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SOME ORGANIC REACTIONS PROMOTED BY SAMARIUM DIIODIDE

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Summary

Various homoallylic alcohols and homobenzylic alcohols were prepared by the reaction between aldehydes and allylic or benzylic halides in the presence of samarium diiodide. This iodide is also a very good reagent for formation of pinacols from aldehydes or ketones. The reactions are especially fast and selective in the case of substituted benzaldehydes. The reactivities of various nitrogen functional groups (imine, oxime, nitro, azo, cyano) towards SmI_2 were also examined.

Introduction

We recently established that samarium diiodide [5] can induce several types of reactions of organic molecules [1–4]. Mechanistic studies showed that the driving force for such transformations is the reducing ability of Sm^{2+} ($E°(Sm^{3+}/Sm^{2+}) = -1.55$ V), which behaves as a one-electron donor [6]. The main reactions we observed were the deoxygenation of sulfoxides or epoxides, the pseudo-Barbier reaction of an organic halide on a ketone, the reduction of alkyl halides, and the coupling of allylic or benzylic halides [1]. Coupling of acid chlorides to give α-diketones was also achieved [2]. More recently others showed SmI_2 to be useful in some fragmentation reactions [7] and in the cleavage of isoxazoles [8]. In this article we wish to describe our results on three topics: (i) reactions between an aldehyde and an organic halide in the presence of SmI_2; (ii) behaviour of aldehydes and ketones in aprotic medium towards SmI_2; and (iii) the action of SmI_2 on some nitrogen compounds. Preliminary reports on part of this work have appeared [3,4].

Reactions between an aldehyde and an organic halide

We previously studied the products from the reaction between octanal and methyl iodide in the presence of two equivalents of SmI_2 [1,9]. After hydrolysis a complex mixture of alcohols **1**, **2**, **4** and ketone **3** was obtained (Fig. 1). The formation of **3** and **4** was attributed to a Meerwein–Ponndorf reaction between octanal and the

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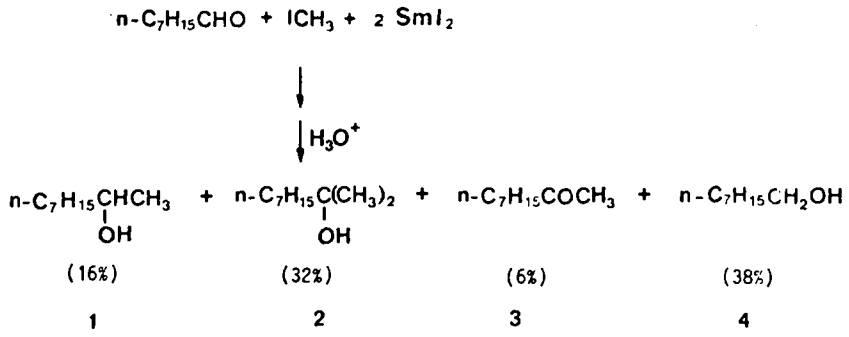


Fig. 1

samarium alcoholate of **1**. The formation of tertiary alcohol **2** was explained in terms of an attack on octanone **3** by methyl iodide, and this was confirmed by direct study of this reaction [1,9]. We tried without success to suppress the competitive Meerwein–Ponndorf reaction by using YbI_2, by changing the experimental conditions, or varying the nature of the aliphatic halide. It was expected that very fast reactions would mean a lower proportion of the unwanted side reaction. For this purpose some allylic and benzylic halides RX were used; it is known that these are prone to self-coupling and to condensation with ketones [1]. It has now been found that octanal and benzyl bromide react almost instantaneously in THF at room temperature in the presence of two equivalents of SmI_2, leading selectively to one product; the homobenzylic alcohol **5a** (Figure 2), which is obtained in 86% yield. This type of reaction is quite general for various aldehydes and allylic or benzylic halides. The main results are listed in Tables 1 and 2.

