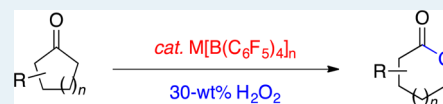


Baeyer–Villiger Oxidation Using Hydrogen Peroxide

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ABSTRACT: The Baeyer–Villiger (BV) oxidation of carbonyl compounds to the corresponding esters or lactones is one of the most important transformations. We recently introduced a highly efficient and selective $\text{LiB}(\text{C}_6\text{F}_5)_4$ - or $\text{Ca}[\text{B}(\text{C}_6\text{F}_5)_4]_2$ -catalyzed BV oxidation of ketones with aqueous hydrogen peroxide to give the corresponding lactones in high yield. In this perspective article, we focus on our discovery and the development of BV oxidation reactions and cascade oxidative transformations through representative metal catalysts and organocatalysts.



KEYWORDS: Baeyer–Villiger oxidation, hydrogen peroxide, transition-metal catalysis, organocatalysis, tetraaryl borate salts

1. INTRODUCTION

In 1899, Adolf Baeyer and Victor Villiger reported the oxidation of menthone to its corresponding lactone using a mixture of persulfate and concentrated sulfuric acid (Caro's acid).¹ Since then, Baeyer–Villiger (BV) oxidation has become one of the most important transformations in organic synthesis, since valuable lactones or esters can be obtained directly from the corresponding ketones.² In general, percarboxylic acids (i.e., *meta*-chloroperbenzoic acid (*m*-CPBA), peracetic acid, etc.) are used for BV oxidation.² However, the use of percarboxylic acid results in the formation of one equivalent of the corresponding carboxylic acid or its salt as waste. Moreover, percarboxylic acids are expensive and/or shock-sensitive. In contrast, the use of hydrogen peroxide has many advantages: it is safe and inexpensive, its active oxygen content is high, it does not require a buffer, and it is clean, since water is the only byproduct formed.³ Attention is now focused on how to replace percarboxylic acids with aqueous hydrogen peroxide. There have been some successful examples of the BV oxidation of ketones with aqueous hydrogen peroxide promoted by homogeneous transition-metal^{4–11} or organocatalysts,^{12–21} and heterogeneous catalysts.^{22–24}

Recently, we developed a highly efficient and selective $\text{LiB}(\text{C}_6\text{F}_5)_4$ - or $\text{Ca}[\text{B}(\text{C}_6\text{F}_5)_4]_2$ -catalyzed BV oxidation of ketones with 30-wt % aqueous hydrogen peroxide to give the corresponding lactones in high yield.²⁵ Additionally, β -silyl cyclohexanones can be oxidized to the corresponding unsaturated carboxylic acids or hydroxylactones in high yields via BV oxidation/ β -elimination reaction sequences and subsequent epoxidation/cyclization reaction sequences.

In this perspective article, we focus on our discovery and the development of BV oxidation reactions and cascade oxidative transformations using aqueous hydrogen peroxide. Representative BV oxidations using transition-metal or other main group metal catalysts and organocatalysts are also briefly highlighted.

2. METAL CATALYSTS

To date, several transition and main group metal complexes have been used as catalysts for the BV oxidation using hydrogen

peroxide. These include $(\text{Me})\text{ReO}_3$,⁴ Lewis acids based on Pt^{II} ,⁵ Sn^{IV} ,⁶ and Sc^{III} ,⁷ chiral Co ,⁸ Zr ,⁹ Pd ,¹⁰ and Pt^{II} complexes developed for the asymmetric BV oxidation, and also some heterogeneous systems based on Sn^{IV} embedded in zeolites²² or mesoporous silicas such as MCM-41²³ or hydrotalcites.²⁴ Among them, Pt^{II} catalysts developed by Strukul and colleagues show the most versatile activity and selectivity (Chart 1).⁵ These features are considered to be the result of the unique electronic properties of the metal combined with a soft Lewis acid character modulated by the proper choice of ancillary phosphine ligands.⁵

