Samarium(II) Iodide[1]

SmI_2

[32248-43-4] I_2Sm (MW 404.16)
InChI = 1/2HI.Sm/h2*1H;/q;;+2/p-2/f2I.Sm/h2*1h;/q2*-1;m
InChIKey = UAWABSHMGXMCRK-ZFDXCKRNCZ

(one-electron reducing agent possessing excellent chemoselectivity in reduction of carbonyl, alkyl halide, and α-heterosubstituted carbonyl substrates;[1] promotes Barbier-type coupling reactions, ketyl–alkene coupling reactions, and radical cyclizations[1])

Physical Data: mp 527 °C; bp 1580 °C; *d* 0.922 g cm^{-3}.
Solubility: soluble 0.1M in THF.
Form Supplied in: commercially available as a 0.10 M solution in THF.
Preparative Methods: typically prepared in situ for synthetic purposes. SmI_2 is conveniently prepared by oxidation of ***Samarium(0)*** metal with organic dihalides.[2]
Handling, Storage, and Precautions: is air sensitive and should be handled under an inert atmosphere. SmI_2 may be stored over THF for long periods when it is kept over a small amount of samarium metal.

Original Commentary

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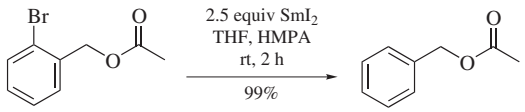
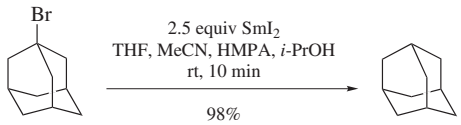
Reduction of Organic Halides and Related Substrates. Alkyl halides are readily reduced to the corresponding hydrocarbon by SmI_2 in the presence of a proton source. The ease with which halides are reduced by SmI_2 follows the order I > Br > Cl. The reduction is highly solvent dependent. In THF solvent, only primary alkyl iodides and bromides are effectively reduced;[2] however, addition of HMPA effects the reduction of aryl, alkenyl, primary, secondary, and tertiary halides (eq 1).[3,4] Tosylates are also reduced to hydrocarbons by SmI_2. Presumably, under these reaction conditions the tosylate is converted to the corresponding iodide which is subsequently reduced.[4,5]



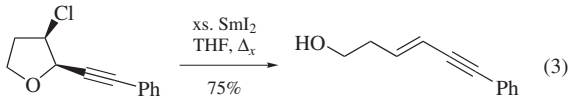
(1)

Samarium(II) iodide provides a means to reduce substrates in which the halide is resistant to reduction by hydride reducing agents (eq 2).



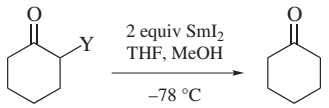
(2)

Samarium(II) iodide has been utilized as the reductant in the Boord alkene-type synthesis involving ring scission of 3-halotetrahydrofurans (eq 3).[6] SmI_2 provides an alternative to the sodium-induced reduction which typically affords mixtures of stereoisomeric alkenes and overreduction in these transformations. When SmI_2 is employed as the reductant, isomeric purities are generally >97% and overreduction products comprise <3% of the reaction mixture.



(3)

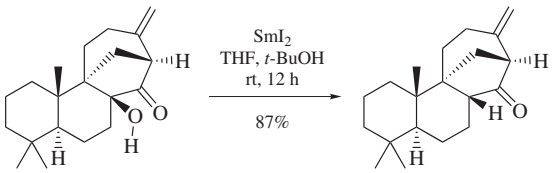
Reduction of α-Heterosubstituted Carbonyl Compounds. Samarium(II) iodide provides a route for the reduction of α-heterosubstituted carbonyl substrates. A wide range of α-heterosubstituted ketones is rapidly reduced to the corresponding unsubstituted ketone under mild conditions (eq 4).[7] The reaction is highly selective and may be performed in the presence of isolated iodides as well as isolated ketones.[7]



(4)

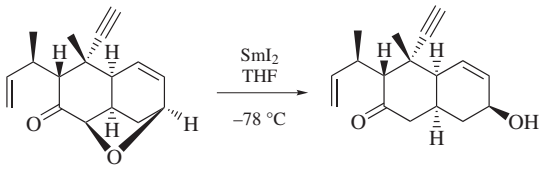
Y	Isolated yield (%)
Cl	100
SPh	76
S(O)Ph	64
SO_2Ph	88

Samarium(II) iodide-induced reductive cleavage of α-hydroxy ketones provides a useful entry to unsubstituted ketones (eq 5).[8]



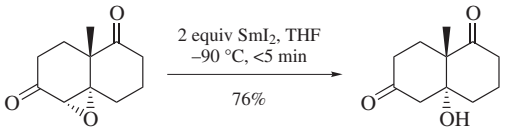
(5)

Samarium(II) iodide promotes the reductive cleavage of α-alkoxy ketones. Pratt and Hopkins have utilized this protocol in synthetic studies en route to betaenone B (eq 6).[9]



(6)

Likewise, this procedure provides a route for the reduction of α,β-epoxy ketones and α,β-epoxy esters to generate the corresponding β-hydroxy carbonyl compounds (eqs 7 and 8).[3,10] The epoxy ketone substrates may be derived from Sharpless asymmetric epoxidation. Consequently, this procedure provides a means to prepare a variety of chiral, nonracemic β-hydroxy carbonyl compounds that are difficult to acquire by more traditional procedures.



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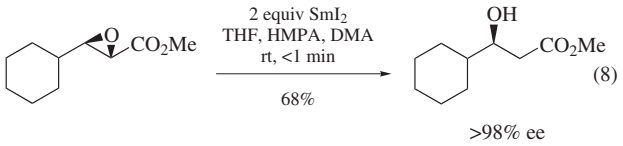
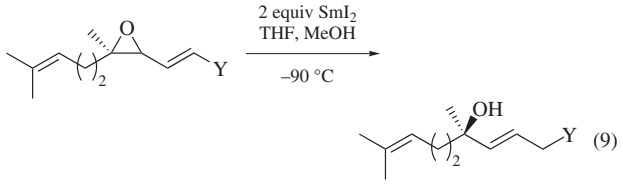


(8)

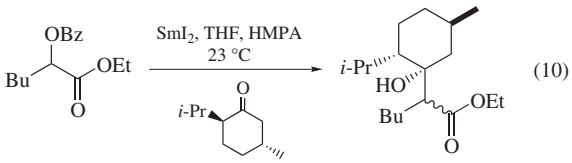
Vinyloxiranes undergo reductive epoxide ring opening with samarium(II) iodide to provide (*E*)-allylic alcohols (eq 9).[3,10b,11] These reaction conditions are tolerant of ketone, ester, and nitrile functional groups. Again, Sharpless asymmetric epoxidation chemistry may be utilized to gain entry to the desired nonracemic substrates, thereby providing a useful entry to highly functionalized, enantiomerically enriched allylic alcohols.



