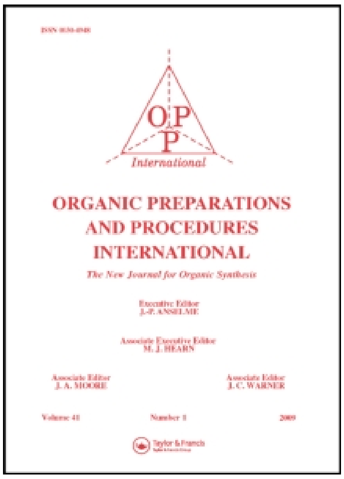

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APPLICATIONS OF TRIMETHYLSILYL HALIDES-OXIDANTS COMBINATIONS IN ORGANIC SYNTHESIS. A REVIEW

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This review is respectfully dedicated to Prof. George A. Olah on the occasion of his 70th birthday

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INTRODUCTION

The use of functionalized organosilicon reagents (R_3SiX, where X is a leaving group) in organic synthesis has experienced rapid growth in the past three decades.[1,2] The extensive use of silicon is largely due to its strong electropositive character compared to carbon and also since silicon forms relatively weak bonds to nitrogen, chlorine, bromine, iodine and sulfur and relatively strong bonds to oxygen and fluorine. In the reagent R_3SiX, the SiX bond is labile and therefore in combination with an oxidant it would have greater tendency to form Si-O-X type of linkage. Thus, a combination of trimethylsilyl halides and some oxidants allows to form modified reagent systems owing to the affinity of oxygen towards silicon. These reagent systems have recently been used in various organic transformations. Among many, the potential of chlorotrimethylsilane (TMSCl)-oxidant system as oxygenating or chlorinating agent has been extensively studied. A number of oxidants such as chromic anhydride (CrO_3), potassium chromate (K_2CrO_4), potassium dichromate ($K_2Cr_2O_7$), manganese dioxide (MnO_2), potassium permanganate ($KMnO_4$), selenium dioxide (SeO_2), sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$) and hydrogen peroxide (H_2O_2) have been employed.

It has been suggested that in the formation of most of these reagent systems, TMSCl first reacts with the oxidant to form a trimethylsiloxy insertion product which then reacts with a second molecule of TMSCl cleaving the trimethylsiloxy-heteroatom bond to produce hexamethyldisiloxane and an oxychloride **1**, which is believed to be responsible for further transformations. This is illustrated in general form and specifically for sodium chlorate-TMSCl combination in *Scheme* 1.

$$Me_3SiCl \longrightarrow Me_3Si{-}O{-}Y \longrightarrow Me_3Si{-}O{-}SiMe_3 + Cl{-}Y$$

1

O-Y : part of the oxidant

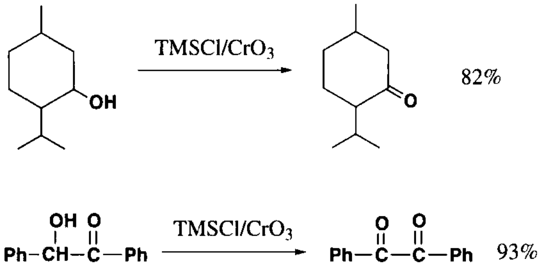
$$Me_3SiCl + NaClO_3 \longrightarrow Me_3Si{-}OClO_2 \xrightarrow{Me_3SiCl} Me_3SiOSiMe_3 + Cl_2O_2$$

Scheme 1

I. TRIMETHYLSILYL HALIDES-OXIDANT COMBINATIONS

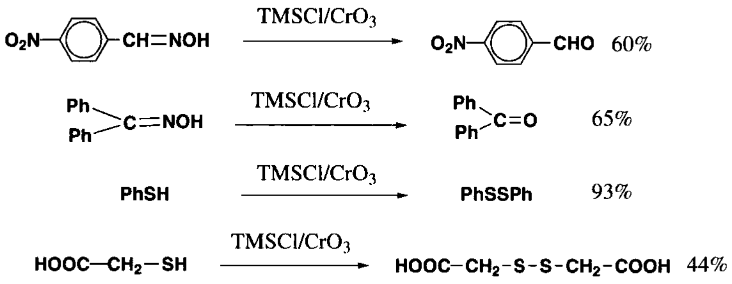
1. Trimethylsilyl Chloride-Chromium (VI) Compounds

Aizpurua and Palomo[3,4] have introduced TMSCl-CrO_3 (1:1), TMSCl-$K_2Cr_2O_7$ (4:1) and TMSCl-K_2CrO_4 (3:1) reagent systems for oxidation of alcohols to the corresponding carbonyl compounds in high yields. Primary, secondary and benzylic alcohols are oxidized with equal ease (*Scheme* 2).

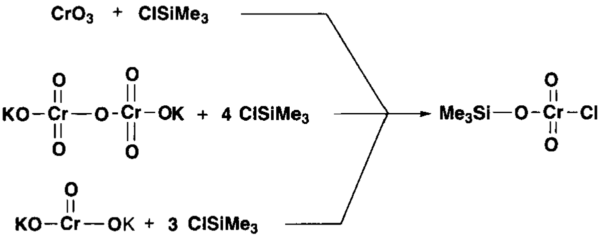


Scheme 2

These reagent systems are also highly efficient for the mild cleavage of oximes to carbonyl compounds and for the selective oxidation of mercaptans to disulfides without over oxidation to sulfones (*Scheme* 3).[3] The deoximation yields are found to be better than those obtained with pyridinium chlorochromate (PCC) and H_2O_2-PCC reagent systems. The versatility of this reagent[3] has been extended further to the oxidation of arylmethanes to aryl aldehydes and benzyl chloride to benzaldehyde in refluxing dichloroethane; however, *p*-nitrotoluene is not oxidized under these conditions. Trimethylsilyl chlorochromate $(Me)_3Si$-O-CrO_2Cl has been suggested[3,4] as the common oxidizing species in the reactions shown below (*Scheme* 4).

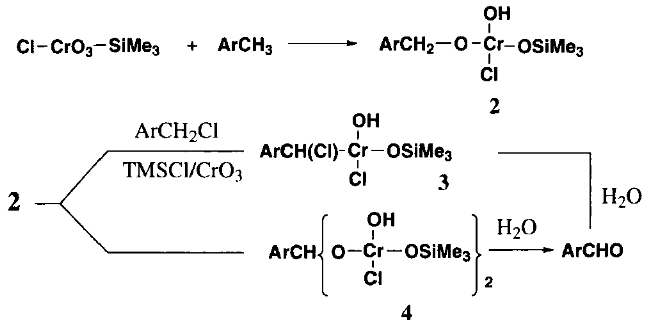


Scheme 3



Scheme 4

The proposed mechanism for this reaction is shown in *Scheme* 5. The isolation of benzyl chloride in the oxidation of toluene supports the intermediacy of $ArCH_2Cl$ in such reactions. In a separate reaction, benzyl chloride was found to undergo oxidation to benzaldehyde under these conditions. Therefore, a 1:4 molar ratio of arylmethane:oxidant is necessary for efficient oxidation; when the molar ratio is decreased, the corresponding benzyl chloride is produced in greater amounts.

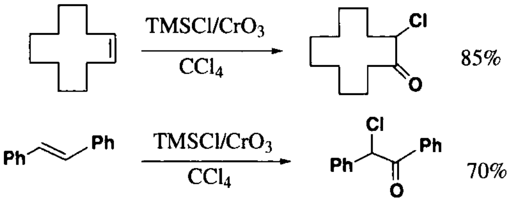


Scheme 5

Benzyl esters are oxidatively[4] cleaved into their corresponding carboxylic acids under mild conditions with $TMSCl/CrO_3$. Thus, treatment of 4-methoxybenzyl ester with $TMSCl/CrO_3$ at room temperature gives the corresponding carboxylic acid in moderate to good yields (30-70%). This is the first oxidative reagent employed for the cleavage of a benzyl ester using chromium (VI) reagent. Although combinations of reagents such as Cl_2SiR_2/CrO_3 ($R = CH_3$ or C_6H_5) have also been used for the deprotection of benzyl ester, the yields are lower in these reactions. It is noteworthy that under similar conditions pyridinium chlorochromate was ineffective for benzyl ester cleavage.[4]

The synthetic potential of the reagent $TMSCl/CrO_3$ is further shown by its potential use as a source of iodonium ion,[4] when combined with molecular iodine in the absence of a catalyst. Such a reagent combination resulted in a great enhancement of iodination reactions under homogeneous and neutral conditions. Here again, $TMSCl/CrO_3$ has been shown to be superior to pyridinium chlorochromate. Thus, in iodination of anisole only 30% of the product is formed with PCC/I_2, whereas $TMSCl/CrO_3$ gives 51% yield of the same product along with 44% of 2,4-diiodoanisole.

