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Lanthanoids in Organic Synthesis. I. The Novel Reduction of Carboxylic Acids with Samarium Diiodide-Base System

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Aromatic and aliphatic carboxylic acids were rapidly reduced with samarium diiodide by the addition of base in the presence of protic solvent at room temperature to the corresponding alcohols. Sodium benzoate was similarly reduced with samarium diiodide in the presence of H_2O in a good yield. In the similar reactions of benzoic acid derivatives bearing carboxyl, formyl, carbamoyl, methoxyl, and chloro groups, these functional groups were also reduced to the corresponding alcohol or amine derivatives. Interestingly, the carboxyl and formyl groups of benzoic acids were partly reduced into the methyl group.

Reduction of carboxylic acid is an important process for the synthetic chemistry. Although the various reduction conditions have been investigated, carboxylic acids are hardly reduced into alcohols with the usual reducing reagents except for diborane,[1)] lithium aluminum hydride,[2)] diisobutylaluminum hydride,[3)] and sodium bis(2-methoxyethoxy)aluminum hydride.[4)] These reducing agents, however, can not be used in the presence of water. Moreover, carboxylic acid is not also easily reduced even by vigorous catalytic hydrogenation.[5)] Taking into account of the utility of direct reduction of carboxylic acid into alcohol, the discovery of truly milder and convenient method has been desirable from a synthetic viewpoint.

Recently, samarium diiodide (SmI_2) has been paid much attention because of its versatile synthetic utility in organic synthesis[6)] since the first paper of Kagan et al.[7)] However, reduction of carboxylic acid using SmI_2 have apparently not been reported so far. We reported that carboxylic acids,[8)] ester, amide and carbonyl compounds[9)] were rapidly reduced with the SmI_2–base system in the presence of protic solvent to the corresponding alcohols in good yields in the proceeding short communications. As a continuation of these studies, the present paper deals with the reduction of carboxylic acids and their derivatives with SmI_2–base system as indicated in Scheme 1.

Results and Discussion

Kagan et al.[6a)] reported that carboxylic acid and ester could not be reduced by SmI_2. As shown in Table 1, irrespective of the addition of methanol, benzoic acid (**1**) could not be reduced into benzyl alcohol (**2**) with only SmI_2 (Entries 1 and 2). However, in this reaction, we expected an increase of one electron donor ability of Sm^{2+} by coexisting base in the present of protic solvent. Our first trial was conducted by the reaction of benzoic acid **1** in 10% aqueous NaOH/tetrahydrofuran (THF). Acid **1** was immediately reduced with SmI_2–NaOH system at room temperature to give the alcohol **2** in a good yield (Entry 6). Compared with the lower yield of the product in the similar reaction using NH_3 or $NaHCO_3$ (Entry 7 or 11), the results using $LiNH_2$ were almost similar to those of using NaOH to give alcohol **2** in good yields. Particularly, the reactions in the presence of H_2O resulted in the shorter reaction time and the good yields of the product **2** (Entries 6 and 10) in comparison with the results in the addition of methanol. On the other hand, in the absence of protic solvent, the reactions gave the lower yields of the alcohol **2** and required the longer reaction time. It is assumed that these reactions were carried out under a heterogeneous system and THF was acted as a hydrogen source in the absence of protic solvent (Entries 3 and 8).[6a)] The similar reaction of sodium benzoate (**3**) in the addition of H_2O afforded the alcohol **2** in excellent yields either with or without base (Entries 14 and 16). These results exhibit that the reduction of carboxylic acid with SmI_2–NaOH in the presence of protic solvent proceeds via carboxylate ion.

Furthermore, as shown in Table 2, mono- and dicarboxylic acids (**4**—**18**) were rapidly reduced with SmI_2–base systems into the corresponding alcohols (**19**—**31**) under similar conditions. Kagan et al. reported that

$$\text{R-COOY} \xrightarrow[\text{Ar, RT}]{\text{SmI}_2\text{, Base in THF/R'OH}} \text{R-CH}_2\text{OH}$$

R: aryl, alkyl Y: H, Na R': H, Me

Base: NaOH, KOH. $LiNH_2$, NH_3, $NaHCO_3$ or none

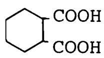
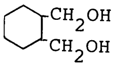
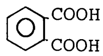
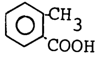
Scheme 1.

