Baeyer–Villiger Oxidation of Cycloalkanones with In Situ Generated Hydrogen Peroxide from Alcohols and Molecular Oxygen Using NHPI as a Key Catalyst

Kenichiro Kamae, Yasushi Obora, and Yasutaka Ishii*

Department of Chemistry and Materials Engineering, Faculty of Chemistry,
Materials and Bioengineering & High Technology Research Center, Kansai University, Suita, Osaka 564-8680

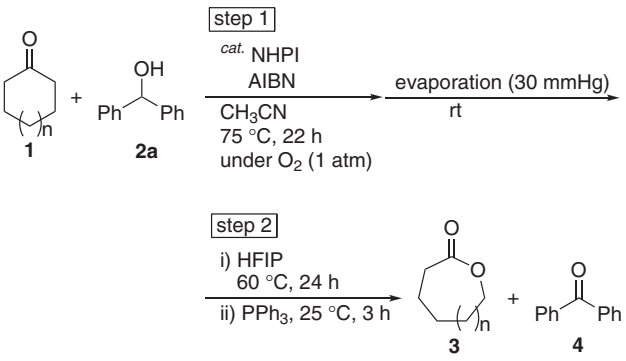
Received March 13, 2009; E-mail: ishii@ipcku.kansai-u.ac.jp

One-pot Baeyer–Villiger oxidation of cycloalkanones was successfully achieved by allowing them to react with hydrogen peroxide generated in situ from benzhydrol and molecular oxygen assisted by *N*-hydroxyphthalimide (NHPI) and 2,2′-azobisisobutyronitrile (AIBN). This method provides an alternative synthetic route to lactones from cycloalkanones using *sec*-alcohols and molecular oxygen assisted by NHPI.

Baeyer–Villiger (BV) oxidation is a frequently used synthetic tool for the production of esters and lactones from ketones.[1] Among lactones, ε-caprolactone is one of the most important lactones as a monomer for producing polylactones and is generally synthesized by the BV reaction of cyclohexanone with peracids like peracetic acid.[2] Because of recent environmental concerns, it has become desirable to produce lactones by the BV oxidation of cyclohexanone with H_2O_2 as a practical oxidant, particularly in industry. There have been several reports on the BV oxidation of cycloalkanones with H_2O_2, but highly concentrated H_2O_2 is used in the presence of arsenic and seleninic acids and platinum complexes as catalysts.[3] Recently, new methods for the BV oxidation of cyclohexanone with aqueous hydrogen peroxide have been reported.[4] Neumann et al. disclosed that cycloalkanones undergo the BV oxidation with 60% H_2O_2 in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) at 60 °C for 20 h to give the corresponding lactones in 60–88% yields.[4a] On the other hand, Berkessel et al. reported the BV oxidation of cyclohexanone with 50% H_2O_2 in the presence of acids like *p*-TsOH in HFIP.[4b] Thereafter, they showed that ε-caprolactone is formed through 7,8,15,16-tetraoxadispiro[5.2.5.2]hexadecane derived from cyclohexanone and H_2O_2 assisted by acid.[4c] In a previous paper, we reported the BV oxidation of cyclohexanone using K/A oil (a mixture of cyclohexanone and cyclohexanol) with molecular oxygen in the presence of a catalytic amount of *N*-hydroxyphthalimide (NHPI) and 2,2′-azobisisobutyronitrile (AIBN) followed by treatment with $InCl_3$.[5] In this reaction, the actual oxidizing agent is the H_2O_2 generated in situ from cyclohexanol and O_2 assisted by the NHPI and AIBN. We also showed that H_2O_2 is efficiently produced from benzhydrol and O_2 under the influence of NHPI and AIBN. Thus, our attention was attracted to the one-pot BV oxidation of various cycloalkanones **1** with H_2O_2 generated in situ from benzhydrol (**2a**) and O_2 by the action of NHPI using AIBN as a radical initiator. The present strategy is illustrated in Scheme 1.

Cyclopentanone (**1a**) was chosen as a model substrate and was allowed to react under various reaction conditions (Table 1).

