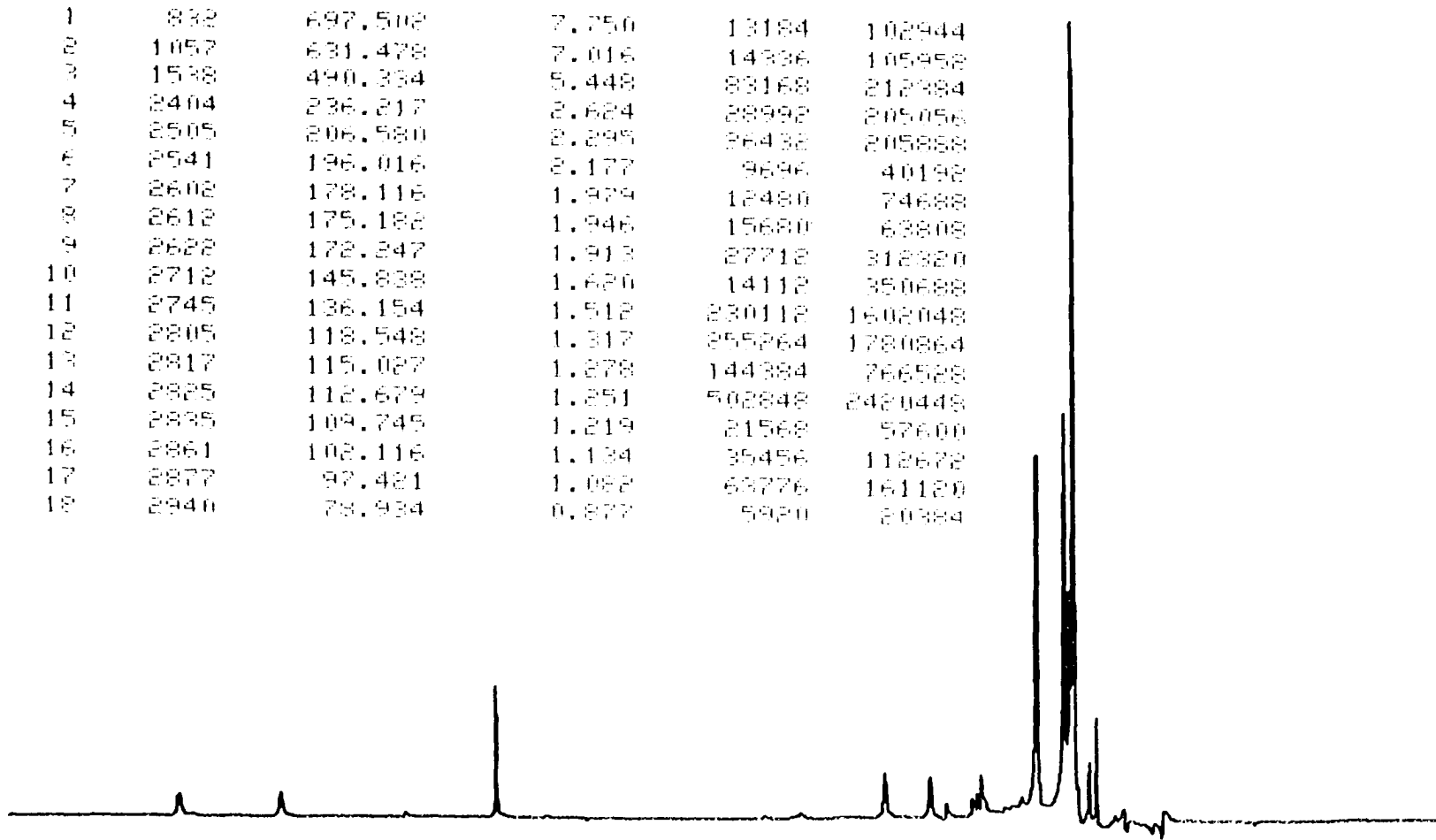


Figure 59. 6 + 15, t=1450 sec.

1	832	697.502	7.750	13824	102688
2	1055	632.065	7.022	13562	97376
3	1538	490.334	5.448	74688	208128
4	2130	316.619	3.517	5856-	25536
5	2191	298.719	3.319	6016-	31712
6	2211	292.850	3.257	12480-	41280
7	2403	236.510	2.627	29024	226944
8	2504	206.873	2.298	25056	194112
9	2537	197.190	2.191	5280-	23840
10	2541	196.016	2.177	10336	64320
11	2603	177.823	1.975	14336	65984
12	2612	175.182	1.946	13152	36128
13	2622	172.247	1.913	36928	575552
14	2711	146.131	1.622	20576	532256
15	2744	136.448	1.516	243616	1732576
16	2805	118.548	1.317	228832	1936832
17	2816	115.320	1.281	122016	676640
18	2825	112.679	1.251	610944	2648736
19	2835	109.745	1.219	9920	13696
20	2842	107.691	1.196	13024-	175264
21	2860	102.409	1.137	7552	9280
22	2877	97.481	1.082	54784	147040

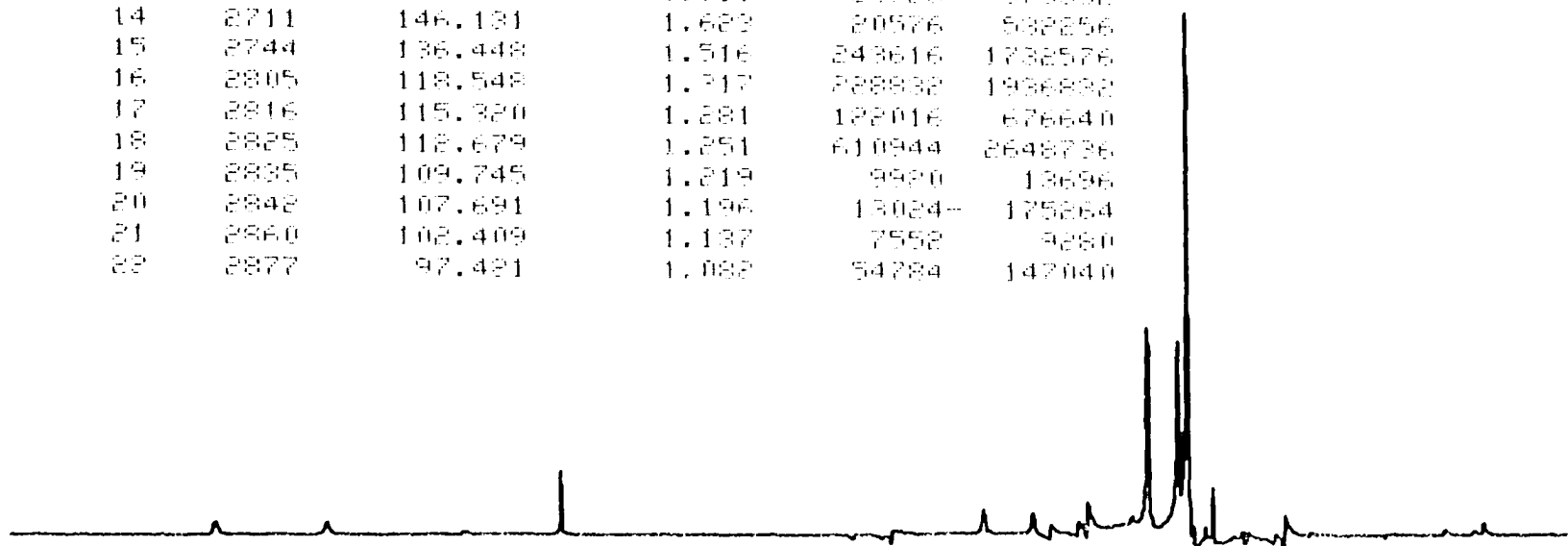
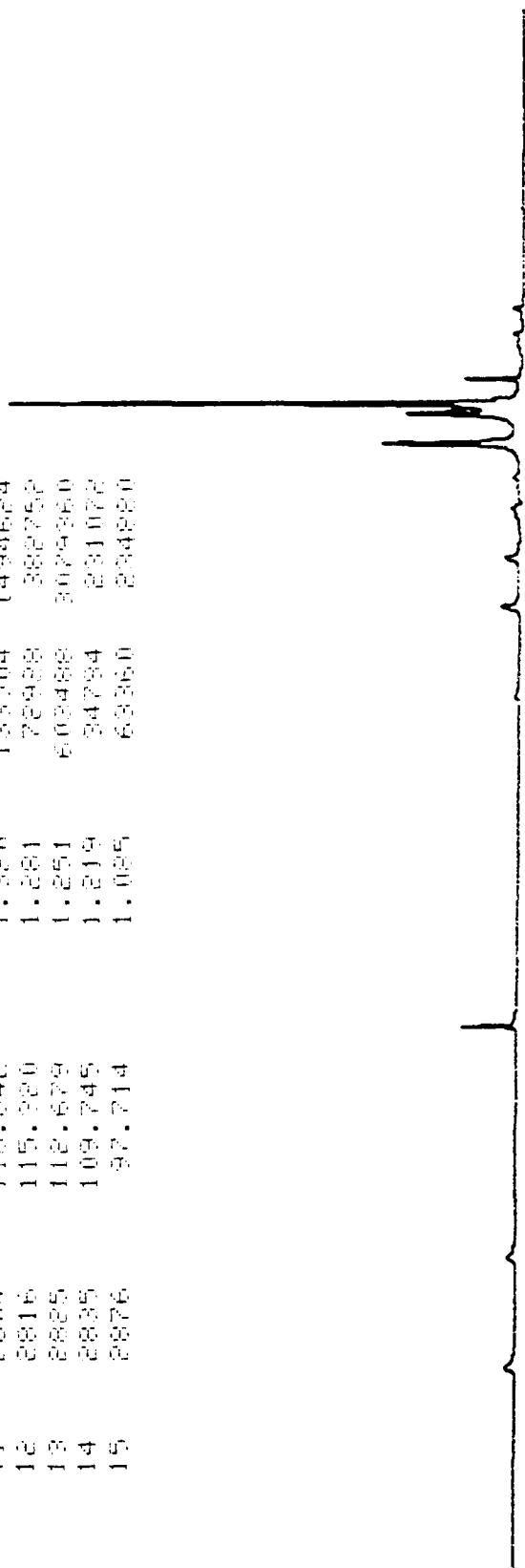


Figure 60. 6 + 15, t=2140.

1	832	697.502	7.750	12928	110015
2	1056	631.772	7.019	11429	93120
3	1538	490.354	5.443	71438	210432
4	2404	236.217	2.624	25696	213824
5	2504	206.873	2.292	21504	195712
6	2603	177.823	1.975	9244	46944
7	2612	125.182	1.946	13736	53600
8	2620	128.834	1.920	15136	115424
9	2708	147.012	1.632	16480	262848
10	2744	136.443	1.516	19880	182208
11	2805	113.943	1.317	17552	167136
12	2816	115.320	1.261	25184	415128
13	2825	112.679	1.251	42402	296928
14	2825	109.745	1.219	3312	126640
15	2841	102.116	1.134	5344	28000
16	2827	97.421	1.032	6324	196768

Figure 61. 6 + 15, t=3520 sec.

1	892	697.502	2.750	11984	106720
2	1056	681.772	2.019	9536	82336
3	1537	490.628	5.451	61760	211424
4	2404	286.217	2.624	22144	205184
5	2504	206.873	2.258	17440	186112
6	2595	180.170	2.001	6464	38400
7	2603	177.823	1.975	7104	23296
8	2611	175.475	1.949	11264	49280
9	2675	156.695	1.741	7808	67552
10	2744	136.448	1.516	16528	175768
11	2804	118.842	1.320	13504	1494624
12	2816	115.320	1.281	72928	382752
13	2825	112.679	1.251	60488	302960
14	2835	109.745	1.219	24784	231072
15	2876	97.714	1.025	63360	234880

Figure 62. 6 + 15, t=6420 sec.

&PF

TPI-T-BUSILYL PERCHLORATE+DI-T-BU METYPIUINE

NO.	CURSOR	FREQ.	PPM	INTENS.	AREA
1	1532	489.748	5.441	72992	242784
2	2745	135.568	1.506	122464	1924096
3	2805	117.961	1.310	97680	1407648
4	2825	112.092	1.245	587680	3445504
5	2877	96.834	1.075	68576	260640

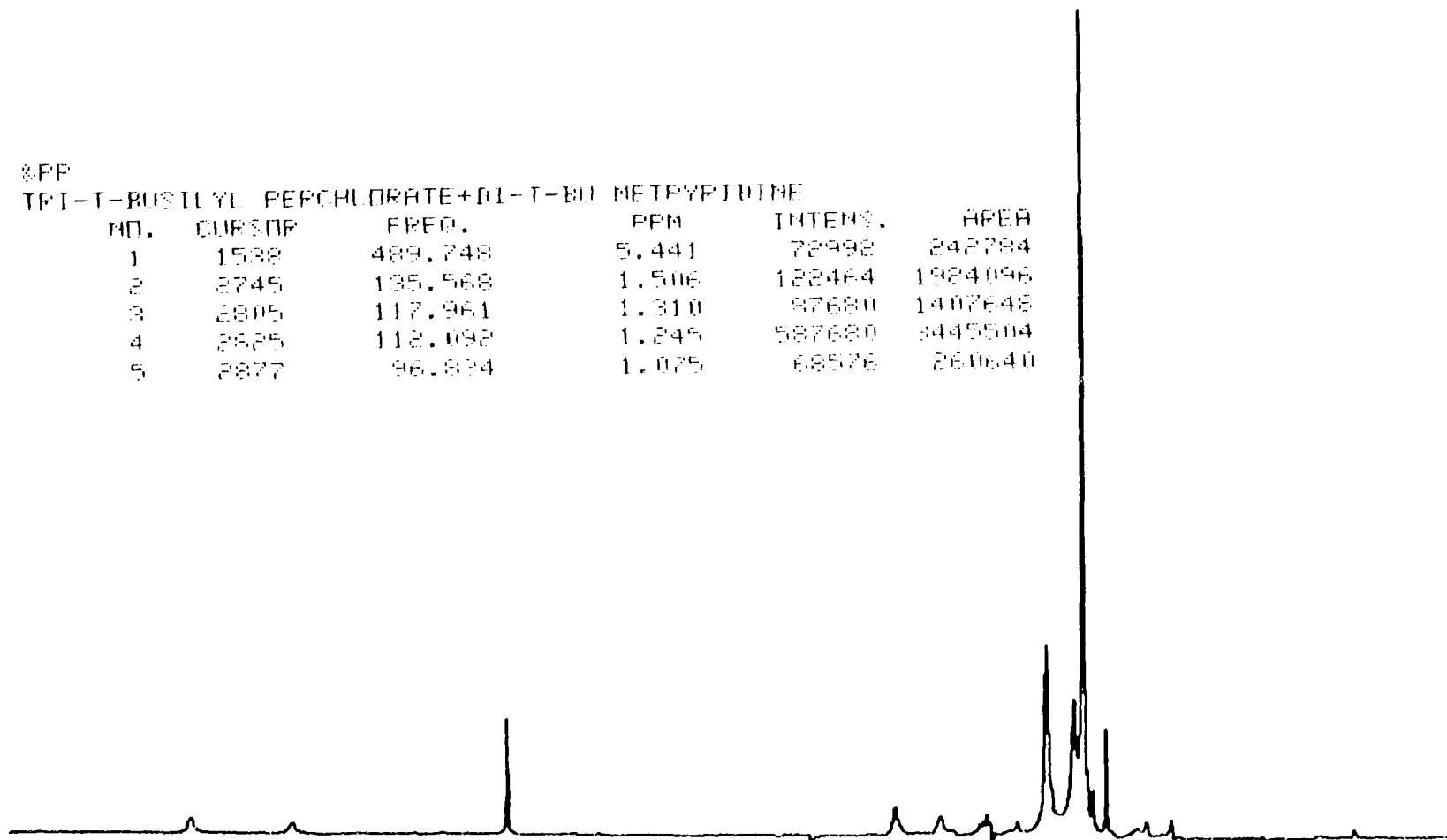
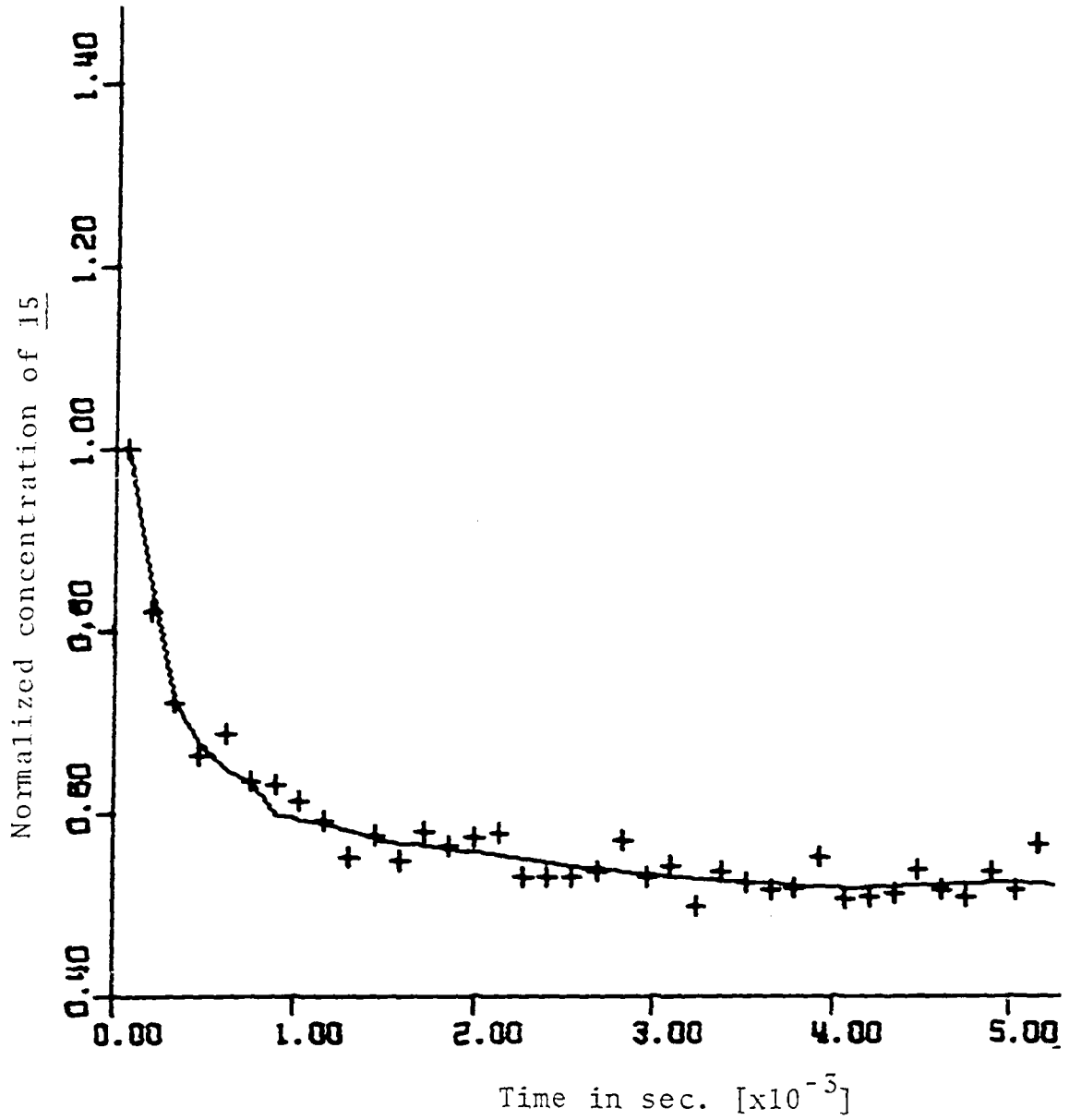


