

THE UNIVERSITY OF CALGARY

New Diazene Systems Incorporating
Chalcogen-Containing Functional Groups

by

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THE UNIVERSITY OF CALGARY
FACULTY OF GRADUATE STUDIES

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ABSTRACT

This thesis describes the preparation, full characterisation, and X-ray structures of two chalcogen-substituted diazenes from the reaction of chalcogen halides with a trisilylated benzamidine, $4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$. A sulfonyl derivative $\text{MeSO}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{NSO}_2\text{Me}$ displays a diazene bond length of $1.20(1)$ Å, slightly shorter than typical $\text{N}=\text{N}$ bond lengths found in similar organic compounds. The structure also is twisted, with an N-N-C-N torsion angle of $63(1)^\circ$. The diazene $4\text{-CH}_3\text{C}_6\text{H}_4\text{SN}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{N}(\text{SC}_6\text{H}_4\text{CH}_3\text{-4})$ is a sulfenyl derivative with an $\text{N}=\text{N}$ bond length of $1.294(14)$ Å. This compound is essentially planar with a corresponding torsion angle of $10(1)^\circ$. It is similar to the structure of a known selenium diazene analogue, and has an intramolecular chalcogen-nitrogen interaction of $2.607(10)$ Å. This compound was prepared unexpectedly from the attempted synthesis of the corresponding S(IV) derivative.

Characterisation of related monosubstituted benzamidine derivatives $\text{ArC}(\text{NER})[\text{N}(\text{SiMe}_3)_2]$ ($\text{ER}=\text{O}_2\text{SMe}$, $\text{OSC}_6\text{H}_4\text{CH}_3\text{-4}$) and related hydrolysis products is also discussed.

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I also thank Dr. Masood Parvez for his perseverance in the two X-ray structural determinations. Lastly, the Department of Chemistry and the University of Calgary are acknowledged for their financial support.

THIS THESIS IS DEDICATED TO MY NEPHEW
JAMES PETER KROUSE

A GOOD THING THAT HAPPENED
DURING A BAD TIME

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LIST OF ABBREVIATIONS AND SYMBOLS

Ar	aryl (aromatic) group
Cp	C ₅ H ₅ cyclopentadienyl
Cp*	C ₅ (CH ₃) ₅
D _{calc}	calculated density
DME	dimethoxyethane
EI-MS	Electron Impact Mass Spectrometry
FAB-MS	Fast Atom Bombardment Mass Spectrometry
FT-IR	Fourier Transform Infrared (Spectroscopy)
GC-MS	Gas Chromatograph Mass Spectrometry
Mes	1,3,5-(CH ₃) ₃ C ₆ H ₂ mesityl
NMR	Nuclear Magnetic Resonance
ORTEP	Oakridge Thermal Ellipsoid Plot
Ph	C ₆ H ₅ phenyl
THF	Tetrahydrofuran
TMEDA	Tetramethylethylenediamine
TMS	Si(CH ₃) ₄ Tetramethylsilane
UV	Ultraviolet (Spectroscopy)
Z	Number of molecules in a unit cell
amu	atomic mass unit
ppm	parts per million
<i>p</i> -tolyl	4-CH ₃ C ₆ H ₄

1.1

GENERAL INTRODUCTION

The silicon-nitrogen bond has the strongest M-N bond strength for Group 14 main-group elements ($M = C < Si > Ge > Sn > Pb$).¹ As a result, silicon-nitrogen compounds are thermally very stable, and many of these compounds can be distilled at high temperatures with little or no decomposition. This trend also exists for the relative bond strengths of M-O, M-F or M-Cl. Consequently, the Si-N bond is highly susceptible to cleavage by halide sources and water. The strength of the Si-N bond, coupled with the lability of the trimethylsilyl group, leads to a vast array of stable silylated compounds that are synthetically very useful.

This chapter contains a brief survey of the chemistry of N,N,N'-trisilylated benzamidines, which will demonstrate the synthetic utility of the Si-N functional group in these compounds and lead to the development of the objectives of this thesis.

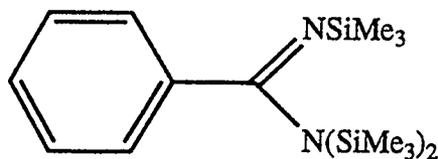
1.2

N,N,N'-TRISILYLATED BENZAMIDINES

A highly important class of silylated compounds are the N,N,N'-trisilylated benzamidines, $ArC(NSiMe_3)[N(SiMe_3)_2]$. These compounds react readily with virtually all main group and transition-metal halides to form inorganic heterocycles or chelated complexes of synthetic usefulness. For the purposes of this thesis, main group elements are defined as the s- and p-block elements of the periodic table, and transition-metals are described as the d-block metals.

1.2.1 SYNTHESIS OF N,N,N'-TRISILYLATED BENZAMIDINES

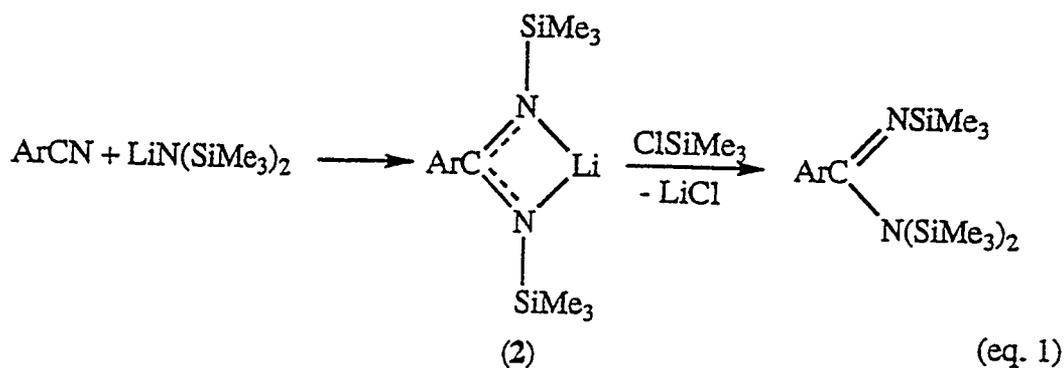
Whereas amidines of the general formula $RC(NH)NH_2$ are useful in synthetic organic chemistry,^{2,3} N,N,N'-trisilylated benzamidine derivatives have been developed extensively as synthetic tools in many branches of inorganic chemistry. The first N,N,N'-trisilylated benzamidine, $PhC(NSiMe_3)[N(SiMe_3)_2]$, (1), was originally discovered by Sanger in 1973.⁴



(1)

Trisilylated benzamidines, in general, are prepared by a 1:1 reaction of lithium bis(trimethylsilyl)amide and an aromatic nitrile. This reaction does not occur if there are any saturated carbons *alpha* to the nitrile. The second step involves the addition of the third trimethylsilyl group, with the concomitant elimination of lithium chloride to give a distillable benzamidine (eq. 1). This route gives access to several persilylated amidines.⁵ A variety of benzamidines are known (Ar = C_6H_5 , $p-CH_3C_6H_4$, $p-ClC_6H_4$, $p-MeOC_6H_4$, $p-Me_2NC_6H_4$, $p-CF_3C_6H_4$, $p-NCC_6H_4$, $p-O_2NC_6H_4$) as well as halogenated amidines such as $CF_3C(NSiMe_3)[N(SiMe_3)_2]$. Recently, the parent formamidine $HC(NSiMe_3)[N(SiMe_3)_2]$ was prepared as well.⁶ These reactions produce oily solids or liquids that are easily purified by vacuum distillation or sublimation to give yields ranging from 50 to 72%. It should also be noted that the lithium derivatives of benzamidines, (2), can be used instead of trisilylated benzamidines for reactions with

main group or transition-metal halides, and usually these reagents give cleaner reactions and higher yields. These lithium salts are normally used *in situ*, but they can be isolated from diethyl ether solutions. Several sodium analogues are known as well.^{7,8} These are moisture-sensitive, white crystalline solids which react with H₂O to give the unsubstituted amidines as hydrolysis products, ArC(NH)(NH₂) in high yields.



1.2.2

MAIN GROUP CHEMISTRY OF N,N,N'-TRISILYLATED BENZAMIDINES

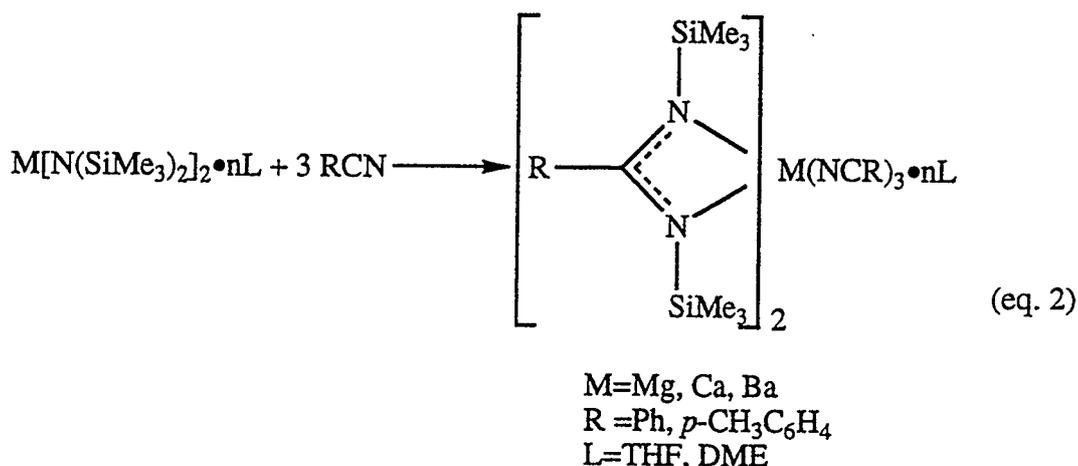
Clearly the possibilities of combining trisilylated benzamidines with main group compounds are plentiful, and as a result the corresponding chemistry is very diverse. Two outcomes are commonly encountered. The first involves coordination complexes with $[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]^\ominus$ anions acting as chelating ligands. Often these compounds can then react further to give the second alternative, the formation of inorganic heterocycles.

1.2.2.1

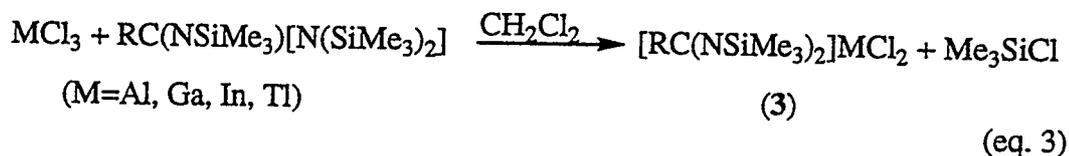
MAIN GROUP DERIVATIVES

INVOLVING THE BENZAMIDINATE ANION AS A CHELATING LIGAND

In discussing main group derivatives, it is recalled that alkali metal derivatives have already been mentioned (section 1.2.1). Also several alkaline earth metal derivatives have been reported for magnesium,⁹ and heavier alkaline earth metals.¹⁰⁻¹⁵ These are formed by using the general reaction (eq. 2).

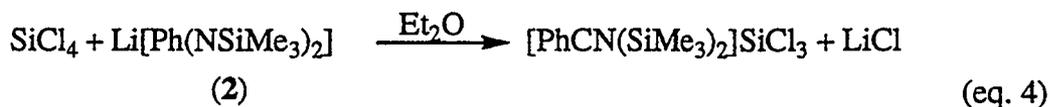


Treatment of the trichlorides of group 13 elements with trisilylated benzamidines in dichloromethane (eq. 3) leads to the monosubstituted products of general formula (3).

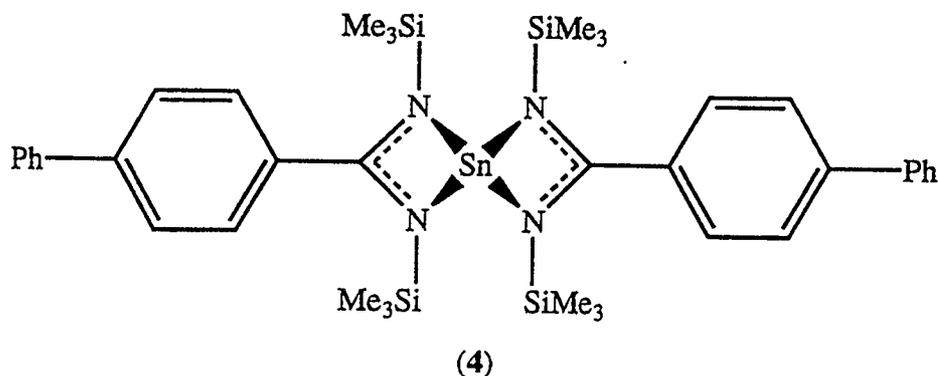


For group 14 elements, apart from the trisilylated benzamidines themselves, only one silicon derivative has been prepared. It was synthesised in an 87% yield by reacting SiCl₄ with Li[PhC(NSiMe₃)₂] in a 1:1 molar ratio (eq. 4). However, no additional

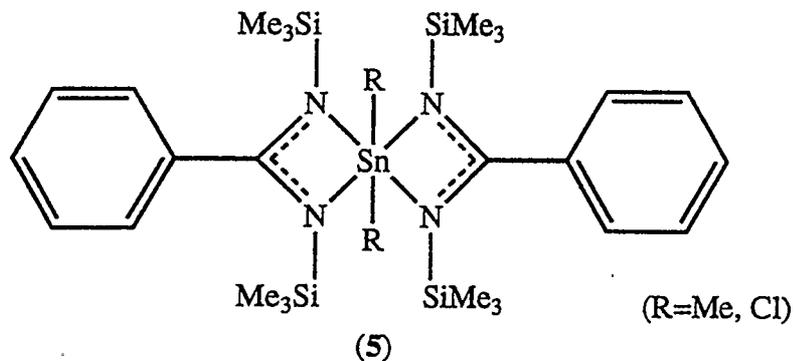
nitrogen coordination to the silicon centre could be achieved.¹⁶



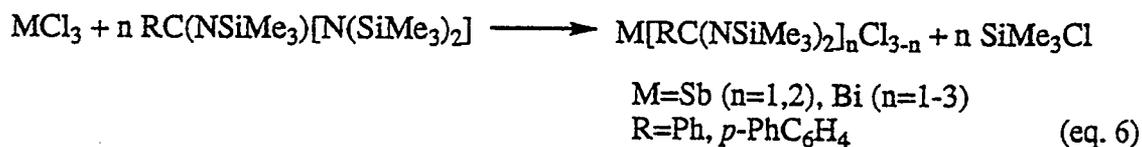
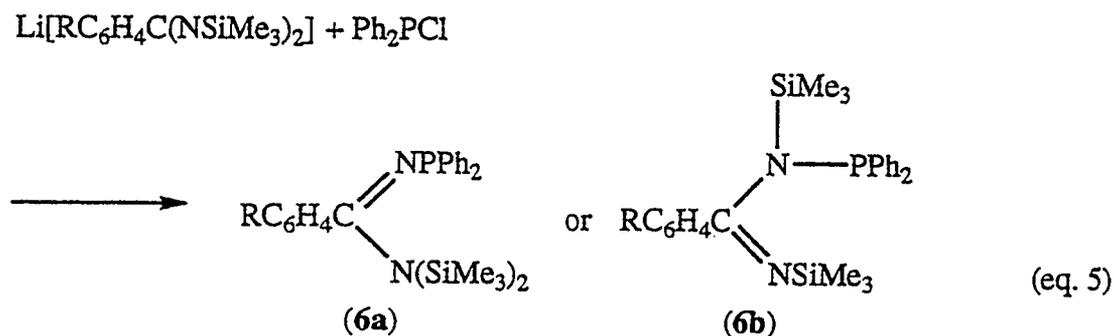
In contrast, tin has shown a vast array of coordination chemistry with the *N,N,N'*-tris(trimethylsilyl) substituted benzamidines. One reaction involved the preparation of a *bis*-substituted square-pyramidal tin(II) compound (4) from the reaction of SnCl_2 with two equivalents of a sodium salt of a trisilylated benzamidine.¹⁷



Analogous reactions of tin(IV) compounds such as SnCl_4 and Me_2SnCl_2 lead to the expected products (5).¹⁶ These complexes display a distorted octahedral coordination about the tin centre. Corresponding lead derivatives have been prepared in an analogous fashion.¹⁷

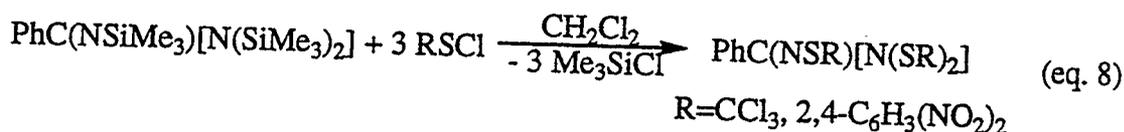
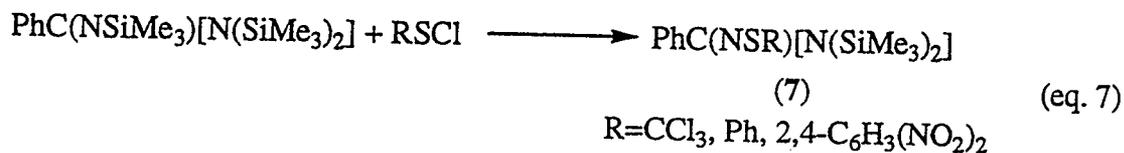


For group 15, several different halides have been reacted to produce various derivatives. In the case of phosphorus, the standard method used is the reaction of Ph_2PCl with a lithium salt of an $\text{N,N}'$ -disilylated benzamidinate (eq. 5). Two isomers are possible, (6a or 6b), but the true structure of these phosphinoamidines is not known since neither of these compounds have been structurally characterised.¹⁸⁻²¹ The 1:1 and 1:2 reactions of benzamidines with trichlorides of antimony and bismuth have been performed with the predicted results (eq. 6). Bismuth trichloride also reacts in a 1:3 fashion with a trisilylated benzamidine to give the only known main group homoleptic *tris*(benzamidine) complex.²²

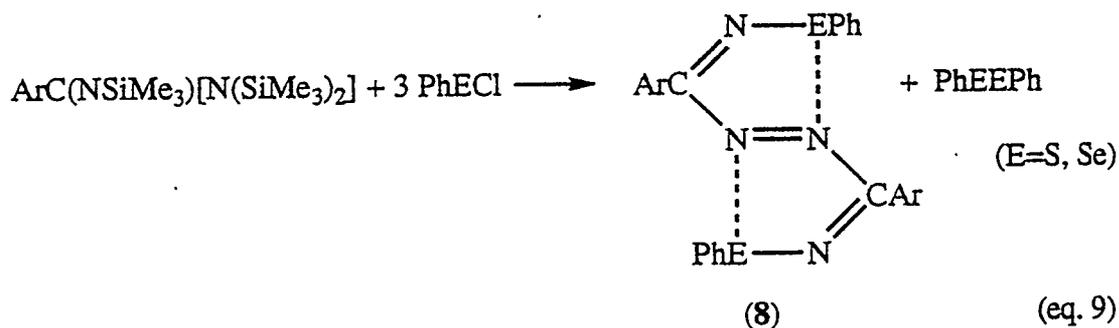


Important reactions have been observed for group 16 main group elements with benzamidines. Addition of one equivalent of benzenesulfonyl chloride leads to a monosubstituted benzamidine, (7), (eq. 7).²³ Further reaction with RSCl (three equivalents of reagent in total) has demonstrated the trisubstitution of a benzamidine for

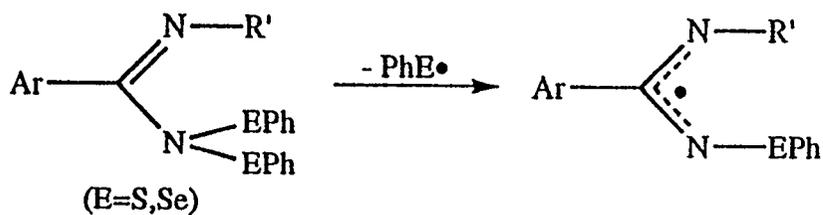
R = CCl₃ and 2,4-C₆H₃(NO₂)₂, leading to the successful isolation and characterisation of two trisubstituted products (eq. 8).²³



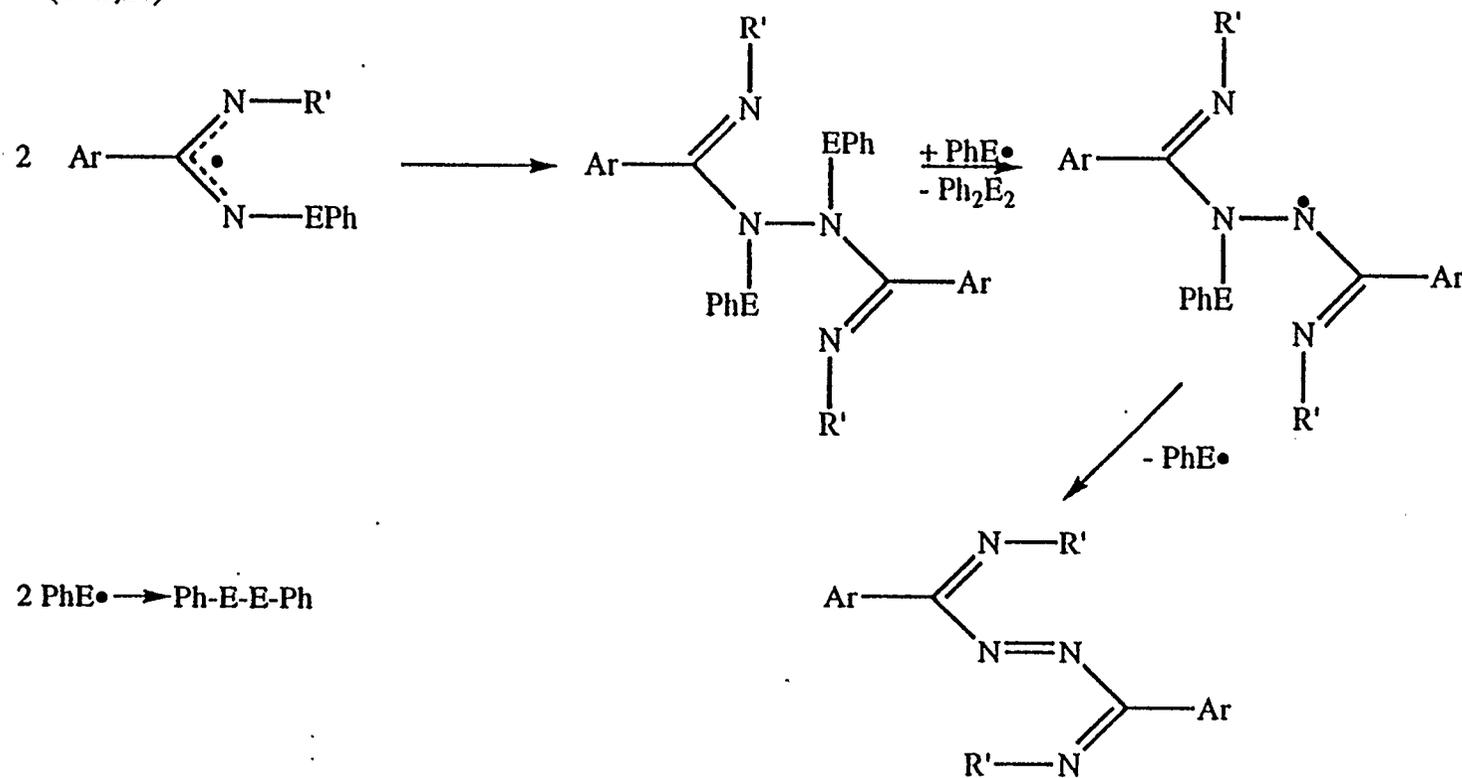
With three equivalents of PhSCl, the resulting trisubstituted product PhC(NSPh)[N(SPh)₂] eliminates diphenyl disulfide to give the diazene derivative PhSN(Ph)CN=NC(Ph)NSPh (8), (eq. 9). This decomposition is believed to occur via the following mechanism (*figure 1*).²⁴ The mechanism is supported by the detection of a radical species, possibly [PhCN₂(SPh)₂][•], (9), by ESR spectroscopy (*figure 2*).²³



Initiation:



Propagation:



Termination: $2 \text{ PhE}\cdot \longrightarrow \text{Ph}-\text{E}-\text{E}-\text{Ph}$

Figure 1: Proposed mechanism for the formation of a diazene from the addition of arylchalcogenyl halide to a trisilylated benzamidine

