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# The use of samarium diiodide in organic and polymer synthesis

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**Abstract. The methods of synthesis and properties of samarium diiodide are examined and the results of its employment for the synthesis of a wide variety of compounds are surveyed. New reactions involving samarium diiodide are described and the prospects for its application in polymer chemistry are indicated. The bibliography includes 87 references.**

## I. Introduction

There has been considerable progress in recent years in the use of the unique properties of divalent lanthanide (Eu, Yb, Sm, etc.) halides in the synthesis of a wide variety of organic compounds.[1–3] Comparison of the oxidation–reduction potentials of lanthanide salts and various transition metal salts has shown that the former, in particular samarium and ytterbium diiodides, belong to the class of the strongest reductants soluble in organic media.

The standard oxidation–reduction potentials of the lanthanides in aqueous solutions are as follows:[2]

$$Eu^{2+}/Eu^{3+} = -0.35\ eV;\ Yb^{2+}/Yb^{3+} = -1.15\ eV;$$

$$Sm^{2+}/Sm^{3+} = -1.55\ eV;\ Tm^{2+}/Tm^{3+} = -2.10\ eV.$$

It is seen from the data presented that $Tm^{2+}$ has the most pronounced reducing properties, but, because of this, it is much less stable than $Sm^{2+}$ and $Yb^{2+}$. It has been shown[4] that, in the absence of $O_2$, solutions of $Eu^{2+}$, $Yb^{2+}$, and $Sm^{2+}$ in THF are stable for a long time (several days),[5] in contrast to $Tm^{2+}$ solutions. Furthermore, thulium is a naturally scarce element.

Bearing these data in mind, it becomes understandable why divalent lanthanide compounds have been isolated only for europium, samarium, and ytterbium.[5] At the same time $Eu^{2+}$ is a very weak electron donor[1] and its reactivity in organic reactions is low. For the same reason, the reactivity of $Yb^{2+}$ is relatively low, which limits significantly the range of reactions in which it is used, such reactions requiring as a rule comparatively severe conditions.

Among all the elements examined, samarium is most preferable because of its high oxidation–reduction potential, which gives rise to its pronounced reducing properties.

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Until recently divalent lanthanide halides have been obtained by complex procedures requiring the reduction of lanthanide trihalides with hydrogen or the corresponding metal at very high temperatures (700–900 °C), their thermal dissociation in a high vacuum, etc.[6,7]

A new comparatively simple method of synthesis of divalent lanthanide diiodides from diiodoethane and the corresponding metal was proposed in 1977,[8] which initiated their wide scale employment in organic and polymer chemistry. Thus the use of $YbI_2$ and especially $SmI_2$ promotes many organic reactions at high rates and with a high yield of the target product even at low temperatures (–78 to 20 °C) and also makes it possible to carry out reactions which could not be performed using other reductants (iodomethylation of carbonyl compounds, synthesis of large lactone rings, selective reduction of the aldehyde group in the presence of the keto-group, etc.[9]).

Using samarium diiodide as the reagent in the chemistry of high-molecular-mass compounds, we obtained a series of new functional polymers and demonstrated for the first time the formation of the Si–Si bond on treatment with $SmI_2$.[10]

In contrast to previously published reviews,[11,12] we shall consider here for the first time the possibility of using samarium diiodide in the chemistry of high-molecular-mass compounds as well as new reactions in organic chemistry.

## II. The synthesis and properties of divalent lanthanide salts

Lanthanide diiodides are obtained nowadays by the reaction of the corresponding metal with 1,2-diiodoethane (DIE) in anhydrous tetrahydrofuran (THF) under an inert atmosphere at room temperature.[5] The $LnI_2$ synthesised in this way are used, without being isolated from solution, in reactions with various compounds.

In contrast to other procedures, an interesting feature of this method is the possibility of obtaining exclusively a $Ln^{2+}$ compound and not a mixture of the $Ln^{2+}$ and $Ln^{3+}$ salts. This is

$$Ln + ICH_2CH_2I \longrightarrow LnI_2 + CH_2{=}CH_2$$

Ln = Sm, Yb.

indicated by the colour of the solutions obtained (blue-green for $SmI_2$ and yellow-green for $YbI_2$) and the results of various analytical methods: iodometric titration, complexometric titration with ethylenediaminetetraacetic acid (EDTA), absorption spectroscopy, NMR, etc.[13,14]

Since the most stable oxidation state of the lanthanides is +3, $Ln^{2+}$ salts should behave as powerful reductants. The stability of solutions of divalent lanthanides is therefore determined primarily by the stability of the solvent employed under the conditions of high reduction potentials.

As mentioned above, THF is one such stable solvent, but the necessity for the thorough removal of the accumulated peroxides from the initial THF and for its preparation in an anhydrous form give rise to certain difficulties.

Apart from THF, certain other aprotic solvents are resistant to powerful reductants.[15] Kamenskaya et al.[16] showed that lanthanide diiodides do in fact react with, for example, hexamethylphosphoramide (HMPA), whereas in common aprotic solvents such as diethyl ether, dioxane, methylal, and 1,2-dimethoxyethane samarium diiodide does not react with DIE at all; in pyrrolidinone the reaction takes place but solutions containing divalent and trivalent lanthanide compounds are then obtained.[17]

The study of the physicochemical properties of divalent Nd, Sm, Yb, Eu, etc. salts showed that these compounds are in fact most stable in THF.[18] Thus THF is nowadays the most suitable solvent for experiments with divalent lanthanide salts, especially $SmI_2$. Unfortunately the solubility of these compounds in THF is limited, amounting to 0.1 mol litre$^{-1}$ for $SmI_2$ and 0.04 mol litre$^{-1}$ for $YbI_2$ at 20 °C.[1]

An improvement in the solubility of $SmI_2$ can be achieved by employing organic complexones such as crown-ethers and sodium tetraphenylborate.[18] Thus the $Yb^{2+}$ and $Sm^{2+}$ ions form complexes readily with crown-ethers, which are 3–4 orders of magnitude more stable than the $Yb^{3+}$ and $Sm^{3+}$ complexes. This is associated with the greater size and smaller charge on the $Ln^{2+}$ ions.[19,20] These complexes are readily soluble in the majority of organic solvents, including even nonpolar or weakly polar solvents such as benzene, hexane, halohydrocarbons, etc. (by virtue of the hydrophobic properties of the aliphatic groups of crown-ethers).[21]

The use of crown-ethers also makes it possible to increase greatly the stability of $Ln^{2+}$ solutions in many solvents, which can be accounted for by the shielding effect of the complexone molecule.[18]

Various diiodoalkanes such as diiodomethane and 2,2-diiodobutane can be used for the preparation of $SmI_2$ instead of DIE.[17] Other haloalkanes react much less effectively. Thus the reaction with 1,2-dibromoethane in THF is very slow and leads to sparingly soluble samarium dibromide,[17] and the reaction with 1,2-dichloroethane does not occur at all.[9]

In contrast to the dichloride and dibromide, samarium diiodide is readily soluble not only in THF but also in HMPA, acetonitrile, and ethanol.[22]

Thus samarium iodide is best among all the salts because of its high reactivity, higher solubility in organic solvents, and the comparative ease of its formation and storage.†