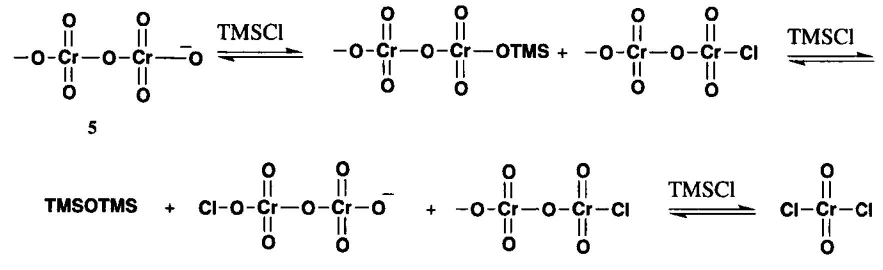
This reagent system (TMSCl/CrO_3) has been further utilized by Lee *et al.*[5] for the selective oxidation of arylmethanes to the corresponding aldehydes in higher yields when 2:2:1 ratio of CrO_3:TMSCl:substrate is used. Further, Lee and Ha[6a] have also used this reagent system for the conversion of olefins to α-chloroketones in high yields (*Scheme* 6).



Scheme 6

According to these authors, "the actual oxidizing species is not trimethylsilyl chlorochromate but a mixture of polyoxochromium dichloride, *viz.* $Cl(CrO_2)_nCl$, where 'n' varies depending on the ratio of chromic anhydride and TMSCl. The polymeric chain of chromic anhydride is broken into smaller fragments with the formation of Cr-OTMS and Cl-Cr bonds. The Cr-OTMS bond is unstable and is replaced with Cr-Cl bond in further reaction with TMSCl. The NMR spectrum of the prepared oxidant shows only two types of methyl protons charactaristic of TMSCl and hexamethyldisiloxane. In a solution containing an equimolar amount of chromic anhydride and TMSCl, about 35% of Cr-O bond in the polymeric chain is believed to be converted to Cr-Cl."

Chlorotrimethylsilane reacts with chromic anhydride[6b] to form a very reactive neutral chromium (VI) oxidizing agent. The active oxidizing species is not trimethylsilyl chlorochromate but chromyl chloride generated in equilibrium concentration. This oxidizing agent proved to be suitable for benzylic oxidations of toluenes and alkylbenzenes to benzaldehyde and aralkyl ketones. The X-ray analysis[6c] of chromic anhydride shows it to be a linear polymer of chromium and oxygen atoms with two additional oxygen atoms linked to each chromium atom viz. **5** (*Scheme* 7). The reaction of chromic anhydride with TMSCl is believed to depolymerize the former, thereby forming O-Si and Cr-Cl bond. The Cr-OTMS bond is replaced upon reaction with another molecule of TMSCl forming hexamethyldisiloxane and another Cr-Cl bond at the terminal chromium atom (*Scheme* 7). Incidentally, a similar type of cleavage of *in situ* generated trimethylsilyl chloroselenite by TMSCl to



5

Scheme 7

form selenium oxychloride and hexamethyldisiloxane has been reported for the reaction of selenium dioxide[12] with TMSCl. Selenium dioxide, like CrO_3, also has a linear polymeric structure.[6c]

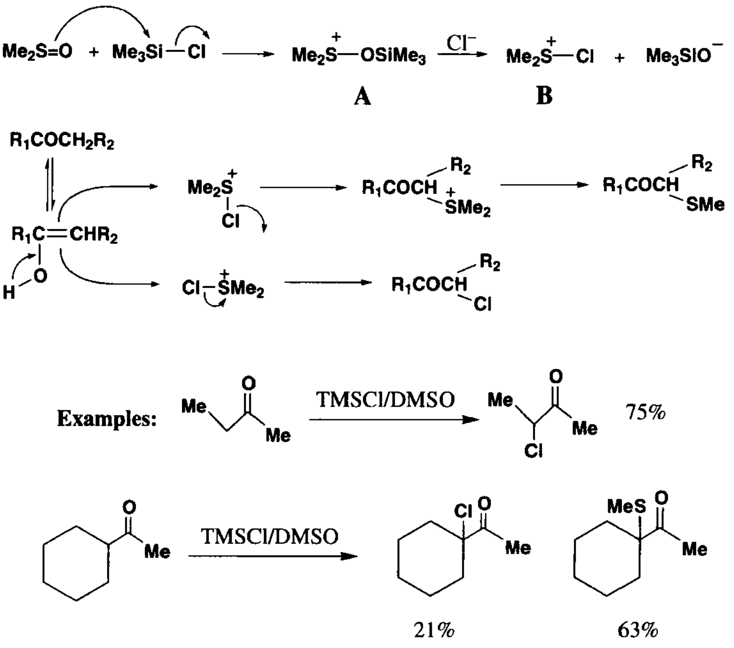
Improved oxidation of arylmethanes and analogous compounds has been reported by Lee and Ha[6b] by using reagents prepared from $TMSCl/CrO_3$ (2:1), Me_2SiCl_2/CrO_3 (2:1) and $MeSiCl_3/CrO_3$ (2:1) in refluxing CCl_4 rather than in dichloroethane as reported earlier by Aizpurua and Palomo.[3] The oxidation of ethylbenzene with $TMSCl/CrO_3$ gives acetophenone as the main product. The other pathway of β-elimination to give styrene is completely suppressed in this reaction. The $TMSCl/CrO_3$ reagent system is milder than chromyl chloride which gives a mixture of phenylacetaldehyde, benzaldehyde and acetophenone (*Scheme* 8). Further, a combination of Me_2SiCl_2 or $MeSiCl_3$ with CrO_3 is found to be superior for such Etard type reactions rather than the combination of TMSCl and CrO_3.

$$PhCHO + PhCH_2CHO + PhCOCH_3 \xleftarrow{CrO_2Cl_2} PhCH_2CH_3 \xrightarrow{CrO_3/TMSCl} PhCOCH_3$$

Scheme 8

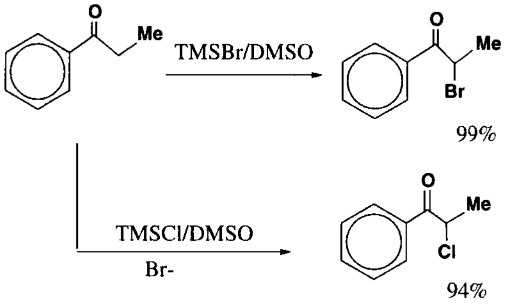
2. Trimethylsilyl Chloride (or Bromide)-Dimethyl Sulfoxide

Pagnoni *et al.*[7a] have found that TMSCl/DMSO system is an efficient reagent for smooth chlorination of unconjugated carbonyl compounds giving α-chloroketones (*Scheme* 9) where chlorine occupies a position at the more substituted carbon atom. On the other hand, β-dicarbonyl compounds are transformed into α-chloro-α-thiomethyl ether derivativesand the poorly reactive phenyl alkyl ketones are recovered unchanged.



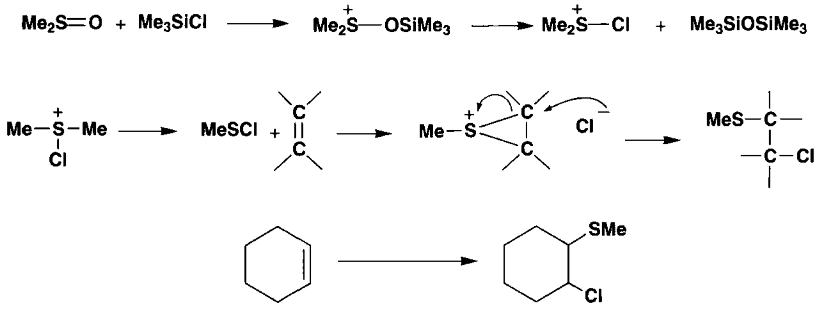
Scheme 9

An extension of the above work has been described by Pagnoni *et al.*[7b] in another report where bromotrimethylsilane-dimethyl sulfoxide (TMSBr/DMSO) reagent system is found to brominate efficiently and regiospecifically at the more alkyl substituted α-position of carbonyl compounds. The added advantage of this system of using bromine instead of chlorine is that α-bromo carbonyl compounds are obtained smoothly and without sulfur containing by-products. The TMSBr/DMSO reagent system also reacts with phenyl alkyl ketones, to give brominated products in 61-99% yields (*Scheme* 10, Eq. 1). These facts are rationalized by considering the stronger electrophilic character at the halogen atom of $Me_2S^+ Br^-$ than that of $Me_2S^+ Cl^-$. In an improved variation of this method, Fraser and Kong[7c] have reported the chlorination of ketones using TMSCl/DMSO with bromide ion (as *n*-$Bu_4N^+ Br^-$) catalysis affording nearly quantitative yields for 1,3-diphenylacetone, benzoylacetone and propiophenone (*Scheme* 10, Eq. 2) apart from acceptable yields for acetophenone, acetylacetone and cyclohexanone were obtained. In the chlorination of propiophenone to 2-chloropropiophenone, the reaction occurs under milder conditions and yields 94% of the product. There is also minimization of the potential side-reactions such as (i) electrophilic attack by the sulfur of $(CH_3)_2S^+ Br^-$ which was reported with $(CH_3)_2S^+ Cl^-$ [7a] (ii) nucleophilic displacement of the halogen of either haloketone, by dimethyl sulfide (iii) enolization of either haloketone, leading to disubstitution.