Figure 62. 6 + 15, t= 16 hrs.

Figure 64. 6 + 15.

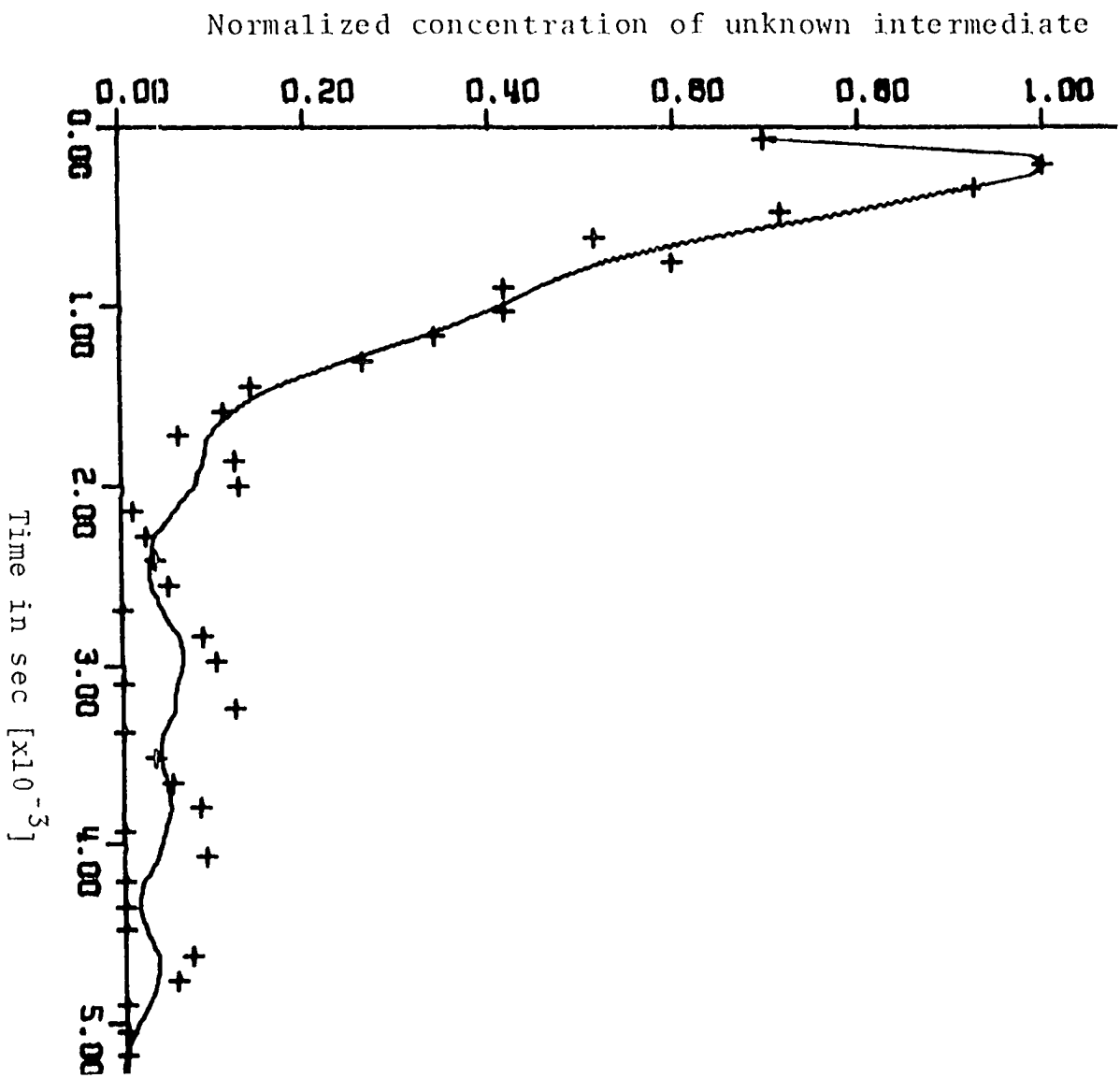


Figure 65. Intermediate at 1.13 in reaction of 6 and 15.

For 12 and 6 the consumption of 15 slows dramatically approaching approximately 50% conversion while the reaction of 11 slows as 30% conversion is approached. These rate curves suggest that perhaps an equilibrium between pyridine and pyridinium is being approached asymptotically and the relative rate at which these equilibria are approached are in the order 11 << 6 < 12. The mysterious intermediate seen in figure 37

Approximate time required to reach equilibrium:

<u>11</u>	16000 sec.
<u>12</u>	800 sec.
<u>6</u>	1000 sec.

again shows up in figures 58-61 at δ 1.13 and a plot of its normalized peak area is shown in figure 65 which indicates that its concentration peaks at ca. 200 sec. and is no longer measureable at 5000 seconds.

The reaction mixtures of all three perchlorates were quenched with methanol after ca. five days as shown in figures 66-71; however, the product mixtures appeared to include a number of products -- not as clean as the

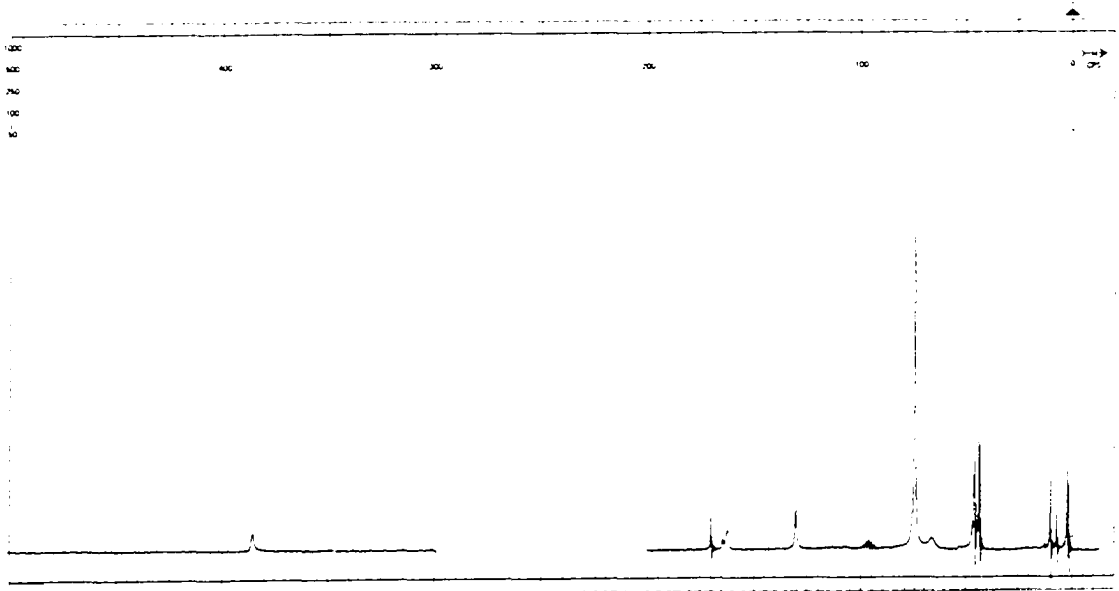


Figure 66. [11 + 15, t=133 hrs] + 1.1 MeOH, t=1 min.

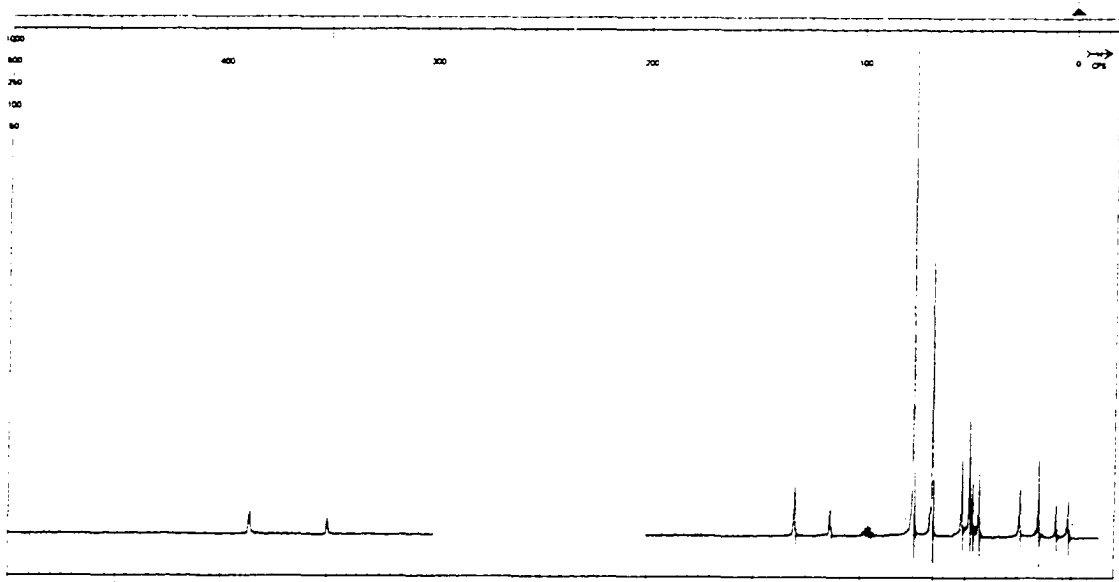


Figure 67. 11 + 15, t=133 hrs.

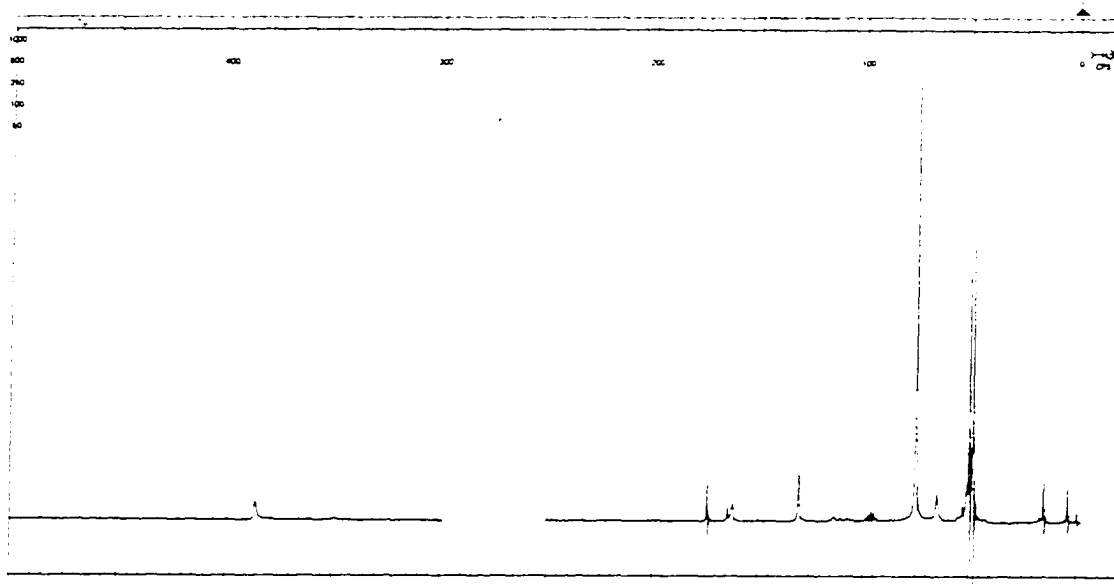


Figure 68. [12 + 15, t=140 hrs] + 1.1 MeOH, t=1 min.

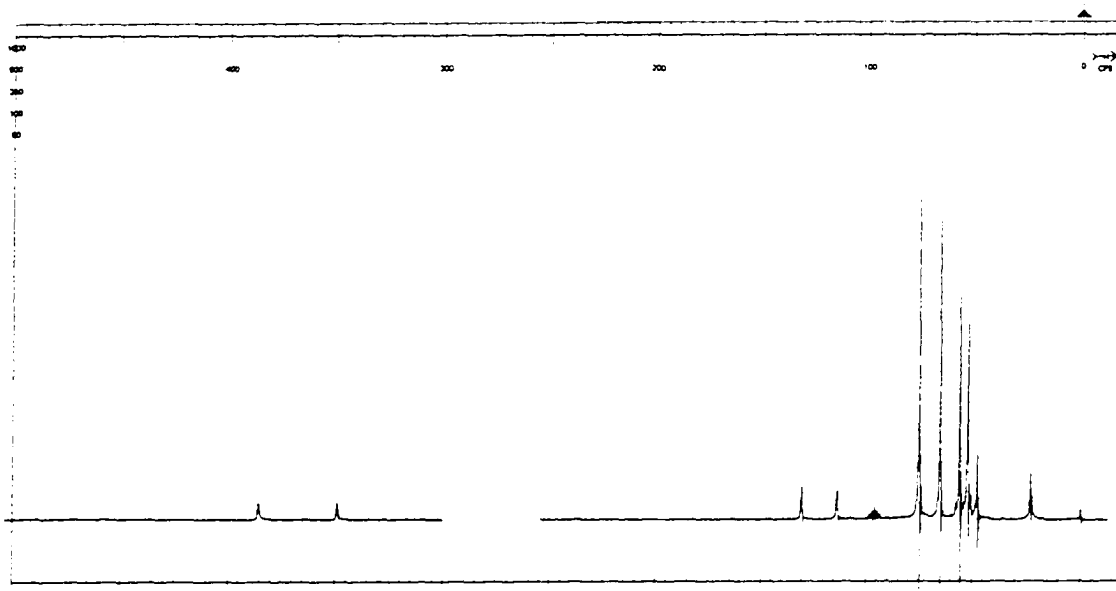


Figure 69. 12 + 15, t=140 hrs.

