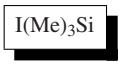
Iodotrimethylsilane[1]



[16029-98-4] C_3H_9ISi (MW 200.11)

(a versatile reagent for the mild dealkylation of ethers, carboxylic esters, lactones, carbamates, acetals, phosphonate and phosphate esters; cleavage of epoxides, cyclopropyl ketones; conversion of vinyl phosphates to vinyl iodides; neutral nucleophilic reagent for halogen exchange reactions, carbonyl and conjugate addition reactions; use as a trimethylsilylating agent for formation of enol ethers, silyl imino esters, and *N*-silylenamines, alkyl, alkenyl and alkynyl silanes; Lewis acid catalyst for acetal formation, α-alkoxymethylation of ketones, for reactions of acetals with silyl enol ethers and allylsilanes; reducing agent for epoxides, enediones, α-ketols, sulfoxides, and sulfonyl halides; dehydrating agent for oximes)

Alternate Name: TMS-I; TMSI; trimethylsilyl iodide.

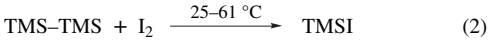
Physical Data: bp 106–109 °C; *d* 1.406 g cm^{-3}; n_D^{20} 1.4710; fp −31 °C.

Solubility: sol in CCl_4, $CHCl_3$, CH_2Cl_2, $ClCH_2CH_2Cl$, MeCN, PhMe, hexanes; reactive with THF (ethers), alcohols, and EtOAc (esters).

Form Supplied in: clear colorless liquid, packaged in ampules, stabilized with copper; widely available.

Analysis of Reagent Purity: easily characterized by ^1H, ^{13}C, or ^{29}Si NMR spectroscopy.

Preparative Methods: although more than 20 methods have been reported[1] for the preparation of TMS-I, only a few are summarized here. ***Chlorotrimethylsilane*** undergoes halogen exchange with either ***Lithium Iodide***[2] in $CHCl_3$ or ***Sodium Iodide***[3] in MeCN, which allows in situ reagent formation (eq 1). Alternatively, ***Hexamethyldisilane*** reacts with ***Iodine*** at 25–61 °C to afford TMS-I with no byproducts (eq 2).[4]



Several other methods for in situ generation of the reagent have been described.[5,6] It should be noted, however, that the reactivity of in situ generated reagent appears to depend upon the method of preparation.

Purity: by distillation from copper powder.

Handling, Storage, and Precautions: extremely sensitive to light, air, and moisture, it fumes in air due to hydrolysis (HI), and becomes discolored upon prolonged storage due to generation of I_2. It is flammable and should be stored under N_2 with a small piece of copper wire. It should be handled in a well ventilated fume hood and contact with eyes and skin should be avoided.

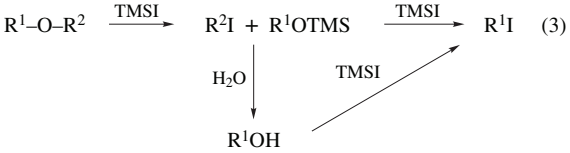
Original Commentary

Michael E. Jung
University of California, Los Angeles, CA, USA

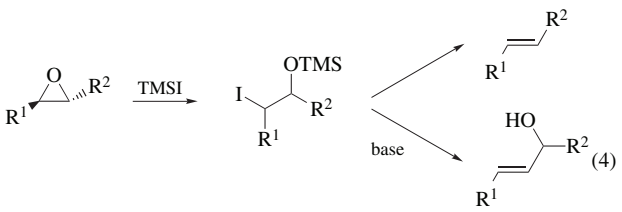
Michael J. Martinelli
Lilly Research Laboratories, Indianapolis, IN, USA

Use as a Nucleophilic Reagent in Bond Cleavage Reactions.

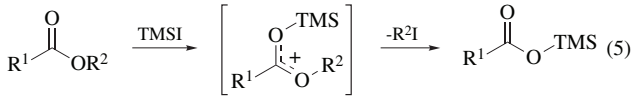
Ether Cleavage.[5,7] The first broad use of TMS-I was for dealkylation reactions of a wide variety of compounds containing oxygen–carbon bonds, as developed independently by the groups of Jung and Olah. Simple ethers initially afford the trimethylsilyl ether and the alkyl iodide, with further reaction giving the two iodides (eq 3).[7,8] This process occurs under neutral conditions, and is generally very efficient as long as precautions to avoid hydrolysis by adventitious water are taken. Since the silyl ether can be quantitatively hydrolyzed to the alcohol, this reagent permits the use of simple ethers, e.g. methyl ethers, as protective groups in synthesis. The rate of cleavage of alkyl groups is: tertiary ≈ benzylic ≈ allylic methyl > secondary > primary. Benzyl and *t*-butyl ethers are cleaved nearly instantaneously at low temperature with TMS-I. Cyclic ethers afford the iodo silyl ethers and then the diiodide, e.g. THF gives 4-iodobutyl silyl ether and then 1,4-diiodobutane in excellent yield.[7,8] Alcohols and silyl ethers are rapidly converted into the iodides as well.[8a,9] Alkynic ethers produce the trimethylsilylketene via dealkylative rearrangement.[4b] Phenolic ethers afford the phenols after workup.[5,7,10] In general, ethers are cleaved faster than esters. Selective cleavage of methyl aryl ethers in the presence of other oxygenated functionality has also been accomplished in quinoline.[11] γ-Alkoxyl enones undergo deoxygenation with excess TMS-I (2 equiv), with the first step being conjugate addition of TMS-I.[12]



Cleavage of Epoxides. Reaction of epoxides with 1 equiv of TMS-I gives the vicinal silyloxy iodide.[8e] With 2 equiv of TMS-I, however, epoxides are deoxygenated to afford the corresponding alkene (eq 4).[13a,b] However, allylic alcohols are efficiently prepared by reaction of the intermediate iodosilane with base.[13c,d] Furthermore, acyclic 2-ene-1,4-diols react with TMS-I to undergo dehydration, affording the corresponding diene.[13e]



Ester Dealkylation.[14] Among the widest uses for TMS-I involves the mild cleavage of carboxylic esters under neutral conditions. The ester is treated with TMS-I to form an initial oxonium intermediate which suffers attack by iodide (eq 5). The trimethylsilyl ester is cleaved with H_2O during workup. Although the reaction is general and efficient, it is possible to accomplish selective cleavage according to the reactivity trend: benzyl, *t*-butyl > methyl, ethyl, *i*-propyl. Neutral transesterification is also possible via the silyl ester intermediate.[15] Aryl esters are not cleaved by TMS-I, however, since the mechanism involves displacement of R^2 by I^-. Upon prolonged exposure (75 °C, 3 d) of simple esters to excess TMS-I (2.5 equiv), the corresponding acid iodides are formed.[14b,16] β-Keto esters undergo decarboalkoxylation when treated with TMS-I.[17] An interesting rearrangement reaction provides α-methylene lactones from 1-(dimethylaminomethyl)cyclopropanecarboxylates (eq 6).[18]



