Divalent Lanthanide Derivatives in Organic Synthesis. 1. Mild Preparation of SmI_2 and YbI_2 and Their Use as Reducing or Coupling Agents[1]

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Abstract: The facile synthesis of SmI_2 and YbI_2 from corresponding metals in THF is described. The reactivity of these potentially powerful reducing agents toward a variety of functional groups is tested. Epoxides and sulfoxides are deoxygenated. Aldehydes are selectively reduced in presence of a ketone. Alkyl halides or tosylates are converted into alkanes. Only coupling products are obtained from benzylic or allylic halides. In the presence of a SmI_2–THF solution, tertiary alcohols are easily obtained from reactions between ketones and alkyl halides. In a similar manner, SmI_2 promotes straightforward alkylation of ketones by alkyl sulfonates. Selective addition of polyfunctional halides or tosylates to ketones may be performed. In these reactions, catalytic amounts of $FeCl_3$ enhance the reactivity.

Introduction

All lanthanide elements and their major derivatives are now readily available in relatively pure form, and furthermore their prices are not prohibitive. They have received wide industrial application.[2] Nevertheless, with the exception of cerium 4+ oxidations[3] and use of europium derivatives as shift reagents in NMR spectroscopy,[4] few reports may be found concerning the use of lanthanide compounds in organic chemistry. In 1975, we described the use of ytterbium trinitrate for the catalytic oxidation of benzoins into benzils.[5] It has since been shown that trivalent lanthanide salts promote pyrimidine formation,[6] selective 1,2 reduction of conjugated ketones by sodium borohydride,[7] or ketalisation.[8] In addition, molecular rearrangements promoted by shift reagents have been described.[9]

Even less attention has been paid to the organic chemistry of divalent lanthanide compounds. Organometallic derivatives prepared from methyl or phenyl iodide and Eu, Sm, or Yb metals exhibit Grignard-type reactions.[10] It was claimed that aqueous solutions of Eu^{2+} salts are able to reduce pyridinecarboxylic acids.[11] Moreover *cis,cis*-1,5-cyclooctadiene was converted into cyclooctatetraenyl dianion by reduction with a mixture of praseodymium trichloride and potassium.[12] Solutions of ytterbium in liquid ammonia are effective in Birch-type reductions.[13] We described in 1977[14] our preliminary results concerning properties of some divalent salts in tetrahydrofuran (THF) solution. We report here a more systematic investigation of the reducing properties of these species.

The most stable oxidation state of the lanthanide elements is +3. Thus divalent lanthanide salts should behave as strong reducing agents. Divalent compounds have been isolated only for Eu, Yb, and Sm.[15] Normal redox potential values in water follow:[16] $Eu^{2+}/Eu^{3+} = -0.43$, $Yb^{2+}/Yb^{3+} = -1.15$, $Sm^{2+}/Sm^{3+} = -1.55$ V. Divalent europium salts are easily obtained by reduction of trivalent salts with amalgamated zinc.[17] Unfortunately these compounds were quite unreactive toward the various organic compounds that we tried to reduce. Known synthetic ways to other divalent lanthanide salts require drastic conditions and/or unusual techniques for organic chemists.[15] We found a very convenient preparation of samarium and ytterbium diiodides. These salts can be stored as THF solutions and are useful precursors to various divalents salts of these metals.[18] Reducing properties of these reagents will be considered.

Discussion

Preparation of SmI_2 and YbI_2. Samarium or ytterbium metal react smoothly with 1,2-diiodoethane in THF to give samarium or ytterbium diiodide according to eq 1.

$$\mathrm{Ln} + \mathrm{ICH_2CH_2I} \longrightarrow \mathrm{LnI_2} + \mathrm{CH_2{=}CH_2} \qquad (1)$$

$$(\mathrm{Ln} = \mathrm{Sm}, \mathrm{Yb})$$

These reactions are performed at room temperature, under inert atmosphere and anhydrous conditions, and yields are quantitative. Various titrations were performed and agreed with a LnI_2 formula. The resulting solutions are colored (blue-green for SmI_2 and yellow-green for YbI_2) and they are easily stored under nitrogen, especially in presence of a small amount of the metal. The solvent may be removed giving SmI_2-*n*THF or YbI_2-*n*THF as powders.

Absorption spectra of SmI_2 and YbI_2 solutions were recorded between 2500 and 300 nm. Broad absorptions were observed at 557 and 618 nm for the Sm^{2+} derivative, at 343 and 383 nm for the Yb^{2+} one. Similar results were obtained for the THF solutions of organometallic compounds of divalent samarium.[10]

Magnetic susceptibilities were measured by an NMR method.[19] Results agreed with quasi-exclusive presence of Sm^{2+} and Yb^{2+} ions: SmI_2–THF solution, $\mu = 3.52\ \mu_B$ at 35 °C (literature 3.64); YbI_2–THF solution, $\mu = 0.00\ \mu_B$ (literature 0.00).[20]

Detailed characterization of SmI_2, YbI_2, and other divalent lanthanide derivatives will be published elsewhere.[18]

From comparison of normal redox potential values of Sm^{2+} and Yb^{2+} derivatives and those of various soluble salts of transition metals, it appears that SmI_2 and YbI_2 are among the strongest reducing agents soluble in organic media.[21] Nevertheless these salts gave mild and selective reactions.

