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Cyclization and Ring-Expansion Processes Involving Samarium Diiodide Promoted Reductive Formation and Subsequent Oxidative Ring Opening of Cyclopropanol Derivatives

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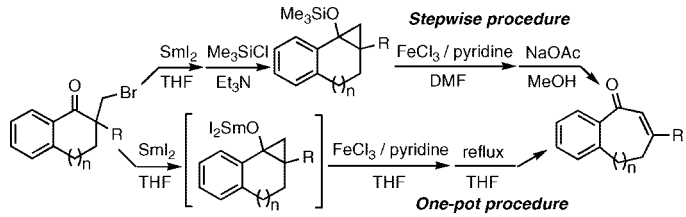

Samarium diiodide promoted reaction of various α-bromomethyl cycloalkanones, followed by subsequent treatment with trimethylsilyl chloride, leads to the production of cyclopropyl silyl ethers embedded in bicyclo[*m*.1.0]alkane frameworks. Treatment of the ethers with oxidative electron-transfer reagents, such as Fe(III), Ce(IV), and Mn(III) salts, generates ring-expanded ketones that convert to cyclic conjugated enones in moderate to good yields. In addition, the reduction−oxidation reaction sequences can be successfully performed in one pot. The regioselectivities of cyclopropane ring opening in the bicyclic substrates depend on the oxidizing agents used. For example, reactions promoted by $FeCl_3$ with pyridine lead to the expected ring-expansion process involving internal-bond cleavage of bicycloalkane and yielding cyclic enones as final products. In contrast, reactions with $Ce(NH_4)_2(NO_3)_6$ or $Mn(OAc)_3$ as oxidizing agents proceed by way of external-bond cleavage to give α-iodomethyl cycloalkanones.

Introduction

Electron transfer (ET) is a fundamental reaction process,[1] and single electron transfer (SET) of neutral organic molecules produces radical ions that often undergo fragmentation reactions to generate free radical intermediates.[2] If carbon radicals are generated in this process, they often participate in synthetically useful carbon−carbon bond-forming reactions.[3] Cyclopropanols and their derivatives are carbocyclic homologues of enols, and as such, they undergo various transformations that are the similar to enol derivatives. As a result, these strained compounds have attracted both the mechanistic and synthetic interest of organic chemists.[4] Single electron transfers from cyclopropanol and enol derivatives produce respective β-carbonyl alkyl and α-carbonyl alkyl radicals (Scheme 1). The alkyl radical intermediates

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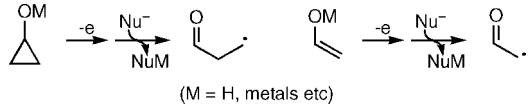
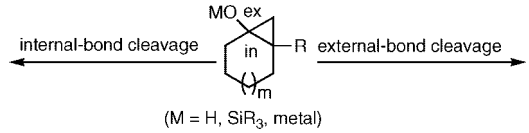
SCHEME 1



SCHEME 2



generated in this manner serve as useful precursors of various carbonyl compounds.[3]

Reactions of cyclopropanol derivatives promoted by various oxidizing agents have been extensively investigated.[5] Photoinduced electron transfer (PET) reactions of these compounds have also been described.[6] In both cases, the reactions that ensue are initiated by cyclopropane ring cleavage. Interesting mechanistic and synthetic issue associated with the regioselectivity of cyclopropane ring opening (internal-bond cleavage vs external-bond cleavage) arise in ET oxidation reactions of substances, in which the cyclopropanol moiety is embedded within a bicyclo[*m*.1.0]alkane framework (Scheme 2).[5,6]

We recently developed a novel cyclization−ring-expansion reaction sequence that is promoted by initial reaction of a substrate with samarium diiodide (SmI_2)[7,8] and followed by oxidative ring opening of intermediate cyclopropanols.[9,10] For example, keto esters I are reductively converted to bicyclic-cyclopropanols II when treated with SmI_2. Metal oxidants promote ring opening of these substances that generates seven-membered ring ketones III (Scheme 3).[9b] Elimination reactions (-HNu) of III produce substituted benzotropolones whose structures are often found in naturally occurring theaflavins.[11]

SCHEME 3

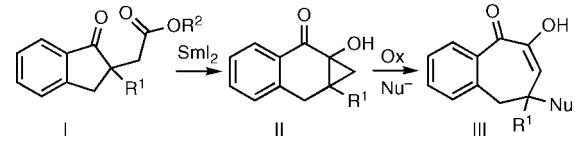
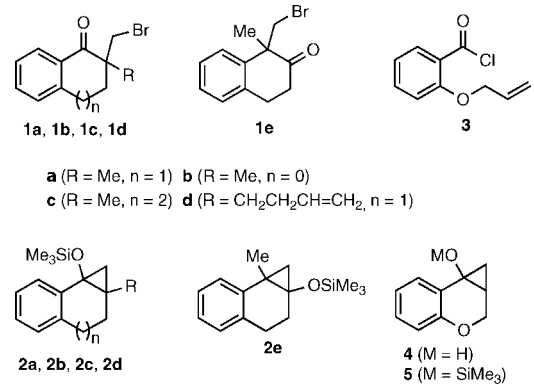


CHART 1



The tandem cyclization−ring-expansion processes serve as an effective protocol for the construction of various cyclic compounds.[12] In light of its potential synthetic significance, we have probed the application of this methodology to other types of substrates. Below, we describe the results of an investigation that demonstrate that intramolecular SmI_2-promoted Barbier reactions[8,13] of α-bromomethyl cycloalkanones can be used to generate bicyclic cyclopropanols,[14] which undergo oxidative ring-opening reactions in an efficient manner. Also, the results of an effort to incorporate these sequential reduction−oxidation processes into a one-pot process are described.

Results and Discussion

Preparation of Cyclopropanol Derivatives. The cyclopropyl silyl ethers **2** (Chart 1) used in these studies were prepared by using SmI_2-promoted intramolecular Barbier reactions of the corresponding α-bromomethyl cycloalkanones **1**,[10a] followed by trimethylsilylation of the resulting cyclopropanols. For example, α-bromomethyl tetralone **1a** was treated with SmI_2, and the crude mixture containing the corresponding cyclopropanol (not shown) was reacted with Me_3SiCl in the presence of Et_3N to give cyclopropyl silyl ether **2a** (Scheme 4).[15] The related cyclopropanol derivatives **2b** (49%), **2c** (79%), **2d** (80%), and **2e** (59%) were synthesized in a similar fashion. Also, the benzopyrane containing fused cyclopropanol **4** (38%) and its

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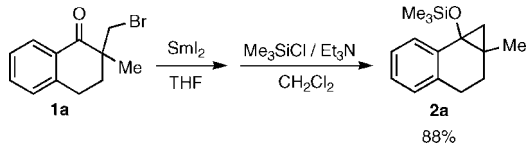
(15) Direct addition of Me_3SiCl to the reaction mixture of **1a** and SmI_2 was not successful.