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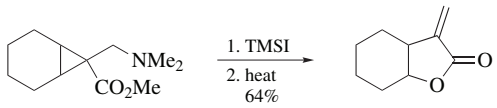
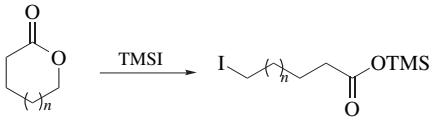


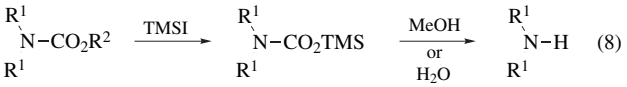
(6)

Lactone Cleavage.[14,19] Analogous to esters, lactones are also efficiently cleaved with TMS-I to provide ω-iodocarboxylic acids, which may be further functionalized to afford bifunctional building blocks for organic synthesis (eq 7). Diketene reacts with TMS-I to provide a new reagent for acetoacylation.[20]



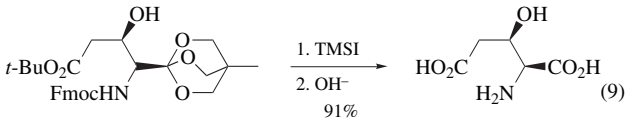
(7)

Cleavage of Carbamates.[21] Since strongly acidic conditions are typically required for the deprotection of carbamates, use of TMS-I provides a very mild alternative. Benzyl and *t*-butyl carbamates are readily cleaved at rt,[22] whereas complete cleavage of methyl or ethyl carbamates may require higher temperatures (reflux). The intermediate silyl carbamate is decomposed by the addition of methanol or water (eq 8). Since amides are stable to TMS-I-promoted hydrolysis,[7a] this procedure can be used to deprotect carbamates of amino acids and peptides.[21d]



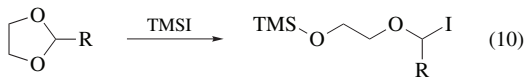
(8)

A recent example used TMS-I to deprotect three different protecting groups (carbamate, ester, and orthoester) in the same molecule in excellent yield (eq 9).[23]



(9)

Cleavage of Acetals.[24] Acetals can be cleaved in analogy to ethers, providing a newly functionalized product (eq 10), or simply the parent ketone (eq 11). Glycals have also been converted to the iodopyrans with TMS-I,[25] and glycosidation reactions have been conducted with this reagent.[26]



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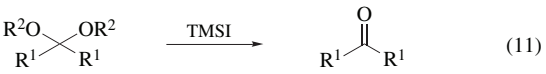
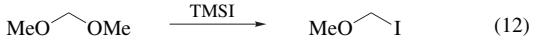


(11)

Orthoesters are converted into esters with TMS-I. The dimethyl acetal of formaldehyde, methylal, affords iodomethyl methyl ether in good yield (eq 12)[27a] (in the presence of alcohols, MOM ethers are formed).[27b] α-Acyloxy ethers also furnish the iodo ethers,[28] e.g. the protected β-acetyl ribofuranoside gave the α-iodide which was used in the synthesis of various nucleosides in good yield (eq 13).[28b] Aminals are similarly converted into immonium salts, e.g. Eschenmoser's reagent, ***Dimethyl(methylene)ammonium Iodide***, in good yield.[29]



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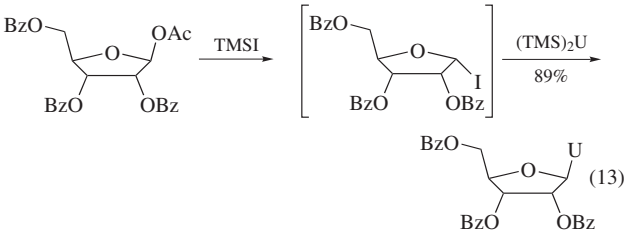
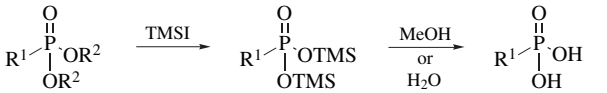


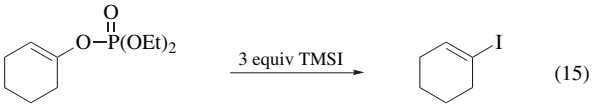
(13)

Cleavage of Phosphonate and Phosphate Esters.[30] Phosphonate and phosphate esters are cleaved even more readily with TMS-I than carboxylic esters. The reaction of phosphonate esters proceeds via the silyl ester, which is subsequently hydrolyzed with MeOH or H_2O (eq 14).



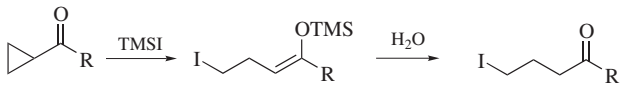
(14)

Conversion of Vinyl Phosphates to Vinyl Iodides.[31] Ketones can be converted to the corresponding vinyl phosphates which react with TMS-I (3 equiv) at rt to afford vinyl iodides (eq 15).



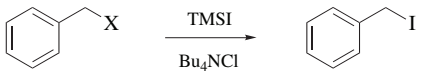
(15)

Cleavage of Cyclopropyl Ketones.[32] Cyclopropyl ketones undergo ring opening with TMS-I, via the silyl enol ether (eq 16). Cyclobutanones react analogously under these conditions.[33]



(16)

Halogen Exchange Reactions.[34] Halogen exchange can be accomplished with reactive alkyl halides, such as ***Benzyl Chloride*** or ***Benzyl Bromide***, and even with certain alkyl fluorides, by using TMS-I in the presence of $(n\text{-Bu})_4NCl$ as catalyst (eq 17).

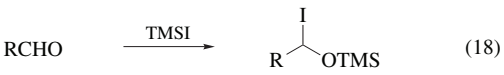


(17)

X = Br, Cl

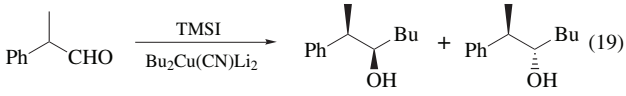
Use of TMS-I in Nucleophilic Addition Reactions.

Carbonyl Addition Reactions.[35] α-Iodo trimethylsilyl ethers are produced in the reaction of aldehydes and TMS-I (eq 18). These compounds may react further to provide the diiodo derivative or may be used in subsequent synthesis.



