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Note

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Sodium Hypochlorite Pentahydrate as a Reagent for the Cleavage of *trans*-Cyclic Glycols

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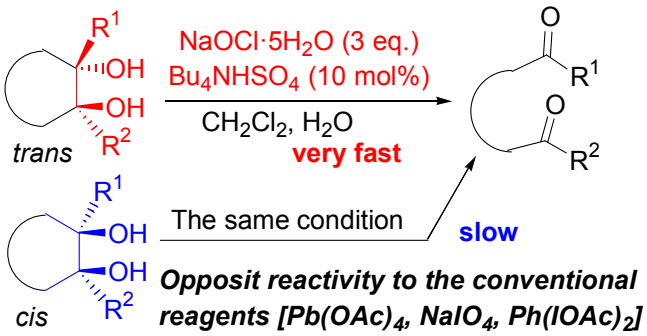
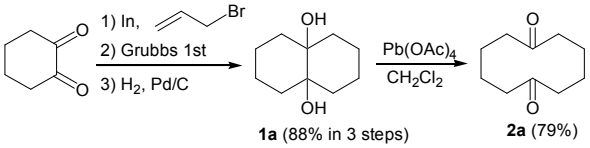


ABSTRACT: Sodium hypochlorite pentahydrate ($NaOCl·5H_2O$) can be used toward the efficient glycol cleavage of *trans*-cyclic glycols, which are generally resistant to this transformation. Interestingly, the reaction of *cis*-cyclic glycols with $NaOCl·5H_2O$ is slower than that observed for the corresponding *trans*-isomer. This *trans* selectivity is in sharp contrast to traditional oxidants used for glycol cleavage. Acyclic glycols can also react efficiently with $NaOCl·5H_2O$ to form their corresponding carbonyl compounds in high yield.

The cleavage of bicyclic bis-tertiary glycols such as octahydronaphthalene- 4a,8a-diol **(1a)** is an attractive procedure for the synthesis of macrocyclic compounds.[1-3] For example, Paquette and co-workers have reported that **1a** can be prepared as a 3:1 diastereomeric mixture upon reaction of cyclohexane-1,2-dione with allyl indium followed by metathesis using 1st generation Grubbs catalyst and hydrogenation (Scheme 1). They then performed the glycol cleavage reaction of **1a** using lead tetraacetate [$Pb(OAc)_4$] to produce the desired ten-membered ring diketone **(2a)**.[2a,b]

Scheme 1. Synthesis of 2a achieved by Paquette et al.

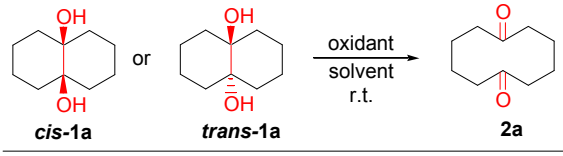


In general, the cleavage of sterically-hindered cyclic glycols, especially *trans*-glycols, is not easy using reagents other than $Pb(OAc)_4$.[4] However, there are serious drawbacks when using $Pb(OAc)_4$. It is highly toxic, and no less than a stoichiometric amount of reagent is required for the reaction, which produces a large amount of toxic lead diacetate over the course of the reaction. Recently, less toxic hypervalent iodine reagents, such as phenyliodine diacetate [$PhI(OAc)_2$],[5] have been used as an alternative to $Pb(OAc)_4$ by Krische and co-workers. The method, however, are required stoichiometric amount (1.2 equiv) of the relatively expensive $PhI(OAc)_2$ reagent.

To avoid the use of large amounts of toxic [$Pb(OAc)_4$] or expensive [$PhI(OAc)_2$] reagents, we have explored the use of several alternative oxidants,[6] and discovered that sodium hypochlorite pentahydrate crystals ($NaOCl{\cdot}5H_2O$) is an extraordinary reagent for glycol cleavage. (**Table 1, run 6**) The reagent reacts easily with hindered *trans*-glycols (such as *trans*-**1a),** which are not particularly reactive using classical oxidants, to form the corresponding dicarbonyl compounds.

We initially focused on aqueous sodium hypochlorite (*aq*. NaOCl) is an inexpensive and environmentally-benign oxidant which has been previously reported to carry out glycol cleavage.[7] However, *aq* NaOCl was useless for the oxidative cleavage of *cis*- and *trans*-**1a. (Table 1, runs 1-4)** The reaction of these compounds with $NaOCl{\cdot}5H_2O$ was next approached, because we recently have reported that $NaOCl{\cdot}5H_2O$ is a superior reagent to conventional aq. NaOCl in the oxidation of organic compounds.[8] For comparison, we also examined the reaction with conventional reagents including sodium periodate ($NaIO_4$),[9] $Pb(OAc)_4$[10] and $PhI(OAc)_2$. Our results are summarized in **Table 1**.