SCHEME 4



SCHEME 5

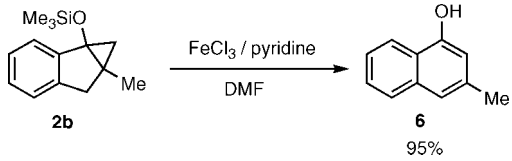
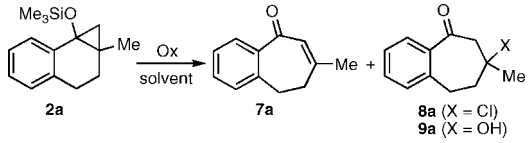


TABLE 1. Reaction of 2a with Oxidizing Reagents (Ox)[a]



entry	Ox	additive (equiv vs **2a**)	solvent	conv of **2a** (%)	yields (%) **7a**	**9a**
1[b]	$FeCl_3$	pyridine (1.0)	DMF	100	72	0
2[b]	$FeCl_3$	Et_2NH (1.0)	DMF	74	33	0
3	CAN[c]	none	MeCN	100	53	0
4	$Mn(OAc)_3 \cdot 2H_2O$	none	AcOH	100	18	27
5	$PhI(OAc)_2$	none	AcOH	100	19	33

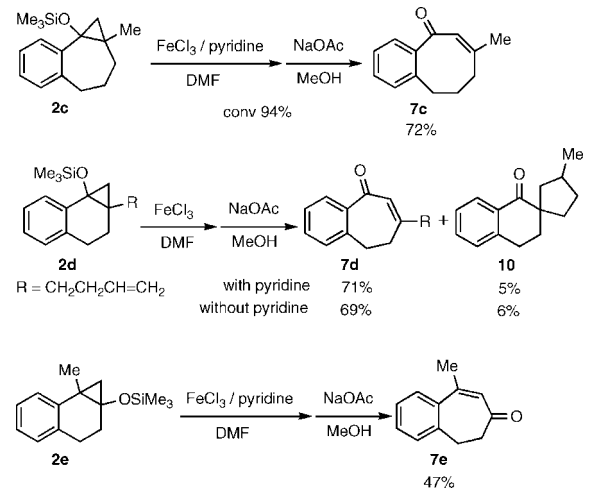
[a] Compound **2a** (0.50 mmol), Ox (2.2 equiv for entries 1, 2, 3, 4; 1.1 equiv for entry 5), solvent (5.0−10.0 mL), at room temperature for 1 h. [b] Crude product mixture was refluxed with NaOAc in MeOH for 2 h. [c] $Ce(NH_4)_2(NO_3)_6$.

silyl ether **5** (28%) (Chart 1) were prepared from *o*-allyloxy benzoyl chloride **3** by using previously described procedures.[16]

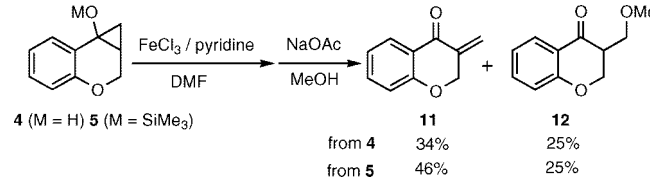
Oxidative Reactions of Cyclopropyl Silyl Ethers. Treatment of cyclopropyl silyl ethers **2b** with $FeCl_3$ in the presence of pyridine at room temperature led to formation of naphthol **6** (Scheme 5). When this process was carried out in the absence of pyridine, the yield of **6** was significantly lowered (67%). In contrast, reactions of **2b** with $Ce(NH_4)_2(NO_3)_6$ (CAN), $Mn(OAc)_3 \cdot 2H_2O$, and $PhI(OAc)_2$ gave complicated product mixtures from which **6** could not be isolated. It is possible that these stronger oxidizing reagents containing Ce(IV) and Mn(III) could cause further oxidation of **6**.[17,18]

The reactions of **2a** with the above oxidizing reagents were explored next (Table 1). Treatment of **2a** with $FeCl_3$ and pyridine led to production of β-chloro benzosuberone **8a** (crude yield 96%). Upon stirring at reflux in a methanolic NaOAc solution, the crude product mixture was converted to the benzocycloheptadienone **7a** (entry 1). When pyridine was replaced by Et_2NH in the $FeCl_3$-promoted reaction, the reaction became sluggish and rather complicated; **7a** was the only isolable product (entry 2). Also, reactions of **2a** with CAN, $Mn(OAc)_3 \cdot 2H_2O$, and $PhI(OAc)_2$ produced **7a** (entries 3−5). In reactions of **2a** with the Mn(III) and I(III) oxidants, β-hydroxy benzosuberone **9a** was the major product (entries 4 and 5).

SCHEME 6



SCHEME 7



On the basis of the observations described above, the $FeCl_3$ and pyridine oxidation conditions were used in reactions of the other cyclopropyl silyl ethers **2** (Scheme 6). Although reaction of **2c** under the conditions employed to react **2a** was slow, **7c** was obtained in 76% yield based on the conversion of **2c**. Reaction of **2d** with $FeCl_3$ in the presence or absence of pyridine generated **7d** as the major product along with a small amount of the spirocyclic product **10**. In the case of **2e**, **7e** was obtained in a moderate yield. Also, CAN could be used to promote the transformation of **2e** to **7e** (52%). We also examined $FeCl_3$/pyridine-promoted reactions of silyl ether **5** and the unprotected alcohol **4** (Scheme 7). Reactions of both **4** and **5** produced the unexpected enone product **11** and the 2-methoxymethylketone **12**, both of which are formed through external cyclopropane bond cleavage.[19]

A plausible mechanism for ring-opening reactions of the bicyclic cyclopropanol derivatives is represented in the pathway proposed for reaction of **2a** (Scheme 8). In the presence of SET oxidizing agents, such as $FeCl_3$, CAN, and $Mn(OAc)_3$,[2a,20] **2a** is transformed to the corresponding radical cation, which then transfers a Me_3Si group to a nucleophile to generate the oxy radical **13a**.[5b,d,e,g,i,j,m] In the presence of the more basic amine Et_2NH versus pyridine (respective pK_a values of their conjugate acids in H_2O are 10.98 and 5.2),[21] the oxidizing ability of Fe(III) would be lowered, leading to a deceleration of the rate of the initial SET event. This is consistent with the observation that the rates of reactions in the presence of pyridine are larger than when Et_2NH is used as a base (see entries 1 and 2, Table 1). Selective internal-bond cleavage of oxy-radical **13a** gives the

(16) Sasaki, M.; Collin, J.; Kagan, H. B. *Tetrahedron Lett.* **1988**, *29*, 6105–6106.

(17) A similar observation was made when **1b** was treated with tris(*p*-bromophenyl)aminium hexachloroantimonate as a SET reagent, which could be due to oxidative decomposition of **6**.[18]

(18) Hasegawa, E.; Ogawa, Y.; Kakinuma, K.; Tsuchida, H.; Tosaka, E.; Takizawa, S.; Muraoka, H.; Saikawa, T. *Teterahedron* **2008**, *64*, 7724–7728.

(19) In the preliminary communication of these results,[14] incorrect structures for the products derived from **4** and **5**, ring-expanded enone and its β-methoxy substituted analog, were reported. Later, it was also found that **11** gradually polymerizes.