(18)

An example of a reaction of an iodohydrin silyl ether with a cuprate reagent is summarized in eq 19.[36] An interesting reaction of TMS-I with phenylacetaldehydes gives a quantitative yield of the oxygen-bridged dibenzocyclooctadiene, which was then converted in a few steps to the natural product isopavine (eq 20).[35,37]



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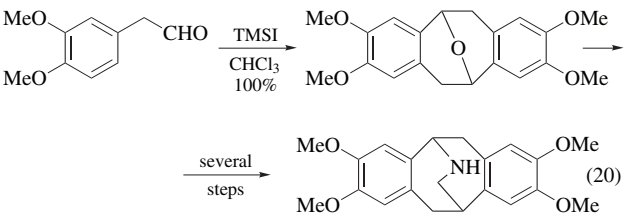
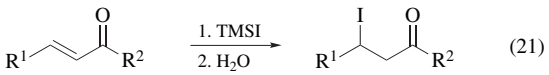


(20)

β-Iodo ketones have been produced from reactions of TMS-I and ketones with α-hydrogens.[38] This reaction presumably involves a TMS-I catalyzed aldol reaction followed by 1,4-addition of iodide.

Conjugate Addition Reactions.[39] α,β-Unsaturated ketones undergo conjugate addition with TMS-I to afford the β-iodo adducts in high yield (eq 21). The reaction also works well with the corresponding alkynic substrate.[40]



(21)

TMS-I has also been extensively utilized in conjunction with organocopper reagents to effect highly stereoselective conjugate additions of alkyl nucleophiles.[41]

Use of TMS-I as a Silylating Agent.

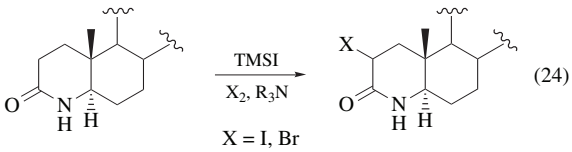
Formation of Silyl Enol Ethers.[42] TMS-I in combination with ***Triethylamine*** is a reactive silylating reagent for the formation of silyl enol ethers from ketones (eq 22). TMS-I with ***Hexamethyldisilazane*** has also been used as an effective silylation agent, affording the thermodynamic silyl enol ethers. For example, 2-methylcyclohexanone gives a 90:10 mixture in favor of the tetrasubstituted enol ether product.[42a] The reaction of TMS-I with 1,3-diketones is a convenient route to 1,3-bis(trimethylsiloxy)-1,3-dienes.[42c]

(22)

In an analogous process, TMS-I reacts with lactams in the presence of Et_3N to yield silyl imino ethers (eq 23).[43a]

(23)

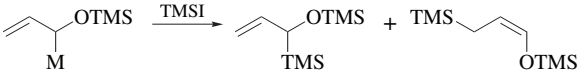
Halogenation of Lactams.[43b] Selective and high yielding iodination and bromination of lactams occurs with ***Iodine*** or ***Bromine***, respectively, in the presence of TMS-I and a tertiary amine base (eq 24). The proposed reaction mechanism involves intermediacy of the silyl imino ether.



(24)

X = I, Br

Reaction with Carbanions.[44] TMS-I has seen limited use in the silylation of carbanions, with different regioselectivity compared to other silylating reagents in the example provided in eq 25.



(25)

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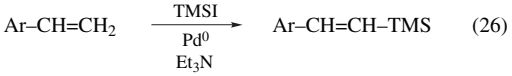
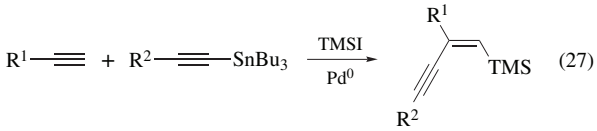
Silylation of Alkynes and Alkenes.[45] A Heck-type reaction of TMS-I with alkenes in the presence of Pd^0 and Et_3N affords alkenyltrimethylsilanes (eq 26).



(26)

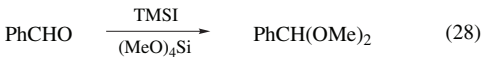
Oxidative addition of TMS-I to alkynes can also be accomplished with a three-component coupling reaction to provide the enyne product (eq 27).



(27)

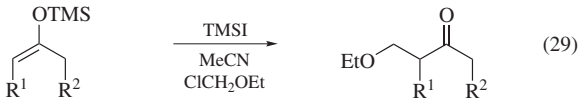
Use of TMS-I as a Lewis Acid.

Acetalization Catalyst.[46] TMS-I used in conjunction with $(MeO)_4Si$ is an effective catalyst for acetal formation (eq 28).



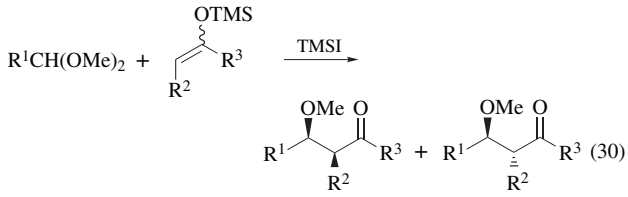
(28)

Catalyst for α-Alkoxymethylation of Ketones. Silyl enol ethers react with α-chloro ethers in the presence of TMS-I to afford α-alkoxymethyl ketones (eq 29).[47]



(29)

Catalyst for Reactions of Acetals with Silyl Enol Ethers and Allylsilanes. TMS-I catalyzes the condensation of silyl enol ethers with various acetals (eq 30)[48] and imines,[49] and of allylsilanes with acetals.[50]



(30)

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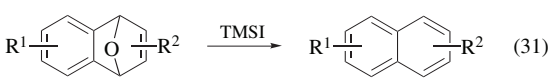
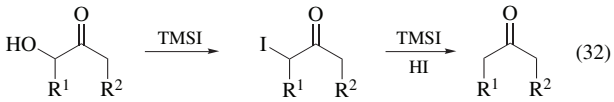
Use of TMS-I as a Reducing Agent. TMS-I reduces enediones to 1,4-diketones,[51] while both epoxides and 1,2-diols are reduced to the alkenes.[13a,b,52] The Diels–Alder products of benzynes and furans are converted in high yield to the corresponding naphthalene (or higher aromatic derivative) with TMS-I (eq 31).[53]



(31)

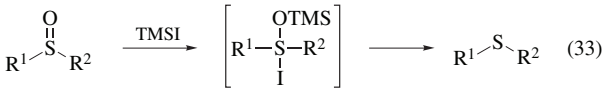
Styrenes and benzylic alcohols are reduced to the alkanes with TMS-I (presumably via formation of HI).[54] Ketones produce the symmetrical ethers when treated with trimethylsilane as a reducing agent in the presence of catalytic TMS-I.[55]

Reduction of α-Ketols.[56,57] Carbonyl compounds containing α-hydroxy, α-acetoxy, or α-halo groups react with excess TMS-I to give the parent ketone. α-Hydroxy ketone reductions proceed via the iodide, which is then reduced with iodide ion to form the parent ketone (eq 32).