A mixture of **1a** (4 mmol) and **2a** (6 mmol) was reacted under O_2 (1 atm) in the presence of NHPI (0.6 mmol) and AIBN (0.3 mmol) in CH_3CN (3 mL) at 75 °C for 22 h (Step 1). After evaporation of the resulting reaction solution under 30 mmHg at room temperature, HFIP (6 mL) was added to the mixture and stirred under air at 60 °C for 24 h. To quench peroxides remaining in the reaction system, the mixture was treated with PPh_3 (3 mmol) (Step 2). The reaction gave δ-valerolactone (**3a**) in 71% yield (76% selectivity) at 94% conversion of **1a**, and **2a** was converted into benzophenone (**4**) in 90% yield (Entry 1). This shows that most of the **2a** reacted with O_2 to liberate hydrogen peroxide and **4**. The reaction of **1a** (6 mmol) with an equimolar amount of **2a** (6 mmol) resulted in the decrease of the yield of **3a** (49%) and **4** (82%) (Entry 2). The reaction using excess **1a** (8 mmol) toward **2a** afforded **3a** in 42% yield (Entry 3). These results indicate that slight excess (1.5 times) of alcohol **2a** to ketone **1a** is suitable to obtain



Scheme 1. Baeyer–Villiger oxidation of cycloalkanones **1** with H_2O_2 generated in situ from benzhydrol (**2a**) and O_2 catalyzed by NHPI/AIBN system.

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Table 1. Baeyer–Villiger Oxidation of Cyclopentanone (**1a**) with H_2O_2 Generated In Situ from Benzhydrol (**2a**) and O_2 by NHPI/AIBN System[a)]

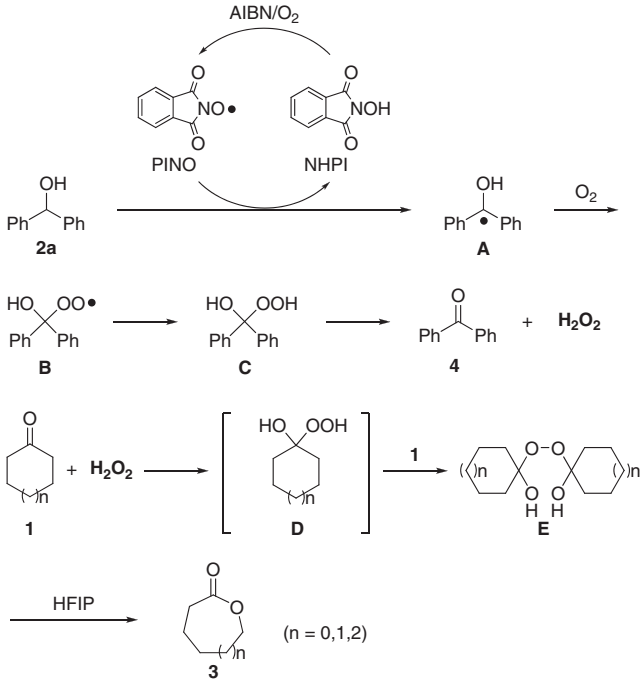
Entry	Ratio/mmol (**1a**/**2a**)	Conv./%		Yield/% (select/%)[b)]	
		1a	**2a**	**3a**[c)]	**4**
1	4/6	94	99	71(76)	90
2	6/6	78	88	49(63)	82
3	8/6	66	99	42(64)	78
4[d)]	4/6	25	99	trace	50
5[e)]	4/6	28	93	9(32)	71
6[f)]	4/6	66	99	42(64)	90
7[g)]	4/6	85	99	64(75)	99
8[h)]	4/6	95	99	62(65)	99
9[i)]	4/6	96	99	83(86)[76]	99
10[j)]	4/6	99	99	81(82)	99
11[k)]	4/6	98	99	71(72)	99
12	4/(6)[l)]	62	—	20(32)	—

a) **1a** (4–8 mmol) was allowed to react with **2a** (6 mmol) in the presence of NHPI (0.6 mmol) and AIBN (0.3 mmol) under O_2 (1 atm) in CH_3CN (3 mL) at 75 °C for 22 h, followed by evaporation (30 mmHg) at room temperature, and then HFIP (6 mL) was added and stirred under air at 60 °C for 24 h. b) Yield and selectivity were determined by GC analysis. c) Yield based on **1a**. Number in the bracket shows isolated yield. d) Reaction was performed without AIBN. e) Reaction was performed without NHPI. f) NHPI (0.3 mmol) and AIBN (0.15 mmol) were used. g) Reaction time was 12 h in 1st step. h) Reaction was performed under Ar in 2nd step. i) *p*-TsOH·H_2O (0.02 mmol) was added in 2nd step. j) HFIP (3 mL) was used. *p*-TsOH·H_2O (0.02 mmol) was added in 2nd step under Ar. k) EtOAc was used instead of CH_3CN. l) Number in parenthesis shows the amount (mmol) of isopropyl alcohol (**2b**).

