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TRIMETHYLSILYLDIAZOMETHANE

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1. INTRODUCTION

The instability and toxicity of diazomethane are hazards which demand extreme caution and the implementation of extra safety measures during its use.[1] On the other hand, trimethylsilyldiazomethane **1** exhibits none of these hazards. It is a liquid which is stable enough to be distilled at atmospheric pressure and handled as one would treat any "normal" organic compound. Its stability is attributed to the presence of the silicon atom on the carbon α to the diazo group resulting in dπ-pπ resonance. Its preparation was first reported in 1967,[2] however, only a few reports of its applications to synthetic organic chemistry as a safe substitute for diazomethane appeared during the following decade. A brief review was published in 1985[3] and Japanese language reviews appeared in 1984[4] and 1986.[5] This review attempts to provide a comprehensive coverage and shows that in most cases **1** can be succesfully substituted for diazomethane and often provides advantages in addition to those of greater safety.

2. PROPERTIES

In contrast to the gaseous diazomethane, **1** is a greenish-yellow liquid, bp 96°C at 775 mm Hg, and refractive index 1.4362 at 25°C. It is soluble in most organic solvents. It is unaffected by neutral water and 20% aqueous potassium hydroxide. It is stable both as a neat liquid and in hydrocarbon solution, but decomposes rapidly on exposure to light.[6]

The stretching vibration of the diazo group in **1** is at a shorter wavelength (2070 cm^{-1}) than alkyl- and aryl-diazomethanes (2049–2020 cm^{-1}). This has been attributed to increased contribution of the resonance structure **2** as a result of carbon–silicon dπ-pπ overlap stabilizing the charge on the carbon adjacent to the silicon atom.[6]

$$(CH_3)_3Si\overset{-}{C}H\text{-}\overset{+}{N}{\equiv}N$$

2

The chemical shift of the proton α to the diazo group in **1** is 2.23 ppm (s) and that of the trimethylsilyl protons is –0.02 ppm (s) in benzene.[6] The former is observed at a higher field than that of other diazomethanes and of *cis-* and *trans-*1,2-bis(trimethylsilyl)ethylene, reinforcing the argument for increased contribution of the resonance structure **2**.

The ^{13}C NMR spectrum of **1** was reported as part of a study of the organometallic diazoalkanes of the main group elements.[7] The chemical shifts reported are –1.6 ppm (methyl on silicon) and 19.1 ppm (diazo carbon).

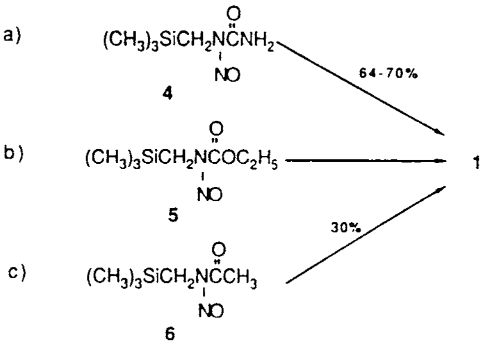
In the UV spectrum, **1** shows absorption at [nm (log ε)] 238(4.00), 402(1.36), 412(1.30), infl.[6]

3. PREPARATION

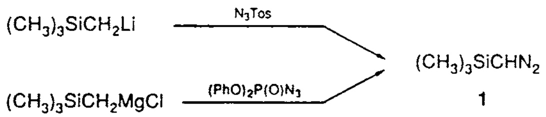
The first reported preparation of **1** was by the reaction of diazomethyllithium **3** with trimethylchlorosilane,[2] a less convenient procedure than methods reported later.

$$\underset{\mathbf{3}}{Li[CHN_2]} \quad + \quad (CH_3)_3SiCl \longrightarrow \underset{\mathbf{1}}{(CH_3)_3SiCHN_2}$$

Other methods generally fall into three main categories: (a) reaction of a base with N-nitroso derivatives; (b) reaction of organometallic derivatives of chloromethyltrimethylsilane with a diazo transfer reagent; and (c) preparations starting from diazomethane. Of the first category, the use of N-nitroso-N-(trimethylsilylmethyl)urea **4** is preferred over ethyl N-nitroso-N-(trimethylsilylmethyl)urethane **5**, giving yields of 64% (in solution) and 70% (neat) from **4**, although the product in both cases is contaminated with hexamethyldisiloxane.[6] In most applications the latter is merely an inert diluent and its presence can be tolerated. A lower yield (30%) is obtained from N-nitroso-N-(trimethylsilylmethyl)acetamide **6**.[8] The N-nitroso precursors for these procedures are themselves prepared by multistep syntheses giving much lower overall yields of **1** from readily available starting materials.



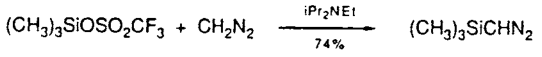
Methods which use a diazo transfer reagent are more convenient as starting materials are often commercially available. Reaction of trimethylsilylmethyllithium with tosyl azide as the diazo transfer reagent gives **1** in 38% yield (unoptimized).[9] Greatly improved yields (85%) are obtained by using diphenylphosphoryl azide as the diazo transfer reagent and the Grignard reagent of chloromethyltrimethylsilane.[10]



$$(CH_3)_3SiCH_2Li \xrightarrow{N_3Tos} (CH_3)_3SiCHN_2 \xleftarrow{(PhO)_2P(O)N_3} (CH_3)_3SiCH_2MgCl$$

1

For those not seeking to avoid the use of diazomethane, a preparation of **1** by simply mixing diazomethane with trimethylsilyl triflate in the presence of diisopropylethylamine as a proton scavenger has been reported to give a 74% yield.[11]