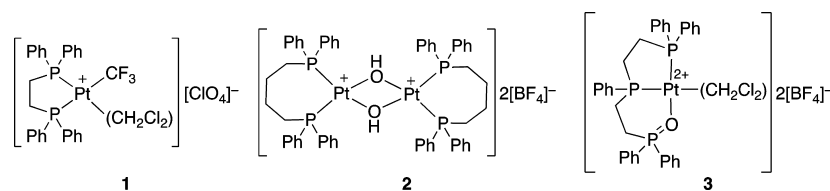
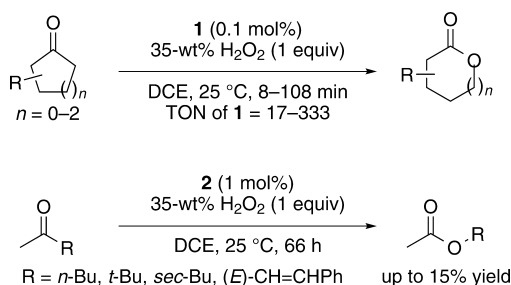
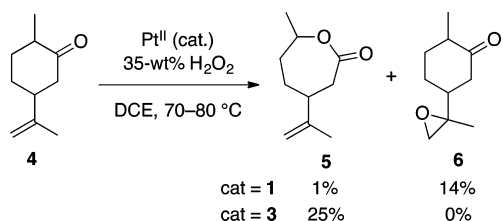
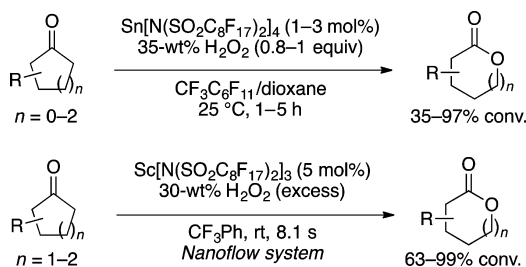
Historically, Pt^{II} catalyst **1** was developed for epoxidation reactions using hydrogen peroxide and was also the first to be found to be active for the BV reaction. Various cycloalkanones (4- to 6-membered rings) can be converted using **1**, and the TON (turnover number) of **1** was shown to reach 233 for the oxidation of cyclobutanone (Scheme 1).^{5a} Catalyst **2** was reactive toward a series of not only cycloalkanones (4- to 6-membered rings), but also acyclic ketones with high efficiency using aqueous 35-wt % H_2O_2 solution (Scheme 1).^{5b,c} However, acyclic ketones were oxidized slowly with poor yields. Catalyst **3** has a double positive charge, which might increase its Lewis acidity, and, similar to **1**, is a single site catalyst. In the oxidation of unsaturated ketone **4**, the use of catalyst **3** gave lactone **5**, albeit in low yield, while the use of **1** gave epoxide **6** as the major product (Scheme 2).^{5d}

Tin bis(perfluoroalkanesulfonyl)imide, $\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$, was successfully used for the BV oxidation of cycloalkanones (4- to 6-membered rings) using 35% aqueous hydrogen peroxide in a fluorosol biphasic catalytic system (Scheme 3).⁶ Furthermore, the catalyst was easily recovered and reused in the fluorosol immobilized phase without a loss of activity. A continuous-flow system was used to achieve high-yielding and selective BV oxidation reactions. Indeed, both the reaction rate and the regioselectivity of the scandium bis-

Received: December 17, 2012

Revised: January 29, 2013

Published: February 22, 2013

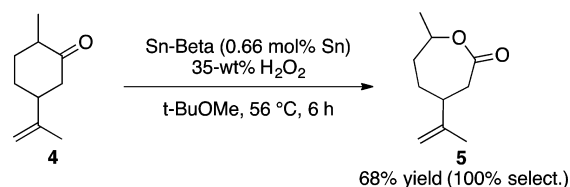
Chart 1. Pt^{II} Catalysts 1–3⁵Scheme 1. Pt^{II}-Catalyzed BV Oxidations of Cyclic and Linear Ketones⁵Scheme 2. Selective Oxidation of Unsaturated Ketone 4 by Pt Catalysts 1 and 3⁵Scheme 3. Sn^{IV}- or Sc^{III}-Catalyzed BV Oxidation of Cycloalkanones^{6,7}

(perfluoroalkanesulfonyl)imide-catalyzed BV oxidation of cycloalkanones were remarkably increased using a nanoflow microreactor even at a low concentration of the catalyst (≤ 0.1 mol %) (Scheme 3).⁷

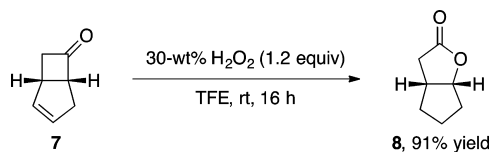
Tin-containing beta zeolites developed by Corma and colleagues have become some of the most chemoselective heterogeneous catalysts for the BV reaction of unsaturated ketones. For instance, these catalysts exhibited enzyme-like selectivity toward lactone for the oxidation of dihydrocarvone using 35-wt % H_2O_2 (Scheme 4).²² These results could be explained by activation of the carbonyl group rather than hydrogen peroxide on the Sn atoms in beta zeolite.

3. ORGANOCATALYSTS

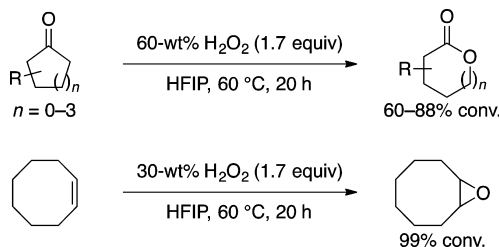
In 1986, Matsumoto and colleagues reported that cyclobutanones were selectively oxidized to give γ -butyrolactones

Scheme 4. Sn-Beta-Catalyzed BV Oxidation of Unsaturated Ketone 4²²

with aqueous hydrogen peroxide in 2,2,2-trifluoroethanol (TFE) without the use of any additional catalyst (Scheme 5).¹²