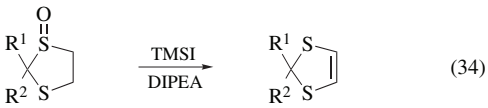
(32)

Sulfoxide Deoxygenation.[58] The reduction of sulfoxides occurs under very mild conditions with TMS-I to afford the corresponding sulfide and iodine (eq 33). Addition of I_2 to the reaction mixture accelerates the second step. The deoxygenation occurs faster in pyridine solution than the reactions with a methyl ester or alcohol.[59]



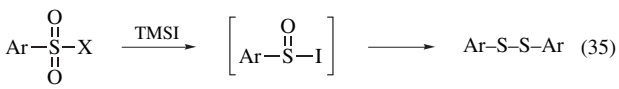
(33)

Pummerer reactions of sulfoxides can be accomplished in the presence of TMS-I and an amine base, leading to vinyl sulfides.[60] An efficient synthesis of dithioles was accomplished with TMS-I and Hünig's base (***Diisopropylethylamine***) (eq 34).[61]



(34)

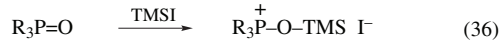
Reaction with Sulfonyl Halides.[62] Arylsulfonyl halides undergo reductive dimerization to form the corresponding disulfides (eq 35). Alkylsulfonyl halides, however, undergo this process under somewhat more vigorous conditions. Although sulfones generally do not react with TMS-I, certain cyclic sulfones are cleaved in a manner analogous to lactones.[63]



(35)

Other Reactions of TMS-I.

Reaction with Phosphine Oxides.[64] Phosphine oxides react with TMS-I to form stable adducts (eq 36). These *O*-silylated products can undergo further thermolytic reactions such as alkyl group cleavage.

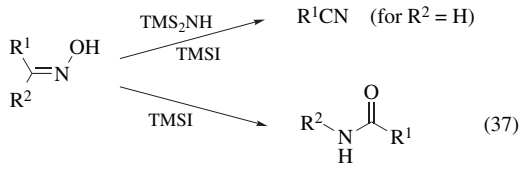


(36)

Chlorophosphines undergo halogen exchange reactions with TMS-I.[65]

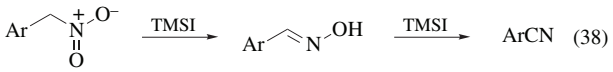
Reaction with Imines. Imines react with TMS-I to form *N*-silylenamines, in a process analogous to the formation of silyl enol ethers from ketones.[66]

Reaction with Oximes.[67] Oximes are activated for dehydration (aldoximes, with hexamethylsilazane) or Beckmann rearrangement (ketoximes) with TMS-I (eq 37).



(37)

Reactions with Nitro and Nitroso Compounds.[68] Primary nitro derivatives react with TMS-I to form the oximino intermediate via deoxygenation, which then undergoes dehydration as discussed for the oximes (eq 38). Secondary nitro compounds afford the silyl oxime ethers, and tertiary nitro compounds afford the corresponding iodide. Nitroalkenes, however, react with TMS-I at 0 °C to afford the ketone as the major product (eq 39).[69]



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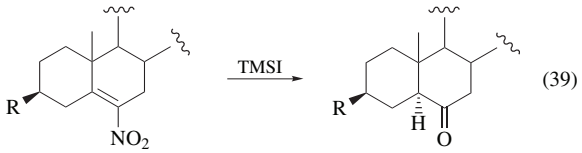
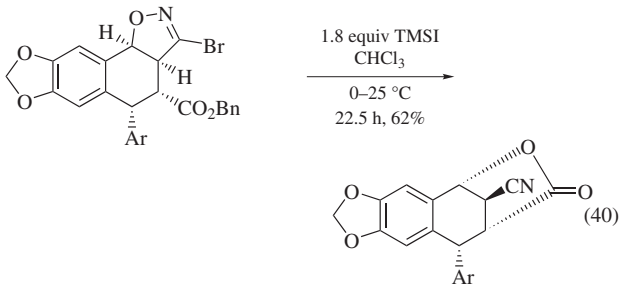


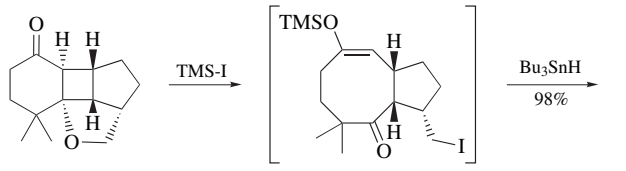
(39)

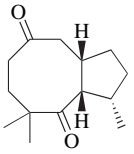
An interesting analogy to this dehydration process is found in the reductive fragmentation of a bromoisoxazoline with TMS-I, which yields the nitrile (eq 40).[70]



(40)

Rearrangement Reactions. An interesting rearrangement occurs on treatment of a β-alkoxy ketone with TMS-I which effects dealkylation and retro-aldol reaction to give the eight-membered diketone after reductive dehalogenation (eq 41).[71] Tertiary allylic silyl ethers α to epoxides undergo a stereocontrolled rearrangement to give the β-hydroxy ketones on treatment with catalytic TMS-I (eq 42).[72]





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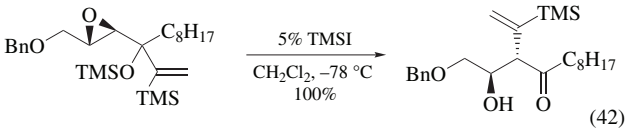


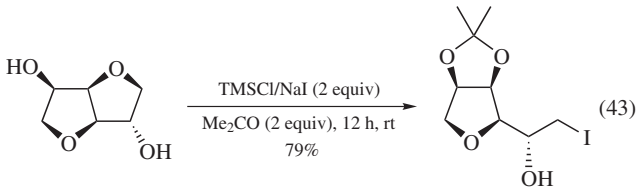
(42)

First Update

George A. Olah, G. K. Surya Prakash, Jinbo Hu
University of Southern California, Los Angeles, CA, USA

Selective Bond Cleavage Reactions.

Ether Cleavage. Iodotrimethylsilane (TMSI) continues to be a versatile ether-cleaving agent in the past decade, and it has been widely applied to complex molecules with high chemoselectivity. Demethylation of 8-methoxy-[2,2]metacyclophanes with TMSI can be accomplished in excellent yields.[73] Treatment of isosorbide and isomannide with TMSI [in situ generated from chlorotrimethylsilane (TMSCl) and sodium iodide] in acetonitrile in the presence of acetone induces the cleavage of only one of the two rings and provides chiral trisubstituted tetrahydrofurans (eq 43).[74] The formation of cyclic sulfonium ions by TMSI-mediated intramolecular displacement of hydroxide or methoxide by sulfide has led to ring contraction reactions from thiepanes to thiolanes (eq 44).[75] The cyclization is especially favored with secondary and tertiary alcohols or ethers, and with an aliphatic more than an aromatic sulfide function.[75]