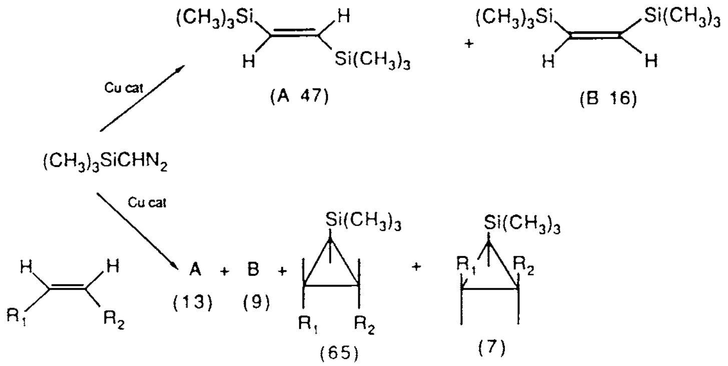
$$(CH_3)_3SiOSO_2CF_3 + CH_2N_2 \xrightarrow[74\%]{iPr_2NEt} (CH_3)_3SiCHN_2$$

1

4. REACTIONS

4.1. Carbene Chemistry

Copper catalyzed decomposition of **1** in benzene is an exothermic reaction giving a mixture of *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene in a ratio of 1 : 2.9, respectively. In the presence of olefins cyclopropane derivatives are obtained in addition to the dimers.[6] Copper(I) chloride catalysis in the presence of cyclohexene gives the dimers in a *cis* : *trans* ratio of 1 : 1.4 and the cyclopropane derivatives in a *syn* : *anti* ratio of 1 : 10.9. The product distribution is unaffected by changes in the ratio of **1** : CuCl. However, different copper catalysts produce

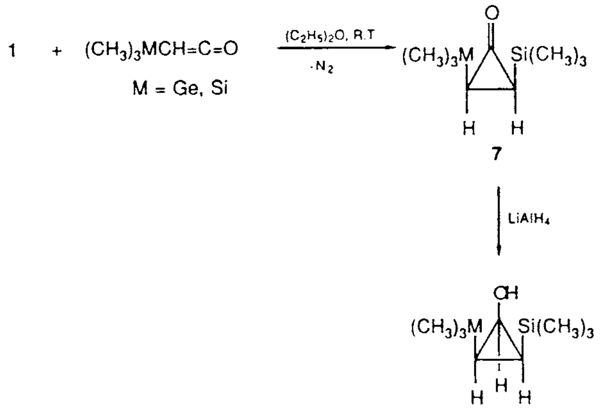


varying yields and ratios of the products.[6] The structure of the olefin also affects the product distribution. With increasing substitution at the olefinic carbons decreasing yields of cyclopropanes result[6,12] to the extent that 2,3-dimethylbut-2-ene gives none of the cyclopropane.[12]

The formation of trimethylsilylcyclopropanes by photolysis of **1** in the presence of olefins is stereospecific, indicating formation of the carbene in the singlet state.[12] In the presence of ethylene a 17% yield of the cyclopropane is obtained along with a 30% yield of the *trans*-dimer. With *trans*-but-2-ene a 23% yield of the cyclopropane and a 61% yield of the *trans*-dimer results. As with the copper catalyzed reaction, 2,3-dimethylbut-2-ene and **1** gives no cyclopropane under photolysis conditions.[12]

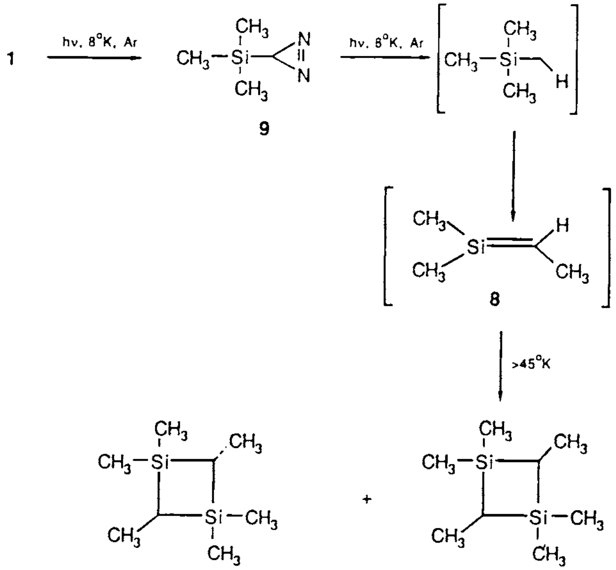
As a synthetic method for the synthesis of silylcyclopropanes, pyrolysis or photolysis of **1** in the presence of olefins is less attractive than the use of lithium 2,2,6,6-tetramethylpiperidide/(chloromethyl)trimethylsilane because of the lower yields obtained and the formation of by-products. An exception to this is the reaction of 1,4-dihydronaphthalene, which with the latter reagent gives insertion products, whereas the expected cyclopropane is obtained by the pyrolysis of **1**.[13]

Reaction of (trimethylsilyl)- and (trimethylgermyl)ketene with **1** at room temperature gives a 64% yield of the corresponding cyclopropanones **7**.[14] It is interesting to note that when diazomethane is reacted with the ketene, low temperatures (–78°C) are necessary to avoid the initiation of polymerization and further reaction of the product **7** to form silacyclobutanones. Reaction of the product cyclopropanones with nucleophiles is highly stereoselective and NMR analysis of these reaction products is used to establish the configuration of the cyclopropanones **7** as the (Z)-isomers.

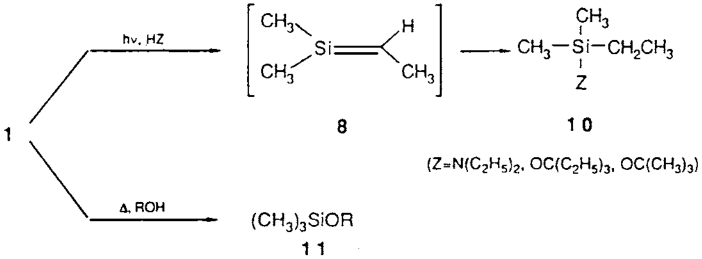


Other studies on the photolysis and thermolysis of **1** reveal its marked ability to undergo methyl migration to form the transient silene species, 2-methyl-2-sila-

2-butene **8**. The existence of **8** resulting from the pyrolysis of **1** at 440°C is demonstrated by (a) trapping experiments with 2-propanol and benzaldehyde, (b) the presence of products from its further reaction, and (c) by a study of 1-deuteriotrimethylsilyldiazomethane.[15] Irradiation of **1** matrix isolated in argon at 8°K produces trimethylsilyldiazirine **9** which on continued irradiation gives **8** which was characterized spectroscopically[16,17,18,19]. Above 45°K **8** dimerizes to the *cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes.