Deoxygenation Reactions Performed with SmI_2 and YbI_2 (Table I). At room temperature diphenyl sulfoxide is converted into diphenyl sulfide in good yield using a stoichiometric amount of SmI_2 (2 equiv). Deoxygenation reaction is faster in refluxing THF or in the presence of a small amount of an alcohol. Some other sulfoxides are reduced as well (Table I). Yields obtained with SmI_2 are similar to those in other published procedures.[22]

Epoxides are deoxygenated to olefins by SmI_2 and to a lesser extent by YbI_2. Use of an excess of SmI_2 in the presence of *tert*-butyl alcohol results in virtually quantitative conversion into olefin without byproducts resulting from epoxide rearrangement[23] or reduction into alcohol. Various examples are listed in Table I. Epoxide deoxygenation reaction performed with other reagents gives similar conversion into olefin.[24]

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Table I. Deoxygenation Reactions by SmI$_2$ in THF

compounds	reaction conditions:^{a} time, temp (°C)	products (% yield)^{b}
1-phenyl-2,3-epoxypropane	1 day, rt^{c}	3-phenylpropene (82), others (18)^{d}
cis-epoxycyclooctane	1 day, rt^{c}	*cis*-cyclooctene (65)
cis-epoxycyclooctane	2 h, 65^{c}	*cis*-cyclooctene (95)
cis-epoxycyclooctane	4 days, 65	*cis*-cyclooctene (92)
1,2-epoxydecane	2 days, rt^{e}	1-decene (92), others (6)^{f}
trans-5,6-epoxydecane	3 h, rt^{c}	*trans*-5-decene (76), others (17)^{g}
trans-5,6-epoxydecane	2 days, rt^{e}	*trans*-5-decene (96)
trans-diphenyl-1,2-epoxyethane	30 min, rt	stilbene (94), 2:1 trans:cis
trans-diphenyl-1,2-epoxyethane	5 min, 65	stilbene (98), 2:1 trans:cis
diphenyl sulfoxide	3 days, rt	diphenyl sulfide (88)
diphenyl sulfoxide	2 h, 65	diphenyl sulfide (90)
p-tolylethyl sulfoxide	4 h, 65	*p*-tolylethyl sulfide (77)
α-naphthylmethyl sulfoxide	1 h, 65	α-naphthylmethyl sulfide (90)

[a] 2 mmol of SmI$_2$, 1 mmol of substrate; rt = room temperature. [b] Determined by GLC analysis by comparison with an internal standard. [c] 2 mmol of *t*-BuOH is added. [d] 3-Phenyl-2-propanone and 3-phenyl-2-propanol. [e] 4 mmol of SmI$_2$, 4 mmol of *t*-BuOH; when only 2 mmol of SmI$_2$ is used, byproducts are obtained in higher yields (17–74%). [f] 2-Decanone and 2-decanol. [g] 5-Decanol.

Table II. Reduction of Conjugated Double Bonds by SmI$_2$ or YbI$_2$ in THF

compounds	reaction conditions,^{a} reducing agent	products (% yield)^{b}
cinnamic acid	SmI$_2$	3-phenylpropionic acid (98)
cinnamic acid	YbI$_2$	3-phenylpropionic acid (98)
ethyl cinnamate	SmI$_2$	ethyl 3-phenylpropionate (98)
ethyl cinnamate	YbI$_2$	ethyl 3-phenylpropionate (98)
trans-cinnamaldehyde	SmI$_2$ or YbI$_2$	polymers
trans-cinnamic alcohol	SmI$_2$ or YbI$_2$	no reaction
3-methylcyclohexenone	SmI$_2$	3-methylcyclohexen-1-ol (67) 3-methylcyclohexanone (28)
citral (*E,Z*)	SmI$_2$	geraniol + nerol (70) citronellal (8) citronellol (18)

[a] 2 mmol of LnI$_2$, 1 mmol of substrate, 2 mmol of MeOH; 1 day, room temperature. [b] Determined by GLC analysis by comparison with an internal standard.

Unfortunately, the phosphine oxides are not reduced by SmI$_2$ or YbI$_2$ under standard conditions.

Reductions of Double Bonds (Tables II and III). Isolated carbon–carbon double bonds remain unchanged on treatment with SmI$_2$ or YbI$_2$. On the contrary, a conjugated double bond can be reduced at room temperature by SmI$_2$ or YbI$_2$. The selectivity is excellent with cinnamic acid or ester. For α,β-conjugated ketones or aldehydes there is competition between C=O or C=C reduction and no attempt was made to improve selectivity (Table II).