Table 1. Glycol cleavage of *cis*-1a and *trans*-1a using several oxidants



***cis*-1a** ***trans*-1a** **2a**

Run	Reaction Condition	Substrate	Time (h)	Yield of **2a** (%)
1	aq. 13% NaOCl[a] (3 eq.) CH_3CN	***cis*-1a**	5	N.R.
2		***trans*-1a**	5	N.R.
3	aq. 13% NaOCl[a] (3 eq.) Bu_4NHSO_4 (10 mol%) CH_2Cl_2	***cis*-1a**	4	2[b]
4		***trans*-1a**	1	6[b]
5	**$NaOCl \cdot 5H_2O$ (3 eq.)** Bu_4NHSO_4 (10 mol%) CH_2Cl_2 / H_2O	***cis*-1a**	**2**	**76**
6		***trans*-1a**	**0.2**	**93**
7	$NaIO_4$ (6 eq.) THF / H_2O	***cis*-1a**	50	74
8		***trans*-1a**	70	N.R.
9	$Pb(OAc)_4$ (2.2 eq.) CH_2Cl_2	***cis*-1a**	0.3	79
10		***trans*-1a**	117	33
11	$PhI(OAc)_2$ (6 eq.) CH_2Cl_2	***cis*-1a**	2.6	89
12		***trans*-1a**	52	64

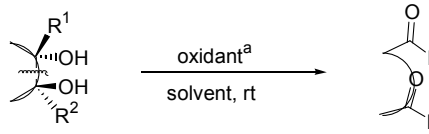
[a]Commercial aqueous solution (Nikkei Ziaso^{TM}) was used.
[b]Most of **1a** was recovered.

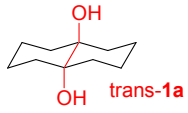
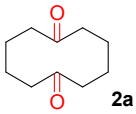
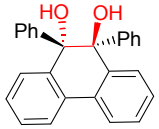
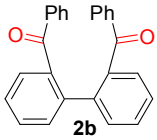
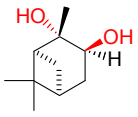
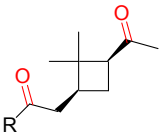
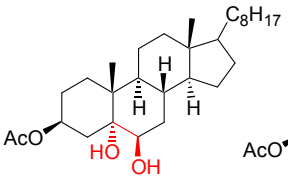
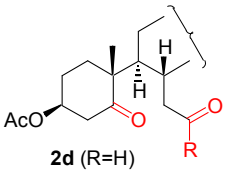
As shown in Table 1, $NaOCl \cdot 5H_2O$ exhibited excellent results (**runs 5 and 6**) more than another reagent systems. Surprisingly, $NaOCl \cdot 5H_2O$ reacted with *trans*-**1a** much faster than *cis*-**1a** to produce **2a** in high yield.[11] This result was in sharp contrast to that observed using conventional reagents [$NaIO_4$, $Pb(OAc)_4$ and $PhI(OAc)_2$], which prefer *cis*-**1a** as the substrate in the glycol cleavage reaction. Conventional reagents cause glycol cleavage via a cyclic intermediate.[12] Therefore, glycols that retard the formation of this cyclic intermediate, (such as *trans*-**1a**) are not good substrates for the reaction. The unique reactivity of $NaOCl \cdot 5H_2O$ means that the mechanism of glycol cleavage using $NaOCl \cdot 5H_2O$ is completely different from that of conventional glycol cleavage reagents. (*vide infra*)

We envisage that $NaOCl \cdot 5H_2O$ will be a superior reagent for the glycol cleavage reaction of sterically hindered *trans*-cyclic glycols which are difficult to react with conventional reagents. The reactions of several *trans*-cyclic glycols (***trans*-1a d**) with $NaOCl \cdot 5H_2O$ were examined, and the results are shown in Table 2.

The reactions using conventional reagents [$NaIO_4$, $Pb(OAc)_4$] were also examined for comparison. For $NaOCl \cdot 5H_2O$, each *trans*-cyclic glycol reacted rapidly to form the corresponding carbonyl compound in high yield. Conversely, $NaIO_4$ did not show any reactivity with the *trans*-cyclic glycols studied. Although $Pb(OAc)_4$ reacted with *trans*-cyclic glycols to produce the desired products, the reactions proceeded slowly and provided the product in lower yield.

Table 2. Glycol cleavage of sterically hindered *trans*-cyclic glycols



Glycol (**1**)	Products	**$NaOCl \cdot 5H_2O$ (3 eq.) Bu_4NHSO_4 (10 mol%) CH_2Cl_2 / H_2O**	$Pb(OAc)_4$ (2.2 eq.) CH_2Cl_2
 trans-**1a**	 **2a**	**93% (0.2 h)**	33% (117 h)[b]
 *trans*-**1b**	 **2b**	**quant (0.2 h)**	92% (3 h)
 *trans*-**1c**	 **2c** (R=H) **3c** (R=OH)	**90% (0.2 h)** (**2c**:70%) (**3c:** 20%)	27% (25 h)[b] (**2c**: trace) (**3c**: 27%)
 *trans*-**1d**	 **2d** (R=H) **3d** (R=OH)	**89% (0.6 h)** (**2d**: 69%) (**3d:** 20%)	30% (25 h)[c] (**2d** only)

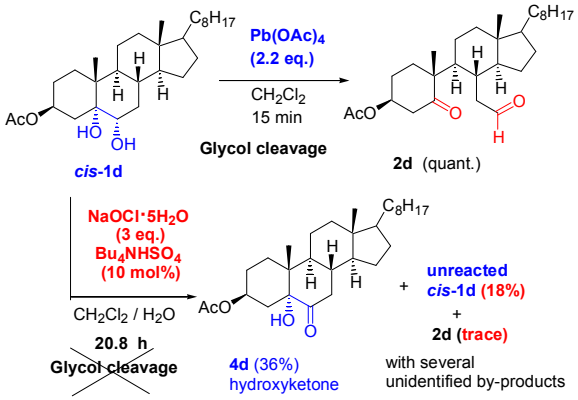
[a] $NaIO_4$ (6 eq.) did not react with any grycols on this table in THF-H_2O for 25 h or more.

[b] While the starting material (***trans*-1c**) disappeared, several unidentified by-products were produced.

[c] Much of the starting material (***trans*-1d**) remained unreacted.