(9)

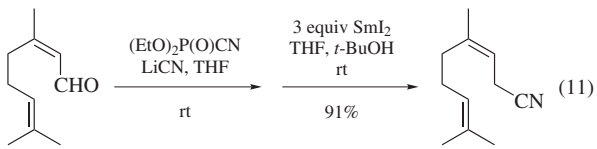
Y	Isolated yield (%)
COSEt	80
SO_2Ph	82
$P(O)(OEt)_2$	84
H	69
Me	42
SPh	54

A useful method for preparation of β-hydroxy esters is accomplished by SmI_2-promoted deoxygenation of an α-hydroxy ester followed by condensation with a ketone (eq 10).[12] In some instances, excellent diastereoselectivities are achieved, although this appears to be somewhat substrate dependent.



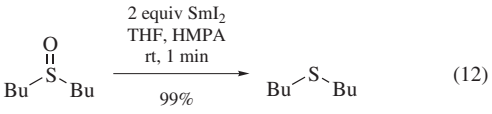
(10)

A useful reaction sequence for transforming carbonyl compounds to one-carbon homologated nitriles has evolved from the ability of SmI_2 to deoxygenate cyanohydrin *O,O′*-diethyl phosphates (eq 11).[13] The procedure is tolerant of a number of functional groups including alcohols, esters, amides, sulfonamides, acetals, alkenes, alkynes, and amines. Furthermore, it provides a distinct advantage over other previously developed procedures for similar one-carbon homologations.



(11)

Deoxygenation Reactions. Sulfoxides are reduced to sulfides by SmI_2 (eq 12).[2,3,14] This process is rapid enough that reduction of isolated ketones is not a competitive process. Likewise, aryl sulfones are reduced to the corresponding sulfides by SmI_2 (eq 13).[3,12]



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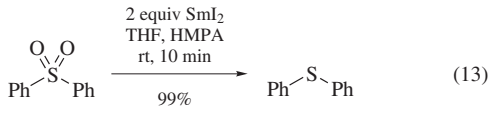
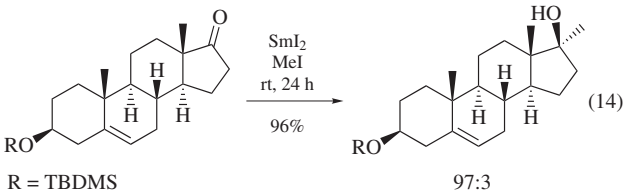


(13)

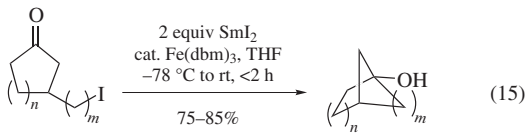
Barbier-type Reactions. Samarium(II) iodide is quite useful in promoting Barbier-type reactions between aldehydes or ketones and a variety of organic halides. The efficiency of SmI_2 promoted Barbier-type coupling processes is governed by the substrate under consideration in addition to the reaction conditions employed. In general, alkyl iodides are most reactive while alkyl chlorides are virtually inert. Typically, catalytic ***Iron(III) Chloride*** or ***Hexamethylphosphoric Triamide*** can be added to SmI_2 to reduce reaction times or temperatures and enhance yields. Kagan and co-workers have recently applied an intermolecular SmI_2-promoted Barbier reaction towards the synthesis of hindered steroidal alcohols. An intermolecular Barbier-type reaction between the hindered ketone and ***Iodomethane*** produced a 97:3 mixture of diastereomers in excellent yield (eq 14).[15]



(14)

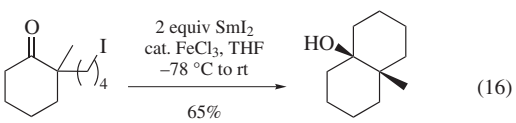
R = TBDMS 97:3

Samarium(II) iodide-promoted intramolecular Barbier-type reactions have also been employed to produce a multitude of cyclic and bicyclic systems.[1] Molander and McKie have employed an intramolecular Barbier-type reductive coupling reaction to promote the formation of bicyclo[*m.n.*1]alkan-1-ols from the corresponding iodo ketone substrates in good yield (eq 15).[16]



(15)

Annulation of five- and six-membered rings proceeds with excellent diastereoselectivity via an intramolecular Barbier-type process (eq 16).[17] The Barbier-type coupling scheme provides a reliable and convenient alternative to other such methods for preparing fused bicyclic systems.

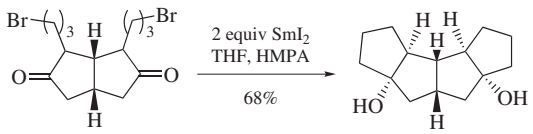


(16)

only diastereomer

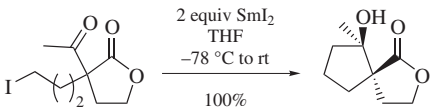
The SmI_2-promoted Barbier-type reaction has also been utilized in the synthesis of polyquinanes. Cook and Lannoye have

employed this method to effect a bis-annulation of an appropriately substituted diketone (eq 17).[18]



(17)

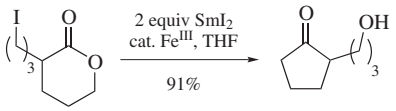
Substituted β-keto esters also provide excellent substrates for the intramolecular Barbier cyclization (eq 18).[19] Diastereoselectivities are typically quite good but are highly dependent on substituent and solvent effects.



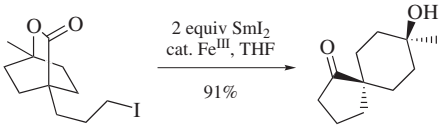
(18)

92% de

Nucleophilic Acyl Substitutions. Samarium(II) iodide facilitates the highly selective intramolecular nucleophilic acyl substitution of halo esters (eqs 19 and 20).[20]

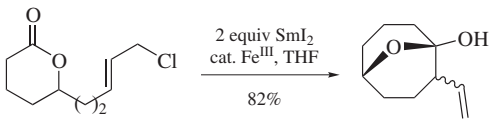


(19)



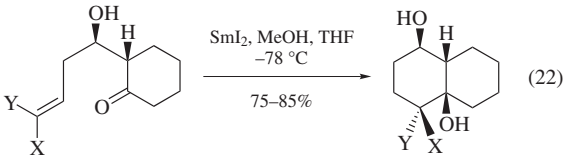
(20)

Unlike organolithium or organomagnesium reagents, SmI_2-promoted nucleophilic substitution does not proceed with double addition to the carbonyl, nor are any products resulting from reduction of the final product observed. With suitably functionalized substrates, this procedure provides a strategy for the formation of eight-membered rings (eq 21).