Table 1. Reduction of Benzoic Acid (**1**) and Sodium Benzoate (**3**) with SmI_2[a)]

Entry	PhCOOY		SmI_2[b)]	Base	Base	Protic solvent	Time	$PhCH_2OH$
No.	Y	mmol	mmol		mmol	ml		Yield/%[c)]
1	H	1	4	None		None	10 h[d)]	0
2	H	0.25	1	None		MeOH (10)	10 h	0.6
3	H	1	2	NaOH	2	None	4.3 h	42
4	H	1	4	NaOH	2	MeOH (10)	5 h	52
5	H	1	1	NaOH	1	H_2O (2)	30 s	48
6	H	1	4	NaOH	8	H_2O (2)	60 s	92
7	H	1	4	NH_3	10	H_2O (2)	3 s	41
8	H	0.5	2	$LiNH_2$	2	None	5 h	25
9	H	0.5	2	$LiNH_2$	2	MeOH (2)	5 h	30
10	H	0.5	2	$LiNH_2$	4	H_2O (1)	60 s	87
11	H	0.5	2	$NaHCO_3$	4	H_2O (2)	74 s	56
12	H	0.5	2	$NaHCO_3$	4	MeOH (10)	2 h	28
13	Na	1	2	None		H_2O (2)	60 s	26
14	Na	1	4	None		H_2O (2)	60 s	92
15	Na	1	2	NaOH	2	H_2O (2)	60 s	72
16	Na	1	4	NaOH	5	H_2O (2.5)	60 s	91

a) Reactions were carried out at room temperature under argon. b) SmI_2 in THF (0.1 M). c) Isolated yields. d) Interrupted reaction time.

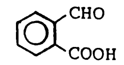
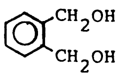
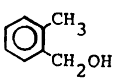
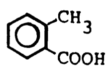
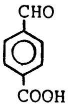
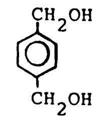
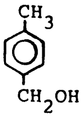
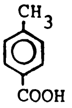
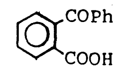
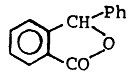
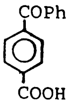
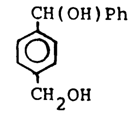
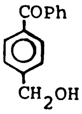
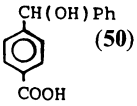
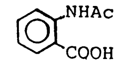
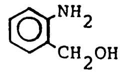
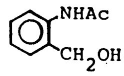
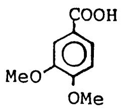
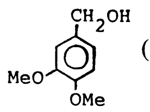
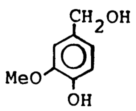
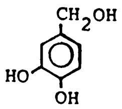
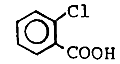
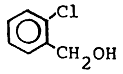
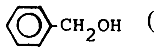
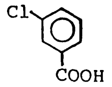
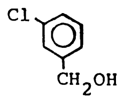
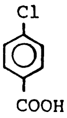
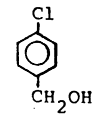
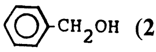
Table 2. Reduction of Carboxylic Acids with SmI_2–Base System[a)]

Substrate[b)] (No.)	SmI_2[c)]	Base	Time	Product (No.)	Yield[d)]
	mol	mmol	min		%
PhCOOH (**1**)	2	NaOH (4)	1	$PhCH_2OH$ (**2**)	92
$C_6H_{11}COOH$ (**4**)	2	NaOH (4)	1	$C_6H_{11}CH_2OH$ (**19**)	78
n-BuCH(Et)COOH (**5**)	2	NaOH (4)	0.2	*n*-BuCH(Et)CH_2OH (**20**)	94
$CH_3(CH_2)_4COOH$ (**6**)	2	NaOH (4)	4.5	$CH_3(CH_2)_4CH_2OH$ (**21**)	61
$CH_3(CH_2)_5COOH$ (**7**)	2	NaOH (4)	5	$CH_3(CH_2)_5CH_2OH$ (**22**)	57
$CH_3(CH_2)_6COOH$ (**8**)[e)]	4	NaOH (8)	18	$CH_3(CH_2)_6CH_2OH$ (**23**)	46
$CH_3(CH_2)_{16}COOH$ (**9**)[e)]	4	NaOH (8)	18	$CH_3(CH_2)_{16}CH_2OH$ (**24**)	13[f)]
$PhCH_2COOH$ (**10**)	2	NaOH (4)	1.2	$PhCH_2CH_2OH$ (**25**)	73
$PhCH_2CH_2COOH$ (**11**)[e)]	4	NaOH (8)	7	$PhCH_2CH_2CH_2OH$ (**26**)	51
PhCH=CHCOOH (**12**)[g)]	4	NaOH (8)	0.1	$PhCH_2CH_2CH_2OH$ (**26**)	39
				$PhCH_2CH_2COOH$ (**11**)	7
$HOOC(CH_2)_4COOH$ (**13**)	4	KOH (8)	1	$HOCH_2(CH_2)_4CH_2OH$ (**27**)	19
$HOOC(CH_2)_5COOH$ (**14**)	4	KOH (8)	0.6	$HOCH_2(CH_2)_5CH_2OH$ (**28**)	25
$HOOC(CH_2)_6COOH$ (**15**)	4	KOH (8)	0.6	$HOCH_2(CH_2)_6CH_2OH$ (**29**)	23
$HOOC(CH_2)_7COOH$ (**16**)	4	KOH (8)	0.7	$HOCH_2(CH_2)_7CH_2OH$ (**30**)	20
 (**17**)	4	KOH (8)	0.5	 (**31**)	18
 (**18**)	4	KOH (8)	1 (s)	 (**32**)	40[h)]