## III. Reactions involving samarium diiodide

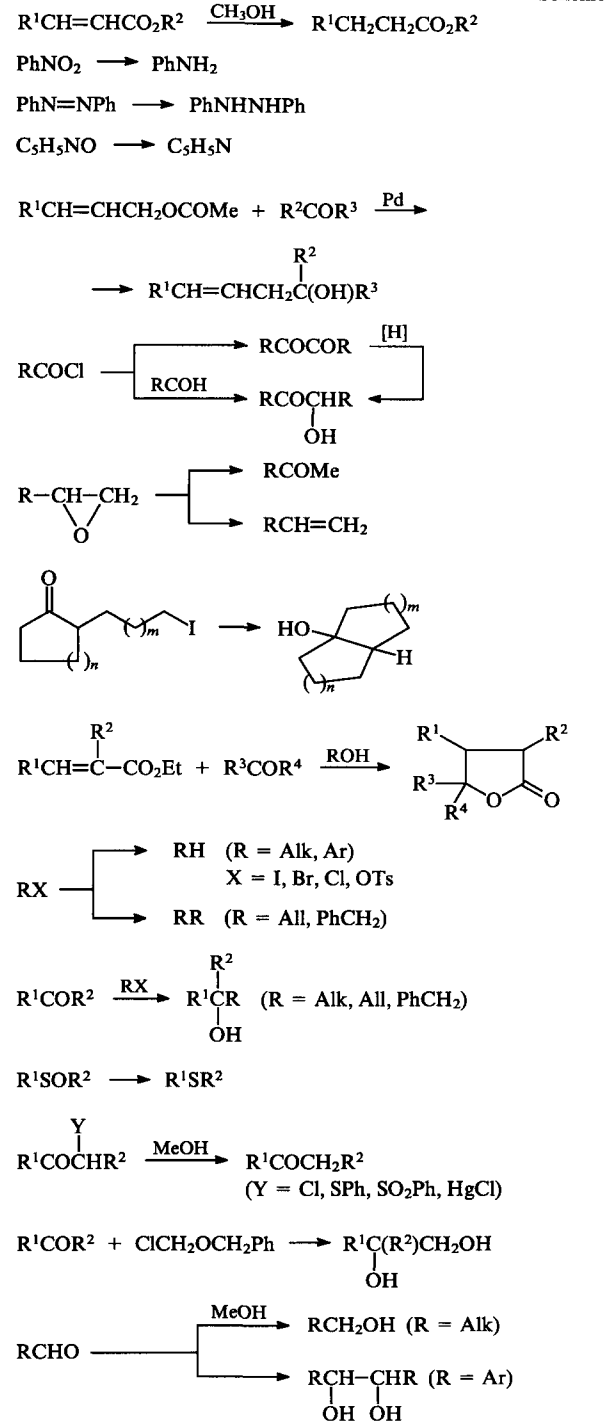
Samarium diiodide is a powerful reductant, soluble in organic solvents, which behaves under the conditions of organic synthesis as an electron donor and is therefore a reagent capable of promoting reactions involving electron transfer.[24]

In a general form, the known reactions that are carried out successfully in the presence of samarium iodide are presented in Scheme 1. The mechanism of organic reactions involving $SmI_2$ can be represented by Scheme 2 in the most general form.

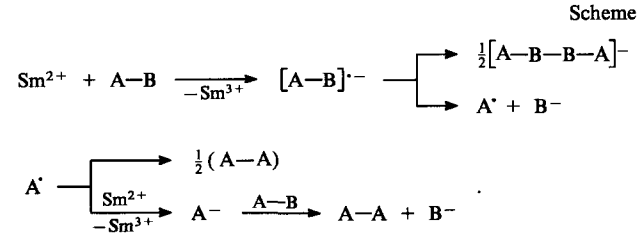
It is noteworthy that the reactions involving electron transfer from $SmI_2$ to the organic substrate A–B with formation of a radical-anion, which subsequently dimerises or is cleaved into an anion and a radical, the latter being capable of reacting subsequently in different ways, have a stepwise radical-ion mechanism.

† $SmI_2$ is distributed by Aldrich in the form of a 0.1 M solution in THF.[23]

Scheme 1



Scheme 2



The ability of $Sm^{2+}$ and $Sm^{3+}$ ions to form highly coordinated compounds also exerts a specific effect on the reaction. This probably accelerates electron transfer and can affect the mode of reactions with participation of a free radical (see below).

It is seen from Scheme 2 that processes with participation of reactive species of three different types can take place in the system: free radicals, radical-anions, and carbanions, which lead to extensive possibilities for a wide variety of chemical reactions — reduction, condensation, addition, and nucleophilic substitution. It is very significant that reactions of this type take place effectively in the given instance in a virtually neutral medium.

Various types of reactions carried out with the aid of $SmI_2$ and their mechanisms are examined below.

## 1. Reduction of halogen-containing hydrocarbons and tosylates

On refluxing for several hours in 0.1 M solution of $SmI_2$ in THF, primary and secondary alkyl bromides and iodides RHal produce the corresponding alkanes RH in a high yield (80%–95%).[5] Hydrocarbons are obtained similarly from the corresponding tosylates ROTs.[5]

$$RX \xrightarrow[65\ ^\circ C,\ 2\ h]{SmI_2,\ THF} RH$$

X = Hal, OTs.

For X = OTs, the reaction is accelerated in the presence of small amounts of NaI. This gives grounds for the hypothesis that the tosylates are initially converted into the iodides and then into the alkanes (small amounts of alkyl iodides have been detected among products of the reation even when the latter was carried out in the absence of NaI).[25]

Inanaga et al.[26] observed that the redution potential of $SmI_2$ increases abruptly after the addition of HMPA to a THF solution of $SmI_2$. Thus phenyl and vinyl halides react with $SmI_2$ only in the presence of 5% HMPA as the catalyst. Tertiary alkyl halides also react under similar conditions and in both cases even chlorides, which do not usually enter into a reaction of this kind, are reduced. It has been shown that the use of the $SmI_2$–THF–HMPA system makes it possible not only to expand significantly the range of halogen-containing hydrocarbons reduced with the aid of $SmI_2$ but also to eliminate the need for prolonged treatment by refluxing. In this case the thermal conditions are milder and the process proceeds at a higher rate and with a quantitative yield of the product.[27]

The addition of HMPA proved to be effective also in a series of other reactions involving samarium diiodide (see below).[28]

In contrast to alkyl halides, benzyl or allyl halides are not reduced by $SmI_2$ but dimerise in several minutes at room temperature.

$$2\ PhCH_2Br + 2\ SmI_2 \xrightarrow[20\ min]{20\ ^\circ C} PhCH_2CH_2Ph + 2\ SmBrI_2$$

The following mechanism has been proposed for the reactions of halogen-containing hydrocarbons with $SmI_2$ in THF:[24]

$$RX + Sm^{2+} \longrightarrow RX^{\cdot -} + Sm^{3+},$$

$$RX^{\cdot -} \longrightarrow \dot{R} + X^-,$$

$$\dot{R} + Sm^{2+} \longrightarrow R^- + Sm^{3+},$$

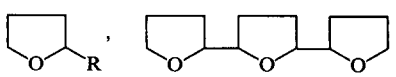
$$\dot{R} + THF \longrightarrow RH + (THF)^{\cdot},$$

$$R^- + THF \longrightarrow RH + (THF)^-,$$

$$\dot{R} + \dot{R} \longrightarrow R{-}R,$$

R = All, $PhCH_2$.

The presence of THF radicals or carbanions in the reaction medium has been confirmed by the formation of small amounts of different 2-substituted THF derivatives, for example:



Under these conditions, the reaction $R^{\cdot} + SmI_2 \rightarrow R^-SmI_2^+$ apparently does not occur because $RSmI_2$ is absent from the reaction products, although in principle such compounds are known and are entirely stable in an organic medium.[1]

It has been suggested[1] that alkyl halides are hydrogenated in the coordination sphere of the samarium(II) ion bound to several THF molecules (like all lanthanide derivatives, samarium diiodide has the high coordination number 8). This can account for the absence of dimerisation products in the reaction of samarium diiodide with aliphatic halides, while benzyl and allyl halides afford only dimerisation products because the radicals formed are too stable to attack THF molecules and can diffuse into the bulk of the solution and recombine there with another radical.