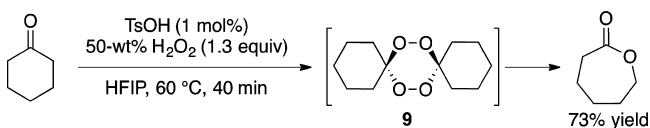
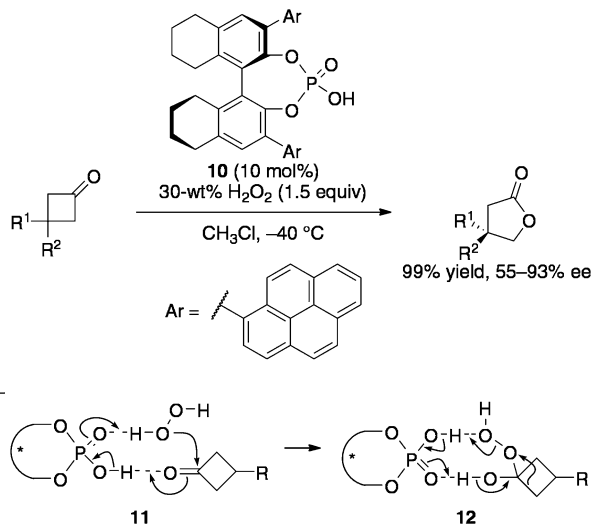
Scheme 5. BV Oxidation of Cyclobutanone 7 In TFE¹²

In 2000, Neumann and colleagues reported the electrophilic activation of hydrogen peroxide by another perfluorinated solvent, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), in the epoxidation of olefins and the BV oxidation of cycloalkanones in the absence of catalysts (Scheme 6).¹³ Based on the result of

Scheme 6. BV Oxidation and Epoxidation Reactions Using Hydrogen Peroxide in HFIP¹³

an NMR analysis, hydrogen bonding was proposed to occur between fluorinated alcohol and hydrogen peroxide, which would make hydrogen peroxide more electrophilic, and which in turn should indeed promote the attack of olefins but not ketones by peroxides.¹³ Later, Berkessel and colleagues explained that Brønsted acid-catalyzed BV oxidations with hydrogen peroxide proceed by a nonclassical mechanism in HFIP through the intermediacy of spirobisperoxide (9), which is activated by the Brønsted acid to give the corresponding lactone (Scheme 7).¹⁴

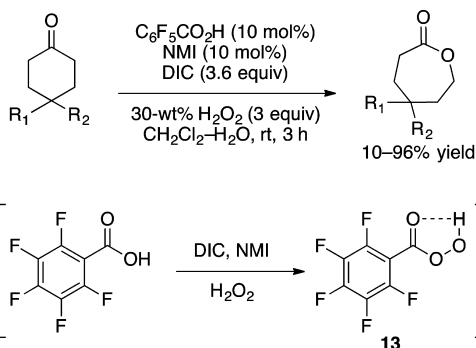
Recently, Ding and colleagues reported the first example of the chiral Brønsted acid (10)-catalyzed enantioselective BV oxidation of 3-substituted cyclobutanones using aqueous hydrogen peroxide (Scheme 8).¹⁵ The corresponding γ -lactones were obtained in high yield and up to 93% ee. The

Scheme 7. TsOH-Catalyzed BV Oxidation of Cyclohexanone Using Hydrogen Peroxide in HFIP¹⁴

Scheme 8. Chiral Phosphoric Acid-Catalyzed Enantioselective BV Oxidation¹⁵


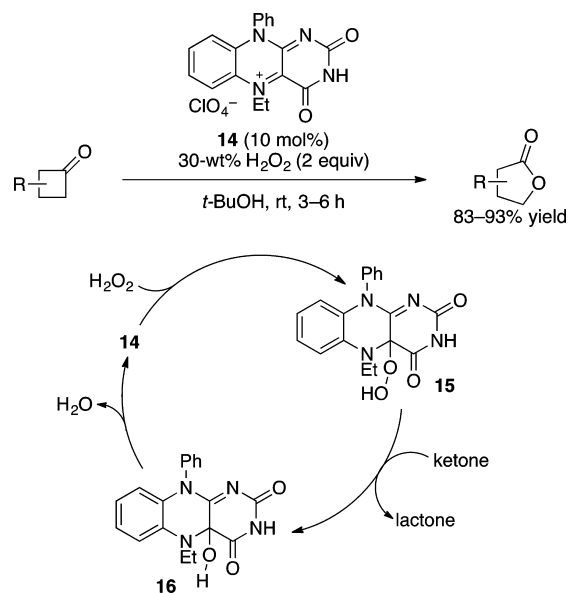
reaction mechanism was investigated based on experimental and theoretical findings, which showed that the catalyst simultaneously acts as a general acid to increase the electrophilicity of the carbonyl carbon and as a Brønsted base to increase the nucleophilicity of hydrogen peroxide in the addition step (11), and facilitated the dissociation of the OH group from the Criegee intermediate in the rearrangement step (12).

In 2008, Miller and colleagues reported another activation method with hydrogen peroxide.¹⁶ The transient peracid **13** could be generated in situ from hydrogen peroxide and pentafluorobenzoic acid catalyst with the use of condensation reagents (DIC, NMI) (Scheme 9).¹⁶ These conditions were especially useful for the BV oxidation of cyclohexanones to give the corresponding ϵ -caprolactones.