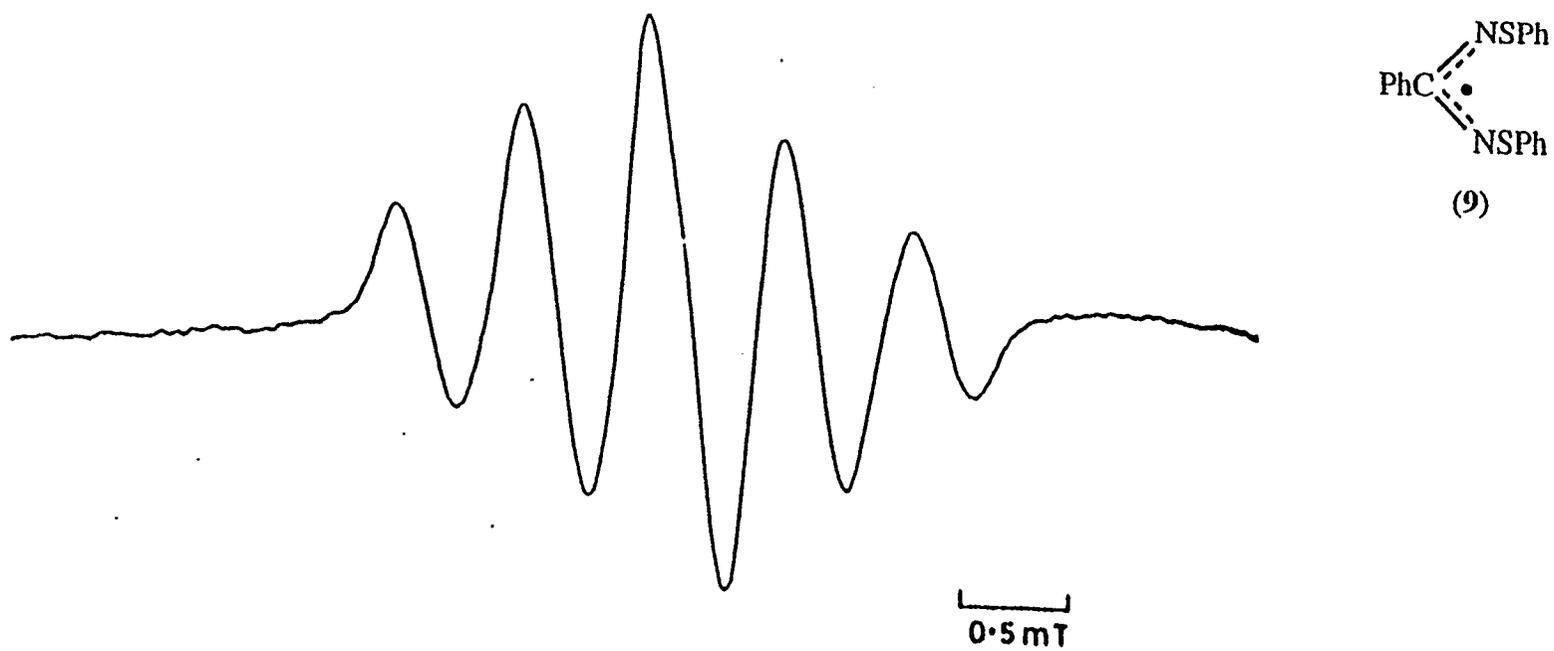


Figure 2: ESR spectrum of a 3:1 mixture of PhSiCl and $\text{PhC}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$ (9) is the proposed radical species observed

The formation of diazenes from benzamidines can also be accomplished by using three equivalents of PhSeCl. Reactions of the benzamidines with one equivalent of RSeCl₃ (R=Me, Ph) were performed as well. These reactions gave moderate yields (40-60%) of the corresponding diazenes.²⁵

The diazenes themselves are intensely coloured compounds ($\epsilon > 10^4$ L mol⁻¹cm⁻¹). Consequently, they have been referred to as 'azo dyes'.²⁵ The intense colour has been attributed to a $\pi \rightarrow \pi^*$ transition involving the Se(4p π)-N(2p π) HOMO interaction. The X-ray structure of a known selenium azo dye, has an essentially planar configuration, (*figure 3*). The individual five-membered rings Se(1)-N(1)-C(1)-N(3)-N(4) and Se(2)-N(2)-C(2)-N(3)-N(4) are planar to within 0.075(4) and 0.028(4) Å, respectively. The intramolecular Se-N contacts (*i.e.* Se(2)-N(3) and Se(1)-N(4)) are approximately 2.65 Å. This is well within the sum of the Van der Waals radii (3.5 Å) for selenium and nitrogen suggesting an appreciable Se-N interaction.²⁶ It is believed that the corresponding sulfur-nitrogen distances in analogous sulfur azo dyes are also less than the sum of the Van der Waals radii; but no sulfur azo-dye has been characterised by X-ray diffraction methods.

Other group 16 compounds of benzamidines have also been prepared. The derivatives [PhC(NSiMe₃)₂]SeCl₃ and [PhC(NSiMe₃)₂]SeOCl have been made by reacting (1) in a 1:1 molar ratio with SeCl₄ or SeOCl₂, respectively.²⁷ An analogous reaction with TeCl₄ has given the only structurally characterised tellurium benzamidinate [PhC(NSiMe₃)₂]TeCl₃.²⁸

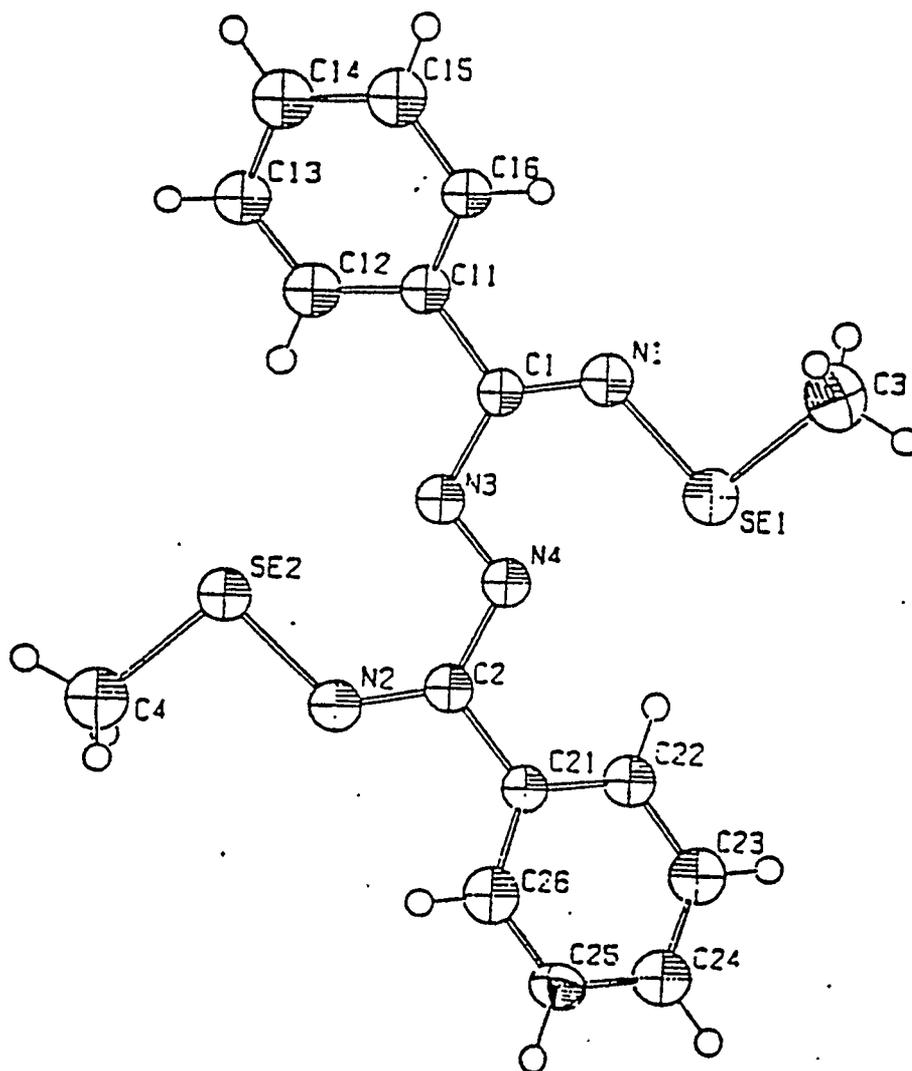
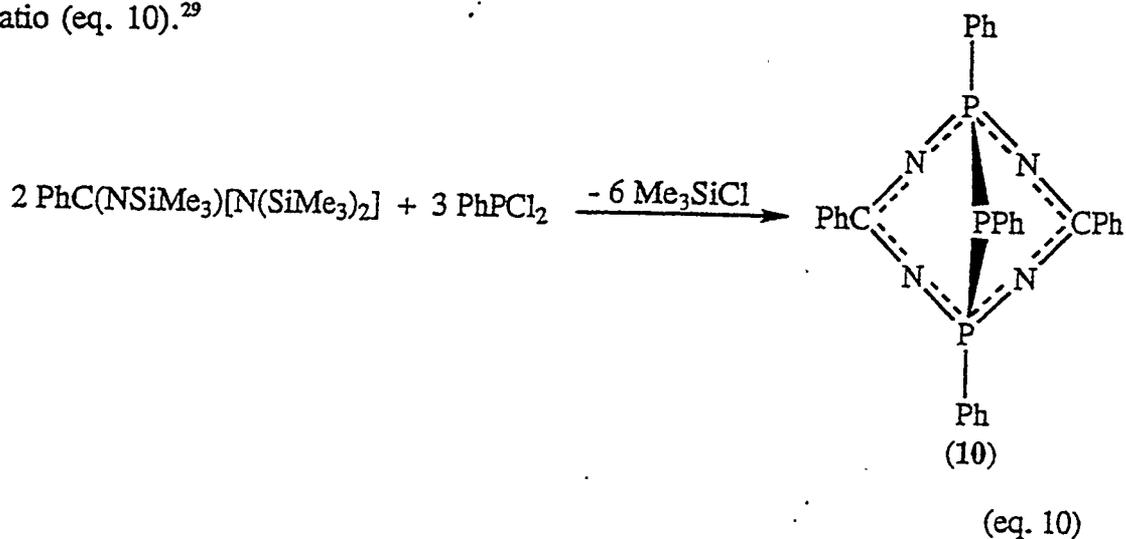


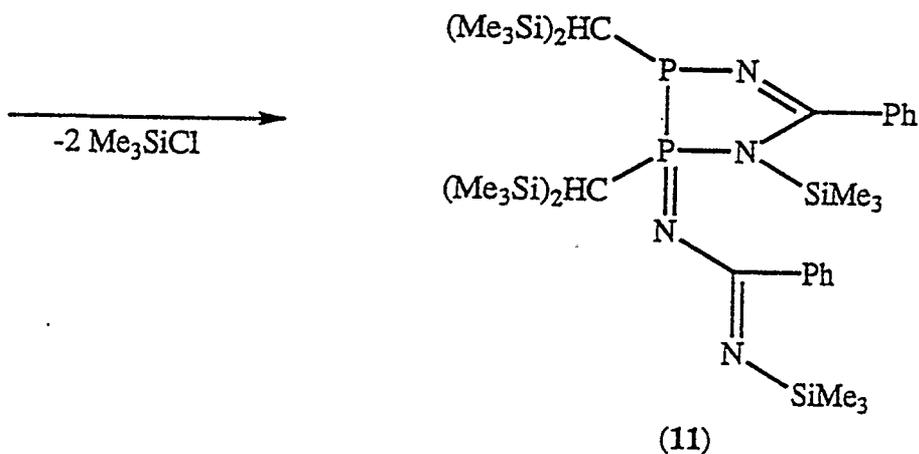
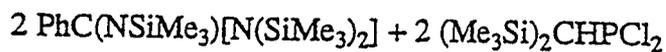
Figure 3: ORTEP of MeSeN(Ph)CN=NC(Ph)NSeMe²⁵

1.2.2.2 MAIN GROUP ELEMENT CHEMISTRY INVOLVING
N,N,N'-TRISILYLATED BENZAMIDINES

Phosphorus-containing heterocycles of benzamidines have been prepared by varying the proportions of RPhCl_2 in reactions with N,N,N'-trisilylated benzamidines. In 1988 the reaction of a trisilylated benzamidine with PhPCL_2 was described for a 2:3 molar ratio (eq. 10).²⁹

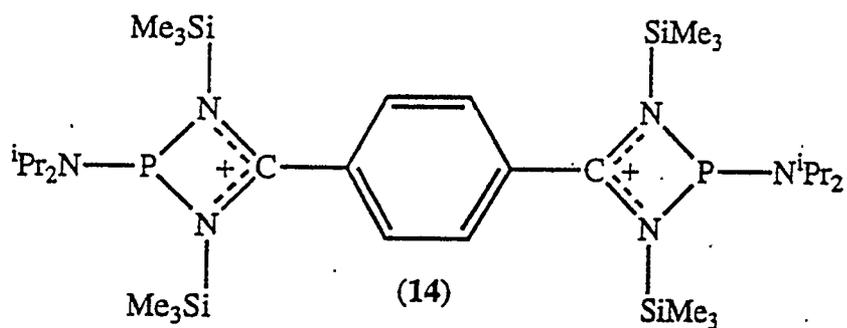
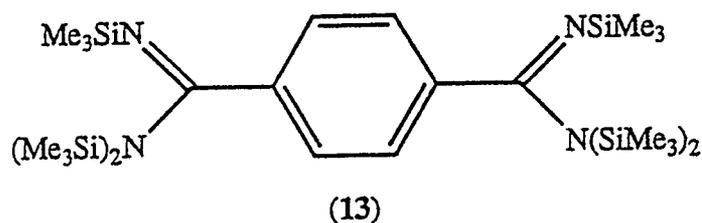
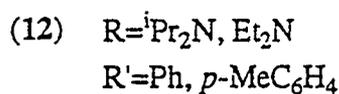
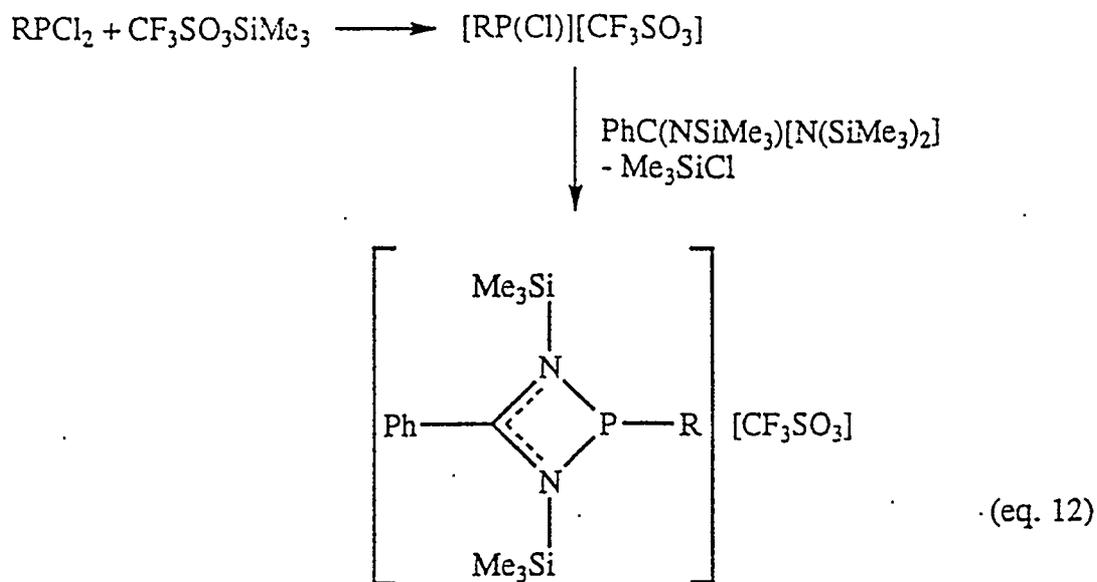


Another phosphorus-containing heterocyclic system was produced when the trisilylated benzamidine was reacted with $(\text{Me}_3\text{Si})_2\text{CHPCl}_2$ (eq. 11).³⁰ Unexpectedly, the 1,4-diaza-2 $\sigma^3\lambda^3$,3 $\sigma^4\lambda^5$ -diphospholene derivative (11) was obtained. Clearly this synthesis is very complex and, although a plausible mechanism has been proposed, no intermediates have been isolated or detected.



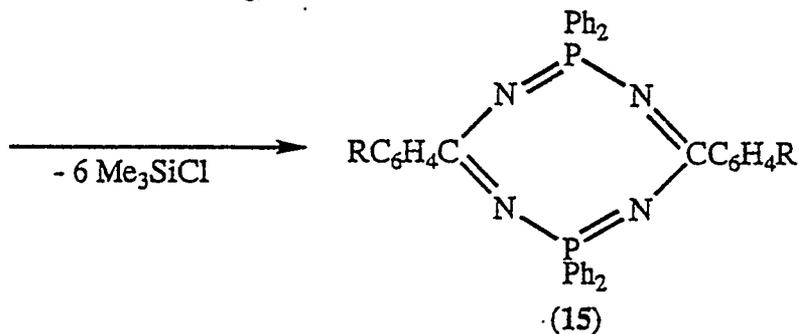
(eq. 11)

A third example of a phosphorus-based heterocycle involves the phosphetene cations (12), (eq. 12), which are observed to be planar four-membered rings. They contain equal C-N bonds that are significantly shorter than a typical carbon-nitrogen single bond. Interestingly, the N-P-N angle in the ring (73.2°) is the smallest angle found in a four-membered heterocycle containing phosphorus. A similar type of reaction was used with a *bis*(trisilylated)benzamidine derivative (13) to give a dicationic *bis*(phosphetene) species (14).¹⁹

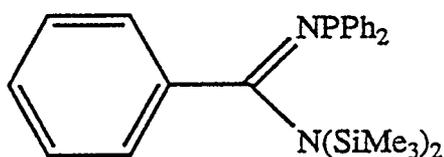


Six- and eight-membered C-N-P heterocycles have been synthesised from the reactions of benzamidines with Ph_2PCl_3 (eq. 13).²⁰ The eight-membered ring is obtained in a relatively low yield (<30%). An alternate synthesis using $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ provides a 31% yield of the eight-membered ring (15) and also a six-membered ring (16)

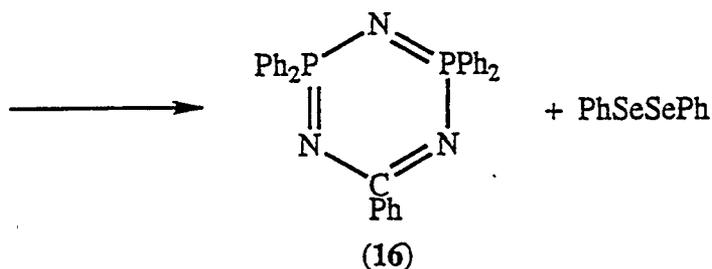
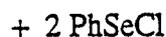
as a minor by-product. This six-membered ring can also be made by the reaction of **6a** (R=H) with two molar equivalents of PhSeCl (eq. 14).



(eq. 13)



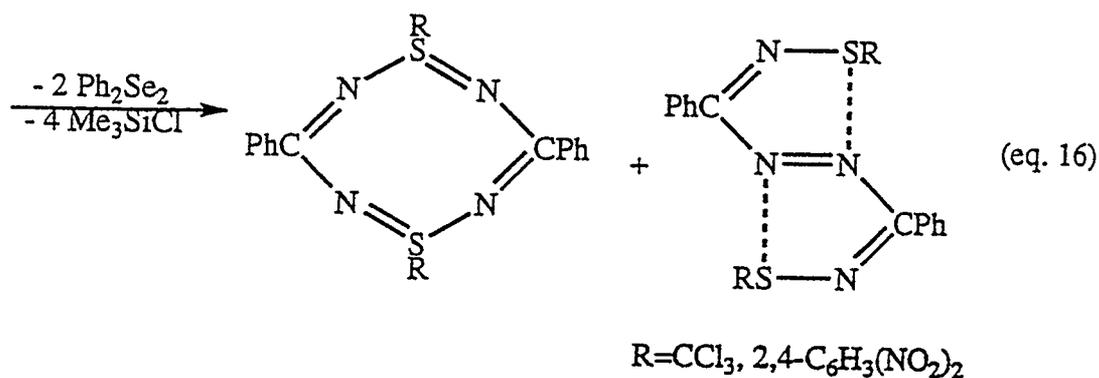
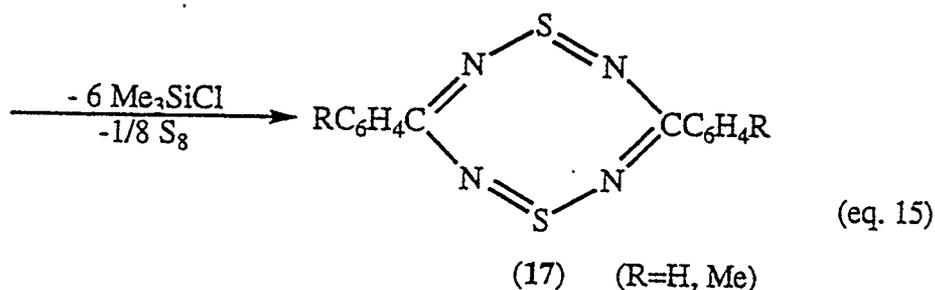
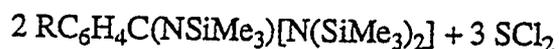
(6a, R=H)



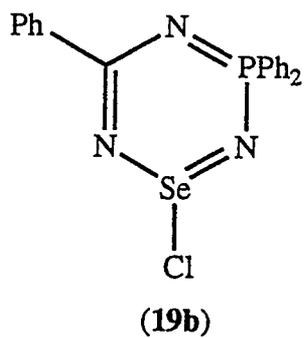
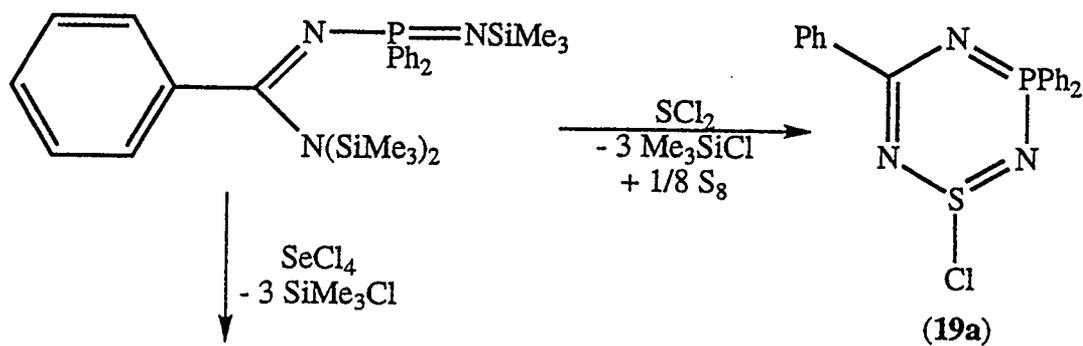
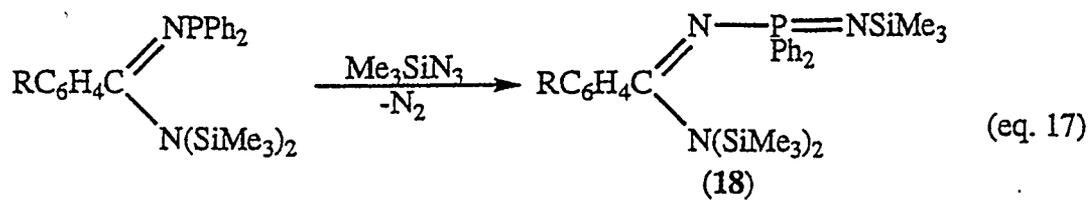
(eq. 14)

The reactions of benzamidines and phosphinated benzamidines with sulfur dichloride have also produced novel inorganic heterocycles. The eight-membered ring (17) was first made in 1981 by the reaction of a trisilylated benzamidine with sulfur dichloride (eq. 15).³¹ This eight-membered ring, which was shown to be planar, possesses a 10π -electron system isoelectronic with the $\text{S}_4\text{N}_4^{2+}$ cation. Low yield syntheses of other eight-membered rings have resulted from the reaction of certain

monochalcogenated benzamidines with benzeneselenenyl chloride in a 1:2 molar ratio (eq. 16).²³ Whereas the S-phenyl derivative leads to the formation of the diazene (8, see section 1.2.2.1), when R=CCl₃ or 2,4-(NO₂)₂C₆H₃, eight-membered rings are obtained in low yield, in addition to the isomeric diazenes.

