Reactions of Carbonyl Compounds with Benzyl Chloromethyl Ether of Diiodomethane in the Presence of Samarium(II) Iodide or Metallic Samarium. New Routes to 1,2-Diols, Iodohydrins and Cyclopropanols
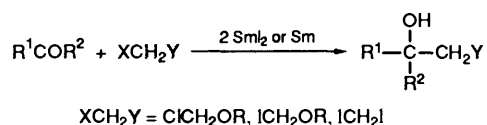
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Carbonyl compounds react with benzyl chloromethyl ether in the presence of samarium(II) iodide to afford the corresponding addition products which, when subsequently hydrogenolysed, yield 1,2-diols. Simple aldehydes and ketones react with diiodomethane in the presence of samarium metal to give iodohydrins in good yields. Under similar reaction conditions, α-halogeno substituted ketones and aromatic 1,4-diketones are converted into cyclopropanols. These cyclopropanations have been shown to proceed through the initial generation of samarium enolates, followed by the Simmons–Smith type reaction. A novel transformation of esters to cyclopropanols *via* tandem one-carbon homologation is also described.

Subsequent to the pioneering work of Kagan and co-workers,[1,2] samarium(II) iodide-mediated organic reactions have been extensively investigated.[3] A number of efficient reductions of organic functional groups have been accomplished by the use of samarium(II) iodide.[4] This reagent has also been employed for the highly stereoselective construction of organic molecules. These results clearly demonstrate that samarium(II) iodide has versatile utility as a one-electron reducing agent in synthetic organic chemistry.

In our continuing study on organic reactions with lanthanides,[5] we have been interested in the use of samarium(II) iodide or metallic samarium as a reagent for carbon–carbon bond forming reactions. Our attention has been focused on the nucleophilic introduction of an alkoxymethyl or iodomethyl group into carbonyl components, since these reactions are quite useful for the preparation of 1,2-diols, iodohydrins, and related compounds. The previously existing methods for these transformations are in general, conducted at very low temperature, because the intermediate α-alkoxymethyl- and iodomethyl-organometallic compounds are unstable at ordinary temperature and readily decompose *via* α-elimination.[6,7] We envisaged that this class of reactions might be produced under ordinary conditions by the use of samarium(II) iodide or metallic samarium (Scheme 1).
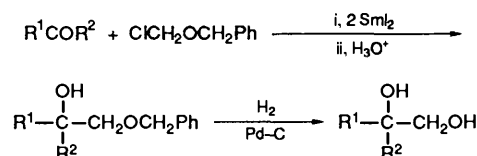
$$R^1COR^2 + XCH_2Y \xrightarrow{\text{2 SmI}_2 \text{ or Sm}} R^1-\underset{\underset{R^2}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2Y$$

$$XCH_2Y = ClCH_2OR, ICH_2OR, ICH_2I$$

Scheme 1

After screening a variety of reaction conditions, we found that nucleophilic alkoxymethylation of carbonyl compounds proceeded smoothly in tetrahydrofuran (THF) at room temperature in the presence of samarium(II) iodide. The introduction of an iodomethyl group and carbonyl components was also achieved by the use of a diiodomethane–samarium reagent system. On the other hand, α-halogeno substituted ketones or some aromatic 1,4-diketones reacted with diiodomethane in the presence of samarium to provide cyclopropanols instead of iodohydrins. Furthermore, it was also found that esters were converted into cyclopropanols on treatment with CH_2I_2/Sm under similar conditions. Here we describe the scope and limitations of these reactions together with the mechanistic aspects.[8]

Results and Discussion

Samarium(II) Iodide-promoted Benzyloxymethylation of Carbonyl Compounds.—Nucleophilic hydroxymethylation of carbonyl compounds provides a useful method for the synthesis of 1,2-diols, and several methods have been described in the literature.[6] However, since the methods reported so far frequently employ toxic organotin compounds or involve multi-step synthetic procedures, there still appears to be a need for new methodology. We sought to exploit a new Barbier-type benzyloxymethylation of carbonyl compounds by the use of divalent samarium. This reaction allows a new method for hydroxymethylation of carbonyl compounds, since the adducts are expected to undergo palladium-catalysed hydrogenolysis to give 1,2-diols (Scheme 2).

$$R^1COR^2 + ClCH_2OCH_2Ph \xrightarrow[\text{ii, H}_3O^+]{\text{i, 2 SmI}_2}$$

$$R^1-\underset{\underset{R^2}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2OCH_2Ph \xrightarrow[\text{Pd–C}]{H_2} R^1-\underset{\underset{R^2}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2OH$$

Scheme 2

Initially we studied the reaction of simple aliphatic ketones with benzyl chloromethyl ether in the presence of SmI_2. The reaction proceeded smoothly in THF at room temperature to give the corresponding addition products in good yields (Table 1).*[9] It is noted that readily enolizable ketones were subjected to benzyloxymethylation in good to high yields. However, the reactions of aldehydes and aromatic ketones resulted in very poor yields of the desired addition products, and instead pinacol coupling products were formed as the major products (80–90%).[10] In order to facilitate the desired Barbier-type reaction with retardation of the pinacol coupling reaction, we used a polyether as an additive. The idea behind these experiments is based on the fact that lanthanide ions possess strong oxophilicity and readily form complexes with polyethers or crown ethers.[11] Thus, we expected that a SmI_2–polyether complex would display strong one-electron transfer ability but, with a reduced ability to coordinate with carbonyl oxygen, pinacol coupling would be retarded. In fact, when a polyether (tetraethylene glycol dimethyl ether or tetraethylene glycol

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* Chloromethyl methyl ether and chloromethyl methoxyethyl ether also reacted with simple ketones in the presence of SmI_2 to give the corresponding adducts in good yields.

Table 1 Reactions of carbonyl compounds with benzyl chloromethyl ether in the presence of SmI_2 [a]

Entry	Carbonyl compound	Product	Yield (%) [b]
1	$(PhCH_2)_2CO$	$(PhCH_2)_2C(OH)CH_2OCH_2Ph$	87
2	$C_6H_{13}COCH_3$	$C_6H_{13}C(OH)(Me)CH_2OCH_2Ph$	84
3	Cyclopentanone	$PhCH_2OCH_2\overline{C(OH)CH_2CH_2CH_2}CH_2$	57
4	Cyclohexanone	$PhCH_2OCH_2\overline{C(OH)CH_2(CH_2)_3}CH_2$	75
5	$Cl(CH_2)_3COCH_3$	$Cl(CH_2)_3C(OH)(Me)CH_2OCH_2Ph$	82
6	$CH_3CO(CH_2)_2CO_2CH_3$	$PhCH_2OCH_2\overline{C(Me)CH_2CH_2C(O)O}$	53
7 [c,d]	C_3H_7CHO	$C_3H_7CHOHCH_2OCH_2Ph$	46
8 [e]	$Ph(CH_2)_2CHO$	$Ph(CH_2)_2CHOHCH_2OCH_2Ph$	66

[a] All reactions were carried out at room temperature unless otherwise state. [b] Isolated yield. [c] Benzyl iodomethyl ether was employed in place of benzyl chloromethyl ether. [d] The reaction was carried out in the presence of tetraethylene glycol dimethyl ether. [e] The reaction was carried out in the presence of tetraethylene glycol dibenzyl ether.
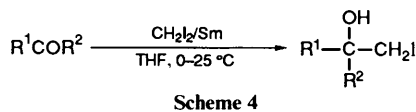
dibenzyl ether) was added to the solution of SmI_2 in THF, the characteristic deep green colour of the solution immediately turned to purple. The use of the resulting polyether complex of SmI_2 significantly improved the yields of the addition products (Entries 7 and 8 in Table 1).