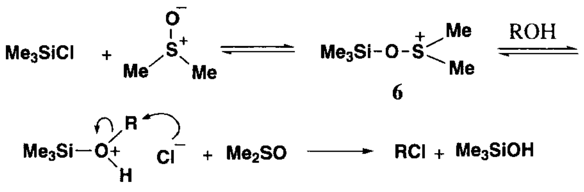
Scheme 10

The scope of these reagents was further explored by Ghelfi *et al.*[7d,e,f] who have reported smooth transformations of alkenes and cycloalkenes by TMSCl/DMSO into 2-chloroalkyl and 2-chlorocycloalkyl methyl sulfides respectively (*Scheme* 11). The addition is both stereo- and regioselective affording *trans*-adducts from a preferential Markovnikov addition. However, TMSBr/DMSO instead gives 1,2-dibromo derivatives from olefins. TMSCl/DMSO is therefore considered equivalent to methanesulfenyl chloride in the reactions with olefins whereas TMSBr/DMSO is like molecular bromine, when reacting with an olefin, in terms of yields and stereochemistry. These results are explained by the stronger electrophilic character of bromine, with respect to sulfur, in the halo-sulfonium intermediate ($Me_2S^+ X^-$), the substrate being transformed into a bromonium rather than into an episulfonium intermediate.



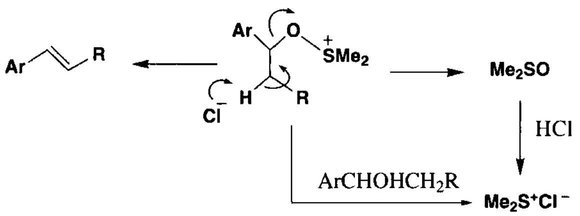
Scheme 11

Conversion of alcohols to chlorides by TMSCl/DMSO has been reported by Snyder.[8a] Both primary and tertiary alcohols can be readily converted to alkyl chlorides by this reagent system in high yields. However, secondary alcohols are unreactive under these conditions. The electrophilicity of the TMSCl silicon is enhanced by the initial transformation of the TMSCl to a new, much more reactive intermediate **6** formed by the reaction with DMSO (*Scheme* 12).

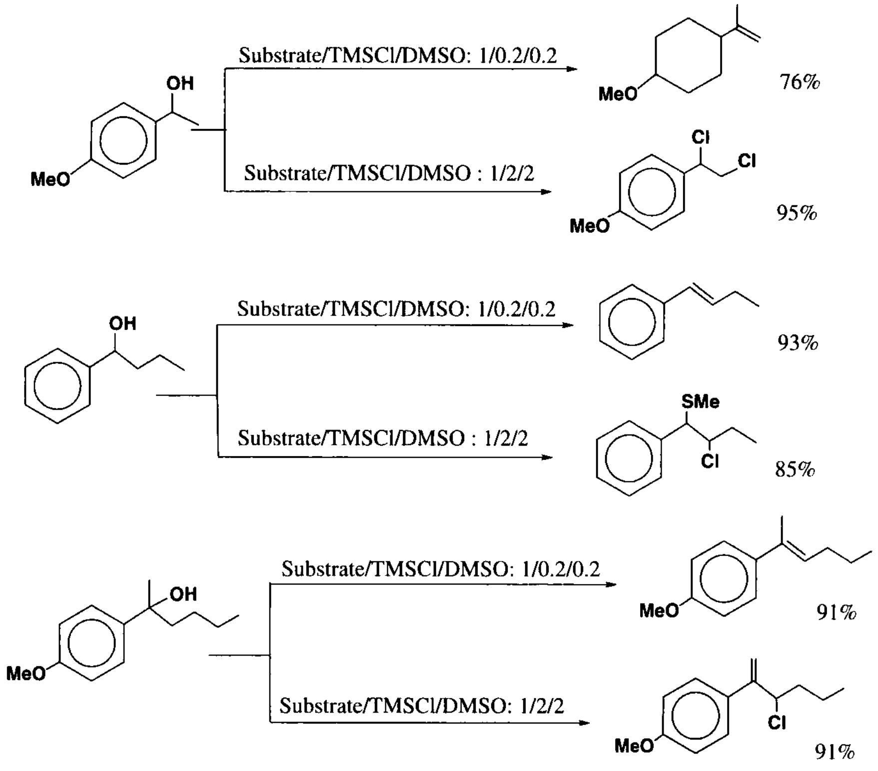


Scheme 12

Pinetti *et al.*[8b] found the reaction of benzylic alcohols with TMSCl/DMSO in acetonitrile to give high yields of styrenes (*Scheme* 13). On the other hand, the use of stoichiometric amounts of reagents led to different reaction pathways. Thus, an elimination-addition sequence occurs with secondary and tertiary alcohols affording vicinal dichloro derivatives, β-chlorothioethers, the corresponding monochloride, or vicinal dichloride, β-chlorothio ethers and allylic chlorides, whereas a nucleophilic substitution occurs to form the corresponding monochlorides starting from primary and sterically hindered substrates (*Scheme* 13). The same authors have earlier reported[8c] that styrenes get smoothly transformed into *vicinal* dichloro derivatives, β-chloro thioethers and allyl chlorides by using stoichiometric amounts of the reagents.



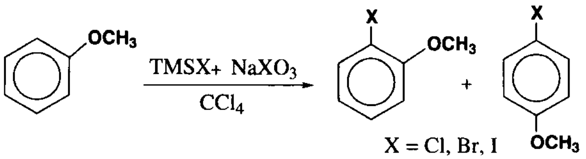
Examples:



Scheme 13 (cont'd)

3. Trimethylsilyl Chloride-Sodium Halates

Halotrimethylsilanes in combination with halates (chlorate, bromate and iodate)[9a] have been reported as efficient nuclear halogenating agents with activated aromatic compounds (*Scheme* 14). Thus, toluene reacted with TMSCl/$NaClO_3$ combination to give 90% yield of a 34:66 mixture of *o*- and *p*-chlorotoluene. Likewise, other aromatic compounds such as xylenes, anisole and phenol were found to give the corresponding *p*-chloro derivatives as chief products in good yields. Bromotrimethylsilane/sodium bromate pair mainly gave ring brominated products with activated aromatic compounds. Anisole, for example, reacted with TMSBr/$NaBrO_3$ to produce *p*-bromoanisole along with a small amount of *o*-bromoanisole. However, toluenes mainly underwent benzylic bromination under these conditions. In case of iodotrimethylsilane/sodium iodate combination, the reaction



Scheme 14

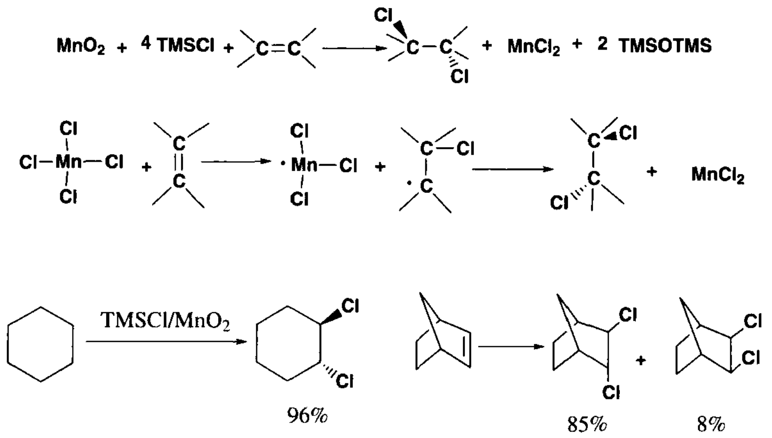
appeared to be sluggish. Among the examples studied, only anisole was found to react, which produced *p*-iodoanisole as the main product. The chemical reactions between TMSX and sodium halates leading to the formation of the effective halogenating agents is not yet clear. Perhaps the first step of the reaction might be the formation of trimethylsilyl esters of halic acids derived from the reaction of TMSX and sodium halate (*Scheme* 15). Further reaction of trimethylsilyl halate with another equivalent of TMSX would remove the trimethylsiloxy group as hexamethyldisiloxane and result in the formation of unstable dichlorine dioxide (Cl_2O_2). It is believed that Cl_2O_2 either decomposes or disproportionates to various chlorine and oxychlorine species. This type of replacement of trimethylsiloxy group with halogen to form halogen heteroatom bonds was observed for the reactions of TMS ester of chromate, chlorochromate, selenite, nitrite and nitrate with chlorotrimethylsilane.[5,6,9b,12] Correspondingly, the formation of chromyl chloride, selenium oxychloride, nitrosyl chloride and nitryl chloride was postulated in these reactions, analogous to the formulation of Cl_2O_2 in the above described reaction.