In the presence of alcohols and amines, photolysis of **1** produces **10**, providing additional evidence for the methyl migration previously discussed[15,20]. Results indicate preferential migration of the methyl group over phenyl. Nonphotolytic thermolysis of **1** in the presence of alcohols gives cleavage product **11**, the reaction occurring by ionic attack on the silicon atom of **1** by the alcohol.[20]



Liquid phase irradiation of **1** in the presence of trimethylsilane results in insertion of the carbene into the Si–H bond to give bis(trimethylsilyl)methane. No products from C–H insertion nor from the dimerization of the carbene are detected.[12]

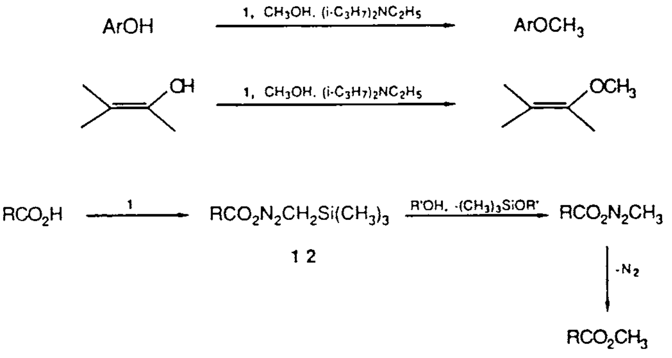
The carbene generated by the WCl_6 initiated decomposition of **1** is found to be a less effective initiator for the polymerization of cyclopentene than the carbenes generated from diphenyldiazomethane and ethyl diazoacetate.[21]

4.2. Other One Carbon Insertion Reactions

4.2.1. Ethers and Esters

Insertion of a one carbon unit into the O–H bond of phenols and enols occurs with **1** to give good yields of the corresponding methyl ethers.[22] The reaction is applicable to a wide variety of substrates. The alcoholic hydroxyl and ketone functionalities in 4-hydroxybenzyl alcohol and estrone remain unchanged. Substrates containing enolizable ketones react to give the corresponding methyl enol ethers. 8-Hydroxyquinoline gives the anticipated product with **1** whereas with diazomethane 1-methyl-8-hydroxyquinolinium betaine is the primary product. The presence of methanol and N,N-diisopropylethylamine are necessary for the reaction to occur.

Carboxylic acids in a methanol-benzene solution at room temperature react with **1** to give, in most cases, quantitative yields of the corresponding methyl esters (a 42% yield of the ester of 1-phenylalanine is obtained).[23] A wide variety of substrates respond to this treatment. Under these reaction conditions other functionalities, such as the phenolic hydroxyl in salicylic acid, the keto group in 1-ketoglutaric acid and the hydroxyl in cholic acid survive unchanged. Reactions are conveniently carried out at room temperature and avoid the hazards associated with the use of diazomethane in analogous procedures. The mechanism of esterification is proposed to go by the diazonium salt **12**.

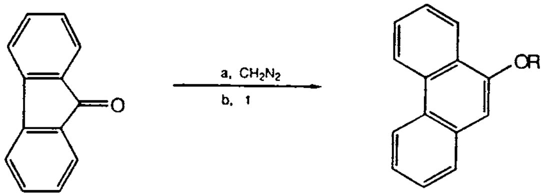


4.2.2. Homologation of Ketones

Acyclic and cyclic ketones react with **1** to give the corresponding homologous products.[24] The presence of one equivalent of boron trifluoride etherate is necessary for the reaction to proceed. The solvent is also important, methylene chloride being the solvent of choice.

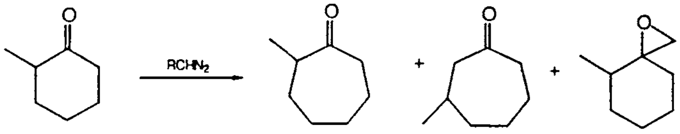
$$RCOR' \xrightarrow[CH_2Cl_2,\ -10°C,\ 2\ hr]{1,\ BF_3O(C_2H_5)_2} RCOCH_2R'$$

Comparison of **1** with the use of diazomethane in this reaction shows several advantages, not the least being higher yields where data is available for comparison. The reaction is also more efficient, for instance in the reaction of 9-fluorenone **13** diazomethane gives predominantly secondary insertion products **14a**, whereas **1** gives the primary insertion product **14b**.



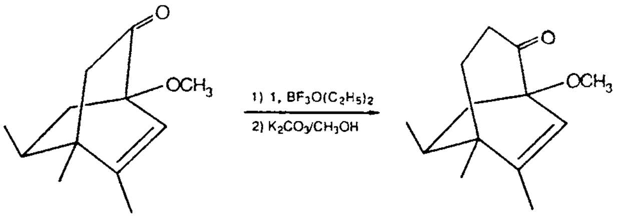
13 14 a, $R=CH_3$ b, $R=H$

Furthermore, **1** shows high regioselectivity, for example 2-methylcyclohexanone **15** gives predominantly 2-methylcycloheptanone **16** with **1**, whereas diazomethane gives a mixture of **16**, 3-methylcycloheptanone **17** and the epoxy derivative **18**. This regioselectivity of the methylene insertion reaction of **1** is presumably due to its bulky trimethylsilyl group.