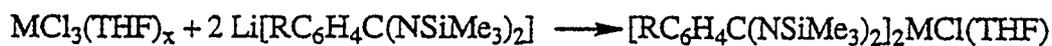


Amidinophosphazenes (18) are another class of phosphorus-based derivatives of N,N,N'-trisilylated benzamidines. They can be formed by reacting trimethylsilyl azide with a phosphinoamidine (6), (eq. 17). The amidinophosphazenes also react with SCl₂ or SeCl₄ (eq. 18) to give interesting six-membered heterocycles (19a and 19b). Both of these rings systems can be made in high yields (> 80%).³²

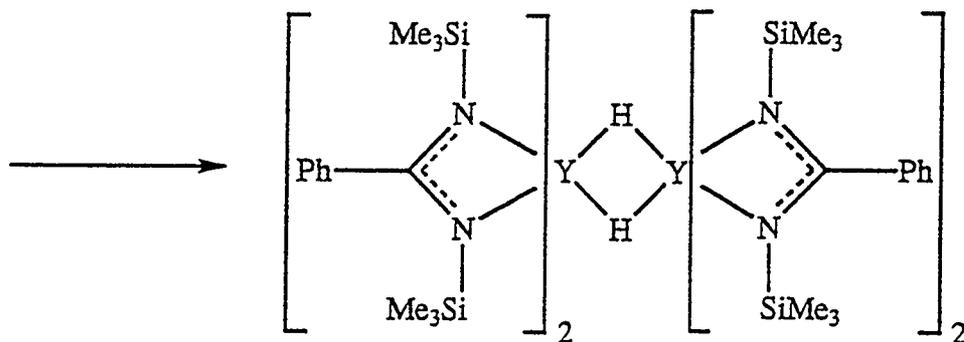
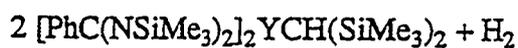
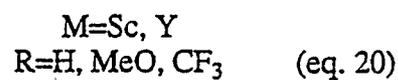


(eq. 18)

controlled reaction (eq. 21) with a one-half molar equivalent of hydrogen gives the dimeric yttrium hydride (21).^{34,35} The reaction with two equivalents of acetylene gives a related bridged dimer (eq. 22).

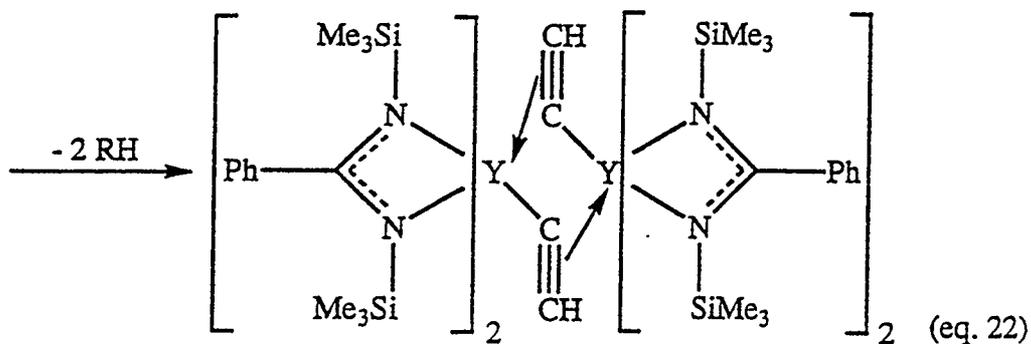
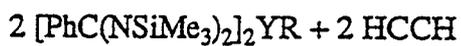


(20)



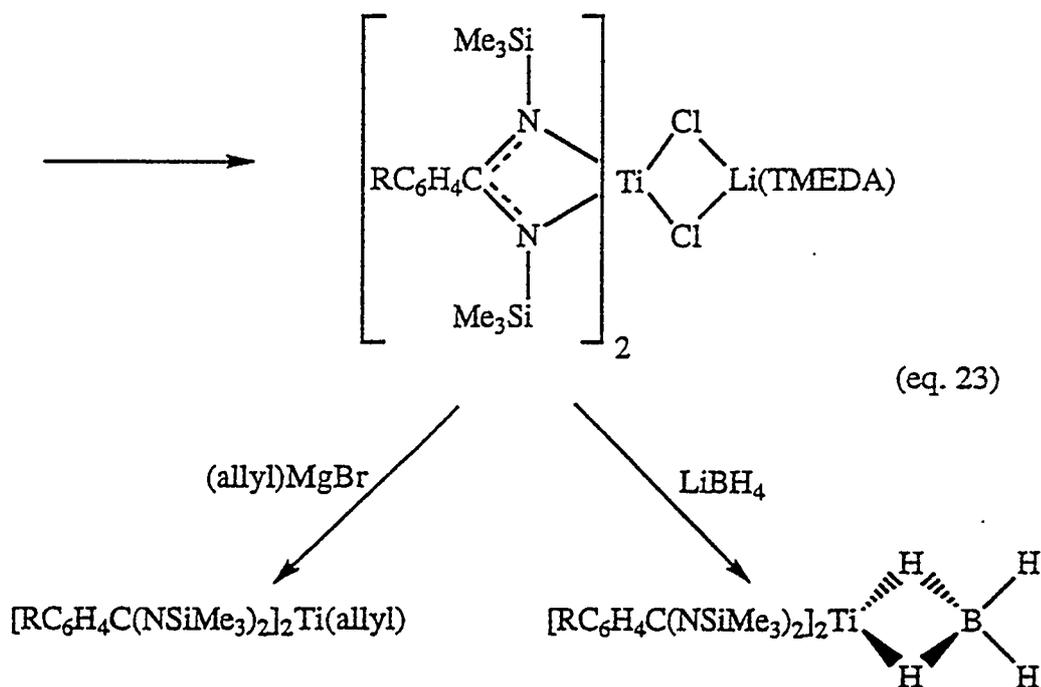
(21)

(eq. 21)

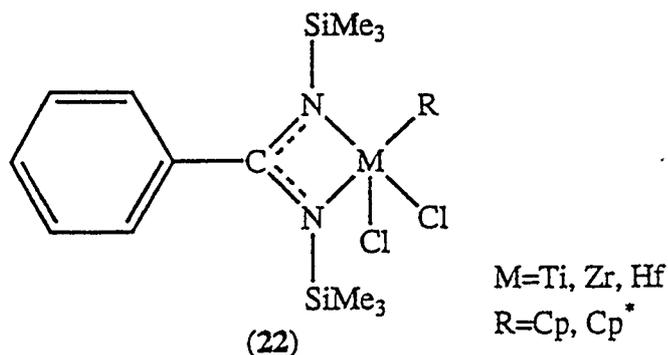


(eq. 22)

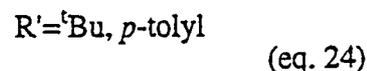
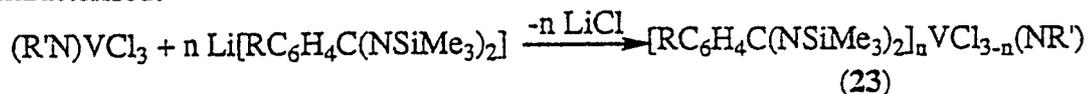
For Group 4 metals, much of the work focuses on adducts of titanium and zirconium. Chelation of the benzamidinate anion can be achieved by the reaction of either $\text{TiCl}_3(\text{THF})_3$ or $\text{TiCl}_2(\text{TMEDA})_2$ with one equivalent of trisilylated benzamidinate or lithiated benzamidinate (2), in the appropriate solvent. These titanium complexes can then react readily with species such as LiBH_4 or Grignard reagents to replace the chloride ion with BH_4^\ominus or allyl groups (eq. 23).³⁸



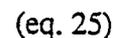
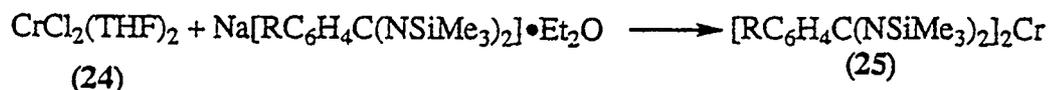
Simple half-sandwich complexes of all Group 4 transition metals, (22),^{22,39} have also been prepared by reacting $(\text{C}_3\text{R}_5)\text{MCl}_3$ ($\text{R} = \text{H}, \text{Me}$) with $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ in a 1:1 fashion. The remaining halide ligands can be replaced by strong nucleophiles such as alkyllithiums or Grignard reagents, giving rise to organometallic benzamidinates.⁴⁰



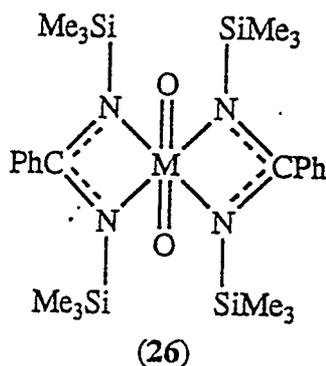
Benzamidinate derivatives of the Group 5 metals have also been prepared. Many vanadium benzamidinate complexes (23) are derived from imido vanadium (V) compounds (eq. 24). These compounds, once formed, undergo substitution reactions with lithium alkoxides.⁴¹ Preliminary studies of the products $[\text{PhC}(\text{NSiMe}_3)_2]\text{MCl}_4$ (M = Nb, Ta) have been reported, but these derivatives are not as yet fully characterised.²⁷



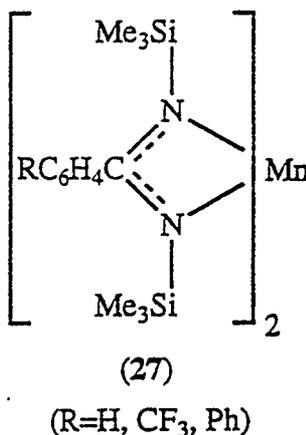
For Group 6 transition metals, several benzamidinate derivatives are well known. In the case of chromium, an interesting square planar four-coordinate complex has been made (25) from the reagent $\text{CrCl}_2(\text{THF})_2$ (eq. 25). This chromium (II) complex is unlike typical transition metal chelated complexes of benzamidinates as it does not adopt an octahedral configuration employing additional THF ligands.²² It is suggested that the coordination sphere about the chromium atom is extremely small and, as a result, occupation of octahedral sites by solvent molecules is not observed. However, preliminary reactions of this complex with "slim" ligands, such as acetonitrile, or carbon monoxide have been described.



Bicyclic compounds of molybdenum and tungsten can be made via the reaction of MO_2Cl_2 ($\text{M} = \text{Mo}, \text{W}$) with $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ in a 1:2 manner. This reaction leads to the formation of $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{MO}_2$, (26).¹⁶

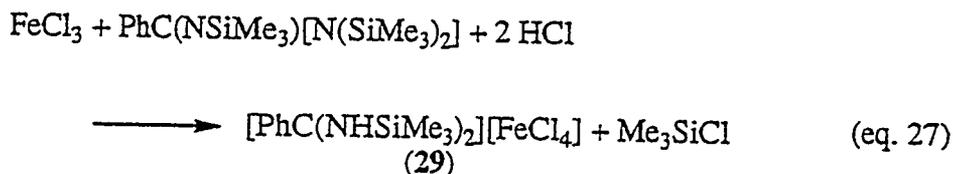
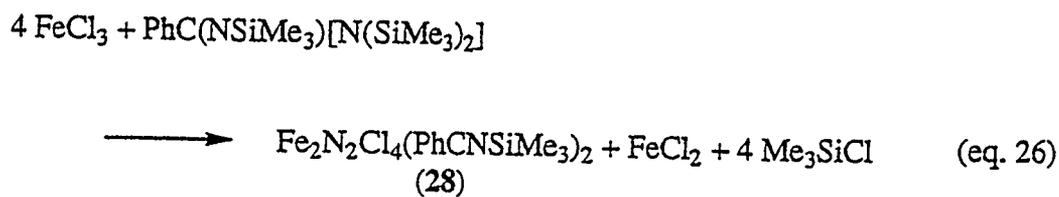


For Group 7, a few manganese benzamidates (27) have been made from $\text{MnCl}_2(\text{THF})_2$.²² No complexes of technetium or rhenium have been reported.

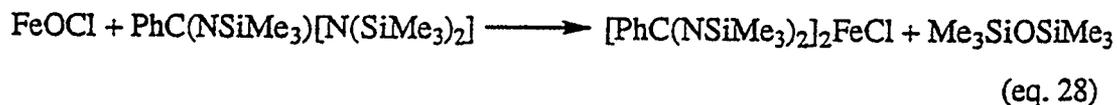


Of the Group 8 and 9 metals, *N,N'*-bis(trimethylsilyl) benzamidinate complexes are known only for iron.² However, the complexation chemistry for iron with these benzamidates is very intriguing. Instead of the expected chelated iron complex (analogous to several other transition metal systems), FeCl_3 gives a dimeric product (28) upon reaction with a silylated benzamidine (eq. 26) in CH_2Cl_2 or CCl_4 .^{42,43} If THF is

present, however, the same reaction also produces an iron-containing side-product, $[\text{PhC}(\text{NHSiMe}_3)_2][\text{FeCl}_4]^\ominus$ (29). It is suggested that the product (28) reacts with HCl, which is formed from a reaction of FeCl_3 with the solvent THF. The formation of (29) is thus shown (eq. 27) and as a result, this reaction leads to two unexpected species instead of the expected chelated product.

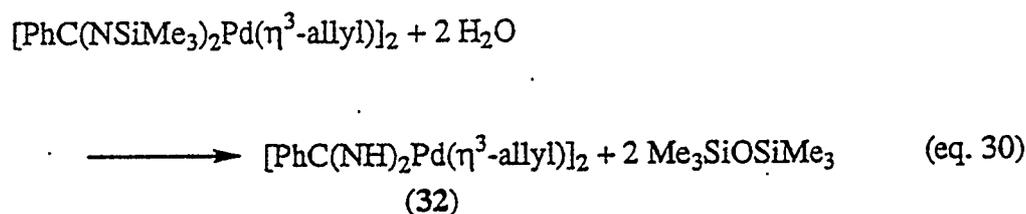
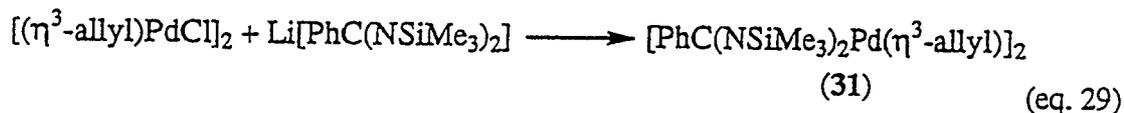
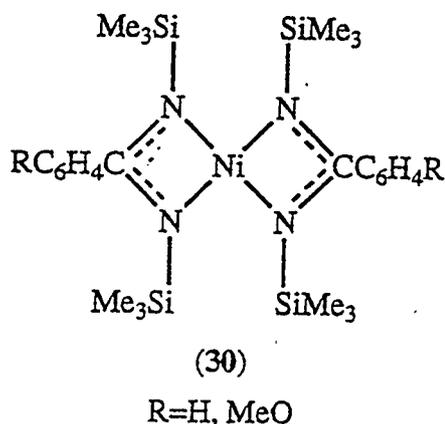


Another chelated iron benzamidinate was synthesised by reacting one equivalent of FeOCl with two equivalents of trisilylated benzamidine in $\text{CH}_3\text{CN}/\text{THF}$ to give an extremely high yield (96%) of dark red moisture-sensitive crystals. Interestingly, the oxygen from the FeOCl was not found in the final product. It is proposed that the oxygen was evolved as *bis*(trimethyl)siloxane in the following reaction (eq. 28).⁴⁴

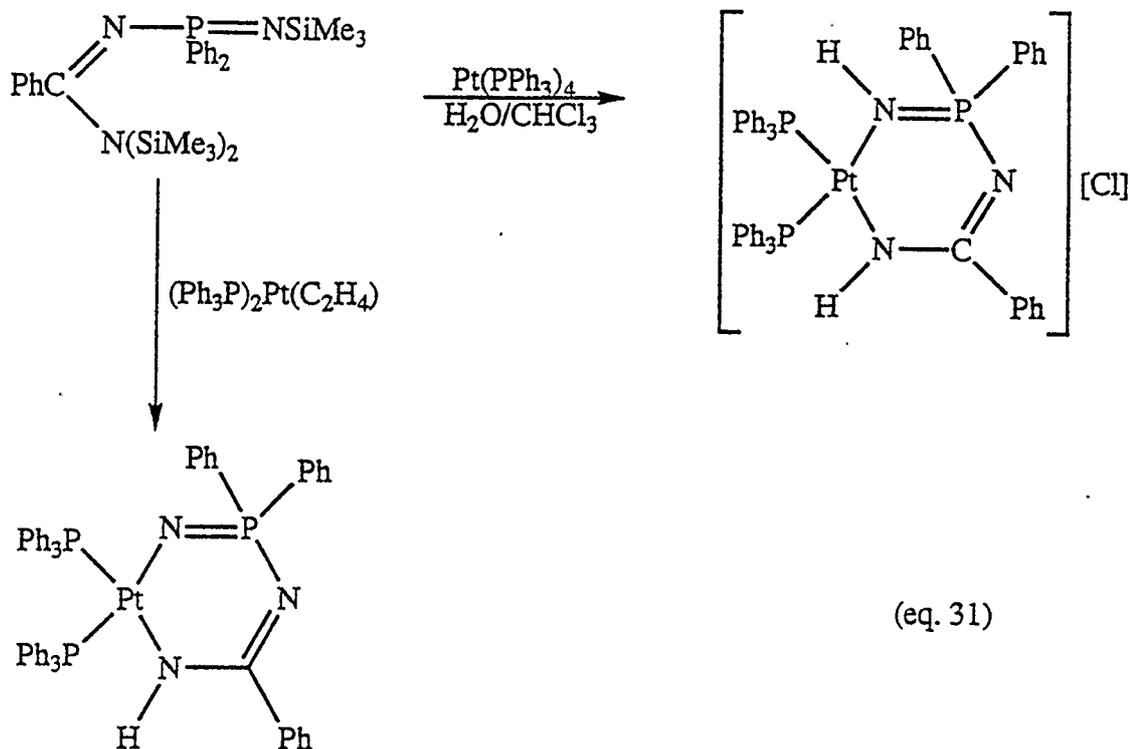


Complexes of Group 10 metals have been established as well. Most recently, Ni(II) derivatives have been made (30),^{45,46} and have been found to react readily with small molecules such as CO and CH_3CN . For palladium, benzamidinated species are readily prepared by conventional methods. However, the benzamidinate ligand tends to

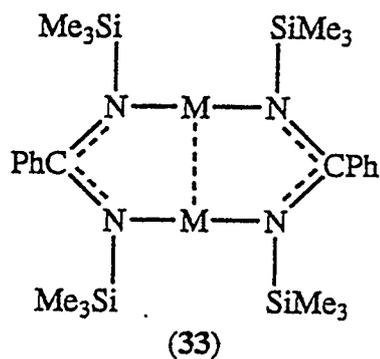
cause dimerisation for the larger metals (eq. 29). The palladium dimer (31) easily undergoes hydrolysis (eq. 30) to give the unique product (32). This is unusual, because previous attempts at hydrolysis resulted in cationic benzamidinium species (e.g. $[\text{PhC}(\text{NHSiMe}_3)_2]^{\oplus}$ and $[\text{PhC}(\text{NH}_2)_2]^{\oplus 2}$) as opposed to metal complexes containing an anionic species.



Although no specific benzamidinate-chelated complexes of platinum are known, two metallacycles involving platinum have been prepared from amidinophosphazenes (eq. 31).⁴⁷ A similar approach has been used to form other platinum and rhodium complexes.²¹

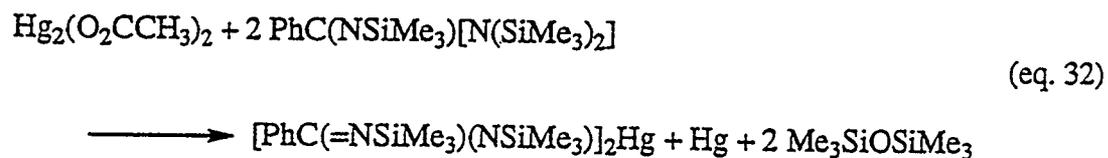


For Group 11 metals, novel binuclear benzamidine-bridged compounds have been made for copper, silver and gold (33).^{48,49} These complexes have close metal-metal distances suggesting weak interactions. Simple gold adducts, made from the reaction of $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ with AuCl_3 , (*e.g.* $[\text{PhC}(\text{NSiMe}_3)_2]\text{AuCl}_2$), are also known.⁵⁰



$M = \text{Cu, Ag, Au}$

For the remaining transition metals of Group 12, only one zinc benzamidinate is completely characterised. This complex is $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zn}$,²² formed by reacting two equivalents of $\text{Na}[\text{PhC}(\text{NSiMe}_3)_2] \cdot 0.5 \text{Et}_2\text{O}$ with ZnCl_2 in THF. For mercury, no similar analogue is known, however a unique monodentate *N,N'*-bis(trimethylsilyl) benzamidinated Hg(II) complex was prepared (eq. 32).⁵¹



1.2.4

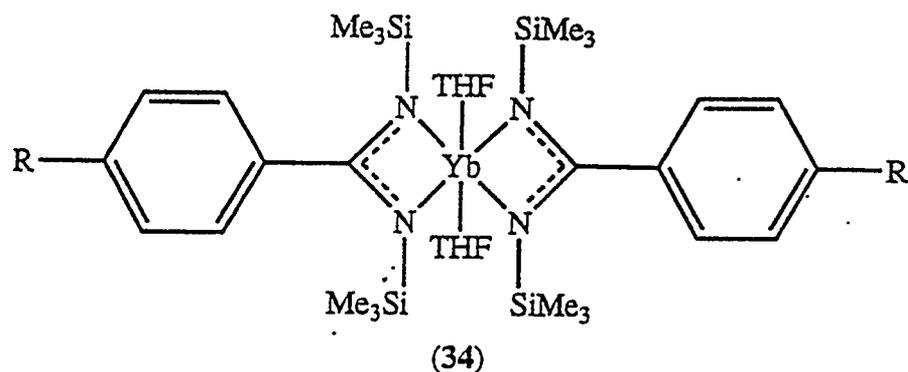
LANTHANIDE AND ACTINIDE

CHEMISTRY OF N,N,N'-TRISILYLATED BENZAMIDINES

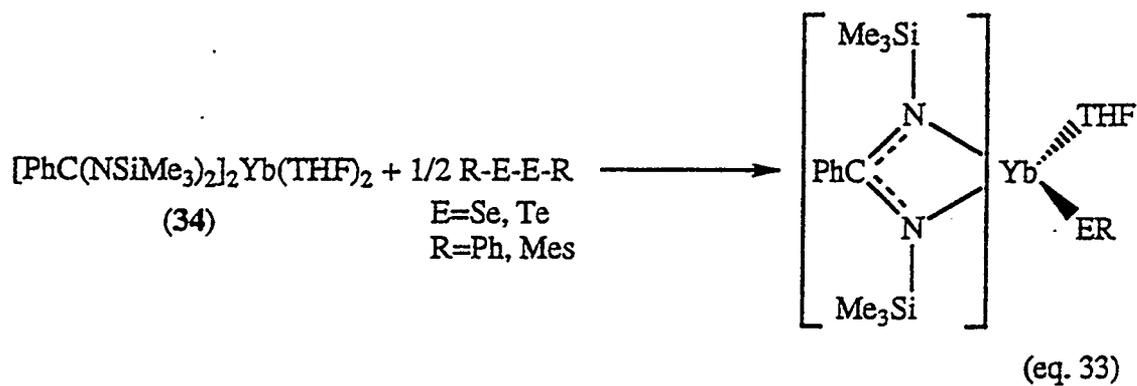
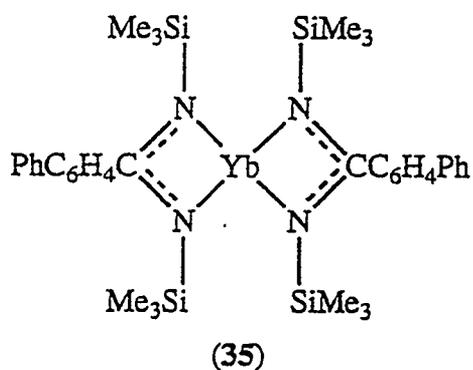
Given the improved availability of simple lanthanide and actinide starting materials in recent years, research in many branches of chemistry has become more involved with these elements. Lanthanides and actinides are generally considered to be very oxophilic and hygroscopic. Ligand systems such as the benzamidates $[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]^\ominus$ and the phosphamidates $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]^\ominus$ have been investigated extensively with these elements. These bulky ligands tend to act as bidentate or tridentate ligands with lanthanide and actinides atoms, leading to sterically saturated N,N'-disubstituted and trisubstituted coordination compounds.² Most lanthanides rely on this octahedral coordination for stabilisation. As mentioned in section 1.2.3 the steric bulk of the benzamidate ligand is roughly analogous to that of a cyclopentadienyl ligand. Not only are the ligands approximately the same bulk and shape, but they also form similar adducts with several metals.