The adducts obtained were converted into 1,2-diols in excellent yields by palladium-catalysed debenzylation. This reaction sequence provides a new synthesis of 1,2-diols from carbonyl compounds. In order to demonstrate the synthetic utility of this method, we tried to synthesize frontalin, a pheromone of Dendroctonus bark beetles, via a short route from heptane-2,6-dione. As shown in Scheme 3, the latter compound when treated with SmI_2 in THF at room temperature provided an addition product **1** in 56% yield. This adduct was hydrogenolysed in the presence of Pd–C to furnish frontalin **2** in 91% yield.

$$MeCO(CH_2)_3COMe \xrightarrow{\quad i \quad} MeCO(CH_2)_3C(OH)MeCH_2OCH_2Ph$$

1
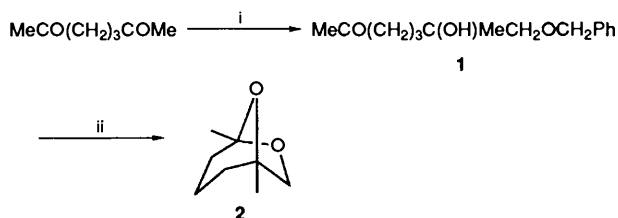
Scheme 3 *Reagents and conditions:* i, benzyl chloromethyl ether, SmI_2. THF, 0 °C; ii, H_2/Pd–C

Iodomethylation of Carbonyl Compounds.—We decided to develop a new method for direct iodomethylation of carbonyl compounds based on an earlier observation that diiodomethane reacts readily with samarium at room temperature.[12] When conducted in the presence of carbonyl compounds some preliminary experiments showed that iodohydrins were produced when a molar ratio of $1:3:2$ (ketone–CH_2I_2–Sm) was employed (Scheme 4).[13,*] The results are summarized in Table 2.

$$R^1COR^2 \xrightarrow[\text{THF, 0–25 °C}]{CH_2I_2/Sm} R^1\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}{-}CH_2I$$
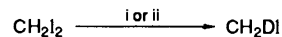
Scheme 4

Simple aliphatic ketones were converted into the corresponding iodohydrins in good to high yields. Easily enolizable ketones such as dibenzyl ketone and β-tetralone were also subjected to iodomethylation. Highly hindered ketones such as 2,4,6-trimethylacetophenone did not react. α,β-Unsaturated carbonyl compounds and aromatic aldehydes also underwent

iodomethylation, although the yields were not satisfactory. Major by-products in these reactions were pinacols. Several diketones, except those ketones having aromatic groups, underwent the iodomethylation at both carbonyl components to give compounds possessing two iodohydrin functionalities.

It is noteworthy that this method provides an approach to various iodohydrins inaccessible by previous methods such as the hydroxyiodonation of olefins.[14]

We were interested in the mechanism of this one-carbon homologation reaction, particularly because of the possible intermediacy of reactive iodomethylsamarium intermediates (ICH_2SmI and ICH_2SmI_2). In order to demonstrate the existence of such species, diiodomethane was treated with Sm or SmI_2 in THF in the presence of Me_2CHOD or MeOD, and the product, iodomethane, was analysed by mass spectrometry. The comparison of the spectra with that of authentic MeI clearly indicates that CH_2DI was produced in essentially quantitative yield in all the cases examined (Scheme 5). These results strongly support that the reaction of CH_2I_2 with samarium or samarium(II) iodide generates ICH_2SmI or ICH_2SmI_2 and that the iodomethylation of carbonyl compounds proceeds through the direct nucleophilic attack of these iodomethylsamarium species to carbonyl components.

$$CH_2I_2 \xrightarrow{\quad i \text{ or } ii \quad} CH_2DI$$

Scheme 5 *Reagents and conditions:* i, Sm, Me_2CHOD (or MeOD)–THF, 0 °C; ii, SmI_2, Me_2CHOD (or MeOD)–THF, 0 °C

Cyclopropanols from α-Halogeno Substituted Ketones or 1,2-Dibenzoylethanes.—α-Halogeno ketones were treated with diiodomethane and samarium in THF at 0 °C ($1:3:3$ halogeno ketone–CH_2I_2–Sm) to give cyclopropanols as the major products (see Scheme 6). It is noteworthy that chloro as well as iodo and bromo ketones reacted smoothly to afford the corresponding cyclopropanols.
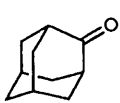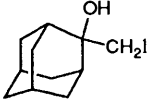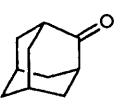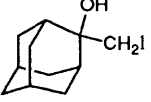
$$R^1COCHXR^2 \xrightarrow[\text{THF, 0 °C}]{CH_2I_2-Sm} \text{[cyclopropanol]}$$
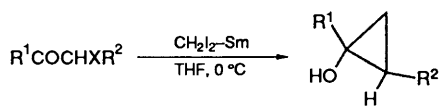
$R^1 = Ph$, $R^2 = H$, $X = Cl$ (37%)
$R^1 = Ph$, $R^2 = H$, $X = Br$ (81%)
$R^1 = Ph$, $R^2 = H$, $X = I$ (88%)
$R^1 = p\text{-}BrC_6H_4$, $R^2 = H$, $X = Br$ (67%)
$R^1 = Ph$, $R^2 = Me$, $X = Cl$ (49%)
$R^1 = Ph$, $R^2 = Me$, $X = Br$ (55%)
$R^1, R^2 = {-}(CH_2)_4{-}$, $X = Br$ (81%)

Scheme 6

Under similar conditions, α-bromo ketones **3** and **4** were converted into biscyclopropanols **5** and **6** in 62 and 29% yields, respectively (Scheme 7). Analysis of these products by ^1H and

* Other lanthanoid metals were also tested for the iodomethylation of acetophenone and benzaldehyde. Although these metals reacted under similar conditions, the yields of the expected iodohydrins were only 10–20%.

Table 2 Synthesis of iodohydrins from carbonyl compounds[a]