It is of interest to note that benzyl and allyl halides in many instances form under the influence of samarium diiodide dimeric hydrocarbons in higher yields than in the presence of other reagents, for example $Cr^{3+}$ salts.[29]

A similar recombination of silyl radicals with formation of the Si–Si bond was first observed by the present authors in a study of the effect of $SmI_2$ on organochlorosilanes.[30] The common method of synthesis of polysilanes used previously, namely from organodichlorosilanes by the Wurtz–Fittig reaction using alkali metals, suffers from a series of disadvantages: severe reaction conditions, low process selectivity, and difficulty in the regulation of the molecular weight characteristics of the polymers formed and in the synthesis of polysilanes with functional group substituents.[31] The methods proposed in recent years are complex, comprise many stages, and are characterised by low yields of the target products.[32]

At the same time, polysilanes, which have specific optical properties, have attracted increased attention.[33] We have developed a single-stage method of synthesis of hexaorganodisilanes from triorganochlorosilanes and $SmI_2$.

$$2\ R^1R^2R^3SiCl + 2\ SmI_2 \longrightarrow (R^1R^2R^3Si)_2 + 2\ SmI_2Cl.$$

| Radicals | Yield (%) |
|---|---|
| $R^1 = R^2 = R^3 = Me$ | < 5 |
| $R^1 = R^2 = Me$, $R^3 = CH_2{=}CH{-}$ | 75 |
| $R^1 = R^2 = Me$, $R^3 = Ph$ | 85 |
| $R^1 = R^2 = R^3 = Ph$ | 90 |

It was established that, as in the case of the carbo-analogues, the mode and rate of the reaction and the yield of the target product depend on the structure of the organochlorosilane employed (compounds with benzyl and allyl substituents dimerise most effectively). It was also shown that the reaction of diorganodichlorosilanes with $SmI_2$ affords oligosilanes.

$$n\,R^1R^2SiCl_2 \xrightarrow{SmI_2} Cl{-}\left(R^1R^2Si\right)_n{-}Cl;$$

$R^1 = R^2 = Me$; $R^1 = CH_3$, $R^2 = Ph$.

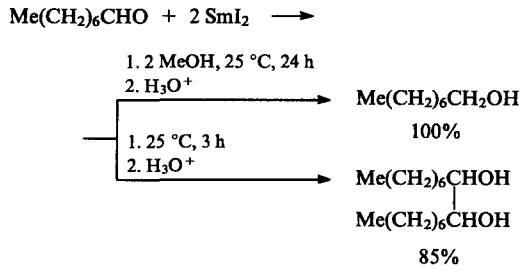
Thus the reduction method based on the use of $SmI_2$ may be assigned to the class of the most progressive and effective methods of synthesis of hydrocarbons and organosilanes from organic and organosilicon halides.

## 2. Reactions with carbonyl compounds

Aldehydes and ketones are reduced by $SmI_2$, the mode of the reaction depends on its conditions and on the structure of the initial compounds. One of the most interesting features of $SmI_2$ is its ability to promote the formation of a C–C bond between ketones and aldehydes, on the one hand, and various organic compounds having the general formula RX (X = Hal, OTs, $OSO_2Me$, OAc), on the other.[24]

**a. Reduction of aldehydes and ketones**

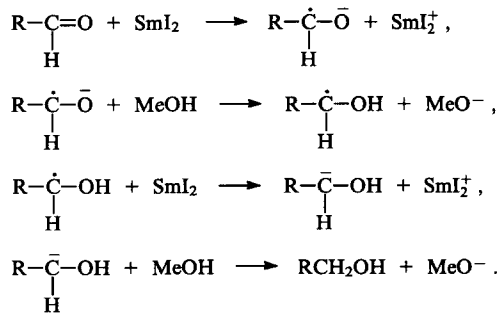
The interaction of aliphatic aldehydes with $SmI_2$ in THF in the presence of a proton donor (for example, 1% methanol solution) affords alcohols, whilst in aprotic media the products are pinacols.[2]




Aliphatic ketones are also reduced under analogous conditions but much more slowly. For example, the yield of 2-octanol in the reaction of 2-octanone with $SmI_2$ is only 12%.[5]

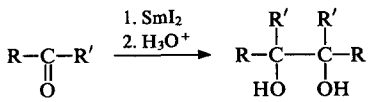
The nature of the proton donor exerts a strong influence on the reaction. Thus, when water is used instead of methanol, 2-octanone is reduced in a satisfactory yield, whereas phenol suppresses the formation of the ketone [alcohol?].[5]

The selective reduction of the aldehyde group in the presence of a keto-group, which constituted previously a complex problem, is based on the significant difference between the reactivities of the above compounds. Suitable reagents, including modified hydroborates and hydroaluminates, have been proposed for this reaction only recently,[34] but $SmI_2$ is the most selective. It has been suggested[1] that the reaction proceeds via the following mechanism:




This mechanism is confirmed by the fact that, when MeOD is used instead of MeOH, 90% of RCHDOH and 10% of $RCH_2OH$ is formed. The formation of a small fraction of the protonated rather than deuteriated product can apparently be accounted for by the possibility that hydrogen may be abstracted from THF by the hyroxyalkyl radical.

**Table 1.** The synthesis of pinacols from aldehydes and ketones by treatment with $SmI_2$.



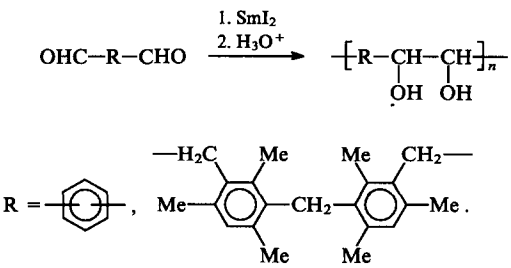

| R | R′ | Reaction time/min | Yield (%) |
|---|---|---|---|
| H | Ph | 0.5 | 95 |
| H | *p*-$CNC_6H_4$ | 0.5 | 95 |
| H | *p*-$NO_2C_6H_4$ | 0.5 | 95 |
| H | *p*-$HOOCC_6H_4$ | 0.5 | 66 |
| H | *p*-$MeOC_6H_4$ | 1.0 | 90 |
| Me | Ph | 0.5 | 95 |
| Me | n-$C_6H_{13}$ | 1440 | 80 |

In the absence of a suitable proton donor (methanol), recombination of the intermediate radical-anions leads to a pinacol. Pinacols are formed almost exclusively from aromatic aldehydes and ketones, the reaction involving aldehydes being very fast (taking only 30–60 s at room temperature) with an almost quantitative yield, while the degree of reaction with aliphatic ketones after 24 h is 80%.[35]

The possibility of obtaining pinacols in high yields from aromatic aldehydes containing various substituents in the *para*-position is especially attractive (Table 1). The above method has significant advantages over other procedures for the synthesis of pinacols because of the attainment of high yields of the target product and the exceptionally high reaction rate.