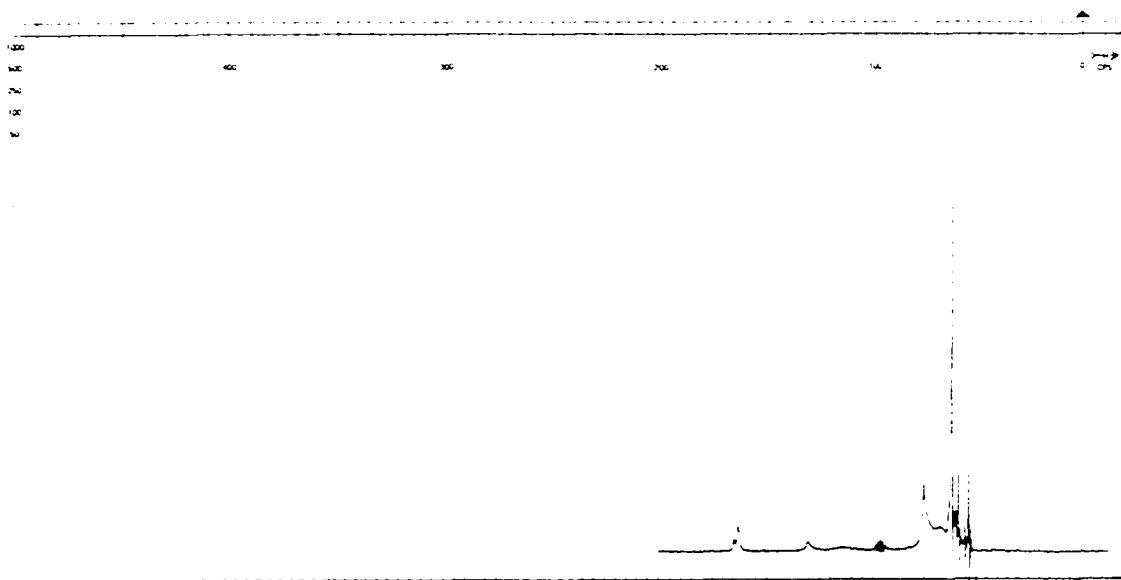


Figure 70. [6 + 15, t=117 hrs] + 1.1 MeOH, t=1 min.

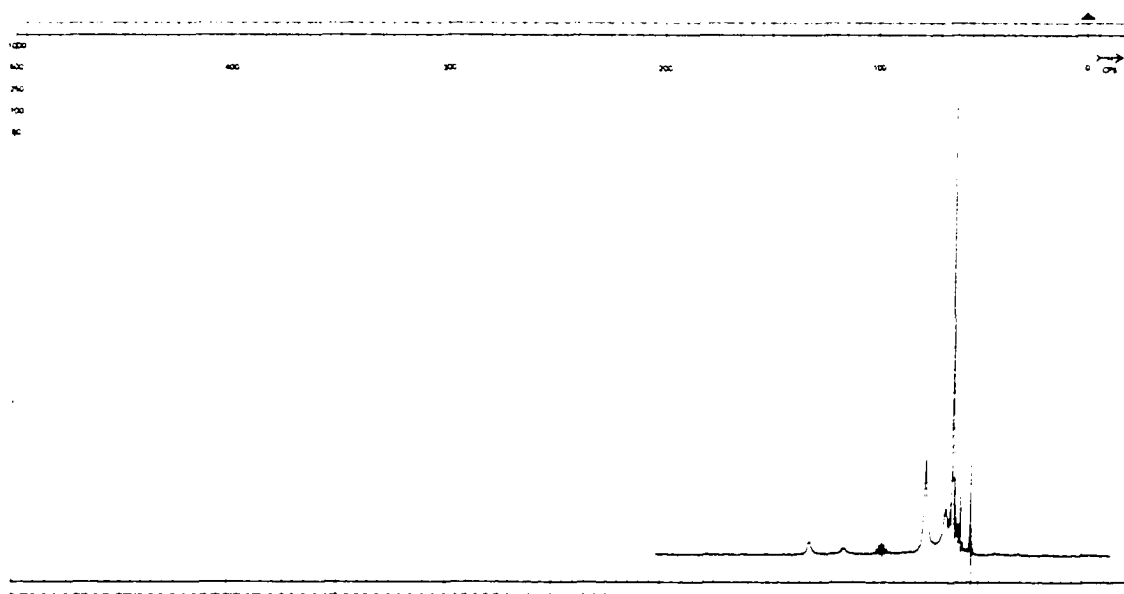
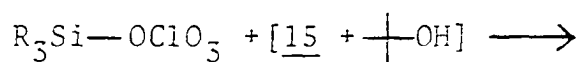


Figure 71. 6 + 15, t=117 hrs.

preliminary experiment with 12 (see figures 39 and 40). In spite of these complicated reactions of the perchlorates with 15, the tertiary butanol solvolysis experiments were attempted.

In order to minimize the reaction of the perchlorates with 15, each perchlorate was added to a solution of t-butanol and 15. The reactivity order of the series was observed to be 6 < 12 < 11.



<u>R₃Si</u>	<u>OC10₃</u>	<u>t_{1/2}</u>
<u>11</u>		<30 sec
<u>12</u>		<60 sec
<u>6</u>		no reaction

It was quite surprizing to discover that for the reaction of 12 it appeared that a considerable amount of isobutene was generated (figures 72 and 73). It is conceivable that steric factors would favor the ejection of a t-butyl cation from an intermediate such as 16. Thus, even though some very interesting reactions of silyl perchlorates had been observed, it seemed that monumental effort might be

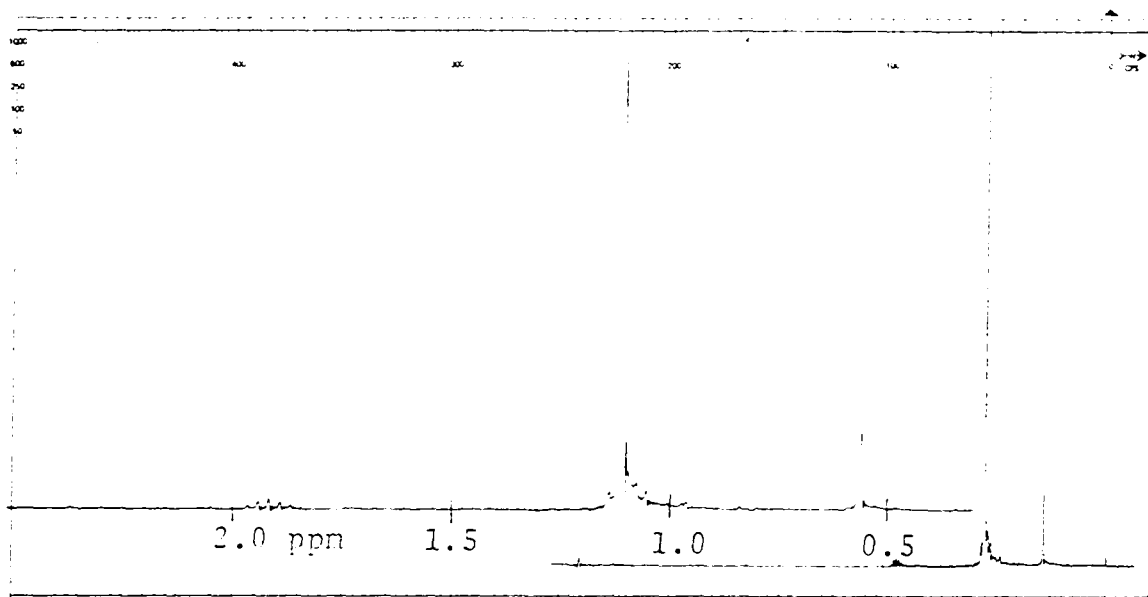


Figure 72. $(\text{CH}_3)_2\text{Si}(\text{OC}_{10}\text{H}_3)\text{Me}$.

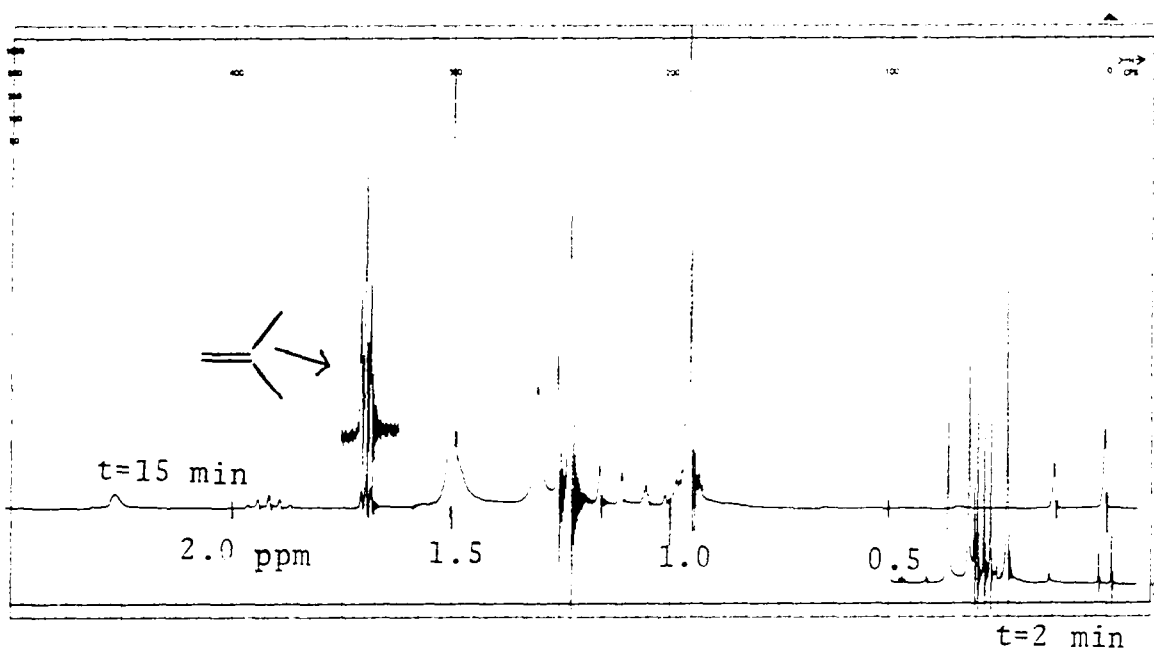
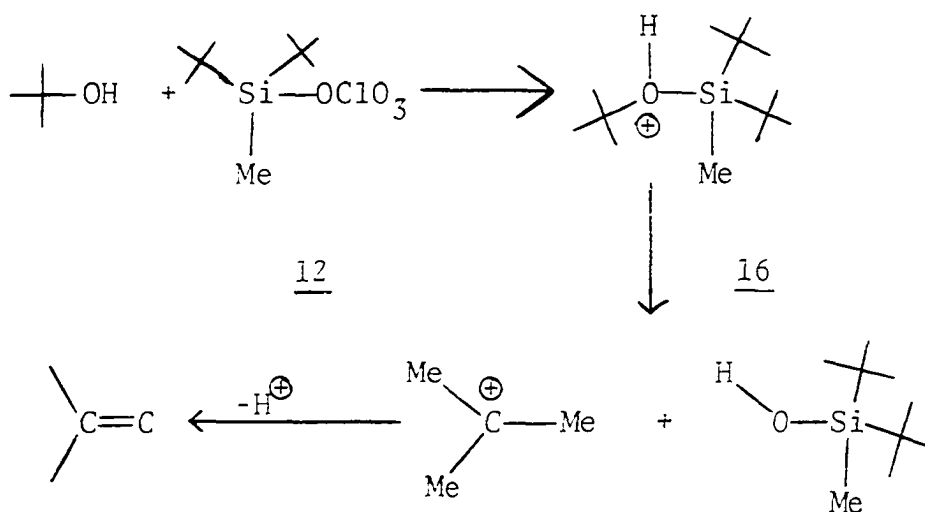
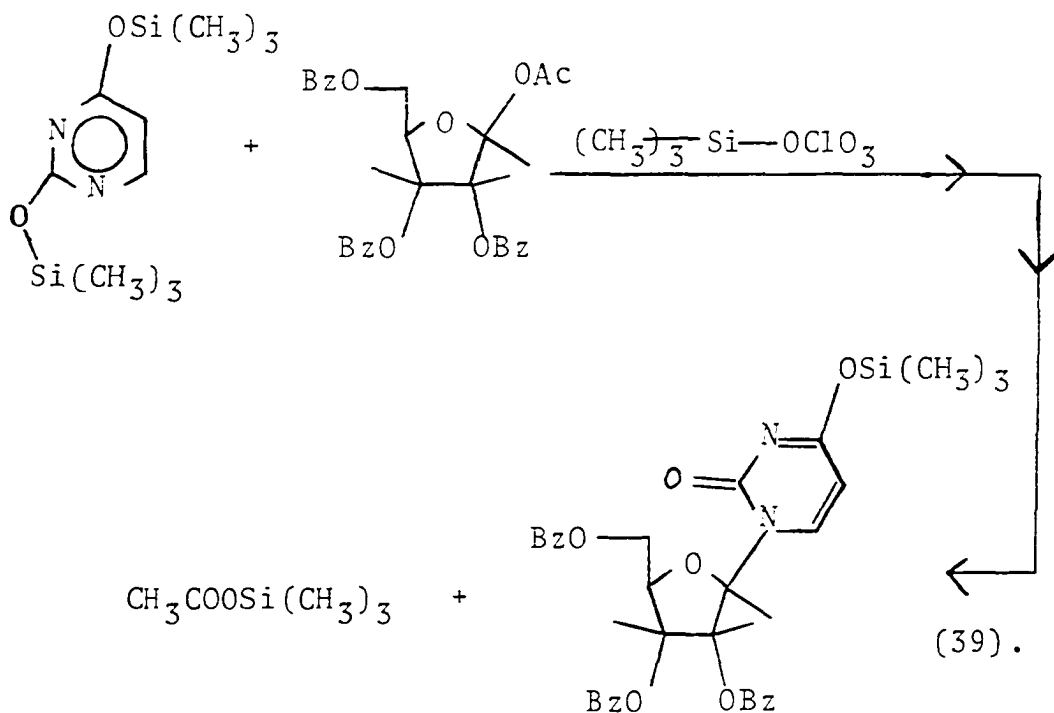


Figure 73. $(\text{CH}_3)_2\text{Si}(\text{OC}_{10}\text{H}_3) + \underline{15} + \text{OH}$.

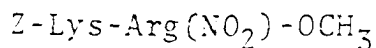
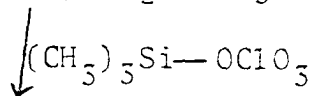
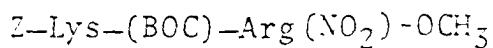
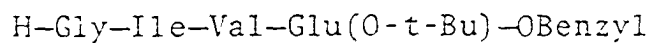
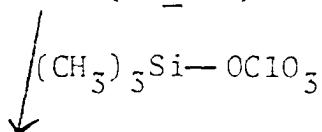
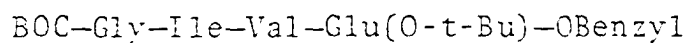


required to elucidate these complex reactions. A decision was made to investigate synthetic uses for this highly reactive class of compounds.

Trimethylsilyl perchlorate has recently received some attention as a Lewis acid catalyst in certain reactions:



and in the selective cleavage of the t-butoxycarbonyl (BOC) group in the presence of the benzyloxycarbonyl (Z) and t-butyl ester groups in nucleoside synthesis:

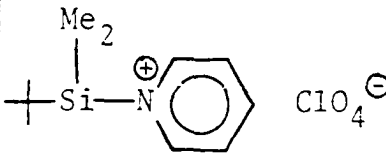
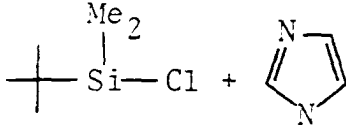
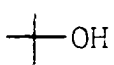
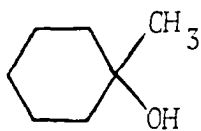


(40).

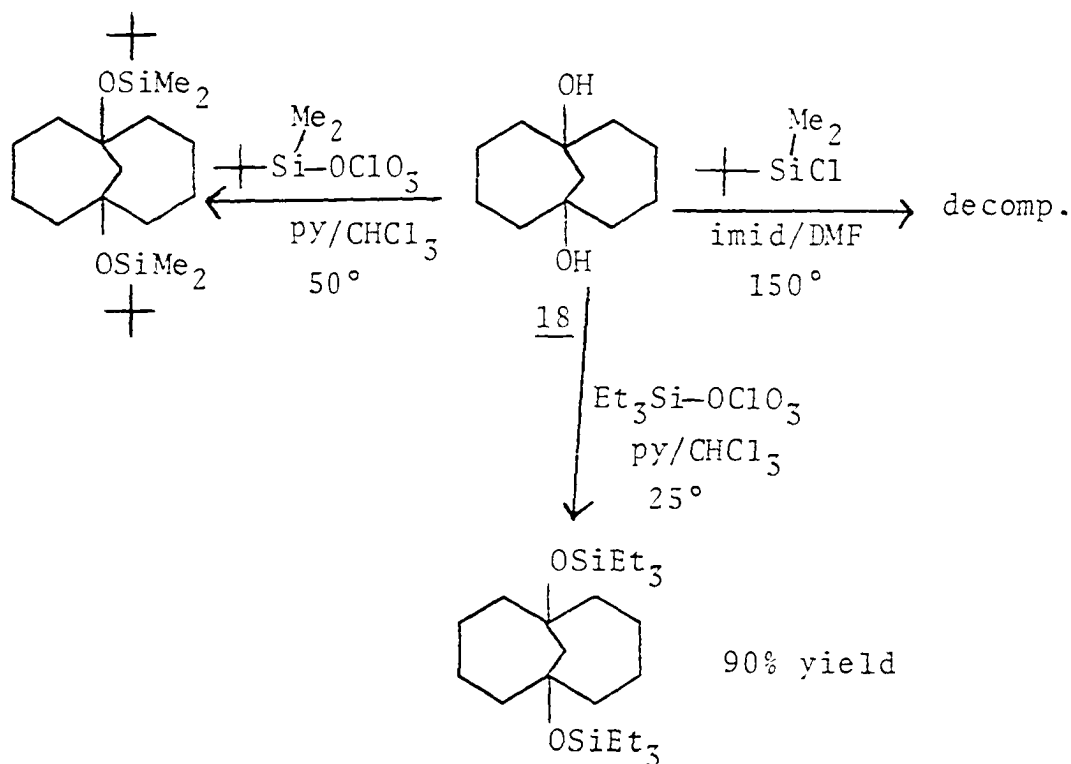
It occurred to us that the perchlorate moiety might find particular utility in effecting silylations that are difficult with other leaving groups. In synthetic chemistry silylating agents are often used to protect alcohols; however, unhindered silyl groups such as trimethylsilyl (TMS) are of limited value because of their extreme reactivity toward acid and base catalyzed solvolysis. Today one of the most popular protecting reagents is t-butyldimethylsilyl chloride (17). Ethers formed from 17 are many times more stable toward solvolysis than TMS ethers (41). Of course, as one might guess the same steric bulk which affords the

additional protection also resists the formation of the silyl ether in the first place; however, Corey found it to be satisfactory for primary and secondary alcohols when imidazole is added as a catalyst though extended reaction times are sometimes required.