15		16	17	18
	R = H	10%	7%	26%
	R = Me_3Si	69%		

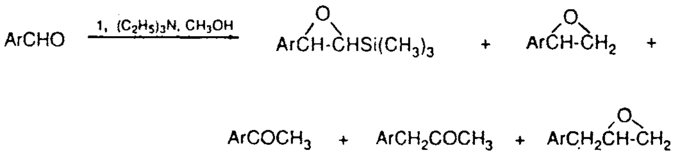
This ring expansion reaction has been applied to the total synthesis of pinguisane-type sesquiterpenes in which the bicyclooctenone **19** is ring-enlarged to **20**.[25]



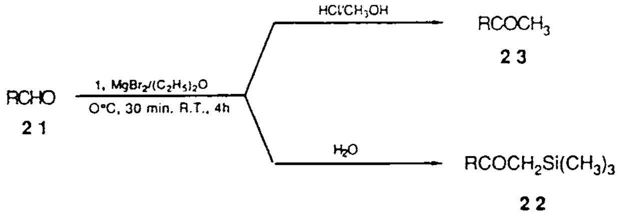
19 **20**

4.2.3. *Conversion of Aldehydes to Homologous Compounds*

Aromatic aldehydes react with **1** in the presence of triethylamine and methanol to give a mixture of homologous epoxides and ketones.[26] The composition of the product mixture is dependent on the reaction solvent and the substituents on the aromatic ring. The lack of selectivity in this reaction limits its use as a synthetic method.



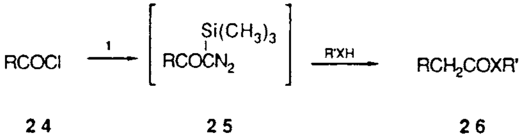
In contrast, aliphatic aldehydes **21** can be converted in a one-pot reaction in moderate yields to pure homologous methyl ketones **22** by reaction with **1** in the presence of magnesium bromide followed by workup with 10% hydrochloric acid/methanol. If desired the corresponding trimethylsilylmethyl ketone **23** can be isolated by using an aqueous workup procedure.[27]



A variety of substrates including primary, secondary, and tertiary aldehydes undergo this reaction. A keto aldehyde (**21**, R = $C_6H_{13}COCH_2CH_2$) undergoes this reaction leaving the original keto group intact.

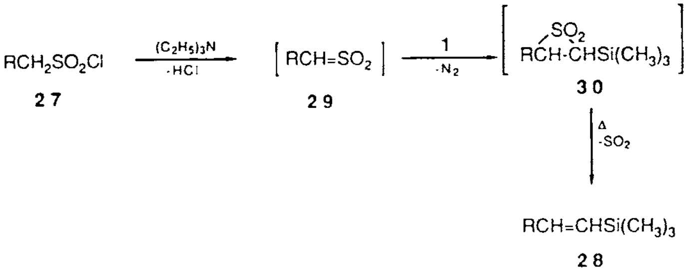
4.2.4. Homologation of Acids

The Arndt-Eistert synthesis, a method for converting carboxylic acids to their homologs via the acid chlorides **24**, is another synthetically important reaction which involves the use of the hazardous diazomethane. Substitution of diazomethane with **1** in this application affords the same products without the associated hazards.[28] In a one-pot system aromatic acid chlorides form the acyl derivatives **25** of **1** in the presence of a base at low temperature. However, aliphatic and alicyclic acid chlorides require two equivalents of **1** and the absence of base. Acetonitrile and tetrahydrofuran (THF), or mixtures thereof, are the preferred solvents. After the formation of the acyl derivative **25** addition of a nucleophile followed by heating to 180°C effects the Wolff rearrangement to the corresponding ester **26** in good yield. Various nucleophiles can be used succesfully in this reaction.



4.2.5. Preparation of Vinylsilanes from Alkanesulfonyl Chlorides

Another example of the use of **1** as a one carbon transfer reagent is the preparation of vinyl silanes **28** from alkanesulfonyl chlorides **27**.[29] This reaction provides good yields at temperatures between 0°C and –70°C in the presence of triethylamine (a strong base is necessary) in THF. The product is either pure (E)-isomer or an E/Z mixture in which the (E)-isomer predominates. This may be due to concomitant isomerization of Z to E. The reaction proceeds via generation of the sulfene **29** followed by formation of the episulfone **30** and extrusion of SO_2.

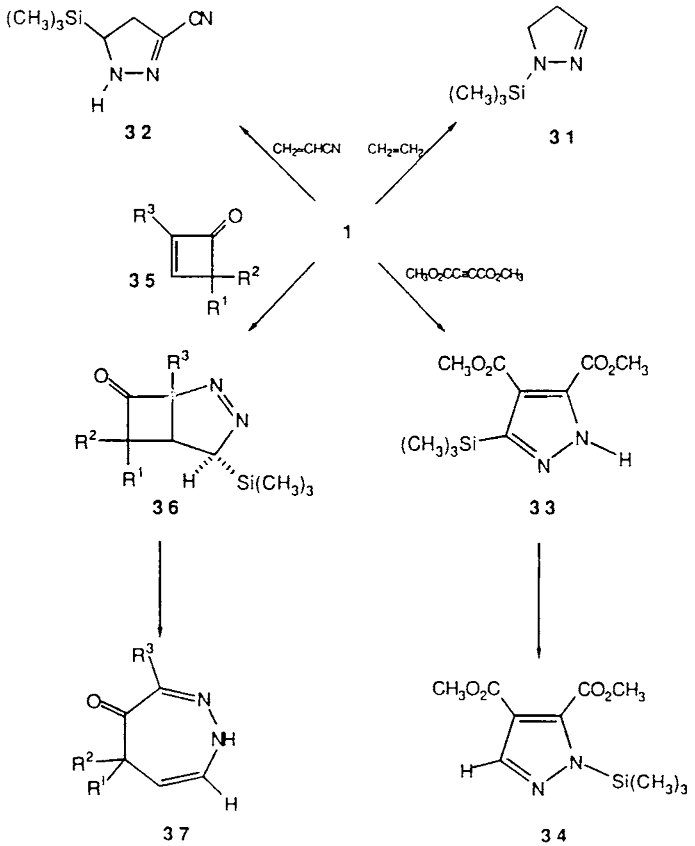


The starting alkanesulfonyl chlorides are readily obtained from alkyl chlorides by reaction with sodium thiosulfate followed by chlorination. This method therefore provides a three-step procedure for converting alkyl chlorides to vinylsilanes.