lactone **3a** in satisfactory yield. Needless to say, the reaction in the absence of either AIBN or NHPI brought about **3a** in trace or poor yield, respectively (Entries 4 and 5). When the amount of AIBN and NHPI was halved under these conditions, the yield of **3a** decreased to 42% (Entry 6). The reaction time in step 1 was shortened to 12 h to form **3a** in slightly lower yield (64%) (Entry 7). The BV oxidation of cyclohexanone with 50% H_2O_2 is reported to be accelerated by adding *p*-toluenesulfonic acid (*p*-TsOH) in HFIP.[4b] Thus, the reaction in step 2 was run by adding a very small amount of *p*-TsOH to result in **3a** in good yield (83%) (Entry 9). By adding *p*-TsOH, the amount of HFIP could be reduced by half (3 mL) to give **3a** in satisfactory yield (81%) (Entry 10). The reaction in EtOAc afforded almost the same result as that in CH_3CN (Entry 11). Unfortunately, the reaction using isopropyl alcohol (**2b**) in place of **2a** as a H_2O_2 source afforded **3a** in low yield (20%) and selectivity (32%) (Entry 12).

On the basis of these results, various cycloalkanones were allowed to react under several reaction conditions (Table 2).

Cyclohexanone (**1b**) was reacted under the same conditions as Entry 1 in Table 1 to give ε-caprolactone (**3b**) in 68% yield (Entry 1). In contrast to the reaction of **1a** where the yield of **3a** was improved by adding a small amount of *p*-TsOH in step 2, no such positive effect was observed in the case of the reaction of **1b** (Entry 2). Isopropyl alcohol (**2b**) was employed in place



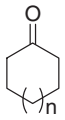
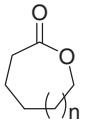
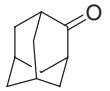
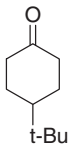
Scheme 2. A possible reaction path for the BV oxidation of **1** with **2a** and O_2 by NHPI/AIBN system.

of **2a** as a H_2O_2 source under these conditions to give **3b** in slightly lower yield (44%). This shows that **2b** is a less effective H_2O_2 source than **2a** (Entry 3). However, excess **2b** was used to give **3b** in good yield (74%) (Entry 4). Cycloheptanone (**1c**) was a slightly reluctant substrate for the BV reaction giving rise to **3c** in 55% yield (Entry 7). However, cyclooctanone (**1d**) underwent the BV oxidation with difficulty under the present reaction conditions, forming α-hydroxy cyclooctanone in preference to lactone **3d** (Entry 8). A similar observation was reported for the BV oxidation of **1d** by Nozaki et al.[6] Cyclododecanone (**1e**) and cyclopentadecanone (**1f**) were also oxidized to the corresponding lactones, **3e** and **3f**, in 69% and 81% yields, respectively (Entries 9 and 10). The compound **3f**, which is known as muscone, is an important perfume. Adamantanone (**1g**) was converted to 4-oxatricyclo-[4.3.1.$1^{3,8}$]undecan-5-one (**3g**) in good yield (93%) (Entry 11). 4-*tert*-Butylcyclohexanone (**1h**) was completely converted into lactone (**3h**) (99%) (Entry 12).

A conceivable reaction pathway in the reaction of **1** is well represented as follows (Scheme 2).

Phthalimide-*N*-oxyl radical (PINO) abstracts a hydrogen atom from **2a** to form 1-hydroxy-1,1-diphenylmethyl radical (**A**). Under O_2, the resulting radical **A** is readily trapped by O_2 to give a hydroperoxide (**C**) which quickly liberates H_2O_2 and benzophenone **4**. For **1a**,[7a] **1b**,[7b] and **1c**,[7a] it is well-known that cycloalkanones **1** react with H_2O_2 to form 1,1′-dihydroxydicycloalkyl peroxides **E** probably through 1-hydroxy-1-cycloalkylhydroperoxides (**D**).[7] Therefore, it is believed that the formed H_2O_2 reacts readily with ketones **1** to form **D** which then undergoes the rearrangement to lactones **3** via **E** assisted by HFIP. The most important feature of the present methodology is that highly reactive anhydrous H_2O_2 is generated in situ from **2a** and O_2 by the action of the NHPI. Thus,