Entry	Carbonyl compound	Product	Yield (%)[b]
1			84
2[c]			25
3	$C_6H_{13}Ac$	$C_6H_{13}C(OH)(CH_2I)Me$	93
4[d]	$C_6H_{13}Ac$	$C_6H_{13}C(OH)(CH_2I)Me$	34
5	$(PhCH_2)_2CO$	$(PhCH_2)_2C(OH)CH_2I$	71
6	3,4-Dihydronaphthalen-2(1H)-one	1,2,3,4-Tetrahydro-2-iodomethylnaphthalen-2-ol	44
7	Cyclopentanone	$ICH_2\overline{C(OH)CH_2(CH_2)_3}CH_2$	84
8	PhCOMe	$PhC(OH)(CH_2I)Me$	71
9	$4\text{-}BrC_6H_4Ac$	$4\text{-}BrC_6H_4C(OH)(CH_2I)Me$	57
10	$4\text{-}NCC_6H_4Ac$	$4\text{-}NCC_6H_4C(OH)(CH_2I)Me$	38
11	3,4-Ethylenedioxyphenyl-Ac	3,4-Ethylenedioxyphenyl-$C(OH)(CH_2I)Me$	87
12	Mesityl-Ac	_____[e]	
13	$\overline{CH_2CH_2}CHAc$	$\overline{CH_2CH_2}CHC(OH)(CH_2I)Me$	77
14	$C_{11}H_{23}CHO$	$C_{11}H_{23}CHOHCH_2I$	72
15	Cyclohex-3-enyl-CHO	Cyclohex-3-enyl-$CHOHCH_2I$	49
16	PhCHO	$PhCHOHCH_2I$	39
17	3,4-Ethylenedioxybenzaldehyde	3,4-Ethylenedioxyphenyl-$CH(OH)CH_2I$	32
18	$4\text{-}NCC_6H_4CHO$	$4\text{-}NCC_4H_4CHOHCH_2I$	44
19	Cyclohex-2-enone	$ICH_2\overline{C(OH)CH_2(CH_2)_2CH=}CH$	22
20[f]	Cyclohex-2-enone	$ICH_2\overline{C(OH)CH_2(CH_2)_2CH=}CH$	55
21[g]	Cyclohex-2-enone	$ICH_2\overline{C(OH)CH_2(CH_2)_2CH=}CH$	80
22	$Me_2C=CH(CH_2)_2CMe=CHCHO$	$Me_2C=CH(CH_2)_2CMe=CHCHOHCH_2I$	31
23	2,6,6-Trimethylcyclohex-1-enyl-CH=CHAc	2,6,6-Trimethylcyclohex-1-enyl-$CH=CHC(CH_2I)(OH)Me^h$	53
24[i]	2,6,6-Trimethylcyclohex-1-enyl-CH=CHAc	2,6,6-Trimethylcyclohex-1-enyl-$CH=CHC(CH_2I)(OH)Me^h$	72
25[j]	CH_2Ac_2	_____[k]	
26[j]	$(C_6H_{13}COCH_2)_2$	$[C_6H_{13}C(OH)(CH_2I)CH_2]_2$	47
27[j]	$CH_2(CH_2Ac)_2$	$CH_2[CH_2C(OH)(CH_2I)Me]_2$	68
28[j]	$CH_2(CH_2Bz)_2$	$CH_2[CH_2C(OH)(CH_2I)Ph]_2$	68
29[j]	$(BzCH_2CH_2)_2$	$[PhC(OH)(CH_2I)CH_2CH_2]_2$	59

[a] All reactions were carried out at 0 °C with a molar ratio of 1:3:2 R^1COR^2–CH_2I_2–Sm, unless otherwise stated. [b] Isolated yield. [c] Molar ratio: 1:1:1 R^1COR^2–CH_2I_2–Sm. [d] Molar ratio: 1:1:0.67 R^1COR^2–CH_2I_2–Sm. [e] No reaction took place. [f] Molar ratio: 1:6:4 R^1COR^2–CH_2I_2–Sm. [g] Molar ratio: 1:6:8 R^1COR^2–CH_2I_2–Sm. [h] This iodohydrin was extremely labile and decomposed to a black tar within a few hours after isolation. [i] Molar ratio: 1:6:3 R^1COR^2–CH_2I_2–Sm. [j] Molar ratio: 1:6:4 diketone–CH_2I_2–Sm. [k] Pentane-2,4-dione was recovered quantitatively.

^{13}C NMR spectroscopy showed that they were single stereoisomers, although the relative configurations have not yet been determined.

PhCOCHBr(CH₂)ₙCHBrCOPh

3, n = 1
4, n = 3

$\xrightarrow{CH_2I_2-Sm}$

5, n = 1
6, n = 3
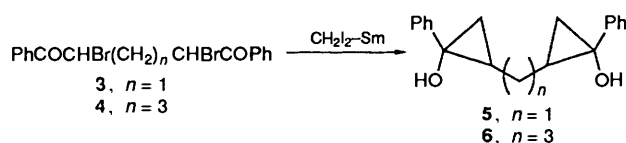
Scheme 7

Another notable finding is that cyclopropanols were produced from 1,4-diketones having aromatic groups (Scheme 8). Thus, the reaction of 1,2-dibenzoylethane provided 1-phenylcyclopropanol in 66% yield. Similarly, 1,2-dibenzoyl-1,1,2,2-tetradeuterioethane was converted into 2,2-dideuterio-1-phenylcyclopropanol. 1,2-Dibenzoylcyclopropane and 1,5-dibenzoylcyclopentane were also converted into the corresponding cyclopropanols 5 and 6 in 69 and 55% yields, respectively. These results clearly indicate that this reaction sequence involves the cleavage of the carbon–carbon bond between two phenacyl groups.
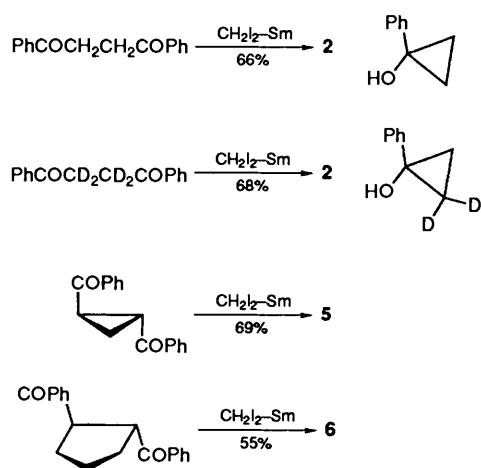
In order to study some mechanistic aspects of these cyclopropanations, we examined the reactions shown in Scheme 9.
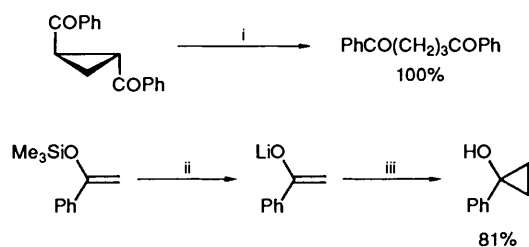
The results for these reactions which proceeded rapidly in THF at room temperature, strongly suggest that the cyclopropanations proceed through the pathway illustrated in Scheme 10. Thus, α-halogeno ketones and 1,4-diketones are reduced by SmI_2 or metallic samarium to generate samarium enolates 7 which, in turn, undergo a Simmons–Smith type cyclopropanation with samarium carbenoid species (ICH_2SmI or ICH_2-SmI_2) to afford 8.*†

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* Molander and Hahn reported that α-halogeno ketones were readily reduced by SmI_2 to generate samarium enolates.[15]
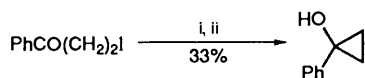
† Molander and Etter reported that samarium(II) carbenoid species (ICH_2SmI) was generated by the reaction of samarium amalgam with diiodomethane. It was also demonstrated by them that the samarium carbenoid underwent the Simmons–Smith type cyclopropanation with allylic alcohols.[16]

PhCOCH$_2$CH$_2$COPh $\xrightarrow[\text{66\%}]{\text{CH}_2\text{I}_2\text{-Sm}}$ 2

PhCOCD$_2$CD$_2$COPh $\xrightarrow[\text{68\%}]{\text{CH}_2\text{I}_2\text{-Sm}}$ 2