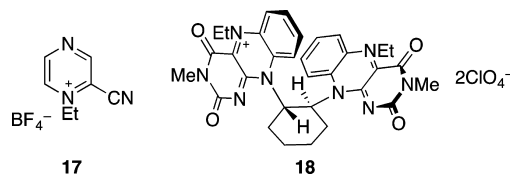
In 1996, Furstoss and colleagues reported the biomimetic activation of hydrogen peroxide using isoalloxazine **14** for

Scheme 9. In Situ-Generated Peracid 13-Promoted BV Oxidation of Cyclohexanones¹⁶


catalyzing the BV oxidation of cyclobutanones (Scheme 10).¹⁷ Hydrogen peroxide and **14** presumably form the peroxide **15**,

Scheme 10. Flavin-Catalyzed BV Oxidation of Cyclobutanones¹⁷


which has also been postulated to be the oxidizing species in enzymatic BV transformations. Compound **15** would then react with ketones to give the corresponding lactones and the hydroxyflavin **16**, which is converted to the catalyst **14** over dehydration. In this context, pyrazinium salt **17**,¹⁸ a simple flavin-like catalyst, and planar-chiral bisflavin catalyst **18**¹⁹ were also recently developed for the BV oxidation of cyclobutanones (Chart 2).

Chart 2. Pyrazinium Salt **17¹⁸ and Bisflavine **18**¹⁹**


Syper reported the first example of the epoxidation and BV oxidation reactions with hydrogen peroxide using benzeneseleninic acid catalysts.²⁰ In 2001, Sheldon and colleagues reported that 3,5-bis(trifluoromethyl)benzeneseleninic acid **20** generated in situ was significantly more active than other previously described selenium catalysts in the epoxidation reaction as well as the BV reactions of cycloalkanes using aqueous hydrogen peroxide in HFIP, TFE, or CH₂Cl₂ (Scheme 11).²¹ Compound **20** could be generated in situ from bis[3,5-bis(trifluoromethyl)phenyl] diselenide **19**, and then reacted with hydrogen peroxide to give perseleninic acid **21**, which was the active oxidant for the oxidation of ketones (Scheme 11).²¹

4. ALKALI OR ALKALINE EARTH METAL BORATE CATALYSTS

Representative examples of previous methods for BV oxidation with hydrogen peroxide as an oxidant are discussed above. Despite the considerable progress in this field, a more selective

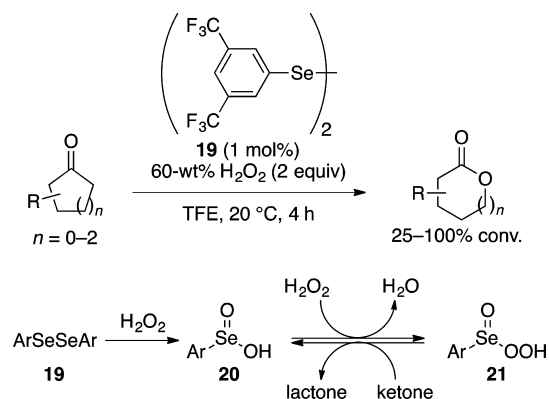
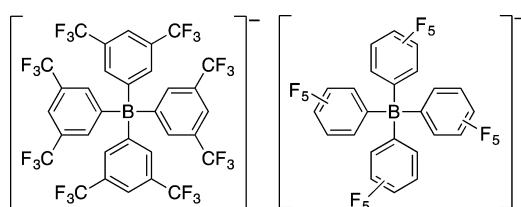
Scheme 11. In Situ-Generated Areneselenenic Acid-Catalyzed BV Oxidation of Cyclobutanones²¹