Table 2. Baeyer–Villiger Oxidation of Cycloalkanone **1** with H_2O_2 Generated In Situ from Benzhydrol (**2a**) and O_2 by NHPI/AIBN System[a)]

Entry	Cycloalkanone **1**	Ratio/mmol (**1**/**2a**)	Conv./%		Lactone **3**	Yield/% (select/%)[b)]	
			1	**2a**		**3**[c)]	**4**
1	 **1b** ($n = 1$)	4/6	96	99	 **3b**	68(70)[63]	99
2[d)]	**1b**	4/6	98	99	**3b**	55(56)	99
3	**1b**	4/(6)[e)]	78	—	**3b**	44(56)	—
4	**1b**	1/(10)[e)]	97	—	**3b**	74(76)	—
5	**1b**	6/(6)[e)]	69	—	**3b**	36(52)	—
6[f)]	**1b**	4/6	70	99	**3b**	21(30)	99
7	**1c** ($n = 2$)	4/6	84	99	**3c**	55(65)	86
8[g),h)]	**1d** ($n = 3$)	4/6	76	99	**3d**	7(8)	99
9[g)]	**1e** ($n = 7$)	2/6	69	99	**3e**	69(99)[63]	99
10[g)]	**1f** ($n = 10$)	1/6	92	99	**3f**	81(88)[70]	99
11[g)]	 **1g**	2/6	98	99	**3g**	93(95)[88]	99
12[d)]	 **1h**	2/6	99	99	**3h**	99(99)[89]	99

a) **1** (1–6 mmol) was allowed to react with **2a** (6 mmol) in the presence of NHPI (0.6 mmol) and AIBN (0.3 mmol) under O_2 (1 atm) in CH_3CN (3 mL) at 75 °C for 22 h, followed by evaporation under 30 mmHg at room temperature, and then HFIP (6 mL) was added and stirred under air at 60 °C for 24 h. b) Yield and selectivity based on GC analysis. c) Yield based on **1**. Numbers in brackets show isolated yields. d) *p*-TsOH·H_2O (0.02 mmol) was added in the 2nd step. e) Number in parenthesis shows the amount (mmol) of **2b**. f) At room temperature in 2nd step. g) *p*-TsOH·H_2O (0.02 mmol) was added in 2nd step under Ar. h) α-Hydroxycyclooctanone was obtained as a major product (16%).

cycloalkanones **1** easily reacts with the anhydrous H_2O_2 to form **D** which then readily reacts with another **1**, giving lactones **3** through a key intermediate **E**.

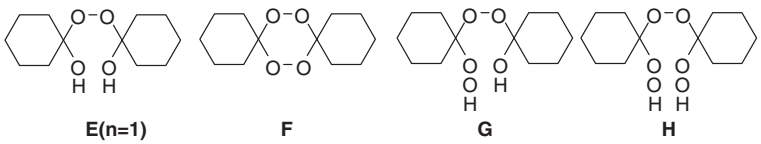
Recently, Berkessel et al. have reported that 7,8,15,16-tetraoxadispiro[5.2.5.2]hexadecane (**F**) is a probable intermediate to **3b** by the BV oxidation of **1b** with 50% H_2O_2 in the presence of *p*-TsOH in HFIP.[4b] In order to confirm whether the peroxide **F** is an intermediate to the **3b** or not, a series of dicyclohexyl hydroperoxides were prepared according to literature procedures[4,7,8] and were allowed to react in HFIP under several conditions (Table 3).