(20) In the case of $PhI(OAc)_2$, an ionic mechanism could be operating instead of a SET mechanism.[5h]

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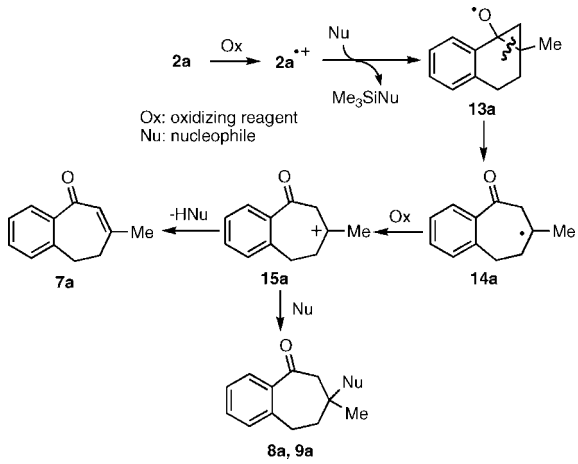
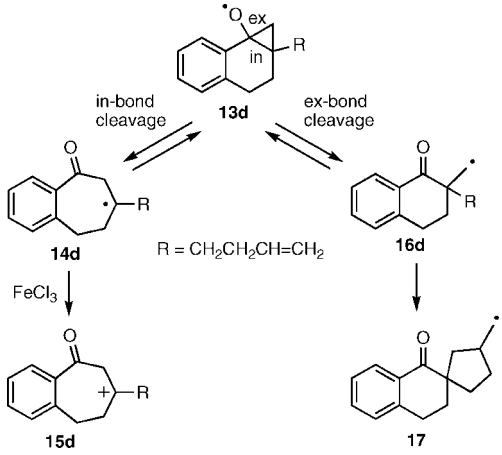
SCHEME 8



SCHEME 9



alkyl radical **14a** that is oxidized by another equivalent of the oxidizing reagent to give carbocation **15a**. Either nucleophilic addition or deprotonation of **15a** is expected to occur, depending on the nature of a coexistent nucleophile/base, to produce the observed products.

In bicyclic cyclopropoxy radicals, such as **13a**, an alternative external-bond cleavage mode is possible. In regard to this issue, observations made in studies of the oxidation reaction of **2d** are notable. In this case, if the intermediate cyclopropoxy radical **13d** undergoes external cyclopropane bond cleavage, the intermediate radical **16d** would be generated and would undergo 5-*exo* radical cyclization[22] to produce **17** (Scheme 9).[23] As described above, the expected product of this reaction mode, the compound **10**, is indeed generated, although in low yield. On the other hand, no products (e.g., α-methyl cycloalkanones) arising from external-bond cleavage were obtained in reactions of the other substrates **2**. A plausible rationalization for these observations invokes the possibility that a rapid equilibrium exists between **14** and **16**.[24] If so, in some cases the thermodynamically less stable radical **16**, formed through external-bond cleavage of **13**, might undergo a fast follow-up reaction leading to formation of the external cyclopropane bond cleavage product (i.e., Curtin−Hammet-type control).[6f,25] However, a fast oxidation of **14** by $FeCl_3$ occurs to give the stable tertiary carbocation intermediates **15** in other cases.

One-Pot Reaction. As described above, the samarium-Barbier reaction of β-bromoketones serves as a useful method for the preparation of cyclopropanol derivatives. In these reactions, samarium cyclopropoxides are generated as intermediates and serve as precursors of the cyclopropanol or siloxycyclopropane products. Owing to the fact that alkoxides are known to be more easily oxidized than the corresponding alcohols,[26] ET oxidation reactions of samarium cyclopropoxides formed in this manner should be possible. If so, it should be possible to carry out the sequential reductive cyclization−oxidative ring-opening reactions in one pot. As shown in Scheme 10, a one-pot procedure would represent a more concise and economical process, which is consistent with green and sustainable chemistry,[27] in contrast to the stepwise procedure described above. Under the one-pot conditions, samarium cyclopropoxide **18** would need to be oxidized by the ET reagents that we have used in the stepwise procedure. In addition, both the reductive cyclization and oxidative ring-opening reactions would need to take place in the same solvent. While SmI_2 is normally prepared in THF,[7,8] THF has not been usually used for oxidative ET reactions of cyclopropanol derivatives.[5]

To explore the one-pot technique, the conversion of **1a** to **7a** was explored (Scheme 11). A THF solution of β-bromoketone **1a** was first treated with SmI_2 followed by the addition of $FeCl_3$ and pyridine, with stirring at room temperature for 1 h and 85 °C for 2 h. As expected, the desired enone **7a** was generated in a 71% yield, which is better than the 65% yield that was obtained by using the stepwise procedure.

A small amount of the α-iodomethyl tetralone **19a**[28] was also formed (3%) in this one-pot reaction. NMR analysis of the crude reaction mixture, generated by using the one-pot method at room temperature, showed that **19a** and β-iodo benzosuberone **20a**[29] were present in a 1:15 ratio. The effects of changes in amines and oxidizing reagents (CAN and $Mn(OAc)_3$) on the efficiencies of the one-pot processes are summarized in Table 2.

As described above, whereas $FeCl_3$-promoted reaction of **1a** in the presence of pyridine gave **7a** as the major product (entry 2), the ratio of **7a** to **19a** was reversed when this process was conducted in the absence of pyridine (entry 1). Replacement of pyridine by Et_2NH led to a significant increase in the yield of **7a** (entry 4).[30] Increasing the equivalents of pyridine from 1 to

(22) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925–3941.

(23) Hasegawa, E.; Takizawa, S.; Iwaya, K.; Kurokawa, M.; Chiba, N.; Yamamichi, K. *J. Chem. Soc., Chem. Commun.* **2002**, 1966–1967.

(24) For a discussion of the reaction pathways for related radical rearrangements involving cyclopropoxy radicals, see: (a) Ryu, I.; Fukushima, H.; Okuda, T.; Matsu, K.; Kambe, N.; Sonoda, N.; Komatsu, M. *Synlett* **1997**, 1265–1268. (b) Chatgilialoglu, C.; Ferreiri, C.; Lucarini, M.; Venturini, A.; Zavitsas, A. *Chem. Eur. J.* **1997**, *3*, 376–387.

(25) Curtin-Hammett principle: *IUPAC. Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"); compiled by McNaught, A. D.; Wilkinson, A.; Blackwell Scientific Publications: Oxford, 1997. An example of Curtin−Hammett-type control of ET-radical reaction: Yoon, U. C.; Kwon, H. C.; Hyung, T. G.; Choi, K. H.; Oh, S. W.; Yang, S.; Zhao, Z.; Mariano, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 1110–1124.

(26) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970.

(27) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.

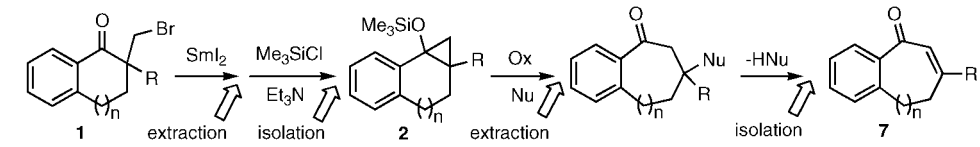
(28) Compound **19a** was identified by the direct comparison with the compound synthesized by α-iodomethylation of α-methyltetralone.