The results obtained in comparing the relative reactivities of Corey's system and the *t*-butyldimethylsilyl perchlorate-pyridine system are shown below. For the protection

	 in CH ₃ CN	 in DMF
	$t_{1/2}$ ca. 30 sec. 100% in 5 min.	30% in 3 days
	$t_{1/2}$ ca. 3 min. 100% in 20 min.	10% in 3 days

of these tertiary alcohols it is apparent that the perchlorate-pyridine system is by far the more useful silylating agent -- rapidly providing quantitative yields of the desired silyl ether. In fact, Warner and Schleis (41) found that Corey's system failed to react with tertiary diol 18 at temperatures of up to 150° where decomposition

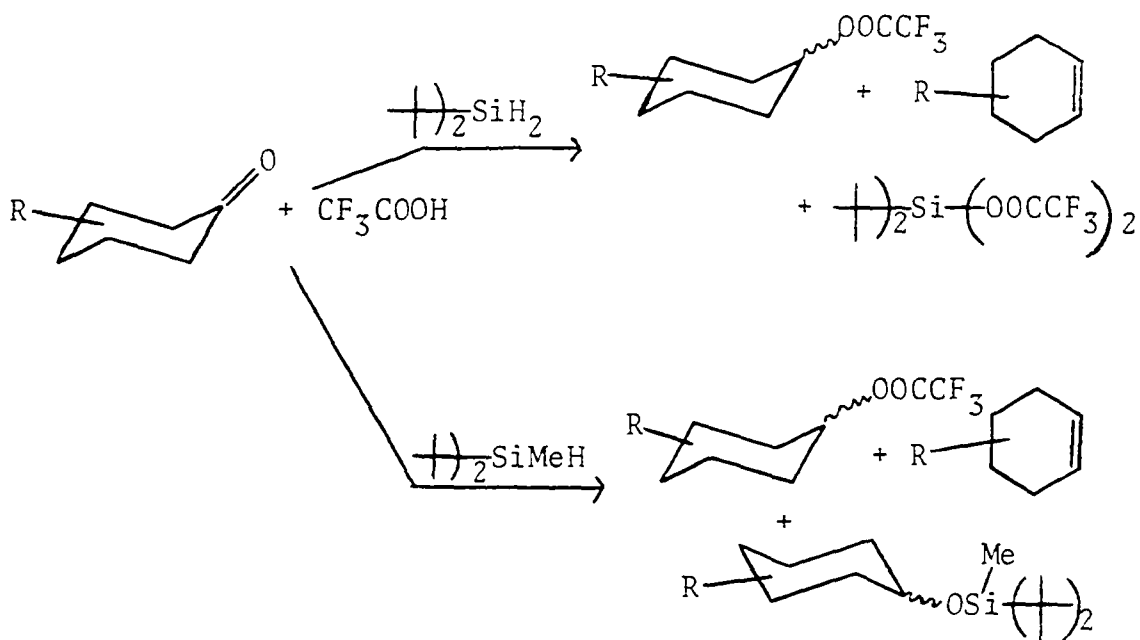


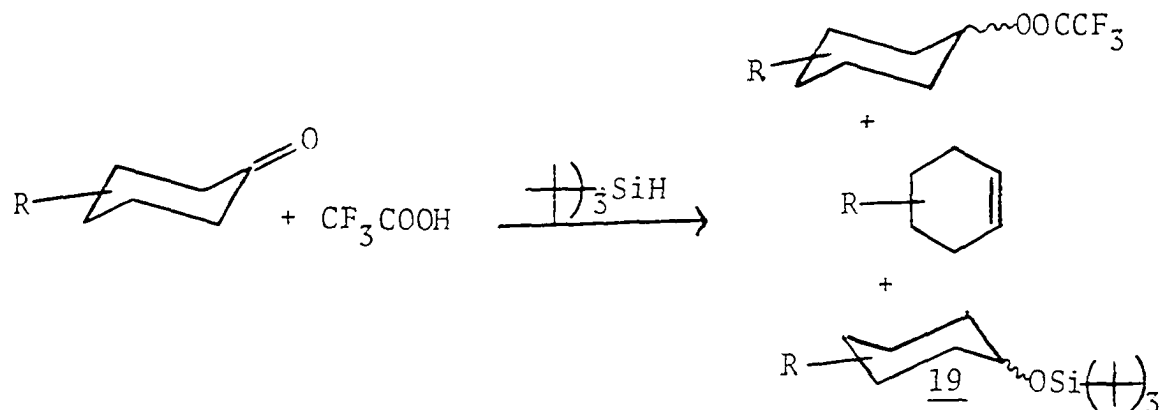
set in. We suggested that they try perchlorates. In dramatic contrast they found that the perchlorate-pyridine system derivatized the diol at 50° in chloroform and that reaction with triethylsilyl perchlorate proceeded almost instantaneously at room temperature to provide the diether in high yield.

The utility of t-butyldimethylsilyl perchlorate had been proven and it appeared that difficulties in the preparation of tri-t-butylsilyl perchlorate would preclude any synthetic utility for it, so the obvious direction of investigation was an examination of di-t-butylmethylsilyl

perchlorate. Both the mono-t-butyl- and di-t-butylsilyl perchlorates can be distilled without difficulty from the reaction mixture of the silane and trityl perchlorate (see page 70). The silanes can be easily prepared from commercially available chlorosilanes and t-butyllithium. A 77% overall yield was attained in the preparation of 11 while 12 was prepared in 71% overall yield. Both are easily handled liquids using syringe and rubber septum techniques, but the question remained as to the synthetic utility of the di-t-butylmethylsilyl perchlorate.

Doyle and West (27) were the first to prepare and investigate the di-t-butylmethylsilyl system. They had prepared di-t-butylmethylsilane (26) and studied the reduction of cyclohexanones by it and other silanes, including di-t-butylsilane and tri-t-butylsilane (43-45).

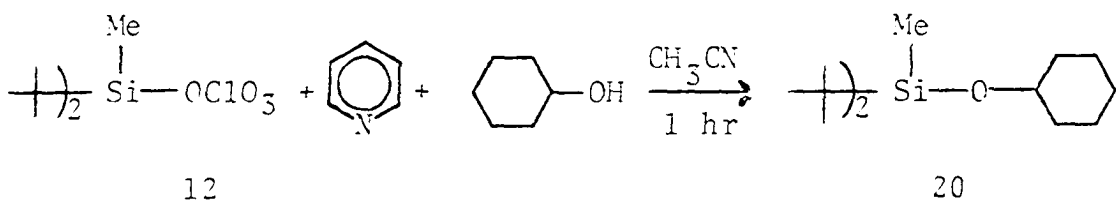




They did report that the tri-t-butyl ether 19 resisted cleavage by "the method successfully employed to remove the t-butyldimethylsilyl protecting group, even when significantly longer reaction times were used". Presumably the method referred to is anhydrous tetra-n-butylammonium fluoride-THF. This made us suspicious that there might be a cleavage problem with the di-t-butylmethylsilyl moiety, but we felt that it could be worked out if a reason could be found for doing so.

One reason for interest in the di-t-butylmethylsilyl (DTBMS) blocking group is that the mono-t-butyldimethylsilyl (TBDMS) ethers are readily cleaved under mildly acidic conditions (HOAc-H₂O-THF) comparable to the tetrahydropyranyl (THP) ethers (41), but the additional steric bulk of the DTBMS group might significantly improve resistance to acidic hydrolysis. Another variation on the TBDMS protecting group, t-butyldiphenylsilyl, has been investigated (46) and was found to provide some added stability. It would be of interest to compare this group with the DTBMS group.

We found that silylation of cyclohexanol with 12 proceeded smoothly at room temperature. The work-up consisted of adding pentane to the reaction mixture, extraction with water, and finally evaporation of the pentane solution to provide a quantitative yield of pure silyl ether 20.



We then compared the stability of 19 relative to the TBDMS and THP ethers of cyclohexanol under acidic and basic conditions. The mono-*t*-butyl system is relatively stable

	1% HCl in 95% EtOH	5% NaOH in EtOH
$\begin{array}{c} \text{Me}_2 \\ \\ \text{---} \text{Si} - \text{OR} \end{array}$	100% removal in 15 min. at R. T.	ca. 15% removal after 9 hrs. at 80° C
$\text{C}_6\text{H}_{10}\text{OR}$	100% removal in 15 min. at R. T.	Stable
$\begin{array}{c} \text{Me} \\ \\ \text{---} \text{Si} - \text{OR} \end{array}$	No dec. after 3 days at R. T.	No dec. after 3 days at 80° C
	50% dec. 24 hrs. at 90°	

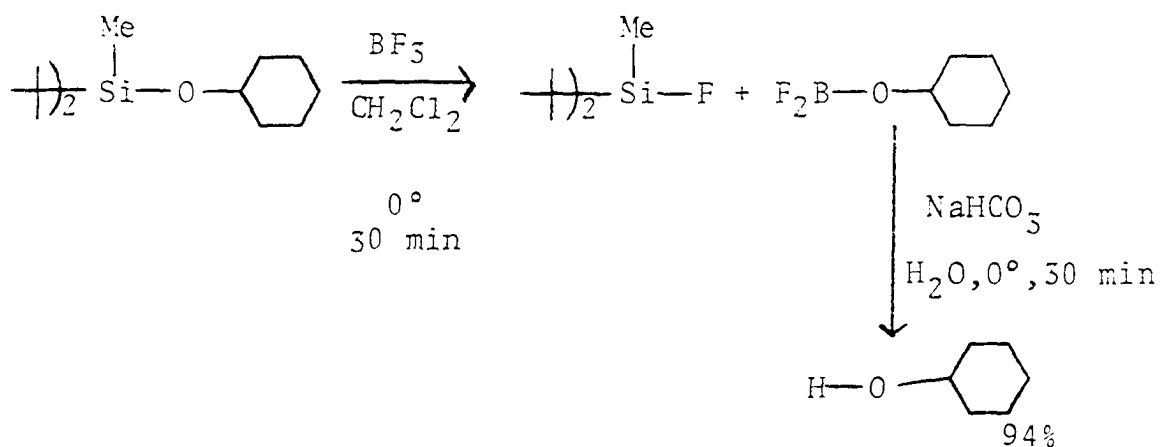
R = cyclohexyl

to base though it does decompose slowly -- the DTBMS system on the other hand was totally inert under these conditions. More importantly, it was found that the DTBMS system answered the complaint of synthetic workers that the mono-t-butyl system is readily cleaved under acidic conditions, in fact it appeared to be totally inert to conditions which rapidly remove both the t-butyldimethylsilyl and THP groups. Now that the DTBMS blocking group had been shown to offer significant advantages over both THP and TBDMS blocking group, the questions remained as to whether it could be useful for tertiary alcohols and as to whether it could be conveniently removed.

As to the first question we were somewhat suspicious that elimination might be a problem with tertiary alcohols in the reaction with the DTBMS perchlorate since it was observed when 2,6-di-t-butyl-4-methylpyridine was used as the base (see figures 72 and 73). Indeed we were amazed to find that a considerable amount of elimination occurred in the reaction of t-butanol with 12 in the presence of a 20% excess of pyridine itself; thus casting doubt of the utility of 12 as a protecting reagent for tertiary alcohols and perhaps others which can readily form a stabilized carbenium ion.

The other question which must be dealt with if 12 is to be used as a protecting reagent is how to remove the DTBMS

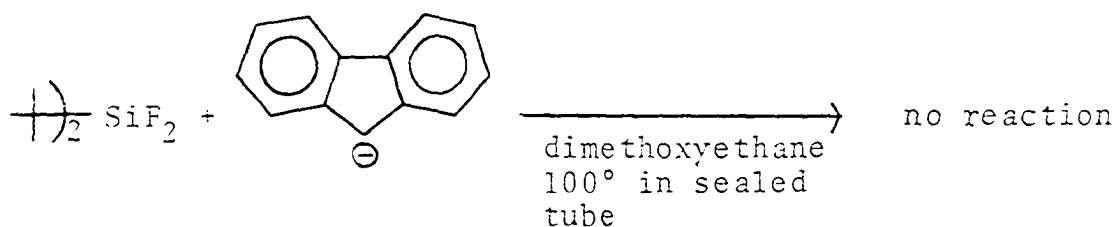
group after its utility has been exhausted. We tried cesium fluoride in DMSO but did not observe any reaction even at elevated temperatures. We did, however, discover that boron trifluoride in methylene chloride cleaved the ether even at 0°. We did not attempt to determine what functional



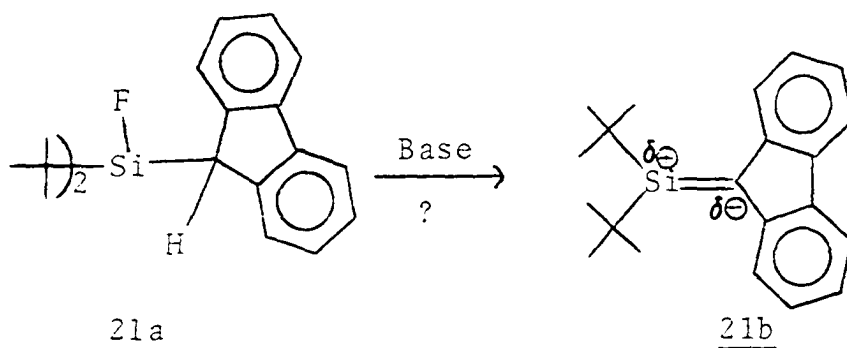
groups are also sensitive to these conditions, but it is expected that BF_3 would certainly cause unwanted side reactions for some molecules of synthetic interest. On the other hand, one would probably not be interested in the DTBMS blocking group unless protection of the alcohol against rather rigorous conditions required to effect the desired transformation was needed.

In addition to our interest in the reactions of alcohols, silyl perchlorates might be used to silylate other types of nucleophiles such as carbanions. It has been generally agreed that for alkylation of sterically hindered

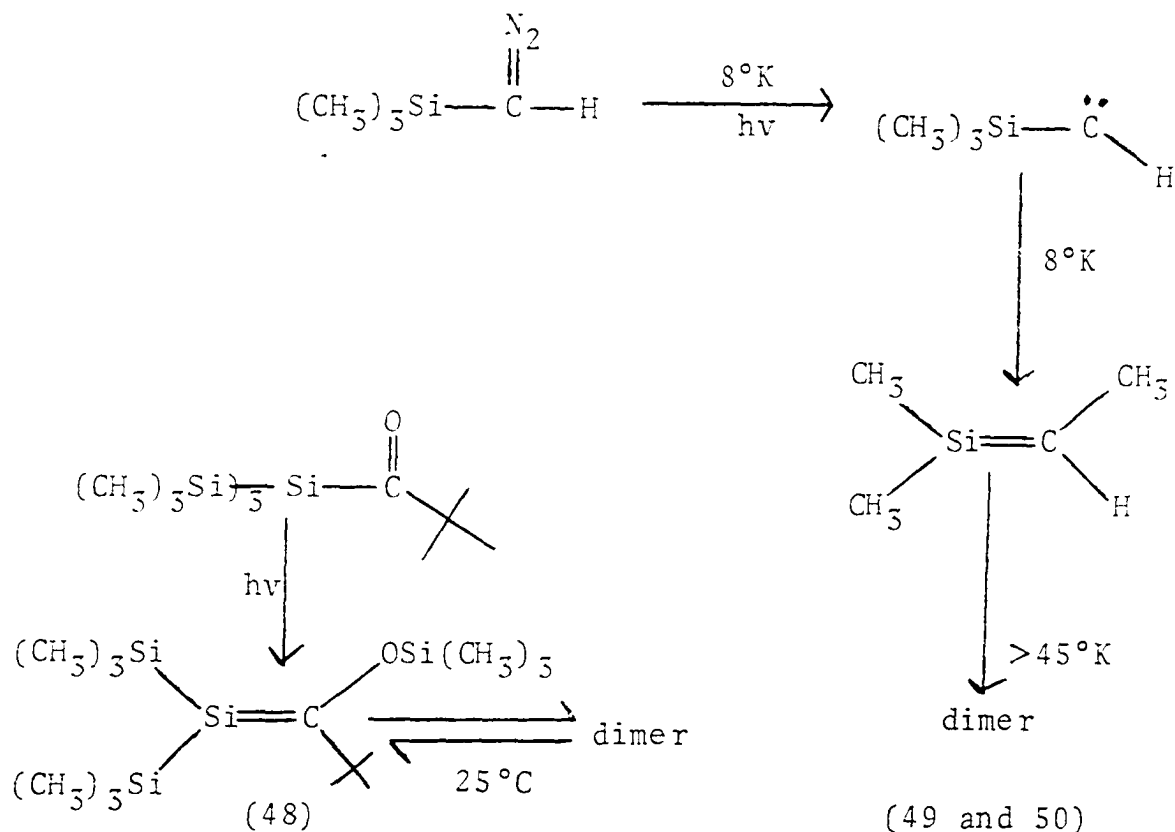
silanes, fluoride is the best leaving group (47); however, our attempt to use a silyl fluoride to synthesize a highly hindered molecule (21a) of particular theoretical interest to us has failed. We were interested in this molecule



because we felt it had potential as a precursor to silene 21b which might be directly observable at room temperature and perhaps isolable.