a) Reactions were carried out at room temperature under argon. b) Carboxylic acid (0.5 mmol) was dissolved in 10% NaOH or 10% KOH of 1 ml. c) 0.1 M solution in THF. d) Isolated yields. e) 1 mmol. f) Reaction was carried out in suspension. g) Kagan et al. reported that reduction of acid **12** with SmI_2 in THF/MeOH (24 h) gave only acid **11** in 98% yield (Ref. 9). h) A mixture (15.4 mg) of the following products was obtained except for acid **32**: 1,2-Benzenedimethanol (**42**), 2-methylbenzyl alcohol (**43**), methyldihydrobenzyl alcohol (from mass data, unidentified), tetrahydrobenzyl alcohol (from mass data, unidentified).

reduction of cinnamic acid (**12**) with SmI_2–MeOH (as hydrogen source) in THF (24 h) gave only 3-phenylpropionic acid (**11**).[9)] However, the acid **12** was reduced with SmI_2–base system to give 3-phenyl-1-propanol (**26**) as a major product (39%). Interestingly, the reduction of phthalic acid (**18**) proceeded smoothly to give *o*-toluic acid (**32**) as a major product in 40% yield accompanied with a mixture of trace amounts of 1,2-benzenedimethanol (**42**), 2-methylbenzyl alcohol (**43**), 2-methyldihydrobenzyl alcohol (from mass data, unidentified) and 2-methyl-3-cyclohexen-1-ol (from mass data, unidentified). It was the remarkable result that the carboxyl group of the acid **18** was partly reduced into the methyl group with this system. The reductions of aliphatic

Table 3. Reduction of Benzoic Acid Derivatives with SmI_2–KOH in THF/H_2O at Room Temperature$^{a)}$

Substrate (No.)		Time / s	Product (No.) Yield/%$^{b)}$					
	(33)	3		(42) 12		(43) 12		(32) 48
	(34)	29		(44) 6		(45) 13		(46) 41
	(35)	3		(47) 98				
	(36)	10		(48) 20		(49) 35		(50) 38
	(37)	164		951) 55		(52) 4		
	(38)	7		(53) 28		(54) 7		(55) 4
	(39)$^{d)}$	30 40$^{c)}$		(56) 35 8		(2) 27 72		
	(40)$^{d)}$	10 40$^{c)}$		(57) 80 84				
	(41)$^{d)}$	30 40$^{c)}$		(58) 52 63		(21) 9 15		

a) Reactions were carried out under argon and 4 mol equiv of SmI_2 (0.1 M solution in THF) and 8 mol equiv of base against substrate (0.5 mmol) were used unless otherwise stated. b) Isolated yields. c) Substrate (1 mmol) was dissolved in 1 cm^3 of 10% aqueous KOH. d) 6 mol equiv of SmI_2 (0.1 M solution in THF) was used.

carboxylic acids with this system exhibited the lower yields compared with the result of acid **1**.