Reduction of some carbonyl compounds was also studied in presence of a proton donor (Table III). Carboxylic acid and ester were not reduced by SmI$_2$ or YbI$_2$. Aldehydes were quantitatively transformed into primary alcohols by SmI$_2$ and methanol. Aliphatic ketones were converted into secondary alcohols in low yield using the same procedure. Under these conditions aromatic ketones were readily reduced. The nature of the proton donor is of importance. Replacing methanol by water allows 2-octanone reduction in good yield. In contrast a small amount of phenol prevents ketone transformation.

A competitive reduction was performed between equimolar amounts of 2-octanone and octanal. Reduction of an aldehyde in the presence of a keto group is a notable feature of SmI$_2$ reactivity, as exemplified by the above experiment. The selective reduction of aldehyde groups in the presence of a ketone has long been a difficult problem and it is only recently that practical selective reagents have been developed for this reaction.[25] In comparison with these reagents, SmI$_2$ seems to be one of the most selective, as demonstrated by the competitive reduction between octanal and 4-*tert*-butylcyclohexanone.[25d] Aldehyde reduction by SmI$_2$ was strongly favored.

Table III. Reduction of Carbonyl Derivatives by SmI$_2$ or YbI$_2$ in THF

compounds	reaction conditons^{a} reducing agents	products (% yield)^{b}
octanoic acid	SmI$_2$ or YbI$_2$	no reaction
methyl octanoate	SmI$_2$ or YbI$_2$	no reaction
octanal	SmI$_2$	1-octanol (99)
octanal	YbI$_2$	1-octanol (5)
2-octanone	SmI$_2$	2-octanol (12)
2-octanone	YbI$_2$	no reaction
acetophenone	SmI$_2$	1-phenylethanol (80)
2-octanone	SmI$_2$^{c}	2-octanol (64)
octanal + 2-octanone	SmI$_2$^{d}	1-octanol (96) 2-octanol (4)
octanal + 4-*tert*-butylcyclohexanone	SmI$_2$^{d}	1-octanol (90) 4-*tert*-butylcyclohexanol (10)

[a] 2 mmol of LnI$_2$, 1 mmol of substrate, 2 mmol of MeOH; room temperature, 1 day. [b] Determined by GLC analysis by comparison with an internal standard. [c] 2 mmol of H$_2$O instead of MeOH. [d] 1 mmol of aldehyde and 1 mmol of ketone; other conditions as in *a*.

Reduction of Halides and Tosylates (Table IV). In aprotic medium at THF reflux, primary bromides and iodides were converted into alkanes in high yields (80–90%). In a similar manner hydrocarbon was readily obtained from the corresponding tosylate. A small amount of alkyl iodide is also detected. This latter conversion of a tosylate into an alkyl iodide is known and was successfully performed with MgI$_2$.[26]

The absence of coupling products from alkyl halides or tosylates is remarkable. Careful examination of the reaction of 1-iodoheptane with SmI$_2$ demonstrated the total absence of tetradecane. Reductions of halides or tosylates to the corresponding alkanes by various reagents have recently been described.[27] In comparison with those reagents yields obtained in reductions by SmI$_2$ are similar.

In contrast to alkyl halides, reactions of benzylic or allylic halides with SmI$_2$ resulted in high yields of coupling products at room temperature. With cinnamyl bromide or chloride and isoprenyl bromide, a mixture of isomeric coupling products is

Table IV. Reaction of Organic Halides with SmI_2 in THF

compounds	reaction time	products (% yield)[a]
1-iodododecane	6 h[b]	dodecane (95)
1-bromododecane	2 days[b]	dodecane (82)
1-chlorododecane	2 days[b]	no reaction
dodecyl tosylate	10 h[b]	dodecane (88) 1-iodo-dodecane (7)
benzyl bromide	20 min[c]	1,2-diphenylethane (82)
benzyl chloride	1.5 h[c]	1,2-diphenylethane (67)
cinnamyl bromide	5 min[c]	(*E*,*E*)-1,6-diphenyl-1,5-hexadiene (55) (*E*)-1,4-diphenyl-1,5-hexadiene (21) 3,4-diphenyl-1,5-hexadiene (6)
cinnamyl chloride	30 min	(*E*,*E*)-1,6-diphenyl-1,5-hexadiene (51) (*E*)-1,4-diphenyl-1,5-hexadiene (23) 3,4-diphenyl-1,5-hexadiene (7)
isoprenyl bromide	1 day[c]	2,7-dimethyl-2,6-octadiene (42) 2,5,5-trimethyl-2,6-heptadiene (25) 3,3,4,4-tetramethyl-1,5-hexadiene (6)

[a] Determined by GLC analysis by comparison with an internal standard. [b] 2 mmol of SmI_2, 1 mmol of substrate; THF reflux. [c] 1 mmol of SmI_2, 1 mmol of halide; room temperature.