$\xrightarrow[\text{69\%}]{\text{CH}_2\text{I}_2\text{-Sm}}$ 5

$\xrightarrow[\text{55\%}]{\text{CH}_2\text{I}_2\text{-Sm}}$ 6

Scheme 8

$\xrightarrow{\text{i}}$ PhCO(CH$_2$)$_3$COPh

100%

81%

Scheme 9 *Reagents and conditions:* i, SmI$_2$ or Sm, THF, room temp.; ii, MeLi, ether–THF, room temp.; iii, CH$_2$I$_2$–SmI$_2$, THF, 0 °C

α–Halogeno ketone or aromatic 1, 4–diketone $\xrightarrow{\text{i}}$

7; n = 1 or 2

8
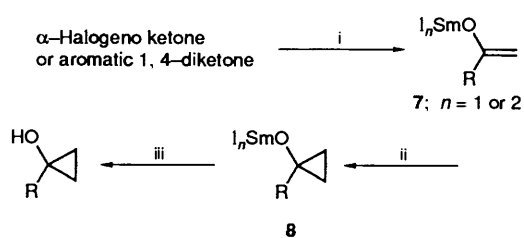
Scheme 10 *Reagents:* i, SmI$_2$ or Sm; ii, ICH$_2$SmI$_2$ or ICH$_2$SmI; iii, H$_2$O

On the other hand, the pathway shown in Scheme 11 might conceivably be a route to cyclopropanol. In order to confirm the possibility of the existence of 2-acyl-1-iodoethane as an intermediate, we examined the model reaction shown in Scheme 12. This reaction was sluggish although it proceeded at room temperature, and the expected product, 1-phenylcyclopropanol, was produced in 33% yield even after 12 h. This result indicates that the reaction does not involve 2-acyl-1-iodoethane as an intermediate.

7 $\xrightarrow{\text{i}}$ RCO(CH$_2$)$_2$I $\xrightarrow{\text{ii}}$ 8
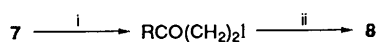
Scheme 11 *Reagents:* i, CH$_2$I$_2$; ii, SmI$_2$ or Sm

PhCO(CH$_2$)$_2$I $\xrightarrow[\text{33\%}]{\text{i, ii}}$

Scheme 12 *Reagents and conditions:* i, SmI$_2$, THF, 12 h; ii, H$_2$O

One-pot Synthesis of Cyclopropanols from Ketones.—The experimental facts described above led us to investigate a one-pot synthesis of cyclopropanols from ketones. Ketones were deprotonated with lithium diisopropylamide (LDA) or triphenyl-methyllithium, and the generated lithium enolates were treated with CH$_2$I$_2$–SmI$_2$ or CH$_2$I$_2$–Sm. As shown in Table 3, simple ketones were converted into cyclopropanols in good yields without isolation of the intermediates.

It is to be noted that the structure of the cyclopropanol obtained is derived from the structure of the initially generated lithium enolate. For instance, 2-methylcyclohexanone was converted into two kinds of lithium enolates under thermodynamic or kinetic conditions. The respective metal enolates underwent a Simmons–Smith type reaction with CH$_2$I$_2$–Sm to give the corresponding cyclopropanols (Table 3, entries 14 and 15). The reaction was also stereospecific. Thus, propiophenone was treated first with LDA, and then with CH$_2$I$_2$–SmI$_2$, to afford *trans*-2-methyl-1-phenylcyclopropanol (56%). This method may be applicable to the synthesis of other synthetically useful cyclopropanols by the employment of the established procedures for regio- and stereo-selective generation of lithium enolates.[17]

One-pot Synthesis of Cyclopropanols from Esters.—On the basis of the results described above, we considered that cyclopropanols might be synthesized from carboxylic acid derivatives *via* tandem one-carbon homologation. Thus, we envisiged that cyclopropanols might be produced through the following reaction pathway shown in Scheme 13.
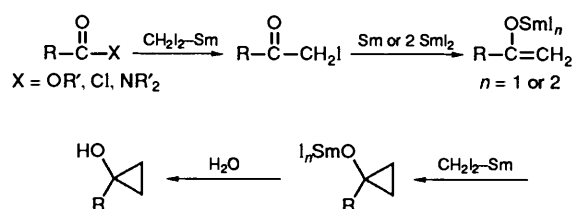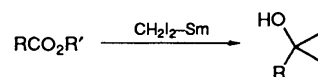

Scheme 13

Our preliminary experiments to demonstrate this possibility were carried out using benzoic acid derivatives; the results are summarized in Table 4. The expected product, 1-phenylcyclopropanol, was produced in all cases except for benzamide; the highest yield was obtained in the case of ethyl benzoate. Benzoyl chloride was converted into the cyclopropanol in 16% yield; significant amounts of benzoin and benzil were produced in this reaction. It is noted that benzoic acid itself was led to the cyclopropanol under these conditions although the yield was not satisfactory.

Other lanthanoid metals (La, Ce, Yb) were also examined for the reaction of ethyl benzoate. The reactions were carried out in THF at 50 °C with a molar ratio of 1:3:4 (ethyl benzoate–diiodomethane–lanthanoid metal). Lanthanum, cerium, and ytterbium provided 1-phenylcyclopanol in 19, 32 and 10% yields, respectively. Other metals or reducing agents such as magnesium, barium, zinc–copper couple, lithium naphthalenide, and diethyl zinc were also tested. However, no, or only a trace amount of the expected cyclopropanol was produced in these cases.

Next, the reactions of other esters with CH$_2$I$_2$–Sm were examined in order to clarify the general scope of this one-pot cyclopropanation. The results are shown in Table 5.

RCO$_2$R' $\xrightarrow{\text{CH}_2\text{I}_2\text{-Sm}}$

Scheme 14

A characteristic feature of this method is that cyclopropanols are synthesized directly from esters *via* tandem one-carbon homologation. It should be also noted that other carbon–carbon double bonds remained unaffected during the reaction.

A further interesting feature is that three methylene components were incorporated in the reaction of phenylthioacetic acid methyl ester. That this reaction provided 1-(2-phenyl-thioethyl)cyclopropanol is reasonably explained by assuming the occurrence of the Stevens rearrangement of a sulphonium

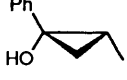**Table 3** Synthesis of cyclopropanols from ketones[a]
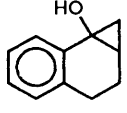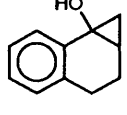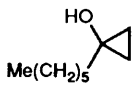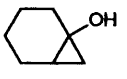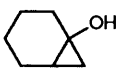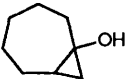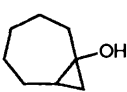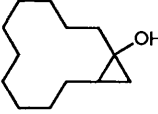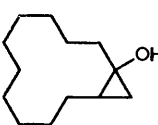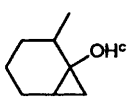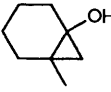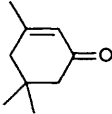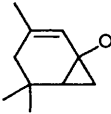
Entry	Ketone	Base	Reagent	Product	Yield (%)[b]
1	PhCOMe	Ph$_3$CLi	CH$_2$I$_2$–SmI$_2$		82
2	PhCOMe	LDA	CH$_2$I$_2$–SmI$_2$		58
3	PhCOMe	Ph$_3$CLi	CH$_2$I$_2$–Sm		60
4	PhCOEt	LDA	CH$_2$I$_2$–Sm		56
5	3,4-Dihydronaphthalen-1(2H)-one	Ph$_3$CLi	CH$_2$I$_2$–Sm		35
6	3,4-Dihydronaphthalen-1(2H)-one	LDA	CH$_2$I$_2$–SmI$_2$		57
7	MeCO(CH$_2$)$_3$Me	Ph$_3$CLi	CH$_2$I$_2$–Sm		52
8	Cyclohexanone	Ph$_3$CLi	CH$_2$I$_2$–Sm		48
9	Cyclohexanone	LDA	CH$_2$I$_2$–SmI$_2$		56
10	Cycloheptanone	Ph$_3$CLi	CH$_2$I$_2$–Sm		68
11	Cycloheptanone	LDA	CH$_2$I$_2$–SmI$_2$		58
12	Cyclododecanone	Ph$_3$CLi	CH$_2$I$_2$–Sm		40
13	Cyclododecanone	LDA	CH$_2$I$_2$–SmI$_2$		46
14	2-Methylcyclohexanone	LDA	CH$_2$I$_2$–SmI$_2$		59