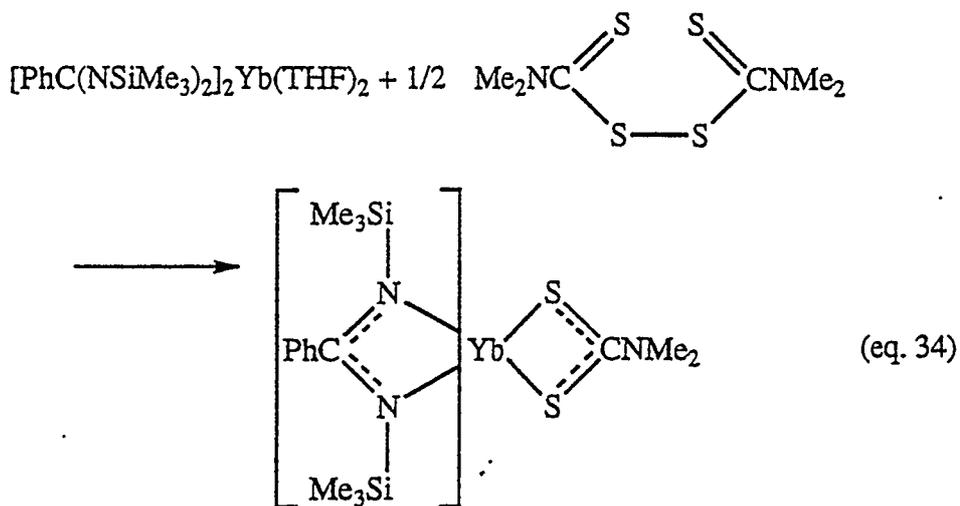
Ytterbium complexes (34) are readily prepared by treating YbI_2 with two equivalents of $\text{Na}[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]$ in THF. These dark red complexes are highly soluble, even in non-polar solvents such as hexane. As expected, they are extremely air- and moisture-sensitive. A similar complex $[\text{PhC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]_2\text{Yb}$, (35), was isolated and shown to be a rare example of tetracoordination about ytterbium. Certain ytterbium complexes can reductively cleave diaryl diselenides and/or ditellurides (eq. 33). These reactions lead to stable Yb(III) complexes with Yb-E bonds.^{52,53} A similar reaction

with thiuram disulfide leads to the formation of a dithiocarbamate ytterbium heterocycle (eq. 34).⁵³ Again, the benzamidinate ligands coordinate to the ytterbium centre in an octahedral fashion.

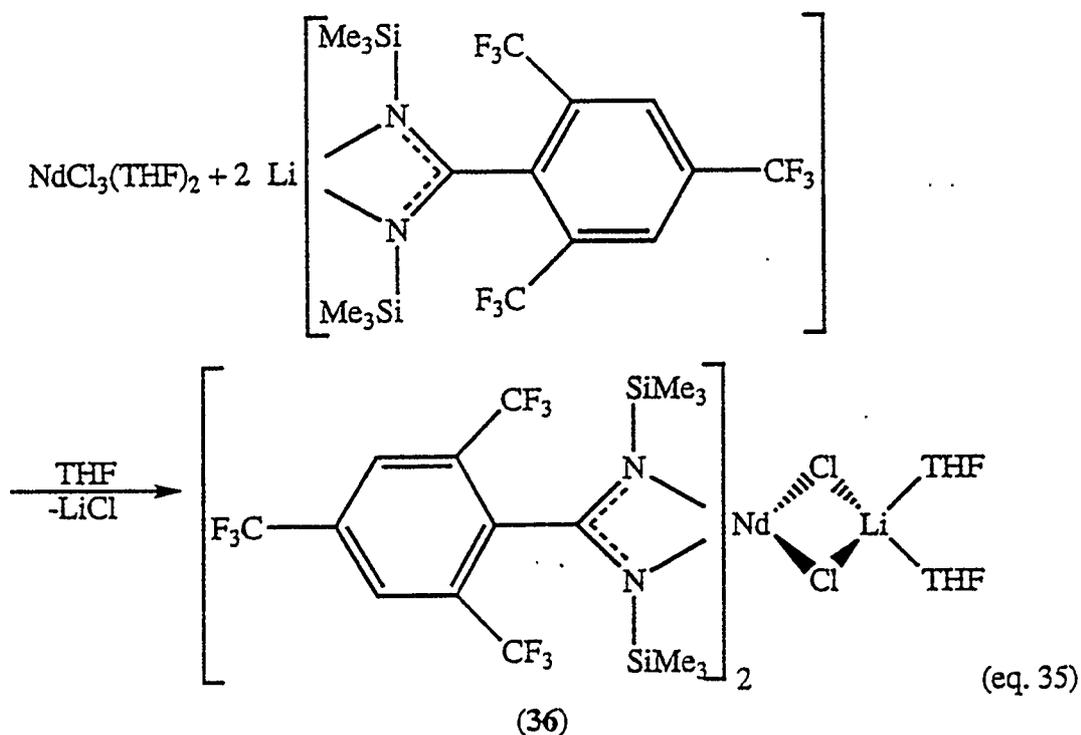


R=H, MeO

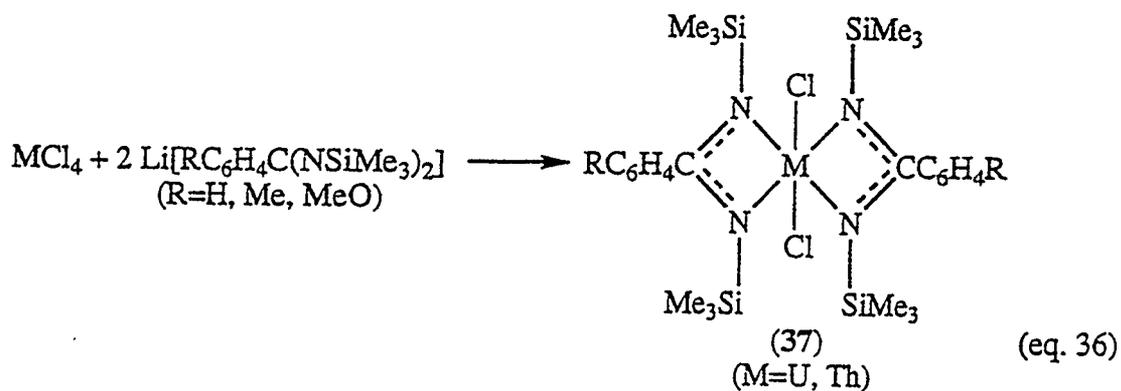




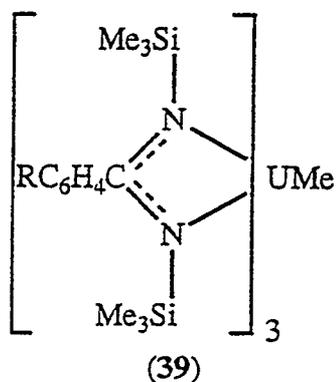
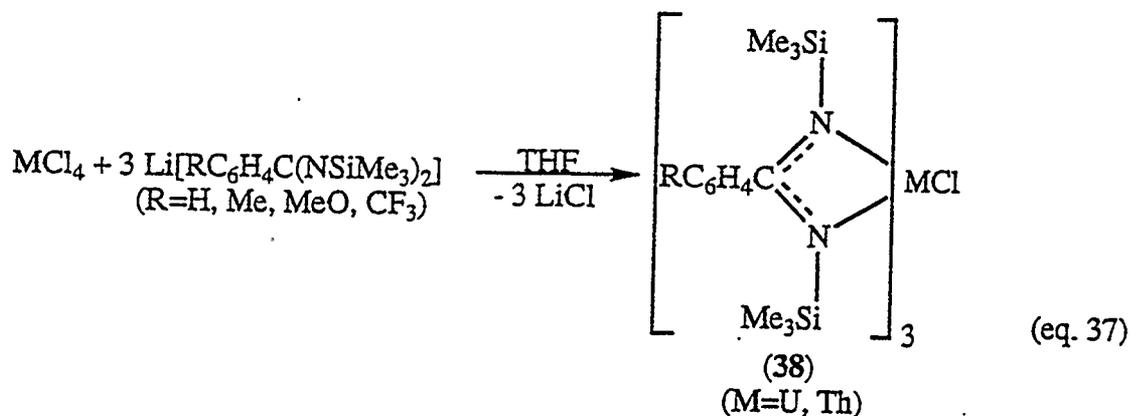
An important goal in the development of lanthanide-based catalysts is the preparation of disubstituted products which have coordinatively unsaturated metal centres.^{54,55} *Tris*(benzamidinated) lanthanides are very useful synthons, but are not particularly good catalysts. The recent synthesis of (36) was accomplished.⁵⁶ It is an analogue of $(\text{C}_5\text{Me}_5)_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$, a reagent useful as a starting material for various organoneodymium homogeneous catalysts.⁵⁷⁻⁵⁹



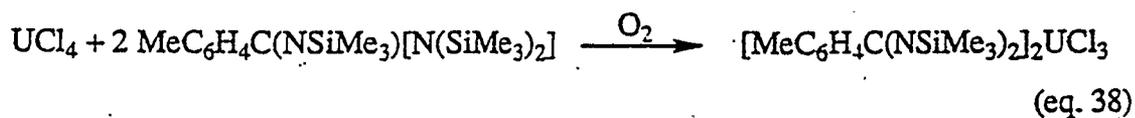
Of the actinides, uranium has been the most investigated metal for benzamidine reactions. Again, these reactions mostly result in the formation of chelates via the reaction of a trisilylated benzamidine with the actinide halide in an appropriate ratio. One of the foremost classes of such compounds are the uranium *bis*(benzamidinate)s, (37). These are prepared via the addition of two molar equivalents of a trisilylated benzamidine (or benzamidinate anion) to UCl_4 (eq. 36).^{7,60} The thorium derivative was prepared in an analogous manner by using ThCl_4 .



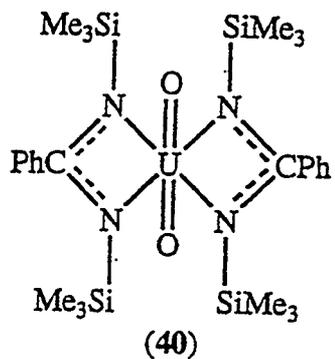
The reaction of UCl_4 with three equivalents of benzamidinate gives the trisubstituted derivative (38), (eq. 37).^{7,60} These compounds are green crystalline solids that are air- and moisture-sensitive. They are also highly thermally stable, and very soluble, even in non-polar solvents. These trisubstituted uranium (IV) complexes are actually seven-coordinated with a capped-octahedral geometry. The Th(IV) analogue has also been made. These uranium(IV) monohalide complexes can then react readily with reagents such as MeLi or NaBH_4 resulting in halide substitution *e.g.* (39).⁶¹



Two benzamidinate complexes are known for higher oxidation states of uranium. An interesting derivative of uranium(V) was made by reacting two equivalents of benzamidine with UCl_4 ; followed by air-oxidation of the reaction mixture (eq. 38). This compound is the first known substitution product of UCl_5 , and the X-ray diffraction study shows the geometry about the uranium to be a distorted pentagonal bipyramid.⁶²



The other known complex is a uranium(VI) derivative (40), which was prepared by the reaction of uranyl chloride (UO_2Cl_2) with the sodium salt of a benzamidinate. Compound (40) is structurally analogous to the octahedral Group 6 complexes (26).



The future of trisilylated benzamidinate chemistry will most likely involve the preparation of many lanthanide and actinide derivatives, for both synthetic and catalytic purposes.

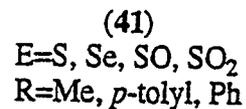
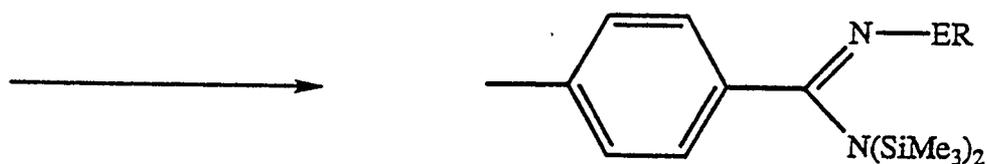
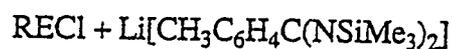
1.3

THESIS OBJECTIVES

The inorganic chemistry of N,N,N' -trisubstituted benzamidines is a rapidly growing area in main group chemistry. There are two separate, but related, objectives to the work described in this thesis. The first concerns the preparation of monosubstituted benzamidines such as (41). These monosubstituted benzamidines may serve as precursors to hybrid inorganic polymers. However, the generation of such polymers is not the goal of this thesis. The primary objective will be to use these derivatives to generate novel chalcogen-substituted diazenes as described in section 1.3.1. The possible synthesis of hybrid (CNSN) inorganic polymers and other related compounds will be discussed in chapter 4.



or



(eq. 39)

1.3.1

PREPARATION OF
CHALCOGEN-SUBSTITUTED DIAZENES

The formation of diazenes (section 1.2.2.1) is initiated by the addition of two equivalents of PhECl to a monosubstituted benzamidine. Previous examples of diazenes (8) have involved E=S, Se. A methyl-selenium species has also been prepared (figure 3).^{25,26} Whereas sulfenylated diazenes have been known for some time,²³ chalcogen derivatives with sulfur (or selenium) in a higher oxidation state than II have not been thoroughly investigated. It is hoped that the synthesis and structural characterisation of chalcogen-substituted diazenes (REN(Ar)CN=NC(Ar)NER) involving sulfonyl (E=SO₂), sulfinyl (E=SO) and sulfenyl (E=S) substituents can be completed. The sulfonylated (S^{VI}) derivative MeSO₂N(4-CH₃C₆H₄)CN=NC(C₆H₄CH₃-4)NSO₂Me has been prepared but not fully characterised.⁶³ Of the chalcogen-substituted diazenes known, only the methyl-selenium diazene has been structurally characterised (figure 3). It is of interest to determine if sulfenylated diazenes have a similar structure to the selenium(II) system, and to observe how the structures and properties of these compounds are changed upon proceeding from E=S, via SO, to SO₂.

Monosubstituted precursors *e.g.* (ArC(NER)[N(SiMe₃)₂]) to these diazenes are extremely air- and moisture-sensitive, and will usually be handled *in situ*. However, the full characterisation of these precursors is desirable, given their potential use as starting materials for hybrid inorganic polymers, as described in chapter 4.

CHAPTER TWO

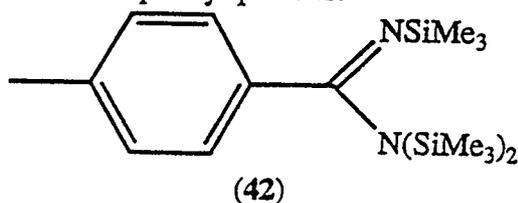
PREPARATION, CHARACTERISATION AND X-RAY STRUCTURE
OF A SULFONYLATED DIAZENE

2.1

INTRODUCTION

As outlined in section 1.3, the primary objective of this thesis is the preparation and characterisation of new diazenes. Preliminary investigations had been carried out on the sulfonylated diazene, $\text{MeSO}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{NSO}_2\text{Me}$.⁶³ The first part of the project was to complete the characterisation of this product in order to compare the structure to the known selenium(II) diazene (*figure 3*). Also desirable was the comparison of the properties of a sulfur(VI)-substituted diazene with those of the known sulfur(II) diazene.^{23,25}

The reagent $4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$, (42), was prepared from $4\text{-CH}_3\text{C}_6\text{H}_4\text{CN}$ by the synthesis developed by Oakley *et al.*,⁵ and it was used as the benzamidine in these preparations. This derivative was chosen on the basis of its straightforward production, as well as the distinctive ¹H-NMR signals for the *p*-tolyl methyl group and the aromatic *p*-tolyl protons.



The synthesis of a sulfonylated diazene is a two-step process. The first step involves the addition of the selected sulfonylating agent. Methanesulfonyl chloride (MeSO₂Cl) was chosen because it is commercially available, easily purified, and has a significantly different ¹H-NMR chemical shift than that of the *p*-tolyl methyl group. The second step is the formation of the diazene via treatment of the initial product with two equivalents of benzeneselenenyl chloride, as discussed in section 1.2.2.1.

2.2

A SULFONYLATED DIAZENE



The sulfonylated diazene, MeSO₂N(4-CH₃C₆H₄)CN=NC(C₆H₄CH₃-4)NSO₂Me, was successfully prepared and fully characterised. The monosubstituted derivative 4-CH₃C₆H₄C(NSO₂Me)[N(SiMe₃)₂], (43), and its hydrolysis products have also been isolated and spectroscopically characterised. Syntheses and experimental data are presented and discussed in the following sections.

2.2.1

PREPARATION AND SPECTROSCOPIC

CHARACTERISATION OF



The substitution of a trimethylsilyl group in (42) with SO₂Me occurred easily and rapidly at room temperature, using neat methanesulfonyl chloride. The by-product

trimethylsilyl chloride was removed *in vacuo* to leave a beige oily product. This product proved to be extremely hygroscopic. Thus, the structure of the product was assigned solely on the basis of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra. This product was handled in an *in situ* manner because of its reactivity with moisture.

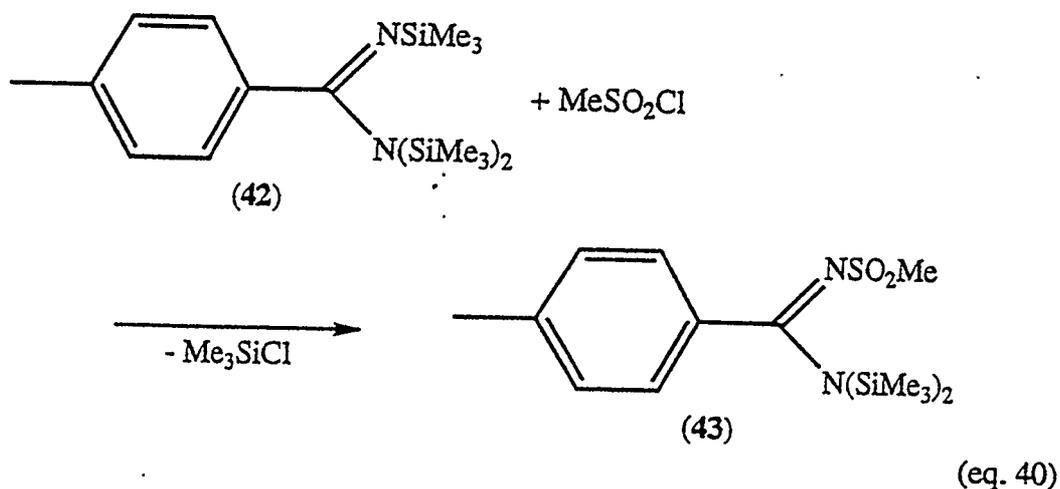


TABLE 1: SPECTROSCOPIC DATA FOR 4-CH₃C₆H₄C(NSO₂CH₃)[N(SiMe₃)₂]

$^1\text{H-NMR}^{a,b}$	δ (ppm)		Integration	Assignment
	7.67-6.86	(AB quartet)	4	CH ₃ C ₆ H ₄
	2.66	(Singlet)	3	CH ₃ SO ₂
	1.97	(Singlet)	3	CH ₃ C ₆ H ₄
	0.11	(Singlet)	18	(CH ₃) ₃ Si
$^{13}\text{C}\{^1\text{H}\}\text{-NMR}^{a,b}$	δ (ppm)		Assignment	
	130.94, 129.18		CH ₃ C ₆ H ₄	
	43.52		CH ₃ SO ₂	
	21.69		CH ₃ C ₆ H ₄	
	3.13		(CH ₃) ₃ Si	

^a Internal Reference C₆D₆

^b Chemical shifts quoted with reference to TMS (Me₄Si)

2.2.2 PREPARATION AND SPECTROSCOPIC
CHARACTERISATION OF HYDROLYSIS DERIVATIVES OF
4-CH₃C₆H₄C(NSO₂Me)[N(SiMe₃)₂]

The monosubstituted derivative (43) readily hydrolyses to form (44) upon addition of excess water in methanol. Water alone is not effective because it is immiscible with dichloromethane. A ¹H-NMR spectrum of the product indicated two small broad proton peaks, suggesting two different N-H environments.

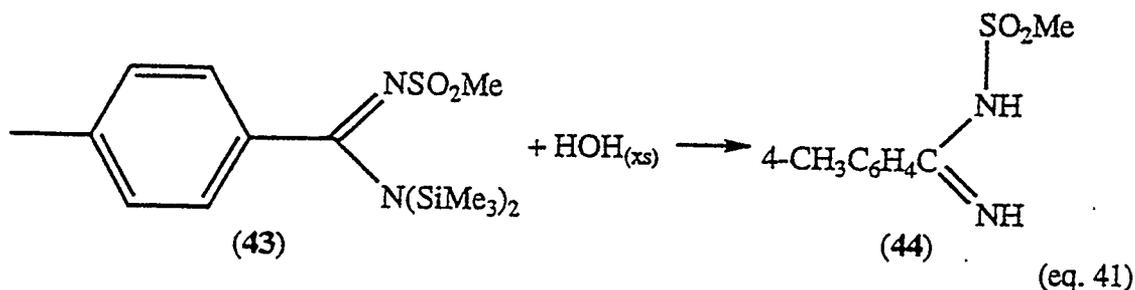


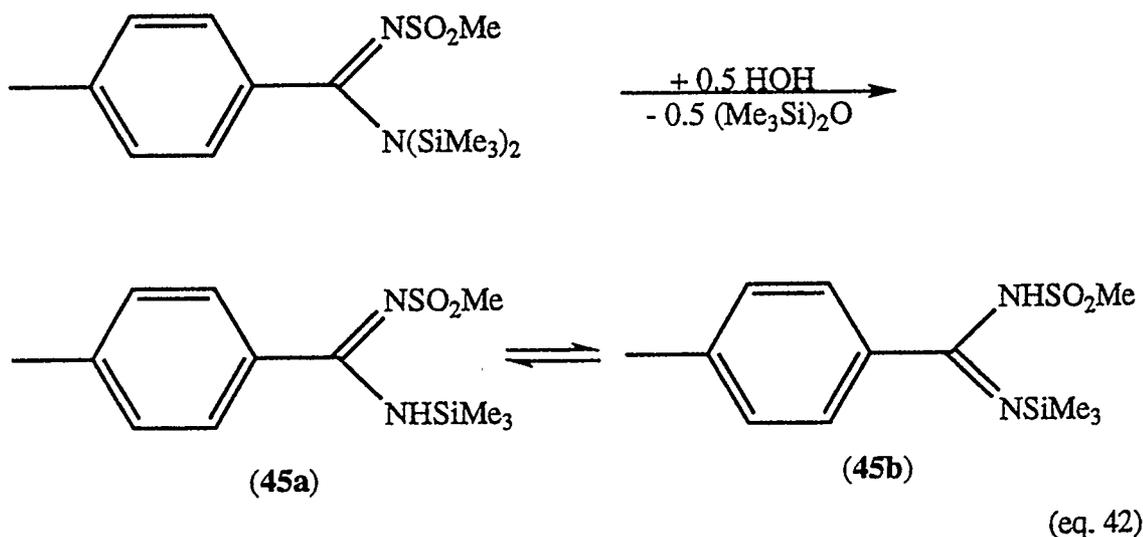
TABLE 2: SPECTROSCOPIC DATA FOR 4-CH₃C₆H₄C(NHSO₂CH₃)[NH]

¹ H-NMR ^{a,b}	δ (ppm)		Integration	Assignment
	8.00	(broad singlet)	0.85	=N-H
	7.74-7.19	(AB quartet)	4.01	CH ₃ C ₆ H ₄
	6.78	(broad singlet)	0.85	NHSO ₂ CH ₃
	3.04	(Singlet)	3.04	CH ₃ SO ₂
	2.37	(Singlet)	3.00	CH ₃ C ₆ H ₄
¹³ C{ ¹ H}-NMR ^{a,b}	δ (ppm)			Assignment
	162.93			C=N
	143.44, 129.37, 127.32			CH ₃ C ₆ H ₄
	42.07			CH ₃ SO ₂
	21.38			CH ₃ C ₆ H ₄

^a Internal Reference CDCl₃

^b Chemical shifts quoted with reference to TMS (Me₄Si)

An attempt to substitute one trimethylsilyl group on (43) with a proton by hydrolysis was performed, but this proved unsuccessful. The $^1\text{H-NMR}$ clearly showed the reaction solution contained a 1:1 mixture of starting material (43) and the hydrolysis product (44). Very recently, however, the derivative (45a, 45b) was prepared independently by Brock, Chivers and Hilts.⁶⁴ The reaction occurred following the addition of Ph_3AsCl_2 (eq. 42) which, presumably, involved the adventitious presence of water.



This hydrolysis product (45a, 45b) was characterised by $^1\text{H-NMR}$ and Electron Impact Mass Spectroscopy (EI-MS) (Table 3). However, the true structures for these species are presently a mystery. A $^1\text{H-NMR}$ spectrum gave an expected result for the proposed skeleton of the compound, except the N-H proton was absent. Curiously, a signal for an N-H proton appears at 193 K, which suggests that the product is fluxional between isomers 45a and 45b. Regardless, satisfactory EI-MS and elemental analyses were obtained to support the empirical formula $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2\text{SSi}$.