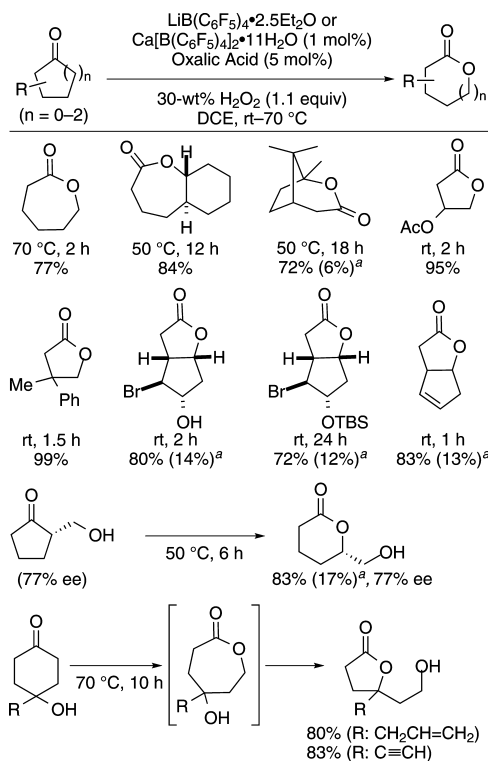
Chart 3. Fluorinated Tetraarylborates

Table 1. Investigation of Li^I or Ca^{II} Salts²⁵

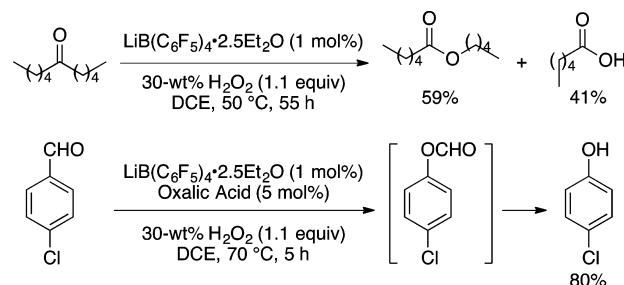
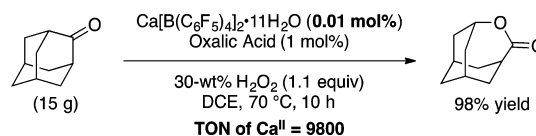
| entry | catalysts (mol %) | time (h) | yield (%) |
|-------|---|----------|-----------|
| 1 | Li[B(C ₆ F ₅) ₄] ₂ ·2.5Et ₂ O (1) | 8 | 94 |
| 2 | LiNTf ₂ (1) | 24 | 28 |
| 3 | LiBF ₄ (1) | 24 | 10 |
| 4 | LiBPh ₄ (1) | 24 | <1 |
| 5 | Li[B(C ₆ F ₅) ₄] ₂ ·2.5Et ₂ O (0.1) | 22 | 98 |
| 6 | Ca[B(C ₆ F ₅) ₄] ₂ ·11H ₂ O (0.1) | 6 | 97 |
| 7 | Ca[B(C ₆ F ₅) ₄] ₂ ·11H ₂ O (0.1) + (CO ₂ H) ₂ (1) | 3 | 98 |
| 8 | (CO ₂ H) ₂ (1) | 24 | <1 |

and efficient BV oxidation process under milder conditions is still needed.²⁶ We expected that water- and oxidant-tolerant and lipophilic acids might be good candidates as catalysts for the BV oxidation with aqueous hydrogen peroxide.

Fluorinated tetraarylborates, such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [B{3,5-(CF₃)₂C₆H₃}₄]⁻ and tetrakis(pentafluorophenyl)borate [B(C₆F₅)₄]⁻ are usually used as weakly coordinating counteranions for transition-metal catalysts to enhance their acidity and/or solubility (Chart 3).²⁷ However, there have been few studies on the use of Group I and Group II metal salts of these borates. In 2000, Sonoda, Mori, and colleagues used dehydrated LiB[3,5-(CF₃)₂C₆H₃]₄ as a Lewis acid catalyst for the Diels–Alder reaction.²⁸ In the same year, Mukaiyama and colleagues reported the use of LiB(C₆F₅)₄ for the benzylation of aromatic compounds and alcohols.²⁹ Later, Liu and colleagues used NaB[3,5-(CF₃)₂C₆H₃]₄·2H₂O for the polymerization of vinyl ethers,^{30a} the Mannich reaction,^{30b} Friedel–Crafts addition,^{30c} and the hydrolysis of acetals.^{30d} Recently, Takenaka and colleagues reported NaB[3,5-(CF₃)₂C₆H₃]₄·2.5H₂O-catalyzed intramolecular nitroalkene Diels–Alder reactions.³¹ However, to the best of our