(29) Isolation and full characterization of the unstable substane **20a** has not been successful. Therefore, the structure of **20a** was tentatively assigned on the basis of the similarity of ^1H and ^{13}C NMR with those of the corresponding chloride **8a**.

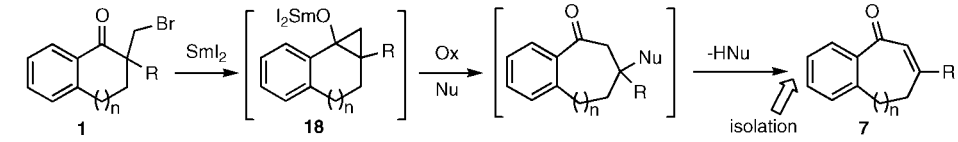
(30) Contrastive effect of Et_2NH on the yield of **3a** in entry 4 in Table 2 compared to that of entry 2 in Table 1 is interesting, although rationalization seems difficult. As expected, samarium alkoxide **18a** is more reactive than silyl ether **2a**, and therefore the reagent system of $FeCl_3$ and Et_2NH still has strong enough oxidizing ability for **18a**.

SCHEME 10

Stepwise procedure



One-pot procedure



SCHEME 11

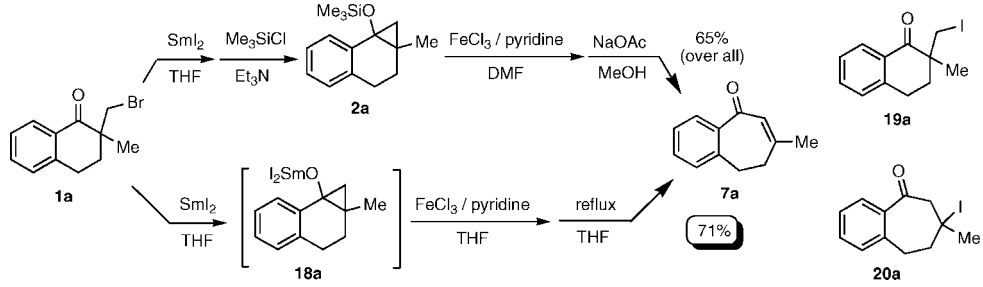
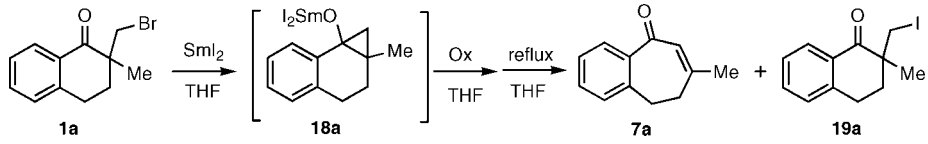


TABLE 2. One-Pot Technique for Sequential Reduction−oxidation-elimination reactions of 1a[a]

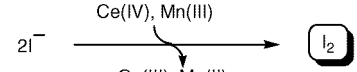


				yields[b] (%)	
entry	Ox	amine (equiv vs **1a**)	conv of **1a** (%)	**7a**	**19a**
1	$FeCl_3$	none	100	25	38
2	$FeCl_3$	pyridine (1.0)	100	71	3
3	$FeCl_3$	pyridine (2.0)	97	67	8
4	$FeCl_3$	Et_2NH (1.0)	100	94	4
5	$FeCl_3$	Et_2NH (5.0)	100	47	18
6	CAN[c]	none	83	tr	88
7	CAN[c]	pyridine (1.0)	100	2	87
8	$Mn(OAc)_3 \cdot 2H_2O$	none	100	tr	90
9	$Mn(OAc)_3 \cdot 2H_2O$	pyridine (1.0)	100	2	84

[a] (i) Compound **1a** (0.50 mmol), SmI_2 (2.2 equiv), THF (12.0 mL), at room temperature for 30 min; (ii) Ox (2.2 equiv), THF (5.0 mL), at room temperature for 1 h; (iii) heated at 85 °C for 2 h. [b] Based on the conversion of **1a**. [c] $Ce(NH_4)_2(NO_3)_6$

2 equiv relative to **1a** caused only a slight change in the ratio and yields of **7a** and **19a**. Similarly, increasing the quantity of Et_2NH (up to 5 equiv) had an impact on the product ratio (entry 5).[31] Notably, **19a** was the exclusive product formed in reactions in which CAN and $Mn(OAc)_3$ were used as oxidants, regardless of whether pyridine was present or absent (entries 6−9).

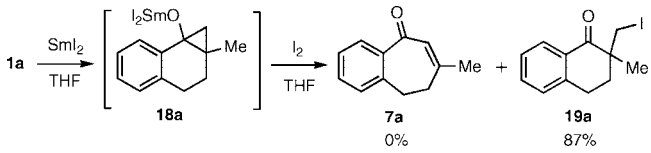
A characteristic color change to brown took place when CAN or $Mn(OAc)_3$ was added. This is likely associated with the formation of iodine molecule (I_2). This observation led to a working hypothesis that iodide ion (I^-) is oxidized by Ce(IV) or Mn(III) to give I_2 on the basis of their redox potentials (see below).[32] In order to determine if this hypothesis is correct, experiments were performed to see if cyclopropanols react with I_2.[33] When I_2 was added to the mixture obtained from the reaction of **1a** with SmI_2, **19a** was produced exclusively (no **7a** was formed) (Scheme 12). Similarly, treatment of silyl ether **2a** with I_2 led to formation of **19a** exclusively (Scheme 13).



	Ce(VI)/Ce(III)	Mn(III)/Mn(II)	Fe(III)/Fe(II)	$I_2/2I^-$
E^o in H_2O (V *vs* NHE)	1.70	1.49	0.75	0.54

We were interested in knowing if the oxidizing reagents used in these processes would oxidize iodide ion. Then, we conducted the reaction of **2a** with $FeCl_3$ and pyridine and with CAN in

SCHEME 12



SCHEME 13

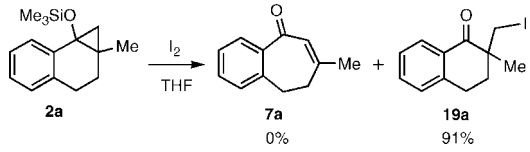
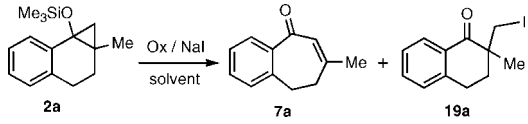


TABLE 3. Oxidation of 2a in the Presence of NaI



entry	Ox	NaI (equiv vs **2a**)	solvent	conv of **2a** (%)	yields (%) **7a**	**19a**
1[b]	$FeCl_3$/pyridine	0.0	DMF	100	72	0
2[b]	$FeCl_3$/pyridine	5.0	DMF	100	70	3
3	CAN[c]	0.0	MeCN	100	53	0
4	CAN[c]	5.0	MeCN	100	1	90

[a] Compound **2a** (0.50 mmol), Ox (2.2 equiv), solvent (5.0−10.0 mL), at room temperature for 1 h. [b] Pyridine (1.0 equiv), crude product mixture was refluxed with NaOAc in MeOH for 2 h. [c] $Ce(NH_4)_2(NO_3)_6$

the presence of NaI. The results are summarized in Table 3. In the reaction of **2a** with $FeCl_3$ and pyridine, **7a** was a major product regardless of whether NaI was present or absent (entries 1 and 2). However, in the reaction with CAN, **19a** became the exclusive product in the presence of NaI (entries 3 and 4).[34] This contrasting result is consistent with the hypothesis that iodide ion is more efficiently oxidized by CAN than by $FeCl_3$ with pyridine.