Yields are always very good, and the reaction is extremely rapid with iodides but very sluggish with tosylates or chlorides. The main limitation is the lack of selectivity in the case of dissymetric allylic halides (in contrast with the use of $CrCl_2$ [10] or $MnCl_2/LiAlH_4$ [11]). The reaction takes place with linear or branched aliphatic aldehydes but not with aromatic aldehydes (pinacol is the main product in these cases as noted later). Benzyl bromide and acetaldehyde give a carbinol which cannot easily be obtained by the classical Grignard reaction [12]. It is of interest that the coupling between two allylic or benzylic moieties is completely suppressed by the presence of an aldehyde. The mechanism that we propose is outlined in Fig. 3; it is based on our previous studies [6] and involves coupling between an allyl or benzyl radical and the radical anion derived from the aldehyde. It is similar to the mechanism recently established for the Barbier reaction with lithium [13]. The reactions of acetylenic halides except propargyl bromide were not investigated. Propargyl bromide, organometallic derivatives of which are not easily available, was coupled with octanal under the conditions shown in Table 2, to give $HC{\equiv}CCH_2CH(OH)C_7H_{15}$ (72%) and $CH_2{=}C{=}CH(CHOHC_7H_{15})$ (16%) after 12 h at room temperature.

The synthesis of homobenzylic or homoallylic alcohols mediated by SmI_2, in spite of the limitations noted, can be compared favourably with established processes [10,14–19] because of its rapidity in many cases and its selectivity towards various functional groups (cyano or ester groups for example).

TABLE 1

PREPARATION OF HOMOBENZYLIC ALCOHOLS **5** (Fig. 2) [a]

RCHO	$ArCH_2X$	Reaction time [b]	Product (yield, %) [c]
$n\text{-}C_7H_{15}CHO$	$C_6H_5CH_2Br$	2.5 min	**5a** (86)
$n\text{-}C_7H_{15}CHO$	$C_6H_5CH_2Cl$	1.1 h	**5a** (23)
$n\text{-}C_7H_{15}CHO$	$C_6H_5CH_2OTs$	–	(0) [h]
$n\text{-}C_7H_{15}CHO$	$p\text{-}(CO_2Ph)C_6H_4CH_2Br$	20 min	**5e** (75)
$n\text{-}C_7H_{15}CHO$	$p\text{-}(CO_2H)C_6H_4CH_2Br$	3 days	(0) [g]
$n\text{-}C_7H_{15}CHO$	$p\text{-}NCC_6H_4CH_2Br$	1 min	**5d** (41) [d,e]
i-PrCHO	$C_6H_5CH_2Br$	3 min	**5b** (87)
i-PrCHO	$C_6H_5CH_2Cl$	1.7 h	**5b** (25)
$c\text{-}C_6H_{11}CHO$	$C_6H_5CH_2Br$	3 min	**5c** (78) [d,f]
$c\text{-}C_6H_{11}CHO$	$C_6H_5CH_2Cl$	2.1 h	**5c** (21)
CH_3CHO	$C_6H_5CH_2Br$	1.5 min	**5f** (36) [d,i]

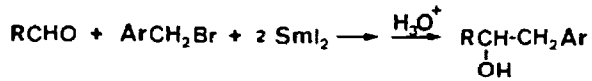
[a] 1 mmol of each reactant, 2 mmol of SmI_2 in 25 ml THF under nitrogen, at room temperature. [b] Measured by the change of colour from deep blue-green (Sm^{2+}) to yellow (Sm^{3+}). [c] Yields measured on the crude product by GLC using a suitable internal standard. [d] Isolated yield on a 5 mmol scale. [e] Purification of the product by recrystallisation in cyclohexane/ethyl acetate (4/1); m.p. 78°C. [f] Recrystallisation in ether; m.p. 39°C. [g] Pinacol and *p*-toluic acid are formed. [h] Reduction of octanal into 1-octanol occurs. [i] Purification of the product by preparative TLC with acetone/$CHCl_3$ (4/96) as eluent.