TABLE 3: SPECTROSCOPIC AND ANALYTICAL DATA FOR



$^1\text{H-NMR}^{a,b,c}$	δ (ppm)		Integration	Assignment
	7.22-7.49	(AB Quartet)	4	$\text{CH}_3\text{C}_6\text{H}_4$
	5.36	(Singlet)	1	N-H
	3.03	(Singlet)	3	CH_3SO_2
	2.40	(Singlet)	3	$\text{CH}_3\text{C}_6\text{H}_4$
	0.18	(Singlet)	9	$(\text{CH}_3)_3\text{Si}$
$^{13}\text{C}\{^1\text{H}\}\text{-NMR}^{a,b}$	δ (ppm)		Assignment	
	129.0, 127.7		$\text{CH}_3\text{C}_6\text{H}_4$	
	42.8		CH_3SO_2	
	21.5		$\text{CH}_3\text{C}_6\text{H}_4$	
	0.24		$(\text{CH}_3)_3\text{Si}$	
Elemental Analysis ^d	%C	%H	%N	
Calculated:	50.67	7.09	9.85	
Observed:	49.88	6.72	9.64	
Electron Impact Mass Spectrum		$\text{M}^\oplus - \text{H}$	283 amu (calc. 284 amu)	
		$\text{M}^\oplus - \text{Me}$	269 amu (calc. 269 amu)	

^a Internal Reference CDCl_3

^b Chemical shifts quoted with reference to TMS (Me_4Si)

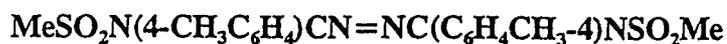
^c $^1\text{H-NMR}$ spectrum was obtained at 193 K

^d Based on empirical formula $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2\text{SSi}$

2.2.3

PREPARATION AND SPECTROSCOPIC

CHARACTERISATION OF



The reaction of the mono-substituted sulfonylated benzamidine (43), prepared *in situ*, with two equivalents of benzeneselenenyl chloride at room temperature, results in the rapid formation of the diazene (46) (eq. 43). After extraction of diphenyl diselenide, this product was isolated as an orange powder in moderately high yields (~60%). X-ray quality crystals were grown by the slow evaporation of a dichloromethane solution over a period of three weeks. The diazene (46) was characterised by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, Fast Atom Bombardment Mass Spectroscopy (FAB-MS), infra-red spectroscopy and elemental analysis.

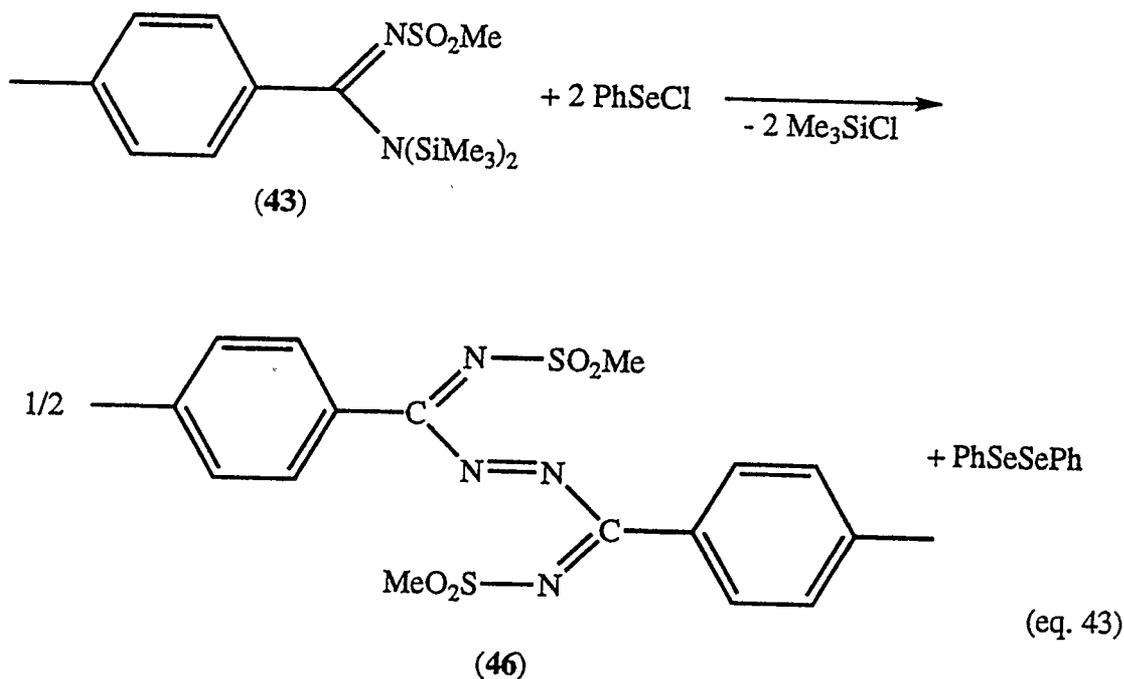
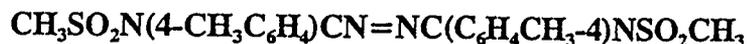


TABLE 4: SPECTROSCOPIC DATA FOR



$^1\text{H-NMR}^{\text{a,b}}$	δ (ppm)		Integration	Assignment
	7.94, 7.32	(AB quartet)	4	$\text{CH}_3\text{C}_6\text{H}_4$
	3.29	(Singlet)	3	CH_3SO_2
	2.45	(Singlet)	3	$\text{CH}_3\text{C}_6\text{H}_4$
$^{13}\text{C}\{^1\text{H}\}\text{-NMR}^{\text{a,b}}$	δ (ppm)			Assignment
	198.2			$\text{CN}=\text{NC}$
	146.3, 131.0, 129.6, 125.4			$\text{CH}_3\text{C}_6\text{H}_4$
	43.2			CH_3SO_2
	21.9			$\text{CH}_3\text{C}_6\text{H}_4$

^a Internal Reference CDCl_3

^b Chemical shifts quoted with reference to TMS (Me_4Si)

The $^1\text{H-NMR}$ spectrum gives the expected pattern, *viz.* the AB quartet for the *p*-tolyl group, and two singlets for the *p*-tolyl and $-\text{SO}_2\text{Me}$ methyl groups with the appropriate intensity ratios. The $^{13}\text{C-NMR}$ spectrum shows a very shielded signal for the skeletal carbon atoms of the diazene at 198.2 ppm. The two *ipso* carbons are assigned at 146.3 ppm (for the carbon nearest to the diazene backbone) and 125.4 ppm.

The infrared spectrum of (46) showed two important features. The first was the appearance of two strong bands at 1377 cm^{-1} and 1307 cm^{-1} , attributed to the $-\text{SO}_2$ group. These band positions are typical for organosulfones.⁶⁵ The next important piece of information gleaned from the IR spectrum was the absence of any broad N-H signals in the $3200\text{-}3500\text{ cm}^{-1}$ region. This suggested that no hydrolysis had occurred.

The FAB mass spectrum of (46) gave an ion peak of 423 amu. The calculated mass is 420 amu, which suggests an $\text{M}+3$ peak is observed. In FAB-MS one can expect

protonation to occur, giving a molecular ion peak $M+n$ (where n =number of additional protons). In the characterisation of both of the diazenes described in this thesis, an $M+3$ peak is observed consistently. The remainder of the mass spectrum displays the expected fragments of the diazene molecule. Typical fragments observed in the mass spectrum were 79 (SO_2Me), 91 ($4\text{-CH}_3\text{C}_6\text{H}_4$), 118 ($4\text{-CH}_3\text{C}_6\text{H}_4\text{CNH}$), and an important peak at 211 ($4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSO}_2\text{Me})[\text{NH}]$), representing one half of the molecule.

Upon measuring the UV-visible spectrum of the compound, it was observed that no absorbance exists above 400 nm. There appears to be a large absorbance at approximately 330 nm, but this could not be measured accurately. In comparison, the known S(II) diazene is a very intensely-coloured species where $\epsilon > 10^4 \text{ M}^{-1}\text{cm}^{-1}$ and λ_{max} is $\sim 550 \text{ nm}$. Clearly, these compounds have very different physical properties. The intensity of the S(II) diazenes is attributed to a significant $\pi \rightarrow \pi^*$ interaction of the chalcogen to the nitrogen. In the case of the S(VI) derivative, this interaction is not expected because the chalcogen is coordinatively saturated. The UV-visible spectrum supports this prediction.

Numerous structural isomers are possible for the diazene (46). It is expected that there are three double bonds present in the compound, each with a possible *E* or *Z* configuration. As a result, there are six possible isomers (*figure 4*). Consequently, an x-ray structural determination was carried out.

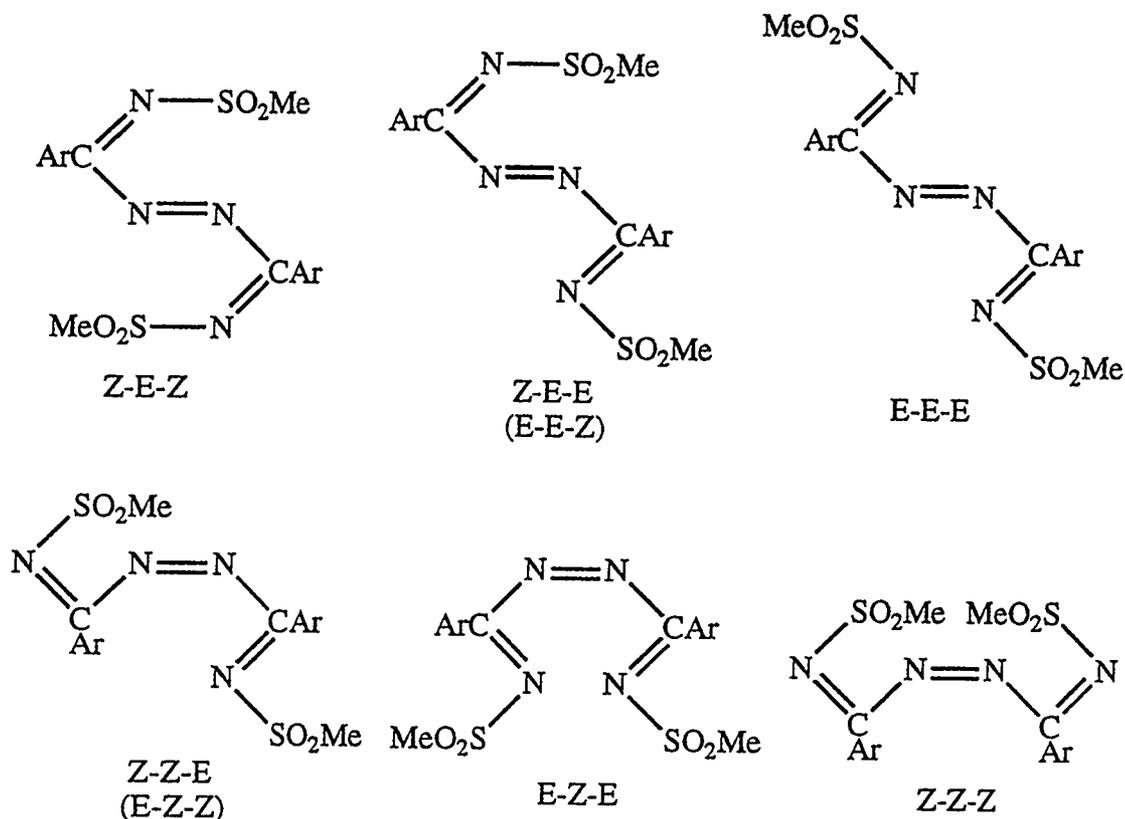
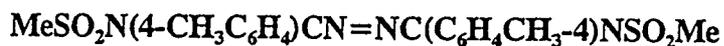


Figure 4: The six isomers of the sulfonated diazene (46)
(Ar = 4- $\text{CH}_3\text{C}_6\text{H}_4$)

2.2.4

X-RAY CRYSTAL STRUCTURE OF



The structure of the diazene (46) was determined by X-ray crystallography by Dr. M. Parvez. The crystallographic data are summarised in Table 5 and selected bond lengths and angles are given in Table 6. *Figure 5* displays an ORTEP drawing⁶⁶ of the compound, and full details of the X-ray structure are available from Dr. M. Parvez.

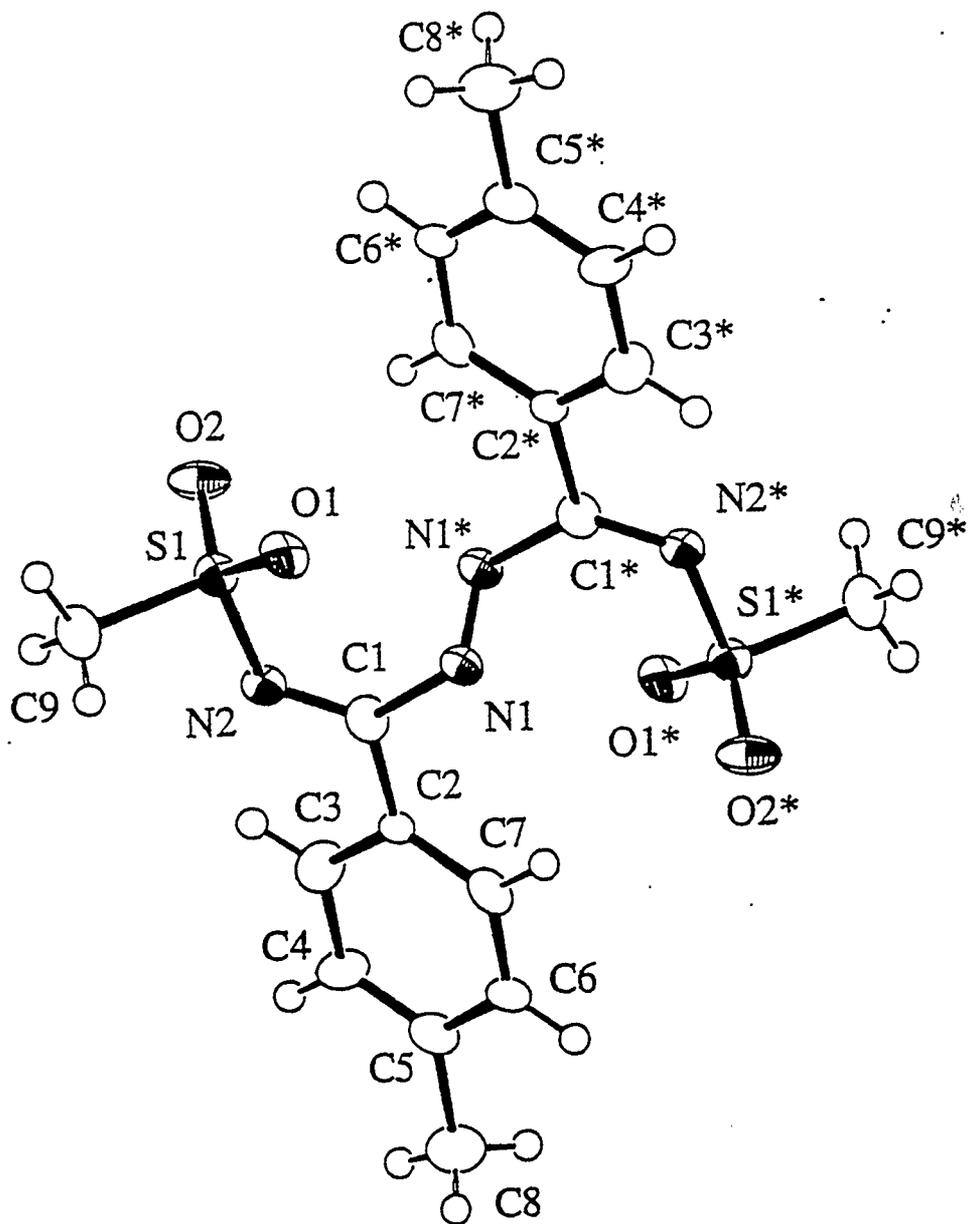


Figure 5: ORTEP of $\text{CH}_3\text{SO}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{NSO}_2\text{CH}_3$

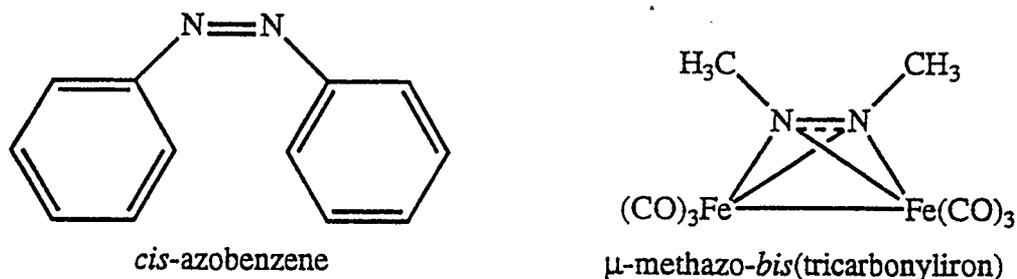
**TABLE 5: CRYSTALLOGRAPHIC DATA FOR
 $\text{CH}_3\text{SO}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-}4)\text{NSO}_2\text{CH}_3$**

M.W. = 420.50 g mol⁻¹ Empirical Formula: C₁₈H₂₀N₄S₂O₄
 monoclinic, space group P2₁/c, β = 101.81(1)°
 a = 10.483(1) Å, b = 5.128(2) Å, c = 18.180(2) Å
 V = 956.6(3) Å³, T = -103.0°C, D_{calc} = 1.460 g cm⁻³
 crystal dimensions = 0.08 x 0.12 x 0.45 mm, Z = 2
 R = 0.064, R_w = 0.063

**TABLE 6: SELECTED BOND LENGTHS AND ANGLES FOR
 $\text{CH}_3\text{SO}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-}4)\text{NSO}_2\text{CH}_3$**

d[C(1)-N(1)]	1.466(9) Å	∠ [C(1)-N(1)-N(1)*]	113.2(9)°
d[N(1)-N(1)*]	1.20(1) Å	∠ [N(2)-C(1)-N(1)]	125.6(7)°
d[C(1)-N(2)]	1.260(9) Å	∠ [N(1)*-N(1)-C(1)-N(2)]	63(1)°
d[S(1)-N(2)]	1.652(6) Å		
d[S(1)---N(1)]	3.16 Å		
d[S(1)---N(1)*]	3.08 Å		

To consider the structure of the S(VI) diazene, (46), one must have a knowledge of typical diazene structures. Azo compounds are usually *trans* (*E*) about the N=N double bond. However, some *cis* (*Z*) examples are known, such as *cis*-azobenzene, or μ -methazo-*bis*(tricarbonyliron). These molecules tend to involve other constraints (steric or electronic) to form the *cis* configuration.



Typically, average dimensions of *trans* azo groups display an N=N bond length of 1.25 Å, a C-N bond length of 1.42 Å, and an N=N-C bond angle of 113° for aromatic substituents (figure 6).⁶⁷ They are also virtually planar.

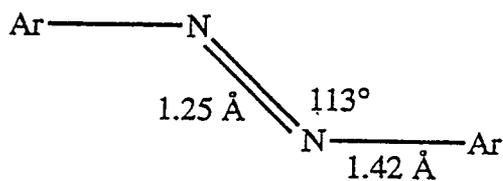


Figure 6: Average dimensions for a *trans* azo moiety with aromatic substituents

The x-ray crystal structure clearly shows that the molecule (46) is a *Z-E-Z* isomer, *i.e.* it is *Z* about both of the C=N double bonds, but *E* about the N=N double bond. Already, the compound appears to be similar to most diazene compounds, with the *trans* N=N bond.

Looking specifically at the backbone of the diazene, certain structural aspects are of importance. The first is the torsion angle defined by N(1)*-N(1)-C(1)-N(2), at 63(1)°.

Whereas in most simple organic diazenes the substituents *trans* to each other tend to lie in the same plane,⁶⁷ this diazene is significantly twisted in this regard. The known selenium diazene [MeSeN(Ph)CN=NC(Ph)NSeMe], (*figure 3*), which is also a *Z-E-Z* compound, has a corresponding torsion angle of $-3.4(5)^\circ$.²⁵ There is a well-established weak selenium-nitrogen interaction in this diazene, which is no doubt somewhat responsible for the near planarity of the molecule. This implies that there are no intramolecular chalcogen-nitrogen interactions occurring in the sulfur(VI) system, which is not surprising as the sulfur(VI) is coordinatively saturated. The S(1)-N(1)^{*} distance is observed to be 3.16 Å. Considering that the sum of the van der Waals radii for sulfur and nitrogen is 3.35 Å,²⁶ this number suggests that there could be, at best, a minimal interaction. It is proposed that, since very little S-N interaction is present, the plane of the diazene has twisted to a lower energy conformation.

The diazene bond length itself is of great significance. The N(1)-N(1)^{*} distance is 1.20(1) Å, as compared to an average diazene bond length of 1.25 Å (*figure 6*).⁶⁷ The selenium (II) diazene (*figure 3*) has a bond length of 1.263(4) Å. The sulfur(VI) system N=N bond is clearly shorter than similar diazene bonds in other systems. In the case of the selenium diazene, the chalcogen is actively interacting with the nitrogen in a $\pi \rightarrow \pi^*$ fashion. As a result, donation into an anti-bonding orbital has lengthened the N=N bond. Since the sulfonylated diazene does not have this contribution, the N=N bond length is somewhat shorter. This is additional evidence that essentially no sulfur-nitrogen interaction is occurring. A more complete discussion of the diazene orbitals is available

in section 3.2.4.

The sulfonylated diazene is not entirely unlike typical diazenes, however. The N(1)-N(1)*-C(1)* angle is $113.2(9)^\circ$, which compares closely to an average 113° , and the C(1)-N(1) bond length is $1.466(9) \text{ \AA}$, only slightly longer than average (*figure 6*).⁶⁷ The C(1)-N(2) bond length is $1.260(9) \text{ \AA}$, as compared to a typical C=N bond length of 1.30 \AA . Comparing it the C(1)-N(1) bond length of $1.466(9) \text{ \AA}$, it is clear that these bonds are significantly different, and that one is a single bond, and one is a double bond. Typical C-N bonds are 1.47 \AA .⁶⁵ This implies that there is only very modest delocalisation between the azo group and the other substituents. This effect is seen quite clearly in the selenium(II) diazene as well.²⁵

CONCLUSIONS

It has been shown that monosubstituted sulfonyl derivatives of trisilylated benzamidines can be prepared. The monosubstituted benzamidine 4- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSO}_2\text{Me})[\text{N}(\text{SiMe}_3)_2]$, (43) has been obtained *in situ*. Hydrolysis products of (43) have also been prepared and spectroscopically characterised. The purity of these products has been confirmed by NMR and elemental analysis. All three of these derivatives should prove to be very important synthons for any future chemistry in this area.

Subsequent reaction of the monosubstituted benzamidine (43) with two equivalents of PhSeCl generates the first S(VI) derivative of an azo dye, (46), which was unambiguously characterised via an X-ray diffraction study. Upon comparison of this S(VI)-containing diazene to the known structure of a Se(II) diazene compound, clear differences were observed. Notably, the diazene bond length for the S(VI) diazene was significantly shorter than for the Se(II) diazene, attributed to the absence of donation into an anti-bonding orbital of the diazene bond. Structural ambiguity concerning the conformation of the double bonds in the compound was eliminated, and the compound was found to be *Z* about the $\text{C}=\text{N}$ bonds and *E* about the $\text{N}=\text{N}$ bond. Analysing the structure clearly shows that there is very little delocalisation of electron density throughout the conjugated $\text{N}=\text{C}-\text{N}=\text{N}-\text{C}=\text{N}$ backbone, which is consistent with the selenium(II) diazene, as well as other known organic diazene compounds.

2.4

EXPERIMENTAL

2.4.1

GENERAL

All distillations and reactions were performed under inert conditions with a dry nitrogen atmosphere. Nitrogen gas (Praxair) was dried by passing it through a column of phosphorus pentoxide (Fisher Scientific Company). This practice eliminates as much moisture as possible from the system, which is vital for the manipulation of these compounds.

With the exception of *p*-tolyl disulfide, all reagents and products were handled under a nitrogen atmosphere using either Schlenk techniques or a glove box (two glove boxes were employed; a Vacuum Atmospheres Corporation glove box and an Innovative Technology glove box). All solutions and solvents were transferred via syringes or cannula.

2.4.2

INSTRUMENTATION

Proton (^1H) and carbon ($^{13}\text{C}\{^1\text{H}\}$) NMR spectra were recorded on a Bruker ACE 200 Spectrometer. A Bruker AM400 Spectrometer was employed for the purposes of variable temperature (VT) NMR. The references for the spectra were internal deuterated solvents. Chemical shifts are quoted relative to tetramethylsilane (0 ppm).