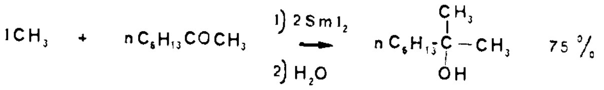
Table V. Alkylations of 2-Octanone by Butyl Halides Mediated by SmI_2

halide RX	reaction conditions,[a] time	5-methylundecan-5-ol, % yield;[b] % yield of others
n-butyl iodide	8 h	76; 9, 3, 1[g]
n-butyl iodide	3 h[c]	73
n-butyl iodide	12 h[d]	97
n-butyl bromide	1 day	67; 20, 4, 2[g]
n-butyl bromide	1.5 day[e]	96
n-butyl chloride	6 days	8
n-butyl tosylate	12 h	49
n-butyl tosylate	10 h[f]	95
n-butyl mesylate	1 day	30
sec-butyl bromide	1.5 day	27; 35, 5, 22[g]
isobutyl bromide	2 days	33; 40, 6, 4[g]
tert-butyl bromide	4 days	9; 39, 21, 24[g]

[a] 2 mmol of SmI_2, 1 mmol of halide, 1 mmol of 2-octanone; THF reflux. [b] Determined by GLC analysis by comparison with an internal standard. [c] In presence of 0.02 mmol of $FeCl_3$; this reaction was performed at room temperature. [d] 3 mmol of SmI_2, 3 mmol of iodide, 1 mmol of 2-octanone. [e] 4 mmol of SmI_2, 4 mmol of bromide, 1 mmol of 2-octanone. [f] 4 mmol of SmI_2, 4 mmol of tosylate, 1 mmol of 2-octanone, and 0.2 mmol of NaI. [g] Respectively unchanged 2-octanone, 2-octanol, 7,8-dimethyl-7,8-tetradecanediol.

obtained. Preferential coupling is head to head (~65%). Yields of coupling obtained using SmI_2 are at least as high as those recently reported using a variety of other reagents.[28] Unfortunately attempts to carry out cross-coupling between 1-iodoheptane and 3-bromo-1-propene or 3-chloro-1-propene failed.

Alkylations of Ketones by Organic Halides or Organic Sulfonates. At room temperature under inert atmosphere, treatment of an equimolar mixture of 2-octanone and methyl iodide with 2 equiv of SmI_2 in THF solution gives 2-methyl-2-octanol in 75% yield (eq 2). This reaction is formally analogous to reactions performed between ketones and Grignard reagents.



$$ICH_3 + nC_6H_{13}COCH_3 \xrightarrow[2)\ H_2O]{1)\ 2\,SmI_2} nC_6H_{13}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_3 \quad 75\,\% \qquad (2)$$

Under similar conditions, reaction between methyl octanoate and methyl iodide in the presence of SmI_2 gives 2-methyl-2-nonanol in low yield (10%). Unchanged ester is recovered. Competitive alkylation experiments performed with equimolar amounts of 2-octanone and methyl octanoate in the presence of SmI_2 and CH_3I show a products distribution of 97:3, establishing an almost exclusive transformation of 2-octanone as described in eq 2. Reaction involving aldehydes is more complex and under investigation.[14] When SmI_2 was replaced by YbI_2 in the previous experiments, no reactions were observed. A systematic study of ketone alkylation using SmI_2 as an electron-donor reagent was undertaken. Alkylations of 2-octanone by alkyl iodide or alkyl bromide are reported in Table V. The standard procedure is described in the Experimental Section. Usually these reactions are performed under nitrogen on a millimole scale with 4×10^{-2} M solutions of SmI_2 in THF. Using 1 equiv of organic halide RX and 2 equiv of SmI_2 per ketone, the reaction requires a few hours in refluxing THF or ~1 day at room temperature. Under these standard conditions, yields of tertiary alcohols are close to 75%. In these reactions, the major byproduct is the alkane arising from the alkyl halide. The order of reactivity is $RI > RBr \gg RCl$ (Table V). With *n*-butyl iodide or *n*-butyl bromide, in addition to the main product, some unchanged ketone and 2-octanol (3%) was recovered. For *n*-butyl chloride, 2-octanone, 2-octanol, and 7,8-dimethyl-7,8-tetradecanediol (12%) were observed as byproducts. Yields of tertiary alcohol can be improved by simultaneous increases of SmI_2 and RX amounts. Tertiary alcohol is then obtained quantitatively. Comparison between isomeric butyl bromides reveals a decrease in yield when replacing primary with secondary and then tertiary bromides. Tertiary alcohols are obtained in moderate yields from *sec*-BuBr and *i*-BuBr in this reaction, while Grignard reagents of these same bromides lead mainly to reduction products, i.e., 2-octanol in the above case.