TABLE 2

PREPARATION OF HOMOALLYLIC ALCOHOLS **6** (Fig. 2) [a]

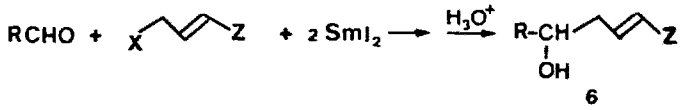
RCHO		Reaction time [b]	Product (yield, %) [c]
$n\text{-}C_7H_{15}CHO$	$CH_2{=}CHCH_2I$	3 min	**5a** (96)
$n\text{-}C_7H_{15}CHO$	$CH_2{=}CHCH_2Br$	10 min	**6a** (53)
$n\text{-}C_7H_{15}CHO$	$CH_2{=}CHCH_2OTs$	25 min	**6a** (17)
$n\text{-}C_7H_{15}CHO$	$CH_2{=}CHCH_2Cl$	6 h	**6a** (10)
$n\text{-}C_7H_{15}CHO$	$CH_3CH{=}CHCH_2Br$	10 min	$CH_3CH{=}CHCH_2CHOHC_7H_{15}$ (60) $CH_2{=}CHCH(CH_3)CHOHC_7H_{15}$ (27)
$n\text{-}C_7H_{15}CHO$	$PhCH{=}CHCH_2Br$	20 sec	$PhCH{=}CHCH_2CHOHC_7H_{15}$ (65) $CH_2{=}CHCHPhCHOHC_7H_{15}$ (35)
$n\text{-}C_7H_{15}CHO$	$ClCH{=}CHCH_2Cl$	40 min	**6e** (31)
i-PrCHO	$CH_2{=}CHCH_2I$	1 min	**6c** (71)
i-PrCHO	$CH_2{=}CHCH_2Br$	1 h	**6c** (28)
i-PrCHO	$CH_2{=}CHCH_2OTs$	1.5 h	**6c** (10)
i-PrCHO	$CH_2{=}CHCH_2Cl$	2 days	**6c** (4)
i-PrCHO	$ClCH{=}CHCH_2Cl$	1.5 h	**6f** (61)
$c\text{-}C_6H_{11}CHO$	$CH_2{=}CHCH_2I$	2 min	**6b** (85)
$c\text{-}C_6H_{11}CHO$	$CH_2{=}CHCH_2Br$	6 min	**6b** (54)
$c\text{-}C_6H_{11}CHO$	$CH_2{=}CHCH_2OTs$	50 min	**6b** (11)
$c\text{-}C_6H_{11}CHO$	$ClCH{=}CHCH_2Cl$	1 h	**6g** (39)
t-BuCHO	$CH_2{=}CHCH_2I$	5 min	**6d** (78) [d,e]

[a] 1 mmol of each reactant, 2 mmol of SmI_2 in 25 ml THF under nitrogen, at room temperature. [b] Measured by the change of colour from deep blue-green (Sm^{2+}) to yellow (Sm^{3+}). [c] Yields measured on the crude product by GLC using a suitable internal standard. [d] Isolated yield on a 5 mmol scale. [e] Purified by distillation of the liquid carbinol.



5

a : R = n-C_7H_{15} Ar = C_6H_5
b : R = i-Pr Ar = C_6H_5
c : R = Cyclohexyl Ar = C_6H_5
d : R = n-C_7H_{15} Ar = p-NCC_6H_4
e : R = n-C_7H_{15} Ar = p-$(CO_2Ph)C_6H_4$
f : R = CH_3 Ar = C_6H_5



6

a : R = n-C_7H_{15} X = Br Z = H
b : R = Cyclohexyl X = Br Z = H
c : R = i-Pr X = Br Z = H
d : R = t-Bu X = Br Z = H
e : R = n-C_7H_{15} X = Cl Z = Cl
f : R = i-Pr X = Cl Z = Cl
g : R = Cyclohexyl X = Cl Z = Cl

Fig. 2

Pinacol formation from aldehydes or ketones

Many aldehydes or ketones were reduced by samarium diiodide in THF solution containing a small amount of methanol acting as a proton source [1,9].