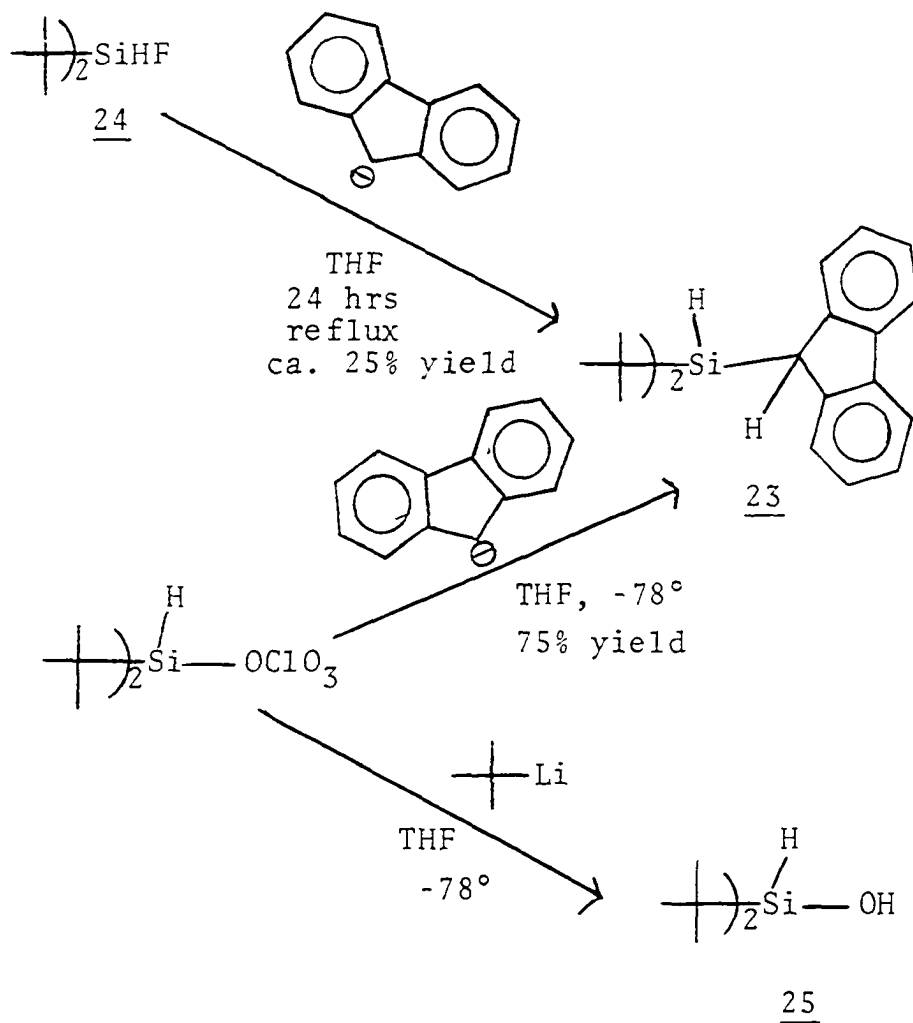
No isolable silene has been prepared to date though quite recently Brooke and Harris (48) have spectroscopic evidence for the direct observation of such a species in solution at room temperature. Other authors (49 and 50) have reported observation of a matrix-isolated silene by IR spectroscopy.



Previously only indirect evidence for the intermediacy of silenes had existed -- typically the isolation of a head to tail dimer or some other trapping product (51).

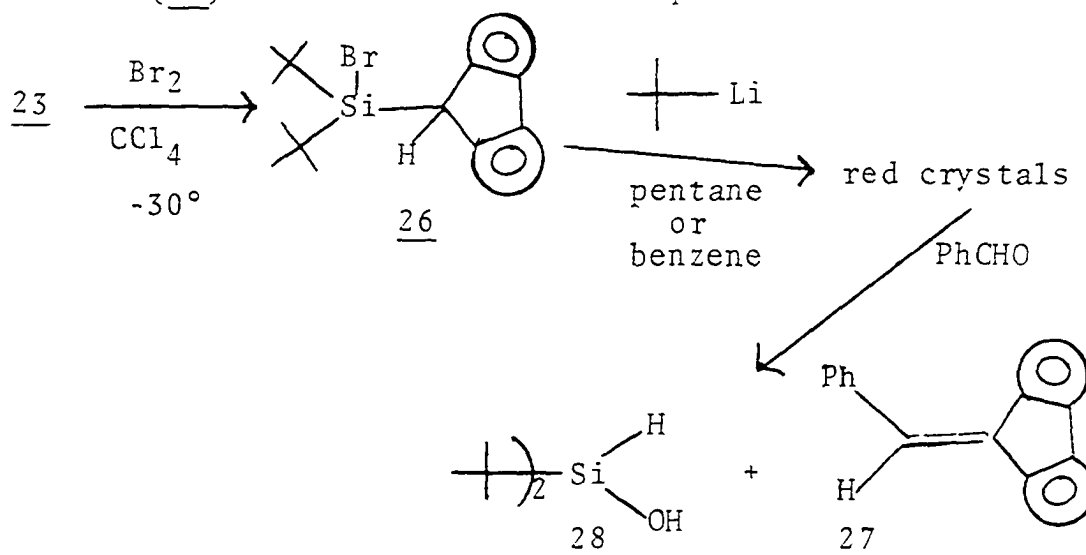
We felt that 21b had both the extreme steric bulk to impede dimerization and the electronic influence of the fluorenyl moiety to stabilize the negative end of the undoubtedly polar silene. At any rate, attempts to react fluorenyllithium with 5 had failed; however, in dramatic contrast fluorenyllithium can be titrated with perchlorate 22

at -78° to give the desired silane (23) in a 75% isolated yield. To provide a strict comparison of the reactivity of a silyl fluoride to a silyl perchlorate a sample of di-t-butylfluorosilane (24) was prepared and treated with fluorenyllithium. After 24 hrs in refluxing THF only about 25% conversion had occurred.

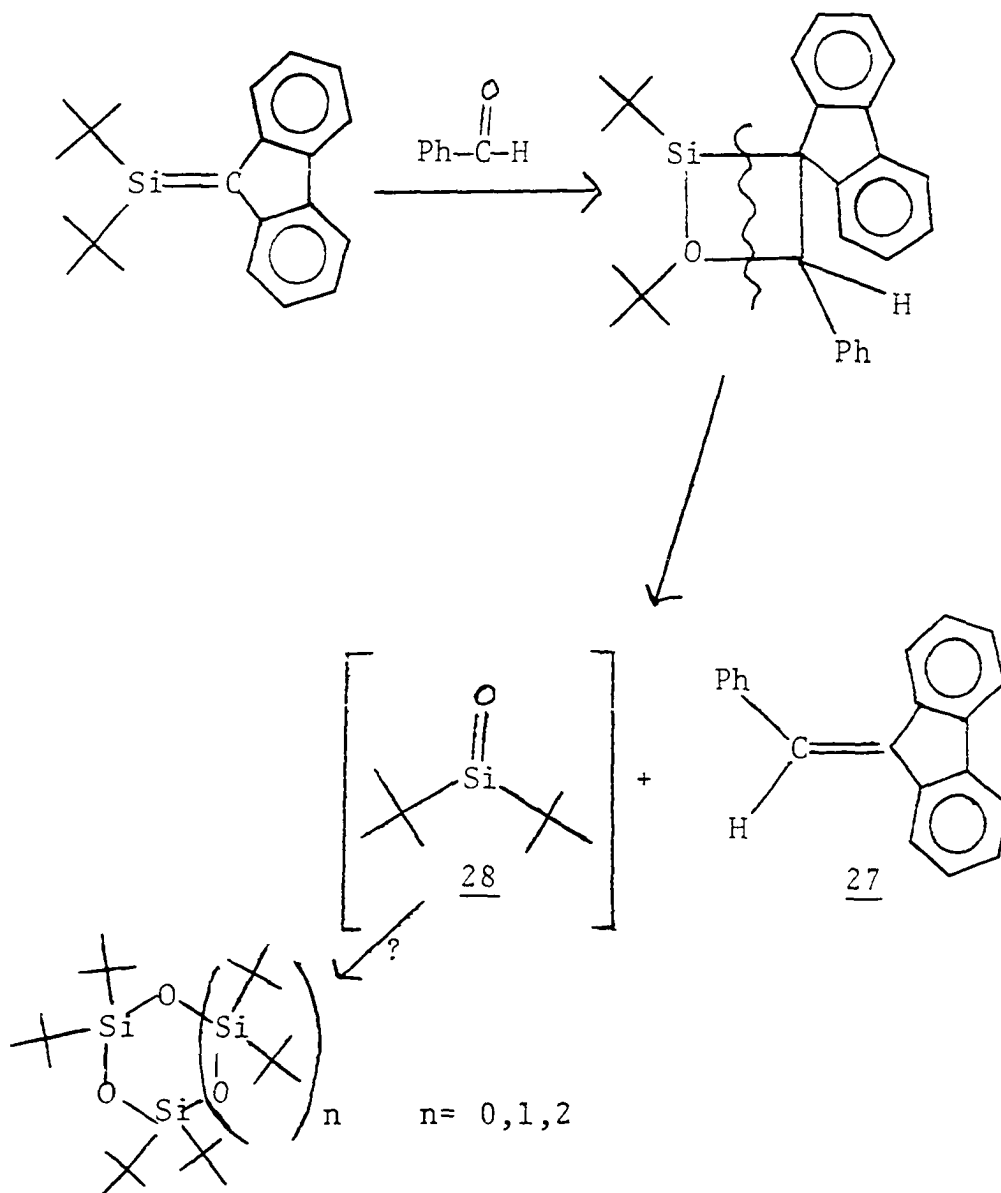


Perchlorate ion may be the world's best leaving group, but we have discovered an important limitation. If the same perchlorate (22) is treated with *t*-butyllithium, reduction of the perchlorate group takes place instead of alkylation on silicon. This reaction is also very rapid at -78° and gives a high yield of silanol 25. The reduction apparently hinges upon the availability of β -hydrogens which the fluorenyl system lacks. At this point large amounts of pure 23 were readily available from 22 and we then set about to effect the transformation of 23 to 21b.

Silane 23 was clearly brominated to 26 and subsequently treated with *t*-butyllithium in either pentane or benzene at ambient temperature to produce a red solution from which beautiful, well-formed, red crystals grew over a period of a couple of days. When these crystals were dissolved in dimethoxyethane and treated with benzaldehyde, 9-benzylidene fluorene (27) was isolated from the product mixture.



Previous work (51) indicated that 27 is an expected trapping product from the desired silene 21b and benzaldehyde; however, the silicon containing product which was isolated from the mixture was di-t-butylsilanol instead of the



expected oligomers of di-t-butylsilanone (28). This does not quite fit the picture and further investigation discovered that quenching of the red crystals with water produced starting silane 23. We also found that the NMR spectrum of these red crystals from 26 (figure 74) could be duplicated by treating 23 with n-butyl or t-butyllithium in THF (figure 75 and 76).

These facts led us to believe that a surprising metallation on silicon was occurring. Though this type of

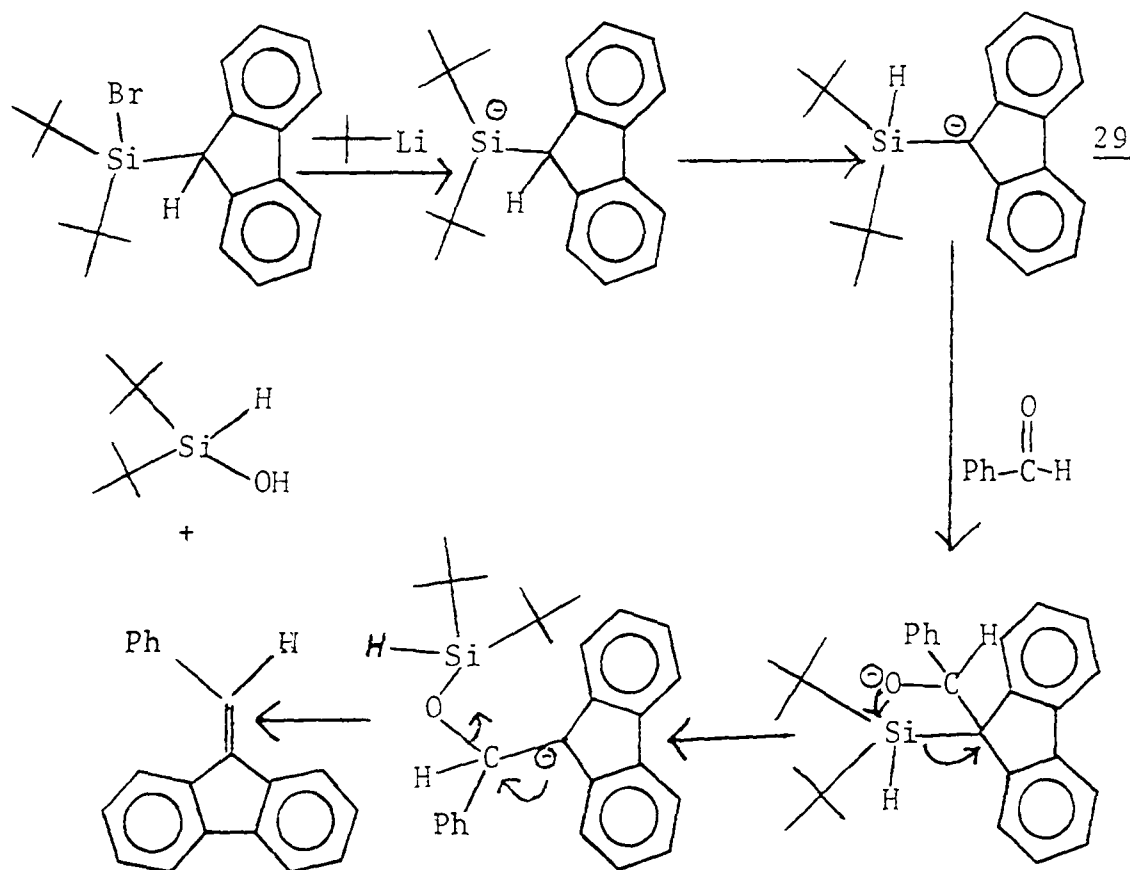
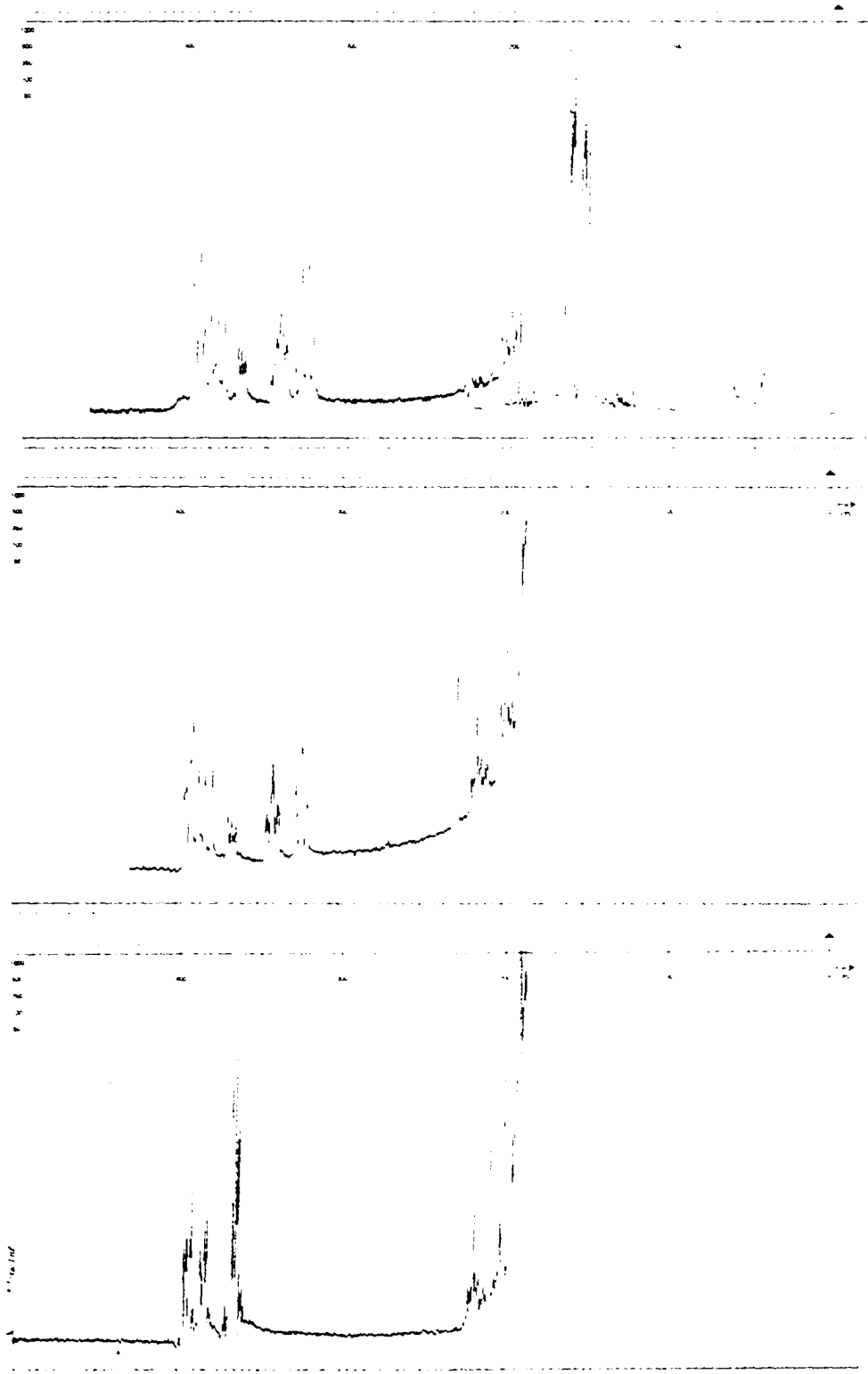


Figure 74. Red, hexane insoluble crystals from di-t-butylfluorenylsilyl bromide and t-butyllithium (nmr solvent is DME).