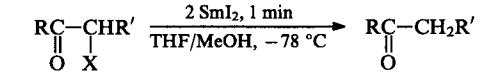
For example, when $CeI_2$ in THF is used, 12 h is required to synthesise a pinacol from benzaldehyde in 94% yield,[36] while in the presence of aqueous $TiCl_3$ in an alkaline medium the reaction with benzaldehyde is rapid, mainly an alcohol being formed as a side product.[37]

By treating dialdehydes with $SmI_2$, we synthesised polypinacols with a molecuar mass of the order of $(12-15) \times 10^3$.[38]



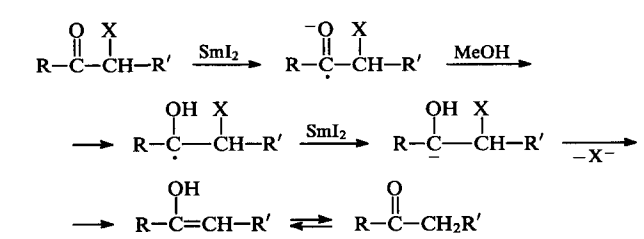

Previously only oligomeric pinacols with a molecular mass not exceeding $2 \times 10^3$ were obtained by treating terephthalic aldehyde with a zinc complex of $TiCl_4$.[39]

Although ketones are reduced via a mechanism similar to that described for aldehydes, α-substituted ketones require special consideration.[40] Analysis of literature data shows that the α-substituent can be abstracted from such compounds only under extremely severe conditions at an elevated temperature.[41,42] The use of $SmI_2$ for this purpose in the presence of a proton donor makes it possible to obtain unsubstituted ketones from a wide range of α-substituted ketones in high yields at low temperatures.




X = OAc, $OSiMe_3$, OTs, Cl, SPh, $SO_2Ph$, $OCO_2CH_2Ph$, HgCl.

It has been suggested[40] that the reaction proceeds via the formation of a ketyl, which is rapidly protonated by methanol. Treatment with a second equivalent of $SmI_2$ leads to the formation of a carbanion from which X is then split off. The unsubstituted ketone is obtained as a result of the tautomerisation of the enol produced.




**b. Reactions of aldehydes and ketones via the CO group**

One of the remarkable properties of samarium diiodide is its ability to promote the formation of a C–C bond between ketones or aldehydes and compounds of different types. It has

been shown that halogen-containing hydrocarbons and tosylates undergo reductive addition to ketones under the influence of $SmI_2$.[5] Formally this reaction is analogous to the reactions of ketones with a Grignard reagent.

$$n\text{-}C_6H_{13}COMe + MeI \xrightarrow[2.\ H_3O^+]{1.\ SmI_2,\ 65\ ^\circ C,\ 1\ h} n\text{-}C_6H_{13}C(OH)Me_2;\quad 75\%$$

$$n\text{-}C_6H_{13}COMe + Bu^nOTs \xrightarrow[2.\ H_3O^+]{1.\ SmI_2,\ THF} n\text{-}C_6H_{13}\overset{\displaystyle Me}{\underset{|}{C}}(OH)\text{—}Bu^n.\quad 95\%$$

Various ketones, both alicyclic and aromatic, interact with the $SmI_2$–RX system and their reactivities hardly differ from that of 2-octanone described above. The reactivity of the halides diminishes in the sequence RI > RBr ≫ RCl. It is of interest to note that allyl and benzyl halides, which usually tend to dimerise rapidly on treatment with $SmI_2$, in the presence of a ketone react readily with the latter, forming tertiary alcohols.

$$n\text{-}C_6H_{13}COMe + ICH_2CH{=}CH_2 \xrightarrow[25\ ^\circ C,\ 25\ min]{2\ SmI_2} n\text{-}C_6H_{13}\overset{\displaystyle Me}{\underset{|}{C}}(OH)CH_2CH{=}CH_2.\quad 72\%$$

On the other hand, vinyl halides and aromatic halo-compounds do not react with ketones in the presence of $SmI_2$; in such cases, only the conversion of the ketones into pinacols to the extent of 10%–20% is observed.[5]

The following mechanism has been proposed for the alkylation of ketones, involving the formation of intermediate radical compounds:[24]

$$RX + SmI_2 \longrightarrow RX^{\cdot-}SmI_2^+ \longrightarrow \dot{R} + SmI_2X, \quad (1)$$

$$\dot{R} + SmI_2 \longrightarrow R^-SmI_2^+, \quad (2)$$

$$R^1R^2C{=}O + SmI_2 \longrightarrow R^1R^2\dot{C}O^-SmI_2^+, \quad (3)$$

$$R^1R^2\dot{C}O^-SmI_2^+ + \dot{R} \longrightarrow RR^1R^2CO^-SmI2^+ \xrightarrow{H_3O^+} RR^1R^2COH, \quad (4)$$

$$R^1R^2C{=}O + R^-SmI_2^+ \longrightarrow RR^1R^2CO^-SmI_2^+ \xrightarrow{H_3O^+} RR^1R^2COH. \quad (5)$$

The mechanism of the reactions of the radical R$^\cdot$ has not been elucidated in detail: it may be that it is reduced by $SmI_2$ to $R^-$ [reaction (2)] or recombines with the ketyl radical arising as a result of electron transfer from $SmI_2$ to the ketone [reaction (4)]. At any rate, the radical mechanism explains the presence in the reaction product of small amounts of compounds such as the α-R-alkylated THF.

The reaction is much faster when small amounts of $FeCl_3$ (1 mass % of $SmI_2$) are added. The catalytic effect of $FeCl_3$ may be due to its ability to promote the formation of ketyl radicals (this was demonstrated for the Grignard reaction) or the conversion of $Sm^{2+}$ into $Sm^{3+}$.[43] In one way or another, $FeCl_3$ behaves as a compound facilitating electron transfer in reactions with $SmI_2$. HMPA also functions as a catalyst of the reaction.[44]

The reduction of aliphatic aldehydes, leading to a mixture of products, proceeds in a more complex manner.[45]

$$n\text{-}C_7H_{15}CHO + MeI \xrightarrow[2.\ H_3O^+]{1.\ SmI_2,\ 25\ ^\circ C} n\text{-}C_7H_{15}CH(OH)Me\ (16\%) + n\text{-}C_7H_{15}COMe\ (6\%) + n\text{-}C_7H_{15}CH_2OH\ (38\%) + n\text{-}C_7H_{15}C(OH)Me_2\ (32\%).$$

The observed reactions may be based on the Meerwein–Ponndorf reaction, which proceeds very rapidly with participation of secondary samarium alkoxides: $n\text{-}C_{17}H_{15}CH(Me)OSmI_2$ is formed initially and then reacts rapidly with the aldehyde, forming $n\text{-}C_7H_{15}COMe$ and $n\text{-}C_7H_{15}CH_2OSmI_2$; a tertiary alcohol is obtained from the ketone and $CH_3I$ in the presence of $SmI_2$.

It has been shown recently[43] that dicyclopentadienylsamarium, readily and rapidly obtained by the exchange reaction between $SmI_2$ and cyclopentadienylsodium, is significantly more effective in the reaction of aliphatic aldehydes with halogen-containing hydrocarbons. In contrast to $SmI_2$, it does not catalyse the Meerwein–Ponndorf or Tishchenko side reaction.