Ultraviolet spectra were obtained using a Cary 219 spectrophotometer. Infrared

spectra were obtained as Nujol mulls on KBr disks with a Mattson Instruments 4030 Galaxy Series FT-IR machine. The crystal structure was determined by Dr. M. Parvez from data collected with a Rigaku AFC6S diffractometer. Data processing was performed with computer programs from the teXsan package⁶⁸ installed on a Silicon Graphics Personal Iris 4D/35 computer. The structure was solved and refined using SHELX,⁶⁹ and plotted using ORTEP.⁶⁶ Elemental analyses and mass spectral analyses were carried out by the Analytical Services division at the Department of Chemistry at The University of Calgary.

2.4.3

SOLVENTS

Solvents used for reactions and crystallisations were of reagent grade. They were all purchased from BDH Incorporated and refluxed over an appropriate drying agent under an inert atmosphere of argon gas (Praxair). The solvents (and drying agents) include: chloroform (phosphorus pentoxide); dichloromethane (first distilled over phosphorus pentoxide and then calcium hydride (BDH)); diethyl ether (sodium wire/benzophenone, both from Aldrich); hexanes (sodium wire/benzophenone); and toluene (sodium wire/benzophenone). Chloroform-d and benzene-d₆ (Aldrich) were not distilled, but used after drying over freshly heated Davison Molecular sieves (purchased from Fisher). Reagent grade methanol was used without any further purification.

2.4.4

REAGENTS

The starting materials *p*-tolunitrile, *p*-tolyl disulfide, benzeneselenenyl chloride, and trimethylsilyl chloride were obtained from Aldrich and used as received. Celite 545 and sea sand for the purposes of filtration were obtained from Fisher Scientific and dried in an oven (110°C) prior to use. Lithium hexamethyldisilylamide, $\text{LiN}(\text{SiMe}_3)_2$, was purchased from Aldrich. It was then dissolved in hexanes and 1.1 equivalents of diethyl ether was added. The lithium hexamethyldisilylamide etherate adduct then precipitated out of solution. It was subsequently washed twice with hexanes and stored in a dry box environment. Commercial samples of methanesulfonyl chloride (Aldrich) were distilled and stored under nitrogen for future use (30°C, 0.01 torr). The ^1H -NMR spectrum of this compound shows a singlet at 3.67 ppm and the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum displays a singlet at 52.46 ppm.

Diphenyl diselenide, produced as a by-product of the preparation of the sulfonylated diazene, was isolated and dissolved in dichloromethane. It was then recycled to PhSeCl , using the method of Engman.⁷⁰

The synthesis of $4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$, (42), was from Oakley *et al.*⁵ It was prepared several times by different people (I. Krouse, I. Vargas-Baca, R. Hilts). The purity was assessed by ^1H -NMR spectroscopy. A typical spectrum of (42) included an AB quartet from 7.22-7.08 ppm (integration ≈ 3.5); a singlet at 2.38 ppm (integration ≈ 3); and a singlet at 0.09 ppm (integration ≈ 26.5).

2.4.5

SYNTHESIS OF



The monosubstituted derivative, (43), was prepared several times in attempts to isolate it. It is extremely hygroscopic and will readily react with any moisture in the system to produce a mixture of the hydrolysis products, (44) or (45a, 45b). Consequently, it was prepared *in situ* for further reactions.

To a clear, colourless solution of $4\text{-CH}_3\text{C}_6\text{H}_4(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$ (1.15 g, 3.28 mmol) in dichloromethane (25 mL), neat MeSO_2Cl (0.25 mL, 0.38 g, 3.32 mmol) was added via syringe at room temperature. The reaction was allowed to stir for 15 min., and then the solvent and Me_3SiCl by-product were removed under vacuum. An off-white crude product remained (1.13 g, 3.15 mmol, 97% yield). Efforts to isolate this product resulted only in the formation of the hydrolysis derivatives. Spectroscopic information for (43) is summarised in section 2.2.1.

2.4.6

SYNTHESIS OF $4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NHSO}_2\text{Me})[\text{NH}]$

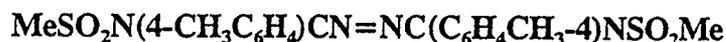
To a clear, colourless solution of $4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$ (1.174 g, 3.35 mmol) in dichloromethane (25 mL), a solution of MeSO_2Cl (0.26 mL, 0.392 g, 3.43 mmol) in dichloromethane (10 mL) was added slowly at room temperature over a 10 minute period. Distilled water (0.06 g, 3.34 mmol) was added

to the reaction mixture and found to be immiscible. Methanol (5 mL) was then added to aid in homogenisation of the mixture, which was allowed to stir for 15 min.. The solvent was then removed *in vacuo* to give off-white crystals of 4-CH₃C₆H₄C(NHSO₂CH₃)[NH], (44) (0.641 g, 3.02 mmol, 90% yield). This material was recrystallised by redissolving entirely in methanol and slowly evaporating the solvent. The recrystallised product was a beige powder. Spectroscopic results are given in section 2.2.2.

The elemental composition was confirmed by combustion analysis. Based on the empirical formula C₉H₁₂N₂SO₂, calculated elemental percentages are: C, 50.93%; H, 5.70% and N, 13.20%. Observed values were: C, 50.67%; H, 5.64% and N, 13.00%.

2.4.7

SYNTHESIS OF



To a clear, colourless solution of 4-CH₃C₆H₄C(NSiMe₃)[N(SiMe₃)₂] (0.60 g, 1.71 mmol) in dichloromethane (25 mL), neat MeSO₂Cl was syringed (0.13 mL, 0.196 g, 1.71 mmol). This mixture was allowed to stir for one hour. Benzeneselenenyl chloride (0.65 g, 3.34 mmol) dissolved in dichloromethane (30 mL) was then added slowly over a period of ten minutes. All steps were performed at room temperature. After two hours an orange solution had resulted, and residual solvent was removed *in vacuo* overnight to give a dark red residue. The product was then washed

with hexanes (2 x 30 mL). The hexane-soluble material was confirmed to be diphenyl diselenide by GC-MS, and the crude yield of extracted material was 0.49 g (theoretical yield was 0.53 g, 92% yield). The hexane-insoluble yellow material massed 0.43 g (0.36 g expected) suggesting that not all PhSeSePh had been extracted. The product was then dissolved in a minimum of dichloromethane and allowed to slowly evaporate over a period of three weeks to afford X-ray diffraction quality crystals of (46). These were used to determine the structure of the molecule. Attempts to purify the product by vacuum sublimation resulted in the apparent decomposition of the product to an orange oil, so this method was not used to isolate further pure product. Further syntheses afforded enough material for complete characterisation (see section 2.2.3 for details). Subsequently, this reaction has been shown to give almost quantitative yields of crude product, but only moderate yields (~60%) of analytically pure product have been isolated. Compound (46) was found to melt between 170-171 °C.

Elemental analysis was obtained from a sample of the diazene that was recrystallised twice from diethyl ether. Careful preparation of the sample was required for these compounds. A key step is the crushing of the sample and the subsequent removal of residual solvent *in vacuo*. Based on the empirical formula $C_{18}H_{20}N_4S_2O_4$, calculated elemental percentages are: C, 51.41%; H, 4.79% and N, 13.32%. Observed values were: C, 50.78%; H, 5.54% and N, 12.20%.

CHAPTER THREE

PREPARATION, CHARACTERISATION AND X-RAY STRUCTURE
OF A SULFENYLATED DIAZENE AND SULFINYL DERIVATIVES OF
 $4\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$

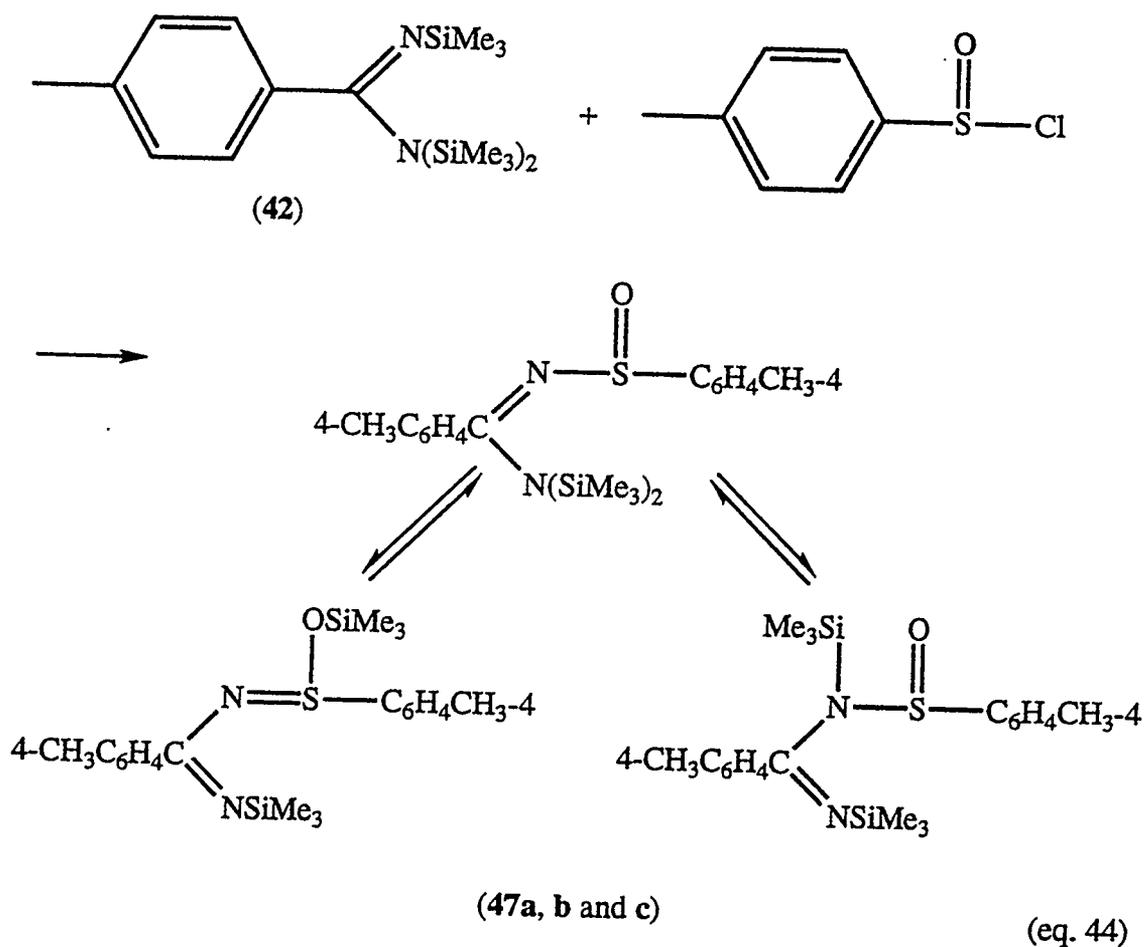
3.1

INTRODUCTION

Upon completion of the preparation of a sulfur(VI) diazene, (46), the natural progression was to attempt to synthesise a sulfur(IV) or sulfinylated diazene in order to complete the series of diazenes with sulfur(II), (IV) and (VI) substituents. The *p*-tolyl trisilylated benzamidine, (42), was used for the preparation of the diazene for the same reasons mentioned previously (section 2.1). The sulfinyl chloride $4\text{-CH}_3\text{C}_6\text{H}_4\text{SOCl}$ was selected on the basis of cost, along with ease of preparation and characterisation. Attempts to prepare MeSOCl by the method of Herrman *et al.*⁷¹ were only partially successful, because the reagent could not be isolated completely free from contaminants. Benzene sulfinyl chloride is difficult to purify, owing to the fact that it often explodes when distilled. *p*-Toluene sulfinyl chloride ($4\text{-CH}_3\text{C}_6\text{H}_4\text{SOCl}$) also explodes when heated under vacuum but, unlike PhSOCl , it can be prepared *in situ* as a very pure material, thereby obviating the need to distil it. It also has a distinctive $^1\text{H-NMR}$ spectrum to aid in characterisation.

The synthetic procedure employed to prepare the sulfinylated diazene mirrored

that used for the sulfonyl derivative in that a monosubstituted benzamidine (47a, b or c) was first prepared (eq. 44). Subsequent addition of two equivalents of benzeneselenenyl chloride is expected to produce $\text{ArC}[\text{NS}(\text{O})\text{Ar}][\text{N}(\text{SePh})_2]$ ($\text{Ar}=\text{4-CH}_3\text{C}_6\text{H}_4$), which, on the basis of precedent, is expected to decompose via PhSeSePh extrusion to give the desired sulfinylated diazene (48). However, this did not prove to be the case.



The monosubstituted derivative 4-CH₃C₆H₄C(NSOC₆H₄CH₃-4)[N(SiMe₃)₂] and its hydrolysis product 4-CH₃C₆H₄C(NHSOC₆H₄CH₃-4)[NH] were also characterised. The syntheses and experimental data are presented in the following sections.

3.2.1

PREPARATION AND SPECTROSCOPIC

CHARACTERISATION OF 4-CH₃C₆H₄C(NSOC₆H₄CH₃-4)[N(SiMe₃)₂]

The substitution of a trimethylsilyl group with a 4-CH₃C₆H₄SO- group occurred easily and rapidly when 4-CH₃C₆H₄C(NSiMe₃)[N(SiMe₃)₂], (42), was treated with a dilute solution of *p*-toluene sulfinyl chloride in dichloromethane at room temperature (eq. 44). The by-product Me₃SiCl was removed *in vacuo* to leave a beige oil. This product proved to be extremely hygroscopic, and was handled *in situ*. The structure could not be assigned on the basis of ¹H-NMR and ¹³C-NMR spectra and three isomers (47a, b and c) are possible.

Crystals of this compound were grown from slow evaporation of a pentane solution. Unfortunately, rapid desolvation and the subsequent decomposition and/or hydrolysis of the species occurred during every attempt to mount the crystals in a capillary tube. This thwarted all attempts at structural elucidation by X-ray diffraction.

The ¹H-NMR spectrum suggested that a mixture of three structural isomers had been formed. Distinct areas corresponding to a 4:3:9 integration (aromatic:methyl:trimethylsilyl) were present in the spectrum. However, these areas were typically composed of several signals. Whereas the methyl region had three

signals, the aromatic and trimethylsilyl regions were complex multiplets. It is on this basis that the three isomers of the product were proposed. The infrared spectrum showed a band at 1045 cm^{-1} , consistent with the S(O) stretch of an organosulfinyl moiety.⁶⁵ The EI-MS displayed a parent ion at 416 amu corresponding to an empirical formula of $\text{C}_{21}\text{H}_{32}\text{N}_2\text{SOSi}_2$. A broad melting point of $90\text{-}95^\circ\text{C}$ suggested that the product was not pure. Upon melting, the white powder became a brown oily liquid, which did not revert to a white solid upon cooling. Because of the highly reactive nature of this product, further characterisation could not be performed. Even at low temperatures this reaction formed three distinct isomers of indeterminate proportions by VT- ^1H -NMR. As a result, it was prepared *in situ* for the subsequent reaction with two equivalents of benzeneselenenyl chloride.

3.2.2

PREPARATION AND SPECTROSCOPIC

CHARACTERISATION OF 4- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{NHSOC}_6\text{H}_4\text{CH}_3\text{-4})[\text{NH}]$

Although the monosubstituted sulfinyl benzamidine apparently formed three isomers (47a, b and c), hydrolysis with excess water produced one product exclusively (50) (eq. 45). Spectroscopic and physical evidence suggests that (50) has the structure depicted.

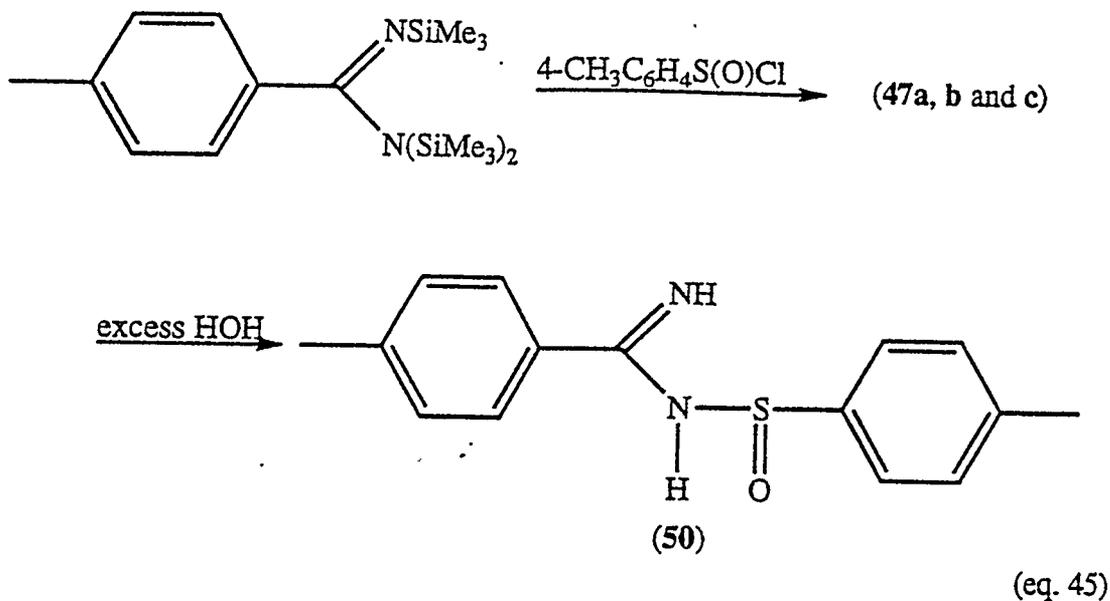


TABLE 7: SPECTROSCOPIC AND PHYSICAL DATA FOR



$^1\text{H-NMR}^{\text{a,b}}$	δ (ppm)		<u>Integration</u>	<u>Assignment</u>
	7.75-7.62	(AB Quartet)	4	$\text{CH}_3\text{C}_6\text{H}_4$
	7.34-7.42	(AB Quartet)	5	$\text{CH}_2\text{C}_6\text{H}_4 + \text{NH}$
	2.41	(Broad singlet)	6.4	$\text{CH}_3\text{C}_6\text{H}_4$
EI-MS	Calculated:	272 amu		
	Observed:	272 amu		
Infrared	1068 cm^{-1} , indicative of S=O stretching			
Elemental Analysis ^c	<u>%C</u>	<u>%H</u>	<u>%N</u>	
	Calculated:	66.15	5.92	10.29
	Observed:	65.79	5.92	10.21

^a Internal Reference CDCl_3

^b Chemical shifts quoted with reference to TMS (Me_4Si)

^c Based on the empirical formula $\text{C}_{15}\text{H}_{16}\text{N}_2\text{OS}$

Neither N-H proton is clearly visible in the proton NMR spectrum. One N-H could be buried underneath the *p*-tolyl AB quartets between 7.3 and 7.8 ppm since the integrated area shows one more proton than expected, but this has not been verified by a D₂O exchange experiment. If a NH₂ moiety was present, the ¹H-NMR spectrum should clearly show a resonance corresponding to two protons, and this is not seen. Elemental analysis is consistent with the proposed formulation of compound (50).

Because the isolation of the monohydrolysed compound (45), described in section 2.2.2, proved to be so difficult, no attempts to prepare the analogous sulfinyl species were made. Furthermore, the existence of isomers complicates the matter. Controlled hydrolysis of (47a, b and c) may result in a monohydrolysis product similar to that described in section 2.4.6.

3.2.2 PREPARATION AND SPECTROSCOPIC CHARACTERISATION

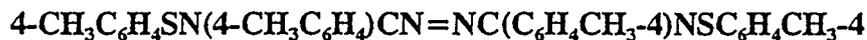
OF 4-CH₃C₆H₄SN(4-CH₃C₆H₄)CN=NC(C₆H₄CH₃-4)NSC₆H₄CH₃-4

The reaction of the monosubstituted benzamidine (47a, 47b and 47c) with two equivalents of benzeneselenenyl chloride at -78°C produced a purple compound initially thought to be the sulfinylated diazene (48). Spectroscopic and analytical evidence, however, suggested an alternate product. A FAB mass spectrum gave a parent ion peak of 511 amu. For compound (48), the calculated parent ion peak would be 540 amu. This suggested that the observed peak is attributable to the sulfur(II) diazene, (49), and the product has formed via loss of oxygen from the sulfinyl moiety (calculated peak is

508 amu). The observed M+3 peak is consistent with the triprotonation observed in the case of the sulfonylated diazene (see section 2.2.3). The infrared spectrum showed the absence of both a S=O moiety and N-H stretching. Elemental analysis was in reasonable agreement with theoretical values for the S(II) diazene, (49). A visible spectrum revealed an absorbance maximum at 550 nm.

The $^1\text{H-NMR}$ data could not differentiate between (48) and (49). It clearly showed two AB quartets for the two *p*-tolyl groups, and two methyl singlets in appropriate integrations. Both (48) and (49) would be expected to give this type of spectrum. As well, the $^{13}\text{C-NMR}$ spectrum could not offer any means to distinguish between the two products.

TABLE 8: SPECTROSCOPIC DATA FOR



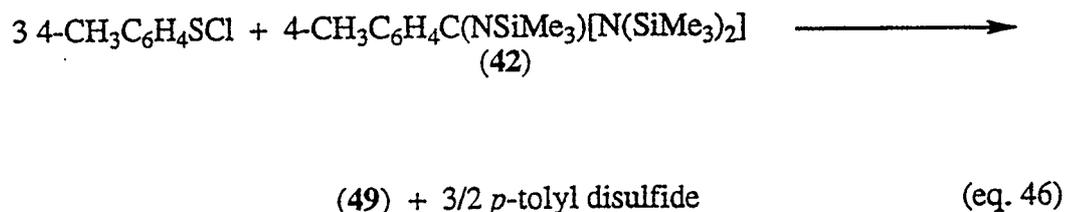
$^1\text{H-NMR}^{\text{a,b}}$	δ (ppm)		Integration	Assignment
	8.32-7.27	(two AB Quartets)	8	$\text{CH}_3\text{C}_6\text{H}_4$
	2.47	(Singlet)	2.5	$\text{CH}_3\text{C}_6\text{H}_4$
	2.41	(Singlet)	3.3	$\text{CH}_3\text{C}_6\text{H}_4$
$^{13}\text{C-NMR}^{\text{a,b}}$	δ (ppm)			Assignment
	198.5			$\text{CN}=\text{NC}$
	138.6, 131.6, 129.8, 129.5			
	129.1, 127.8, 127.4, 125.3			$\text{CH}_3\text{C}_6\text{H}_4$
	21.50			$\text{SCH}_3\text{C}_6\text{H}_4$
	21.22			$\text{CH}_3\text{C}_6\text{H}_4$

^a Internal Reference CDCl_3

^b Chemical shifts quoted with reference to TMS (Me_4Si)

The ^{13}C -NMR spectrum showed several aromatic carbons between the region of 125 and 131 ppm. The carbon *ipso* to the S(II) atom is assigned at 131.6 ppm, and the *ipso* carbon closest to the diazene skeleton at 138.6 ppm (based on a similar carbon in compound (46)). All other aromatic carbons cannot be assigned with confidence without further experimentation such as isotope exchange reactions.

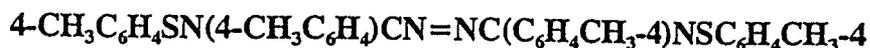
To provide further evidence for the identity of (49), the same product was prepared in quantitative yield via the reaction of three equivalents of *p*-toluene sulfonyl chloride with the trisilylated benzamidine (42) (eq. 46). The spectroscopic data for this product was found to correspond with data obtained for the product from the reaction of (47) with two equivalents of benzeneselenenyl chloride.



An X-ray crystallographic study showed that the oxygen on sulfur atoms was no longer present. As a result, the first crystal structure of a sulfur(II) azo dye, (49), was serendipitously determined, from the attempted preparation of a S(IV)-containing compound.

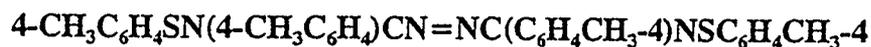
3.2.3

X-RAY CRYSTAL STRUCTURE OF



The structure of the sulfenyl diazene (49) was determined by an X-ray diffraction study performed by Dr. M. Parvez. The crystallographic data are summarised in Table 9, and selected bond lengths and angles are given in Table 10. *Figure 7* displays an ORTEP drawing⁶⁶ of the compound and *figure 8* is a packing diagram of the unit cell, showing the sheet-like layering of the molecules. Full details of the X-ray structure are available from Dr. M. Parvez.