The reduction presumably involves an initial electron transfer from SmI_2 with formation of a ketyl radical [6]. Only minor amounts of pinacols could be detected in these experiments. In most of the condensations between ketones and organic

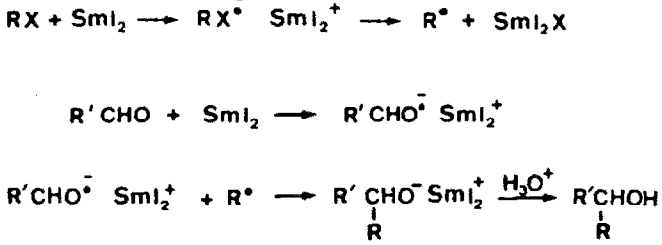
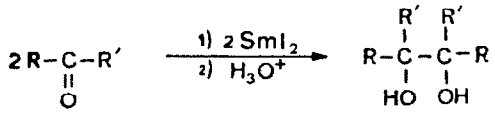


Fig. 3

halides mediated by SmI_2, pinacols were not formed although an electron transfer to the carbonyl group was postulated [6]. It was recently found that aldehydes react unexpectedly rapidly with SmI_2 in THF in the absence of electrophilic species (such as alcohol, carboxylic acids, or organic halides). The reaction usually takes place within a few minutes at room temperature for aromatic aldehydes or aromatic ketones, with almost quantitative formation of pinacol. A few hours are needed for aliphatic aldehydes and one day is needed for aliphatic ketones. The results are shown in Table 3. Yields are often high. The method is very competitive with various previous pinacol preparations [20–23]. It is especially useful for the coupling of aromatic aldehydes because of its rapidity and its selectivity with respect to many reducible functional groups. Thus substituents as CN, NO_2, CO_2R remain intact if the stoichiometric amount of SmI_2 (1 eq./aldehyde group) is used. It is known that ester carboxylic and nitrile functions are not easy to reduce with SmI_2. Since the nitro group is reduced by samarium diiodide (see later) it was surprising to find such a good selectivity in the pinacol formation starting from *p*-nitrobenzaldehyde **7**. Competitive experiments (Fig. 4) throw some light on the reactivity of **7**. Equimolar amounts of benzaldehyde and nitrobenzene were treated with one equivalent of SmI_2 under the experimental conditions of Table 3. A complex mixture of products

TABLE 3

FORMATION OF PINACOLS FROM ALDEHYDES OR KETONES UNDER THE INFLUENCE OF SAMARIUM DIIODIDE [a]



R	R′	Reaction time [b]	Yield (%) [c,d]
H	C_6H_5	0.5 min	95
H	*p*-NO_2-C_6H_4	0.5 min	95
H	*p*-CN-C_6H_4	0.5 min	95
H	*p*-COOH-C_6H_4	0.5 min	66
H	*p*-CH_3O-C_6H_4	1 min	90
H	*p*-$(CH_3)_2N$-C_6H_4	0.5 min	90 [e]
H	2,4,6-$(CH_3)_3$-C_6H_2	0.5 min	95
H	n-C_7H_{15}	3 h	85
H	Cyclohexyl	4 h	95
H	CH_3	1 min	0 [f]
CH_3	n-C_6H_{13}	24 h	80
CH_3	C_6H_5	0.5 min	95
C_6H_5	$(CH_2)_4COC_6H_5$	2 h [g]	32 [g]

[a] 2 mmol of substrate, 2 mmol of SmI_2 in 25 ml of THF at room temperature under nitrogen. For other details see the text. [b] Measured by the change of color from deep-blue green (Sm^{2+}) to yellow-orange (Sm^{3+}). [c] Isolated yields. [d] The pinacol was formed as a *dl-meso* mixture, which was analysed only in the case of benzaldehyde (*dl/meso* 56/44). [e] Hydrolysis under neutral conditions. Under acidic conditions the product remains in the aqueous phase as a soluble ammonium salt. [f] In this case, ethyl acetate is the major product. A reaction of the Tischchenko type is probably a competitive process. [g] A 2×10^{-2} *M* solution of the diketone in THF was added dropwise during 2 h to a 0.1 *M* SmI_2 solution. A brown color appeared at the end of the addition. The product is 1,2-diphenyl-1,2-cyclohexanediol.