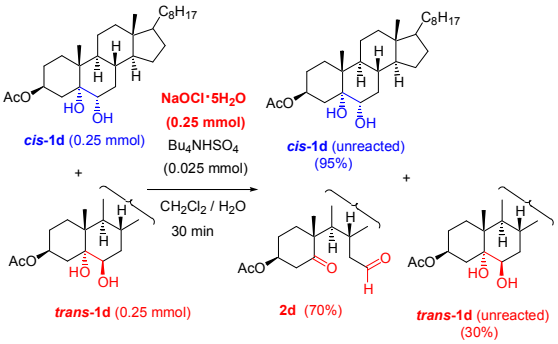
Subsequently, we examined the glycol cleavage of ***cis*-1d** (Scheme 2). ***cis*-1d** immediately reacted with $Pb(OAc)_4$ to produce the desired products in quantitative yield. Interestingly, $NaOCl{\cdot}5H_2O$ hardly reacted with ***cis*-1d** and produced only a trace amount (< 1%) of the desired glycol cleavage compound (**2d**)**.** After 20.8 h, a significant amount of unreacted ***cis*-1d** remained in the reaction mixture**,** and the corresponding hydroxyl ketone (**4d**) was obtained as the major product (36% yield) together with several unidentified by-products.

Scheme 2. Reaction of *cis*-1d with $Pb(OAc)_4$ or $NaOCl{\cdot}5H_2O$



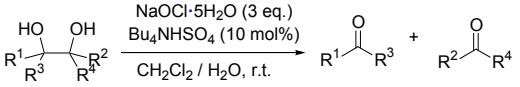
When an equimolar mixture of ***cis*-1e** and ***trans*-1e** was treated with $NaOCl{\cdot}5H_2O$ under the same reaction conditions, the selective reaction of ***trans*-1e** was observed with ***cis*-1e** recovered in almost quantitative yield (Scheme 3). The control experiment clearly exhibits that the cleavage of *trans*-glycol is much faster than that of *cis*-glycol.

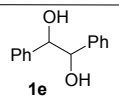
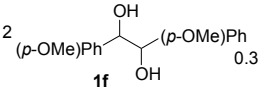
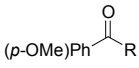
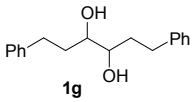
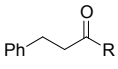
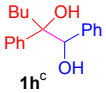
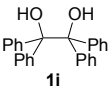
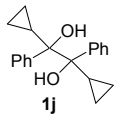
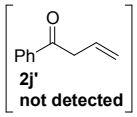
Scheme 3. Glycol cleavage of an equimolar mixture of *cis*- and *trans*-1d using $NaOCl{\cdot}5H_2O$



Next, the reactions of several acyclic glycols (**1e-j**) using $NaOCl·5H_2O$ were then investigated (**Table 3**). Glycol cleavage was observed in all cases and the corresponding aldehydes, carboxylic acids, and ketones were obtained in high yield. The glycol substrate containing a cyclopropyl moiety (**1j**) provided the corresponding cyclopropyl phenyl ketone (**2j**) as the sole product. Allyl phenyl ketone (**2j'**) was not observed (**Table 3**, **run 6**). This result meant that radical intermediates were not produced during the glycol cleavage reaction.

Table 3. Glycol cleavage of acyclic-glycols



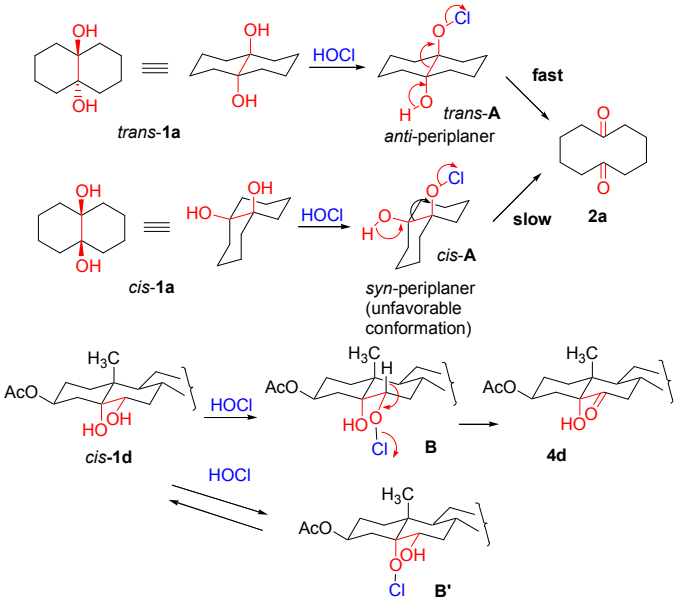
Run	Glycol	Time (h)	Products
1	 **1e**	0.3	 75%[a] **2e**(40%[a] R=H) **3e** (35%[a] R=OH)
2	 **1f**	0.3	 75%[b] **2f** (68%[b] R=H) **3f** (7%[b] R=OH)
3	 **1g**	6	 78%[a] **2g** (2%[a] R=H) **3g** (76%[a] R=OH)
4	 **1h**[c]	0.3	 93%[a] **2e** (92%[a] R=H) **3e**(1%[a] R=OH)  **2h (quant[a])**
5	 **1i**	0.5	 **2i** (82%[d])
6	 **1j**	1	 **2j** (89%[d])  **2j'** **not detected**

[a] GC-yield using 1-chloronaphthalene as an internal standard.
[b] GC-yield using decalin as an internal standard.
[c] 2.0 eq. $NaOCl·5H_2O$ was used.
[d] Isolated yield.