$$Me_3SiCl + NaClO_3 \longrightarrow Me_3Si{-}OClO_2 \xrightarrow{Me_3SiCl} Me_3SiOSiMe_3 + Cl_2O_2$$

Scheme 15

4. Trimethylsilyl Chloride-Manganese Dioxide

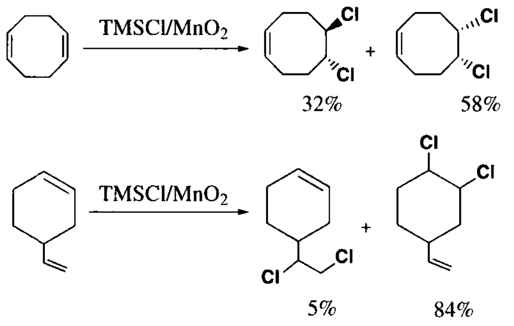
Ghelfi *et al.*[10a] have introduced a new reagent system which gives rise to a smooth and high-yield chlorination of unconjugated alkenes without isomerization. The *trans*-vicinal dichloro derivatives were obtained from cyclic substrates with high stereoselectivity. These results have been explained by invoking the participation of a manganese (IV) chloride species (*Scheme* 16). During its reduction, the TMSCl/MnO_2 reagent apparently inserts two chlorine atoms stepwise. Ths high selectivity of addition rules out the involvement of free chlorine atoms in these reactions. Thus, the



Scheme 16

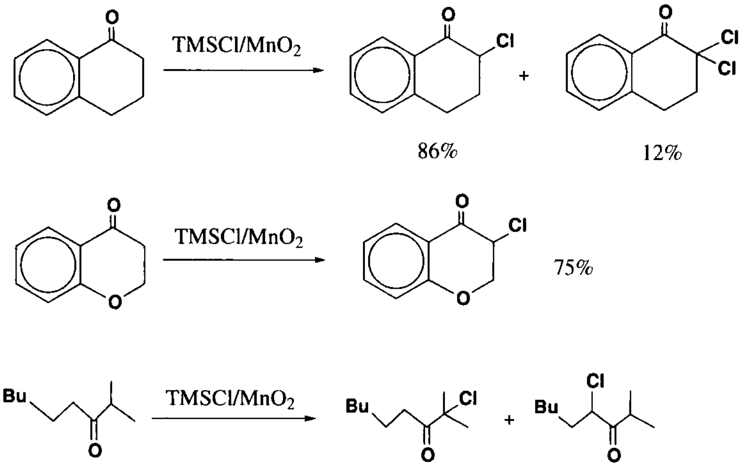
addition product can derive from the interaction between the alkene and the chlorine carrier in solution involving a non-chain radical mechanism. Since in this case a remarkable *trans*-stereoselectivity (see examples in *Scheme* 16) is observed, TMSCl/MnO$_2$ reagent may be considered as an efficient radical-quenching system.

Ghelfi and coworkers[10b] have shown that dienes react with this reagent system to give chemoselectively the addition product at the more heavily alkyl substituted olefinic bond (*Scheme* 17). Further, with the exception of norbornadiene, no molecular skeleton rearrangement is observed in the compounds studied. These reactions are also expected to proceed through manganese (IV) complex involving a non-chain radical pathway.



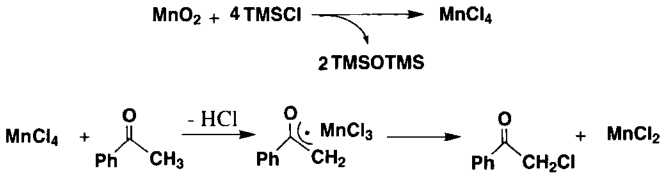
Scheme 17

The same workers have also utilized[10c,d] this reagent system for the chlorination of ketones. High yields of the chlorinated products are obtained at relatively low temperatures (15°-20°) in acetic acid as a medium. α-Monochloro derivatives are generally produced in agreement with lower reactivity of α-chloroketones (*Scheme* 18) for further chlorination. However, when the amount of TMSCl/MnO$_2$ was increased, the relative proportion of α,α- and α,α'-di-substitution rose. An



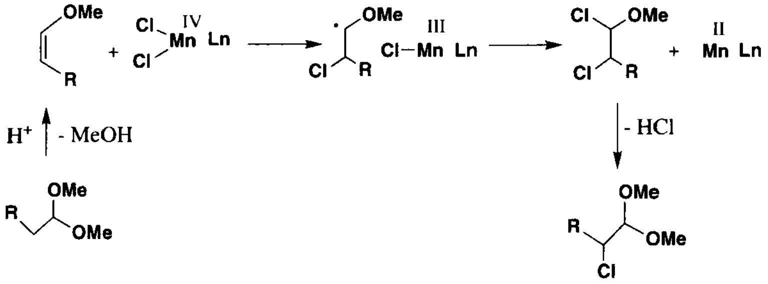
Scheme 18

advantage of this reagent is relatively low acidity of the medium. In case of aliphatic substrates, which generally undergo disubstitutions more easily, the amount of α-monochlorinated derivative is optimized by using 10% molar excess of MnO_2 over the ketone. Manganese (IV) chloride, an elusive species, is postulated as an intermediate in these reactions also. This forms an α-keto radical upon reaction with a ketone which ultimately gives the product *i. e.* α-chloroketone (*Scheme* 19). Chlorotrimethylsilane[10e] can be replaced by the less expensive acetyl chloride (AcCl) giving essentially identical results in terms of product distribution and their isolation.



Scheme 19

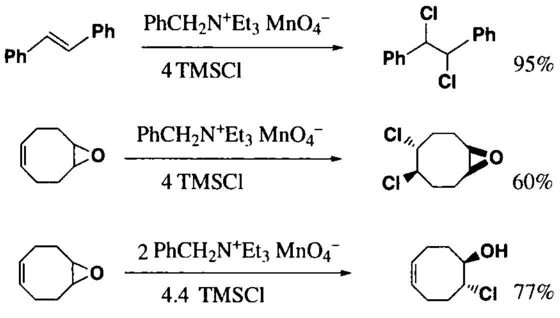
Ghelfi and coworkers[10f] have reported the α-chlorination of acetals using $TMSCl/MnO_2$ as an indirect method to obtain α-chloroaldehydes which are not easily accessible by chlorination of aldehydes. The halogenation has been explained by a ligand-transfer process on an enol ether intermediate, mediated by a Mn(IV) chloride species (*Scheme* 20). The yields of α-chloro acetals are excellent.



Scheme 20

5. Trimethylsilyl Chloride-Potassium Permanganate

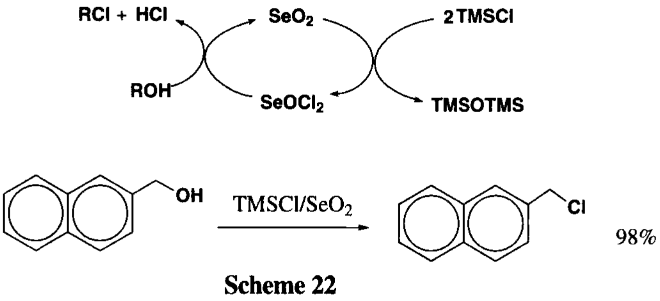
Very recently,[11] a novel manganese reagent generated from $TMSCl/KMnO_4$ in the presence of a quaternary ammonium salt is shown to smoothly dichlorinate alkenes, open epoxides and chemoselectively oxidize sulfides to sulfoxides. With the exception of the aryl substituted olefins, which give a mixture of *syn* and *anti*-dichlorides, the reaction proceeds exclusively by *anti*-dichlorination of alkenes. The manganese reagent also tolerates various protecting groups (e.g. $-OSiMe_2t$Bu) and displays excellent levels of chemoselectivity. For example, chlorohydrin formation by direct epoxide opening is not observed during the chlorination of monoepoxide of 1,5-cyclooctadiene (*Scheme* 21). Interestingly, in the presence of an excess of TMSCl, smooth and chemoselective epoxide opening takes place affording the corresponding *anti*-chlorohydrin in the case of mono epoxide of cyclooctadiene. Under these conditions a variety of epoxides are converted to *anti*-chlorohydrins.