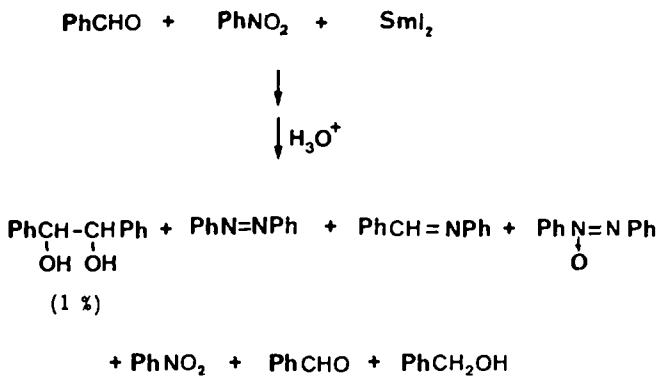
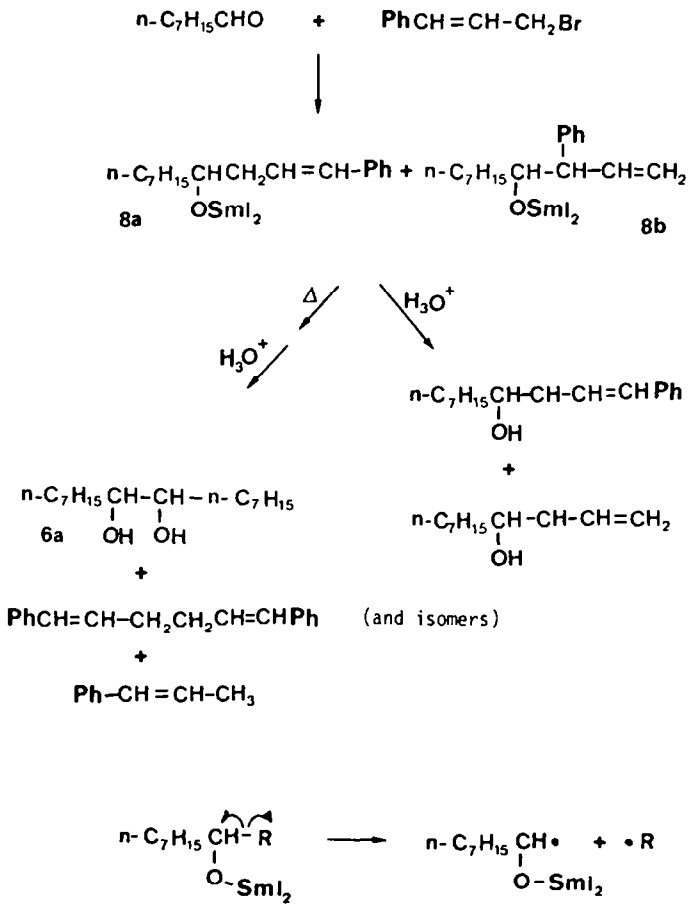

PhCHO + PhNO2 + SmI2
H3O+
PhCH-CHPh + PhN=NPh + PhCH=NPh + PhN=NPh
OH OH
O
(1 %)
+ PhNO2 + PhCHO + PhCH2OH