With regard to the reduction of acids bearing the other functionalities (**33**—**41**), the corresponding products were immediately obtained under the similar conditions (Table 3). On these reductions, a few of the interesting results were recognized as follows:

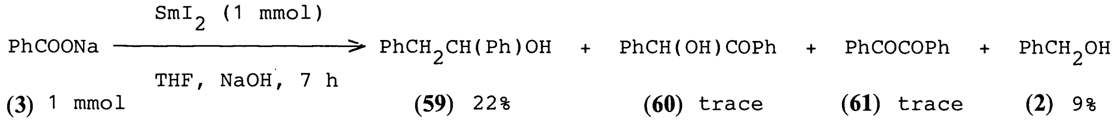
1) The aldehyde moiety of *o*- and *p*-formylbenzoic acids (**33** and **34**) was reduced into the methyl group to afford the corresponding products (**32**, **43**, **45**, and **46**) similarly to the reduction results of phthalic acid (**18**) in Table 2.

2) The amide moiety of 2-acetamidobenzoic acid (**37**) was reduced into the amino group along with the reduction of carboxyl group to give 2-aminobenzyl alcohol (**51**) as a major product.[10]

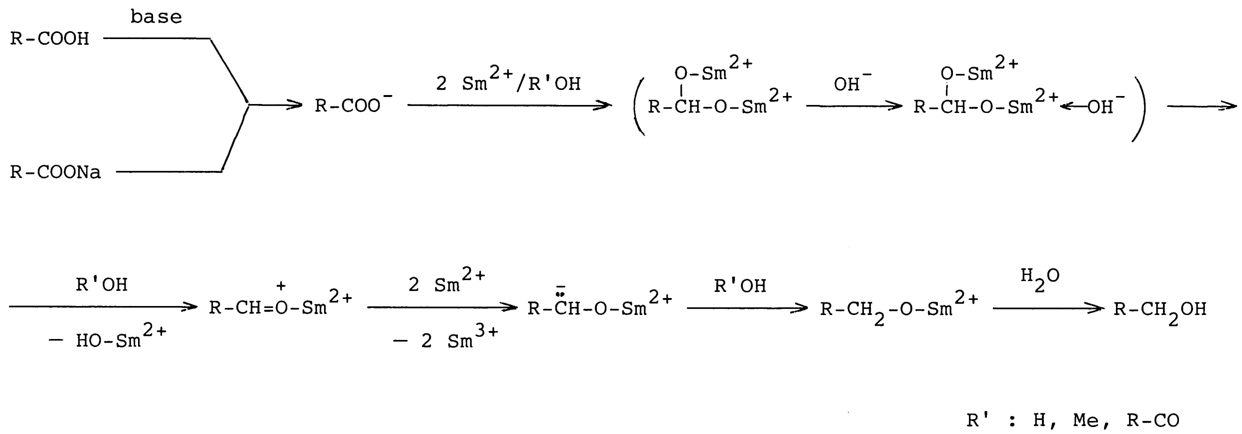
3) Reduction of the methoxyl moiety of veratric acid (**38**) proceeded partially to afford 4-hydroxy-3-methoxybenzyl alcohol (**54**) and 3,4-dihydroxybenzyl alcohol (**55**) as by-products.

4) Reactions of chlorobenzoic acids **39** and **41** using 6 mol equiv of SmI_2 afforded benzyl alcohol **2** in 72 and 15% yields accompanied with *o*- and *p*-chlorobenzyl alcohol (**56** and **58**), respectively. However, the similar reduction of the acid **40** afforded only *m*-chlorobenzyl alcohol (**57**) in 84% yield.

As described above, sodium benzoate **3** was reduced into the alcohol **2** with this system in the presence of H_2O (Table 1) in good yields. In contrast to these results, the reaction of benzoate **3** with SmI_2 in the absence of protic solvent (in THF) resulted in the reductive carbon–carbon coupling reaction to afford 1,2-diphenylethanol (**59**), benzoin (**60**) and benzil (**61**) accompanied with benzyl alcohol **2**. Accordingly, the formation of carbon–carbon coupling products is suggestive of acyl radical as an intermediate in the absence of hydrogen source.



Scheme 2.



Scheme 3.

In these reductions, it is presumed that the hydrogen source was in any event the hydrogen of H_2O, methanol or carboxylic acid since the similar reduction of sodium benzoate **3** using $LiNH_2$ in D_2O afforded $C_6H_5CD_2OH$ in 90% yields. Kagan et al. reported that the mechanism of the reduction of carbonyl group with aprotic THF solution of SmI_2 involves an electron transfer from Sm to the substrate and hydrogen abstraction from THF.[6a,7] Taking into account of these reports, it is presumed that the hydrogen of THF was also used as the hydrogen source in the reductions of benzoic acid **1** in the absence of protic solvent (Entries 3 and 8 in Table 1).