Scheme 21

6. Trimethylsilyl Chloride-Selenium Dioxide

A simple, inexpensive and high-yield conversion of alcohols to the corresponding alkyl chlorides has been reported by Lee and Kang[12] using TMSCl and a catalytic amount of SeO_2. Selenium oxychloride ($SeOCl_2$) is believed to be the effective chlorinating agent (*Scheme* 22) in these reactions. Since SeO_2 cannot escape out of the reaction medium only catalytic amount of it is needed to effectively chlorinate alcohols provided that enough chlorine source is present to convert SeO_2 back to $SeOCl_2$. Thus, for example, when benzyl alcohol was mixed with slightly more than two equivalents of TMSCl and 2-3 mole % of SeO_2, hydrochloric acid soon started to evolve and benzyl chloride was formed in nearly quantitative yield. Likewise, a wide variety of alcohols were smoothly converted into the corresponding chlorides. Only in the case of tertiary alcohols did the problem of elimination become apparent. Thus, *t*-butanol gave *t*-butyl chloride in only 30% yield since the rest of the alcohol was eliminated to isobutylene which escaped along with HCl.

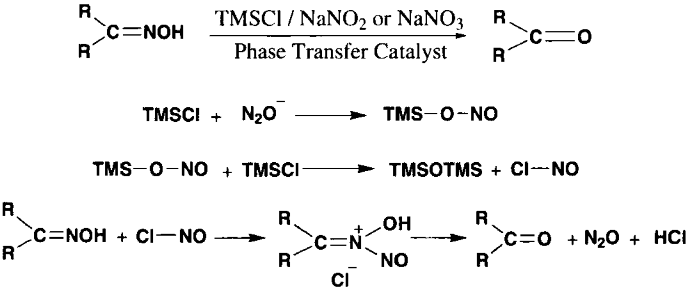


Scheme 22

Generally no skeletal migration was observed. Thus, for example, neopentyl alcohol gave neopentyl chloride and allylic alcohols gave the corresponding chlorides in nearly quantitative yields, although exceptions have been observed. Thus, geraniol gave a 1:1 mixture of geranyl and linallyl chlorides. In short, this reagent is superior to thionyl chloride and other chlorinating agents, not only in terms of yields and mildness of the reaction conditions but also because the competing side reactions are greatly suppressed.

7. Trimethylsilyl Chloride-Sodium Nitrite (or Sodium Nitrate)

A mixture of chlorotrimethylsilane and sodium nitrite (or nitrate)[13a] was found to be effective in deoximation reactions. Trimethylsilyl nitrite (or nitrate) seems to be initially formed which further reacts with chlorotrimethylsilane to produce nitrosyl chloride (or nitryl chloride) and hexamethyldisiloxane (*Scheme* 23).



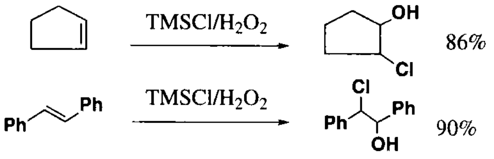
Scheme 23

To facilitate the solubilization of the sodium salts in organic solvent about 5 mole % of the benzyltriethylammonium chloride or Aliquat 336 was used, although the use of a phase-transfer catalyst is not essential. The nitrosonium ion adds to the nitrogen atom of the oxime followed by decomposition to the carbonyl compound and dinitrogen monoxide. Despite the fact that a large number of oxidative deoximation reagents are available,[13b] the yield of the deoximation of benzaldoxime is generally poor[13c] with Cr(VI) reagents as compared to the present reagent system. Although nitrous acid and derivatives were also used for the deoximation of ketoximes,[13d] the yields with TMSCl/$NaNO_3$ or TMSCl/$NaNO_2$ are quantitative for most of the carbonyl compounds, though the yields are slightly lower for aliphatic aldoximes. However, the deoximation of oximes derived from α,β-unsaturated carbonyl compounds was not clean. Thus, cinnamaldoxime gave a mixture of cinnamaldehyde and benzaldehyde in moderate yields.

Intermediacy of NOCl in the reaction of $NaNO_2$ and TMSCl is further confirmed[13e] when anilines were effectively transformed into aryl chlorides under these conditions at 0°. Thus, a variety of anilines have been reported to yield aryl halides in a one-pot reaction using $NaNO_2$ and halotrimethylsilanes in CCl_4. Halotrimethylsilanes are used both for the generation and halogen substitution of a diazonium group.

8. Trimethylsilyl Chloride-Hydrogen Peroxide

Ho[14] has reported that a combination of TMSCl and hydrogen peroxide gives trimethylsilyl hydroperoxide which possesses bonding arrangement similar to that found in percarboxylic acids. Both these types of compounds are made up of soft acid-soft base pair with respect to the O-O linkage. Several cycloalkenes and stilbenes react with TMSCl/H_2O_2 to produce α-chlorohydrins (*Scheme* 24). Although oxiranes are not isolated under the reaction conditions in which hydrochloric acid is present, the high yield production of chlorohydrins implicates their intermediacy. In other words, silyl hydroperoxides are indeed able to transfer an oxygen atom to alkenes.



$Me_3SiCl + H_2O_2 \longrightarrow Me_3SiOOH + HCl$

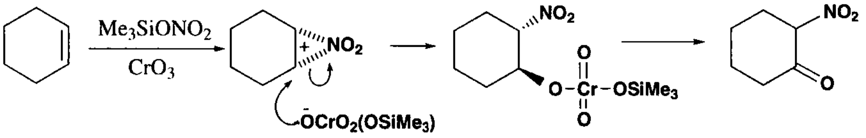
$\text{Alkene} + Me_3SiOOH \longrightarrow \text{Oxirane} + Me_3SiOH$

$\text{Oxirane} + HCl \longrightarrow \text{Chlorohydrin}$

Scheme 24

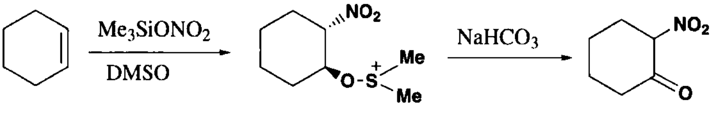
9. Trimethylsilyl Nitrate-Chromium Trioxide

A combination of TMSCl, $AgNO_3$ and CrO_3 has recently been reported by Vankar *et al.*[15a] to convert olefins into α-nitroketones. Both cyclic and acyclic olefins readily react to give α-nitroketones in good to excellent yields with the exception of α-nitrocyclopentanone (yield 27%). Unsymmetrical olefins give α-nitroketones regioselectively with the nitro group entering at the less substituted carbon. It is believed that $AgNO_3$ and TMSCl form trimethylsilyl nitrate (Me_3SiONO_2) which then reacts with CrO_3 to generate a yet another intermediate viz. $Me_3SiOCrO_2ONO_2$. This intermediate then reacts with olefins to form α-nitroketones (*Scheme* 25).



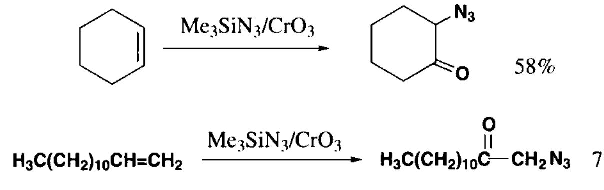
Scheme 25

In a variation, Vankar *et al.*[15b] have further observed that CrO_3 in the above reaction could be replaced by dimethyl sulfoxide (DMSO). Under these conditions, after the reaction, a basic work up was followed to ensure oxidation. These reactions resemble the Kornblum type[16] oxidation which is known for the conversion of aliphatic halides (or any good leaving group) into aldehydes or ketones. The proposed mechanism is shown in *Scheme* 26. The nature of Me_3SiONO_2 suggests that it could be a reasonably good source of $^+NO_2$.[17] Therefore it might be expected that it may react with other functional groups in a manner analogous to $^+NO_2\,BF_4^-$.[18]



Scheme 26

Trimethylsilyl azide (which may be prepared from TMSCl and NaN_3) reacts with CrO_3 to form a reagent system which has been found[19] to react with aldehydes to yield α-acyl azides in good to excellent yields. It is proposed that chromyl azide is the actual species that brings about this conversion. This reagent combination has been used to convert olefins into α-azidoketones in good yields (*Scheme* 27).[20] Previously, Me_3SiN_3 has been utilized to transform olefins into α-azidoketones by reaction in conjunction with oxidants such as $Pb(OAc)_4$ or $PhI(OAc)_2$.[21]



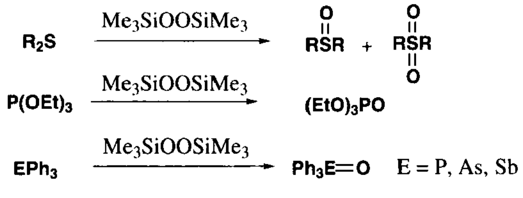
Scheme 27

10. *bis*(Trimethylsilyl)peroxide

bis(Trimethylsilyl) peroxide (BTSP)[22a] is an important non-aqueous substitute for hydrogen peroxide and therefore it has generated great interest among chemists to explore its potential for the past several years and it is becoming increasingly more popular. Recently, the structure of BTSP has been sudied in detail by Königstein and Jansen[22b] using X-ray analysis.