A very promising feature of the SmI_2-promoted alkylation method is the ability to replace alkyl halides with alkyl sulfonates. Under standard conditions, yields of tertiary alcohols are moderate but can be increased considerably by addition of a catalytic amount of sodium iodide. The reaction then proceeds in fairly good yield and is very valuable as a synthetic tool. In contrast, Grignard reactions using alkyl sulfonates are quite impossible.

Allylic, benzylic, and propargylic halides easily react with ketones in presence of SmI_2 (Table VI). Yields are often appreciable (60–85%) under standard conditions at room temperature and can be rendered quantitative using an excess of SmI_2 and alkyl halide. Allylic or propargylic halides lead to mixtures of the two isomeric tertiary alcohols. The major product formally arises from reaction of unrearranged halide.

It is interesting to note that, in the absence of ketones, benzylic or allylic halides rapidly react with SmI_2 to yield coupling products exclusively (Table IV), while only tertiary alcohols are obtained when 2-octanone is present (Table VI). For example benzyl bromide leads to dibenzyl in 82% yield in 20 min. In the presence of 2-octanone, however, alkylation is slower and gives the tertiary alcohol in 69% yield in 30 min as the only product.

Vinylic or aromatic halides are unreactive in the presence of SmI_2 and a ketone. Pinacolization of ketones occurs in these cases in 10–20% yield. Various ketones may be allylated by the SmI_2–RX system, including cyclic and aromatic ketones (Table VII). There is no significant differences in reactivity between these and 2-octanone. Allylation of 4-*tert*-butylcyclohexanone was performed, and equatorial attack predominated (87:13). Almost the same results were obtained using $allyl_2Zn$ (85:15) or mixtures of $LiAlH_4$–$CrCl_3$ and allyl halide (81:19–88:12).[29]

Taking advantage of the inertness of some functional groups

Table VI. Alkylations of 2-Octanone by Unsaturated Halides

unsaturated halides	reaction conditions,[a] time	products (% yield)[b]
allyl iodide	15 min	4-methyl-1-decen-4-ol (71)
allyl bromide	25 min	4-methyl-1-decen-4-ol (66)
allyl chloride	1.5 day	4-methyl-1-decen-4-ol (60)
cinnamyl bromide	20 min	1-phenyl-4-methyl-1-decen-4-ol (52) 3-phenyl-4-methyl-1-decen-4-ol (31)
cinnamyl chloride	40 min	1-phenyl-4-methyl-1-decen-4-ol (50) 3-phenyl-4-methyl-1-decen-4-ol (35)
isoprenyl bromide	30 min	2,5-dimethyl-2-undecen-5-ol (37) 3,3,4-trimethyl-1-decen-4-ol (27)
propargyl bromide	20 min	4-methyl-1-decyn-4-ol (37) 4-methyl-1,2-decadien-4-ol (36)
benzyl bromide	30 min	1-phenyl-2-methyl-2-octanol (69)
benzyl chloride	3 h	1-phenyl-2-methyl-2-octanol (71)
β-bromostyrene	3 days[c]	no alkylation product
iodo- or bromobenzene	3 days[c]	no alkylation product

[a] 2 mmol of SmI_2, 1 mmol of ketone, 1 mmol of halide; room temperature. [b] Determined by GLC analysis by comparison with an internal standard. [c] Reaction performed in refluxing THF.

toward SmI_2, we investigated some alkylations using difunctional halides or tosylates in order to perform selective reactions (Table VIII).

Ethyl α-bromopropionate readily reacts with cyclohexanone in the presence of SmI_2 at room temperature to give the β-hydroxy ester. This smooth conversion is formally similar to the Reformatsky reaction. Ethyl β-bromopropionate or $TsO(CH_2)_9COOCH_3$ reacts with cyclohexanone or 2-octanone at THF reflux in the same way. With the tosylate ester, two byproducts were also detected in the reaction medium, methyl 1-iodo-decanoate and methyl decanoate.

As expected, selective alkylations of 2-octanone were observed with functionalized chlorides. Thus, use of $I(CH_2)_6Cl$ permits the addition of the $-(CH_2)_6Cl$ group to a ketone. $TsO(CH_2)_4Cl$ reacts with 2-octanone only at the sulfonate. In this experiment, 1-iodo-4-chlorobutane was also detected. In the same way, 1,3-dichloropropene reacts only through its allylic chloride.

These reactions of samarium diiodide in THF are easy to carry out, although often some hours are required for the reaction to go to completion. However addition of a catalytic amount of ferric chloride[30] (1% with respect to SmI_2) significantly decreases the reaction time (Table V).

Conclusion

The reactions described in this publication show that SmI_2 is a new versatile reagent of wide use in varied synthetic procedures. In the Table IX are reported isolated yields in some representative reactions selected from Tables I–VIII, experiments being performed on 10-mmol scale. Thus yields reported in Tables I–VIII and measured by GLC analysis are a good indication of the isolated yields.