As mentioned above, the striking characteristic of these reductions is the extremely short reaction time at room temperature and is based on the highly promoted electron transfer from SmI_2 by coexisting sodium hydroxide or the other bases in the presence of protic solvent. SmI_2 presents a high coordination number, a great affinity for oxygen atom and the highest reduction potential among species soluble in organic medium. The single electron donor ability of Sm^{2+} is strongly affected by the nature of ligands around Sm^{2+}. Generally, it would be expected to facilitate relatively the release of electron from metal ion when a sufficient electron is supplied from ligands around metal ion. Accordingly, it has been surmised that the reducing ability can greatly be enhanced by the addition of base to SmI_2. Therefore, it is assumed that the reductant for these reductions may also be $R_1{-}Sm{-}R_2$ (R_1, R_2: I, OH or OCH_3) or the coordinated Sm^{2+} with base in addition to SmI_2. Thus, the coordinated Sm^{2+} with base in addition to SmI_2. Thus, the coordination of base to SmI_2 highly accelerates the electron transfer process from Sm^{2+} by the addition of base to SmI_2. In contrast to the results of the benzoate **3** in the absence of protic solvent, which is suggestive of acyl radical, carboxylic acids were directly reduced to alcohols without the carbon–carbon coupling product with SmI_2–base system in the presence of hydrogen source. Therefore, as shown in Scheme 3, it is assumed that $\mathrm{R{-}\overset{-}{C}{=}\overset{+}{O}{-}Sm^{2+}}$ forms by the elimination of $HO{-}Sm^{2+}$ from $R{-}CH(OSm^{2+})_2$ allowing the action of OH^- after carboxylate ion is reduced with 2 equivalents of Sm^{2+} or the coordinated Sm^{2+} with base in the presence of hydrogen source. Compared with the result of the acid **1** with this system, yields of alcohols from the similar reactions of aliphatic carboxylic acids were unsatisfactory. The cause could be the difference of resonance stability of intermediates (such as $\mathrm{R{-}\overset{-}{C}(O{-}Sm^{2+})_2}$ or $\mathrm{R{-}\overset{-}{C}{=}\overset{+}{O}{-}Sm^{2+}}$) between the acid **1** and aliphatic carboxylic acids. Though the actual reductant and the detailed mechanism of these reductions have remained obscure at the present stage, a possible mechanism for the present reduction is proposed in Scheme 3, which may explain the experimental results.

Little work has been reported on the direct reduction of carboxyl and formyl group into methyl group with SmI_2. As described above (Tables 2 and 3), the carboxyl and formyl moieties of benzoic acid derivatives were unexpectedly reduced into methyl group. Though detailed mechanism of these reduction has also remained obscure, these results can be presumed that the intermediate bearing *o*- or *p*-$CH_2{-}O{-}Sm^{2+}$ moiety in a molecule tends to eliminate $(Sm^{2+})_2O$ with SmI_2 and protic solvent to form methyl group. In the reduction of veratric acid **38**, its *o*- and *p*-methoxyl groups were reduced with SmI_2–base system to give phenol derivatives (**54** and **55**). Taking into account the conditions of this reaction and the reducing ability of this system, it is suitable to consider that the cleavage of methoxyl moiety is due to the reduction by this system rather than hydrolysis by Sm^{3+} as Lewis acid. Considering the reduction result of *o*-chlorobenzoic acid **39** in Table 3, it can be also presumed that an electron pair of Cl atom forms chelation with Sm atom in which is the intermediate bearing $-CH_2-O-Sm^{2+}$ moiety in the ortho position and the chelate is easily reduced with this system. As described in Table 3, the *p*-methoxyl and *o*- or *p*-chloro groups of benzoic acid were easily reduced with this system more than those of the meta position. The reactivity of ortho and para positions of carboxyl group seems to be the reason for the higher resonance stability of ketyl anion compared with that of meta position.[11)]

As mentioned above, comparing the reduction of carboxylic acid by SmI_2 alone[7)] with the present results, it seems reasonable to assume that the reducing ability of SmI_2–base system is greater than that of only SmI_2. Remarkably, the present method can be used for the direct conversion of carboxylic acids to alcohols by the mild and facile reduction, so the new SmI_2–base system provides a promising method for synthetic chemistry.