It has also been found that secondary alcohols are formed from aldehydes in a satisfactory yield when the more reactive benzyl or allyl halides are employed.[45]

$$n\text{-}C_7H_{15}CHO + ICH_2CH{=}CH_2 \xrightarrow[25\ ^\circ C,\ 5\ min]{2\ SmI_2,\ THF} n\text{-}C_7H_{15}\overset{\displaystyle OH}{\underset{|}{C}}HCH_2CH{=}CH_2\quad 75\%$$

A mechanism similar to that discussed above for the reduction of ketones has been proposed for this reaction.

$$RX + SmI_2 \longrightarrow RX^{\cdot-}SmI_2^+ \longrightarrow \dot{R} + SmI_2X$$

$$R'CHO + SmI_2 \longrightarrow R'CHO^{\cdot-}SmI_2^+$$

$$R'CHO^{\cdot-}SmI_2^+ + \dot{R} \longrightarrow RR'CHO^-SmI_2^+ \xrightarrow{H_3O^+} RR'CHOH$$

It is interesting to note that the CN, $NO_2$, $CO_2R$, and other groups are not then involved.[35]

$$n\text{-}C_6H_{13}COMe + TsO(CH_2)_9CO_2Me \xrightarrow[2.\ H_3O^+]{1.\ 2\ SmI_2,\ 65\ ^\circ C,\ 2\ h} n\text{-}C_6H_{13}\overset{\displaystyle OH}{\underset{|}{C}}(CH_2)_9CO_2Me\quad \overset{\displaystyle CH}{\underset{|}{}}\quad 63\%$$

γ-Hydroxynitriles have been obtained in a low yield in the reaction of ketones with acrylonitrile.[47]

$$R^1COR^2 + CH_2{=}CH{-}CN \xrightarrow[THF,\ KOH]{2\ SmI_2} R^1R^2\overset{\displaystyle OH}{\underset{|}{C}}{-}CH_2CH_2CN\quad 17\%-20\%$$

It has been observed recently that, on treatment with samarium diiodide, allyl acetates also interact with carbonyl compounds in the presence of catalytic amounts of a palladium complex [$Pd(OAc)_2$ + $PPh_3$ or $Pd(PPh_3)_4$] to form homoallyl alcohols in a good yield.[46]

$$R^1CH{=}CHCH_2OCOCH_3 + R^2COR^3 \xrightarrow[SmI_2,\ 0\ ^\circ C,\ 2\ h]{Pd(PPh_3)_4} R^1CH{=}CHCH_2C(OH)R^2R^3.$$

Aromatic and α,β-unsaturated carbonyl compounds react differently, affording mainly dimerisation products — pinacols.[46] The use of readily available allyl acetates in the aldehyde and ketone reduction reactions makes it possible to replace allyl halides, which are difficult to obtain, unstable, and toxic.

In the presence of $SmI_2$, aldehydes and ketones also react with chloromethyl sulfides $ClCH_2SR$ to form hydroxythioethers.[48]

$$ClCH_2SR + R^1R^2CO \xrightarrow{SmI_2,\ THF} R^1R^2C(OH)CH_2SR$$

R = Me, Ph.

A reaction involving the coupling of carbonyl compounds $R^1C(O)R^2$ [$R^1 = PhCH_2$, $R^2 = Me$; $R^1 + R^2 = (CH_2)_{11}$; $R^1 = cyclo\text{-}C_6H_{11}$, $R^2 = H$] with alkynes $R^3C{\equiv}CX$ (X = Ph, $CH_2OAc$, $Bu^t$) has also been described. The reaction is promoted by the $SmI_2$–HMPA–THF system ($Bu^tOH$, 20 °C, 5 min); it results in the formation of the allyl alcohols $R^1R^2C(OH)CH = CHX$.[49]

Thus the use of samarium diiodide in reactions involving reductive addition to the carbonyl group makes it possible to obtain alcohols with a wide variety of structures in satisfactory yields.

**c. Hydroxymethylation of carbonyl compounds**

The interesting reaction involving the hydroxymethylation of carbonyl compounds on treatment with samarium diiodide has been recently achieved by Imamoto et al.[50] Ketones readily interact in this reaction with benzyl chloromethyl ether at room temperature, forming alcohols, which afford diols on subsequent hydrogenation.

$$R'\overset{\overset{O}{\|}}{C}R + ClCH_2OCH_2Ph \xrightarrow{2\ SmI_2,\ 20\ °C}$$

$$\longrightarrow RR'\underset{OH}{\overset{|}{C}}CH_2OCH_2Ph \xrightarrow[Pd/C]{H_2} RR'\underset{OH}{\overset{|}{C}}CH_2OH$$

Aldehydes are not reduced to alcohols but are converted into pinacols in 80%–90% yield. However, in the presence of equimolar amounts of the dimethyl or dibenzyl ether of tetraethylene glycol, which form a complex with $SmI_2$, it is possible to obtain alcohols in 50%–70% yield.

$$PhCH_2CH_2CHO + ClCH_2OCH_2Ph \xrightarrow{2\ SmI_2,\ 20\ °C}$$

$$\longrightarrow PhCH_2CH_2CH(OH)CH_2OCH_2Ph \xrightarrow[Pd/C]{H_2}$$

66%

$$\longrightarrow PhCH_2CH_2\underset{OH}{\overset{|}{C}}HCH_2OH$$

90%

In the interaction of carbonyl compounds with diiodomethane in the presence of metallic samarium or $SmI_2$, an iodohydrin is formed as an intermediate, its hydrolysis subsequently affording the corresponding diol.[51, 52]

$$R^1\overset{\overset{O}{\|}}{C}R^2 + CH_2I_2 \xrightarrow{SmI_2\ or\ Sm} R^1R^2\overset{\overset{OH}{|}}{C}CH_2I$$

Thus the hydroxymethylation of carbonyl compounds may be an effective reaction in the synthesis of 1,2-diols.

**d. Reactions with carboxylic acids and their derivatives**

Carboxylic acids and their derivatives (esters, amides, and anhydrides) are as a rule resistant to the action of $SmI_2$.[5] However, it has been shown recently that, in the presence of bases and a proton donor, they are readily reduced by $SmI_2$ to the corresponding alcohols at room temperature.[53]

$$PhCOOR^1 \xrightarrow[THF,\ R^1OH,\ 20\ °C]{SmI_2,\ HB} PhCH_2OH$$

$$+ \left\{[PhCH(OH)]_2 + PhCH_2CH(OH)Ph + PhCH_2COPh\right\}$$

$R^1$ = Me, PhCO; HB = $LiNH_2$, LiOMe, KOH.

$$PhCONHR^2 \xrightarrow[THF,\ R^2OH,\ 20\ °C]{SmI_2,\ HB} PhCH_2OH + PhCH_2NHR^2$$

$R^2$ = H, Ph.

Carboxylic acid chlorides do not form the expected reduction products, such as aldehydes or primary alcohols, on reaction with $SmI_2$. On the other hand, they enter very rapidly into an addition reaction. The main product obtained is then an α-diketone RCOCOR in a yield ranging from 40% (R = Alk) to 80% (R = Ar), an α-ketol RCOCH(OH)R being formed as a side product.[55]

$$2\ RCOCl + 2\ SmI_2 \xrightarrow{25\ °C,\ 2-4\ min} R\text{–}\overset{\overset{O}{\|}}{C}\text{–}\overset{\overset{O}{\|}}{C}\text{–}R + 2\ SmI_2Cl$$

R = Ph (78%), *p*-$ClC_6H_4$ (72%), *p*-$MeOC_6H_4$ (69%), $Cl(CH_2)_4$ (54%).

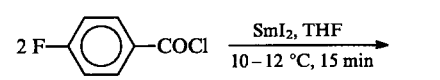
The product yields vary depending on R.