4.3. 1,3-Dipolar Addition Reactions

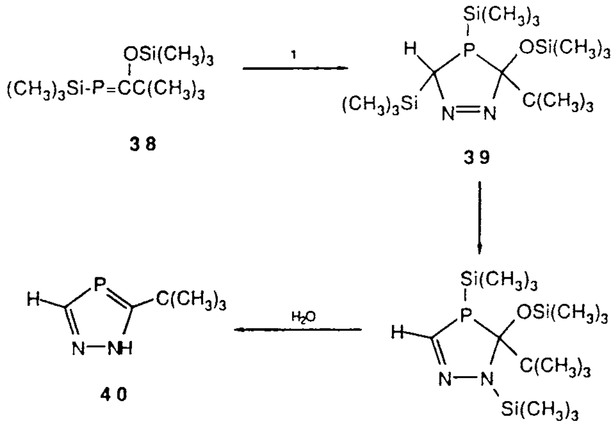
The 1,3-dipolar addition reactions of **1** provide an entry to a series of five-membered heterocycles. An important characteristic of this chemistry is the propensity of the trimethylsilyl group to undergo migration from carbon to nitrogen.

With the unactivated olefin, ethylene, the cycloaddition reaction of **1** requires 13 days at 55°C to complete.[30] The product is 1-trimethylsilyl-2-pyrazoline **31** which is formed by a 1,3-silyl shift. Activated 1,3-dipolarophiles react more readily; for instance, acrylonitrile gives the hydrolytically unstable adduct **32**.[6,31] Dimethyl acetylenedicarboxylate gives product **33** which is also believed to undergo the 1,3-silyl migration to form **34**.[31]

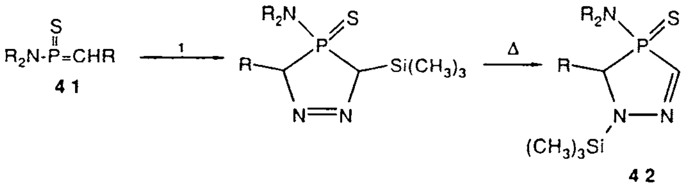


With some dipolarophiles, for example phenyl isothiocyanate, phenyl isocyanate, and carbon disulfide, **1** reacts with loss of nitrogen.[31] Addition to the cyclobutenone **35** gives the pyrazoline **36**. Desilylation of this product with methanol causes isomerization to the dihydrodiazotropenone **37**.[32]

A series of 1,3-dipolar addition reactions of **1** to organophosphorus compounds show a similar pattern of silyl group migrations. The phosphaalkene **38** reacts with **1** to produce the dihydrodiazophosphole **39** which undergoes the 1,3-silyl shift. Subsequent desilylation and hydrolysis affords the 1,2,4-diazophosphole **40**.[33]

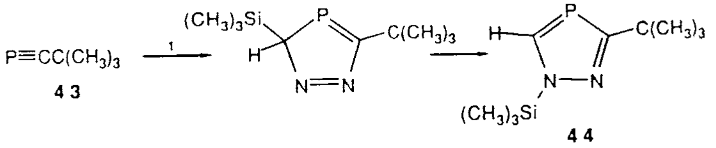


The substituted phosphaalkene **41** undergoes similar chemistry involving a 1,3-silyl shift to form the diazaphospholine **42**.[34]



The reaction product of **1** with the phosphaalkyne **43** undergoes a 1,5-silyl migration to give the 1,2,4-diazaphosphole **44**.[35]

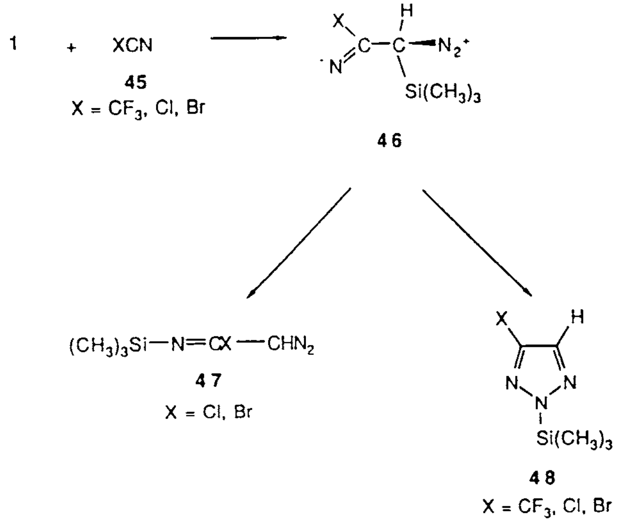
(Additional 1,3-dipolar cycloaddition reactions of **1** are discussed in Section 6.1.)



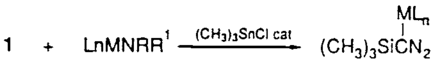
4.4. Miscellaneous Reactions

The reaction of **1** with trifluoroacetonitrile and cyanogen halides gives 1,2,3-triazoles **48**. Although these may be formed by a 1,3-dipolar addition mechanism, the presence of isomeric diazo-substituted imines **47** in the reaction product from the cyanogen halides suggest a mechanism involving nucleophilic attack by the diazoalkane on the nitrile carbon to afford intermediate **46**. Ring closure, followed by trimethylsilyl migration, would give the 1,2,3-triazole or rearrangement by nucleophilic attack of nitrogen on silicon would give **47**.[36]

(The preparation of 1,2,3-triazoles from lithium trimethylsilyldiazomethane is described in Section 5.3.2.)