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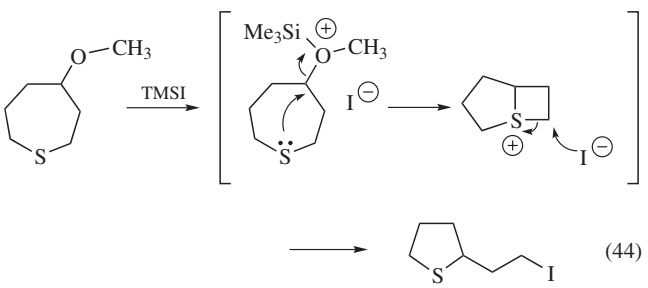
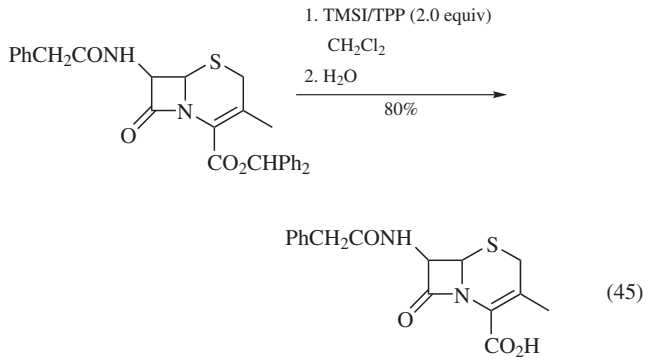


(44)

Ester and Lactone Cleavage. TMSI has been combined with triphenylphosphine (TPP) (in dichloromethane solution) as a more stable, milder, and more selective ester-cleaving agent compared with TMSI itself.[76] TPP increases the stability of TMSI as well as the selectivity by decreasing its reactivity and plays a significant role in preventing side reaction by scavenging the reactive alkyl iodides, generated from the cleavage of ester compounds, to give the corresponding phosphonium iodide salts that are inactive under the reaction conditions.[76] *p*-Methoxybenzyl and diphenylmethyl esters can be easily converted into the corresponding carboxylic acids using TMSI/TPP in dichloromethane at room temperature in good yields (eq 45).[76]



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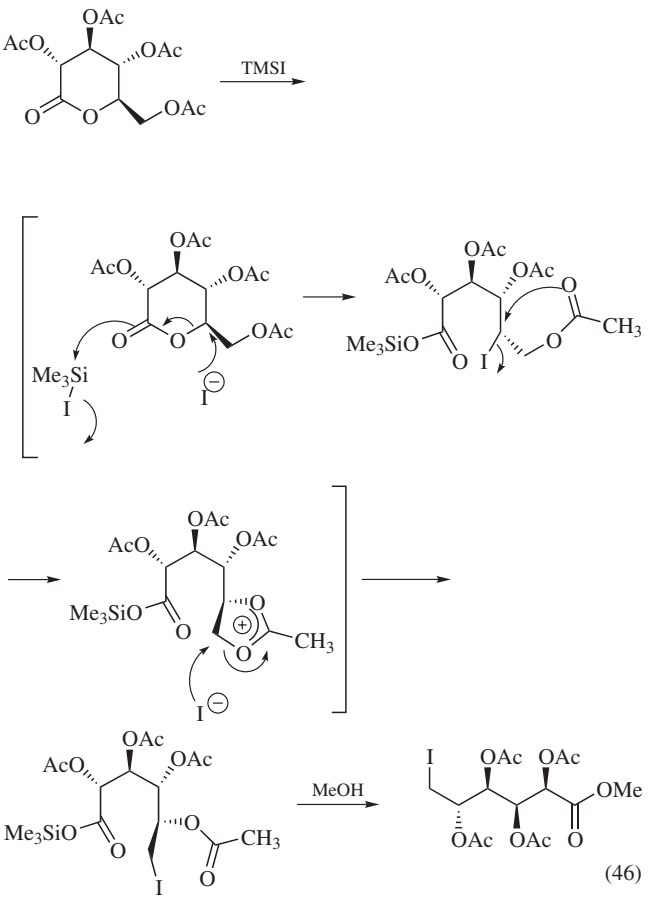
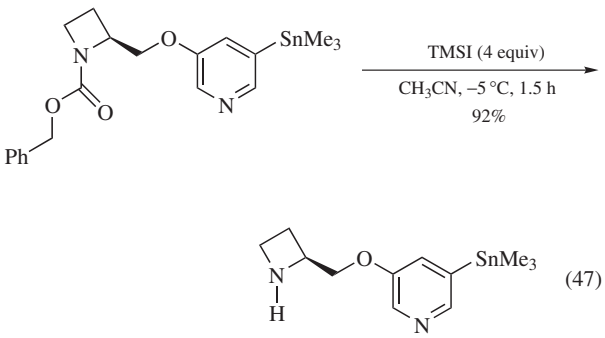


(46)

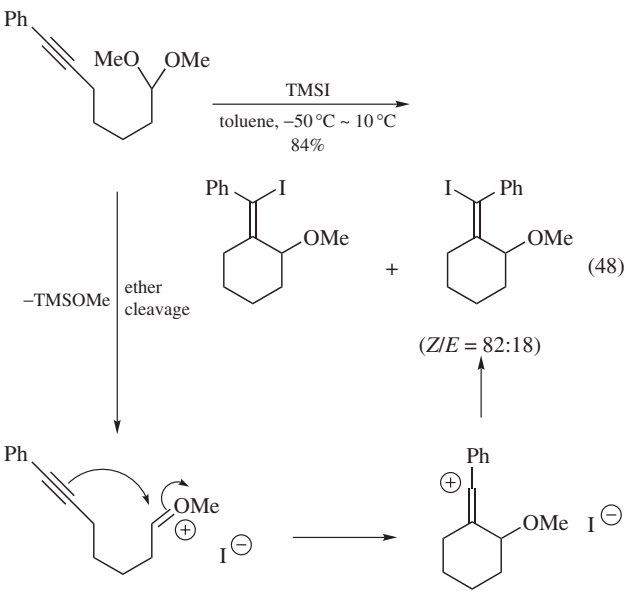
An unusual sugar lactone cleavage reaction, followed by an intramolecular rearrangement, leads to the formation of primary iodides with the same configuration. The lactone is proposed to be opened by an iodide anion, with inversion of configuration at C-5. The formation of acetoxonium ion then occurs from secondary iodide, with a second inversion at C-5. The acetoxonium ion is then opened regioselectively by an iodide ion, leading to the primary iodide (eq 46).[77]

Cleavage of Carbamates. TMSI has been used as a deblocking agent for the benzyloxycarbonyl group (Cbz) in the synthesis of the nicotinic receptor tracer 5-IA-85380 precursor (eq 47).[78] The TMSI-mediated selective carbamate cleavage can be achieved to afford amino-tin compounds without removing the stannyl moiety, which becomes the key step in the multiple-step synthesis.[78] TMSI has also been applied to the selective cleavage in chiral *N*-substituted 4-phenyl-2-oxazolidinones, and this method allows a more versatile use of 4-phenyl-2-oxazolidinone as a chiral auxiliary and *N*-protective group in the synthesis of carbacephems.[79]