Table 3 (*continued*)

Entry	Ketone	Base	Reagent	Product	Yield (%)[b]
15[d]	2-Methylcyclohexanone	LDA	CH_2I_2 SmI_2		62
16		LDA	CH_2I_2 SmI_2		62

[a] All reactions were carried out in THF at −78 °C through to room temperature. See experimental section. [b] Isolated yield. [c] A mixture (*ca.* 2:3) of stereoisomers. [d] The lithium enolate was generated by treatment of 2-methylcyclohexanone with LDA at room temperature for 6 h.

Table 4 One-pot synthesis of cyclopropanols from benzoic acid derivatives

PhCOX	Molar ratio of PhCOX–CH_2I_2–Sm	Conditions	Yield (%)
$PhCO_2Et$	1:2:3	reflux, 0.7 h	42
$PhCO_2Et$	1:3:4	reflux, 0.7 h	66
$PhCO_2Et$	1:3:4	50 °C, 1.5 h	71
$PhCO_2Et$	1:3:4	20 °C, 1.5 h	58
$PhCO_2Et$	1:4:4	20 °C, 0.7 h	66
$PhCO_2Et$	1:4:6	reflux, 0.7 h	56
$PhCO_2Et$	1:5:6	reflux, 0.7 h	65
$PhCO_2Et$	1:5:6	50 °C, 1.2 h	76
$PhCO_2Et$	1:5:6	0 °C, 1.0 h	45
$PhCO_2Et$	1:5:6	−78 to −0 °C, 2.0 h	33
$PhCO_2Et$	1:8:6	reflux, 0.7 h	44
$PhCO_2CMe_3$	1:3:4	50 °C, 1.5 h	34
PhCOCl	1:3:4	50 °C, 1.5 h	16
$PhCOSC_4H_9$	1:3:4	50 °C, 1.5 h	23
$PhCONMe_2$	1:3:4	50 °C, 1.5 h	34
$PhCONH_2$	1:3:4	50 °C, 1.5 h	0
$PhCO_2H$	1:3:4	50 °C, 1.5 h	19

ylide produced by the reaction of the sulphide with the samarium carbenoid (Scheme 15).

Scheme 15
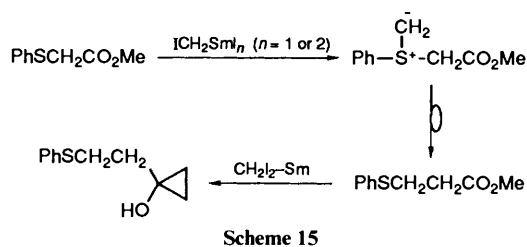
Experimental

Materials.—Rare earth ingots (Sm, La, Ce, Nd, Yb) were purchased from Nippon Yttrium Company Ltd. and were scraped to powder (50–200 mesh) before use by the use of a lasp. Anhydrous THF (tetrahydrofuran) was distilled from sodium–benzophenone prior to use. Simple organic chemicals were purchased and purified by distillation under reduced pressure. *J* Values are given in Hz.

The following compounds were synthesized according to the procedures described in the literature: hexadecane-7,10-dione,[18] heptane-2,6-dione,[19] 1,2-dibenzoylethane,[20] 1,3-dibenzoylpropane,[21] 1,4-dibenzoylbutane,[22] *trans*-1,2-dibenzoylcyclopropane,[23] *trans*-1,2-dibenzoylcyclopentane,[24] and 1,3-dibenzoyl-1,3-dibromopropane.[25]

1,5-*Dibromo*-1,5-*dibenzoylpentane.* This *compound* was prepared by the reaction of 1,5-dibenzoylpentane with bromine in chloroform at room temperature. M.p. 108.5–109.5 °C (from

EtOH) (Found: C, 52.1; H, 4.2. $C_{19}H_{18}Br_2O_2$ requires C, 52.08; H, 4.14%): ν_{max}(KBr)/cm⁻¹ 1680, 1355, 1255, 805 and 710; δ_H(CDCl₃) 1.48–2.18 (6 H, m), 5.06 (2 H, t, *J* 7.2) and 7.20–8.07 (10 H, m).

1,1,2,2-*Tetradeuterio*-1,2-*dibenzoylethane.* This compound was prepared from 1,2-dibenzoylethane by H/D exchange reaction in D_2O–THF in the presence of catalytic amount of KOH.

Alkoxymethylation of Carbonyl Compounds (*General Procedure*).—A solution of samarium diiodide (0.1 mol dm⁻³ THF solution; 30 cm³) was added to a mixture of carbonyl compound (1 mmol) and alkoxymethyl halide (1 mmol). The mixture was stirred until the reaction was complete when it was treated with aqueous acetic acid. The product was extracted with ethyl acetate, and the combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residual oil was purified by preparative TLC on silica gel.

Spectral and analytical data of new compounds prepared are as follows.

2-*Benzyloxymethyl*-1,3-*diphenylpropan*-2-*ol* (*Table* 1, *entry* 1). An *oil* (Found: C, 83.1; H, 7.15. $C_{23}H_{24}O_2$ requires C, 83.10; H, 7.28%); ν_{max}(neat)/cm⁻¹ 3520, 3010, 2900, 2840, 1495, 1450, 1090 and 740; δ_H(CCl₄) 1.72 (1 H, s), 2.78 (4 H, s), 2.95 (2 H, s), 4.34 (2 H, s), 7.13 (10 H, br s) and 7.24 (5 H, br s).

2-*Benzyloxymethyloctan*-2-*ol* (*Table* 1. *entry* 2). An *oil* (Found: C, 76.85; H, 10.4. $C_{16}H_{26}O_2$ requires C, 76.75; H, 10.47%); ν_{max}(neat)/cm⁻¹ 3420, 2910, 2840, 1455, 1205 and 750; δ_H(CCl₄) 0.7–1.6 (13 H, m), 1.09 (3 H, s), 1.43 (1 H, s), 3.20 (2 H, s), 4.46 (2 H, s) and 7.24 (5 H, br s).
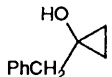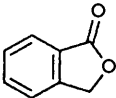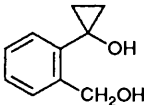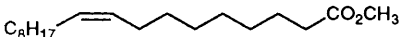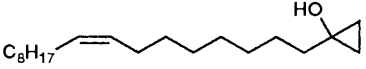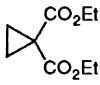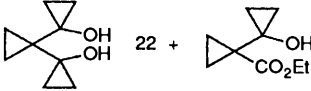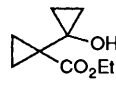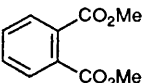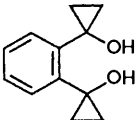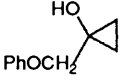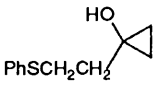
1-*Benzyloxymethylcyclopentanol* (*Table* 1. *entry* 3). An *oil* (Found: C, 75.6; H, 8.7. $C_{13}H_{18}O_2$ requires C, 75.69; H, 8.80%); ν_{max}(neat)/cm⁻¹ 3420, 2940, 2850, 1450, 1100 and 750; δ_H(CCl₄) 1.4–1.9 (8 H, m), 2.44 (1 H, s), 3.36 (2 H, s), 4.54 (2 H, s) and 7.29 (5 H, br s).