Hahn and Metzinger[22c] were the first to report the preparation of BTSP from the reaction of TMSCl with H_2O_2 in the presence of pyridine. In a modified procedure, Buncel and Davies[22d] obtained BTSP from the reaction of DABCO-H_2O_2 complex (formed from 35% H_2O_2 and DABCO) with TMSCl. The major drawback of this route is the high cost of DABCO, thus preventing its large scale usage. Another procedure for the preparation of BTSP reported by Jackson,[22f] employs a urea-H_2O_2 complex in place of DABCO-H_2O_2 complex. The intermediate *bis*(trimethylsilyl)urea [$(Me_3SiNH)_2CO$] reacted further with urea-H_2O_2 complex to afford BTSP and urea was recovered as an innocuous by-product. BTSP can also be prepared by using an inexpensive polyamine *viz.* hexamethylenetetramine[22g] ($C_6H_{12}N_4$) and hydrogen peroxide to form a complex $C_6H_{12}N_4.H_2O_2$ which reacts with TMSCl to give BTSP in 80% yield.

BTSP is used to carry out a number of oxidative transformations.[23a] Thus, sulfides,[23b] phosphines,[24a,b] phosphites[25a] give correspondingly sulfoxides (or sulfones), phosphine oxides and phosphates respectively in good to excellent yields (*Scheme* 28). Non-aqueous oxidation of nucleoside



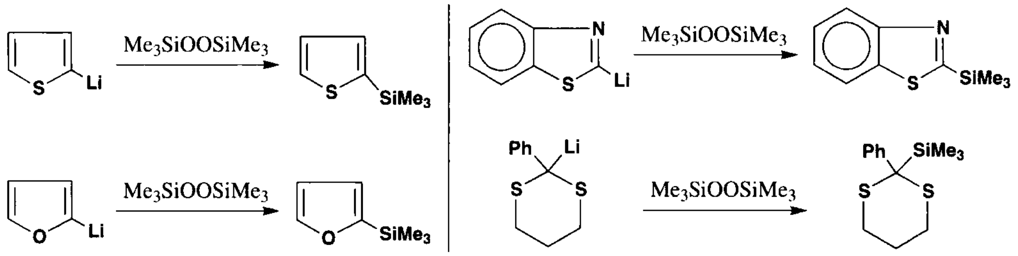
Scheme 28

phosphites to the corresponding phosphates has been reported by Noyori *et al.*[25b] using BTSP and trimethylsilyl triflate (TMSOTf). They have also reported[25c] a solid phase synthesis of oligodeoxyribonucleotides using BTSP oxidation of phosphites to synthesize hexanucleoside (AAGATC). BTSP has also been used[26a,b,c,d,e] in the regiospecific introduction of a hydroxy group in aromatic and aliphatic compounds in good yields *via* electrophilic hydroxylation of their organometallic derivatives (R-Li) (*Scheme* 29).

$$\mathrm{RX} \xrightarrow{n\text{-}\ C_4H_9Li} \mathrm{RLi} \xrightarrow{Me_3SiOOSiMe_3} \mathrm{ROSiMe_3} \xrightarrow{HCl/CH_3OH} \mathrm{ROH}$$

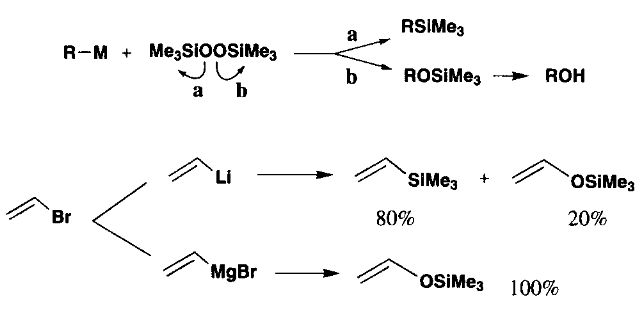
Scheme 29

Surprisingly, irrespective of the nature of the heterocyclic ring, reaction of BTSP[26] with lithium derivatives of thiophene, furan and dithiane and a benzothiazole at carbanionic centres α- to the hetero atoms afforded the corresponding trimethylsilyl derivatives. No traces of the expected trimethylsiloxy derivatives were detected (*Scheme* 30).



Scheme 30

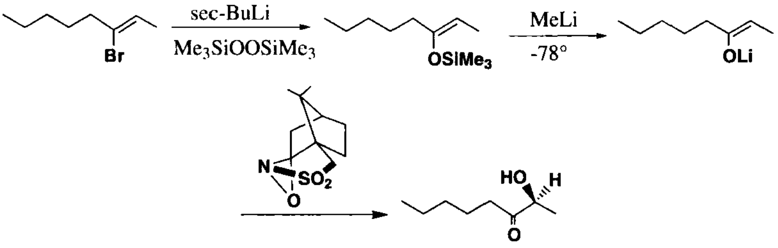
BTSP has also been used with allyl, vinyl, alkynyl, aromatic and hetero aromatic anions to form trimethylsiloxy and hydroxy compounds. Depending on the reaction conditions, the trimethylsiloxy derivatives can be obtained alone or together with the corresponding trimethylsilyl derivatives, which are sometimes the major products (*Scheme* 31).



Scheme 31

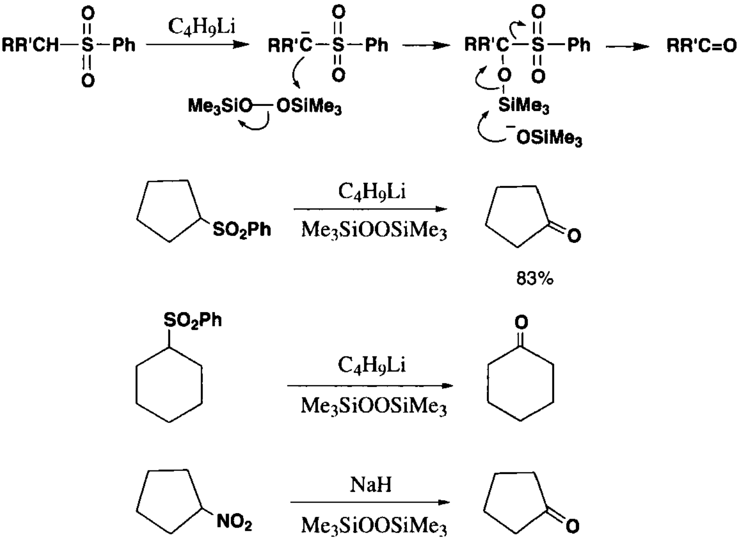
Davis *et al.*[27] have shown that vinyl bromides undergo stereoselective oxidation to silyl enol ethers when they are treated with *sec*-BuLi followed by BTSP (or *t*-BuSiOOSi *t*-Bu) at -78° in THF.

These silyl enol ethers then stereoselectively are transformed into lithium enolates upon treatment with MeLi and subsequently employed in the synthesis of α-hydroxy ketones (*Scheme* 32).