A plausible reaction mechanism for the glycol cleavage of *trans*- and *cis*-**1a** using $NaOCl·5H_2O$ is shown in **Scheme 4**.[13] Hypochloric acid (HOCl) derived from $NaOCl·5H_2O$ and Bu_4NHSO_4 may be the active species,[8b] which reacts with one of the hydroxyl groups in the glycol substrate to form hypochlorite intermediate (**A**). In the case of the *trans*-isomer, the resulting hypochlorite substituent and the unreacted hydroxyl group of *trans*-**A** are fixed in an *anti*-periplanar configuration, and therefore, a Grob-type fragmentation occurs immediately to produce

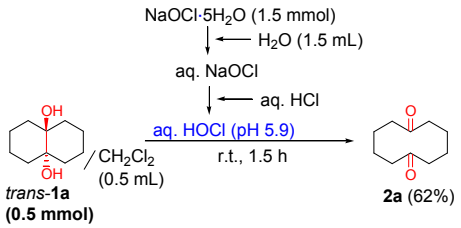
the desired product (**2a**). On the other hand, *cis*-**A** must be *syn*-periplanar for the glycol cleavage reaction to occur, but this conformation is not thermodynamically favorable for *cis*-**A**. Therefore, *cis*-**1a** reacts much slower than *trans*-**1a**. In the case of ***cis*-1d**, since the *syn*-periplanar conformation of either mono-chlorinated intermediate (**B**, **B'**) are unfavored, the glycol cleavage reaction is very difficult. The secondary alcohol in ***cis*-1d** was oxidized to the corresponding carbonyl group *via* intermediate **B** to form **4d**.

Scheme 4. A plausible reaction mechanism for glycol cleavage reaction.



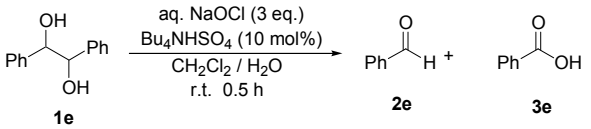
In order to prove hypochloric acid (HOCl) is an active species, the reaction of *trans*-**1a** in dichloromethane with aqueous HOCl prepared from $NaOCl \cdot 5H_2O$ being adjusted to pH 5- 6 upon adding conc. HCl was examined. In this biphasic mixture *trans*-**1a** in the organic phase was slowly converted to **2a** (**Scheme 5**). This result indicates that HOCl in the aqueous phase was gradually transferred into the organic phase and reacted with *trans*-**1a** to cause glycol the cleavage reaction. This result strongly suggests that HOCl is the active species.

Scheme 5. The reaction of *trans*-1a with aq. HOCl.



Although conventional *aq*. NaOCl has been used as an oxidant for glycol cleavage,[7] it is not effective in cleaving highly hindered bicyclic glycol **1a**, as shown in Table 1 (**runs 1- 4**). This is because *aq*. NaOCl is not effective to have high pH value (>13) compared to be low pH (10 11) of NaOCl·$5H_2O$ crystals in several oxidation reactions. [8] Therefore, the effect of pH on the glycol cleavage reaction was examined using **1e** as a substrate (**Table 4**). Although the reaction rate of the glycol cleavage of **1e** using conventional aq. 13% NaOCl was slow to be recovered a half of **1e** (**run 2**), the reaction of **1e** using aq. 13% NaOCl prepared from NaOCl·$5H_2O$ and water exhibited faster (**run 1**). Furthermore, conventional aq. NaOCl adjusted using hydrochloric acid to lower the pH (**run 3**) gave results similar to those of aq. NaOCl prepared from NaOCl·$5H_2O$, but they were not identical.

Table 4. Effect of pH on glycol cleavage

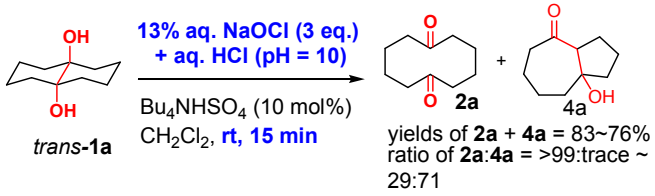


1e **2e** **3e**

Run	aq. NaOCl	pH of aq. NaOCl	Yield (GC%)		
			2e	**3e**	Total
1	13% aq NaOCl prepared from NaOCl·$5H_2O$ and water	10.4	40.2	35.4	75.6
2	Conventional 13% NaOCl aq.	13.3	50.7	1.3	52.0
3	Conventional 13% NaOCl aq. + aq.HCl	10.4	47.0	30.2	77.2

Hence, we have carefully examined the reaction of *trans*-**1a** with *aq*. NaOCl (pH = 10) prepared from conventional 13% *aq* NaOCl and hydrochloric acid (**Scheme 6**). Although the reaction went to completion immediately, recyclized compound **4a**, (produced *via* an intramolecular aldol reaction of **2a**) was formed. When several experiments were carried out under the same reaction conditions, the ratio of **2a** to **4a** varied widely. This phenomenon was a difference in the reaction of *trans*-**1a** with NaOCl·$5H_2O$ which consistently produced **2a** as the major product. Conventional *aq*. NaOCl is not as pure as NaOCl·$5H_2O$ and contains some impurities (NaCl, $NaOCl_3$ etc.) which may affect the product ratio.