(47)

Cleavage of Acetals. The action of TMSI on 7-phenyl-6-alkynal dimethylacetals gives the oxonium ion intermediates, which undergo an intramolecular electrophilic reaction with the carbon-carbon triple bond to afford 2-(1-iodobenzylidene)cyclohexyl methyl ether (eq 48).[80] TMSI has also been used in a one-pot conversion of tetraacetal tetraoxa-cages to aza-cages in alkyl nitriles at room temperature via the ring expansion intermediates, which was interpreted to involve a Ritter-type of reaction mechanism (eq 49).[81] Interestingly, the reaction of tetraacetal tetraoxa-cages with TMSCl and NaI in nitriles at room temperature gives the amido-cages.[81]



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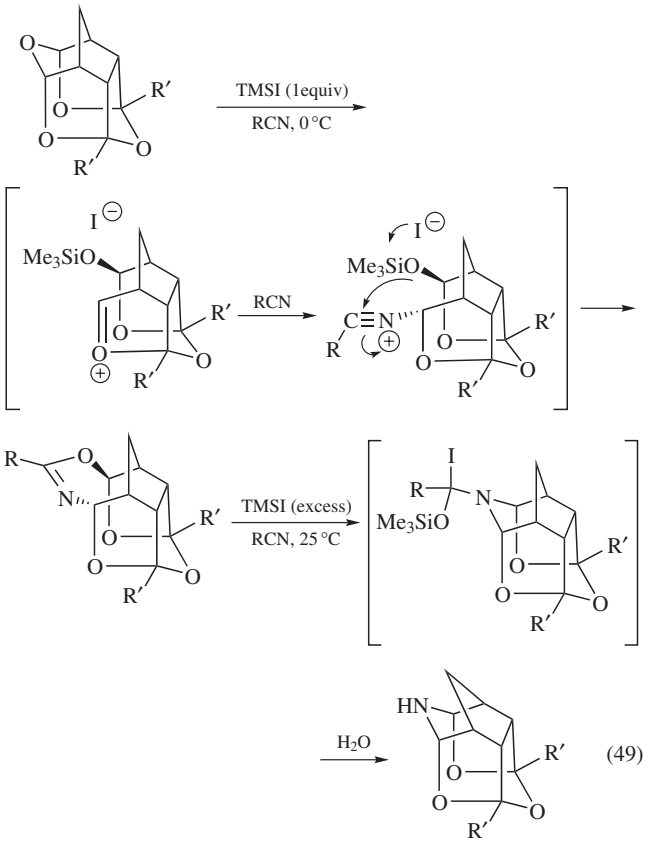
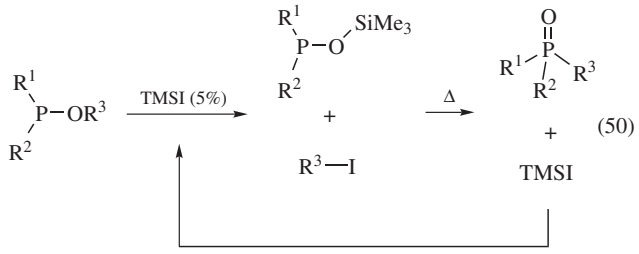


(49)

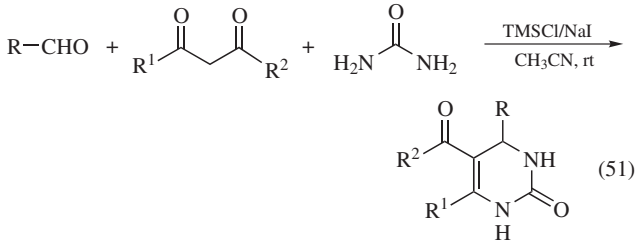
Cleavage of Phosphorous(III) Esters Leading to a Michaelis–Arbuzov Rearrangement. A new and catalytic version of the Michaelis-Arbuzov rearrangement has been reported by directly forming an alkyl halide through the action of trimethylsilyl halide (TMSX, X = I, Br) on phosphorous(III) esters (eq 50).[82] This rearrangement occurs at temperatures from 20 to 80 °C, and only a catalytic amount (5 mol%) of TMSI (or TMSBr) is needed. Unlike the usual Arbuzov rearrangement, alkyl halides are not required for this type of direct and easy-to-handle TMSX-catalyzed Michaelis-Arbuzov-like rearrangement.[82]



(50)

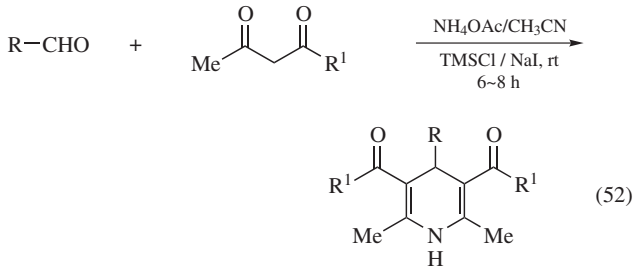
Use of TMSI as a Lewis-acidic Activation Agent.

For Biginelli Reaction. TMSI (in situ generated from TMSCl and NaI) is an excellent promoter for the one-pot synthesis of dihydropyrimidinones via the Biginelli reaction (eq 51), which involves the condensation of an aldehyde, a β-ketoester and urea (or thiourea).[83] The traditional Biginelli reaction commonly proceeds under strongly acidic conditions, and this protocol often suffers from low yields particularly in case of substituted aromatic or aliphatic aldehydes. However, when TMSI is applied as a promoter, the reaction usually affords excellent yields of dihydropyrimidinones even at ambient temperature (eq 51).[83]



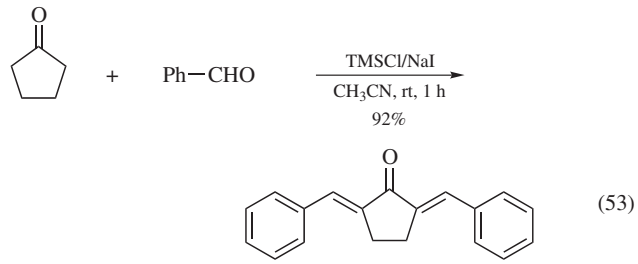
(51)

For the Synthesis of Hantzsch 1,4-Dihydropyridines. TMSI (in situ generated) has been used in the efficient synthesis of various substituted Hantzsch 1,4-dihydropyridines using both the classical and modified Hantzsch procedures at room temperature in acetonitrile (eq 52).[84] The usage of TMSI enables the reaction to proceed smoothly with good to excellent yields of products.[84]