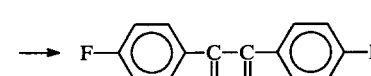
The asymmetric reduction of benzil to benzoin takes place in the presence of optically active compounds such as quinine or quinidine. This reaction proceeds even more effectively in the presence of HMPA.[54]

$$Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}\overset{\overset{O}{\|}}{C}\text{–}Ph \xrightarrow[[H]]{SmI_2} Ph\text{–}\overset{\overset{H}{|}}{C}\text{–}\overset{\overset{O}{\|}}{C}\text{–}Ph$$

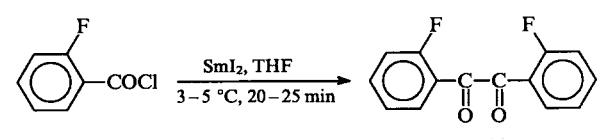
OH

We have obtained difluorobenzils by condensing under mild conditions the chlorides of *p*- and *o*-fluorobenzoic acids by treatment with $SmI_2$ in THF.[10]




50%




65%

These products were then used to synthesise high-molecular-mass aromatic ethers by the nucleophilic substitution of the fluorine atom by alkali metal bisphenoxides and subsequent conversion of the α-diketone groups into quinoxaline groups.[10]

A paraffin-like admixture of $C_{23-25}$ alkanes was also detected in the unpurified product of the reactions of acid chlorides or fluorides.[56] They can be produced in the oligomerisation

of ethylene, formed at an early stage in the interaction of metallic samarium with diiodoethane. $SmI_2$ or $SmI_2Cl$ might have served as the oligomerisation initiator both in the samarium diiodide formation stage and in the stage involving the synthesis of the diketones.

According to ideas put forward in the literature,[57] the acid chloride condensation reaction proceeds via the formation of radical-ions, which are cleaved to acyl radicals and these are reduced to acyl anions. The latter react in their turn with a second molecule of the acid chloride, affording an α-diketone (the direct recombination of the acyl radicals is insignificant).

$$RCOCl + SmI_2 \longrightarrow [RCOCl]^{\cdot -}\ SmI_2^+$$

$$[RCOCl]^{\cdot -} \longrightarrow RC\dot{O} + Cl^-$$

$$RC\dot{O} + SmI_2 \longrightarrow$$

$$\longrightarrow RCO^-SmI_2^+ \xrightarrow{RCOCl} ROC{-}COR + SmI_2Cl$$

$$2\,RC\dot{O} \longrightarrow ROC{-}COR$$

The last process takes place to a very insignificant extent. The proposed mechanism explains the satisfactory yield (75%) of the α-diketone from $PhCH_2COCl$. It is known that the acyl radical $PhCH_2CO^{\cdot}$ is rapidly decarbonylated ($k_c = 5.2 \times 10^7\ s^{-1}$) to $PhCH_2^{\cdot}$. The absence of toluene and 1,2-diphenylethane from the reaction products is evidence that the acyl radical is reduced to the acyl anion at a rate greatly exceeding $5.2 \times 10^7\ s^{-1}$. The anion is then acylated by the acid chloride, affording the α-diketone. The presence of the intermediate acyl anion $RCO^-SmI_2^+$ in the reaction is also confirmed by its interaction with electrophiles other than RCOCl, for example aldehydes and ketones, which results in the formation of α-hydroxyketones after hydrolysis: their formation can be accounted for by nucleophilic acylation.[57]

$$Bu^tCOCl + EtC(=O)H \xrightarrow[20\ ^\circ C,\ 4\ min]{2\ SmI_2} Bu^tC(=O)CH(OH)Et$$

64%

The direct synthesis of α-diketones from carboxylic acid chlorides by treatment with $SmI_2$ has undoubted advantages over other methods of synthesis of these compounds based on multistage procedures such as the oxidation of monocarbonyl compounds or their α-substituted derivatives (for example acyloins, derivatives of enediols, glycols, etc.) or their synthesis from aromatic compounds and oxalyl chloride by the Friedel–Crafts reaction.[58]

A new strategy for the synthesis of α-hydroxyketones by the reaction of an alkyl halide, isonitrile, and a carbonyl compound with $SmI_2$ has also been proposed.[59]

$$R^1Hal + ZNC \xrightarrow[-15\ ^\circ C,\ 3\ h]{2\ SmI_2,\ THF/HMPA} R^1C(=NZ)SmI_2 \xrightarrow[0\ ^\circ C,\ 14\ h]{R^2R^3C=O}$$

$$\longrightarrow R^1C(=NZ)CR^2R^3(OH) \xrightarrow{H_3O^+} R^1C(=O)CR^2R^3(OH)$$

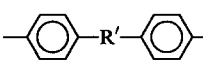
Z = 2,6-dimethylphenyl

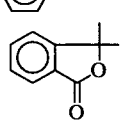
The mild conditions make it possible to employ this method for the synthesis of compounds with various functional groups, including, for example, terminal acetylenic and trimethylsilyl ether groups, and also for the synthesis of α-hydroxyaldehydes.

The formation of α-diketones in the reaction of carboxylic acid chlorides with $SmI_2$ may serve as a basis for the formation of the corresponding polymers. The available information about the synthesis of such polymers by other methods is extremely scant. The possibility of obtaining polyhydroxyketones and polybenzoins by the acyloin or benzoin condensation of terephthalic acid chloride and terephthalic anhydride respectively, which were oxidised to poly-α-diketones by prolonged refluxing in nitric acid, has been described.[60,61] Only insoluble high-molecular-mass oligomers were obtained in 50%–70% yield.[62]

We synthesised for the first time α-diketone homopolymers and copolymers in a quantitative yield[63] by the reaction of aromatic dicarboxylic acid chlorides with $SmI_2$ in THF at room temperature for 10–15 min. It was found that the acid fluorides are also reactive in this process.

$$XOCRCOX + SmI_2 \longrightarrow -[R{-}CO{-}CO]_n-$$

R = , ;

R′ = —O—, —C(CF₃)₂—, ;

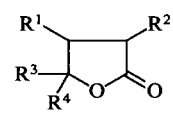
X = Cl, F.

The polymers synthesised have an amorphous structure, a molecular mass of the order of $25 \times 10^3$, and a softening temperature of 250–290 °C. They are readily soluble in various organic solvents.

**e. The cyclisation reactions of carbonyl compounds**

**Intermolecular cyclisation.** In the presence of samarium diiodide and a proton donor, aldehydes and ketones interact with alkenes containing electron-accepting substituents.[47]

$$R^1CH{=}CR^2CO_2Et + R^3COR^4 \xrightarrow[ROH,\ 3\ h]{2\ SmI_2}$$



Methyl, ethyl, and especially butyl alcohols can be used as the proton donor. In order to suppress the reduction of the ketone, the dimethyl ether of tetraethylene glycol, which forms a complex with $SmI_2$, is added to the reaction mixture.[64]

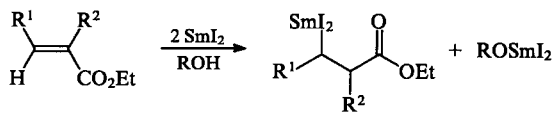
Whereas in the routinely used method of the electrochemical synthesis of γ-lactones from activated olefins and ketones or aldehydes in the presence of chlorotrimethylsilane only aliphatic compounds are reactive, when samarium diiodide is used the reaction can be extended to aromatic aldehydes and ketones.[64] The reaction apparently proceeds via a radical mechanism.[47]

$$R^3R^4C{=}O \xrightarrow{SmI_2} R^3R^4\dot{C}{-}OSmI_2 \xrightarrow{H\ =\ CR^1CO_2Et}$$

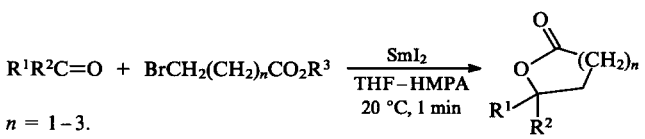
$$\longrightarrow R^3R^4C(OSmI_2){-}HCR^1{-}\dot{C}R^2{-}CO_2Et \longrightarrow$$

$$\xrightarrow[-EtOSmI_2]{ROH,\ SmI_2} R^3R^4C{-}HCR^1{-}HCR^2{-}CO_2Et$$

However, another mechanism involving the formation of samarium homoenolate is not ruled out either.