Further studies on the application toward other functionalities and the reaction mechanisms are in progress.

Experimental

Commercially available SmI_2 (0.1 M in THF, Aldrich and Strem) was used throughout this work. Melting points were determined on a Yanagimoto micro-melting point apparatus, model MP-S3, and were uncorrected. Infrared (IR) spectra were measured in Nujol mulls or as liquid films with a JASCO A-100 (Nihon Bunko) infrared spectrometer, and nuclear magnetic resonance (NMR) spectra were recorded on the JEOL JSX 500, JEOL FX 90-Q and JEOL JNM-PMX 60 spectrometers (Nihon Denshi). Gas chromatography (GC) was done on a GC-8A (Shimadzu) gas chromatography, yields of isolated products were calculated by GC on a capillary column, packed with CBP1-S50-050 (50 m, 0.33 mm, Shimadzu), at 150 and 220 °C and 0.5 kg cm^{-2} nitrogen pressure, by comparison with standard amounts of authentic samples. Chromatography columns of alumina were prepared with aluminum oxide 90 (70—230 mesh ASTM, Merck). Mass spectra (MS) and GC-MS were recorded on a JMS-D100 and JMS AX505W mass spectrometers, respectively.

General Procedure for the Reduction of Carboxylic Acids with the SmI_2-Base System. The procedure for the reduction of benzoic acid (**1**) with SmI_2–NaOH is described in detail as a typical example. A 10% sodium hydroxide (1 ml) solution of the acid **1** (0.5 mmol) was added to a THF solution of SmI_2 (20 ml, 0.1 M (1 M=1 mol dm^{-3}), 2 mmol (4 mol equiv)) and sodium hydroxide (4 mmol (8 mol equiv)) with stirring at room temperature under an atmosphere of argon. After the typical deep blue color of SmI_2 was disappeared, an aqueous sodium hydroxide (50%, 5 ml) was added to the reduction mixture and the mixture was stirred at room temperature for 10 min. The THF layer was separated and the aqueous layer was extracted with ether. The combined extract was dried over magnesium sulfate, concentrated, and the residue was purified by column chromatography (alumina) to give benzyl alcohol (**2**) in 92% yield. In the reduction of acids (**12**, **18**, **33**, **34**, **36**, and **38**), the aforesaid basic aqueous layer was acidified with concd hydrochloric acid and extracted with ether. The extract was treated by the usual method to give the corresponding products (**11**, **32**, **46**, **50**, **54**, and **55**), respectively.

The other products were obtained under the similar conditions and these products were identified by comparison of their IR, GC-MS, NMR spectra, and gas chromatographic behavior with those of the corresponding authentic samples, and the yields are listed in Tables 2 and 3.

Reduction of Sodium Benzoate (3) with SmI_2–NaOH System in the Presence of H_2O. A solution of compound **3** (1 mmol) and sodium hydroxide (5 mmol) in H_2O (2.5 ml) was added to a THF solution of SmI_2 (40 ml, 0.1 M, 4 mmol) with stirring at room temperature under an atmosphere of argon. After the typical color of SmI_2 was disappeared (1 min), an aqueous sodium hydroxide solution (50%, 10 ml) was added to the reaction mixture and the mixture was stirred at room temperature for 10 min. The THF layer was separated and the aqueous layer was extracted with ether. The combined extract was dried over magnesium sulfate, concentrated, and the residue was purified by column chromatography (alumina) to give benzyl alcohol **2** in 91% yield.

Reduction of Sodium Benzoate (3) with SmI_2–NaOH System in THF. To a mixture of compound **3** (1 mmol) and sodium hydroxide (1 mmol) was added a THF solution of SmI_2 (10 ml, 0.1 M, 1 mmol) with stirring at room temperature under argon. After the typical color of SmI_2 was disappeared (7 h), an aqueous sodium hydroxide solution (50%, 5 ml) was added and the mixture was stirred at room temperature for 10 min. The THF layer was separated and the aqueous layer was extracted with ether. The combined extract was dried ($MgSO_4$), concentrated, and followed by column chromatographic purification (alumina). The following products were obtained: 1,2-diphenylethanol (**59**) (22%), benzoin (**60**) (trace), benzil (**61**) (trace), and benzyl alcohol (**2**) (9%).

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