1-*Benzyloxymethylcyclohexanol* (*Table* 1. *entry* 4). An *oil* (Found: C, 76.3; H, 9.15. $C_{14}H_{20}O_2$ requires C, 76.33; H, 9.15%); ν_{max}(neat)/cm⁻¹ 3420, 2920, 2840, 1455, 1105 and 745; δ_H(CCl₄) 1.2–1.7 (10 H, m), 1.98 (1 H, s), 3.23 (2 H, s), 4.48 (2 H, s) and 7.27 (5 H, br s).

1-*Benzyloxy*-5-*chloro*-2-*methylpentan*-2-*ol* (*Table* 1, *entry* 5). An *oil* (Found: C, 64.4; H, 7.9. $C_{13}H_{20}ClO_2$ requires C, 64.32; H, 7.89%); ν_{max}(neat)/cm⁻¹ 3400, 2850, 1455, 1370, 1105 and 750; δ_H(CCl₄) 1.08 (3 H, s), 1.4–1.9 (4 H, m), 2.00 (1 H, s), 3.17 (2 H, s), 3.42 (2 H, t, *J* 6.0), 4.43 (2 H, s) and 7.13 (5 H, br s).

2-*Benzyloxymethyl*-2-*methylbutan*-4-*olide* (*Table* 1, *entry* 6). An *oil* (Found: C, 70.8; H, 7.3. $C_{13}H_{16}O_3$ requires C, 70.89; H, 7.32); ν_{max}(neat)/cm⁻¹ 2850, 1770, 1450, 1105, 950 and 750; δ_H(CCl₄) 3.51 (3 H, s), 1.7–2.8 (4 H, m), 3.44 (2 H, s), 4.57 (2 H, s) and 7.32 (5 H, br s).

Table 5 On-pot synthesis of 1-substituted cyclopropanols from esters[a]

Entry	Ester	Molar ratio of Ester–CH_2I_2–Sm	Product	Yield (%)[b]
1	$PhCO_2Et$	1 : 3 : 4		71
2	$PhCO_2CMe_3$	1 : 3 : 4		34
3	$PhCH_2CO_2Et$	1 : 3 : 4		51
4		1 : 3 : 4		59
5	C_8H_{17}———————CO_2CH_3	1 : 3 : 4		70
6		1 : 6 : 8	22 +	14
7		1 : 6 : 8		21
8	$PhOCH_2CO_2Me$	1 : 3 : 4		60
9	$PhSCH_2CO_2Me$	1 : 3 : 4		9[c]

[a] All reactions were carried out in THF at 50 °C. [b] Isolated yield. [c] Thioanisole and (phenylthio)acetone obtained in 29 and 12% yields, respectively.

1-*Benzyloxypentan-2-ol* (*Table* 1, *entry* 7). An *oil*; ν_{max}-(neat)/cm^{-1} 3360, 2900, 2850, 1440, 1100 and 740; δ_H(CDCl$_3$) 0.78–1.16 (3 H, m), 1.18–1.64 (4 H, m), 2.3–2.5 (1 H, br s), 3.24–3.54 (2 H, m), 3.7–3.92 (1 H, m), 4.54 (2 H, s) and 7.1–7.5 (5 H, br s); m/z (EI) 194 (M$^+$, 3%), 107 (20), 92 (52), 91 (100), 73 (36) and 55 (52).

1-*Benzyloxy-4-phenylbutan-2-ol*. (*Table* 1, *entry* 8). An *oil*; ν_{max}(neat)/cm^{-1} 3360, 2950, 2800, 1465, 1420, 1080, 720 and 680; δ_H(CDCl$_3$) 1.6–1.84 (2 H, m), 2.38–2.96 (3 H, m), 3.2–3.4 (2 H, m), 3.46–3.8 (1 H, m), 4.42 (2 H, s), 7.24 (5 H, br s) and 7.32 (5 H, br s); m/z (EI) 256 (M$^+$, 1%), 105 (35), 92 (22), 91 (100) and 65 (17).

Iodomethylation of Carbonyl Compounds (*General Procedure*).—Freshly scraped samarium powder (300 mg, 2 mmol) was placed in a two-necked flask with a dropping funnel containing a carbonyl compound (1 mmol) and diiodomethane (804 mg, 3 mmol) in THF (6 cm^3). The THF solution was slowly added at 0 °C under argon. Usually, the reaction was initiated within a few minutes, and the addition of the solution required

about 20 min. After addition, stirring was continued for an additional 20 min at the same temperature. The reaction mixture was treated with 1 mol dm^{-3} HCl and extracted with ether. The combined extracts were washed with aqueous Na$_2$-S$_2$O$_3$ and brine, dried (MgSO$_4$) and evaporated. The product was isolated by chromatography of the residue on silica gel.

Spectral and analytical data of new iodohydrins prepared are as follows.

1-*Iodo-2-methyloctan-2-ol* (*Table* 2, *entry* 1). M.p. 39–40 °C (from hexane) (Found: C, 40.05; H, 6.9. C$_9$H$_{19}$IO requires C, 40.01; H, 7.09%); ν_{max}(KBr)/cm^{-1} 3380, 2905, 2840, 1465, 1375, 1135 and 780; δ_H(CDCl$_3$) 0.75–1.75 (13 H, m), 1.32 (3 H, s), 2.05 (1 H, s) and 3.32 (2 H, s).

2-*Iodomethyl-1,3-diphenylpropan-2-ol* (*Table* 2, *entry* 5). An oil; ν_{max}(neat)/cm^{-1} 3500, 3000, 2900, 1490, 1080, 1030, 760, 735 and 700; δ_H(CDCl$_3$) 1.78 (1 H, s), 2.95–3.15 (6 H. m) and 7.22 (10 H, br s); m/z (EI) 352 (M$^+$, 0.2%), 261 (33), 260 (37), 134 (11), 133 (15), 116 (10), 105 (15), 92 (36), 91 (100) and 65 (22).

1,2,3,4-*Tetrahydro-2-iodomethyl-2-naphthol* (*Table* 2, *entry* 6). An oil: ν_{max}(neat)/cm^{-1} 3350, 2900, 1480 and 740: δ_H(CDCl$_3$)

2.24 (2 H, s), 2.68–3.04 (4 H, m), 3.38 (2 H, s) and 7.16 (4 H, br s); m/z (EI) 288 (M$^+$, 3%), 161 (34), 143 (100), 129 (20), 128 (36), 127 (20), 117 (29), 115 (28), 104 (23), 91 (34), 78 (12), 77 (13) and 51 (12).