Reaction of **1** with metal amides gives the metallated derivatives **49**.[37]



$$1 + \mathrm{LnMNRR^1} \xrightarrow{(CH_3)_3SnCl\ cat} (CH_3)_3Si\overset{ML_n}{\overset{|}{C}}N_2$$

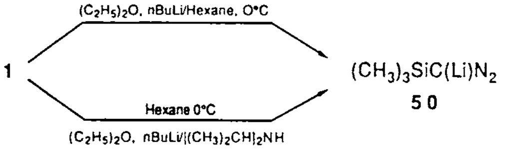
49

M = Sn, Pb, Sb, Bi, As

$L_n = (CH_3)_3$

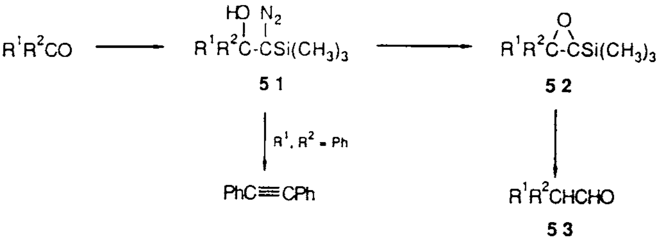
5. REACTIONS OF LITHIO TRIMETHYLSILYLDIAZOMETHANE

Lithio trimethylsilyldiazomethane **50** is a reagent which has a number of synthetically useful applications. It is usually prepared *in situ* by the reaction of **1** with either *n*-butyllithium or with lithium diisopropylamide at low temperature.[38]



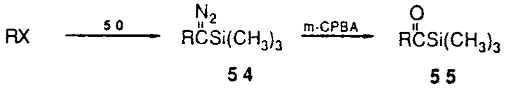
5.1. Reaction with Carbonyl Compounds

The products obtained from the reaction of **50** with carbonyl compounds are dependent upon the type of groups attached to the carbonyl and the reaction conditions. Protonation of the initially formed intermediate from aliphatic ketones, aralkyl ketones, and aromatic aldehydes produces the 1-diazo-1-trimethylsilyl-2-alkanols **51** in moderate yields under low-temperature conditions.[39] At room temperature these compounds lose nitrogen to produce trimethylsilyl epoxides **52** which can undergo desilylation to the aldehyde homolog **53** of the starting carbonyl compound. When benzophenone is the carbonyl compound the intermediate undergoes loss of nitrogen and elimination to give diphenylacetylene.[40]



5.2. Preparation of Acylsilanes

Acylsilanes are synthetically useful functional compounds. The reaction of alkyl halides with **50** offers a convenient route to these compounds. The first step produces 1-trimethylsilyldiazoalkanes **54** which can be subsequently oxidized with *m*-chloroperbenzoic acid to produce the acylsilanes **55**.[41] The yields in both steps are good. Chlorides, bromides, and iodides all respond to this reaction with similar yields. The oxidation conditions are mild enough to leave the double bond of 11-iodoundec-1-ene intact.

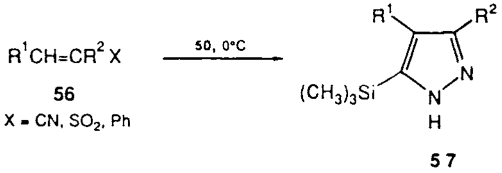


$$RX \xrightarrow{50} \overset{N_2}{\overset{\|}{RCSi(CH_3)_3}} \xrightarrow{m\text{-CPBA}} \overset{O}{\overset{\|}{RCSi(CH_3)_3}}$$

5.3. Preparation of Heterocyclic Compounds

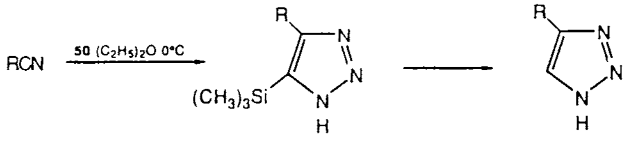
5.3.1. *Preparation of Pyrazoles*

Unsaturated nitriles **56** react with **50** to form trimethylsilylpyrazoles **57** in good yields. The latter can be readily desilylated with base or fluoride.[42] The proposed mechanism for this reaction is a nucleophilic attack at the α-unsaturated carbon followed by cyclization and elimination of LiCN. A wide variety of substituted nitriles respond to this chemistry. However, if the reactant contains bulky substituents 1,2,3-triazoles can be formed by competitive reaction at the nitrile unsaturation (see Section 5.3.2.). This side reaction can be minimized by using tetrahydrofuran as the solvent in place of ether. A much improved synthesis of the pyrazoles involves the use of the corresponding sulfones instead of the α,β-unsaturated nitriles.[43] This method is not solvent dependent.



5.3.2. *Preparation of 1,2,3-Triazoles*

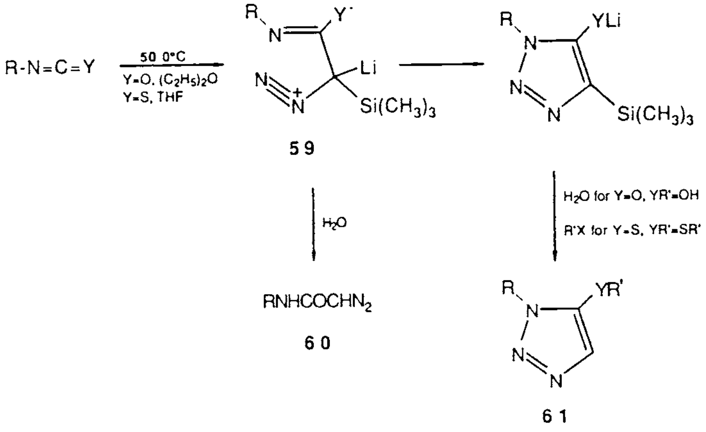
With no alpha unsaturation, a wide variety of substituted nitriles, including aliphatic, aromatic, and heteroaromatic, react with **50** at the nitrile unsaturation to give 4-substituted-5-trimethylsilyl-1,2,3-triazoles **58** in good yields. Desilylation of **58** can be readily accomplished in high yields.[44]



58

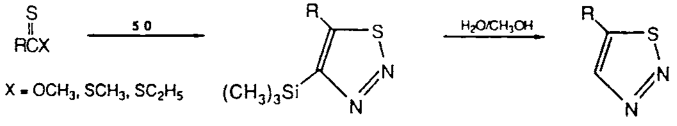
5-Hydroxy- and 5-alkylthio-1,2,3-triazoles **61** are obtained when isocyanates[45] and isothiocyanates[46] are reacted with **50**. The reaction proceeds stepwise via the intermediate **59** resulting from nucleophilic attack on the carbon of the isocyanate group. In the case of 5-hydroxy-1,2,3-triazoles the diazoacetamide **60** can be isolated by thermolysis of the reaction mixture or by quenching prior to the completion of the reaction. In the case of the 5-alkylthio derivatives the product is obtained by quenching the reaction mixture with an alkyl halide.