(21)

Ketone–Alkene Coupling Reactions. Ketyl radicals derived from reduction of ketones or aldehydes with SmI_2 may be coupled both inter- and intramolecularly to a variety of alkenic species. Excellent diastereoselectivities are achieved with intramolecular coupling of the ketyl radical with α,β-unsaturated esters.[21] In the following example, ketone–alkene cyclization took place in a stereocontrolled manner established by chelation of the resulting Sm(III) species with the hydroxyl group incorporated in the substrate (eq 22).[21b]

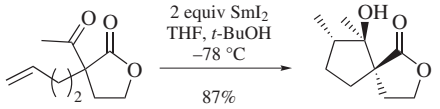


(22)

X = CO_2Me, Y = H
X = H, Y = CO_2Me

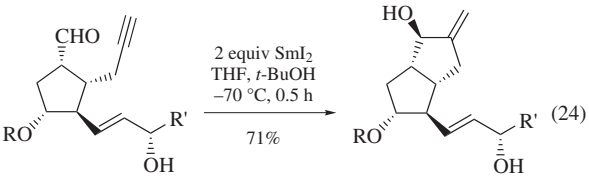
X = CH_2CO_2Me, Y = H
X = H, Y = CH_2CO_2Me

A similar strategy utilizing β-keto esters provided very high diastereoselectivities in the ketyl–alkene coupling process. In these examples, chelation control about the developing hydroxyl and carboxylate stereocenters was the source of the high diastereoselectivity achieved (eq 23).[22]



(23)

Alkynic aldehydes likewise undergo intramolecular coupling to generate five- and six-membered ring carbocycles. This protocol has been utilized as a key step in the synthesis of isocarbacyclin (eq 24).[23] SmI_2 was found to be superior to several other reagents in this conversion.

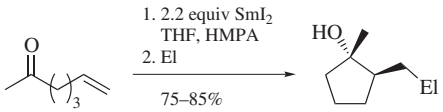


(24)

R = TBDMS, R' = C_5H_{11}

80% de

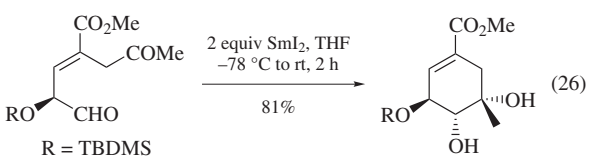
Samarium(II) iodide in the presence of HMPA effectively promotes the intramolecular coupling of unactivated alkenic ketones by a reductive ketyl–alkene radical cyclization process (eq 25). This protocol provides a means to generate rather elaborate carbocycles through a sequencing process in which the resulting organosamarium species is trapped with various electrophiles to afford the cyclized product in high yield.[24]



(25)

El = RCHO, RCOR, CO_2, Ac_2O, O_2

Pinacolic Coupling Reactions. In the absence of a proton source, both aldehydes and ketones are cleanly coupled in the presence of SmI_2 to the corresponding pinacol.[25] Considerable diastereoselectivity has been achieved in the coupling of aliphatic 1,5- and 1,6-dialdehydes, providing near exclusive formation of the *cis*-diols (eq 26).[26]

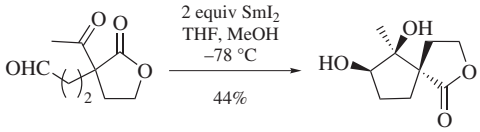


(26)

R = TBDMS

92% de

Intramolecular cross coupling of aldehydes and ketones proceeds with excellent diastereoselectivity and high yield in suitably functionalized systems wherein chelation control by the resulting Sm III species directs formation of the newly formed stereocenters (eq 27).[22a,27] A similar strategy has been utilized with a β-keto amide substrate to provide a chiral, nonracemic oxazolidinone species. This strategy permits entry to highly functionalized, enantiomerically pure dihydroxycyclopentanecarboxylate derivatives (eq 28).



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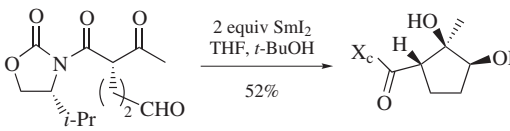
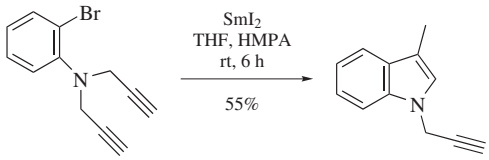


(28)

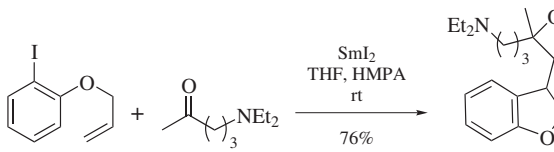
Radical Addition to Alkenes and Alkynes. Samarium(II) iodide has proven effective for initiation of various radical addition reactions to alkenes and alkynes. Typically, tin reagents are used in the initiation of these radical cyclization reactions; however, the SmI_2 protocol often provides significant advantages over these more traditional routes.

Samarium(II) iodide-mediated cyclization of aryl radicals onto alkene and alkyne acceptors provides an excellent route to nitrogen- and oxygen-based heterocycles (eq 29).[28]



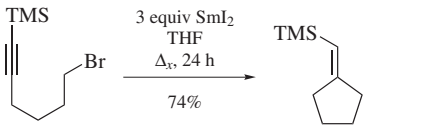
(29)

The SmI_2 reagent is unique in that it provides the ability to construct more highly functionalized frameworks through a sequential radical cyclization/intermolecular carbonyl addition reaction.[29] Thus the intermediate radical formed after initial cyclization may be further reduced by SmI_2, forming an organosamarium intermediate which may be trapped by various electrophiles, affording highly functionalized products (eq 30).



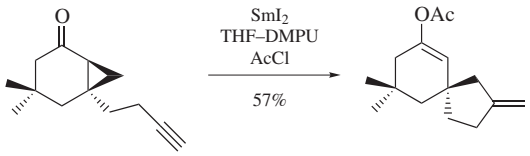
(30)

Samarium(II) iodide further mediates the cyclization reactions of alkynyl halides (eq 31).[30] When treated with SmI_2, the alkynyl halides are converted to the cyclized product in good yield. Addition of DMPU as cosolvent provides slightly higher yields in some instances.