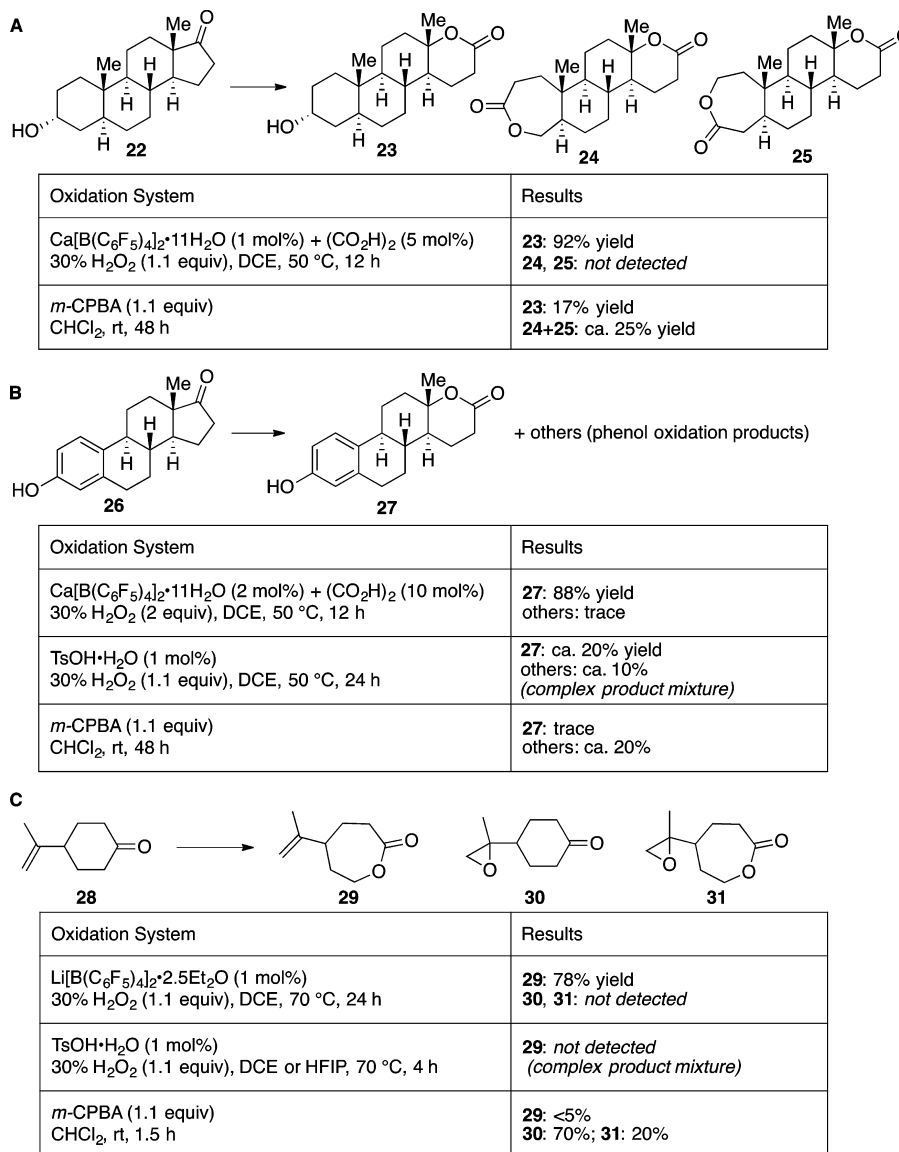
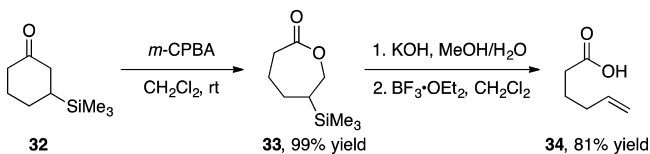
Scheme 12. Li^I- or Ca^{II}-Catalyzed BV Oxidation of Cycloalkanones Using Hydrogen Peroxide²⁵

^aYields of the minor regiomers are shown in parenthesis.

Scheme 13. BV Oxidation of Linear Ketone and Aldehyde²⁵Scheme 14. Gram-Scale Oxidation of Adamantanone²⁵

knowledge, these alkali or alkaline-earth metal tetraarylborates have never been used for oxidation reactions.

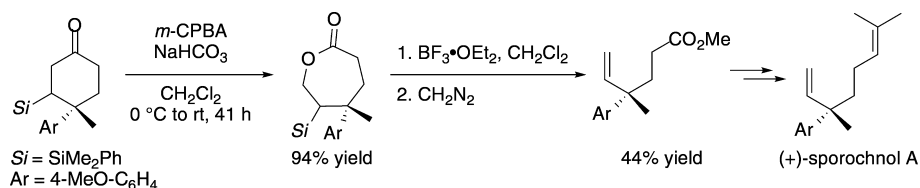
Because of the high lipophilicity of fluorinated tetraarylborates,²⁷ we envisioned that these alkali or alkaline-earth metal salts might exhibit efficient catalytic activity for BV oxidation with aqueous hydrogen peroxide under biphasic conditions. Thus, these salts were expected to promote both the nucleophilic attack of the carbonyl group by hydrogen peroxide and the subsequent rearrangement of a Criegee intermediate through the acidic activation of the carbonyl group in the organic phase or interface. In sharp contrast, conventional hydrophilic Lewis or Brønsted acids serve as catalysts in the aqueous phase or interface, and consequently lead not only to

Scheme 15. Chemoselective Oxidations of Bifunctional Ketones 22, 26, and 28²⁵Scheme 16. BV Oxidation of β -Silyl Ketone 33 with *m*-CPBA³³

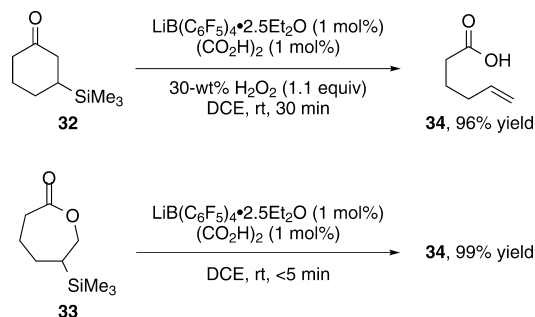
BV oxidation to give lactones but also to the subsequent hydrolysis of lactones. Furthermore, as discussed above, when

unsaturated ketones were used as starting materials in the presence of conventional acid catalysts, epoxidation competed with BV oxidation.