Fig. 4


n-C7H15CHO + PhCH=CH-CH2Br
n-C7H15CHCH2CH=CH-Ph + n-C7H15CH-CH-CH=CH2
OSmI2 OSmI2
Ph
8a 8b
Δ
H3O+
H3O+
n-C7H15CH-CH-CH=CHPh
OH
+
n-C7H15CH-CH-n-C7H15
OH OH
6a
n-C7H15CH-CH-CH=CH2
OH
+
PhCH=CH-CH2CH2CH=CHPh (and isomers)
+
Ph-CH=CH-CH3

n-C7H15CH-R
O-SmI2
n-C7H15CH• + •R
O-SmI2

9

Fig. 5

was obtained containing no more than 1% of benzaldehyde pinacol (Fig. 4). The products shown in Fig. 4 were identified but their distribution was not determined. It is clear that the electronic interaction between NO_2 and CHO groups in *p*-nitrobenzaldehyde plays a major part in the initial formation of the anion radical which is the intermediate in the pinacol formation. An unusual process giving rise to pinacol, depicted in Fig. 5, is noteworthy. As previously noted (Table 2) octanal and cinnamyl bromide in the presence of SmI_2 at room temperature rapidly produce a mixture of two homoallylic alcohols. If the samarium alcoholates are heated (THF refluxing for 12 h) prior to hydrolysis then homoallylic alcohols are no longer obtained. Instead pinacol **6a**, identified by NMR and GLC, is obtained (65% by respect to octanal). Isomeric diphenylhexadienes and β-methylstyrene were also produced. This unusual cleavage of the samarium alkoxides **8** could occur via the homolysis **9**, facilitated by the stabilisation of the cinnamyl radical R; followed by irreversible reactions such as R–R or R–H formation (the latter after H atom abstraction from THF). A similar cleavage was noted in the reaction between some conjugated anils and an allylmagnesium compound [24].

Nitrogen compounds (Table 4)

The behaviour of various nitrogen functional groups towards diiodosamarium was examined. It was found that aromatic or aliphatic nitriles are inert in the presence of SmI_2. A Schiff base such as benzalaniline is reduced to amine if methanol is present. Oximes give complex mixtures; in the case of benzaldehyde

TABLE 4

ACTION OF SAMARIUM DIIODIDE ON SOME NITROGEN FUNCTIONAL GROUPS

Compound	Reaction conditions [a]	Products and yields (%) [b]
PhCH=NPh	2 SmI_2, 2 MeOH 24 h	$PhCH_2NHPh$ (50), PhCH=NPh (50) [c]
PhCH=NOH	4 SmI_2, 4 MeOH 5 min	$PhCH(NH_2)CH_2Ph$ (75), $PhCH_2NHCH_2Ph$ (25)
PhN=NPh	8 SmI_2, 4 MeOH 24 h	$PhNH_2$ (50)
$PhNO_2$	8 SmI_2, 2 MeOH 5 min	$PhNH_2$ (25), PhN=NPh (25), $PhNO_2$ (50)
PhCN	4 SmI_2, 2 MeOH	No reaction
$n\text{-}C_{11}H_{23}CN$	4 SmI_2, 2 MeOH	No reaction
$m\text{-}NCC_6H_4NO_2$	6 SmI_2, 2 MeOH 5 min	$m\text{-}NCC_6H_4NH_2$ (95)
$p\text{-}NCC_6H_4NO_2$	6 SmI_2, MeOH 5 min	$p\text{-}NCC_6H_4NH_2$ (84)
PhNHNHPh	2 SmI_2, 4 days	$PhNH_2$ (55)
PhCH=NPh + n-BuI	2 SmI_2	PhCH(n-Bu)NHPh(20), PhCH(C(CH$_2$)$_3$O)NHPh (60)
	24 h	$PhCH_2NHPh$ (10)

[a] Reactions performed at room temperature with THF solutions 10^{-1} *M* in SmI_2. [b] Yields measured on the crude reaction mixture by GLC with a suitable internal standard. [c] With 2.5 SmI_2 the yield of $PhCH_2NHPh$ is 80%.

oxime the products were isolated and found to be isomeric amines. The reaction mechanism was not elucidated. Azobenzene and nitrobenzene are reduced by SmI_2 to give moderate yields of amines. The selective reduction of *meta*- or *para*-nitrobenzonitrile to the corresponding cyanoanilines is noteworthy; the reaction is fast (a few minutes at room temperature) and the yields are almost quantitative. Possibly the electron-withdrawing effect of the cyano group enhances the reactivity of the nitro group.