On the basis of above results, a plausible mechanism for the one-pot reaction of the bromomethyl ketone **1a** involves SET oxidation of the cyclopropoxy-samarium intermediate **18a** by $FeCl_3$ to produce the corresponding radical cation that then undergoes samarium ion elimination and subsequent internal-bond cleavage of cyclopropoxy radical **13a** (Scheme 14, *path A*). The formed alkyl radical **14a** is oxidized by another equivalent of $FeCl_3$ to form the tertiary carobocation **15a** that is trapped by iodide ion to give **20a**, which undergoes elimination to produce **7a**. On the other hand, in the cases of oxidations promoted by the relatively strong oxidants CAN and $Mn(OAc)_3$, iodide ion is transformed to I_2 (Scheme 14, *path B*). A following electrophilic attack of I_2 on the cyclopropane ring of **18a** results in production of carbocation **21a**, and elimination of samarium ion gives **19a** as an isolable product. *Paths A* and *B* both operate in the reaction promoted by $FeCl_3$ in the absence of an amine (see entry 1 of Table 2).[35]

As described above, the combination of $FeCl_3$ and amine is effective for the one-pot transformation of **1a** to **7a**. Sequential reductive cyclization−oxidative ring-opening reactions utilizing these conditions were applied to reactions of other substrates. The results are summarized in Scheme 15. In most of the cases, the yields of desired 3-substituted-enones **7** were greater than those arising from application of the stepwise procedure. Importantly, the one-pot method was effective in transforming the nonbenzocyclic substrates **22** to the enone **23**. It should be noted that when pyridine was replaced by Et_2NH, the yield of **6** (61%) in the one-pot reaction of **1b** did not significantly change. However the one-pot reaction of **1d** in the presence of Et_2NH was not efficient, resulting in the formation of **7d** in only a 39% yield. Thus, it appears that the method using pyridine gives more consistent results than that using Et_2NH. Finally, the one-pot reaction of **3** did not form **11**.

Summary. As shown by the results described above, β-bromo ketones undergo cyclization and ring-expansion reactions that involve sequential reductive formation and oxidative ring opening of cyclopropanol intermediates. Characteristic features of this unique two-step process are the operation of an intramolecular samarium-Barbier reaction of α-bromomethyl cycloalkanones and regioselective oxidative ring opening of the resulting cyclopropanols embedded in bicyclo[*m*.1.0]alkane frameworks. This reaction sequence leads to the production of various 3-substituted cyclic-enones that serve as precursors for the formation of quarternary carbon-centered systems.[36] A further notable observation made in this effort is that this sequence can be performed by using a one-pot procedure.[37] Under the one-pot conditions, contrasting regioselectivities of cyclopropane ring opening are observed depending upon the nature of the oxidizing reagent used. The oxidizing reagent dependency of these one-pot processes can be explained by whether or not molecular iodine is produced. When the oxidizing reagent is sufficiently strong to transform iodide ion into iodine, the predominant pathway followed involves external-bond cleavage of bicycloalkane framework.

Experimental Section

Preparations of Bromoalkyl-cycloalkanones: 2-Bromomethyl-2-methyl-1-tetralone (1a). To the suspension of NaH (1.06 g, 26.4 mmol) in THF (13.0 mL) was added HMPA (4.6 mL, 26.4 mmol). Subsequently, 2-methyl-1-tetralone (3.53 g, 22.0 mmol) in THF (12.0 mL) was added, and the mixture was stirred under N_2 at room temperature. After 1 h, CH_2Br_2 (4.6 mL, 66 mmol) was added, and the mixture was stirred at reflux (85 °C) for 22 h. Then, it was

(31) At the moment, the origin of the amine effect causing the considerable formation of **19a** is unclear. It might be that the amine coordinates with the samarium ion to weaken the Sm-O bond of cyclopropoxide, which then assists the external bond cleavage of cyclopropoxy anion.

(32) *Lange's Handlectron Transfer in Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985; Section 6.

(33) To the best of our knowledge, reactions of cyclopropanol derivatives with iodine are unprecedented, whereas those with bromine have been reported.[4] Also see: Murai, S.; Seki, Y.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1974**, 1032–1033.

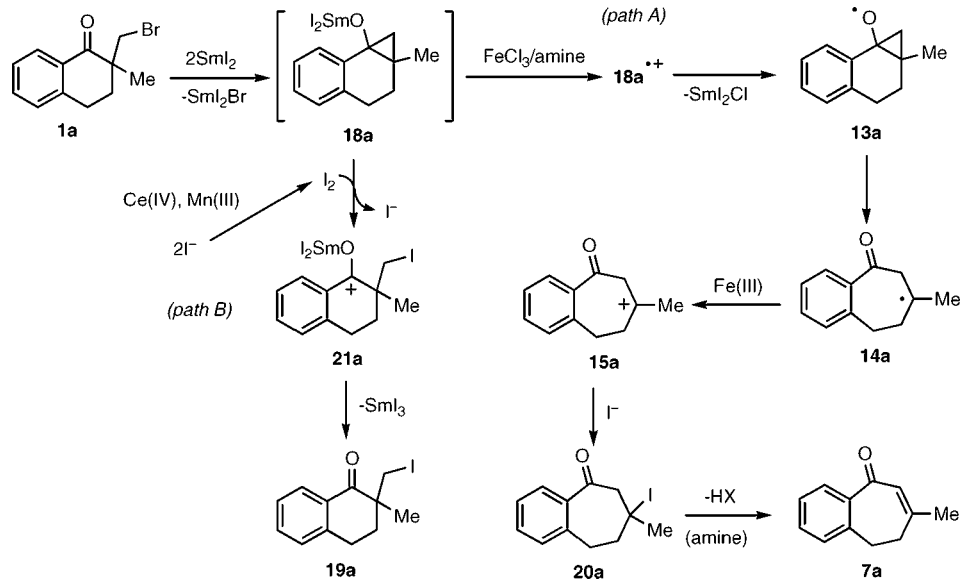
(34) Our observation might be related to those made by Flowers[5m] in which cyclopropanol ring-opening reactions are promoted by CAN in the presence of certain nucleophiles.

(35) A question raised in this effort concerns why the weaker oxidizing reagent $FeCl_3$ promotes SET reaction of **18a** but the stronger oxidizing reagents CAN and $Mn(OAc)_3$ do not. A clear explanation of this finding is not available at the moment. It is possible to hypothesize that **18a** more efficiently reacts with iodine than with the metal reagents and that the latter SET steps between **18a** and the reagents is reversible.