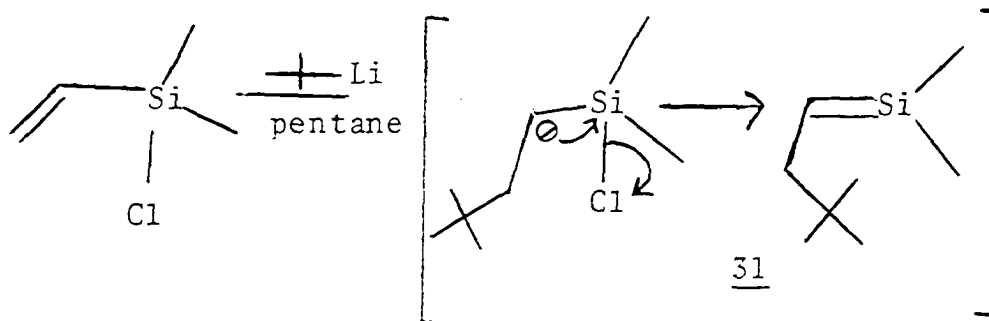
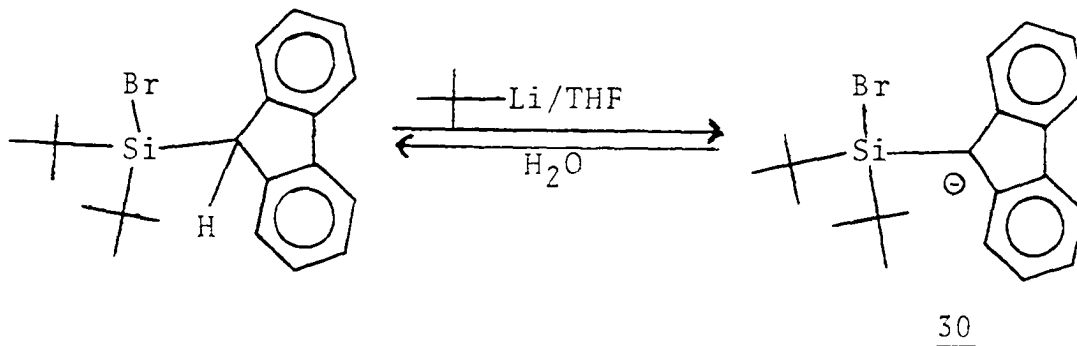
Figure 75. Di-t-butylfluorenylsilane plus 1.2 eq n-butyllithium in THF.

Figure 76. Di-t-butylfluorenylsilane in THF.

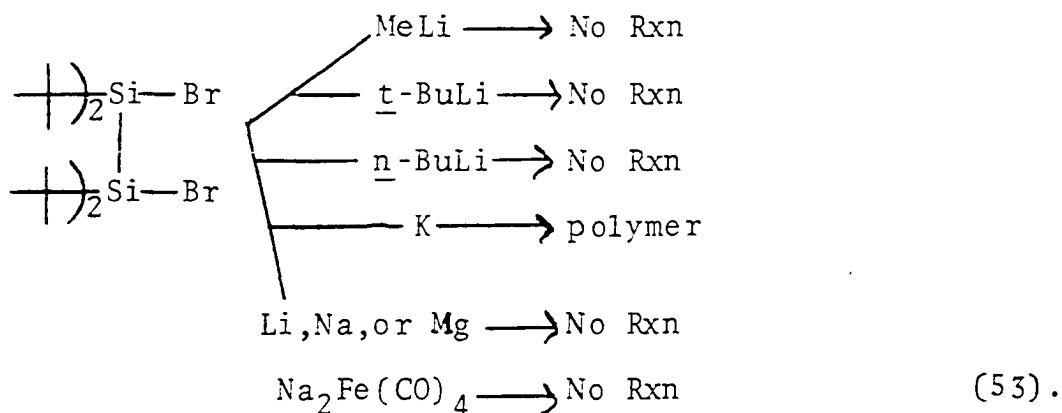


transmetallation is quite common for organic halides it has never been observed in silicon chemistry. A better anion can be made by hydrogen migration so that gives us our disappointing red crystals. Thus substituted fluorenyl-lithium salt 29 reacts with benzaldehyde to give a α -silyl alkoxide, a type of system which is known to decompose to olefin and silanol (52).

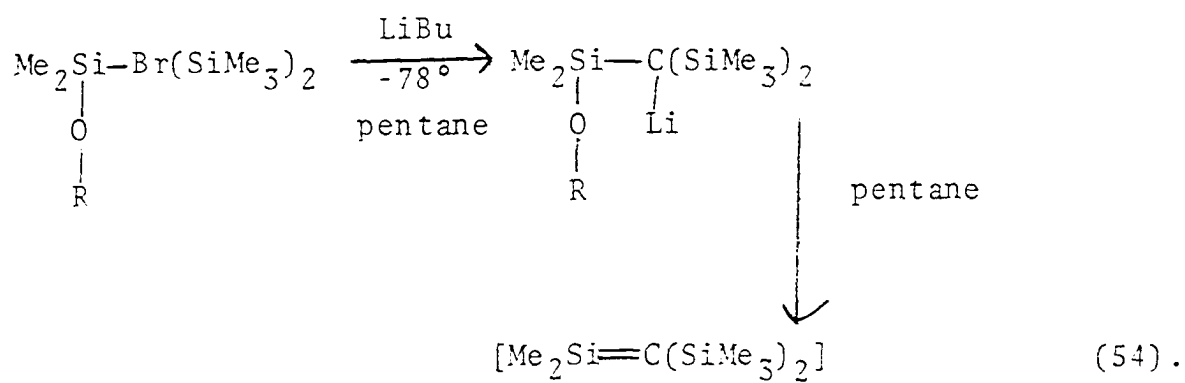
In THF the reaction is quite different where either t-butyl or n-butyllithium cleanly removes the fluorenyl proton giving the desired intermediate carbanion (30). The



unfortunate fact is that this carbanion is quite stable (figures 77 and 78). This is particularly distressing in view of the report of Jones and Lim (52) that α -halosilyl-carbanion 31 immediately eliminates chloride at low temperature to form the intermediate silene. The difference between the stability of 30 and 31 must surely be either the solvent system (pentane for 31 versus THF for 30) or perhaps the stability of the carbanion (the fluorenyl anion may be so stable that the system loses more than it gains by elimination). This provides us with the first stable α -halosilyl carbanion. Other workers have also met with failure in attempting to prepare highly hindered silicon-silicon double bonds:



More recently Wiberg and Preiner have succeeded in preparing a silene by elimination from several substituted α -silyl carbanions:



R	(> °C)
Ph ₂ PO	90
(PhO)PhPO	12
(PhO) ₂ PO	-15
Tos	-50

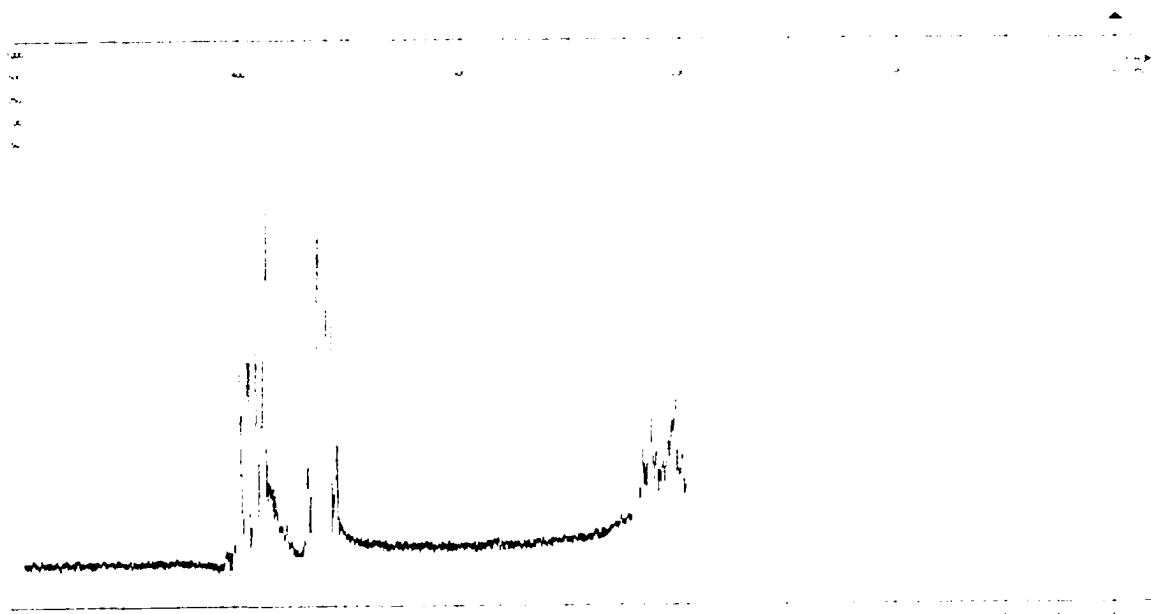


Figure 77. Di-t-butylfluorenylsilyl bromide in THF.

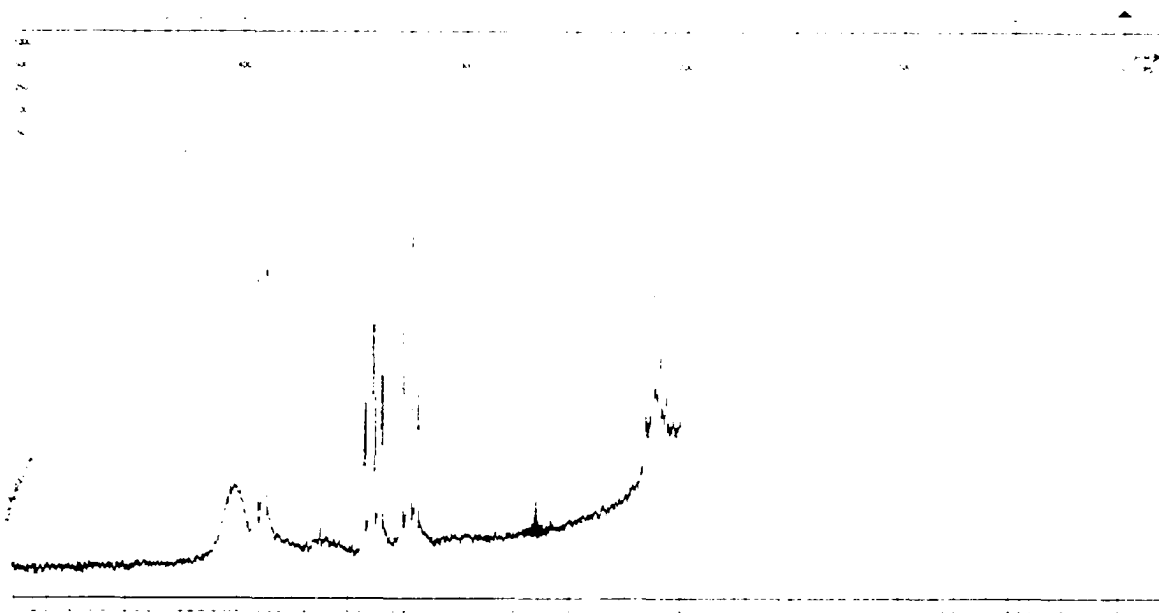


Figure 78. Di-t-butylfluorenylsilyl bromide in THF plus 1.3 n-butyllithium.

EXPERIMENTAL

General

Infrared spectra (ir) were recorded on a Beckman spectrophotometer. Routine nmr spectra were determined on a Varian HA-100 instrument and chemical shifts are reported as parts per million (δ scale) from tetramethylsilane though it was not always used as the internal standard (benzene and methylene chloride were often used). ^{13}C and ^{29}Si nmr were recorded on a Bruker 90MHz FT spectrophotometer as were the kinetic experiments of the silyl perchlorates with 2,6-di-t-butyl-4-methylpyridine. Spectra were occasionally obtained on a Varian A-60 nmr spectrophotometer and will be designated as 60 MHz nmr's.

The kinetic experiments involving the trityl salts were monitored with a Cary 14 ultraviolet (UV) spectrophotometer. Routine and high resolution mass spectra (ms) were recorded on the MS-902. Gas chromatographic/mass spectral (gcms) analysis was accomplished on a Perkin-Elmer 270 mass spectrometer. Routine analytical gas chromatography (gc) was accomplished on a Varian aerograph 600-C flame ionization instrument using a 1/8" diameter, 6 ft. long column packed with 10% Dexel 300 on Chromasorb P. GC yields were accomplished by adding known amounts of an inert standard

to the reaction mixture and comparing the relative responses of the materials of interest to those previously determined for authentic mixtures of known composition. Melting points were determined on a Thomas Hoover instrument and are uncorrected.

The vast majority of the reactions described in the experimental section involve moisture and/or oxygen-sensitive compounds. Reactions were run under nitrogen and only dried solvents were used. Generally, molecular sieves provided sufficient drying if the materials to be dried were stored over molecular sieves for at least one week prior to use.

Reactions

Preparation of tri-t-butylsilane (4) and tri-t-butylsilyl iodide (7)

The method of Dexheimer and Spialter (29) was used to prepare 4, and 7 was prepared from 4 by the method of Weiderbruch and Peter (28) and recrystallized from acetonitrile. All spectral and physical properties of the materials so prepared matched those previously reported for the two compounds. Some additional spectral data was obtained for 7: ^{13}C nmr showed singlets at δ (CDCl_3 , ^1H -decoupled) 30.7 and 24.5 in the ratio of 4.1:1 and its Si^{29} -nmr- (CHCl_3) showed a singlet at δ 47.9.

Preparation of tri-t-butylsilyl perchlorate (6)

A sample of AgClO_4 was placed in a flask and was dried by heating at 150° under vacuum overnight. This sample of AgClO_4 and a sample of (7) were placed in a "dry box" in which all subsequent manipulations were carried out. A quantity of 7 (2.25 g; 6.91 mmoles) and AgClO_4 (1.30 g; 6.31 mmoles) were placed in 40 ml acetonitrile and heated to 75° with the immediate formation of a yellow precipitate presumed to be AgI. Heating was continued for 5 hrs. After the mixture had cooled it was filtered and the yellow precipitate (AgI) was washed with acetonitrile and allowed to dry (1.44 g; 98%). The filtrate was extracted several times with 15 ml portions of hexane and then evaporated to yield 1.83 g of a slightly yellow solid which was sublimed at 95° and 0.02 mm pressure to furnish white crystalline 6 (1.71 g; 5.74 mmoles; 91% based on AgClO_4). It was later found that the material could be prepared outside of the "dry box" using Schlenk tube, syringe, and rubber septum techniques.

The white crystalline material was found to soften and begin to decompose at 150° . It became completely black at ca. 185° : ^1H nmr (CD_3CN) δ 1.27(s); ^{13}C nmr (CD_3CN , ^1H decoupled) δ 29.18, 23.18; ^{29}Si (CD_3CN) δ 29.27; ir (film was prepared by placing a small amount of a very concentrated CH_2Cl_2 solution between two salt plates, pressing the plates

together, and evacuating them in a vacuum desiccator) 2960m, 2910m, 2880m, 1486m, 1476m, 1399m, 1374m, 1270m, 1231s, 1034s, 1021w, 1014w, 9352, 820s, 808s, 743s, 708w, 690w.