(31)

Highly functionalized bicyclic and spirocyclic products are obtained in good yield and high diastereoselectivity by a tandem reductive cleavage–cyclization strategy (eq 32).[31] Radical ring opening of cyclopropyl ketones mediated by samarium(II) iodide-induced electron transfer permits the elaboration of a tandem ring opening–cyclization strategy wherein the resultant samarium enolate may be trapped by either oxygen or carbon electrophiles.



(32)

First Update

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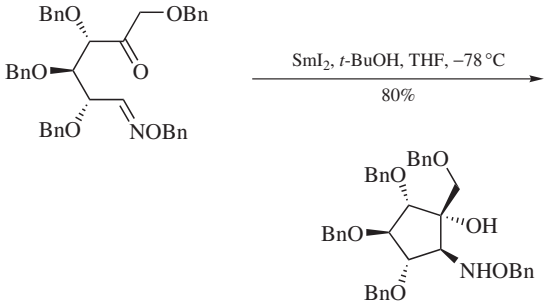
Reductive Cross-coupling of Imines and Aldehydes. Samarium iodide-mediated intramolecular reductive cross-coupling of aldehydes or ketones with oximes (eq 33),[32] hydrazones (eq 34),[33] and imines (eq 35)[34] is well-documented.



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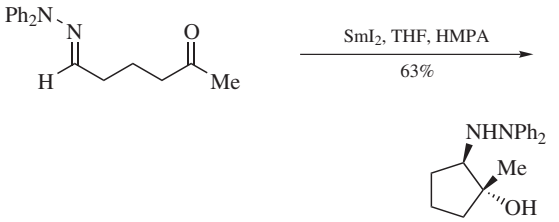

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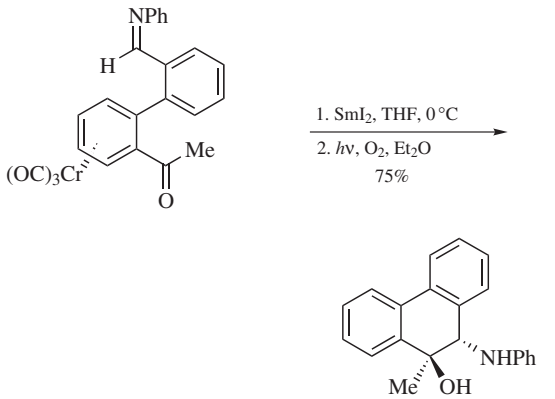
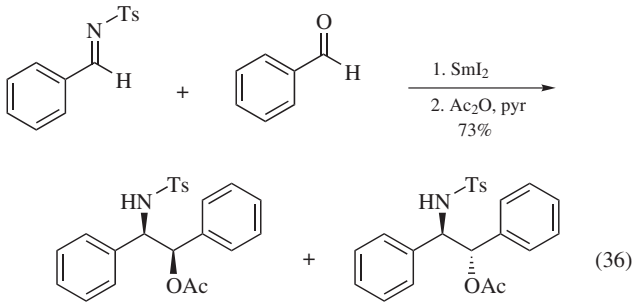


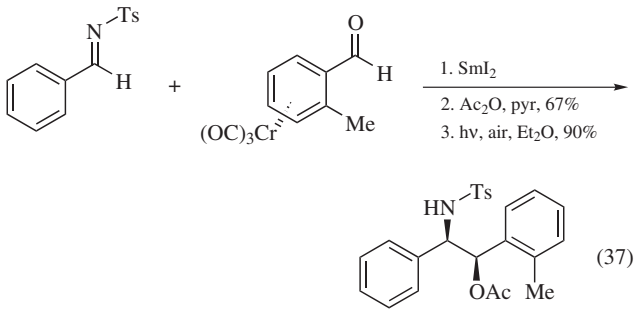
(35)

The intermolecular coupling of imine derivatives and aldehydes can be achieved using samarium iodide. For example,

N-tosylimines and aldehydes gave *syn*-β-amino alcohol derivatives in good yields and diastereoselectivities (eq 36).[35] Access to enantiopure *syn*-β-amino alcohols can be achieved if chiral chromium complex of the aldehyde is used (eq 37).

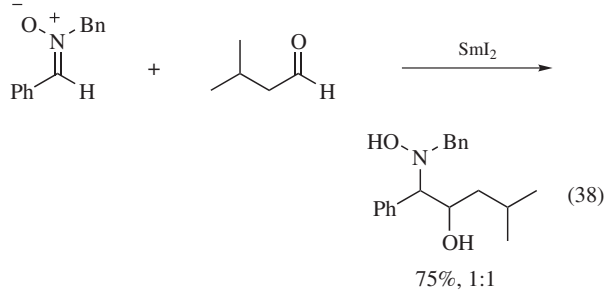


(36)



(37)

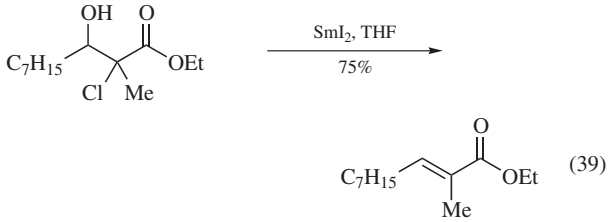
It is also possible to couple planar chiral ferrocenecarboxaldehydes with imines with excellent diastereocontrol.[36] Oximes can be coupled with aldehydes in good to excellent yields. However, the level of diastereocontrol is usually quite modest (eq 38).



(38)

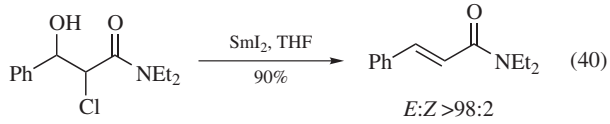
It is possible to use samarium iodide catalytically in several reactions if a cheap alloy of the light lanthanides (La, Ce, Nd, Pr, Sm) called Mischmetall is used.[37]

Synthesis of Alkenes by Reductive Elimination. The treatment of 2-halo-3-hydroxy esters and amides with samarium iodide leads to the corresponding di- or trisubstituted (*E*)-α,β-unsaturated derivatives in high yields and diastereoselectivities (eqs 39 and 40).[38] The precursors are readily accessible by condensation of the lithium enolate of α-haloesters or amides. If the substrate contains γ,δ-unsaturation, the β,γ-unsaturated ester is generated in the process (eq 41).