SmI_2 and YbI_2 are easy to prepare and to handle. Generally reactions using these reagents are clean. In addition, the lanthanide metals and salts are not known to be toxic and are easily available materials. Some of the reactions mediated by SmI_2 resemble those carried out with mixtures of $LiAlH_4$ and various transition metal salts.[31] However, SmI_2 promotes the formation of carbon–carbon bonds in mild conditions and in cases when $LiAlH_4$-$CrCl_3$ reagent[29] works only with allylic halides. The mechanism of reactions induced by SmI_2 is related to electron transfers from samarous ion to organic substrates. Mechanism of alkylation of carbonyl compounds will be discussed in a forthcoming paper.[32] The scope of the reactivity of SmI_2 or YbI_2 is not yet fully established.[33] Nevertheless, results described in this publication lead us to hope that divalent lanthanide derivatives could form a novel class of useful reagents for organic synthesis.

Table VII. Alkylations of Various Ketones by Allyl Halides

compounds	reaction conditions,[a] time in min	products (% yield)[b]
2-octanone + allyl bromide	25	4-methyl-1-decen-4-ol (66)
cyclohexanone + allyl bromide	20	1-allylcyclohexanol (69)
acetophenone + allyl bromide	15	4-phenyl-1-penten-4-ol (71)
4-*tert*-butylcyclohexanone + allyl iodide	15	1-allyl-4-*tert*-butylcyclohexanol (72)[c]

[a] 2 mmol of SmI_2, 1 mmol of ketone, 1 mmol of halide; room temperature. [b] Determined by GLC analysis by comparison with an internal standard. [c] Mixture of epimers. Equatorial attack to axial attack: 87:13.

Experimental Section

Infrared and UV visible spectra were recorded on a Perkin-Elmer 237 and a Cary 17 spectrophotometer, respectively. Proton magnetic resonance spectra (^1H NMR) were recorded using a Perkin-Elmer Model R 32 at 90 MHz. Chemical shifts in $CDCl_3$ are reported in parts per million on the δ scale relative to tetramethylsilane as internal standard. Mass spectra were obtained on a GC–MS Hewlett-Packard Model 5992 A. Gas chromatographic analyses were carried out on a Carlo Erba Model FTV 2150. Peak area integration was performed by electronic integration. Yields measured by GLC were all calculated by comparison with an internal standard. Optical rotations were measured using a Perkin-Elmer Model 241 polarimeter.

Reagents. Samarium and ytterbium were 40 mesh powders from Research Chemicals (Phoenix, Ariz.). Their prices follow: Sm, \$0.90 per gram; Yb, \$2.50 per gram. (Distilled metals: Sm, \$230 per kilogram; Yb, \$500 per kilogram.) 1,2-Diiodoethane (Merck) in ether was washed with an aqueous sodium thiosulfate solution and then with water; after the solution was dried over $MgSO_4$, ether was removed and 1,2-diiodoethane was obtained as a white powder. Diiodomethane (Fluka) was distilled before use under reduced pressure. THF must be quite anhydrous and deoxygenated. It was carefully distilled under nitrogen from sodium benzophenone ketyl. Sodium iodide and ferric chloride were dehydrated before use by heating under diminished pressure.

Most organic compounds used were commercial samples purified by distillation or recrystallization. (+)-Ethyl α-bromopropionate,[34] 1-phenyl-2,3-epoxypropane,[35] *cis*-epoxycyclooctane, 1,2-epoxydecane, *trans*-5,6-epoxydecane,[36] *p*-tolylethyl sulfoxide, α-naphthylmethyl sulfoxide,[37] and sulfonates[38] were prepared according to literature procedures. Many spectra of reaction products can be compared with those of authentic samples prepared by Grignard reactions or Reformatsky reactions.

Preparation of SmI_2 and YbI_2. While all operations were performed in a dry glove filled with nitrogen, this precaution is not necessary for synthetic purposes; apparatus and procedures appropriate for Grignard reactions can be employed.

In a standard procedure, 3 g (0.02 mol) of samarium powder[39] was placed in a reaction flask fitted with a dropping funnel containing 2.82 g of 1,2-diiodoethane (0.01 mol) in 250 mL of THF. Metallic excess can be reused later on. THF solution was slowly added and the content of the flask was magnetically stirred. If solvent was very pure no induction period was observed. Finally a 4×10^{-2} M intense blue-green solution of SmI_2 in THF was obtained (10^{-1} M solutions of SmI_2 in