Reaction of 7 with alkali

A quantity of 7 (40 mg; 0.12 mmoles) was placed in an nmr tube with 0.5 ml of CD₃CN and 5 μ l (0.28 mmoles) of water. After heating overnight at 75° there was no change in the nmr spectrum relative to the starting solution. To the reaction mixture was added 25 μ l of a 50% aqueous KOH solution. After again heating overnight at 75° it appeared that the ¹H nmr absorption of 7 at δ 1.24 was being slowly replaced by a singlet at δ 1.15 and one at δ 1.06.

Reaction of 6 with water

The nmr tube used to obtain the proton spectrum of 6 contained ca. 40 mg (0.13 mmoles) in ca. 0.4 ml CD₃CN. To this solution was added 3 μ l (0.17 mmoles) of water and the nmr spectrum was changed immediately from a singlet at δ 1.27 to a singlet at δ 1.08. A duplicate of this reaction is described later in the experimental.

Reduction of 6 with NaBH₄

In the dry box 0.36 g (1.1 mmoles) of 6 was dissolved in 2 ml diglyme. This solution was added dropwise with stirring to a solution of 0.05 g (1.3 mmoles) NaBH₄ in

2 ml diglyme (some of the perchlorate solution was spilled during the transfer). A considerable amount of gas was evolved (presumably BH_3) with each addition. When the addition was complete (5 min) the evolution of gas ceased. Stirring was continued for 1 hr and the solution was then removed from the dry box and poured onto a mixture of ice and pentane. The pentane solution was extracted several times with water and evaporated. GLC of the product mixture showed only one product and it had a retention time identical to that of 4. The ir spectrum showed the mixture to be primarily 4 (compared with authentic 4) with the characteristic Si-H frequency of 2080 cm^{-1} . The nmr of the residue was somewhat poorly resolved. After simple distillation at high vacuum the only absorption observed in the nmr was that of 4: δ 1.15 (27H,s), 3.33 (1H,s).

Preparation of triethylsilyl perchlorate

A quantity of trityl perchlorate (10.59 g; 30 mmoles) was placed in a flask equipped with a rubber septum and a magnetic stirrer. The flask was cooled in an ice bath and 40 ml methylene chloride were added (yellow-orange slurry). Triethylsilane (3.5 g; 30 mmoles) was added dropwise via syringe. As the addition was completed the mixture became homogeneous and colorless. After warming to room temperature the rubber septum was removed and quickly replaced by a

short-path distilling head (some fuming was observed). The system was heated to 50° at atmospheric pressure for 30 min to drive off the methylene chloride. The residue was then carefully evacuated (tends to bump and foam) and distilled at 10 mm to furnish 5.91 g (92% yield) of a clear, colorless liquid: b.p. 43-45° @ 0.5 mm; lit (5) b.p. 45-46° @ 1 mm.; 60 MHz ¹H nmr: δ 0.95 (m); ²⁹Si nmr (neat with 10% C₆D₆) δ 45.6.

Reduction of triethylsilyl perchlorate with NaBH₄

A solution of 0.10 g (2.6 mmoles) NaBH₄ in 10 ml diglyme was added via syringe to a solution of triethylsilyl perchlorate (0.55 g, 2.6 mmoles) in 20 ml methylene chloride at -40°. A slight evolution of gas was observed. The work-up was identical to that for the reduction of 6 except that the pentane solution was fractionally distilled at atmospheric pressure until the temperature of the distillate reached 40°. The pot residue weighed 0.59 g and gc indicated that it consisted of only triethylsilane and pentane. NMR analysis indicated that the solution was ca. 47% triethylsilane (91% yield).

Kinetics of trityl salt-silyl hydride exchange reactions

All solutions of the trityl salts were prepared in a dry box using freshly distilled (from P₂O₅) methylene chloride.

A solution of trityl salt (25 ml) was placed in a 50 ml volumetric flask and 25 ml of silyl hydride solution was placed in a 25 ml volumetric flask. The openings of the two flasks were joined using a folded piece of polyethylene tubing. The reaction was begun by unfolding the connecting tube allowing the silane solution to pass into the 50 ml volumetric flask with vigorous shaking.

The reaction mixture was quickly poured into a quartz uv cell and placed in the temperature controlled sample compartment of a Cary 14 spectrophotometer. The absorption of the trityl cation at 430 nm was monitored as a function of time. The initial concentration of trityl ion was determined by diluting another 25 ml aliquot of the same trityl stock solution used for the reaction of the 50 ml reaction volume. The absorption was measured and initial concentration of cation was calculated assuming an extinction coefficient of 38,250 as reported for a number of trityl salts (55).

The "neat addition" method was similar except that a 50 ml solution of the trityl salt was prepared and a quantity of silane was added via syringe. After a few seconds of vigorous shaking the reaction solution was placed in the spectrometer as before. More details, specific concentrations, and other data are given in the results and discussion section.

Preparation of *t*-butyldimethylsilane

Freshly distilled chlorodimethylsilane (9.46 g, 0.1 mole) was added to 20 ml pentane cooled in an ice bath. Dropwise addition of *t*-butyllithium in pentane (50 ml 2.0 M solution, 0.1 mole) was accomplished using a syringe and after the addition was complete the reaction mixture was allowed to warm to room temperature overnight. The product mixture was poured into a mixture of ice and bicarbonate solution. After extraction with water the pentane solution was distilled to afford 10.4 g (90% yield) of *t*-butyldimethylsilane:

b.p. 81-83°; ^1H nmr (CCl_4) δ 3.61 (h, 1H, J=3.5), 0.89 (s, 9H), 0.01 (d, 6H, J=3.5); ir (film) 2950s, 2925s, 2895m, 2880m, 2855s, 2099s, 1460m, 1420w, 1382w, 1358m, 1252s, 1060m, 1004m, 9822, 872s, 830s, 791w, 771w, 751m, 713m; ms m/e (rel intensity) 116(14), 101(2), 75(20), 73(30), 59(100), 58(34), 57(43), 56(49); ms calculated for $\text{C}_6\text{H}_{16}\text{Si}$ m/e 116.1021; found m/e 116.1022.

Preparation of *t*-butyldimethylsilyl perchlorate (11)

The title compound was prepared from *t*-butyldimethylsilane (1.16 g, 10 mmoles) and trityl perchlorate (3.65 g, 10.5 mmoles) in the same manner as triethylsilyl perchlorate to afford 1.95 g (91% yield) of clear, odorless 11:
b.p. 35° at 0.06 mm; ^1H nmr (CD_3CN) δ 0.99 (s, 9H), 0.51 (s, 6H); ir (film) 2955m, 2935m, 2885w, 2865m, 1471m, 1465m,

13942, 1367w, 1226s, 1101m, 1032s, 10112, 10012, 938w,
850m, 780s, 708m, 662m.

Preparation of di-t-butylmethylsilane

The title compound was prepared from t-butyllithium (110 ml, 2.1 M in pentane, 0.23 moles) and methylchlorosilane (12.6 g, 0.11 mole) in the manner used to prepare t-butyldimethylsilane except that aqueous NH_4Cl was used to neutralize the product mixture. Fractional distillation produced 14.59 (82% yield) of di-t-butylmethylsilane (b.p. 152-154°) which was found to have identical spectral properties to the impure material (b.p. 148-155°) prepared by the more tedious multistep method of Doyle and West (27).

Preparation of di-t-butylmethylsilyl perchlorate (12)

The title compound was prepared from the silane (7.21 g, 45.6 mmoles) and trityl perchlorate (15.7 g, 45.6 mmoles) in 30 ml methylene chloride by the same method used for triethylsilyl perchlorate (except the reaction mixture was stirred 1 hr at room temperature). Distillation furnished 10.2 g (39.8 mmoles, 87% yield) of clear, colorless 12: b.p. 65° at 0.1 mm; ^1H nmr (CD_3CN) to δ 1.11 (s, 18H), 0.57 (s, 3H); ir (film) 2975s, 2945s, 2900m, 2870s, 1472s, 1395w, 1371m, 1230s, 1114s, 1034s, 10102, 938w, 826m, 790s, 739m 680m.

NMR tube reactions of silyl perchlorates 11, 12 and 6

All the reactions shown in figures 1-73 were conducted in essentially the same fashion. A small septum was placed on an nmr tube and the tube was purged with dry nitrogen via a long, syringe needle. Deuteroacetonitrile (CD_3CN , 0.5 ml) was injected into the tube along with 30 μl of methylene chloride as an internal lock. A quantity of silyl perchlorate (0.126 mmoles) was injected into the tube and its spectrum then obtained. For the two liquid perchlorates 11 and 12 volumetric measurements of the pure materials were used based on the approximate densities of 1.15 g/ml for 11 and 1.08 g/ml for 12. For the solid 6 a stock solution was prepared by diluting 0.74 g (2.5 mmoles) of 6 to 5 ml with CD_3CN to provide a 0.5 M solution. The requisite volume (250 μl , 0.125 mmole) of this solution was injected into an nmr tube containing 0.280 ml CD_3CN and 30 μl CH_2Cl_2 to approximate the final concentrations used for 11 and 12. Sufficient information regarding the amounts of additional reagents are given in the figure captions for the individual reactions. For the reaction products of the perchlorates with water and those of the perchlorate-pyridinium complexes with water some additional spectral data was obtained and is described in the following sections.

Reactions of 11 and the 11-pyridinium complex with water

To each of the nmr tube reaction mixtures was added 0.4 ml each of water and pentane. After vigorous shaking the pentane layer was removed and gcms of each product mixture was obtained and a single product was found from both reactions. The remaining pentane solutions were allowed to evaporate in open vials. A small amount of CCl_4 was added to the residue and solution ir and nmr spectra were obtained which showed the products of the two reactions to be identical and the structure was assigned as n-butyldimethylsiloxane: ^1H nmr (CCl_4) δ 0.86 (s,9H), 0.01 (s,6H); ir (CCl_4) 3090w, 3070w, 3035w, 2950s, 2925s, 2860s, 1470m, 1390w, 1362w, 1255s, 1170s, 1105m, 940w, 840s, 675s; gcms m/e (rel intensity) 246(0.4), 231(1), 189(24), 147(100), 133(4), 132(4), 117(5), 73(15), 66(2), 59(2), 57(1), 45(1), 41(2).

Reactions of 12 and the 12-pyridinium complex with water

Spectral data on the pentane extracts was obtained in identical fashion as for 11. Again only one product was found for both reactions and its structure was assigned as di-t-butylmethylsilanol: ^1H nmr (CCl_4) δ 1.10 (s,1H) - for the reaction of the perchlorate itself this peak was seen at 0.91, 0.96 (s,18H), 0.01 (s,3); ir (CCl_4) 3700m, 3090w, 3075w, 3035w, 2960s, 2930s, 2885m, 2855s, 2470m, 1385w,

1361w, 1250m, 1005w, 981w, 696w, 670s; gcms m/e (rel intensity) 174(2), 117(12), 75(100), 61(4), 60(4), 57(3), 56(2).

Reactions of 6 and the 6-pyridinium complex with water

Spectral data on the pentane extracts was obtained in identical fashion as for 11; however for 6 there was a significant difference between the reactions. The reaction of 6 with water produced a single product whose structure was assigned to be tri-t-butylsilanol: ^1H nmr (CCl_4) δ 1.09(s); ir (CCl_4) 3700m, 2980m, 2955s, 2905m, 2875s, 1480m, 1385m, 1368w, 10102, 965w, 620m; gcms m/e (rel intensity) 159(16), 117(35), 87(2), 75(100), 61(3), 57(3), 41(5). Silanol prepared by Dexheimer and Spialter (29) from the ozonolysis of tri-t-butylsilane was reported to have the following spectral properties: ^1H nmr (CCl_4) δ 3.12 (s,1H) and 1.10 (s,27H); ir 3448w, 2950s, 2874s, 1481m, 1393w, 1368w, 1075w, 821s; ms parent ion peak 216.

The product mixture from the reaction of the 6-pyridinium complex with water was found to be primarily tri-t-butylsilanol and the gcms showed nothing more; however, the nmr showed some new absorptions at δ 1.22 and 1.19 and the ir showed new absorptions at 3410w, 2210m, 1620m, 1593w, 1455m, 1445m, 885w, 693w. The source of these new absorptions remains unidentified.

Comparison of the reactivities of *t*-butyldimethylsilyl perchlorate--pyridine system to the silyl chloride--imidazole system

These reactions were conducted in nmr tubes in a fashion similar to previous descriptions. For the reactions of 11 with *t*-butanol and 1-methylcyclohexanol a quantity of 11 (46 mg, 0.215 mmoles) was injected into an nmr tube containing 0.75 ml CD₃CN and 5 μl of benzene as an internal lock. Pyridine (20 mg, 0.25 mmoles) was then added. To this solution was added 14.5 mg (0.196 mmoles) *t*-butanol and the change in the O-*t*-butyl absorption was monitored in the nmr. The *t*-butanol peak at δ 1.22 was gradually replaced by the Si-O-*t*-butyl peak at δ 1.26. The conversion was over 50% at 30 sec and was complete at 5 min: ¹H nmr (CD₃CN reaction solution) δ 1.26 (s,9H), 0.89 (s,9H), 0.12 (s,6H).

The reaction was repeated with 1-methylcyclohexanol (22 mg, 0.193 mmoles) replacing the *t*-butanol. The methyl peak of the alcohol at δ 1.18 was gradually replaced by a peak at δ 1.26. The conversion was ca. 50% at 3 min and complete at 20 min: ¹H (CD₃CN reaction solution) δ 1.49 (m, 10H), 1.19 (s,3H), 0.87 (s,9H), 0.07 (s,6H).

Attempts to derivatize these tertiary alcohols using *t*-butyldimethylsilyl chloride were then made to provide a strict comparison. The chloride (32 mg, 0.213 mmoles) and imidazole (30 mg, 0.44 mmoles) in the proportions suggested

by Corey and Venkateswarlu (42) were added to 0.75 ml of DMF. The same amounts of each of the two alcohols were added as before and the changes in nmr spectrum of the solution were monitored. After three days the conversion of t-butanol to ether was ca. 30%. For 1-methylcyclohexanol it was ca. 10%.

Preparative scale reaction of 11 with 1-methylcyclohexanol

To a flask equipped with a magnetic stirrer and a rubber septum was added 0.862 g (4.03 mmoles) of 11 and 5 ml acetonitrile. Pyridine (0.332 g, 4.2 mmoles) was added slowly and finally 0.45 g (3.95 mmoles) of 1-methylcyclohexanol was injected to the stirred solution. Just after the mixture became homogeneous a phase separation occurred. Stirring was continued for 1.5 hrs. The reaction mixture was then poured into a small separatory funnel containing 15 ml pentane and 15 ml saturated NaHCO₃ solution. The pentane layer was then extracted several times until the smell of pyridine could no longer be detected in the aqueous phase. Evaporation of the pentane solution then afforded 0.891 g (99% yield) of the desired silyl ether (>95% pure by GC): ¹H nmr (CCl₄) δ 1.48 (m, 10H), 1.18 (s, 3H), 0.86 (s, 9H), 0.05 (s, 6H); ir (film) 2930s, 2855s, 1460m, 1445w, 1372w, 1358w, 1275w, 1253s, 1168m, 1135m, 1061s, 1024s, 1000m, 831s, 768s; ms m/e (rel intensity) 228(2), 213(6), 185(6),

177(26), 95(11), 75(100), 59(11), 57(4); ms calculated for $C_{13}H_{28}OSi$ m/e 228.1909; found, m/e 228.1905.

Preparative scale rxn of 11 with cyclohexanol

Silyl perchlorate 11 (0.854 g, 4.0 mmoles) was reacted with pyridine (0.38 g; 4.8 mmoles) and finally 0.401 g (4.0 mmoles) cyclohexanol in the fashion described above. Work-up as above furnished 0.848 g (99% yield) of the desired silyl ether (>95% pure by gc): 1H nmr (CCl_4) δ 3.58 (broad s, 1H), 1.47 (m, 10H), 0.88 (s, 9H), 0.02 (s, 6H); ir (film) 2930s, 2860s, 1465m, 1445w, 1371w, 1360w, 1255m, 1132w, 1096s, 1050m, 1018w, 1002w, 992w, 935w, 883w, 868m, 834s, 790w, 771m; ms m/e (rel intensity) 214(1), 199(1), 157(63), 75(100), 73(11); ms calculated for $C_{12}H_{26}SiO$ m/e 214.1753; found m/e 214.1759.