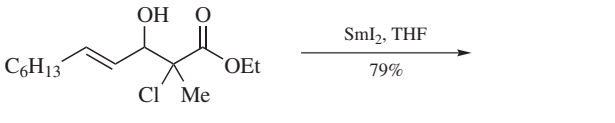
(39)

E:*Z* >98:2



(40)

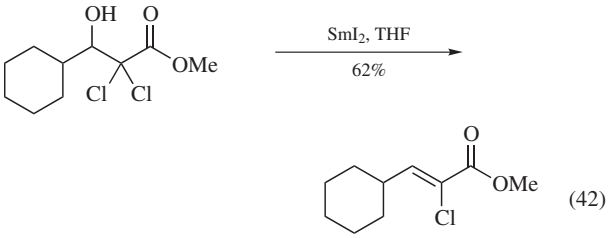
E:*Z* >98:2



(41)

E:*Z* >98:2

The stereoselective reduction of α,α-dichloro-β-hydroxy esters using samarium iodide yields (*Z*)-α-chloro-α,β-unsaturated esters (eq 42).[39]

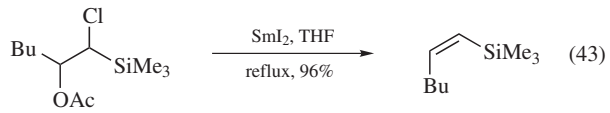


(42)

Z:*E* >98:2

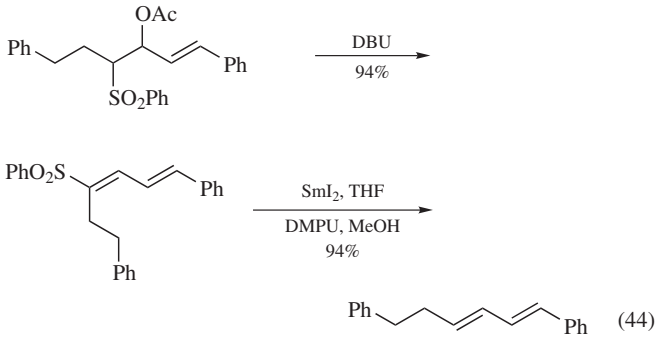
Similarly, γ-acetoxy-α,β-enoates are reduced by samarium diodide to generate dienolates which are kinetically trapped at the α-position by electrophiles (proton, aldehydes, or ketones).[40]

(*Z*)-Alkenylsilanes are obtained in high diastereoselectivities if *O*-acetyl-1-chloro-1-trimethylsilylalkan-2-ols are treated with samarium iodide (eq 43). The stereochemical outcome is independent from the relative stereochemistry of the starting material.[41]



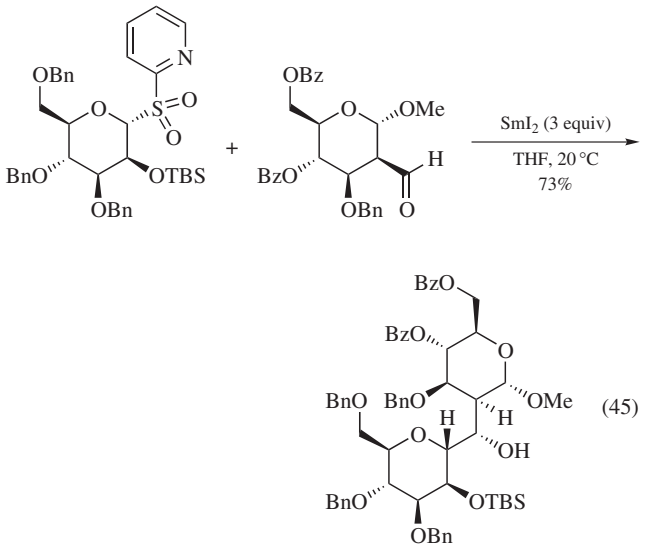
(43)

Samarium iodide can also be used as an alternative to sodium/mercury amalgam for the reductive elimination of 1,2-acetoxysulfones in the Julia-Lythgoe olefination.[42] The alkene is generated in a two-step process that first involves DBU or LDA treatment to generate a vinyl sulfone that is then reductively cleaved with samarium iodide (eq 44). The diastereoselectivity of both transformations is usually quite good and the method is compatible with the synthesis of monoalkenes as well as dienes and trienes.



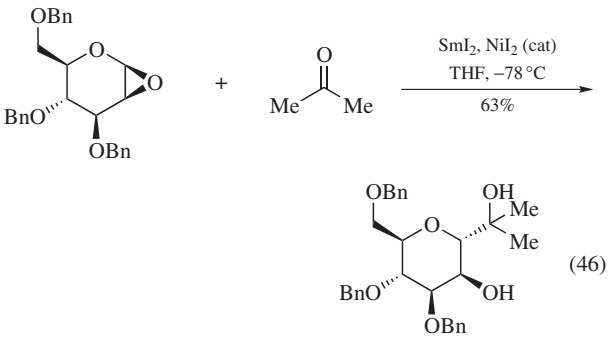
(44)

Synthesis of α-Heteroalkyl Samarium. Samarium iodide is the reagent of choice to generate α-alkoxyalkylsamarium species from suitable precursors. For example, the anomeric position of glycosides can be functionalized by treating a pyridylsulfone precursor with samarium iodide (eq 45). A subsequent quench with an aldehyde generates the corresponding *C*-glycoside via the Barbier reaction with outstanding diastereoselectivity.[43] It is also possible to generate similar reactive intermediates from the corresponding glycosyl phenylsulfones[44] or glycosyl phosphates.[45]



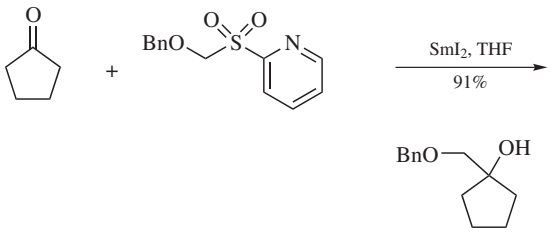
(45)

An alternative but related approach involves the coupling of epoxides and carbonyl compounds (eq 46).[46] In this reaction, the addition of a catalytic amount of nickel(II) iodide[47] produced slightly higher yields of the *C*-glycoside.



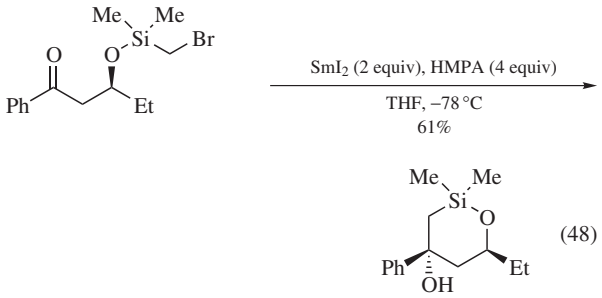
(46)

In a related fashion, benzyloxymethyl 2-pyridylsulfone can be used as a hydroxymethylation equivalent to provide a convenient approach for the one-carbon homologation of carbonyl compounds (eq 47).[48] The pyridylsulfone derivative is a superior precursor than the corresponding chloride.