The use of small amounts of HMPA in this reaction makes it possible to achieve the direct synthesis of γ-, δ-, or ε-lactones from the corresponding bromoesters, in particular from the readily available industrially produced β-bromopropionate, γ-bromobutyrate, or δ-bromovalerate, in satisfactory yields. [52,65]



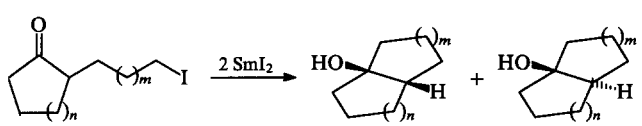
$n = 1-3$.

75%–82%

Thus the use of $SmI_2$ has made it possible to develop a new single-stage method of synthesis of lactones, the distinctive features of which are simplicity, technological convenience, and effectiveness.

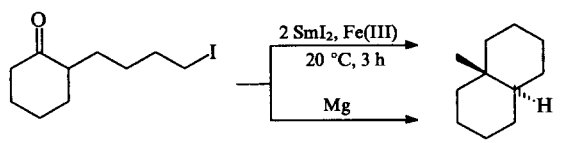
**Intramolecular cyclisation.** Molander and coworkers [66–68] have shown that, when $SmI_2$ is used as the reagent, the Barbier as well as Reformatsky reactions take place readily and smoothly. [69]

The intramolecular cyclisation reaction (the Barbier reaction) plays an important role in organic synthesis. A series of methods for carrying out a reaction of this type have been developed. [70] The most common include the cyclisation of 2-(ω-iodoalkyl)cycloalkanones with formation of the corresponding mixture of diastereoisomeric bicyclic alcohols.



By regulating the length of the iodoalkyl side chain and the ring size in the initial cycloalkanone, it is possible to obtain a wide variety of bicyclic compounds. However, the use of traditional reductants, in particular alkali [71] and alkaline earth metals, [72] in this process led to the formation of bicyclic alcohols with only three-, four-, and five-membered rings.

The use of $SmI_2$ makes it possible to achieve the intramolecular cyclisation of haloketones accompanied by the formation of bicyclic alcohols with six-membered and in certain cases also with seven-membered rings in a high yield. [66]

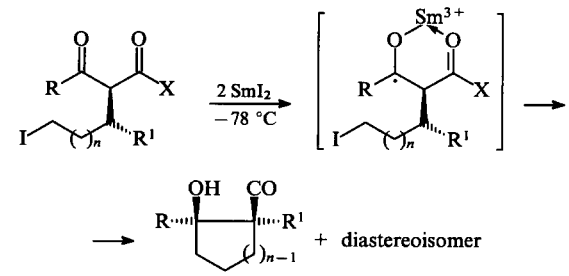


95%

In addition, the stereocontrolled cyclisation of 2-(ω-iodoalkyl)β-ketoesters and 2-(ω-iodoalkyl)-β-ketoamides‡ takes place on treatment with $SmI_2$, affording high yields of the esters and amides respectively of *cis*-2-hydroxycycloalkanecarboxylic acids with five-, six-, and even seven-membered rings. [67]

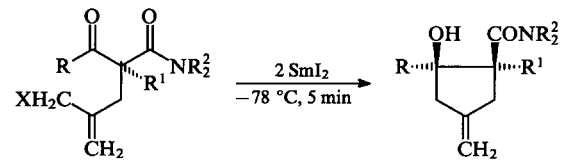
‡ When activated magnesium is used at room temperature, cyclisation does not occur and the initial reagent is isolated. [73]

In view of the very strong affinity of the samarium ion for the oxygen atom in the reactions of carbonyl compounds with $SmI_2$, a stable chelate is formed fairly readily and the process proceeds via an intermediate stage involving the formation of a samarium-containing metallocycle. The stereoselectivity of all the processes is exceptionally high under these conditions.



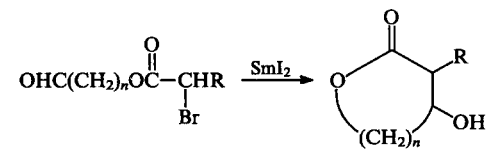
$X = NR^2_2, OR^2$.

2-(ω-Haloallyl)-β-ketoamides also cyclise readily.



In the presence of $SmI_2$, the reaction proceeds under mild conditions, which makes it possible to obtain cyclic systems with various functional groups which remain unaffected. Thus $SmI_2$ proved to be an extremely effective reagent in the stereocontrolled intramolecular Barbier reactions.

Tabuchi et al. [74] established that the use of $SmI_2$ proved to be most effective in the synthesis of medium and large lactone rings. In particular, eight- and nine-membered rings, the synthesis of which by the traditional method has been extremely difficult, can now be obtained fairly readily. Inanaga and coworkers have also been working on these lines. [12]

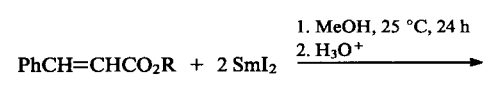


76%–96%

$n = 4-10$.

## 3. Reduction of C=C double bonds

On treatment with $SmI_2$ solutions, the conjugated double bond is reduced even at room temperature in contrast to an isolated double bond. [5] Thus α,β-unsaturated acids and esters are reduced in a high yield by samarium diiodide in THF in the presence of methanol. [1]



R = H, Et.

However, for conjugated esters, this reaction is not the only one possible. For example, when an unsaturated ester having a more complex structure is acted upon by $SmI_2$, the following reaction takes place with 90% conversion: [2]

$$MeCH(OH)CH{=}C(Me)CO_2Et + 2\,SmI_2 \xrightarrow[2.\,2\,H_2O^+]{1.\,THF} MeCH{=}CHCH(Me)CO_2Et\,.$$

The carbonyl groups in α,β-unsaturated ketones and aldehydes are also partially reduced, so that competing reactions involving the reduction of the C=O and C=C groups are possible.

## 4. Reactions with nitrogen-containing compounds

The effect of $SmI_2$ on various nitrogen-containing functional groups has been investigated. Aromatic and aliphatic nitriles do not undergo any changes in its presence.[75] Aromatic nitro- and azo-compounds are readily reduced by $SmI_2$ in THF at room temperature.[76]

$$PhNO_2 \xrightarrow[20\ ^\circ C,\ 5\ min]{8\,SmI_2} PhNH_2 \quad 85\%$$

$$NO_2C_6H_4NH_2 \xrightarrow[20\ ^\circ C,\ 5\ min]{8\,SmI_2} NH_2C_6H_4NH_2 \quad 89\%$$

$$Ph{-}N{=}N{-}Ph \xrightarrow[2\%\ MeOH,\ 20\ ^\circ C]{2\,SmI_2} PhNHNHPh \quad 95\%$$

Picoline and pyridine *N*-oxides are converted into the corresponding bases.[75]

$$MeC_5H_4NO \xrightarrow[20\ ^\circ C,\ 5\ min]{2\,SmI_2} MeC_5H_4N \quad 83\%$$

$$C_5H_5NO \xrightarrow[65\ ^\circ C,\ 10\ min]{2\,SmI_2} C_5H_5N \quad 80\%$$

Arsenic oxides are reduced similarly.[76]

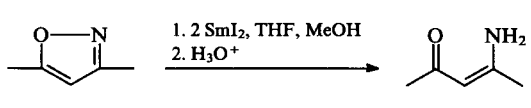
The rapid and selective reduction of *m*- and *p*-nitrobenzonitriles to the corresponding cyanoanilines is particularly remarkable.[75]

$$m\text{-}NCC_6H_4NO_2 + 8\,SmI_2 \xrightarrow[MeOH,\ 25\ ^\circ C]{THF} m\text{-}NCC_6H_4NH_2\,.$$

It may be that the reactivity of the nitro-group in these compounds is enhanced by the electron-accepting effect of the CN group.[75]

Schiff bases, for example benzylideneaniline, are reduced to the amines by samarium diiodide in the presence of methanol. Oximes form complex mixtures; isomeric amines have been isolated for benzaldehyde oxime.