Table VIII. Alkylations of Ketones by Some Functionalized Halides

compounds	reaction conditions,[a] time	products (% yield)[b]
cyclohexanone + (+)-ethyl α-bromopropionate	10 min[c]	(±)-ethyl 2-(1′-hydroxycyclohexyl)propionate (51)
cyclohexanone + ethyl β-bromopropionate	1 day[d]	ethyl 3-(1′-hydroxycyclohexyl)propionate (28)
2-octanone + $TsO(CH_2)_9COOCH_3$	10 h[d,e]	methyl 11-hydroxy-11-methylheptadecanoate (63) methyl 10-iododecanoate (16) methyl decanoate (6)
2-octanone + 1-iodo-6-chlorohexane	12 h[d]	1-chloro-7-methyltridecan-7-ol (58)
2-octanone + $TsO(CH_2)_4Cl$	1 day[d,e]	1-chloro-5-methylundecan-5-ol (62) 1-iodo-4-chlorobutane (14)
2-octanone + 1,3-dichloropropene	2 days[c]	1-chloro-4-methyl-1-decen-4-ol (64)

[a] 2 mmol of SmI_2, 1 mmol of ketone, 1 mmol of halide. [b] Determined by GLC analysis by comparison with an internal standard [c] Room temperature. [d] THF reflux. [e] 0.1 mmol of NaI was added to reaction mixture.

Table IX. Reactions of SmI_2 on a Preparative Scale

compounds	reaction conditions,[a] time, temp *in* °C	products (% yield)[b]
trans-5,6-epoxydecane	2 days,[c] rt	*trans*-5-decene (73)
diphenyl sulfoxide	2 days,[d] rt	diphenyl sulfide (95)
ethyl cinnamate	1 day,[e] rt	ethyl 3-phenylpropionate (85)
octanal	1 day,[e] rt	1-octanol (85)
dodecyl tosylate	12 h,[d] 65	dodecane (76)
benzyl bromide	30 min,[f] rt	1,2-diphenylethane (83)
ethyl α-bromopropionate + cyclohexanone	20 min,[g] rt	ethyl 2-(1′-hydroxycyclohexyl)propionate (90)
1-iodo-6-chlorohexane + 2-octanone	1 day,[g] 65	1-chloro-7-methyltridecan-7-ol (74)
1,3-dichloropropene + 2-octanone	2 days,[g] rt	1-chloro-4-methyl-1-decen-4-ol (84)

[a] Reaction performed on 10-mmol scale with an excess of SmI_2. [b] Isolated yield after distillation or chromatography. [c] 30 mmol of SmI_2, 10 mmol of compound, 30 mmol of *t*-BuOH. [d] 25 mmol of SmI_2, 10 mmol of compound. [e] 25 mmol of SmI_2, 10 mmol of compound, 25 mmol of MeOH. [f] 12.5 mmol of SmI_2, 10 mmol of compound. [g] 25 mmol of SmI_2, 12 mmol of halide, 10 mmol of ketone.

THF could be readily prepared). These solutions could be stored for a long time, apparently without decrease in Sm^{2+} concentration if kept under inert atmosphere and in the presence of a small amount of metal. Nevertheless, to ensure reproducible results, these solutions should be used within a few days.

YbI_2 was prepared using exactly the same procedure: solutions of YbI_2 in THF were light yellow-green; 4×10^{-2} M solutions of YbI_2 in THF were the most concentrated that we could obtain.

Characterization. The species in THF solution are characterized as follows: the titrations used were acidometric titration, reaction with iodine in toluene, hydrolysis and iodimetric titration,[10] silver nitrate titration of halides, and EDTA titration;[40] absorption spectroscopy was employed; magnetic susceptibilities were measured using a NMR method.[19] Detailed characterization will be published later.[18]

Reductions Performed with SmI_2 and YbI_2. (Tables I–IV). In a typical experiment 2 mmol of SmI_2 in THF (50 mL) was placed in a 100-mL flask; 1 mmol of substrate in 5 mL of THF was added. If required, 2 mmol of methanol or *tert*-butyl alcohol was then introduced. Reactions were performed under nitrogen, either at room temperature or at THF reflux. With SmI_2 the initial blue-green solution turned yellow, indicating the end of the reaction. Sometimes a yellow precipitate appeared. With YbI_2 similar decoloration was observed. If required, an internal standard for GLC analysis was then added. The mixture was worked up with dilute HCl (0.1 N) in order to dissolve the Ln^{3+} species. Organic products were extracted twice with ether. The organic layer was washed with water, sodium thiosulfate, water, and brine. After the solution was dried over $MgSO_4$, ether and THF were removed. The remaining material was then analyzed. Precipitated materials were Ln^{3+} species; for instance, the mineral product obtained through reduction of 1-iodobutane by SmI_2 was identified as SmI_3.