The use of tetrahydrofuran solvent was found to be essential for the preparation of the 5-alkylthio-1,2,3-triazoles. Totally different chemistry occurs when the solvent is changed (see Section 5.3.4.). For the 5-hydroxy derivatives diethyl ether is the solvent of choice. Yields from these reactions are good (80% for hydroxy derivatives) to excellent (>90% for alkylthio derivatives). As a method for the preparation of the hydroxy derivatives the use of **50** provides a more convenient and safer method than other reported procedures.

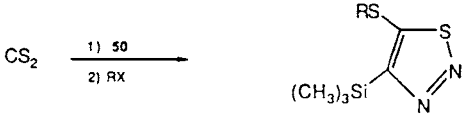


5.3.3. Preparation of 1,2,3-Thiadiazoles

When thiocarbonyl derivatives (thionoesters and dithioesters) are subjected to reaction with **50** 5-substituted-1,2,3-thiadiazoles **62** are obtained after quenching with aqueous methanol.[47] When carbon disulfide is reacted and the reaction mixture quenched with an alkyl halide 5-alkylthio-1,2,3-thiadiazoles **63** are obtained.



62

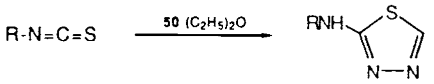


63

Thioketones also react with **50** to give **62** although different products, alkenes, alkynes, and 1,2,3-thiadiazoles, can be obtained depending upon the structure of the substituents and reaction solvent.[48]

5.3.4. Preparation of 2-Amino-1,3,4-thiadiazoles

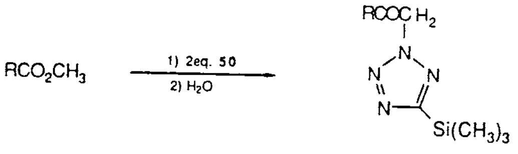
When the reaction of isothiocyanates with **50** is carried out in diethyl ether solvent the reaction products are 2-amino-1,3,4-thiadiazoles **64**.[49] Compared to the use of tetrahydrofuran as a solvent, which gives the 1,2,3-triazole ring structure (see Section 5.3.2.), it is evident that the nature of the solvent plays a significant role in the cyclization.



64

5.3.5. Preparation of Tetrazoles

Methyl esters of carboxylic acids react with two equivalents of **50** to give tetrazoles **65** in good yields.[50] The products are readily desilylated with methanolic hydrochloric acid.

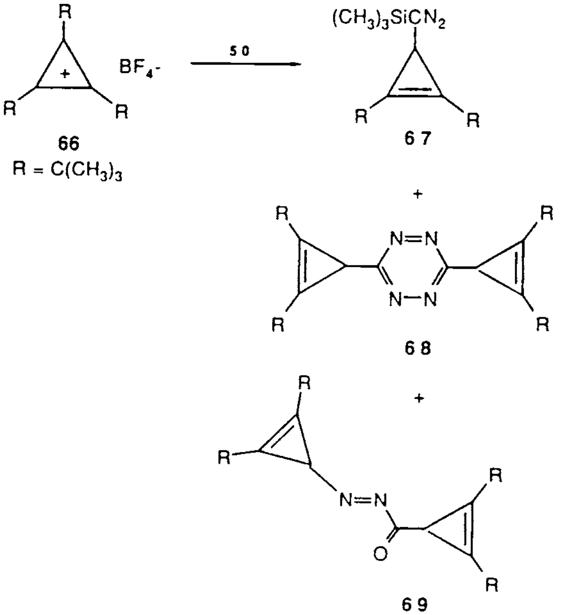


65

5.4. Miscellaneous Reactions

As part of an attempt to prepare a tetrahedrane ring structure, **50** was reacted with tri-*tert*-butylcyclopropenylium tetrafluoroborate **66** leading to a 15% yield of the cyclopropenyldiazo derivative **67**.[51] Other products obtained from this reaction were the tetrazine **68**, resulting from the dimerization of **67** followed by hydrolysis, and the acyldiimide **69** which resulted from the reaction between **66** and **67**.[52]

In other applications **50** can be used to prepare germanium and silicon substituted trimethylsilyldiazomethanes **70** and **71**,[37,53] the diazophosphine **72**,[54] and the rhodium-substituted diazomethane **73**.[55] All of these products can be used as carbene precursors.



66
R = $C(CH_3)_3$

67

68

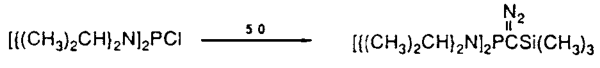
69

$$(CH_3)_3MCl \xrightarrow{50} (CH_3)_3M[(CH_3)_3Si]CN_2$$

M = Si, Ge **70**

$$(CH_3)_3SiSi(CH_3)_2Cl \xrightarrow{50} (CH_3)_3SiSi(CH_3)_2[(CH_3)_3Si]CN_2$$

71



$$[\{(CH_3)_2CH\}_2N]_2PCl \xrightarrow{50} [\{(CH_3)_2CH\}_2N]_2P\overset{N_2}{\overset{\|}{C}}Si(CH_3)_3$$

72

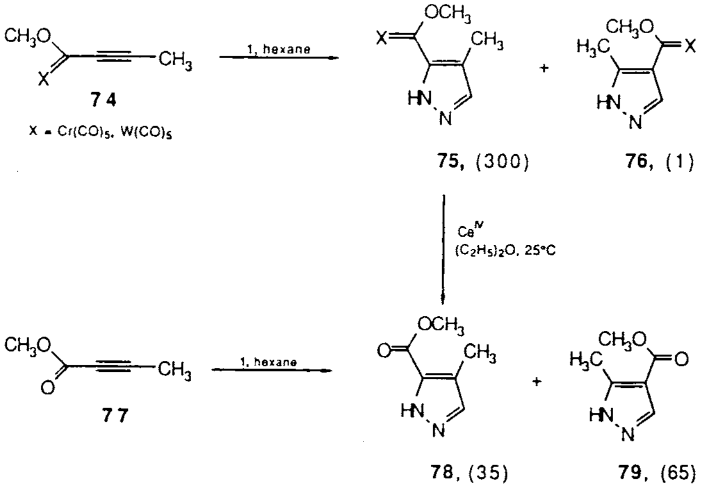
$$Rh[P(CH_3)_3]_4Cl \xrightarrow{50} Rh[P(CH_3)_3]_4\{C(N_2)Si(CH_3)_3\}$$