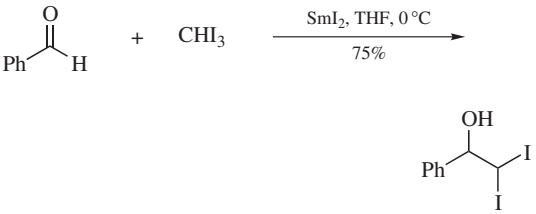
(47)

Another hydroxymethyl equivalent is the silylmethyl group. Tamao oxidation of the product obtained from the samarium iodide-promoted intramolecular reductive cyclization of bromosilyloxy derivatives leads to the hydroxymethyl group (eq 48).[49]



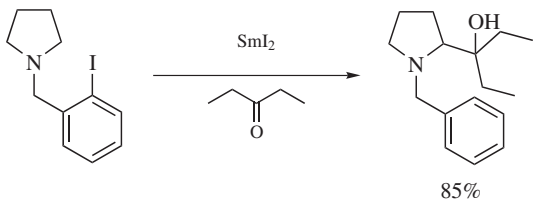
(48)

The diiodomethylation of carbonyl compounds is also possible if samarium iodide is used in conjunction with iodoform.[50] The products are synthetically useful since they are easily converted into α-hydroxyacids or α-iodoaldehydes upon basic treatment (eq 49).



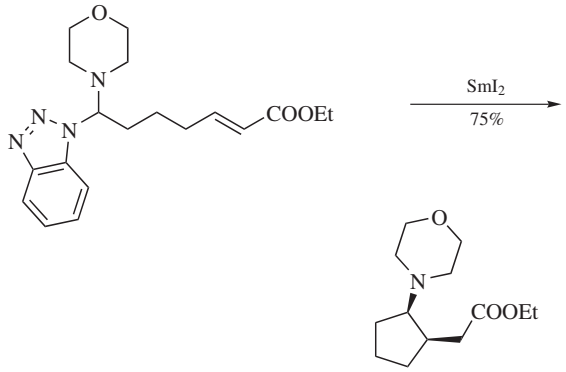
(49)

It is possible to generate an α-heteroalkyl radical by a 1,5-hydrogen atom transfer from the radical obtained from an *o*-iodobenzyl protected amine (eq 50). It can then be subjected to several reactions such as condensation with a ketone.[51]



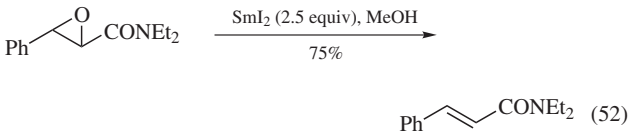
(50)

Alternatively, an α-amino radical can be generated from an α-benzotriazolylamine precursor (eq 51).

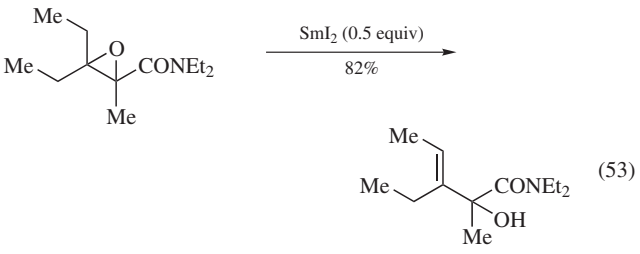


(51)

Opening of α,β-Epoxy Esters and Amides. Treatment of aromatic α,β-epoxyamides with samarium iodide leads to the highly stereoselective synthesis of α,β-unsaturated amides with high diastereocontrol (eq 52).[52] If the reaction is run on a substrate that contains γ-protons, then a base-promoted reaction produces the (*E*)-α-hydroxy-β,γ-unsaturated amide (eq 53).[53]

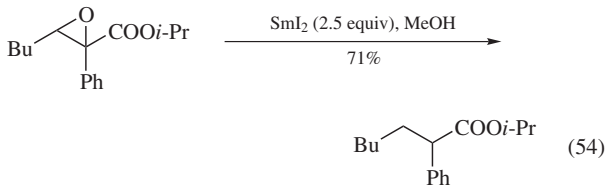


(52)



(53)

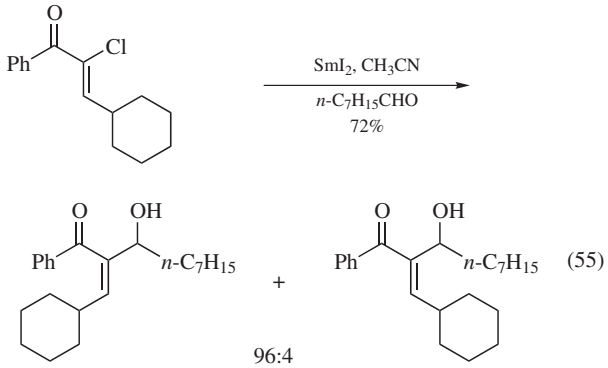
Analogous reactions with the α,β-unsaturated ester generates the saturated ester derivative (eq 54).[54]



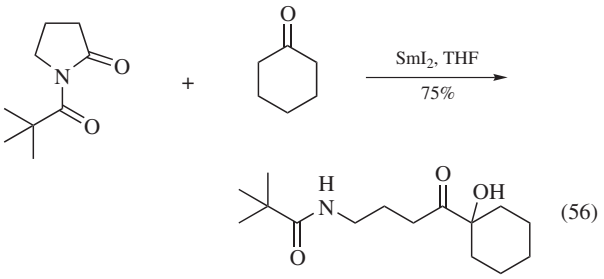
(54)

Addition of Vinylsamarium to Aldehydes. Treatment of (*Z*)-α-chloro-α,β-unsaturated ketones with samarium iodide leads to the vinylsamarium reagent that can be trapped with aldehydes or ketones to produce Baylis-Hillman type adducts with inversion of stereochemistry at the alkene (eq 55).[55]

Coupling of *N*-Acyl Lactams with Aldehydes or Ketones. Treatment of *N*-acyl lactams with samarium iodide leads to an acylsamarium species that is trapped by ketones or aldehydes (eq 56).[56]