Treatment of the **F** (0.5 mmol) without *p*-TsOH in HFIP (3 mL) under stirring at room temperature and 60 °C for 0.5 and 20 h resulted in the recovery of the starting **F** unchanged, while reaction in the presence of *p*-TsOH under these conditions led to **3b** as described by Berkessel et al. (Entries 1–4).[4b] **F** was found to be the stable peroxide even in HFIP in the absence of *p*-TsOH. This observation makes unlikely the possibility of **F** as a precursor in our reaction, because **1b** was converted into **3b** in substantial yield in the absence of *p*-TsOH. On the other hand, it was found that 1,1′-dihydroxydicyclohexyl peroxide [**E**(***n* = 1**)] reacted readily in HFIP without *p*-TsOH even at room temperature to give rise to an approximately 1:1 mixture of ketone **1b** (0.53 mmol) and lactone **3b** (0.47 mmol) within 0.5 h and that the reaction of **E**(***n* = 1**) in the presence of *p*-TsOH afforded the same result as that in the absence of *p*-TsOH (Entries 5 and 6). However, the same treatment of 1-hydroxy-1′-hydroperoxydicyclohexyl peroxide (**G**) at room temperature for 20 h led to **1b** without formation of lactone **3b**, while the reaction was prolonged to 20 h to produce **1b** (0.42 mmol) and **3b** (0.48 mmol) (Entry 7). The treatment of **G** at 60 °C gave almost the same results as that at room temperature (Entry 8). It is believed that **G** rearranged through somewhat different reaction steps from those of **E**. The reaction of **G** in the presence of *p*-TsOH at room temperature for 0.5 and 20 h afforded lactone **3b** in 0.31 and 0.63 mmol, respectively (Entry 9). The rearrangement of **G** to **3b** was found to be accelerated by adding a small amount of *p*-TsOH (Entry 10). 1,1′-Dihydroperoxydicyclohexyl peroxide (**H**), prepared by a literature procedure,[8] was allowed to react in HFIP at room temperature, producing **1b** without formation of lactone **3b** even at 60 °C for 20 h (Entry 12), while **H** rearranged to lactone **3b** in good yield in the presence of a small amount of *p*-TsOH in HFIP for 20 h even at room temperature (Entries 13 and 14).

Table 3. Reaction of Dicyclohexylhydroperoxides in HFIP under Several Conditions[a)]

Entry	Hydroperoxides	*p*-TsOH/mmol	Temp/°C	Yield/mmol[b)]	
				1b	**3b**
1	**F**	—	rt	0 (0.09)	0 (0)
2	**F**	—	60	trace (0.10)	0 (0)
3	**F**	0.02	rt	0.14 (0.21)	0.07 (0.24)
4	**F**	0.02	60	0.23 (0.24)	0.18 (0.45)
5	**E($n = 1$)**	—	rt	0.53	0.47
6	**E($n = 1$)**	0.02	rt	0.53	0.47
7	**G**	—	rt	1.00 (0.42)	0 (0.48)
8	**G**	—	60	0.92 (0.12)	trace (0.56)
9	**G**	0.02	rt	0.16 (0.02)	0.31 (0.63)
10	**G**	0.02	60	0.06 (0)	0.51 (0.67)
11	**H**	—	rt	1.00 (1.00)	0 (trace)
12	**H**	—	60	1.00 (0.93)	0 (0.06)
13	**H**	0.02	rt	0.29 (0)	0.10 (0.71)
14	**H**	0.02	60	0.03 (0)	0.58 (0.74)

a) Hydroperoxides (0.5 mmol) were reacted at room temperature for 0.5 and 20 h in the presence or absence of *p*-TsOH·H_2O (0.02 mmol) in HFIP (3 mL) followed by treatment with PPh_3 (3 mmol) at room temperature for 3 h. b)Yield and selectivity based on GC analysis. Numbers in the parentheses show results for 20 h.



In contrast to **E($n = 1$)** which produced a mixture of **1b** and **3b** in HFIP alone at room temperature within 0.5 h, **F** and **H** did not rearrange to ketone **3b** in the absence of *p*-TsOH. On the basis of these results, **F** and **H** can be excluded from precursors of the BV oxidation of **1b** to **3b** in this reaction.

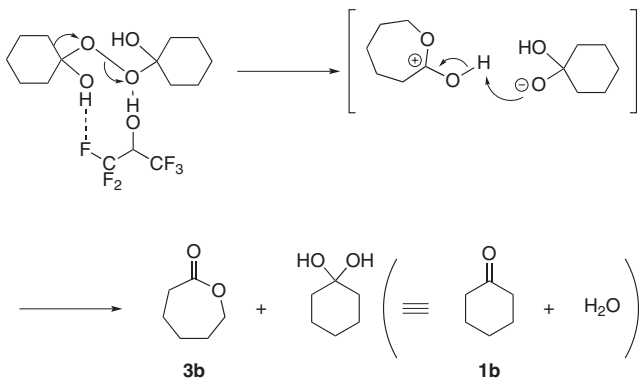
Owing to the complexity of the reaction medium and the difficulty of isolating peroxides from the reaction solution, it seems rather hazardous to make an accurate assessment about the reaction pathway in the present reaction, but the fact that only **E** rearranged in HFIP to **3b** in the absence of any acid is in fair agreement with the experimental results. Accordingly, it seems reasonable to assume that the present one-pot BV oxidation of **1b** to the **3b** by the present reaction system proceeds mainly through the formation of **E** as a precursor.