Scheme 6. The reaction of *trans*-1a with *aq*. NaOCl (pH = 10.1) prepared from conventional 13% *aq* NaOCl and *aq*. HCl



In conclusion, the glycol cleavage of *trans*-cyclic glycols using $NaOCl \cdot 5H_2O$ proceeded much faster than their corresponding *cis*-cyclic glycols. This reactivity was in sharp contrast with that observed using the conventional glycol cleavage oxidants for which *cis*-glycols react much faster. $NaOCl \cdot 5H_2O$ was a superior reagent for glycol cleavage of sterically hindered *trans*-glycols. Hypochloric acid (HOCl) derived from $NaOCl \cdot 5H_2O$ was likely to be the active species.

Experimental Section

General Information: All reagents were purchased from Nacalai Tesque, Wako Pure Chemicals Industries, Kanto Kagaku, Kishida Reagents Chemical Co., Tokyo Chemical Industry or Aldrich, and used without any further purification. Melting points were measured on a Yanaco micro melting point apparatus (MP-J3) and are uncorrected. NMR spectra were recorded on a JEOL (JNM-EX400) spectrometer as solutions in $CDCl_3$ using TMS or the residual solvent peak as an internal standard. GC analyses were run on a Shimadzu GC-2014 instrument with flame-ionization detectors, equipped with an NB-1 (0.25 mm×60 m, df¼0.4 mm) GC column using helium as the carrier gas. GC yields were determined using 1-chloronaphtalene (for the reaction of **1e**, **1g** and **1h**) or decalin (for the reaction of**1f**) as an internal standard.

Preparation of the starting materials (glycols): All of the starting materials (glycols) are known compounds. Several of them were prepared according to the literature (*cis*-**1a**,[14] *trans*-**1a**,[14] **1b**,[15] **1c**[16] and **1d**[17]), and one was purchased as a commercial reagent [benzopinacol (**1j**)]. Glycols **1e**,[18] **1f**,[2a] **1g**,[19] **1h**[20] and **1j**[21] were prepared *via* the following procedures. Most of the glycols (**1e**, **1f**, **1g**, **1h** and **1j**) were prepared as a mixture of diastereomers.

1,2-Diphenylethane-1,2-diol (1e).[18] Sodium borohydride (1.14 g, 30.1 mmol) was added to a stirred solution of benzoin (4.25 g, 20.0 mmol) in methanol (100 mL) at 0 °C and the reaction mixture was stirred at room temperature for 80 min. Water was added and the mixture was concentrated in vacuo. The residue was partitioned with dichloromethane and water. The organic layer was separated and dried using anhydrous sodium sulfate. The dried extract was filtered and concentrated *in vacuo* to give the crude product as a white solid. Recrystallization from toluene methanol gave pure **1e** [18] (3.66 g, 85%) as colorless crystals.

1,2-Di-*p*-anisilethane-1,2-diol (1f). [2a] Sodium borohydride (0.568 g, 15.0 mmol) was added to a stirred solution of 1,2-di-*p*-anisil-2-hydroxyethan-1-one (2.72 g, 10.0 mmol) in methanol (100 mL) at 0 °C and the resulting reaction mixture was stirred at room temperature for 50 min. Water was added and the mixture was concentrated in vacuo. The residue was partitioned with ethyl acetate and water. The organic layer was separated and dried using anhydrous sodium sulfate. The dried extract was filtered and concentrated *in vacuo* to provide the crude product as a white solid. The crude product was purified by silica gel column chromatography using hexane ethyl acetate = 2:1 (v/v) as the eluent to give **1f**[2a] (1.52 g, 50%) as pale yellow crystals.

1,6-Diphenylhexane-3,4-diol (1g). [19] Sodium borohydride (284 mg, 7.51 mmol) was added to a stirred solution of 1,6-diphenyl-4-hydroxyhexan-4-one (1.34 g, 5.00 mmol) in methanol (10 mL) at 0 °C and the reaction mixture was stirred at room temperature for 40 min. Water was added and the mixture was concentrated in vacuo. The residue was partitioned with dichloromethane and water. The organic layer was separated and dried using anhydrous magnesium sulfate. The dried extract was filtered and concentrated *in vacuo* to provide the crude product as a white solid. The crude product was purified by silica gel column chromatography using hexane ethyl acetate = 5:1 (v/v) as the eluent to give **1g** [19] (798 mg, 63%) as colorless crystals.

1,2-Diphenylhexane-1,2-diol (1h). [20] A hexane solution of butyllithium (1.59 M, 13.0 mL, 20.7 mmol) was added to a stirred solution of benzoin (1.00 g, 4.71 mmol) in tetrahydrofuran (10 mL) at 78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 1 h under the same conditions. Saturated aqueous ammonium chloride (3 mL) was added to the reaction mixture, which was then warmed to room temperature. Water (5 mL)

was added and the resulting mixture was extracted with dichloromethane (20 mL × 3). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane ethyl acetate = 5:1 (v/v) as the eluent to give **1h** [20] (798 mg, 63%) as colorless crystals.

1,2-Dicyclopropyl-1,2-diphenylethane-1,2-diol (1j). [21] A tetrahydrofuran solution of cyclopropylmagnesium bromide (0.5 M, 22 mL, 11 mmol) was slowly added to a stirred solution of benzyl (1.05 g, 5.0 mmol) in tetrahydrofuran (60 mL) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 4 h 10 min at room temperature. Saturated aqueous ammonium chloride (3 mL) was added to the reaction mixture, which was then extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane ethyl acetate = 10:1 (v/v) as the eluent to give **1j** [21] (416 mg, 28%) as colorless crystals.