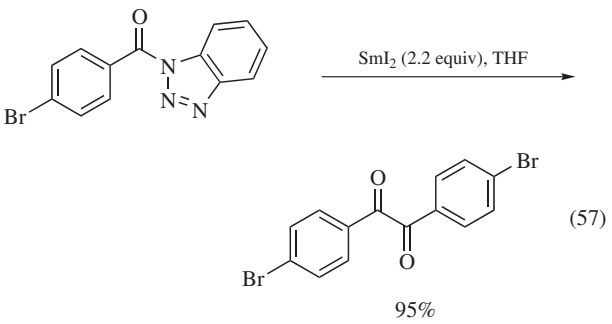
(55)



(56)

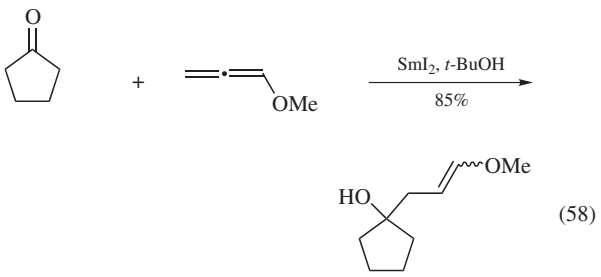
It is also possible to couple imides with alkyl halides both interintramolecularly[57] and intramolecularly.[58] Alternative precursors to generate acylsamarium species also include acyl chlorides[59] and amides.[60]

Synthesis of 1,2-Dicarbonyl by Coupling Reactions. It is possible to generate 1,2-diketones easily by treating an appropriate precursor with samarium iodide. For example, the transformation of *N*-acylbenzotriazoles into 1,2-diketones can be achieved in good to excellent yields (eq 57).[61]



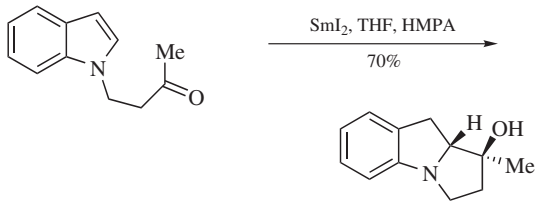
(57)

Synthesis of Homoenolate Equivalent. The samarium iodide-induced coupling of carbonyl derivatives with methoxyallene provides 4-hydroxy 1-enol ethers in high yields (eq 58).[62] An almost equimolar mixture of the two enol ethers are usually observed but acid hydrolysis leads to the aldehyde.

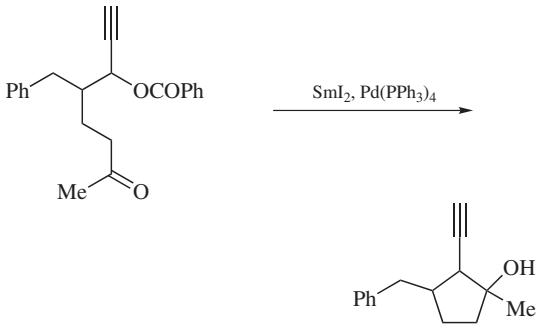


(58)

Related examples include the coupling of ketones with indole (eq 59)[63] and alkynyl moieties (eq 60).[64] In the latter case, tetrakis(triphenylphosphine)palladium must also be added to generate the electrophilic component.

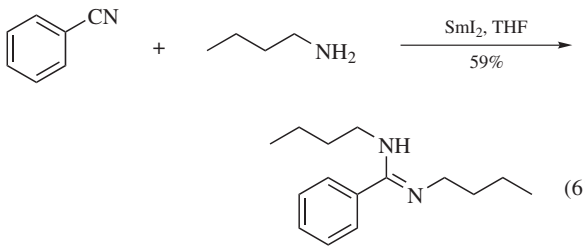


(59)



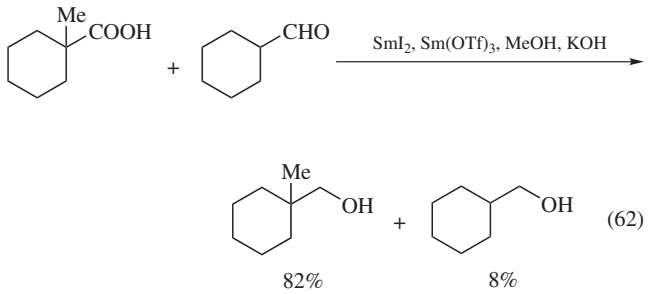
(60)

Synthesis of Amidines from Amines and Nitriles. An efficient one-step preparation of *N*,*N*′-disubstituted amidines is possible by direct nucleophilic addition of an amine to a nitrile using catalytic amounts of samarium iodide (eq 61).[65] Alternatively, an azide can be used instead of an amine.[66]



(61)

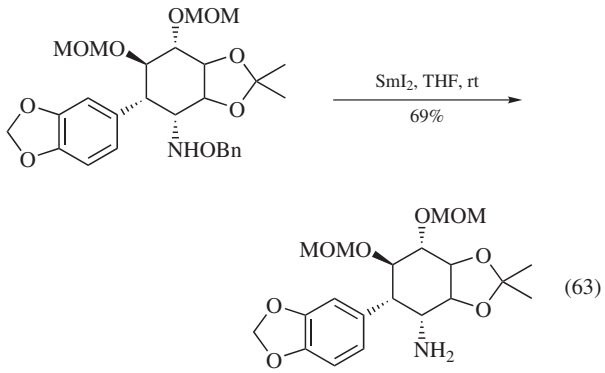
Chemoselective Reduction of Carboxylic Acids. The facile chemoselective reduction of carboxylic acids in the presence of an aldehyde proceeds smoothly with samarium iodide in combination with lanthanide triflate and methanol (eq 62).



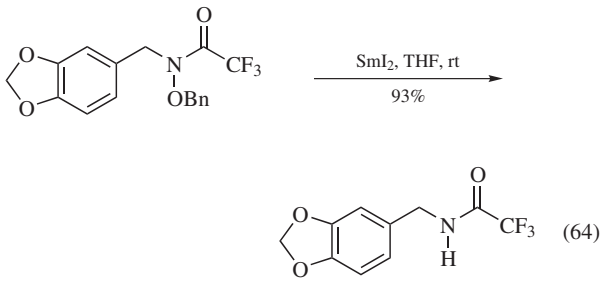
(62)

Reduction of Azides. Reduction of alkyl, aryl, and aroylazides to the corresponding primary amine or amide occurs in good yield upon treatment with excess samarium iodide in THF.[67,68]

Reductive Cleavage of N–O Bonds. An efficient process for the reductive cleavage of N–O bonds using samarium iodide that is compatible when base sensitive substrate is available (eqs 63 and 64). [69] This reagent is sometimes superior to aluminum amalgam or sodium amalgam. Furthermore, the direct quenching of the reduction mixture with acylating agents provides high yields of the corresponding protected amine.