An attempt was made to couple an alkyl halide with a Schiff base, by analogy with the reaction between alkyl halides and ketones [1]. Benzalaniline and butyl iodide gave only minor amount of the expected PhCH(n-Bu)NHPh. The main product results from addition of THF to the double bond of the Schiff base. It was recently found that the N–O bond in isoxazoles can be selectively cleaved [8].

Conclusion

This study has given a better picture of the scope of the behaviour of SmI_2 towards organic compounds. It has been possible for the first time to use aldehydes in SmI_2 pseudo-Barbier reactions by using reactive organic halides whose reaction can compete efficiently with the subsequent Meerwein–Ponndorf reaction or with pinacol formation. The reductive coupling of aldehydes to produce pinacols is very easy in the absence of organic halides or protic compounds. Under the same conditions the pinacol formation from ketones is slow. Cyano groups are unreactive towards SmI_2 but nitro compounds, imines, and oximes are reduced to some extent in the presence of methanol. Many transformations of organic compounds are known to include some steps involving an electron transfer [25]. As we stated in an earlier paper [6], most of the reactions observed here can also be interpreted in terms of initiation by electron transfer from Sm^{2+} to an organic reactant.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 237 spectrophotometer. Proton magnetic resonance spectra (^1H NMR) were recorded using a Perkin–Elmer Model R32 spectrometer at 90 MHz. Chemical shifts are reported in parts per million on the δ scale relative to tetramethylsilane as internal standard. Mass spectra were obtained with a GC-MS Ribermag R 10-10 instrument. GLC analyses were carried out on a Carlo Erba Model FTV 2150 chromatograph.

Reagents

Samarium was 40 mesh powder from Labelcomat (Sterrebeck-Belgium). A solution of 1,2-diiodoethane (Merck) in ether was washed with an aqueous sodium thiosulfate and then with water. The solution was dried over $MgSO_4$, and the ether was removed to leave 1,2-diiodoethane as a white powder. The THF must be completely anhydrous and deoxygenated before use. The product was carefully distilled under nitrogen from sodium benzophenone ketyl.

Most organic compound used were commercial samples purified by distillation or recrystallisation. Allyl and benzyl tosylates [29], and *para*-substituted benzyl bromides [30] were prepared according to literature procedures.

Preparation of 0.1 M SmI_2 solution in THF

Samarium powder (3 g, 0.02 mol) was placed under nitrogen in a Schlenk tube: A solution of 2.82 g of 1,2-diiodoethane (0.01 mol) in 100 ml of anhydrous THF was prepared. A few drops of this THF solution were added to the metal and the typical blue color of SmI_2 appeared. The whole solution could subsequently be added within a few minutes. There was an exothermic effect without THF reflux, and sometimes formation of a yellow green precipitate. At the end of the preparation no precipitate remained. The SmI_2 preparation is quite fast (typically 15 min) if freshly distilled THF is used. Any excess of metal can be reused.

Reaction between aldehydes and organic halides

In a standard procedure, 2 mmol of SmI_2 in THF (20 ml) were placed under nitrogen. A solution of 1 mmol of aldehyde and 1 mmol of organic halide in 5 ml of THF; was then added at room temperature with magnetic stirring. The blue color (of Sm^{2+}) changed to yellow and a yellow precipitate appeared. Excess of 0.1 *N* HCl was then added, and, if necessary, an internal standard for GLC analysis was introduced. The organic products were extracted twice with water, and the organic layer was washed with saturated NaCl solution and then dried over $MgSO_4$. Ether and THF were removed and the remaining material was then analysed by NMR spectroscopy and GLC.