Standard experimental procedure for the glycol cleavage reaction using $NaOCl·5H_2O$: Sodium hypochlorite pentahydrate (606 mg, 3.68 mmol) was added to a stirred solution of *trans*-**1a** (210 mg, 1.23 mmol) and tetrabutylammonium hydrogen sulfate (42.2 mg 0.12 mmol) in dichloromethane (10 mL) and water (3 mL) at 0°C, and the resulting mixture was stirred for 0.2 h under the same conditions. Water (3 mL) was added, and the reaction mixture was extracted with dichloromethane (40 mL×2). The combined organic layers were dried over anhydrous sodium sulfate, filtered and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane ethyl acetate = 10:1 (v/v) as the eluent to give 1,6-cyclodecanedione **2a** (183 mg, 93%) as colorless crystals.

1,6-Cyclodecanedione (2a).[1a] m.p.: 99 °C (lit.[1a]: 99 100 °C). ^{1}H-NMR ($CDCl_3$): δ (ppm) 1.84 1.86 (m, 8H), 2.35 2.36 (m, 8H). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 23.4, 42.2, 214.1.

[1,1'-Biphenyl]-2,2'-diylbis(phenylmethanone) (2b).[22] Following the standard procedure, **1b** (182 mg, 0.50 mmol) was reacted with sodium hypochlorite pentahydrate (247 mg, 1.5 mmol) and tetrabutylammonium

hydrogen sulfate (17.0 mg 0.05 mmol) for 0.2 h to produce **2b** (182 mg, quant.) as colorless crystals. This product was sufficiently pure and required no further purification. m.p.: 174 175 °C (lit.[22]: 172 173 °C). ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.15 7.35 (m, 14H), 7.61 7.64 (m, 4H). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ (ppm) 126.7, 127.9, 129.3, 130.0, 130.3, 131.4, 132.7, 137.3, 138.2, 140.2, 197.5.

(*1S,3S*)-3-Acetyl-2,2-dimethylcyclobutaneacetaldehyde (2c)[23] **and (*1S,3S*)-3-acetyl-2,2-dimethylcyclobutaneacetic acid (3c).**[24] Following the standard procedure, **1c** (85.7 mg, 0.50 mmol) was reacted with sodium hypochlorite pentahydrate (495 mg, 3.0 mmol) and tetrabutylammonium hydrogen sulfate (17.0 mg 0.05 mmol) for 0.2 h to produce a mixture of **2c** and **3c**. The crude mixture was dissolved in ethyl acetate (30 mL) and extracted with saturated sodium bicarbonate (10 mL). The remaining ethyl acetate solution was washed with brine (5 mL × 2), dried over anhydrous sodium sulfate and concentrated *in vacuo* to give crude product **2c**. Crude **2c** was purified by silica gel column chromatography using hexane ethyl acetate = 1:1 (v/v) as the eluent to give **2c** (84.1 mg, 70% yield) as a pale yellow oil. The combined saturated sodium bicarbonate layers were acidified using concentrated hydrochloric acid and extracted with ethyl acetate (30 mL × 2). The combined organic layers were washed with brine (5 mL × 2), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to give **3c** (21.5 mg, 23%) as colorless crystals. This product was sufficiently pure and required no further purification.

2c: Pale yellow oil. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.83 (s, 3H), 1.32 (s, 3H), 1.90-1.99 (m, 2H), 2.03 (s, 3H), 2.38-2.48 (m, 3H), 2.90 (m, 1H), 9.72 (m, 1H). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ (ppm) 17.6, 22.8, 30.1, 30.3, 35.7, 43.3, 54.1, 54.3, 201.4, 207.4 .

3c: Colorless crystals. m.p.: 64 65 °C (lit.[24]: 68 °C). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.86 (s, 3H), 1.31 (s, 3H), 1.87 1.99 (m, 2H), 2.03 (s, 3H), 2.24 2.40 (m, 3H), 2.86 (m, 1H). $^{13}C\{^{1}H\}$-NMR($CDCl_3$): δ (ppm) 17.3, 23.0, 30.2, 30.2, 34.8, 37.7, 43.3, 54.2, 178.0, 207.7.

Reaction of *trans*-1d with NaOCl·5H$_2$O: 3β-Acetoxy-5-oxo-5,6-secocholestan-6-al (2d)[25] **and 3β-acetoxy-5-oxo-5,6- secocholestan-6-oic acid (3d).** [26] Following the standard procedure, ***trans*-1d** (232 mg, 0.50 mmol) was reacted with sodium hypochlorite pentahydrate (250 mg, 1.5 mmol) and tetrabutylammonium hydrogen sulfate (17.0 mg 0.05 mmol) for 0.6 h to give a mixture of **2d** and **3d**. Purification by silica-gel column chromatography using hexane ethyl acetate = 5:1 → 2:1 (v/v) as the eluent gave **2d** (159 mg, 69%) and **3d** (49 mg, 20%).

2d: Colorless oil. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.68 (s, 3H), 0.85 2.46 (m, 42H), 3.06 (dd, *J* = 14.0, 4.8 Hz, 1H), 5.37 (brs, 1H), 9.61 (brs, 1H). ^{13}C{^{1}H }-NMR ($CDCl_3$): δ (ppm) 11.5, 17.6, 18.5, 21.2, 22.5, 22.8, 23.1, 23.7, 25.1, 25.3, 27.8, 28.0, 34.3, 34.8, 35.7, 36.0, 39.4, 39.8, 42.1, 42.5, 43.2, 44.0, 52.3, 54.1, 56.1, 73.4, 170.2, 202.6, 216.1.