Preparative scale reaction of 12 with cyclohexanol

A quantity of 12 (5.60 g, 21.9 mmoles) in 20 ml CH_3CN was reacted with pyridine (1.9 g, 24 mmoles) and finally 2.19 g (21.9 mmoles) of cyclohexanol. Again a phase separation occurred immediately after the dissolution of the cyclohexanol. After stirring the mixture for 1 hr, 20 ml of pentane were added and the mixture extracted once with dilute HCl and twice with water. Evaporation of the pentane solution provided 5.62 g (100%) of the desired silyl ether

(>95% pure by gc): ^1H nmr (CCl_4) δ 3.62 (broad s, 1H), 1.50 (m, 10H), 0.95 (s, 18H), 0.04 (s, 3H); ir (film) 2930s, 2860s, 1465m, 1445w, 1381w, 1368m, 1250m, 1128w, 1092s, 1048m, 1016m, 1006m, 992w, 931w, 883w, 871w, 856m, 820s, 776m, 750m, 692m; ms m/e (rel intensity) 256(6), 241(3), 199(36), 157(48), 75(100), 73(18), 61(12), 41(15); ms calculated for $\text{C}_{15}\text{H}_{32}\text{OSi}$ m/e 256.2222; found m/e 256.2210.

Stability comparison of t-butyltrimethylsilyl (TBDMS), di-t-butylmethylsilyl (DTBMS), and tetrahydropyranyl (THP) ethers of cyclohexanol

For the acid stability test a stock solution of a 1% HCl in aqueous ethanol was prepared by adding 2.9 g concentrated (35%) aqueous HCl to 97.1 g of 95% ethanol. A sample of each ether (50 μl) was placed in a test tube containing 0.5 ml of the 1% HCl in aqueous ethanol solution and a septum placed over the mouth of the tube. The decomposition of the ethers was followed by gc. Both the TBDMS and THP ethers were completely removed in 15 min at room temperature; however, the DTBMS ether showed no decomposition after 5 days at room temperature. Upon heating some decomposition was observed, but after 24 hrs at 80° less than 50% decomposition had occurred.

For the alkaline stability test a stock solution of 5% NaOH in aqueous ethanol was prepared by dissolving 5 g of NaOH in 95 g of 95% ethanol. The THP ether was assumed

to be stable under basic conditions, but samples of both silyl ethers (50 μ l) were placed in nmr tubes containing 0.9 ml of the 5% NaOH in aqueous ethanol solution. The spectrum of the DTBMS ether showed no change after heating at 80° for 3 days; however, the TBDMS ether was found to decompose slowly under these conditions as ca. 15% of the silyl ether methyl absorption at δ 0.03 had been converted to a new peak at δ -0.07 after 9 hrs at 80°.

Cleavage of the di-*t*-butylmethylsilyl ether of cyclohexanol with BF₃

A sample of the title ether (0.278 g) was placed in a flask with 10 ml of methylene chloride. Decane (0.081 g) was added as an internal gc standard. The flask was cooled in an ice bath and BF₃ was slowly passed over the stirred solution for 30 min. Saturated aqueous NaHCO₃ (15 ml) was added to the mixture and it was allowed to stir at room temperature for 5 hrs. The mixture was placed in a separatory funnel and the methylene chloride layer drained off. The aqueous layer was then extracted once with 10 ml of diethyl ether and the ether extract combined with the methylene chloride layer. After stirring the solution was found (by gc) to contain di-*t*-butylmethylfluorosilane and cyclohexanol (94% yield--cyclohexanol was further identified by comparison of gcms with authentic material).

Reaction of di-t-butyldifluorosilane with fluorenyllithium

Fluorenyllithium was prepared by adding n-butyllithium (5 ml of 1.6 M solution in hexane, 8.0 mmoles) to a solution of 1.33 g fluorene and 25 ml DME in a sealable pyrex tube with cooling. After 0.5 hr at room temperature, 1.44 g (80 mmoles) of di-t-butyldifluorosilane was added to the red solution and the tube was cooled, evacuated and sealed. After heating at 100° for 24 hrs the tube was opened and the red solution was quenched with aqueous NH₄Cl and found to contain only starting materials (by gc and nmr).

Preparation of di-t-butylsilane

Di-t-butyldifluorosilane (60 g, 0.33 mole) was added slowly to a slurry of LAH (12 g, 0.33 mole) in 100 ml THF at reflux. After refluxing an additional 2 hrs the reaction mixture was slowly poured over a mixture of ice and aqueous NH₄Cl. Pentane (150 ml) was then added to the mixture and the pentane layer was extracted several times with water until the aqueous extract no longer smelled of THF. The pentane layer was then distilled (b.p. 126-128°) to furnish 40.5 g (84%) of the title compound which had identical spectral properties to those reported by Doyle and West (27) though this preparation is a vast improvement over their preparation.

Preparation of di-t-butylsilyl perchlorate

The title compound was prepared in the manner of triethylsilyl perchlorate from 15.8 g (46 mmoles) trityl perchlorate in 40 ml CH_2Cl_2 and 6.87 g (47 mmoles) to di-t-butylsilane. Distillation as before afforded 10.2 g (91% yield) of di-t-butylsilyl perchlorate: b.p. 49° at 0.07 mm; 60 MHz ^1H nmr (CCl_4) δ 4.57 (s,1H), 1.15 (s,18H).

Preparation of di-t-butylfluorenylsilane (23)

Fluorenyllithium (20 mmoles) was prepared by adding 15.5 ml of 1.6 M solution of n-butyllithium (24.8 mmoles) to an ice cooled solution of 3.32 g (20 mmoles) fluorene in 70 ml THF. The characteristic bright red-orange color of the fluorenyl anion was produced immediately. After stirring at room temperature for 1 hr the solution was cooled to ca. -75° with a dry ice-ethanol bath. Approximately 7 ml di-t-butylsilyl perchlorate was drawn into a 10 ml syringe and weighed. The perchlorate was added dropwise to the dry ice cooled, red-orange solution of fluorenyllithium. An immediate reaction was apparent and when the light yellow end-point was reached the syringe was weighed again and the difference was 5.97 g (24.7 mmoles) of silyl perchlorate. The light yellow solution contained a white precipitate which appeared to dissolve as the mixture warmed to room temperature. The mixture was poured into 100 ml of hexane and extracted with

water several times. The hexane solution was evaporated and after 10 hrs under high vacuum, 7.22 g of yellow, mushy crystals were obtained. The product mixture was determined (by gc) to consist primarily of a single product and fluorene. The material was loaded on a silica gel column and eluted with Skelly B. The elution was followed by gc -- fluorene came off first and the product closely behind it. Evaporation of all the eluent containing substantial amounts of product afforded 4.81 g (78% yield) of a white crystalline material (m.p. 89-91°) which contained small amounts (< 5%) of fluorene. Recrystallization from CH₃CN afforded a total (2 crops) of 4.0 g (65% yield) of pure di-t-butylfluorenylsilane: m.p. 93-94°; ¹H nmr (CCl₄) δ 7.61 (m,4H), 7.19 (m,4H), 4.01 (s,1H), 3.92 (s,1H), 0.87 (broad s,18H); ir (CCl₄) 3060m, 3038w, 3020w, 2970s, 2930s, 2883s, 2858s, 2100s, 1467s, 1441s, 1386m, 1361m, 1330w, 1303w, 1231w, 1178m, 1100w, 1072s, 1029w, 1010m, 932m, 869s, 848s; ms m/e (rel intensity) 308(8), 251(6), 210(6), 196(5), 194(5), 181(3), 165(14), 101(10), 75(100); ms calculated for C₂₁H₂₈Si m/e 308.1960; found m/e 308.1914.

Preparation of di-t-butylfluorosilane

A sample of the title compound was prepared from trityl fluoroborate and di-t-butylsilane by M. J. Maroney in the same fashion as the preparation of triethylsilyl perchlorate.

All physical and spectral properties of the material were identical to those reported by Weidenbruch and Peter (28).

Reaction of di-t-butylfluorosilane with fluorenyllithium

Fluorenyllithium (1.0 mmole) was prepared as before from fluorene (0.166 g, 1.0 mmole) and n-butyllithium (0.63 ml of 1.6 M hexane solution, 1.0 mmole) in 3 ml THF. After stirring 30 min at room temperature, di-t-butylfluorosilane (0.2 g, 1.2 mmole) was added causing a darkening of the characteristic red-orange color of the fluorenyl anion. No further color change was noted after 1 hr at room temperature so the solution was heated at 65° for an additional 24 hrs. The color of the solution appeared darker so the mixture was quenched by adding pentane and extracting first with saturated NH₄Cl solution and then with water. The pentane solution was evaporated and nmr and gc analysis indicated that the residue contained fluorene and di-t-butylfluorenylsilane in the approximate ratio of 3:1, in addition to minor amounts of unidentified materials. Thus indicating that only about 25% conversion had occurred.

Reaction of di-t-butylsilyl perchlorate with t-butyllithium

A solution of t-butyllithium (27 ml of 1 M pentane solution, 27 mmoles) in 30 ml diethyl ether was cooled to ca. -75° by a dry-ice--ethanol bath. The title perchlorate

(5.0 g, 20 mmoles) was added dropwise very slowly via syringe and an immediate reaction was observed as a white precipitate formed. After the addition was complete the Pyrex syringe exploded but the reaction flask was left intact. The colorless reaction mixture was warmed to room temperature and poured over ice. After extraction with aqueous NH_4Cl and finally water, evaporation of the pentane-ether layer afforded 2.96 g of mushy, white crystals which were determined to be di-t-butylsilanol: m.p. of sublimed material 64-66°; ^1H nmr (CCl_4) δ 3.96 (2,1H), 1.56 (s,1H), 0.97 (s,18H); ir (CCl_4) 3700m, 2500w, 2985s, 2935s, 2895m, 2860s, 2092s, 1469s, 1442w, 1388w, 1363m, 1010m, 938w, 831s; ms calculated for $\text{C}_8\text{H}_{20}\text{OSi}$ m/e 160.1283; found m/e 160.1287.

Preparation of di-t-butylfluorenylsilyl bromide

Bromine (1.14 g, 7.1 mmoles) in 4 ml CCl_4 was added to a solution of 2.0 g (6.5 mmoles) di-t-butylfluorenyl silane in 20 ml CCl_4 at -30°. After stirring ca. 15 min at this temperature the evolution of HBr ceased. The solution was stirred 15 min more, then rotary evaporated to afford 3.23 g of a light brown solid residue. Sublimation of the residue under high vacuum afforded 2.41 g (95% yield) of the title compound: white crystals, m.p. 81-82°; ^1H nmr (CCl_4) δ 7.78 (m,4H), 7.19 (m,4H), 4.24 (s,1H), 0.85 (s,18H); ir (CCl_4): 3062m, 3035w, 2960s, 2895s, 2861s, 1472s, 1444s,

1390m, 1365m, 1170w, 1072s, 1028w, 1008w, 935m, 871m,;
ms m/e (rel intensity) 388(11), 386(11), 223(15), 221(15),
181(52), 179(52), 165(96), 139(81), 137(81), 58(100); ms
calculated for $C_{21}H_{27}SiBr$ m/e 386.1065; found m/e 386.1028.

Reaction of di-*t*-butylfluorenylsilyl bromide with
t-butyllithium

Silyl bromide (0.1 g, 0.26 mmoles) was placed in an nmr tube equipped with a rubber septum and dissolved with 0.4 ml pentane. To this solution was added 0.30 mmoles (150 μ l of 2 M solution in pentane) of *t*-butyllithium. The solution turned a light red-orange color and the formation of tan precipitate was noted. The precipitation continued over a period of 2 days and it was noted that beautifully formed, red crystals had also appeared. The supernatant liquid was withdrawn via syringe and the solids were washed once with pentane. After withdrawal of the pentane wash, 0.5 ml DME was added and the solids dissolved to produce a red solution (see figure 74 for nmr). The solution was divided in half and one portion was quenched with benzaldehyde (20 mg, 0.22 mmoles). After 30 min at room temperature hexane (0.5 ml) and water (0.5 ml) were added to the product mixture. After vigorous shaking the hexane layer was removed and evaporated and the residue chromatographed on a silica-gel column. The column was eluted with hexane first followed by a 10% ether-hexane solution. Evaporation of the hexane eluent furnished

a white solid residue which was determined to consist primarily of 9-benzylidene fluorene: ^1H nmr (CCl_4) δ 7.71-6.85 (m) with an approximately equal volume of nondescript aliphatic absorption from 1.7 to 0.8 (presumably hexane) and a small singlet at 1.30; ir (CCl_4) 3062m, 3023m, 2961w, 2925w, 2858w, 1491m, 1448s, 940m, 694s; ms m/e (rel intensity) 254(100), 253(87), 252(58), 251(8), 250(17), 126(17), 125(8), 113(12), 112(4), 76(8); ms calculated for $\text{C}_{20}\text{H}_{14}$ m/e 254.10956; found m/e 254.1104.

Evaporation of the 10% ether-hexane eluent furnish a redish solid. No evidence for oligomers of di-t-butylsilanone could be found. The nmr spectrum was suggestive of di-t-butylsilanol (as compared to authentic material): ^1H nmr (CCl_4) δ 7.71-6.85 (weak multiplet: small amount of 9-benzylidene fluorene), 3.98 (s,1H), 0.96 (s,18H), also small amounts of nondescript aliphatic absorption and as in the previous fraction (but here greatly diminished) a singlet at 1.30. The ir and ms of the material contained all the requisite peaks for di-t-butylsilanol but it appeared to be a relatively minor component of a complex mixture.

The other portion of the red DME solution was quenched with water (0.5 ml) and extracted with hexane (0.5 ml). Evaporation of the hexane afforded a tan residue whose gc, ir and nmr were essentially superimposable with authentic di-t-butylfluorenylsilane.

The red crystals were thus presumed to be the silyl-fluorenyllithium salt 20. The nmr of these red crystals could be duplicated by treatment of di-t-butylfluorenylsilane with 1.1 equivalents of either n-butyl or t-butyllithium (figures 75 and 76). In fact, the red crystals themselves could be obtained in pentane or benzene by treatment of di-t-butylfluorenylsilane with 1.1 equivalents of t-butyllithium over a period of 2 to 3 days.

Reaction of di-t-butylfluorenylsilyl bromide with t-butyl or n-butyllithium in THF

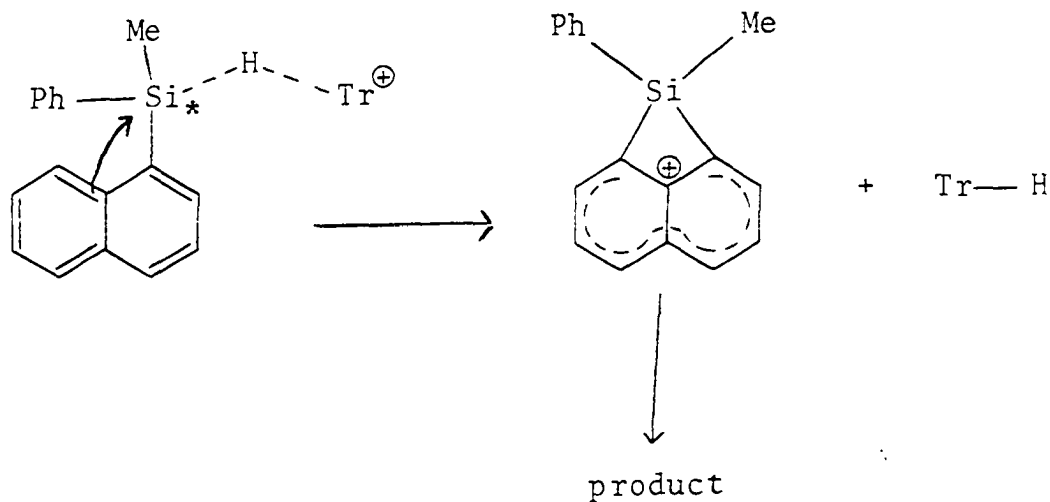
A sample of silyl bromide (53 mg, 0.14 mmoles) was placed in an nmr tube along with 0.5 ml THF and the solution cooled -75° . n-Butyllithium (0.115 ml 1.6 M in hexane, 0.18 mmoles) was injected and an immediate reaction took place and with mixing the solution turned a bright yellow-green color which appeared to have a fluorescent character (see figures 77 and 78). Similar treatment with t-butyllithium (0.09 ml 2 M in pentane, 0.18 mmoles) afforded a dark green solution with an essentially identical nmr: ^1H nmr (THF) δ 8.07 (broad hump--seemed to vary somewhat in relative intensity from one run to the next), 7.84 ((d, J=7, these protons appeared to be weakly coupled (J=1) to another proton)), 6.83 ((t, J=7, also weakly coupled to another proton (J=1)), 6.50 ((t, J=7, also weakly coupled to another proton (J=1))), the integration of

these four absorptions is approximately equal, there is also a spurious peak at δ 5.35 present in all reactions but varying greatly in intensity, and in the t-butyllithium reaction there is a heptet ($J=1$) which was ascribed to isobutene (the aliphatic region was obscured by THF). Quenching of these solutions from either n-butyl or t-butyllithium with water furnish a single product whose gc, nmr and ir were identical to starting silyl bromide.

SUGGESTIONS FOR FUTURE WORK

Certainly the reactions of the t-butylsilyl perchlorates deserve further investigation as some very stimulating data has been presented here without a complete explanation. A particularly good place to start would be to identify the unknown product obtained from the quenching of the 6-pyridine complex.

For the trityl salt-silyl hydride exchange reaction the stereochemistry should be determined, preferably with a silane other than α -NpMePhSiH, which might racemize without the involvement of a silylenium ion:



On the synthetic front it would certainly be of interest to examine the utility of silyl perchlorates in the preparation of enol ethers.

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