Pinacol formation from aldehydes or ketones

In a typical experiment 2 mmol of SmI_2 in THF (20 ml) were placed under nitrogen, and a solution of 2 mmol of carbonyl compound (aldehyde or ketone) in 5 ml of THF was added at room temperature with magnetic stirring. In the case of aromatic aldehydes or ketones the blue color (of Sm^{2+}) immediately changed to orange and a yellow precipitate appeared after a few minutes. In the case of aliphatic carbonyl compounds, the blue color disappeared slowly (several hours for aldehydes and one day for ketones), turning green, then yellow; a yellow precipitate appeared during these color change. The work-up was the same as described above.

Reduction of nitrogen functional groups with samarium diiodide

The procedure was the same as described in ref. 1. The work-up was carried out under neutral conditions.

1,2-Diphenyl-1,2-cyclohexanediol: ^{1}H NMR ($(CD_3)_2CO$) δ 8.05–6.95 (m,10), 5.1 (s, 2), 2.90–1.40 (m, 8); MS *m/e* (relative intensity) chemical ionisation NH_3 286 (100), 268 (37), 251 (79), 233 (4.6), 209 (2.1), 173 (5.1), 146 (11.1), 133 (14.7), 105 (29.6); IR (Nujol mull) 3120–3660 (OH).

p-$CNC_6H_4CH_2CH(OH)C_7H_{15}$: m.p. 78°C; ^{1}H NMR ($CDCl_3$) δ 7.70–7.25 (q, 4), 3.95–3.70 (m, 1), 2.90–2.70 (m, 2), 1.65 (s, 1), 1.55–1.10 (m, 12), 0.90 (t, 3) IR (Nujol mull) 3100–3400 (OH), 2220 (CN); Microanalysis: C, 78.2; H, 9.2; O, 6.9; N, 5.5. $C_{16}H_{23}NO$ calcd.: C, 78.4; H, 9.4; O, 6.5; N, 5.7%.

[p-$CH_3OC_6H_4CH(OH)]_2$: ^{1}H NMR (DMSO) δ 7.5–6.6 (m, 8), 5.3–4.8 (m, 2-OH), 4.8–4.5 (m, 2), 3.9–3.5 (m, 6).

[p-$CNC_6H_4CH(OH)]_2$: ^{1}H NMR (DMSO) δ 8–7.2 (m, 8), 5.9–5.1 (m, 2-OH), 4.9–4.5 (t, 2).

[p-$NO_2C_6H_4CH(OH)]_2$: ^{1}H NMR (DMSO) δ 8.5–7.5 (m, 8), 7.3–6.5 (m, 2-OH), 5.6–4.7 (m, 2).

[p-$CO_2HC_6H_4CH(OH)]_2$: ^{1}H NMR (DMSO) δ 8.2–7.2 (m, 8), 4.9–4.6 (t, 2), 1.4 (s, 2-OH).

[p-$(CH_3)_2NC_6H_4CH(OH)]_2$: ^{1}H NMR (DMSO) δ 7.4–6.4 (m, 8), 5.4–4.9 (m, 2-OH), 4.9–4.4 (m, 2), 3–2.8 (m, 12H).

[2,4,6-$(CH_3)_3C_6H_2CH(OH)]_2$: ^{1}H NMR (DMSO) δ 7.1–6.5 (m, 4), 5.8–5.3 (m, 2), 2.9–1.9 (m, 20).

p-$(CO_2Ph)C_6H_4CH_2CH(OH)C_7H_{15}$: ^{1}H NMR ($CDCl_3$) δ 8.24 (m, 2), 7.55–7.10 (m, 7), 3.90–3.70 (m, 1), 2.90–2.70 (m, 2) 2.45 (s, 1), 1.90 (m, 12), 0.90 (t, 3); IR (neat) 3150–3600 (OH), 1715 (C=O ester), 1595 and 1610 (C=C aromatic), 1275 (C–O benzoate).

[Cyclohexyl-$CH(OH)]_2$: ^{1}H NMR ($CDCl_3$) δ 3.95–3.80 (d, 1.1) *meso* compound, 3.50–3.30 (m, 0.9) *dl* compound, 2.45–0.90 (m, 24); IR (Nujol mull) 3040–3600 (OH).

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