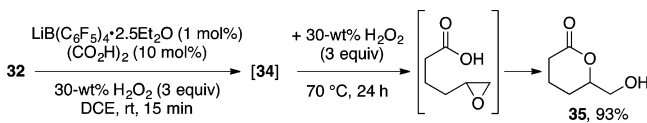
To prove our concept, various Li^I or Ca^{II} salts were examined as catalysts for the BV oxidation of cyclopentanone to δ -valerolactone in the presence of 1.1 equiv of 30-wt % H₂O₂ in dichloroethane (DCE) (Table 1). Commercially available LiB(C₆F₅)₄ (1 mol %) gave lactone in 94% yield (entry 1). In sharp contrast, other conventional lithium salts such as LiNTf₂, LiBF₄, and LiBPh₄ exhibited very poor catalytic activities under similar conditions (entries 2–5). The catalyst

Scheme 17. Application of β -Silyl Ketone Oxidation to the Formal Synthesis of Natural Products³⁴

Scheme 18. Transformation of β -Silyl Cyclohexanone **32 to Unsaturated Acid **34** through BV Oxidation/ β -Elimination Reaction Sequences²⁵**



Scheme 19. Transformation of **32 to Hydroxylactone **35** through BV Oxidation/ β -Elimination and Subsequent Epoxidation/Cyclization Reaction Sequences²⁵**



loading of $\text{LiB}(\text{C}_6\text{F}_5)_4$ could be reduced to 0.1 mol % without affecting the chemical yield (entry 6). Moreover, the $\text{Ca}(\text{II})$ salt, $\text{Ca}[\text{B}(\text{C}_6\text{F}_5)_4]_2$, which was easily prepared from the corresponding $\text{Li}(\text{I})$ salt by a cation exchange reaction, showed higher catalytic activity (entry 6). The fact that the use of water-miscible organic solvents such as acetonitrile, dimethyl formamide, ethanol, and so forth led to rather low conversion suggested that the biphasic nature was essential for the efficiency of the present BV oxidation. It was expected that the hydrated metal complexes, $\text{M}[\text{B}(\text{C}_6\text{F}_5)_4]_m \cdot n\text{H}_2\text{O}$, might act as a Lewis acid-assisted Brønsted acid (LBA)³² catalyst under aqueous conditions. Thus, we found that the reaction rate was significantly accelerated with oxalic acid (entry 7). Therefore, in

situ-generated highly reactive LBA species, $\text{M}[\text{B}(\text{C}_6\text{F}_5)_4]_m \cdot [(\text{CO}_2\text{H})_2]_n$, might be an active catalyst when oxalic acid is used as a cocatalyst.

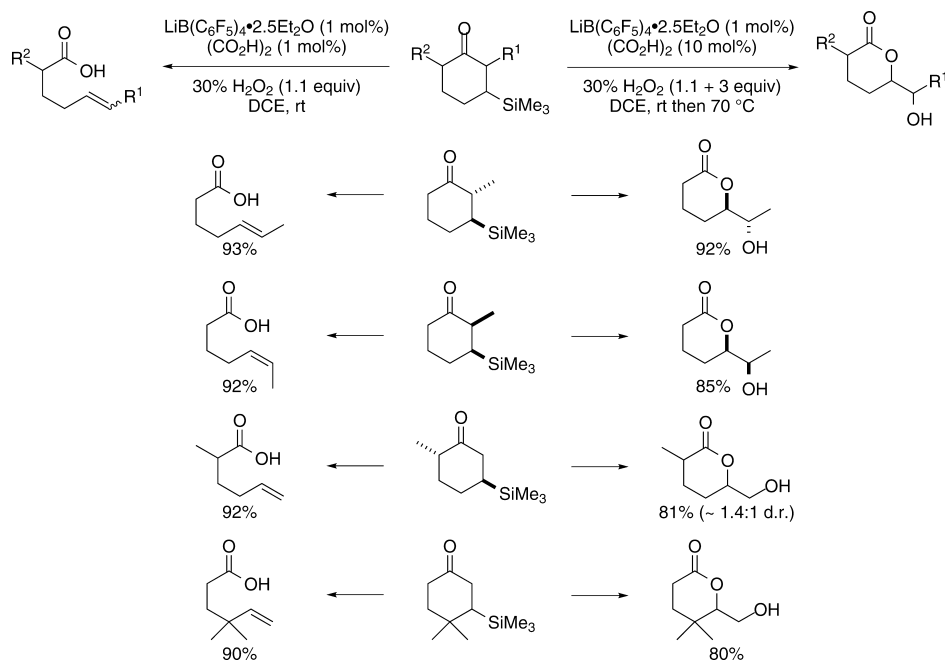
Selected examples of the BV oxidation of several cycloalkanones are shown in Scheme 12.²⁵ The usual regioselectivities were observed for the oxidations of unsymmetrical cycloalkanones. Notably, both Ca^{II} and Li^{I} could be used as catalysts in most cases. However, the Ca^{II} salt gave slightly better results than the Li^{I} salt, particularly for the oxidation of 5- and 6-membered cycloalkanones. Although the oxidation rate was accelerated in the copresence of oxalic acid, hydrolysis of the lactone products was also activated in some cases (especially 7-membered ring lactones). Several functional groups such as terminal or internal alkenyl, hydroxy, acetoxy, silyloxy, and halo groups were tolerated under the present conditions. In fact, these BV oxidations gave the corresponding lactones in high yields chemoselectively. Moreover, the BV oxidation of optically active ketone gave the corresponding lactone without racemization. In addition, the BV oxidation of 4-hydroxycyclohexanones gave more stable 5-membered hydroxylactones through successive intramolecular transesterification.