Reactions between Ketones and Organic Halides (Tables V–VIII). In a typical experiment 2 mmol of SmI_2 in THF (50 mL) was placed in a 100-mL flask, 1 mmol of carbonyl compound in 5 mL of THF was added; then 1 mmol of halide or sulfonate in 5 mL of THF was introduced. If required, 0.1 mmol of NaI or 0.01 mmol of $FeCl_3$ were added. Reactions were performed under nitrogen, either at room temperature or in refluxing THF. The initial blue-green solution of SmI_2 turned yellow, indicating the end of the reaction. Sometimes a yellow precipitate appeared. An internal standard for GLC analysis was then added. The mixture was worked up with dilute HCl (0.1 N) in order to dissolve the Ln^{3+} species. Organic products were extracted twice with ether. The organic layer was washed with water, sodium thiosulfate, water, and brine. After the solution was dried over $MgSO_4$, ether and THF were removed. The remaining material was then analyzed.

Ethyl 3-(1′-hydroxycyclohexyl)propionate: ^1H NMR ($CDCl_3$) δ 1.15 (d, 3, *J* = 6.5 Hz), 1.22 (t, 3, *J* = 6.5 Hz), 1.35–1.75 (m, 10), 2.46 (q, 1, *J* = 6.5 Hz), 4.15 (q, 2, *J* = 6.5 Hz); MS *m/e* (rel intensity) 200 (12), 182 (4), 157 (58), 155 (13), 144 (64), 111 (42), 99 (54), 98 (47), 83 (31), 81 (65), 74 (56), 73 (17).

Methyl 11-hydroxy-11-methylheptadecanoate: ^1H NMR ($CDCl_3$) δ 0.85 (t, 3, *J* = 7.5 Hz), 1.09 (s, 3), 1.15–1.50 (m, 26), 2.1–2.4 (m, 2), 3.6 (s, 3); MS *m/e* (rel intensity) 229 (25), 197 (65), 129 (82), 128 (23), 111 (28), 95 (30), 87 (42), 83 (37), 69 (100).

Methyl 10-iododecanoate: ^1H NMR ($CDCl_3$) δ 1.05–1.47 (m, 14), 2.27 (t, 3, *J* = 7.5 Hz), 3.13 (t, 3, *J* = 7.5 Hz), 3.62 (s, 3); MS *m/e* (rel intensity) 185 (10), 153 (12), 149 (63), 87 (47), 74 (100), 55 (37), 41 (24).

1-Chloro-7-methyltridecan-7-ol: ^1H NMR ($CDCl_3$) δ 0.9 (t, 3), 1.12 (s, 3), 1.25–1.50 (m, 20), 3.52 (t, *J* = 6.5 Hz); MS *m/e* (rel intensity) 235 (4), 233 (15), 165 (32), 163 (87), 129 (100), 109 (24), 71 (26), 69 (54).

1-Chloro-5-methylundecan-5-ol: ^1H NMR ($CDCl_3$) δ 0.9 (t, 3), 1.10 (s, 3), 1.20–1.85 (m, 18), 3.45 (t, 2, *J* = 6.5 Hz); MS *m/e* (rel intensity) 207 (1), 205 (3), 137 (18), 135 (36), 129 (34), 99 (78), 71 (13), 69 (28), 43 (100).

1-Chloro-4-methyl-1-decen-4-ol: ^1H NMR ($CDCl_3$) δ 0.9 (t, 3), 1.18 (s, 3), 1.25–1.55 (m, 10), 2.42 (dd, 2, *J* = 7, *J′* = 1 Hz), 5.89 (dd, 1, *J* = 7 Hz), 6.16 (dd, 1, *J* = 7, *J′* = 1 Hz); MS *m/e* (rel intensity) 189 (2), 129 (100), 119 (24), 87 (8), 59 (77), 43 (74).

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Reactivity of Alkyne Tungsten and Molybdenum Complexes. Heterolytic C–H Bond Activation in Coordinated Alkynes

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Abstract: A general preparative method for [M(C$_5$H$_5$)(CO)(2-butyne)$_2$]PF$_6$ complexes (**6**, M = Mo, W) is described. The alkyne ligands were shown to be very labile at temperatures above 100 °C. The reactions of **6** with phosphine and methoxide were investigated. Using triethylamine as cocatalyst, **6** was shown to promote hydrogen exchange between 2-butyne and acetonitrile or acetone.

Introduction

Alkyne complexes of transition metals are intermediates in a number of catalytic and stoichiometric processes.[1] We have investigated the mechanisms of a number of these, e.g., oligomerization reactions,[2] insertion reactions yielding vinyl metal complexes and cyclic ketones,[3] and 1,2 addition of alkyl groups across alkynes.[4] Basic features of the metal–alkyne interaction (such as lability, metal–alkyne bond rotation, and propargyl hydrogen acidity) are therefore of interest. The potential for alkynes to act as four-electron rather than two-electron donors raises the possibility that the chemistry of their complexes may differ substantially from that of the corresponding alkenes due to stabilization of intermediates with unusually low formal valence electron counts.

Indeed, recent papers report[5,6] a number of formally 16-electron molybdenum complexes containing alkyne ligands (e.g., **1** and **2**) for which the closest alkene analogues are[5] 18-electron species (e.g., **3** and **4**). Similarly it might be ex-

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