Scheme 32

In an excellent exploration of the chemistry of BTSP, Hwu[28a] has reported desulfonylation of sulfones to form the corresponding carbonyl compounds upon treatment with BTSP in the presence of n-BuLi (*Scheme* 33). This method has been successfully applied with some alkyl, allylic, benzylic and cycloalkyl sulfones. β,γ-Unsaturated sulfones are converted to α,β-unsaturated ketones without the double bond being affected (Eq. 1, *Scheme* 33). Owing to the weak strength of O-O bonds and the high energy of O-Si bonds, the trimethylsiloxyl anion (Me_3SiO^-) can behave as both an efficient leaving

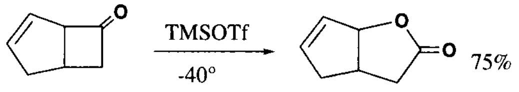


Scheme 33

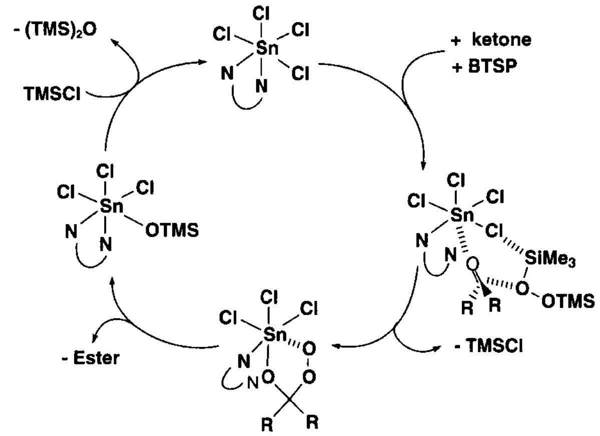
group and a back-attacking moiety. Another advantage of this method is easy removal of byproducts. As one of the oxygens of BTSP becomes the carbonyl oxygen of the product, it is possible to label an oxygen at a specific position *in situ* if an appropriate sulfone is used. In a variation of the Nef reaction, aliphatic nitro compounds are converted into the corresponding carbonyl compounds in high yields (*Scheme* 33).[28b] Instead of a sulfonyl group, as reported by Hwu,[28a] in this case the nitro group acts as a leaving group.

The Baeyer-Villiger oxidation[29a] has been carried out with BTSP under aprotic conditions in the presence of a catalytic amount of TMSOTf. The oxidation occurs specifically at carbonyl groups and C=C are not affected (*Scheme* 34). Takai *et al.*[29b] have reported the Baeyer-Villiger reaction by using BTSP and a Lewis acid such as $SnCl_4$ (or $BF_3.Et_2O$); however, one mole equivalent of the catalyst was necessary for the reaction to occur. In an improved procedure, Shibasaki *et al.*,[29c] have recently reported a new catalyst system comprised of $SnCl_4$ and *trans*-1,2-diaminocyclohexane (1:1) which promotes the reaction of a variety of carbonyl compounds with BTSP. The use such a catalyst system is expected to accomplish the Baeyer-Villiger reaction in an enantioselective manner. It is noteworthy that the catalyst is needed in only 5-10 mol percent. The choice of BTSP is obvious as it is available in water free state. A proposed mechanism is shown in *Scheme* 35.

$$R_2C{=}O + Me_3SiOOSiMe_3 \xrightarrow{\text{TMSOTf (cat.)}} RCOOR$$



Scheme 34

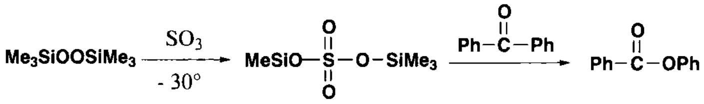


Scheme 35

The potential of BTSP has been further explored by its use in combination with many other reagents to carry out a number of useful transformations. This has been possible mainly due to its non-aqueous nature in comparison to hydrogen peroxide which is available only as an aqueous solution. The following text outlines such combinations and their uses in organic synthesis.

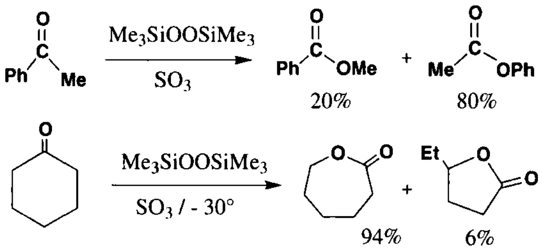
11. *bis*(Trimethylsilyl)peroxide-Sulfur Trioxide

BTSP reacts with SO_3 at -30° to furnish a species called *bis*(trimethylsilyl) monoperoxy sulfate which is a derivative of Caro's acid (*Scheme* 36).[30a] This reagent is found to be an excellent reagent for the Baeyer-Villiger (BV) oxidation of aliphatic, aromatic, acylic and cyclic ketones yielding



Scheme 36

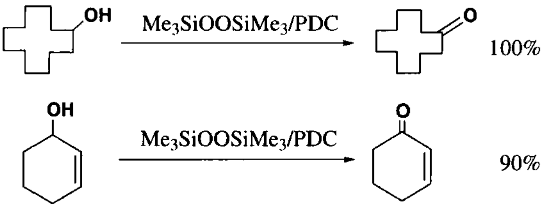
the corresponding esters in high yields. This has distinct advantages over Caro's acid in similar transformations as it gives high yields and purer products. The limitations of this oxidant are that α,β-unsaturated ketones react sluggishly, double bonds are oxidized and that the products of aralkyl ketones such as *p*-bromoacetophenone are hydrolyzed to the corresponding phenols under the reported reaction conditions. Curci *et al.*[30b] have studied the mechanistic aspect of the BV oxidation of ketones with BTSP-SO_3 and have shown the intermediacy of dioxiranes in such reactions. Interestingly, the BV oxidation of acetophenone not only gives phenyl acetate (80%) but also sizable amounts of methyl benzoate 20% (*Scheme* 37). Conversion of a dioxirane intermediate to esters in these reactions *via* polar rearrangement is expected to be due to the Lewis acid [$(Me_3Si_2)SO_4$ or $(Me_3Si)_2SO_3$] catalysis.



Scheme 37

12. *bis*(Trimethylsilyl)peroxide-Pyridinium Dichromate

A system[31] comprising of BTSP and a catalytic amount of pyridinium dichromate (PDC) has been found to be effective for the oxidation of alcohols to the corresponding carbonyl compounds (*Scheme* 38) in excellent yields. Chromic anhydride (CrO_3) and pyridinium chlorochromate (PCC) were found to be less effective as catalysts.

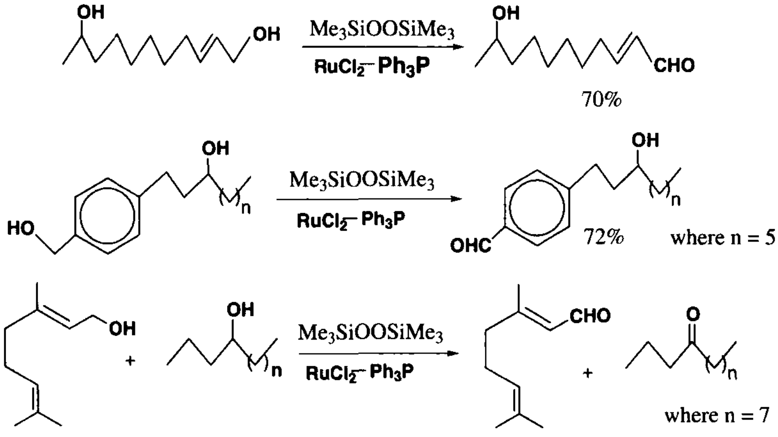


Scheme 38

13. *bis*(Trimethylsilyl)peroxide-Dichloro*tris*(triphenylphosphine) Ruthenium

It has been reported that a reagent system consisting of BTSP and $RuCl_2P(Ph)_3$ also efficiently oxidizes various kinds of alcohols to the corresponding carbonyl compounds (*Scheme* 39).[31]

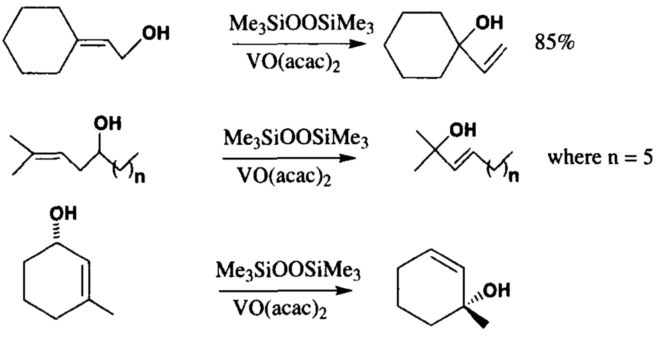
Interestingly, selective oxidation of primary allylic alcohols in the presence of secondary ones is possible and allylic and benzylic alcohols are oxidized faster than secondary alcohols.