When linear ketones or aldehydes were oxidized, ester products were also hydrolyzed simultaneously. In fact, the oxidation of 6-undecanone gave the corresponding ester together with hexanoic acid (Scheme 13). Additionally, the oxidation of *p*-chlorobenzaldehyde gave the *p*-chlorophenol in 80% yield after hydrolysis of the corresponding formate (Scheme 13).

The present method could be applied to a gram-scale oxidation. The oxidation of 2-adamantanone on a 15 g scale with only 0.01 mol % of $\text{Ca}(\text{II})$ salt catalyst gave the desired lactone in 98% isolated yield (TON up to 9800) (Scheme 14).

The present method is very useful for the oxidation of a bifunctional substrate. For instance, the oxidation of hydroxysteroidal ketones **22** and **26**, and unsaturated ketone **28** gave the corresponding lactones **23**, **27**, and **29**, respectively, in high

Scheme 20. Oxidative Cascade Reactions of β -Silyl Cyclohexanones²⁵



yields without any other oxidation products (Scheme 15). In contrast, the use of *m*-CPBA in place of H₂O₂ for the oxidation of **22** or **26** gave alcohol or phenol oxidation byproducts (Scheme 15, A and B). In addition, the oxidation of unsaturated ketone **28** with *m*-CPBA under usual conditions mainly gave the epoxides **30** and **31** (Scheme 15C). The use of TsOH as a catalyst for the BV oxidation of **28** with hydrogen peroxide gave a complex reaction mixture or very low conversions (Scheme 15C).

Next, we focused on the oxidation of β -silyl cyclohexanones. According to Hudrlik and colleagues, the BV oxidation of β -silyl ketones with *m*-CPBA is directed by the silyl group to selectively give esters of β -hydroxysilanes, which are useful for the synthesis of unsaturated esters or acids (Scheme 16).³³ This method can also be applied to the formal synthesis of (+)-sporochonol by Kotsuki and colleagues (Scheme 17).³⁴ Interestingly and unexpectedly, the oxidation of β -trimethylsilyl cyclohexanone **32** with 1.1 equiv of 30-wt % H₂O₂ in the presence of LiB(C₆F₅)₄ (1 mol %) and oxalic acid (1 mol %) at room temperature afforded 5-hexenoic acid **34** in 94% yield as a sole product (Scheme 18).²⁵ The expected lactone **33**, which was obtained by oxidation with *m*-CPBA (Scheme 16),³³ was not detected. Notably, the oxidation rate was significantly accelerated by the substitution of a β -silyl group; hence the reaction proceeded rapidly even at room temperature. In contrast, the oxidation rate was not affected by β -silyl substitution under oxidation conditions with *m*-CPBA.³³ Apparently, **34** was generated via the BV oxidation of **32** and the subsequent fast β -elimination of silyl lactone intermediate **33**. In sharp contrast, treatment with acid (excess BF₃·Et₂O) was needed under harsh conditions for the β -elimination of silyl lactones to give the corresponding unsaturated carboxylic acids.^{33,34}

This catalytic oxidation system can also be used for the oxidative cyclization of unsaturated acids (Scheme 19).²⁵ Notably, a higher loading of oxalic acid (10 mol %) and a high temperature (70 °C) were needed for the oxylactonization step. To the best of our knowledge, this is the first example of the transition metal-free catalytic oxylactonization of unsaturated carboxylic acids using hydrogen peroxide.³⁵

Thus, several synthetically valuable unsaturated acids or hydroxylactones could be obtained from the corresponding β -silyl cyclohexanones by controlling the amounts of hydrogen peroxide and oxalic acid under optimized conditions (Scheme 20). Notably, the oxidation of 2-substituted β -silyl ketones gave the corresponding unsaturated acids or hydroxylactones as sole products in a stereospecific manner.

5. CONCLUSION

The BV oxidation method has been upgraded several times, from the original use of Caro's acid to more atom-efficient and mild oxidants such as hydrogen peroxide. There have been some successful examples of the BV oxidation of ketones with aqueous hydrogen peroxide promoted by several types of catalysts. Despite the considerable progress in this field, a more selective and efficient BV oxidation process under mild conditions is still needed. Recently, we developed a highly efficient and selective LiB(C₆F₅)₄- or Ca[B(C₆F₅)₄]₂-catalyzed BV oxidation of various cycloalkanones with 30-wt % aqueous hydrogen peroxide to give the corresponding lactones in high yield. Additionally, we found that the reaction rate was accelerated with the use of oxalic acid as a cocatalyst. Moreover, β -silyl cyclohexanones could be oxidized to the corresponding

unsaturated carboxylic acids or hydroxylactones in high yields via successive BV oxidation/ β -elimination reactions and/or subsequent successive epoxidation/cyclization reactions, by controlling the amounts of hydrogen peroxide and oxalic acid. The success of the catalytic BV oxidation of β -silyl cyclohexanones with hydrogen peroxide in place of *m*-CPBA led to the development of unique oxidative cascade reactions. These reactions proceed under mild conditions and tolerate various functional groups.

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Notes

The authors declare no competing financial interest.

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