73

6. TRANSITION METAL COMPLEX CHEMISTRY

6.1. 1,3-Dipolar Cycloaddition Reactions

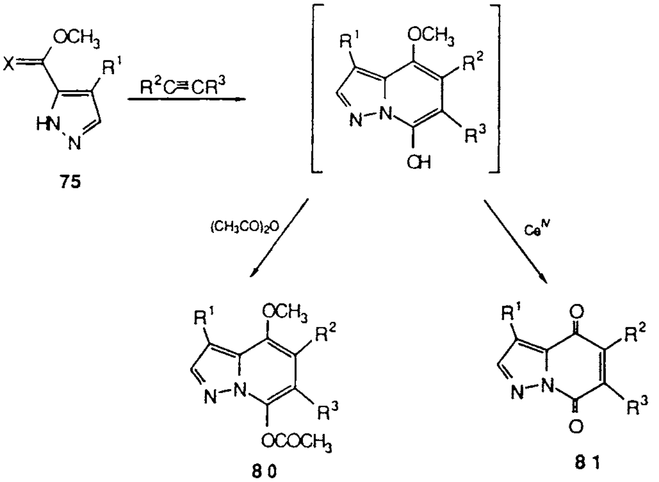
Transition metal carbene complexes containing α,β-unsaturation **74**, X=Cr(CO)5, W(CO)5, readily undergo 1,3-dipolar cycloaddition reactions with **1**.[56] In this chemistry diazomethane can also be used as the dipolarophile; however, further reaction of this reagent with the metal–carbon double bond of the pyrazole



complex produces an undesirable enol ether by-product. The use of **1** suppresses the formation of this by-product. The trimethylsilyl group is lost during the workup procedure to give pyrazole carbene complexes **75** and **76**.

As a synthetic route for the formation of the pyrazole nucleus, the use of the transition metal complexes **74** offers the advantages of a much faster reaction and a reaction product in which only one regioisomeric cycloadduct predominates as compared to the use of the corresponding esters **77**, which produce a mixture of the two regioisomers **78** and **79**. Conversion of the carbene complex **75** to the ester **78** is accomplished by oxidation with ceric ammonium nitrate.

The pyrazole carbene complexes **75** are useful precursors of the pyrazolo[1,5-α]pyridines **80** and quinones **81**.[56] The presence of the metal and its ligand allows **75** to undergo annulation reactions with alkynes, a reaction which cannot occur with the corresponding esters **78**. The initial intermediate formed can either be transformed with acetic anhydride to the pyridine **80** or oxidized with ceric ammonium nitrate to the quinone **81**. Best yields (40–50%) are obtained from disubstituted acetylenes.

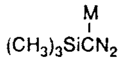


6.2. 1,3-Organometallic Insertion Reactions

The reaction of **1** with the transition metal complexes **82** represents the first reported example of a 1,3-organometallic insertion into the M–H bond leading to the formation of trimethylsilylmethylazo-transition metal complexes **83**.[57]

$$\underset{\textbf{82}}{\pi\text{-}C_5H_5(CO)_3M\text{-}H} \xrightarrow{1} \underset{\textbf{83}}{\pi\text{-}C_5H_5(CO)_2MN{=}NCH_2Si(CH_3)_3}$$

$$MN(CH_3)_2 \xrightarrow{1}$$



$$\overset{M}{(CH_3)_3SiCN_2}$$

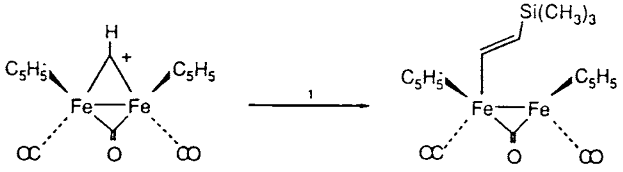
84

M = $(CH_3)_3Sn$, $1/2(\pi\text{-}(C_5H_5)_2Zr)$

Delocalization of the N=N π-electrons into the *d*-orbitals of the transition metal and/or silicon atoms accounts for the stability of the products. Insertion into the M–R, M–Cl, and M–NR2 bonds cannot be achieved, although from the latter reaction the transition metal diazoalkane **84** is obtained.[57]

6.3. Alkylidene Complexes

Nucleophilic attack by a series of diazo compounds, including **1**, at the methylidyne carbon of the complex **85** followed by loss of nitrogen produces the μ-methylidene complex **86**.[58] Alkyl and aryl substituted μ-alkylidyne complexes do not undergo this reaction.



85 **86**

Following a similar mechanism, the electrophilic nature of the carbon in the methylidyne ligand **87** is evidenced by the formation in high yield of the μ-alkylidene complex **88**.[59]

$$\underset{\textbf{87}}{HOs_3(CO)_{10}(CH)} \xrightarrow{1} \underset{\textbf{88}}{HOs_3(CO)_{10}(CH{=}CHSi(CH_3)_3)}$$

The μ-alkylidene complex **90** is formed when **1** is reacted with the rhodium complex **89**, but rapid rearrangement to **91** occurs in solution.[60]

$$\underset{\textbf{89}}{(C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)} \xrightarrow{1}$$

$$\underset{\textbf{90}}{(C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CHSi(CH_3)_3)(\mu\text{-}CF_3C_2CF_3)} \longrightarrow$$

$$\underset{\textbf{91}}{(C_5H_5)_2Rh_2(CO)[\mu\text{-}C(CF_3)C(CF_3)CHSi(CH_3)_3]}$$

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