TABLE 9: CRYSTALLOGRAPHIC DATA FOR



M.W. = 508.70 g mol⁻¹ Empirical Formula: C₃₀H₂₈N₄S₂

monoclinic, space group p2₁/n, β = 95.56(4)°

a = 6.140(2) Å, b = 10.492(6) Å, c = 20.728(9) Å

V = 1325(1) Å³, T = -53.0°C, D_{calc} = 1.275 g cm⁻³

crystal dimensions = 0.08 x 0.20 x 0.42 mm, Z = 2

R = 0.056, R_w = 0.052

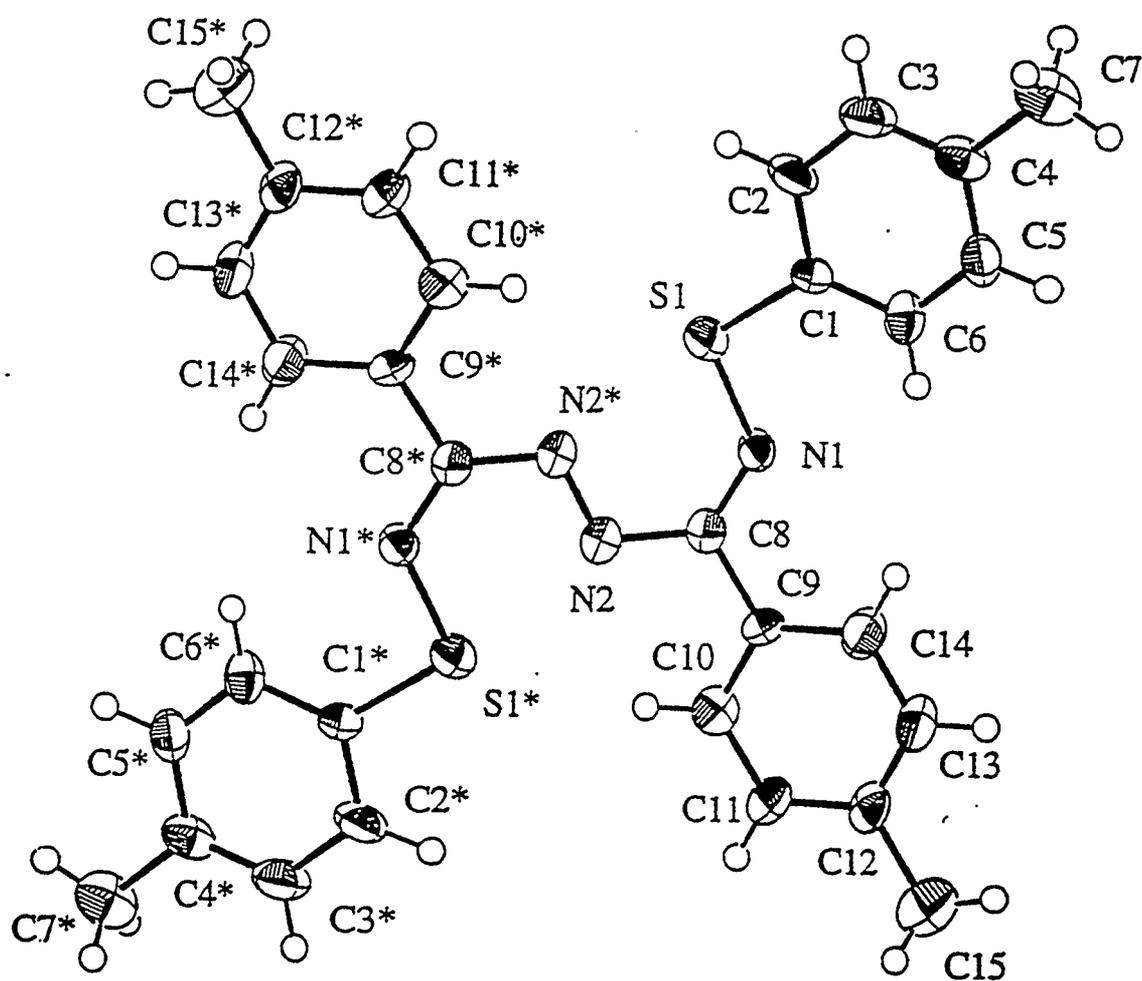


Figure 7: ORTEP of the sulfenylated diazene
 $4\text{-CH}_3\text{C}_6\text{H}_4\text{SN}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-}4)\text{NSC}_6\text{H}_4\text{CH}_3\text{-}4$

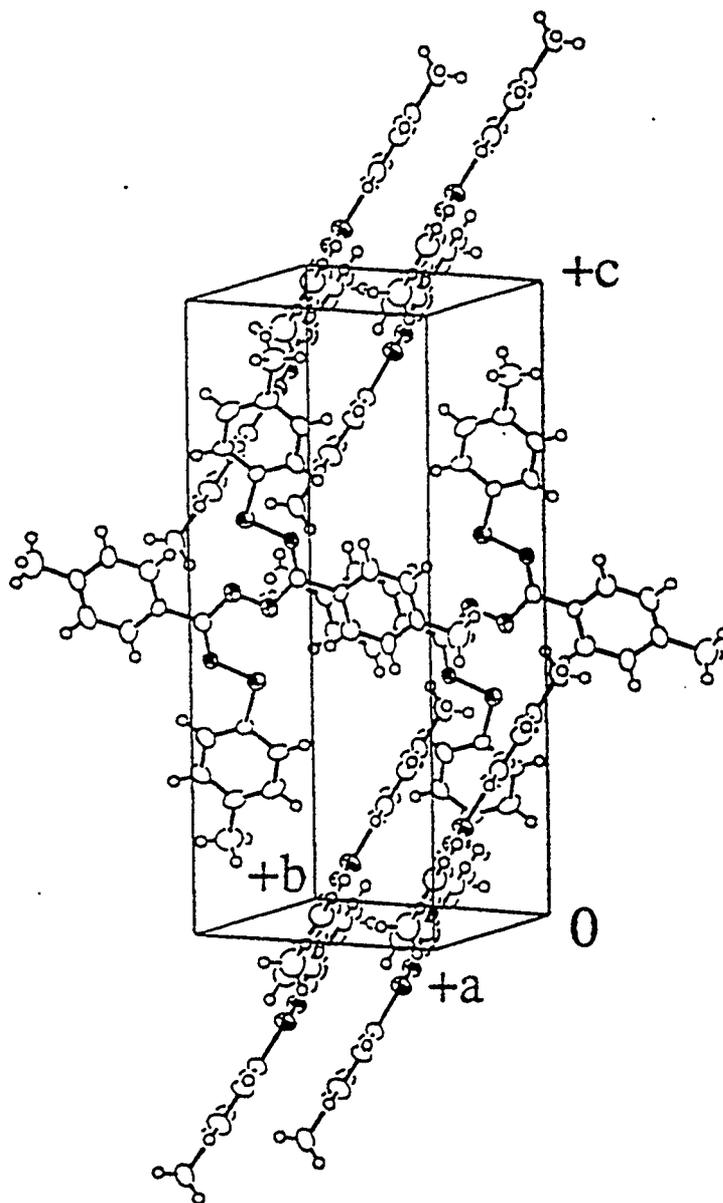
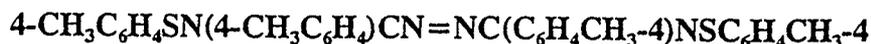


Figure 8: Packing diagram of the monoclinic unit cell for the sulfenylated diazene
 $4\text{-CH}_3\text{C}_6\text{H}_4\text{SN}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{NSC}_6\text{H}_4\text{CH}_3\text{-4}$

TABLE 10: SELECTED BOND LENGTHS AND ANGLES FOR



$d[\text{C}(8)\text{-N}(2)]$	1.415(11) Å	$d[\text{S}(1)\text{---N}(2)^*]$	2.607(10) Å
$d[\text{N}(2)\text{-N}(2)^*]$	1.294(14) Å	$\angle [\text{C}(8)\text{-N}(2)\text{-N}(2)^*]$	112.7(7)°
$d[\text{C}(8)\text{-N}(1)]$	1.303(11) Å	$\angle [\text{N}(1)\text{-C}(8)\text{-N}(2)]$	126.9(10)°
$d[\text{N}(1)\text{-S}(1)]$	1.641(8) Å	$\Phi[\text{N}(2)^*\text{-N}(2)\text{-C}(8)\text{-N}(1)]$	10(1)°

As with the sulfonylated diazene (46), there are three double bonds expected to be present in compound (49). As a result, there are six potential isomers of (49) (figure 9). There is also the possibility of isomers resulting from rotation about the C-N single bond. A representative example of these rotamers has been isolated.⁷²

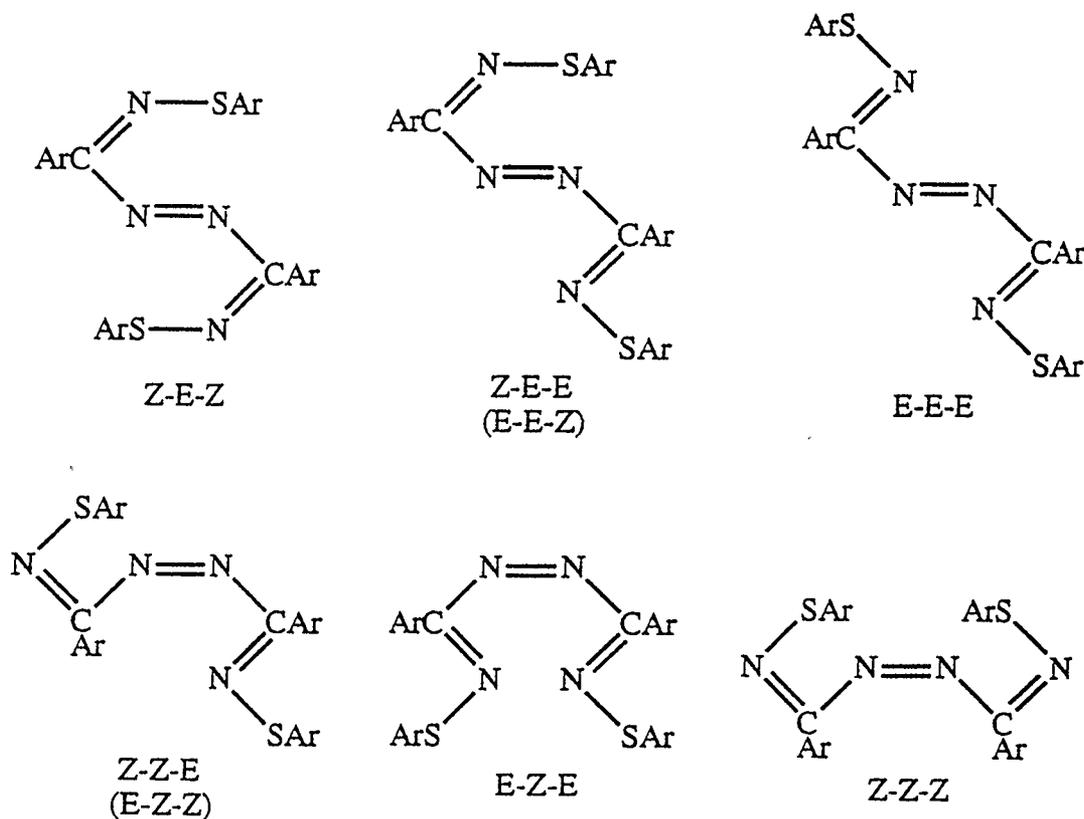


Figure 9: The six isomers of the sulfenylated diazene (49)
(Ar = 4-CH₃C₆H₄)

The crystal structure confirms that the *Z-E-Z* configuration was the actual isomer of (49) prepared. This is consistent with the structure of the known Se(II) diazene (*figure 3*).²³ This isomer was predicted, as the compound is expected to adopt this configuration as a consequence of intramolecular chalcogen-nitrogen interactions, which are observed in the selenium(II) system. The distance between S(1) and N(2)* is 2.607(10) Å, which is well within the sum of the van der Waals radii of sulfur and nitrogen (3.35 Å).²⁶ By comparison, the sulfonyl diazene, (46), has virtually no chalcogen-nitrogen interaction, as there is no electron donation available from the S(VI) centre. It is available for the S(II) case, however. As a result, the torsion angle about the S(II) diazene is only 10(1)°, which is similar to the selenium(II) diazene (*figure 3*) with $\Phi[\text{N-N-C-N}] = -3.4(5)^\circ$. The S(VI) diazene is twisted, again indicating that no intramolecular interactions are present.

Figure 8 is a packing diagram of the unit cell of compound (49). There are two important aspects of note here. First, one can clearly see the planarity of the actual molecules, and how they pack essentially in 'sheets'. However, also of interest, is the absence of any intermolecular interactions. The molecules are greater than 4 Å apart, so no chalcogen-nitrogen donation is present between different molecules.

Another important feature in the structure is the N=N bond length of 1.294(14) Å as compared to 1.263(4) Å for the Se(II) azo dye.²³ As seen in *figure 5*, typical N=N bond lengths in aromatic-substituted diazenes are 1.25 Å,⁶⁷ suggesting that the N=N bonds in (49) are slightly elongated. In distinct contrast, the S(VI) diazene (46) has an N=N bond length of only 1.20(1) Å, which is significantly shorter. Clearly,

in the sulfur(II) and selenium(II) azo dyes, the chalcogen-nitrogen $\pi \rightarrow \pi^*$ interaction (figure 10) results in a longer N=N bond length. Figure 10 displays the molecular orbital diagram for the S(II) diazene system.²⁴ The lone pair donation from the sulfur(II) system results in occupation of the b_g antibonding orbital. It is this interaction that causes elongation of the N=N bond.

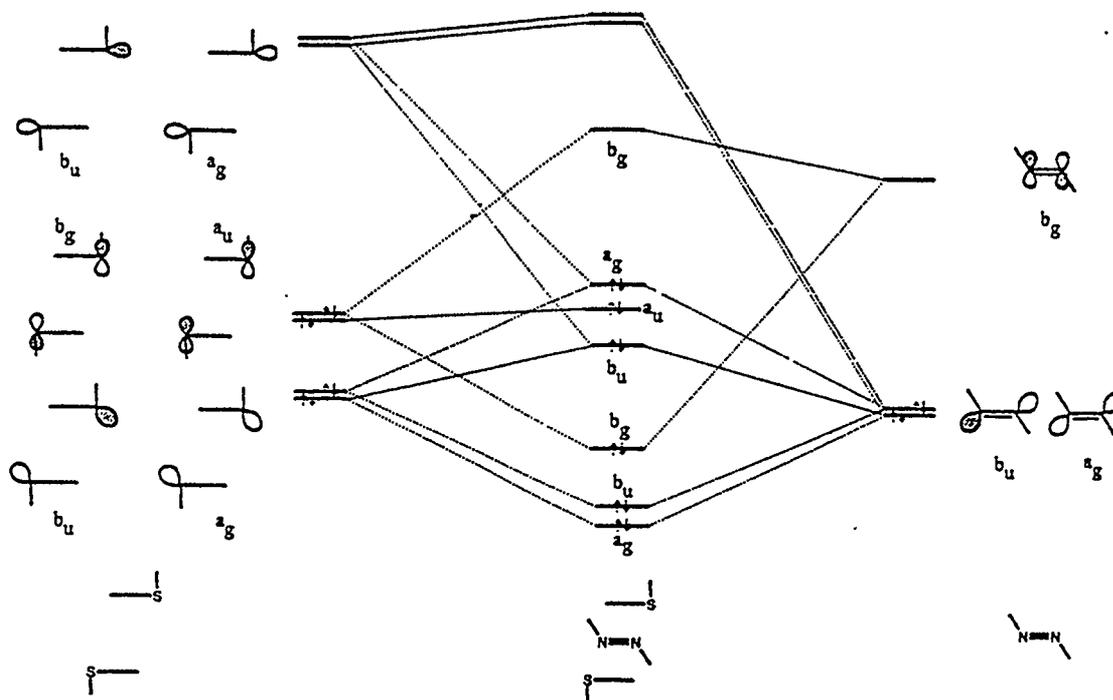


Figure 10: Orbital interaction diagram for the sulfur(II) diazene system

Significant delocalisation over the N=C-N=N-C=N backbone is not observed in (49). The C(8)-N(2) and C(8)-N(1) bond lengths are 1.415(11) Å and 1.303(11) Å, respectively. Typical C-N bond lengths are 1.47 Å, and C=N bond lengths are 1.30 Å,⁶⁵ suggesting that only modest delocalisation is present. This is consistent with the results obtained for both the selenium(II) azo dye (*figure 3*)²³ and the sulfur(VI) derivative (46) (see section 2.2.4 for additional details).

Very recently, other diazene products (*figures 11* and *12*) have been prepared in the Chivers group.^{72,73} These compounds appear to be kinetic products formed from the same type of reaction used to prepare diazenes (*figure 13*), namely the addition of arylchalcogenyl chloride to a trisilylated amidine. However, these products have adopted hitherto unknown conformations. They were obtained by varying reaction conditions and the substituents attached to the central carbon in the trisilylated amidine. For example, by using a trisilylated formamidine, I. Vargas-Baca has prepared a *Z-E-Z* product, (*figure 11*), which involves very weak sulfur-nitrogen interactions (2.83 Å).⁷² By using large halogenated substituents, P. Zoricak has prepared a *E-E-E* product (*figure 12*), as well as eight-membered rings, which are isomers of the more thermodynamically stable diazenes, and sixteen-membered rings.⁷³

T. Chivers, I. Vargas-Baca and T. Ziegler have shown by Density Functional Theory that the potential energies for these diazene compounds (*figures 11* and *12*) compounds are much higher than for the 'closed' diazene systems involving chalcogen-nitrogen interactions (*i.e.* azo dyes such as *figure 3* and 49) (*figure 14*).²⁴ It has been proposed that the *Z-E-Z* (or 'closed' diazene) isomers are the final thermodynamic

products of these reactions.

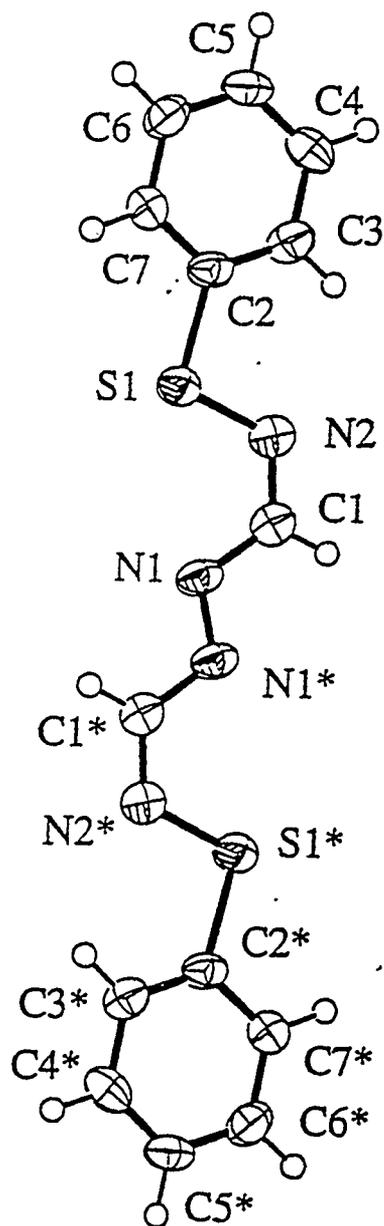


Figure 11: ORTEP of $C_6H_5SNCHN=NCHNSC_6H_5$ ⁷²

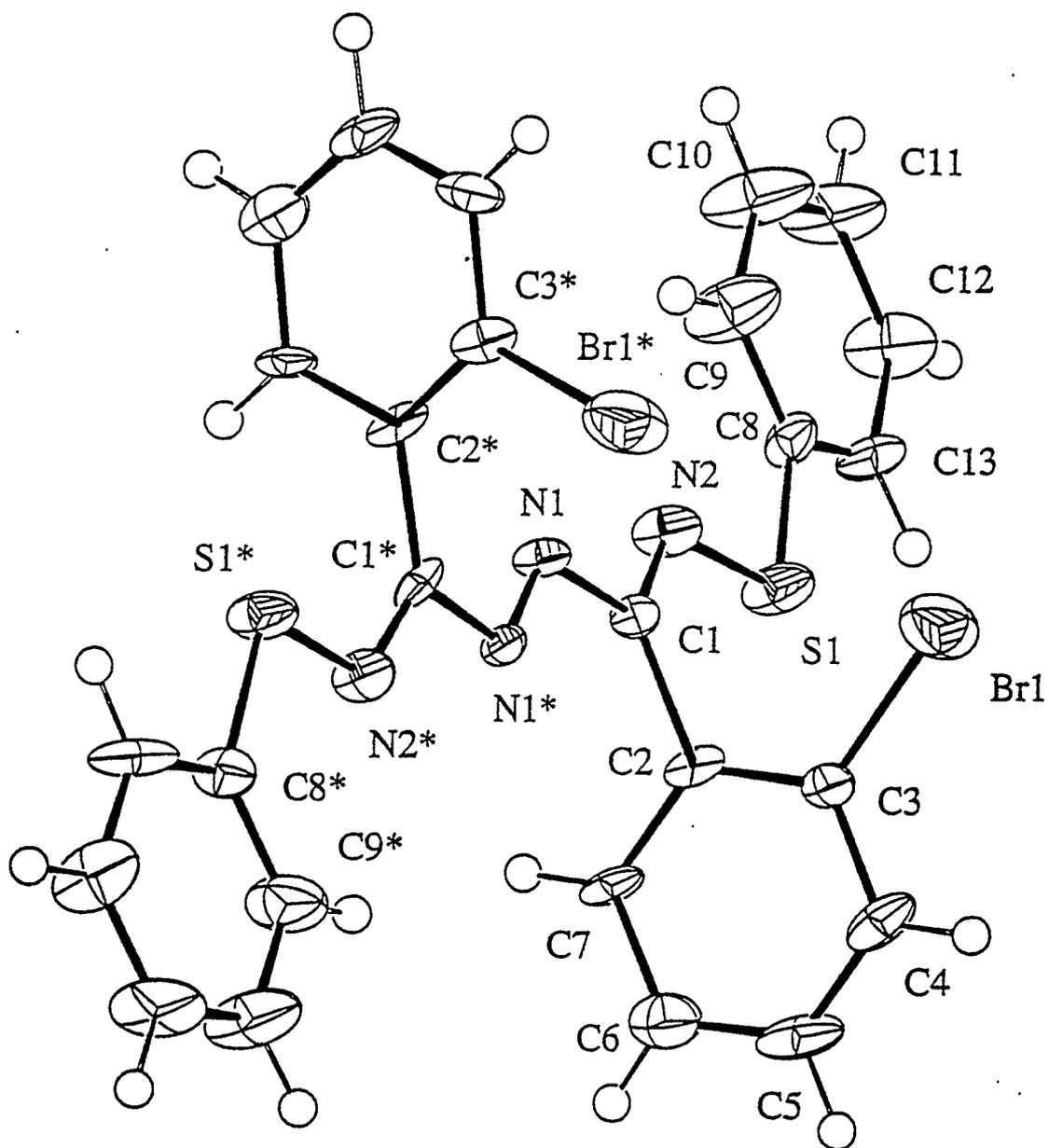


Figure 12: ORTEP of $C_6H_5SN(2-BrC_6H_4)CN=NC(2-BrC_6H_4)NSC_6H_5$ ⁷³

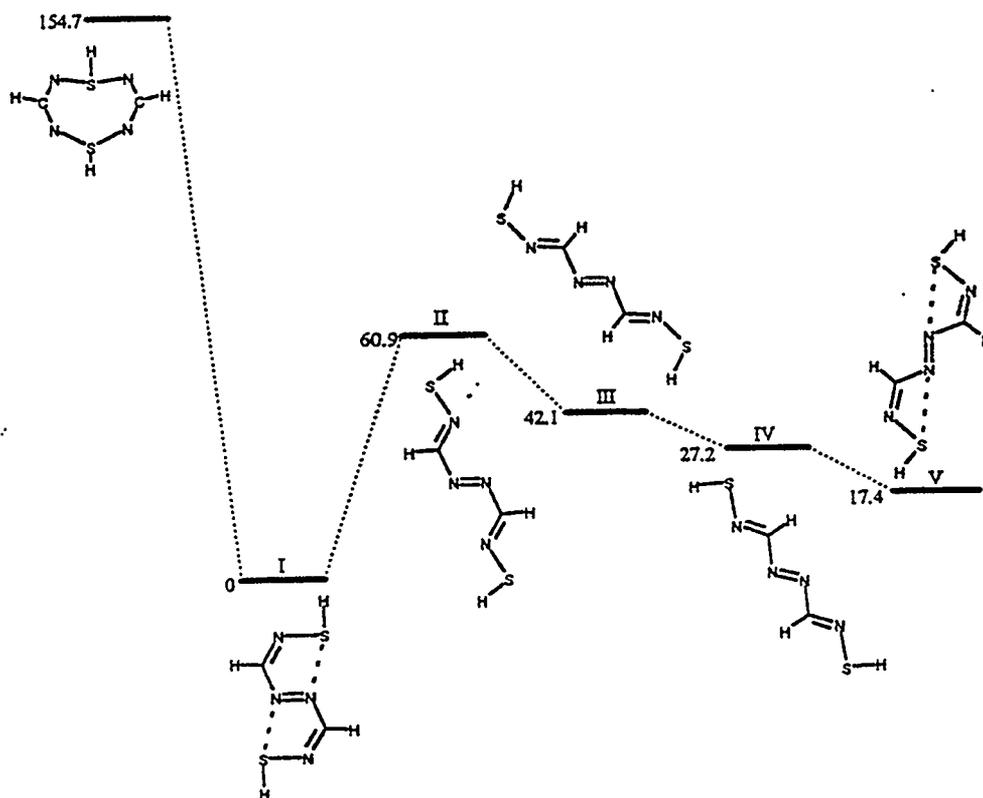


Figure 14: Calculated relative energies (kJ mol^{-1}) of $(\text{HS})\text{NC}(\text{H})\text{N}=\text{NC}(\text{H})\text{N}(\text{SH})$ isomers and the eight-membered ring $\text{HSN}_2\text{C}_2(\text{H})_2\text{N}_2\text{SH}$

From a structural viewpoint, the diazene shown in *figure 11* has a $\text{N}=\text{N}$ bond length of $1.254(8) \text{ \AA}$. This is in close agreement with average $\text{N}=\text{N}$ bond lengths in diazenes with aliphatic substituents (a typical molecule, *trans*-azomethane has an $\text{N}=\text{N}$ bond length of $1.254(3) \text{ \AA}$).⁶⁷ This suggests that a small sulfur-nitrogen interaction is occurring; in fact, the intramolecular distance between these atoms is 2.83 \AA . The difference of the chalcogen-nitrogen interaction distances could be because of the size of the rings. The 'closed' azo-dye type structure contains five-membered rings, whereas the formamidine-based compound in *figure 11* has four-membered moieties. This

molecule is virtually planar with a torsion angle $\Phi[\text{N}=\text{N}-\text{C}=\text{N}]$ of $179.2(6)^\circ$, and the planes defined by $\text{N}(1)^*-\text{C}(1)^*-\text{N}(2)^*$ and $\text{N}(1)-\text{C}(1)-\text{N}(2)$ are less than one degree out from each other.