1-*Iodomethylcyclohexanol* (*Table 2, entry* 7). M.p. 69–70 °C (from hexane) (Found: C, 35.3; H, 5.5. C$_7$H$_{13}$IO requires C, 35.02; H, 5.46%); ν_{max}(KBr)/cm^{-1} 3370, 2900, 2830, 1445, 1170, 980 and 735; δ_H(CDCl$_3$) 0.8–2.0 (10 H, m), 1.87 (1 H, s) and 2.32 (2 H, s).

1-*Iodo-2-phenylpropan-2-ol* (*Table 2, entry* 8). An oil; ν_{max}-(neat)/cm^{-1} 3400, 2950, 1440, 1180, 770 and 710; δ_H(CDCl$_3$) 1.68 (2 H, s), 2.21 (1 H, s), 3.62 (2 H, s) and 7.64–7.3 (5 H, m); m/z (EI) 262 (M$^+$, 1%), 243 (30), 135 (30), 127 (17), 121 (100), 117 (72), 115 (61), 91 (40), 78 (15), 77 (29) and 51 (39).

2-p-*Bromophenyl*-1-*Iodopropan-2-ol* (*Table 2, entry* 9). An oil; ν_{max}(neat)/cm^{-1} 3400, 2950, 1480, 1080, 1010 and 830; δ_H-(CDCl$_3$) 1.68 (3 H, s), 2.36 (1 H, s), 3.56 (2 H, s) and 7.2–7.5 (4 H, m); m/z (EI) 342/340 (M$^+$, 6/6%), 324 (16), 322 (17), 215 (14), 213 (15), 201 (100), 199 (99), 127 (16), 116 (73), 115 (47), 91 (28), 75 (20) and 51 (25).

2-p-*Cyanophenyl*-1-*iodopropan-2-ol* (*Table 2, entry* 10). M.p. 89.5–90.0 °C (from hexane) (Found: C, 42.05; H, 3.55; N, 4.6. C$_{10}$H$_{10}$INO requires C, 41.84; H, 3.51; N, 4.88%); ν_{max}-(KBr)/cm^{-1} 3400, 2200, 1600, 1400, 1200, 1160 and 840; δ_H(CDCl$_3$) 1.72 (3 H, s), 2.84 (1 H, br s), 3.62 (2 H, s) and 7.66 (4 H, br s).

1-*Iodo*-2-[3′,4′-(*methylenedioxy*)*phenyl*]*propan-2-ol* (*Table 2, entry* 11). An oil; ν_{max}(neat)/cm^{-1} 3400, 2950, 2860, 1480, 1240, 1030, 930 and 820; δ_H(CDCl$_3$) 1.66 (3 H, s), 2.4 (1 H, s), 3.52 (2 H, s), 5.88 (2 H, s) and 6.62–6.86 (3 H, m).

2-*Cyclopropyl*-1-*iodopropan-2-ol* (*Table 2, entry* 13). An oil; ν_{max}(neat)/cm^{-1} 3400, 2950, 1370, 1200 and 1030; δ_H(CDCl$_3$) 0.4–0.7 (4 H, m), 0.9–1.24 (1 H, m), 1.32 (3 H, s), 1.72–1.96 (1 H, br s) and 3.48 (2 H, s); m/z (EI) 226 (M$^+$, 0.3%), 127 (11), 85 (100), 81 (16), 58 (14) and 53 (20).

1-*Iodotridecan-2-ol* (*Table 2, entry* 14). M.p. 42.0–43.0 °C; ν_{max}(KBr)/cm^{-1} 3300, 2900, 1460, 1100 and 1070; δ_H(CDCl$_3$) 0.8–1.7 (23 H, m), 2.0–2.2 (1 H, br s) and 3.2–3.7 (3 H, m).

2-*Iodo*-1-[3′,4′-(*methylenedioxy*)*phenyl*]*ethanol* (*Table 2, entry* 17). M.p. 91.5–92.0 °C; ν_{max}(KBr)/cm^{-1} 3100, 2850, 1480, 1440, 1240, 1140 and 820; δ_H(CDCl$_3$) 2.52 (1 H, br s), 3.36–3.56 (2 H, m), 4.7–4.88 (1 H, m), 6.04 (2 H, s) and 6.84–7.08 (3 H, m).

1-p-*Cyanophenyl*-2-*iodoethanol* (*Table 2, entry* 18). M.p. 101–102 °C (from hexane) (Found: C, 39.8; H, 2.85; N, 4.9. C$_9$H$_8$INO requires C, 39.59; H, 2.95; N, 5.13%); ν_{max}(KBr)/cm^{-1} 3450, 2200, 1410, 1290, 1190, 1060 and 850; δ_H(CDCl$_3$) 2.96 (1 H, br s), 3.28–3.56 (2 H, m), 4.74–4.9 (1 H, m) and 7.36–7.7 (4 H, m).

1-*Iodomethylcyclohex-2-enol* (*Table 2, entry* 19). An oil; ν_{max}-(neat)/cm^{-1} 3350, 2900, 1170, 980 and 720; δ_H(CDCl$_3$) 1.3–2.2 (7 H, m), 3.34 (2 H, s) and 5.5–6.0 (2 H, m).

(E)-1-*Iodo*-2-*methyl*-4-(2,6,6-*trimethylcyclohex*-1-*enyl*)*but*-3-*en*-2-*ol* (*Table 2, entry* 23). An oil; ν_{max}(neat)/cm^{-1} 3400, 2900, 1450 and 980; δ_H(CDCl$_3$) 0.99 (6 H, s), 1.0–2.2 (6 H, m), 1.49 (3 H, s), 1.66 (3 H, s), 2.13 (1 H, s), 3.38 (2 H, s), 5.41 (1 H, d, *J* 16) and 6.14 (1 H, d, *J* 16).

Synthesis of Cyclopropanols from α-*Halogeno Ketones or* 1,2-*Dibenzoylethanes: General Procedure.*—The reaction was carried out in a similar manner with a molar ratio of 1:3:3 (α-halogeno ketone–CH$_2$I$_2$–Sm) and with a molar ratio of 1:4:4 (diketone–CH$_2$I$_2$–Sm). Work-up of the reaction mixture and isolation of the products were carried out in the same procedure described above.

Spectral and analytical data of new cyclopropanols synthesized are as follows.

2,2-*Dideuterio*-1-*phenylcyclopropanol* **2**. An oil; ν_{max}(neat)/cm^{-1} 3330, 2310, 1500, 1450, 1240, 775 and 710; δ_H(CDCl$_3$) 0.88–1.05 (1 H, m), 1.13–1.28 (1 H, m), 2.46 (1 H, br s) and 7.07

(5 H, br s); m/z (EI) 136 (M$^+$, 42%), 135 (100), 117 (8), 106 (64) and 77 (48).

1,1-*Bis*(2′-*hydroxy*-2′-*phenylcyclopropyl*)*methane* **5**. M.p. 125–127 °C (Found: C, 81.4; H, 7.25. C$_{19}$H$_{20}$O$_2$ requires C, 81.40; H, 7.19); ν_{max}(KBr)/cm^{-1} 3220, 2970, 2860, 2820, 1595, 1440, 1245, 1025, 760 and 705; δ_H(CDCl$_3$) 0.89–0.93 (2 H, m), 1.14–1.33 (3 H, m), 1.52–1.66 (2 H, m), 2.53–2.61 (1 H, m), 4.2 (2 H, br s) and 7.1–7.6 (10 H, br s); δ_C(CDCl$_3$) 20.93 (t), 27.33 (t), 29.69 (d), 59.09 (s), 124.75 (d), 126.07 (d), 128.06 (d) and 145.00 (s); m/z (EI) 280 (M$^+$, 3%), 185 (5), 134 (10), 133 (18), 120 (9), 105 (100), 91 (9), 77 (43) and 55 (19).