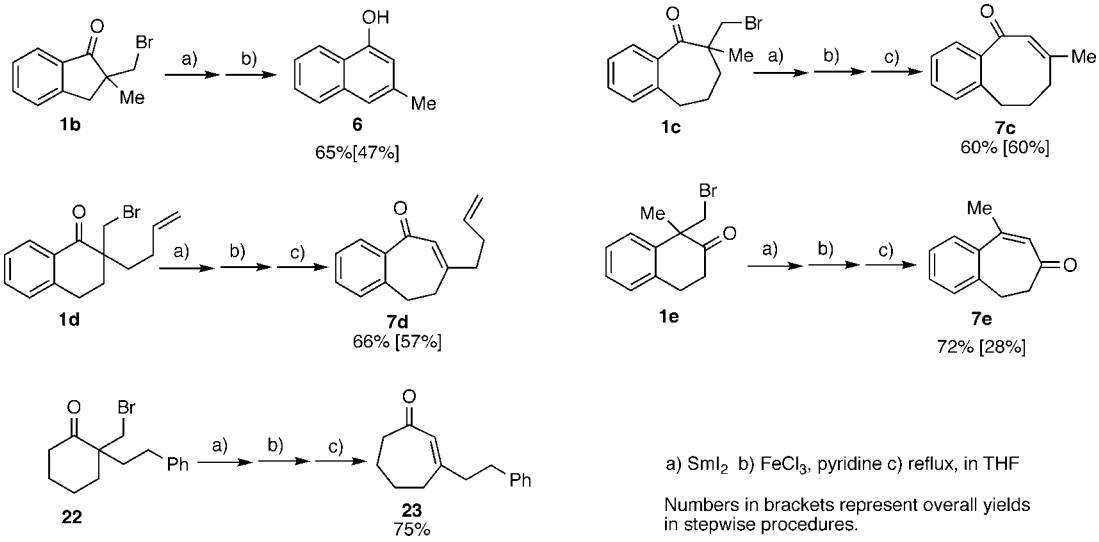
(36) *Quaternary Stereocenters: Challenge and Solutions for Organic Synthesis*; Christoffers, J., Baro, A., Eds; Wiley-VCH: Weinheim, 2005.

(37) A reviewer suggested the applicability of the reductive regeneration of samarium(II) from the produced samarium(III) to our reaction system, which might be an interesting future subject to investigate since catalytic use of samarium is also consistent with green and sustainable chemistry. Representative examples of reductive regeneration of samarium(II): (a) Nomura, R.; Matsuno, T.; Endo, T. *J. Am. Chem. Soc.* **1996**, *118*, 11666–11667. (b) Corey, E. J.; Zheng, G. Z. *Tetrahedron Lett.* **1997**, *38*, 2045–2048. (c) Parrisha, J. D.; Little, R. D. *Tetrahedron Lett.* **2001**, *42*, 7767–7770. (d) Shean, J. J.; Fang, J. M. *J. Org. Chem.* **2001**, *66*, 3533–3537.

SCHEME 14



SCHEME 15



extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography on silica gel (CH_2Cl_2/*n*-hexane = 1/1) to give 2-bromomethyl-2-methyl-1-tetralone **1a** (2.71 g, 10.7 mmol, 49%). Compound **1b**, **1c**, **1d**, and **1e** were similarly prepared. Data for **1a**: pale yellow oil; IR (Neat) 1680 cm^{-1}; ^1H NMR (200 MHz) δ 1.30 (s, 3H), 1.96−2.09 (m, 1H), 2.30−2.44 (m, 1H), 2.91−3.05 (m, 1H), 3.50 (d, J = 10.3 Hz, 1H), 3.81 (d, J = 10.3 Hz, 1H), 7.22−7.35 (m, 2H), 7.44−7.52 (m, 1H), 8.04 (m, 1H); ^{13}C NMR (50 MHz) δ 21.1, 25.1, 32.6, 40.6, 45.9, 126.8, 128.0, 128.7, 131.0, 133.6, 143.1, 199.0; LRMS (EI) *m*/*z* (relative intensity) 252 (M^+, 30), 254 (M^+ + 2, 30), 173 (100); HRMS (EI) calcd for $C_{12}H_{13}O^{79}Br$ 252.0149, found 252.0150 (M^+), calcd for $C_{12}H_{13}O^{81}Br$ 254.0129, found 254.0122 (M^+ + 2). Data for **1b**: colorless oil; IR (KBr) 1702 cm^{-1}; ^1H NMR (200 MHz) δ 1.34 (s, 3H), 2.95 (d, J = 17.3 Hz, 1H), 3.39−3.66 (m, 3H), 7.35−7.79 (m, 4H); ^{13}C NMR (50 MHz) δ 23.9, 39.3, 39.6, 50.0, 122.4, 126.6, 127.6, 135.2, 135.3, 152.2, 207.1; LRMS (EI) *m*/*z* (relative intensity) 238 (M^+, 2), 240 (M^+ + 2, 2), 159 (100). Data for **1c**: pale yellow oil; IR (Neat) 2924, 1668, 1442, 1250, 960, 738 cm^{-1}; ^1H NMR (200 MHz) δ 1.29 (s, 3H), 1.66−2.03 (m, 4H), 2.75−2.81 (m, 2H), 3.49 (d, J = 10.0 Hz, 1H), 3.62 (d, J = 10.0 Hz, 1H), 7.09−7.40 (m, 4H); ^{13}C NMR (50 MHz) δ 22.2, 22.6, 32.8, 41.7, 49.7, 126.6, 127.6, 128.4, 131.1, 137.0, 140.7, 211.0; LRMS (EI) *m*/*z* (relative intensity) 266 (M^+, 1), 268 (M^+ + 2, 1), 91 (100). Data for **1e**: yellow oil; IR (Neat) 1714 cm^{-1}; ^1H NMR (200 MHz) δ 1.50 (s, 3H), 2.62−2.86 (m, 2H), 2.98−3.18 (m, 2H), 3.57 (d, J = 9.9 Hz, 1H), 4.09 (d, J = 9.9 Hz, 1H), 7.19−7.33 (m, 4H); ^{13}C NMR (50 MHz) δ 27.0, 28.0, 37.9, 39.1, 52.6, 126.0, 127.1, 127.2, 128.3, 136.3, 139.6, 211.4; LRMS (EI) *m*/*z* (relative intensity) 252 (M^+, 16), 254 (M^+ + 2, 15), 131 (100); HRMS (EI) calcd for $C_{12}H_{13}O^{79}Br$ 252.0149, found 252.0152 (M^+), calcd for $C_{12}H_{13}O^{81}Br$ 254.0129, found 254.0125 (M^+ + 2).