It has been observed recently that the N–O bond in isoxazoles is cleaved selectively by $SmI_2$.[77]




96%

## 5. Reactions with epoxides and sulfoxides

On treatment with samarium diiodide, epoxides are converted into olefins even at room temperature.[5]

$$PhCH_2CH{-}CH_2 \xrightarrow[25\ ^\circ C,\ 24\ h]{2\,SmI_2} PhCH_2CH{=}CH_2\,.$$

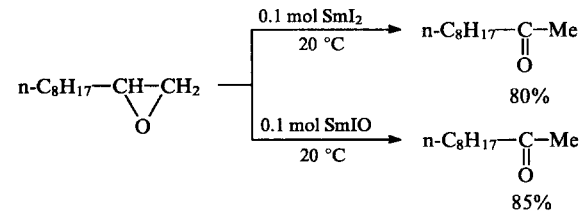
82%

Sulfoxides are similarly reduced to sulfides.

$$R{-}\overset{\overset{O}{\|}}{S}{-}R^1 \xrightarrow[65\ ^\circ C,\ 2\ h]{2\,SmI_2} R{-}S{-}R^1 \quad 90\%$$

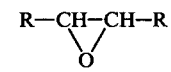
The deoxidation of organic heteroatomic oxides takes place almost instantaneously in the presence of HMPA in a quantitative yield; even triphenylphosphine oxide is reduced under these conditions.[23]

$RCOCH_3$ is obtained as a side product in the reactions of $SmI_2$ with terminal epoxides. Its formation is apparently associated with the effect of $Sm^{3+}$, which accumulates during the reduction process.[78] During the reaction, $SmI_2$ is converted into $I_2SmOSmI_2$, which decomposes slowly, affording a mixture of $SmI_3$ and SmIO. The authors suggest that it is in fact the latter compound which acts as the catalyst of the rearrangement of the terminal epoxide to the corresponding methyl ketone. The following reactions indicate this:

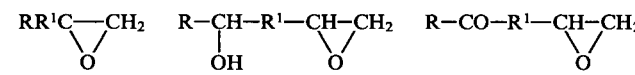



Consequently small amounts of samarium diiodide catalyse the isomerisation of terminal epoxides RCOMe, in contrast to other catalysts which lead to the exclusive formation of an aldehyde.[74]

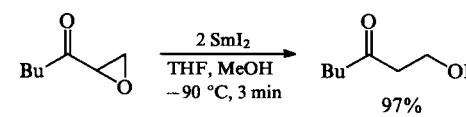
The rearrangement of 1,2-disubstituted epoxides to the corresponding methyl ketones proceeds with greater difficulty. Internal epoxides



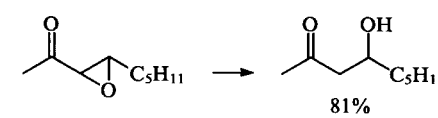

are also converted into ketones very slowly. The reaction is altogether uncharacteristic of epoxides of other types.




It has been shown recently that α,β-epoxyketones are converted into β-hydroxyketones (aldols) on treatment with $SmI_2$.[79]



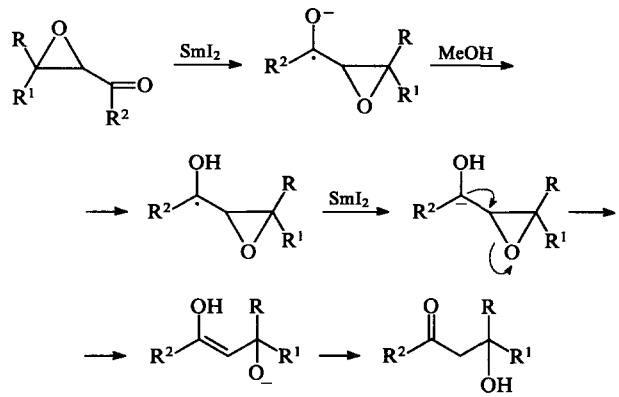

97%




81%

Primary, secondary, and tertiary cyclic and alicyclic aldols can be obtained in high yields by this procedure.

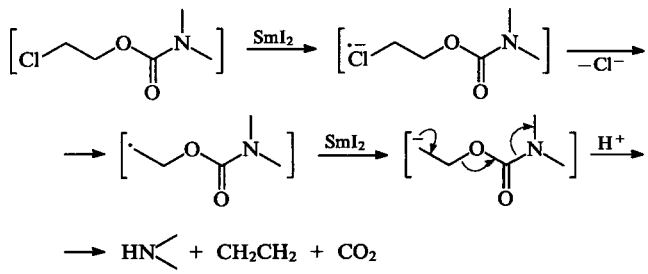
It has been suggested[79] that the reaction proceeds via the formation of a ketyl, which is rapidly protonated by methanol. On treatment with a second equivalent of samarium diiodide, a carbanion, which induces the opening of the epoxide ring, is obtained. Tautomerisation of the enol formed leads to the formation of a ketone.



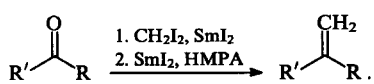
Thus a wide variety of aldols, including chiral aldols which are not obtainable by traditional methods, can be synthesised by treatment with samarium diiodide.[80–82]

### 6. Other reactions

The use of $SmI_2$ as a very powerful reducing agent frequently makes it possible to solve problems in organic chemistry of the kind which it has not so far been possible to solve using other reductants. Thus it has been impossible for a long time to obtain an amine from 2-chloroethyl carbamate; the use of all the reagents known for reactions of this kind led to the formation of hydroxyethyl carbamate as the main product.[83] On the other hand, samarium diiodide cleaves 2-chloroethyl carbamate effectively, forming an amine.[84] The rapid and selective course of the reaction can be accounted for by the ability of samarium diiodide to reduce rapidly the intermediate radical to the anion.



It has also been possible to achieve the monoiodomethylation of carbonyl groups at room temperature (with subsequent reductive elimination), i.e. to achieve a reaction which had been regarded hitherto as impossible.[27,85] The process is completed after 3 min and the product yield is extremely high (73%–80%).



Thus, by virtue of the very high reduction potential of divalent samarium, it has become possible to carry out various kinds of substitutions for functional groups which cannot be achieved by traditional methods.

* * *

The range of organic reactions with participation of $SmI_2$ has been expanding continuously. Thus it has been possible to achieve recently the reduction of triple bonds (in combination with a catalyst based on transition metals),[12] the cyclisation of aromatic radicals,[86] dimerisation reactions with reduction of derivatives of conjugated unsaturated carboxylic acids,[12] intramolecular cyclisation of nonactivated unsaturated ketones,[87] etc.

Samarium diiodide is used in the synthesis of new functional polymers and oligomers. It is of interest to employ the reactions with $SmI_2$ not only for the synthesis of new polymers but also for the modification of known polymers by incorporating reactive groups in their main chain. This leads to extensive prospects for subsequent chemical reactions of the polymers, including the formation of heat-resistant and thermostable linear, branched, and network heterochain high-molecular-mass compounds, including organometallic compounds.

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