1,3-*Bis*(2′-*hydroxy*-2′-*phenylcyclopropyl*)*propane* **6**. M.p. 85–87 °C; ν_{max}(KBr)/cm^{-1} 3310, 2900, 2830, 1490, 1440, 1240, 1030, 760 and 705; δ_H(CDCl$_3$) 0.65–0.82 (2 H, m), 1.05–1.25 (4 H, m), 1.16–1.84 (6 H, m), 3.02 (2 H, br s) and 7.16 (10 H, br s); m/z (in beam) 308 (M$^+$, 3%), 290 (32), 199 (23), 189 (100), 170 (82), 146 (25), 120 (100), 105 (100) and 77 (84) (Found: M$^+$, 308.1751. C$_{21}$H$_{24}$O$_2$ requires M, 308.1778).

One-pot Synthesis of Cyclopropanols from Ketones: General Procedure.—A carbonyl compound (1 mmol) was added at −78 °C to a solution of LDA or triphenylmethyllithium (1.2 mmol) in THF–hexane (3:1) (4 cm^3). The mixture was stirred at the same temperature for 1 h, after which a suspension of SmI$_2$, prepared from (6 mmol) and diiodoethane (5 mmol) in THF (10 cm^3), was added with a pipette. Diodomethane (2.5 mmol) was then added and the mixture was warmed to and stirred at room temperature during 1 h. The reaction mixture was treated in a similar manner described above and the product was isolated by preparative TLC.

Spectral data of a new cyclopropanol synthesized are as follows.

1-*Hydroxycyclopropylhexane*. An oil; ν_{max}(neat)/cm^{-1} 3300, 2900, 1450, 1000, 960 and 920; δ_H(CDCl$_3$) 0.4–1.72 (17 H, m) and 2.2 (1 H, br s); m/z (EI) 142 (M$^+$, 0.2%), 113 (12), 85 (47), 72 (74) and 57 (100).

Synthesis of Cyclopropanols from Esters: General Procedure.—Samarium powder (600 mg, 4 mmol) was placed in a 30 cm^3 two-necked flask and covered with dry THF (2 cm^3). The mixture was warmed to 50 °C, and to this mixture was added a solution of ester (1 mmol) and diiodomethane (804 mg, 3 mmol) in THF (8 cm^3) under argon. The reaction was usually initiated within a few minutes after addition of several drops of the solution. The remainder of the solution was slowly added during 1.5 h with vigorous stirring. After addition, the mixture was cooled, treated with 1 mol dm^{-3} HCl, and extracted with ether. The product was isolated by chromatography on silica gel.

Spectral and analytical data of new cyclopropanols prepared by this method are as follows.

1-*Benzylcyclopropanol* (*Table 5, entry* 3). An oil; ν_{max}-(neat)/cm^{-1} 3300, 1260, 1100 and 720; δ_H(CDCl$_3$) 0.6–0.76 (2 H, m), 0.76–0.92 (2 H, m), 1.9 (1 H, br s), 2.94 (2 H, s) and 7.4 (5 H, br s); m/z (EI) 148 (M$^+$, 19%), 130 (18), 91 (100) and 57 (58).

o-(1-*Hydroxycyclopropyl*)*benzyl alcohol* (*Table 5, entry* 4). An oil (Found: C, 73.3; H, 7.45. C$_{10}$H$_{12}$O$_2$ requires C, 73.14; H, 7.37); ν_{max}(neat)/cm^{-1} 3300, 2920, 2860, 1450, 1235, 1020 and 770; δ_H(CDCl$_3$) 0.75–0.95 (2 H, m), 1.00–1.25 (2 H, m), 4.0–4.4 (2 H, br s), 4.76 (2 H, s) and 7.20 (5 H, br s).

(Z)-(1-*Hydroxycyclopropyl*)*heptadec-8-ene* (*Table 5, entry* 5). An *oil* (Found: C, 81.4; H, 12.9. C$_{20}$H$_{38}$O requires C, 81.56; H, 13.01); ν_{max}(neat)/cm^{-1} 3350, 2920, 2860, 1475, 1020 and 740; δ_H(CDCl$_3$) 0.21–0.38 (2 H, m), 0.56–0.70 (2 H, m), 0.83 (3 H, t, *J* 7), 1.1–1.4 (14 H, m), 1.42 (1 H, br s), 1.8–2.0 (4 H, m) and 5.04–5.22 (2 H, m).

1,1-*Bis*(1-*hydroxycyclopropyl*)*cyclopropane*. (*Table 5, entry* 6). M.p. 94–95 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3300, 1230,

1020 and 970; δ_H(CDCl$_3$) 0.36–0.56 (6 H, m), 0.6–0.84 (4 H, m), 1.2–1.36 (2 H, m) and 3.4 (2 H, br s).

Ethyl 1-(1-hydroxycyclopropyl)cyclopropane-1-carboxylate (*Table* 5. *entry* 6). An oil; ν_{max}(neat)/cm^{-1} 3400, 2950, 1700, 1300, 1200, 1130 and 1020; δ_H(400 MHz) (CDCl$_3$) 0.4–0.43 (2 H, m), 0.76–0.82 (4 H, m), 1.23–1.26 (2 H, m), 1.27 (3 H, t, *J* 7.1) and 4.18 (2 H, q, *J* 7.1); *m/z* (EI) 170 (M$^+$, 2%), 142 (15), 124 (70), 109 (13), 96 (50), 68 (100) and 55 (88).

1,2-Bis(1-hydroxycyclopropyl)benzene (*Table* 5, *entry* 7). M.p. 144.5–145.5 C (from hexane) (Found: C, 75.5; H, 7.6. C$_{12}$H$_{14}$-O$_2$ requires C, 75.76; H, 7.42%); ν_{max}(KBr)/cm^{-1} 3100, 1440, 1240, 1020, 940, 860 and 780; δ_H(CDCl$_3$) 0.7–1.1 (4 H, m), 1.1–1.4 (4 H, m). 3.24 (2 H, s) and 7.1–7.9 (4 H, m).

1-Phenoxymethylcyclopropanol (*Table* 5, *entry* 8). An oil; ν_{max}(neat).cm^{-1} 3300, 1580, 1490, 1240, 1040, 760 and 700; δ_H(CDCl$_3$) 0.6–1.1 (4 H, m), 3.1 (1 H, br s), 4.08 (2 H, s) and 6.96–7.54 (5 H, m); *m/z* (EI) 164 (M$^+$, 3%), 94 (100) and 77 (18).

1-(2-Phenylthioethyl)cyclopropanol (*Table* 5, *entry* 9). An oil; ν_{max}(neat)/cm^{-1} 3300, 1480, 1440, 1250, 740 and 690; δ_H(CDCl$_3$) 0.44–0.68 (2 H, m), 0.72–0.96 (2 H, m), 1.3 (1 H, br s), 1.84 (2 H, t, *J* 8), 3.16 (2 H, t, *J* 8) and 7.0–7.4 (5 H, m); *m/z* (EI) 194 (M$^+$, 23%), 165 (14), 137 (23), 123 (75), 110 (88), 83 (70), 77 (23) and 57 (100).

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