Preparation of 2-Bromomethyl-2-phenethylcyclohexanone (22). 2-Phenethyl-2-mesyloxymethylcyclohexanone (915 mg, 2.95 mmol) and LiBr (852 mg, 9.81 mmol) were added to acetone (7.0 mL), and the mixture was refluxed at 65 °C for 42 h. Then, it was extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography on silica gel (EtOAc/*n*-hexane = 1/10) and distilled under reduced pressure to give 2-bromomethyl-2-phenethylcyclohexanone **22** (521.5 mg, 1.77 mmol, 60%). Data for **22**: pale yellow oil; IR (Neat) 2932, 1704 cm^{-1}; ^1H NMR

(270 MHz) δ 1.63−2.62 (m, 12H), 3.55 (d, J = 10.8 Hz, 1H), 3.81 (d, J = 10.8 Hz, 1H), 7.14−7.32 (m, 5H); ^{13}C NMR (68 MHz) δ 20.7, 27.3, 29.9, 36.2, 36.9, 39.4, 39.6, 52.1, 126.0, 128.2, 128.4, 141.2, 212.2; LRMS (EI) *m*/*z* (relative intensity) 296 (M^+, 2), 298 (M + 2, 2), 192 (100).

Preparation of Cyclopropyl Silyl Ethers: 6-Methyl-1-trimethylsilyloxy-2,3-benzobicyclo[4.1.0]hepta-2-ene (2a). To a solution of SmI_2 (0.1 M in THF, 11.0 mL, 1.10 mmol) was added **1a** (127 mg, 0.50 mmol) in THF (1.0 mL). The mixture was stirred under N_2 at room temperture for 30 min. Then, it was extracted with Et_2O after addition of 0.1 N aqueous HCl. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine. The ether solution was dried over $MgSO_4$, and the filtrate was concentrated. Then, Et_3N (0.21 mL, 1.50 mmol) and Me_3SiCl (0.15 mL, 1.20 mmol) were added to the residue in CH_2Cl_2 (3.0 mL). The mixture was stirred at room temperture for 30 min. Then, it was extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, brine, and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography on silica gel (EtOAc/*n*-hexane = 1/5) to give 6-methyl-1-trimethylsilyloxy-2,3-benzobicyclo[4.1.0]hepta-2-ene **2a** (111.0 mg, 0.44 mmol, 88%) as a colorless oil. **2b**, **2c**, **2d**, and **2e** were similarly prepared. Data for **2e**: colorless oil; IR (Neat) 2924, 1248, 836 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.19 (s, 9H), 0.80 (d, J = 5.7 Hz, 1H), 1.28 (d, J = 5.7 Hz, 1H), 1.53 (s, 3H), 1.97−2.11 (m, 1H), 2.25 (m, 1H), 2.52−2.74 (m, 2H), 6.97−7.07 (m, 2H), 7.15 (m, 1H), 7.37 (m, 1H); ^{13}C NMR (68 MHz) δ 1.4, 16.6, 22.9, 23.5, 27.6, 28.0, 64.6, 124.5, 125.5, 126.0, 128.1, 133.4, 141.6; LRMS (EI) *m*/*z* (relative intensity) 246 (M^+, 5), 75 (100).

Preparation of 6a,7-Dihydrobenzo[*b*]cyclopropa[*d*]pyran-7a-ol (4).[16] To 2-allyloxybenzoic acid (172 mg, 0.96 mmol) in benzene (5.0 mL) was added Et_3N (0.51 mL, 3.6 mmol). The mixture was cooled to 0 °C, and $SOCl_2$ (0.18 mL, 2.4mmol) was added. The mixture was stirred at 0 °C for 30 min and warmed to room temperature. After 1.5 h, the filtrate was concentrated to obtain 2-allyloxybenzoyl chloride **3**. Then, **3** in THF (2 mL) was added to a solution of SmI_2 (0.1 M in THF, 21.1 mL, 2.11 mmol). The mixture was stirred at room temperature for 30 min. Then, it was extracted with Et_2O after addition of 0.1 N aqueous HCl. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography on silica gel (EtOAc/benzene = 1/1) to give 6a,7-dihydrobenzo[*b*]cyclopropa[*d*]pyran-7a-ol **4** (58.6 mg, 0.36 mmol, 38%). Data for **3**: brown oil; ^{1}H NMR (270 MHz) δ 4.46 (m, 2H), 5.32 (m, 1H), 5.51 (m, 1H), 5.97−6.13 (m, 1H), 6.93−7.12 (m, 2H), 7.56 (m, 1H), 8.08 (m, 1H). Data for **4**: brown oil; IR (Neat) 3336, 1256, 1206 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.17 (t, J = 6.1 Hz, 1H), 1.34 (dd, J = 9.7, 5.4 Hz, 1H), 1.84 (m, 1H), 3.23 (broad s, 1H), 3.79 (d, J = 10.8 Hz, 1H), 4.15 (dd, J = 10.5, 1.1 Hz, 1H), 6.81 (m, 1H), 6.98 (m, 1H), 7.10 (m, 1H), 7.57 (m, 1H); ^{13}C NMR (68 MHz) δ 18.1, 27.3, 51.8, 62.3, 116.8, 121.6, 124.3, 126.9, 129.4, 150.7; LRMS (EI) *m*/*z* (relative intensity) 162 (M^+, 51), 120 (100); HRMS (EI) calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0677.

Preparation of 1,1a,2,7b-Tetrahydro-7b-trimethylsilyloxy-benzo[*b*]cyclopropa[*d*]pyran (5). To **4** (145 mg, 0.89 mmol) in CH_2Cl_2 (3.0 mL) were added Et_3N (0.37 mL, 2.68 mmol) and Me_3SiCl (0.27 mL, 2.14 mmol). The mixture was stirred at room temperture for 30 min. Then, it was extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to column chromatography on silica gel (EtOAc/*n*-hexane = 1/10) to give 1,1a,2,7b-Tetrahydro-7b-trimethylsilyloxy-benzo[*b*]cyclopropa[*d*]-pyran **5** (151.5 mg, 0.65 mmol, 73%). Data for **5**: pale yellow oil; IR (Neat) 2952, 1250, 1210, 834 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.17 (s, 9H), 1.16 (t, J = 5.8 Hz, 1H), 1.35 (dd, J = 9.7, 5.4 Hz, 1H), 1.90 (m, 1H), 3.90 (d, J = 10.3 Hz, 1H), 4.21 (d, J = 10.5 Hz, 1H), 6.80 (m, 1H), 6.98 (m, 1H), 7.09 (m, 1H), 7.52 (m, 1H); ^{13}C NMR (68 MHz) d 1.4, 18.0, 26.3, 53.3, 62.1, 116.7, 121.4, 125.1, 126.6, 129.9, 150.6; LRMS (EI) *m*/*z* (relative intensity) 234 (M^+, 93), 75 (100); HRMS (EI) calcd for $C_{13}H_{18}O_2Si$ 234.1076, found 234.1079.