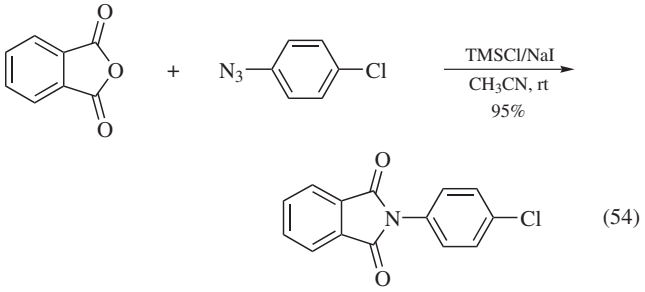
(52)

For Aldol and Related Reactions. The TMSI/$(TMS)_2NH$ combination can be used for the synthesis of polycyclic cyclobutane derivatives by tandem intramolecular Michael-aldol reaction.[85] TMSI-induced diastereoselective synthesis of tetrahydropyranones by a tandem Knoevenagel-Michael reaction, has also been developed.[86] More recently, the facile synthesis of α,α'-bis(substituted benzylidene)cycloalkanones has been reported, using TMSI (in situ generated) mediated cross-aldol condensations (eq 53).[87]



(53)

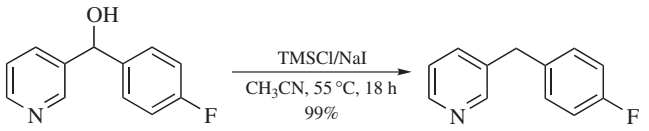
For the Synthesis of N-Substituted Phthalimides/Naphthalimides. *N*-Substituted phthalimides and naphthalimides can be synthesized in good to excellent yields, employing TMSI (in situ generated) from corresponding azides and anhydrides under mild conditions (eq 54).[88]



(54)

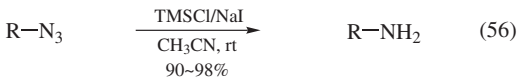
Use of TMSI as a Reducing Agent.

Selective Reduction of α,α-Diaryl Alcohols. TMSI has been utilized as a reducing agent for the rapid and highly selective reduction of α,α-diaryl alcohols to the corresponding alkanes.[89] The reaction proceeds particularly well for electron-rich substrates, which may be associated with the proposed intermediacy of an aryl-stabilized benzylic carbocation at the reduction site.[90] The moderately electron-deficient benzylic alcohols can also be selectively reduced to analogous toluenes, and the reaction condition tolerates other reduction-sensitive functional groups such as ketone, aldehyde, nitrile, and nitro groups (eq 55).[90] The preparation of biarylmethanes, involving benzylation via tandem Grignard reaction-TMSI-mediated reduction, has also been reported.[91]



(55)

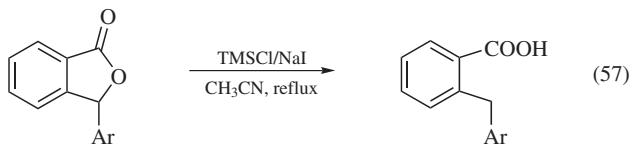
Reduction of Azides to Amines. In situ generated TMSI has been found to be a useful reducing agent for the reduction of azides to amines (eq 56).[92] The reaction is carried out under extremely mild and neutral conditions, and a number of aryl, alkyl, and aroyl azides are suitable for this tranformation. This methodology has also been applied to the synthesis of pyrrolo[2,1-*c*][1,4]benzodiazepines via reductive cyclization of ω-azido carbonyl compounds.[93]



(56)

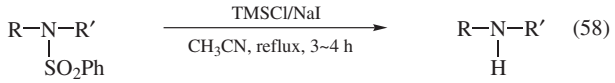
(R= alkyl, aryl, and aroyl)

Reductive Cleavage of Phthalides and Sulfonamides. 3-Arylphthalides can be readily cleaved reductively by means of TMSI (in situ generated) to give corresponding 2-benzylbenzoic acids (eq 57) or 2-(2-thienylmethyl)benzoic acids.[94]



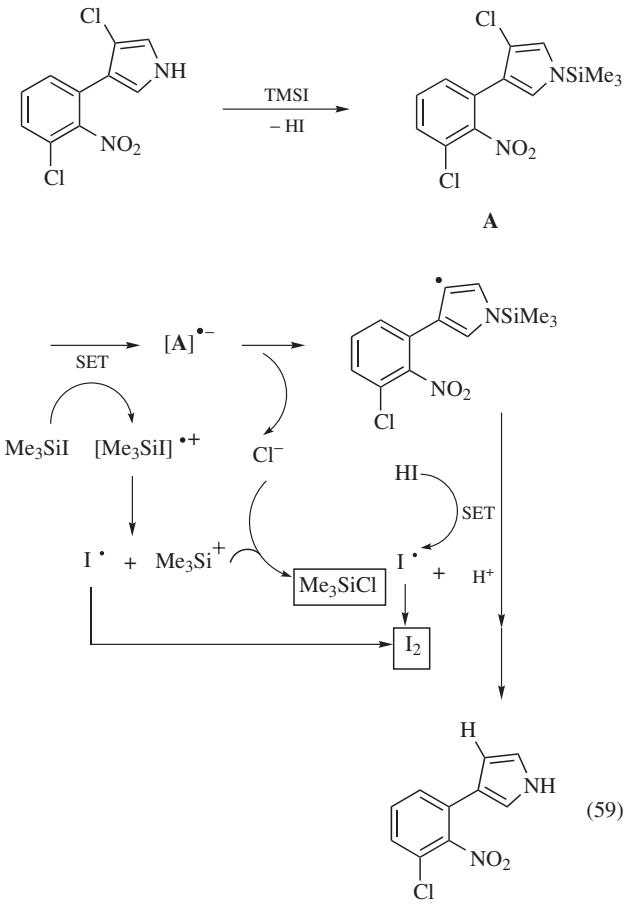
(57)

TMSI, in situ generated from TMSCl and NaI, is also a robust reagent for the deprotection of sulfonamides (eq 58).[95] The reductive desulfonylation usually proceeds in good yields with 1.5 equiv of TMSI in acetonitrile under reflux for 3~4 hours. The mild reaction conditions employed in this deprotection method allow the selective deprotection of sulfonamides in the presence of *N*-alkyl and *N*-benzyl groups.[95]



(58)

Reductive Cleavage of Heteroaryl C-Halogen Bonds. Regioselective reductive dehalogenation of heterocyclic antibiotic compounds, such as pyrrolnitrins, halo-uridines and pyrimidines, has been successfully accomplished (eq 59).[96a] A single-electron transfer (SET) mechanism was proposed for this type of dehalogenation (eq 59).[96a] TMSI-mediated reductive C-2 dechlorination of some 5-allyl(allenyl)-2,5-dichloro-3-dialkylamino-4,4-dimethoxy-2-cyclopentenones has also been successful.[96b]

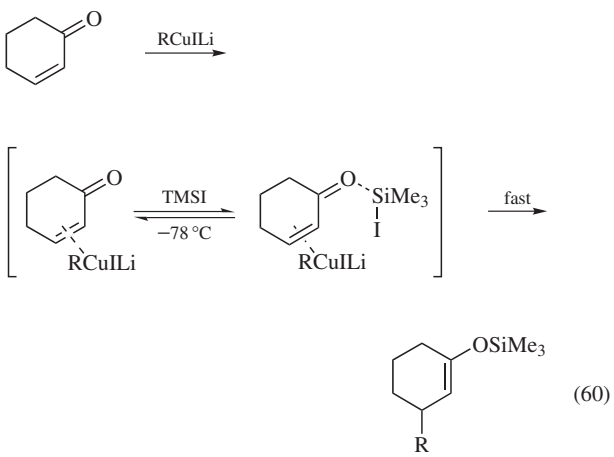


(59)

Use of TMSI in Conjunction with Organometallic Reagents.