The formation of **3b** from **E** is thought to pass through the following reaction pathway (Scheme 3).

It is well known that HFIP possesses strong hydrogen bonding ability with a OH group.[9] Thus, the HFIP activates the hydroxy function of **E** to induce heterolytic cleavage of the peroxide bond followed by proton transfer to lead to a 1:1 mixture of lactone **3b** and ketone **1b**.

In fact, the treatment of **E** in HFIP at room temperature produced an approximately 1:1 mixture of **1b** and **3b** as shown in Entry 5 of Table 3.

In conclusion, we have developed a one-pot BV oxidation of various cycloalkanones to the corresponding lactones with in situ generated hydrogen peroxide from benzhydrol (**2a**) and O_2 by NHPI as a key catalyst. From the reaction of hydroperoxides derived from cyclohexanone and H_2O_2 in HFIP, a probable precursor of the rearrangement of **1b** to **3b** is proposed to be the 1,1′-dihydroxydicyclohexyl peroxide **E**. In addition, no rearrangement occurred from **F** and **H** in the absence of *p*-TsOH.



Scheme 3. A possible disproportionation of **E($n = 1$)** to **1b** and **3b** induced by HFIP.

Experimental

All starting materials except **F**,[7,10] **E($n = 1$)**,[7] **G**,[7] and **H**[8] were commercially available and used without further purification. GLC analysis was performed with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-1) using an internal standard. ^1H and ^{13}C NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. The products were characterized by ^1H NMR, ^{13}C NMR, and GC-MS. The yields of products were estimated from the peak areas based on an internal standard using GLC.

Compounds **3a**,[11] **3b**,[11] **3c**,[11] **3d**,[12] **3e**,[12] **3f**,[13] **3g**,[11] **3h**,[14] **E($n = 1$)**,[7] **F**,[10] **G**,[7] and **H**,[8] were reported previously.

A Typical Reaction Procedure for the Formation of δ-Valerolactone (3a) is as Follows (Table 1, Entry 9). A mixture of NHPI (98 mg, 0.6 mmol) and AIBN (49 mg, 0.3 mmol) was added to a mixture of cyclopentanone (**1a**) (336 mg, 4 mmol) and benzhydrol (**2a**) (1105 mg, 6 mmol) in MeCN (3 mL) under O_2. The reaction mixture was stirred at 75 °C for 22 h. After evaporation of the resulting solution under 30 mmHg at room temperature, HFIP (6 mL) and *p*-TsOH·H_2O (4 mg, 0.02 mmol) were added to the mixture and stirred under air at 60 °C for 24 h. After the reaction, PPh_3 (787 mg, 3 mmol) was added to quench peroxides remaining in the reaction system. Removal of solvent under reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to give the product, δ-valerolactone (**3a**) (304 mg, 3.04 mmol) in 76% isolated yield as a pure form.

Reaction of 1,1′-Dihydroxydicyclohexyl Peroxide [E($n = 1$)] in HFIP (Table 3, Entry 5). Compound **E**($n = 1$) (115 mg, 0.5 mmol) was stirred at room temperature for 30 min in HFIP (3 mL). GC analysis of the reaction mixture showed that cyclohexanone (**1b**) (0.53 mmol) and ε-caprolactone (**3b**) (0.47 mmol) were formed.

Reaction of 1-Hydroxy-1′-hydroperoxydicyclohexyl Peroxide (G) in HFIP (Table 3, Entry 7). Compound **G** (123 mg, 0.5 mmol) was stirred at room temperature for 20 h in HFIP (3 mL). After the reaction, PPh_3 (787 mg, 3 mmol) was added. GC analysis of the reaction mixture showed that **1b** (0.42 mmol) and **3b** (0.48 mmol) were formed.

Reaction of 1,1′-Dihydroperoxydicyclohexyl Peroxide (H) in HFIP (Table 3, Entry 11). Compound **H** (131 mg, 0.5 mmol) was stirred at room temperature for 30 min in HFIP (3 mL). After the reaction, PPh_3 (787 mg, 3 mmol) was added. GC analysis of the reaction mixture showed that **1b** (1.00 mmol) was formed.

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