Reaction of Cyclopropyl Silyl Ether with $FeCl_3$. To $FeCl_3$ (1.10 mmol) and pyridine (0.50 mmol) in DMF (2.0 mL) was added **2** (0.50 mmol) in DMF (3.0 mL) under N_2. The mixture was stirred under N_2 at room temperature for 1 h. Then, it was extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine. The ether solution was dried over anhydrous $MgSO_4$, and the filtrate was concentrated. Then, NaOAc (2.5 mmol) and MeOH (5.0 mL) were added to the residue, and the mixture was refluxed at 85 °C. After 2 h, it was extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to TLC (CH_2Cl_2/*n*-hexane = 1/1) and **7** was obtained. Same treatment of **4** and **5** with $FeCl_3$ gave **11**[38] and **12**. Data for **7e**: yellow oil; IR (Neat) 1656 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.34 (d, J = 1.1 Hz, 3H), 2.67 (m, 2H), 2.97 (m, 2H), 6.28 (s, 1H), 7.29 (m, 3H), 7.48 (m, 1H); ^{13}C NMR (50 MHz) δ 26.1, 29.9, 44.1, 126.9, 128.1, 128.7, 129.2, 129.6, 136.9, 141.0, 148.5, 202.5; LRMS (EI) *m*/*z* (relative intensity) 172 (M^+, 51), 129 (100); HRMS (EI) calcd for $C_{12}H_{12}O$ 172.0888, found 172.0890. Data for **9a**: white solid, mp 110.9−111.7 °C; IR (Nujol) 3408, 1662 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.44 (s, 3H), 1.88−2.10 (m, 2H), 2.15 (broad s, 1H), 2.93 (dd, J = 15.8, 10.1 Hz, 1H), 2.96 (d, J = 11.1 Hz, 1H), 3.81 (d, J = 10.3 Hz, 1H), 3.09 (d, J = 11.6 Hz, 1H), 3.27 (dd, J = 16.7, 8.4 Hz, 1H), 7.27 (m, 2H), 7.40 (m, 1H), 7.78 (m, 1H); ^{13}C NMR (68 MHz) δ 29.9, 31.1, 42.3, 55.9, 71.7, 126.4, 128.6, 130.2, 131.7, 138.1, 144.0, 200.5; LRMS (EI) *m*/*z* (relative intensity) 190 (M^+, 0.3), 129 (100). Data for **11**:[38] pale yellow oil; IR (Neat) 2912, 1664, 1598, 1282 cm^{-1}; ^{1}H NMR (270 MHz) δ 5.00 (t, J = 1.5 Hz, 2H), 5.58 (d, J = 0.8 Hz, 1H), 6.31 (d, J = 1.1 Hz, 1H), 6.95−7.10 (m, 2H), 7.48 (m, 1H), 7.99 (m, 1H); ^{13}C NMR (68 MHz) δ 71.2, 118.0, 121.8, 122.4, 127.9, 136.0, 138.7, 160.5, 161.8, 181.8; LRMS (EI) *m*/*z* (relative intensity) 160 (M^+, 100); HRMS (EI) calcd for $C_{10}H_8O_2$ 160.0524, found 160.0523. Data for **12**: brown oil; IR (Neat) 1690, 1606, 1478 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.98−3.11 (m, 1H), 3.38 (s, 3H), 3.64−3.83 (m, 2H), 4.42 (dd, J = 11.4, 9.9 Hz, 1H), 4.63 (dd, J = 11.4, 4.9 Hz, 1H), 6.95−7.05 (m, 2H), 7.47 (m, 1H), 7.89 (m, 1H); ^{13}C NMR (50 MHz) δ 46.4, 59.2, 68.2, 69.0, 117.8, 120.8, 121.3, 127.2, 135.9, 161.7, 192.0; LRMS (EI) *m*/*z* (relative intensity) 192 (M^+, 36), 120 (100); HRMS (EI) calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0784.

One-Pot Reduction−Oxidation Reaction of α-Bromomethyl Cycloalkanone. To a solution of SmI_2 (0.1 M in THF, 11.0 mL, 1.10 mmol) was added **1** or **22** (0.50 mmol) in THF (1.0 mL), and the mixture was stirred under N_2 at room temperature. After 30 min, $FeCl_3$ (1.10 mmol) and pyridine (0.50 mmol) in THF (5.0 mL) was added, and the mixture was stirred. After 1 h, the mixture was stirred at reflux (85 °C) for 2 h. Then, it was extracted with Et_2O after addition of water. The extract was treated with water, saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to TLC (CH_2Cl_2/*n*-hexane = 1/1), and **7** or **23**[39] was obtained. The same treatment of **3** with $FeCl_3$ gave a complicated mixture. Data for **19a**: orange oil; IR (Neat) 1674 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.30 (s, 3H), 2.03 (m, 1H), 2.23 (m, 1H), 2.98 (m, 1H), 3.33 (d, J = 10.0 Hz, 1H), 3.61 (d, J = 9.7 Hz, 1H), 7.20−7.35 (m, 2H), 7.47 (m, 1H), 8.04 (m, 1H); ^{13}C NMR (68 MHz) δ 16.2, 22.7, 25.4, 34.9, 45.0, 126.8, 128.1, 128.7, 130.9, 133.5, 143.0, 197.9; LRMS (EI) *m*/*z* (relative intensity) 300 (M^+,

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16), 145 (100); HRMS (EI) calcd for $C_{12}H_{13}OI$ 300.0011, found 300.0015. Data for **23**:[39] pale yellow oil; IR (Neat) 2932, 1658 cm^{-1}; ^1H NMR (270 MHz) δ 1.78 (m, 4H), 2.14−2.60 (m, 6H), 2.80 (m, 1H), 5.93 (s, 1H), 7.16−7.33 (m, 5H); ^{13}C NMR (68 MHz) d 21.2, 25.1, 32.8, 34.1, 42.2, 42.7, 126.0, 128.1, 128.3, 129.3, 140.6, 160.7, 203.6; LRMS (EI) *m*/*z* (relative intensity) 214 (M^+, 48), 91 (100); HRMS (EI) calcd for $C_{15}H_{18}O$ 214.1358, found 214.1360. Data for **8a**:[6f] white solid, mp 56.2−60.3 °C; ^1H NMR (200 MHz) δ 1.78 (s, 3H), 2.02 (ddd, J = 15.4, 10.3, 1.2 Hz, 1H), 2.55 (ddt, J = 15.4, 8.1, 1.2 Hz, 1H), 3.05 (dd, J = 17.0, 7.9 Hz, 1H), 3.12 (dd, J = 11.7, 1.4 Hz, 1H), 3.41 (dd, J = 17.8, 10.8 Hz, 1H), 3.53 (d, J = 11.7 Hz, 1H), 7.24−7.46 (m, 3H), 7.79 (m, 1H); ^{13}C NMR (50 MHz) δ 31.4, 32.4, 44.9, 57.6, 69.3, 126.6, 129.0, 130.3, 132.0, 137.8, 143.8, 198.0. Data for **20a**: yellow oil; ^1H NMR (270 MHz) δ 1.70 (dd, J = 15.9, 10.0 Hz, 1H), 2.18 (s, 3H), 2.90 (dd, J = 15.9, 7.8 Hz, 1H), 3.03−3.12 (m, 1H), 3.23−3.35 (m, 1H), 3.80 (d, J = 11.9 Hz, 1H), 7.30 (m, 2H), 7.42 (m, 1H), 7.77 (m, 1H); ^{13}C NMR (68 MHz) δ 33.2, 37.5, 46.7, 49.4, 62.1, 126.5, 128.9, 130.4, 131.9, 137.8, 143.8, 197.1.

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Supporting Information Available: ^1H NMR, ^{13}C NMR, and IR charts of new compounds; additional procedures for the preparation of some intermediate compounds and their ^1H NMR data and charts. This material is available free of charge via the Internet at http://pubs.acs.org.

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