The diazene shown in *figure 12* has a diazene $\text{N}=\text{N}$ bond length of $1.26(1) \text{ \AA}$. This is in good agreement with average $\text{N}=\text{N}$ bond lengths in aromatic-substituted diazenes (*figure 6*).⁶⁷ The bulky substituents appear to prevent the potential chalcogen-nitrogen interactions from occurring sterically, as these atoms are more than 3.60 \AA apart. With a $\Phi[\text{N}=\text{N}-\text{C}=\text{N}]$ of $173.8(7)^\circ$, the molecule is planar. The planes defined by $\text{N}(2)-\text{C}(1)-\text{C}(2)$ and $\text{N}(2)^*-\text{C}(1)^*-\text{C}(2)^*$ are less than 7° out from each other.

In summary, the differences between the known sulfur(II) diazenes and the sulfur(VI) diazene are marked and many. Whereas the S(II) molecules are all virtually planar, the S(VI) diazene is significantly twisted. The $\text{N}=\text{N}$ bond length in the sulfur(VI) diazene is notably shorter than typical diazene bond lengths, and any known S(II) diazene systems that have been discussed herein. As for the azo dye (49), it is significantly different from other known sulfur(II) diazenes. A pronounced chalcogen-nitrogen interaction is present, which clearly elongates the $\text{N}=\text{N}$ bond length. Potential energy calculations (*figure 14*) show that diazenes of this type appear to be the most thermodynamically stable isomers of the possible products that are available, and have been isolated thus far. Clearly, the potential number of products resulting from the addition of arylchalcogenyl halides to silylated amidine systems is considerable (*figure 13*), and the known characterised compounds have thus far only scratched the surface of this area of chemistry.

diazene. Suggested approaches for alternate syntheses of the sulfinyl systems are proposed in chapter 4.

3.3

CONCLUSIONS

Although a sulfinylated diazene system was not isolated, the unexpected formation and subsequent crystallographic characterisation of the sulfenyl azo dye (49) nevertheless helped to advance understanding of these novel chalcogen-nitrogen compounds. Sulfinylated derivatives (47 and 50) were also characterised. The analytical data and chemical properties obtained from these compounds may prove to be very useful for future work with these systems.

3.4 EXPERIMENTAL

3.4.1 GENERAL

Unless otherwise discussed, all instrumentation, reagents and solvents are the same as in chapter 2.

3.4.2 INSTRUMENTATION

No additional instrumentation was employed for the research in this chapter, other than that mentioned in section 2.4.2.

3.4.3 SOLVENTS

The only solvent used in this chapter other than the ones mentioned in section 2.4.3 was pentane (BDH). It was dried by distilling over sodium wire (obtained from Aldrich).

3.4.4 REAGENTS

In addition to reagents used in section 2.4.4, purified acetic acid was obtained from W. Cristofoli (obtained by distillation over anhydrous CrO_3). *p*-Toluene sulfinyl

chloride was prepared *in situ* following the method of Herrman *et al.*⁷¹

3.4.5

SYNTHESIS OF



To a clear colourless solution of 4-CH₃C₆H₄C(NSiMe₃)[N(SiMe₃)₂] (1.20 g, 3.42 mmol) in dichloromethane (25 mL), a dichloromethane (25 mL) solution of *p*-toluene sulfinyl chloride (4-CH₃C₆H₄SOCl) (0.48 mL, 0.60 g, 3.43 mmol) was added at -78°C. The solution immediately turned yellow. After stirring for one hour at room temperature, the solvent was removed *in vacuo* to give a semi-crystalline material (1.22 g, 2.93 mmol, 85.6%, based on an empirical formula C₂₁H₃₂N₂SOSi₂). Colourless crystals were grown from saturated pentane solutions; however handling of the product quickly resulted in hydrolysis. Based on NMR data, it was proposed that this compound is actually three distinct isomers (47a, b and c) all giving the same empirical formula (eq. 44). Because several of the resonances overlap in the proton spectrum, none of the structural isomers can be unambiguously identified. See section 3.2.1 for details.

3.4.6

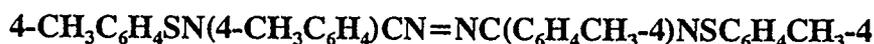
SYNTHESIS OF 4-CH₃C₆H₄C(NHSOC₆H₄CH₃-4)[NH]

To a clear, colourless solution of 4-CH₃C₆H₄C(NSiMe₃)[N(SiMe₃)₂] (1.34 g, 3.82 mmol) in dichloromethane (25 mL), *p*-toluene sulfinyl chloride

(0.55 mL, 0.667 g, 3.82 mmol) was added in a dichloromethane (25 mL) solution. After fifteen minutes of stirring, 0.07 mL of water in methanol (5 mL) was added via syringe. The solvent was then removed *in vacuo* to give a crude beige residue (0.95 g, 91.35% yield). The product was then recrystallised from methanol to give a very pure sample of (50), characterised by ¹H-NMR, elemental analysis and mass spectrometry (see section 3.2.2 for details).

3.4.7

SYNTHESIS OF



A clear, colourless dichloromethane solution (25 mL) of 4-CH₃C₆H₄C(NSiMe₃)[N(SiMe₃)₂], (42) (1.31 g, 3.74 mmol) was added to a dichloromethane solution (10 mL) of *p*-toluene sulfinyl chloride (0.654 g, 3.74 mmol) at -78°C. The *p*-toluene sulfinyl chloride had been prepared *in situ* prior to use.⁷¹ The reaction mixture was allowed to stir for one hour and then allowed to warm slowly to room temperature. Benzeneselenenyl chloride (1.43 g, 7.47 mmol) in dichloromethane (25 mL) was added slowly over a period of ten minutes at -78°C and allowed to stir for one hour at 23°C. The resultant mixture was evaporated *in vacuo* giving a purple residue. This residue was extracted with hexanes (2 x 30 mL) (1.07 g, 3.43 mmol Ph₂Se₂ removed) and pumped to dryness giving

4-CH₃C₆H₄SN(4-CH₃C₆H₄)CN=NC(C₆H₄CH₃-4)NSC₆H₄CH₃-4 as a purple solid (0.89g, 1.75 mmol, 93.7%). X-ray quality crystals were grown from a diethyl ether solution stored at -20°C for one week. Elemental analysis was in agreement with that based on the empirical formula C₃₀H₂₈N₄S₂. Calculated: C, 70.83%; H, 5.55% and N, 11.01%. Observed: C, 70.07%; H, 5.59% and N, 10.85%. UV-visible spectroscopy revealed a molar absorptivity of 1.79 x 10⁴ M⁻¹cm⁻¹ in dichloromethane at a maximum absorbance wavelength of 550 nm. The material was observed to melt at 112-114°C. Spectroscopic data for (49) are discussed in section 3.2.3.



Three equivalents of *p*-toluene sulfenyl chloride (0.746 g, 4.70 mmol) were added to a clear, colourless solution of (42) (0.55 g, 1.57 mmol) at -78°C in dichloromethane (25 mL). The resulting purple solution was allowed to stir for one hour at 23°C, and subsequent removal of solvent *in vacuo* was performed. The theoretical combined yield of diazene (49) and di-*p*-tolyl disulfide was 0.79 g. The crude yield was found to be 0.80 g. The disulfide was then extracted with pentane. The remaining diazene weighed 0.28 g (0.55 mmol, 71.8%) and the pentane-soluble extractions were 0.30 g (1.22 mmol, 75%). The diazene product was shown by ¹H-NMR and FAB-MS to be identical to (49).

CHAPTER FOUR

CONCLUSIONS AND FUTURE WORK

4.1 GENERAL CONCLUSIONS

Addressing the objectives presented in section 1.3, new diazene compounds have been prepared. A sulfonylated diazene, (46), $\text{H}_3\text{CSO}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-}4)\text{NSO}_2\text{CH}_3$, was prepared and fully characterised. It was found to have a *Z-E-Z* structure about its three double bonds, and was observed to be a twisted molecule.

In the attempts to synthesise a similar compound containing a S(IV) moiety, a sulfenylated azo dye $4\text{-CH}_3\text{C}_6\text{H}_4\text{SN}(4\text{-CH}_3\text{C}_6\text{H}_4)\text{CN}=\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-}4)\text{NSC}_6\text{H}_4\text{CH}_3\text{-}4$, (49), was produced unexpectedly. The subsequent characterisation of these compounds has illuminated and clarified certain aspects of their structure and bonding. The nature of the N=N bond is found to be affected by weak chalcogen-nitrogen interactions in most S(II) and Se(II) systems, however, no such interaction is observed for the one S(VI) system that is now known. Whereas all known S(II) and Se(II) systems prepared from the addition of arylchalcogenyl chloride to silylated amidine systems appear to be relatively planar, the corresponding S(VI) system is notably twisted.

Calculations by I. Vargas-Baca have shown that the 'closed' diazene isomer is the most thermodynamically stable product of reactions of this type.²⁴ Several other products have been prepared from the trisilylated amidine-PhSCl system (*figure 13*). Eight-

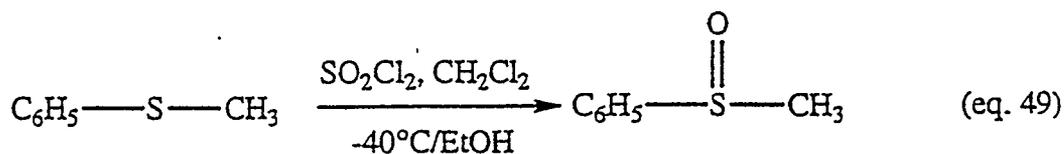
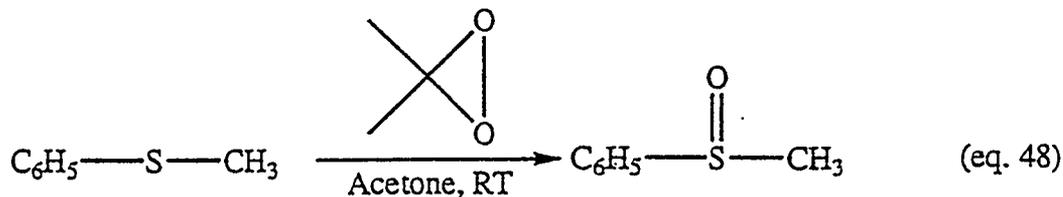
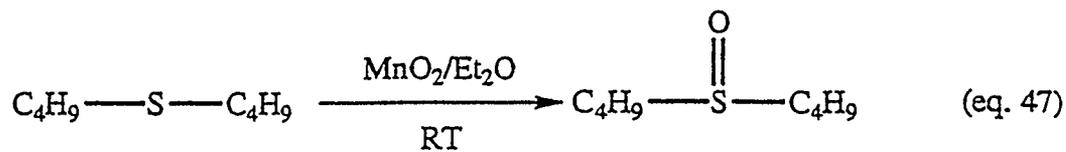
membered rings, sixteen-membered macrocycles and different conformational isomers of the diazenes have all been isolated (see section 3.2.4 for some well-characterised examples).⁷²⁻⁷⁴ Clearly, the molecules characterised and discussed herein represent only a few of the possible products that are available. One immediately apparent extension of this project would be to attempt to isolate other possible products from these reactions. By adjusting the reaction conditions (*e.g.* temperature, concentration, reaction times, *etc.*) one could conceivably prepare other isomers of these diazenes, employing the same repeating unit. For example, in the case of the S(VI) system, the basic unit would be a $\text{H}_3\text{CSO}_2\text{NC}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{N}$ moiety. The possibility for the preparation of oligomers or polymers is present. Perhaps, even asymmetric compounds could be generated (all the compounds isolated thus far have a centre of inversion). For S(II) systems, cyclic products of repeating units have been isolated, and by applying different reaction conditions or techniques, perhaps larger oligomers and polymers can be prepared.

The secondary objective concerned the derivatives and precursors to the diazenes prepared. These compounds have the potential to serve as building blocks for new molecules. The monosubstituted benzamidine systems such as (43) and (47) have wide applications in several different types of reactions. In fact, these systems have been used in preliminary studies for the preparation of polymers (see section 4.3). Other extensions of this project are also discussed.

4.2 PREPARATION OF A SULFINYLATED DIAZENE

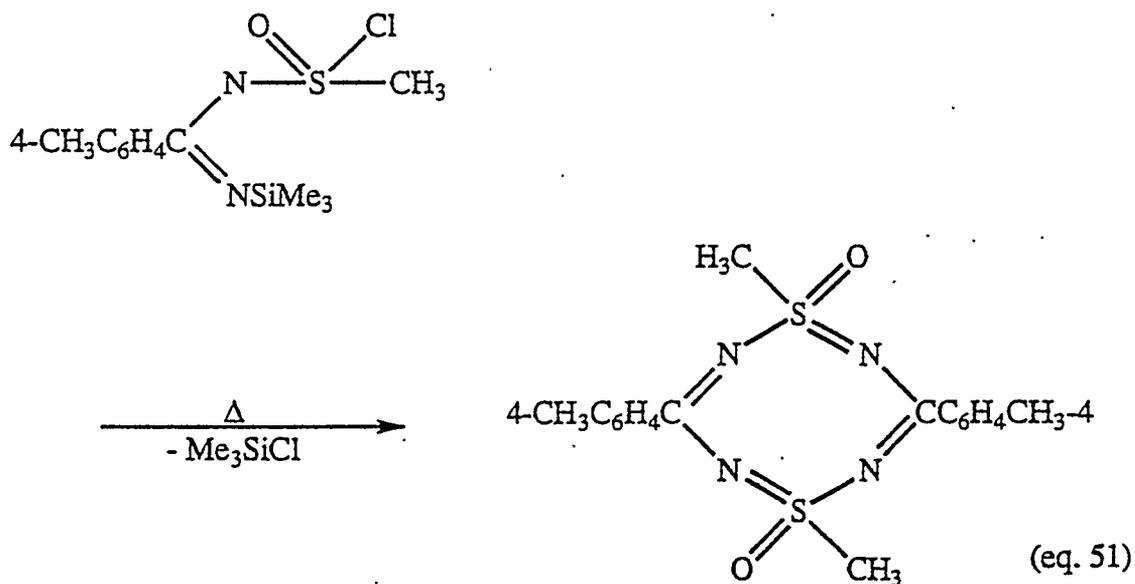
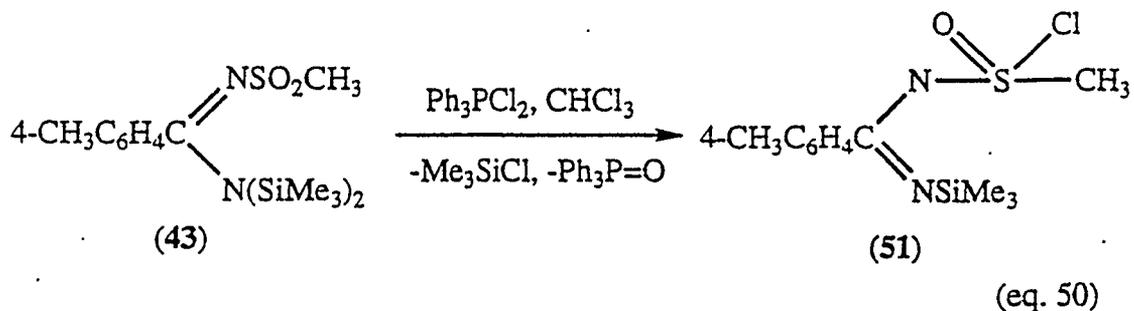
The preparation of a S(IV) analogue of the diazene system was not successful in this thesis. A direct route reproducibly gave a sulfenylated product. As discussed in section 3.2.5, it is not known why the oxygens are lost, but loss during workup was proposed.

Assuming the preparation of a sulfinylated diazene cannot be achieved directly, it may be possible to mildly oxidise a S(II)-containing diazene to produce the desired compound. There are many ways used regularly in organic chemistry to achieve such an oxidation;⁷⁵ however, one must consider a reagent that will not attack the diazene bond itself. It is suggested that any water-based approach should be avoided to deter any hydrolysis of S-N linkages. Equation 47 involves the addition of MnO_2 in petroleum ether. This mild oxidation has been observed to give a 71% sulfoxide product exclusively.⁷⁶ Using dioxirane, 65% exclusive sulfoxide product was observed in eq. 48.⁷⁷ In equation 49, a 95% synthesis of the sulfoxide product was achieved.⁷⁸ All three of these methods promote exclusive sulfoxidation. This is advantageous, because if a sulfone is produced as a side-product, separation of the compounds may prove difficult.

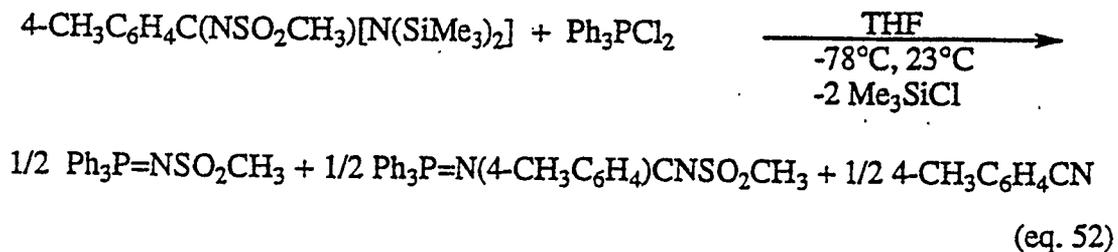


**4.3 EMPLOYING A MONOSUBSTITUTED BENZAMIDINE
4-CH₃C₆H₄C(NSO₂CH₃)[N(SiMe₃)₂] AS A PRECURSOR
TO POLYMERS**

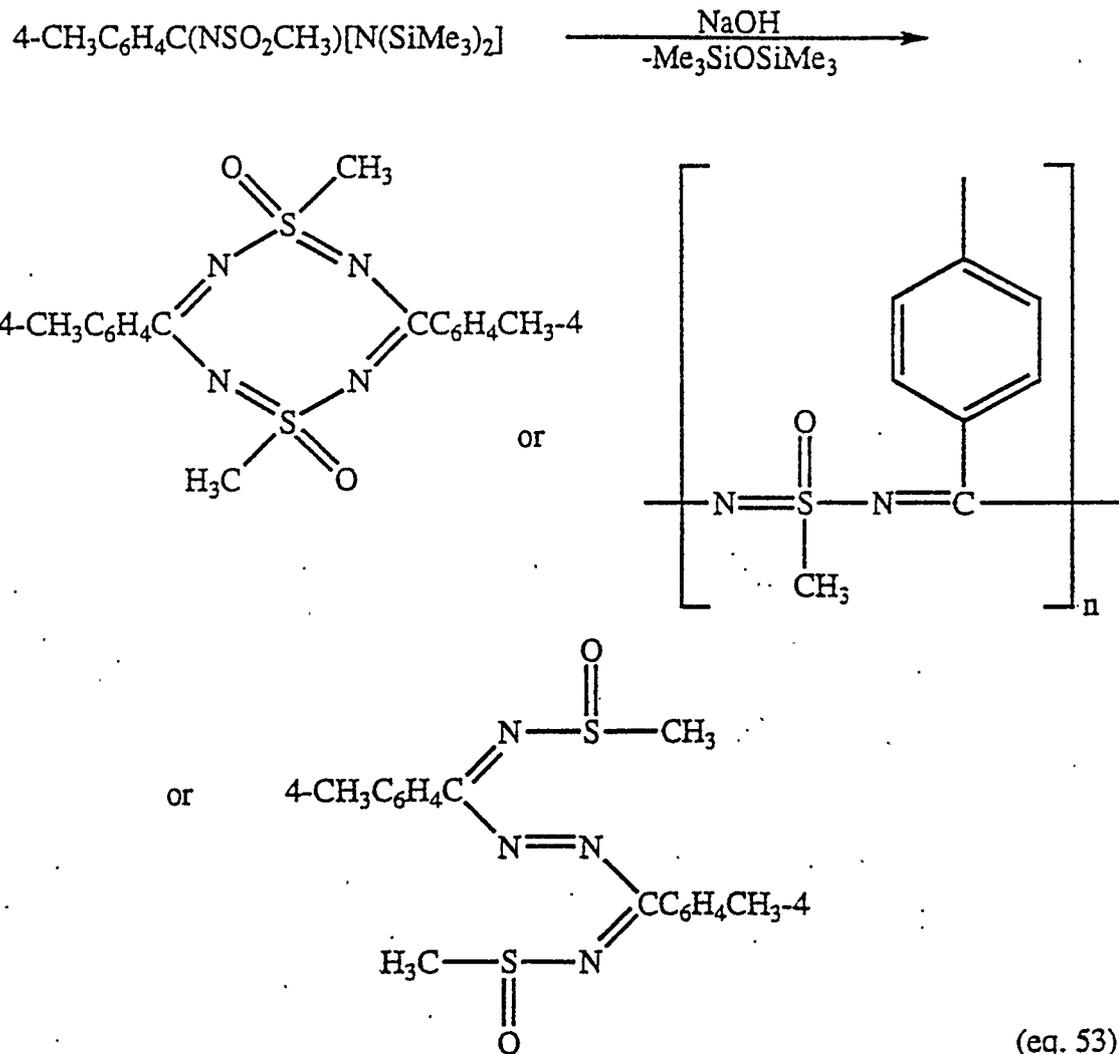
Upon characterisation and isolation of monosubstituted benzamidines such as (43) and (47), the potential for using them as polymer precursors was evaluated.⁶⁴ Specific attention was given to the monosulfonylated derivative, (43). Drawing upon the work of Roy *et al.*,⁷⁹ it was hypothesised that sulfonimidoyl chloride derivatives such as (51) could be prepared. Thermally induced elimination of Me₃SiCl from such compounds could produce heterocycles, oligomers or, perhaps, polymers (eq. 51 is an example of the production of a heterocycle).



Equation 50 has been investigated,⁶⁴ but the desired result did not occur. Triphenylphosphine appears to have a greater affinity for the amino nitrogen than for an oxygen atom in (43). As a result, in contrast to the observations of Roy,⁷⁹ the phosphinimines $\text{Ph}_3\text{PNSO}_2\text{CH}_3$ and $\text{Ph}_3\text{PNC}(\text{NSO}_2\text{CH}_3)(\text{C}_6\text{H}_4\text{CH}_3\text{-4})$ are formed (eq. 52).



Another possibility for using derivatives of type (43) as polymer precursors is to attempt a base catalysis. This approach is useful for the promotion of the elimination of *bis*(trimethyl)siloxane. It was used by Regitz *et al.* as a step in the preparation of phosphalkynes, via the elimination of $(\text{SiMe}_3)_2\text{O}$ from an acylated *bis*(trimethylsilyl)phosphino centre.⁸⁰ It may yield a ring system, oligomers or polymers based on the repeating unit $(4\text{-CH}_3\text{C}_6\text{H}_4\text{CNS}(\text{CH}_3)(\text{O})\text{N})$. It may even produce the corresponding sulfinyl azo dye.



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