3d: Colorless oil. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.69 (s, 3H), 0.85 2.46 (m, 43H), 3.19 (dd, *J* = 14.4, 4.4Hz, 1H), 5.39 (br s, 1H). ^{13}C{^{1}H }-NMR ($CDCl_3$): δ (ppm) 11.7, 17.7, 18.6, 21.2, 22.5, 22.8, 23.0, 23.8, 24.4, 25.2, 27.9, 28.0, 34.0, 34.4, 35.6, 35.7, 36.0, 39.4, 39.7, 41.5, 42.6, 43.1, 52.3, 54.4, 55.9, 73.5, 170.3, 178.5, 216.3.

Reaction of *cis*-1d with NaOCl·5H$_2$O: 3-Acetocy-5-hydroxy-10,13-dimethyl-17-octyl-6-oxohexadecahydrocyclopenta[a]phenanthrene (4d).[25] Following the standard procedure, c***is*-1d** (232 mg, 0.50 mmol) was treated with sodium hypochlorite pentahydrate (250 mg, 1.5 mmol) and tetrabutylammonium hydrogen sulfate (17.0 mg 0.05 mmol) for 20 h 50 min to give a mixture of ***cis*-1d** and **4d** and several other compounds. The yields of ***cis*-1d** (18%) and **4d** (36%) were determined by ^{1}H-NMR spectroscopy using 1-chloro-4-(trifluoromethyl)benzene as an internal standard.

Benzaldehyde (2e)[27] **and benzoic acid (3e).** [28] Following the standard procedure, **1e** (214 mg, 1.00 mmol) was reacted with sodium hypochlorite pentahydrate (500 mg, 3.0 mmol) and tetrabutylammonium hydrogen sulfate (35.1 mg 0.10 mmol) to produce the crude product as a mixture of **2e** and **3e**. The yields of **2e** (40%) and **3e** (35%) were determined by GC.

***p*-Methoxybenzaldehyde (2f)**[29] **and *p*-methoxybenzoic acid (3f).** [30] Following the standard procedure, **1f** (274 mg, 1.00 mmol) was reacted with sodium hypochlorite pentahydrate (500 mg, 3.0 mmol) and

tetrabutylammonium hydrogen sulfate (35.1 mg 0.10 mmol) to produce the crude product as a mixture of **2f** and **3f**. The yields of **2f** (68%) and **3f** (7%) were determined by GC.

3-Phenylpropanal (2g)[31] **and 3-phenylpropanoic acid (3g).** [32] Following the standard procedure, **1g** (270 mg, 1.00 mmol) was reacted with sodium hypochlorite pentahydrate (500 mg, 3.0 mmol) and tetrabutylammonium hydrogen sulfate (35.1 mg 0.10 mmol) for 6 h to produce the crude product as a mixture of **2g** and **3g**. The yields of **2g** (2%) and **3g** (76%) were determined by GC.

Benzaldehyde (2e), benzoic acid (3e) and 1-phenylpentan-1-one (2h). [33] Following the standard procedure, **1h** (270 mg, 1.00 mmol) was reacted with sodium hypochlorite pentahydrate (500 mg, 3.0 mmol) and tetrabutylammonium hydrogen sulfate (35.1 mg 0.10 mmol) to produce the crude product as a mixture of **2e**, **3e** and **2g**. The yields of **2e** (40%), **3e** (35%) and **2g** (quant.) were determined by GC.

Benzophenone (2i).[34] Following the standard procedure, **1i** (367.5 mg, 1.00 mmol) was reacted with sodium hypochlorite pentahydrate (500 mg, 3.0 mmol) and tetrabutylammonium hydrogen sulfate (35.1 mg 0.10 mmol) to produce crude product **2i**. Purification by silica gel column chromatography using hexane ethyl acetate = 10:1 (v/v) as the eluent gave pure **2i** (297.1 mg, 82%) as colorless crystals. m.p.: 48 °C (lit.[34]: 47.8 49.4 °C). ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.47 7.50 (m, 4H), 7.57 7.61 (m, 2H), 7.80 7.82 (m, 4H). ^{13}C{^{1}H }-NMR ($CDCl_3$): δ (ppm) 128.2, 130.0, 132.4, 137.6, 196.7.

Cyclopropylphenylmethanone. (2j)[35] Following the standard procedure, **1j** (147.5 mg, 0.50 mmol) was reacted with sodium hypochlorite pentahydrate (250 mg, 1.5 mmol) and tetrabutylammonium hydrogen sulfate (17.0 mg 0.05 mmol) to produce crude product **2j**. Purification by silica gel column chromatography using hexane ethyl acetate = 15:1 (v/v) as the eluent gave pure **2j**(130.1 mg, 89%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ (ppm) 1.02 1.07 (m, 2H), 1.23 1.27 (m, 2H), 2.68 (septet, *J*=4.1 Hz, 1H), 7.48 (m, 2H), 7.56 (m, 1H), 8.02 (m, 2H). ^{13}C{^{1}H }-NMR ($CDCl_3$): δ (ppm) 11.6, 17.1, 128.0, 128.5, 132.7, 138.0, 200.6.

Standard experimental procedure for glycol cleavage using $Pb(OAc)_4$: Lead tetraacetate (975 mg, 2.2 mmol) was added to a stirred solution of glycol **1a** (170.1 mg, 1.00 mmol) in dichloromethane (10 mL) at room

temperature, and stirred for 117 h under the same conditions. Water (3 mL) was added, and the reaction mixture was extracted with dichloromethane (40 mL×2). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane ethyl acetate = 10:1 v/v as the eluent to give 1,6-cyclodecanedione **2a** (56.5 mg, 33%) as colorless crystals. This product was identical to **2a** prepared using sodium hypochlorite pentahydrate.