Scheme 39

14. *bis*(Trimethylsilyl)peroxide-Vanadyl Acetylacetonate

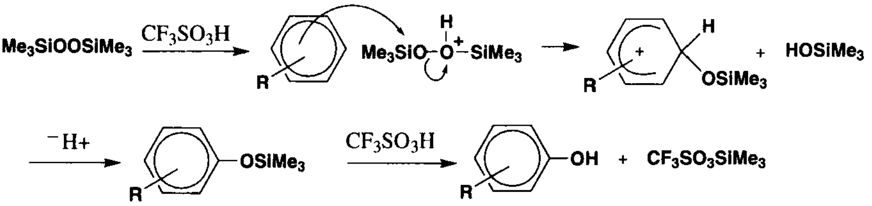
Isomerization of primary allylic alcohols to tertiary alcohols has been reported by Takai *et al.*[32a] by means of BTSP/VO(acac)$_2$ in aprotic solvents under mild reaction conditions. Usually tertiary esters are isomerized to allylic primary esters with acetic anhydride[32b] or with palladium (II) complexes.[32c] But this report shows a reverse conversion, *i. e.* primary alcohol → tertiary alcohol isomerization. This rearrangement was found to occur with BTSP/MoO$_2$(acac)$_2$ combination as well. However, the isomerization of a primary allylic to a secondary alcohol was found to be less satisfactory. Interestingly, α,β-epoxy alcohols were scarcely produced with BTSP-VO(acac)$_2$ system in sharp contrast to the Sharpless epoxidation reagent of *t*-BuOOH-VO(acac)$_2$. In these reactions, the hydroxyl group was found to migrate mainly on the same side of the olefinic double bond. Thus, for example (S)-(-)-3-methyl-2-cyclohexen-1-ol (**7**, 40% e/e) gave (R)-(+)-1-methyl-2-cyclohexen-1-ol in 35% yield (**8**, 29% e/e) and 40% of the unchanged starting alcohol was recovered (*Scheme* 40). This result suggests that the isomerization does not proceed *via* a free allylic cation.



Scheme 40

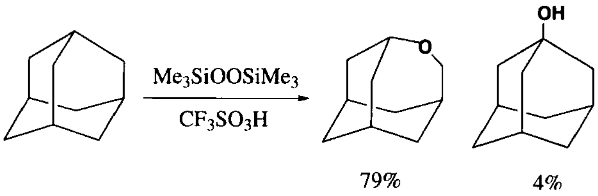
15. *bis*(Trimethylsilyl)peroxide-Triflic Acid

Olah and Ernst[33a] have found that *bis*(trimethylsilyl) peroxide/trifluoromethane sulfonic acid (triflic acid) [TfOH] is a convenient reagent system for one step hydroxylation of aromatics in high yields (*Scheme* 41). Prior to this report, electrophilic hydroxylation of *o*- and *p*-xylene had been reported by reaction with BTSP and $AlCl_3$[33b] which gave mixtures of phenols including those derived by *ipso* attack followed by rearrangement.



Scheme 41

The reagent system BTSP-TfOH was further found by Olah *et al.*[34] to be an efficient electrophilic oxygenating agent for adamantane and diamantane. With adamantane, the major product was 4-oxohomoadamantane arising *via* C-C bond insertion along with very little 1-adamantol, the C-H insertion product (*Scheme* 42). However, in diamantane two isomeric oxahomodiamantanes were obtained along with two isomeric bridgehead diamantanols corresponding to C-C and C-H-bond insertions.



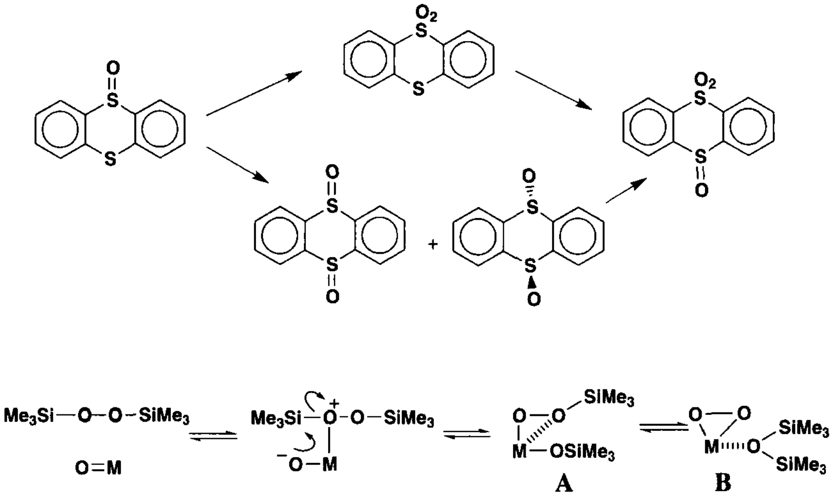
Scheme 42

Curci *et al.*[35] carried out a comparative study of BTSP and *tert*-butyl(trimethylsilyl) peroxide based oxidations of thioxane and N,N-dimethyl *p*-anisidine and concluded that silyl peroxides are superior to alkyl hydroperoxides or H_2O_2. This is mainly because silyl peroxides have much higher solubility in aprotic solvents and yield easily separable reduction products, *e. g.* $(Me_3Si)_2O$ or $ROSiMe_3$.

bis(Trimethylsilyl)peroxide can be activated by various oxo and peroxo complexes[36] of molybdenum, tungsten and vanadium which were subsequently used as catalysts for sulfoxidation of thianthrene 5-oxide (SSO). The most efficient activator for BTSP was the $[MoO_5(OPtBu_3)]$ complex (*Scheme* 43). In this case it is suggested that the bisperoxo metal complex is the active oxygen transfer species.

16. *bis*(Trimethylsilyl)peroxide-Fe(II) and Fe(III) Salts

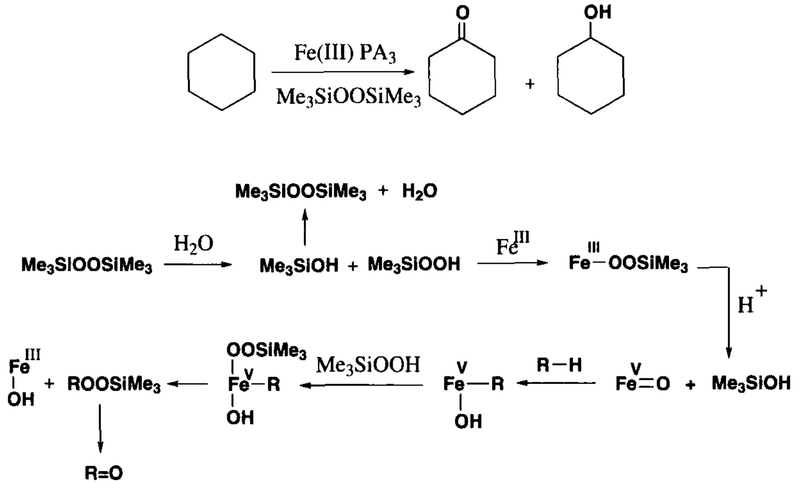
During the search for new oxidants for Gif chemistry Barton *et al.*[37] have reported the use of BTSP to be suitable for the activation of saturated hydrocarbons. The selective oxidation of alkanes to



where M=O is the metal complex

Scheme 43

ketones (*Scheme* 44) using Fe(III)(PA)$_3$ and Fe(III)(PA)$_2$ Cl$_2$Pyr$_2$H with BTSP is thus reported[37a] to proceed by a non-radical mechanism (*Scheme* 44). Here the ligand PA (picolinic acid) is very essential in the absence of which only molecular oxygen is formed.



Scheme 44

Another advance of this reagent system, developed by Barton *et al.*,[37b] is that Fe(II)Cl_2 salt and BTSP in pyridine can also bring about the oxidations of hydrocarbons. Thus, a system composed of an $Fe^{II}Cl_2$ salt and BTSP in a mixture of hydrocarbon and pyridine afforded in 1 h, alkyl chloride or alkyl radical products trapping in good yield. The addition of a reducing agent to keep Fe^{II} in solution gave impressive results. This system is found to involve Fe^{IV}=O which produces a carbon radical. Unlike the H_2O_2 system, no carboxylate ligand is needed to perform the reaction thus providing a very simple system. The advantage in using this oxidant is the possibilty of carrying out experiments under very dry conditions at room temperature or even at relatively higher tempearture without any risk of decomposition (no exothermic reaction between Fe^{II} or Fe^{III} and BTSP occurs as it does with H_2O_2). Further, the efficiency with respect to the iron catalyst is higher.

bis(Trimethylsilyl)peroxide was found by Katsuki *et al.*[38] to serve as an effective terminal oxidant in (salen) manganese (III) complex catalyzed asymmetric epoxidation of chromene derivatives using N-methylimidazole as an axial ligand.

II. Conclusion and Future Outlook

In conclusion, halotrimethylsilanes (especially chlorotrimethylsilane) in combination with several oxidizing agents permit a variety of reactions to be performed. Many of them offer distinct selectivities. It is hoped that the scope of such combinations will be explored further and many new combinations of TMSX and oxidants and thereby new reactions (or modifications of older reactions) will be reported in the future.

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