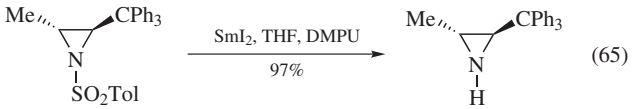
(63)



(64)

Cleavage of Haloethyl Derived Protecting Groups. Samarium diiode is a mild and effective reagent for the deprotection of 2-bromoethyl and 2-iodoethyl esters[70] and (2,2,2-trichloroethoxy) methoxy ethers.[71]

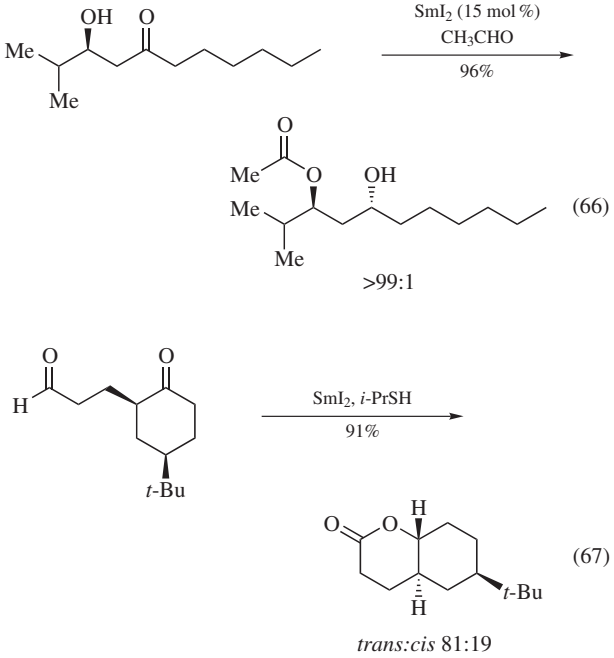
Cleavage of *N*-Tosyl Protecting Groups. The deprotection of *N*-benzenesulfonamides or *N*-*p*-toluenesulfonamides of the parent primary or secondary amines occurs in good yield upon heating with excess samarium iodide in a mixture of THF and DMPU (eq 65).[72] The method has also been used in the epimerization-free deprotection of protected α-chiral amines.[73]



(65)

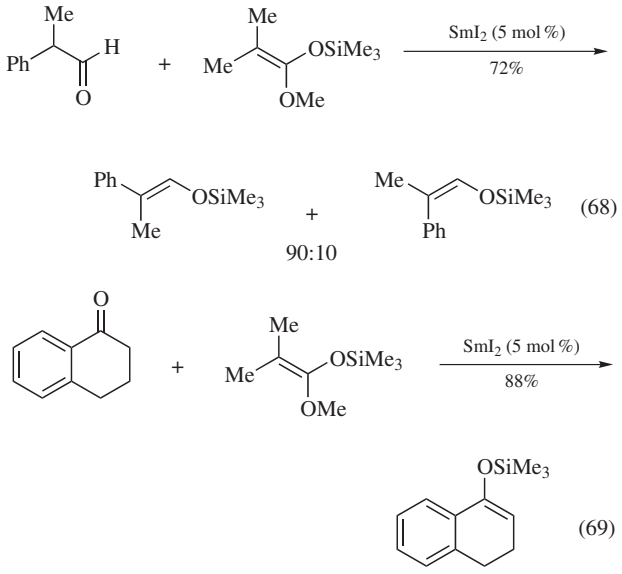
It is also possible to deprotect *N*-sulfonylated amides under similar conditions.[74]

Tishchenko Reduction of Carbonyl Derivatives. The samarium iodide-catalyzed Tishchenko reaction has been used quite extensively in synthesis. Interesting examples include the diastereoselective synthesis of *anti*-1,3-diols (eq 66)[75] and δ-lactones (eq 67).[76]

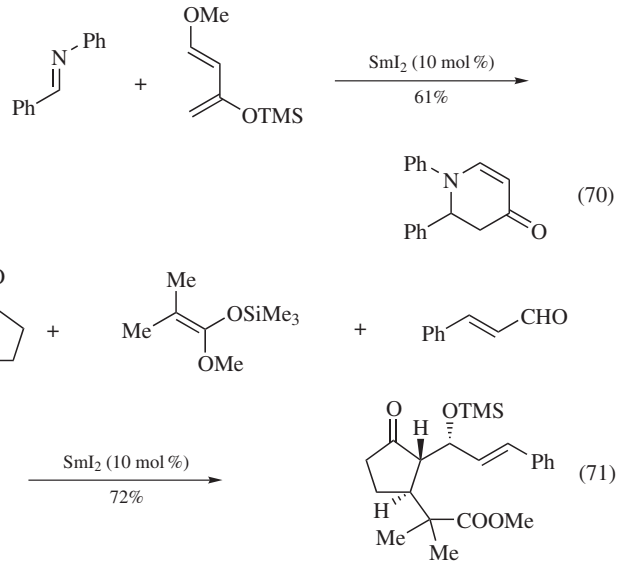


A mechanistically different stereoselective reduction of β-hydroxy ketones leading to *anti*-1,3-diol using stoichiometric amounts of samarium iodide has been reported.[77]

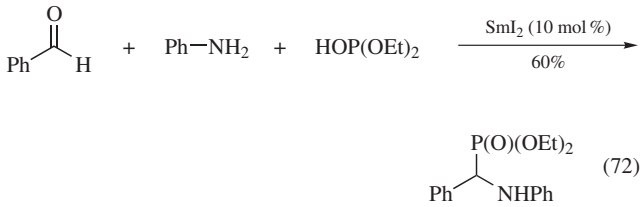
Preparation of Silyl Enol Ethers. Ketones and α-substituted aldehydes are converted into their corresponding silyl enol ethers by the reaction with trimethylsilyl ketene acetal derived from methyl isobutyrate in the presence of a catalytic amount of samarium iodide (eqs 68 and 69).[78] Mixtures are usually obtained with unsymmetrical ketones.



Lewis Acid Catalyzed Reactions. Samarium iodide catalyzes several transformations by presumably acting as a Lewis acid. For example, it is an efficient catalyst for the imino-Diels-Alder (eq 70) and for imino-aldol reactions.[79] Tandem Mukaiyama-Michael-aldol (eq 71)[80] and Michael imino-aldol processes have also been reported.[81]



Three-component α-Amino Phosphonate Synthesis. A simple and efficient synthesis of α-amino phosphonates is possible under relatively mild conditions by the reaction of aldehydes, amines, and a dialkylphosphite using samarium iodide in catalytic amounts (eq 72).[82]



Related Reagents. Samarium(II) Iodide–1,3-Dioxolane.

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