[1,1'-Biphenyl]-2,2'-diylbis(phenylmethanone) (2b). According to the standard procedure, **1b** (199 mg, 0.55 mmol) was reacted with lead tetraacetate (536 mg, 1.20 mmol) for 3 h to produce **2b** (181 mg, 92%) as colorless crystals. This product was identical to **2b** prepared using sodium hypochlorite pentahydrate.

(*1S,3S*)-3-Acetyl-2,2-dimethylcyclobutaneacetaldehyde (2c) and (*1S,3S*)-3-acetyl- 2,2-dimethylcyclobutaneacetic acid (3c). Following the standard procedure, **1c** (85.0 mg, 0.50 mmol) was reacted with lead tetraacetate (488 mg, 1.1 mmol) for 25 h to produce **3c**, accompanied by a trace amount of **2c** and several byproducts. The crude mixture was dissolved in ethyl acetate (30 mL) and extracted with saturated sodium bicarbonate (10 mL). The combined saturated sodium bicarbonate layers were acidified using concentrated hydrochloric acid and extracted with ethyl acetate (30 mL × 2). The combined organic layers were washed with brine (5 mL × 2), dried over anhydrous sodium sulfate, filtered and evaporated to provide **3c** (26.6 mg, 27%) as colorless crystals. This product was identical to the **3c** prepared using sodium hypochlorite pentahydrate. Since the amount of **2c** produced was very small and accompanied by many other by-products, it was impossible to obtain **2c** in its pure form from the residual ethyl acetate solution.

Reaction with *trans*-1d: 3β-Acetoxy-5-oxo-5,6-secocholestan-6-al (2d). Following the standard procedure, *trans*-**1d** (231 mg, 0.50 mmol) was reacted with lead tetraacetate (488 mg, 1.1 mmol) for 25 h to produce the crude product. Purification by silica gel column chromatography using hexane ethyl acetate = 5:1 → 2:1 (v/v) as the eluent gave **2d** (69.4 mg, 30%) as a colorless oil. This product was identical to **2d** prepared using sodium hypochlorite pentahydrate.

Reaction of *cis*-1d: 3β-Acetoxy-5-oxo-5,6-secocholestan-6-al (2d). Following the standard procedure, ***cis*-1d** (232 mg, 0.50 mmol) was reacted with lead tetraacetate (508 mg, 1.1 mmol) in dichloromethane (5 mL) for 15 min to produce **2d**. Purification by silica-gel column chromatography using hexane ethyl acetate = 5:1 → 2:1 (v/v) as the eluent gave **2d** (230 mg, quant.) as a colorless oil. This product was identical to **2d** prepared using sodium hypochlorite pentahydrate.

Glycol cleavage of an equimolar mixture of *cis*-1d and *trans*-1dwith NaOCl·5H$_2$O: Sodium hypochlorite pentahydrate (45.7 mg, 0.25 mmol) was added to a stirred solution of *cis*-**1d** (115.8 mg, 0.25 mmol), *trans*-**1d** (116.0 mg, 0.25 mmol) and tetrabutylammonium hydrogen sulfate (17.3 mg 0.25 mmol) in dichloromethane (10 mL) and water (3 mL) at 0 °C, and the resulting mixture was stirred for 40 min at room temperature. Water (3 mL) was added, and the react ion mixture was extracted with dichloromethane (40 mL × 2). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to produce the crude product as a mixture of *cis*-**1d**, *trans*-**1d** and **2d**. The yields of *cis*-**1d** (95%), *trans*-**1d** (30%) and **2d** (70%) were determined by ^{1}H-NMR spectroscopy using 1-chloro-4-(trifluoromethyl)benzene as an internal standard.

Glycol cleavage of *trans*-1a using aq. HOCl prepared from NaOCl·5H$_2$O, water and hydrochloric acid: The pH was adjusted to 5.9 by adding conc. hydrochloric acid to aq. NaOCl prepared upon dissolving NaOCl·5H$_2$O (248 mg, 1.5 mmol) in water (1.5 mL). The resulting aq. HOCl was added to a stirred solution of *trans*-**1a** (85 mg, 0.5 mmol) in dichloromethane (5 mL) at room temperature. The resulting suspension was stirred for 1.5 h under the same conditions. The reaction mixture was cooled to 0 °C, diluted with water (10 mL) and extracted with dichloromethane (20 mL × 2). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to provide the crude product as a colorless solid. Analysis of the crude product by ^{1}H-NMR spectroscopy using 1-chloro-4-(trifluoromethyl)benzene as an internal standard indicated that the yield of **2a** was 62%.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra of the obtained products. (PDF)

GC trace for reactions of **1e**, **1f**, **1g** and**1h.** (Table 3, runs 1 4), (PDF)

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(6) We developed the aerobic oxidative cleavage of bis-tertiary glycols catalyzed by oxytrichlorovanadium ($VOCl_3$) as an environmentally benign reaction (Kirihara, M.; Yoshida, K.; Noguchi, T.; Naito, S.; Matsumoto, N.; Ema, Y.; Torii, M.; Ishizuka, Y.; Souta, I. Effective cleavage of ditertiary glycols via vanadium(V)-catalyzed aerobic oxidation. *Tetrahedron Lett.* **2010**, *51*, 3619 3622). Therefore, a $VOCl_3$-catalyzed aerobic oxidative cleavage of **1a** was examined. Contrary to our expectation, **1a** proved to be unreactive under catalytic $VOCl_3$-O_2 conditions. The reaction of **1a** with an excess of $VOCl_3$ was similarly unsuccessful. Thus, we believe that highly hindered bicyclic glycols such as **1a** do not react with vanadium compounds.

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