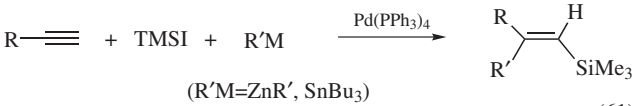
In Conjugate Monoorganocopper Addition to α,β-Unsaturated Carbonyl Compounds. TMSI has been demonstrated to efficiently promote the reaction of conjugate 1,4-additions of monoorganocopper compounds into a

variety of α,β-unsaturated carbonyl compounds, such as cyclic and acyclic enones, β-alkoxy enones, enoates, and lactones, often at $-78\,^{\circ}C$ (eq 60).[97] The RCu(LiI)-TMSI reagent gives a good economy of group transfer with good to excellent yields of conjugate adducts. Lithium iodide, present from preparation of the organocopper compounds, increases the rate of the reaction and is a favorable component.[97] The mechanistic study of the role of TMSI in the conjugate addition of butylcopper-TMSI to α-enones shows that a direct silylation of an intermediate π-complex by TMSI is most likely (eq 60).[98]The conjugate additions of MeCu, PhCu, and *n*-BuCu to the chiral enoylimides in the presence of TMSI and LiI in THF give the adducts in excellent yields and high diastereoselectivity ($80 \sim 93\%$ *de*).[99] In the presence of TMSI and LiI in THF, the otherwise unreactive copper acetylides can add to enones present as *s-trans* conformers to provide good yields of the silyl enol ethers of β-acetylido carbonyl compounds.[100] Similaly, TMSI-promoted diastereoselective conjugate additions of monoorganocuprates Li[RCuI] to different α,β-unsaturated *N*-acyl oxazolidinones with high yields and diastereomeric ratios have also been reported.[101]



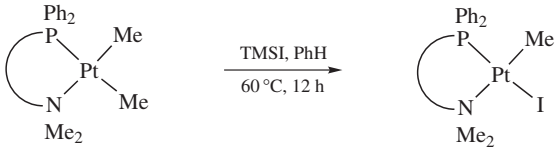
(60)

Pd-catalyzed Coupling Reactions. The reaction of terminal acetylenes with TMSI and organozinc reagents (or organostannanes) in the presence of $Pd(PPh_3)_4$ results in addition of the trimethylsilyl group of TMSI and an alkyl group of the organozinc reagent (or alkynyl group of organostannane) to the acetylenes to give vinylsilanes (eq 61).[102] This catalytic reaction involves an oxidative addition of the Si-I bond in TMSI to Pd(0) leading to a silylpalladium(II) species, and silylpalladation of an acetylene with the Si-Pd species followed by coupling with organozinc reagents (or organostannanes).[102]



(61)

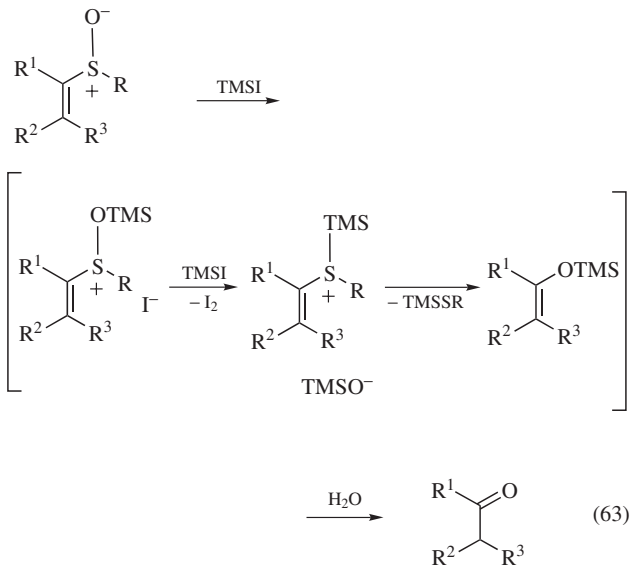
TMSI as Iodination Agent in Organometallic Complexes. TMSI has been applied as an iodinating agent in organometallic complexes.[103–105] For example, reaction of the P,N-chelated dimethylplatinum complexes with TMSI stereoselectively gives the corresponding methyl iodo complexes in which only the methyl group trans to the phosphorus atom is exchanged (eq 62).[103] TMSI was also used as a halogen-exchange reagent in the thorium(IV) complex to form Th-I bond.[104] The application of TMSI as a Cl-I exchange reagent in transition metal coordination chemistry, has also been studied.[105]



(62)

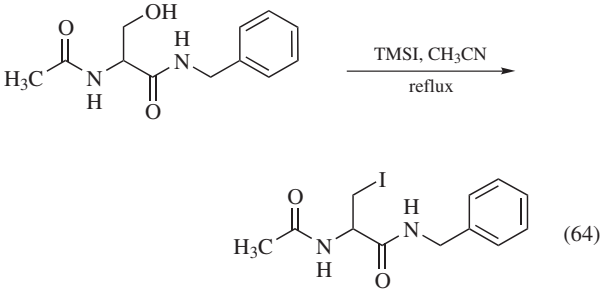
Other Reactions of TMSI.

Reaction with α,β-Unsaturated Sulfoxides. The reaction of TMSI with α,β-unsaturated sulfoxides in chloroform at ambient temperature is a mild, efficient, and general method for the preparation of carbonyl compounds (eq 63).[106] The proposed reaction mechanism is shown in eq 63.[106a] Formation of a strong oxygen-silicon bond is followed by reduction of the sulfur function and oxidation of iodide to iodine, the latter precipitating in chloroform. The trimethylsiloxy anion attacks the unsaturated carbon linked to the sulfur function, which leaves the substrate, allowing the formation of the silyl enol ether species. Finally, hydrolysis converts the silyl enol ether into the carbonyl compound.[106a]



(63)

Iodination of β-Hydroxy Amino Acid Derivatives. TMSI has been used as an iodinating agent to convert β-hydroxy amino acid derivatives into corresponding β-iodo amino acid derivatives (eq 64).[107] The low yields for the reaction have been attributed in part to the sensitivity of the β-iodo products to the reflux conditions. Higher yields can be obtained when TMSCl and TMSBr are used as chlorinating and brominating agents.[107]



(64)

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