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Hypervalent λ^n-Iodane-Mediated Fragmentation of Tertiary Cyclopropanol Systems

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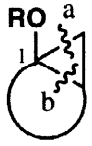
Abstract: The oxidation of tertiary cyclopropyl silyl ethers with hypervalent λ^n-iodanes caused fragmentation which produced alkenoic acids or esters.

Keywords: Fragmentation reactions; Hypervalent elements; Cyclopropanes

INTRODUCTION

Cyclopropyl compounds are widely used in organic synthesis due to their high reactivity. Among them, tertiary cyclopropyl silyl ethers (**1**), easily prepared from the cyclopropanation of enol silyl ethers, are recognized as useful synthetic intermediates,[1] and simple fragmentation at their cyclopropanol system is familiar as a procedure for the α homologation of ketones. Several methods have been developed to achieve the specific cleavage at bond "a" or "b" of **1**.

The C_1-C_3 bond (bond a) in **1** can be specifically cleaved with zinc(II) iodide,[2] base,[3,4] halogen,[5] mercury(II) acetate,[6] silver(I) tetrafluoroborate,[7,8] copper(II) tetrafluoroborate,[7,8] tin(IV) chloride,[9] phenylpalladium(II) triflate,[10] or Zeise's dimer.[11] With iron(III) chloride,[12-16] electrolysis[17] or manganese(III) picolinate[18-20] C_1-C_2 cleavage (bond b) occurs with a mechanism that has been assumed to involve radical intermediates.



1 (R = TMS)
2 (R = H)

a: $Hg(OAc)_2$, ZnI_2, base, halogen, $AgBF_4$, $Cu(BF_4)_2$, $SnCl_4$, PhPdOTf, $[Pt(C_2H_4)Cl_2]_2$
b: $FeCl_3$, $Mn(pic)_3$, electrolysis
a & b: $Pb(OAc)_4$

Scheme 1

Rubottom reported that the reaction of **1** with lead(IV) tetraacetate (LTA) in acetic acid lead to the cleavage of two bonds to yield alkenoic acids in moderate to high yields.[21,22] The reaction involves the fission

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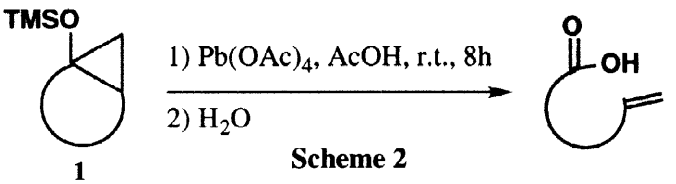
PII: S0040-4020(98)00862-X

of both bonds connected to the carbon bearing the siloxy group (the C_1-C_3 bond and the C_1-C_2 bond). This reaction is synthetically useful, however, the high toxicity of LTA is a serious drawback to its utility.



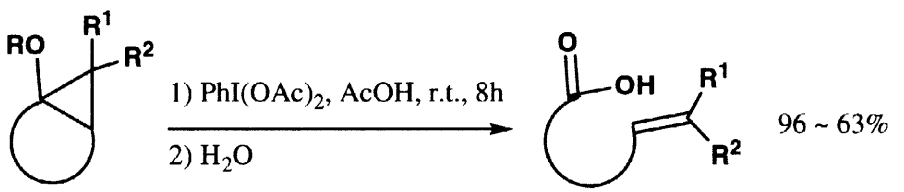
1

Scheme 2

We found that the treatment of **1** or **2** with phenyliodine(III) diacetate (PIDA) efficiently gave the alkenoic acids or their corresponding esters, and described it in preliminary communications.[23,24] We now report the full detail and further results of this reaction.

RESULTS AND DISCUSSION

The oxidation of **1** or **2** with 1.1 eq. PIDA in acetic acid at room temperature caused the two-bond cleavage (a and b) to afford alkenoic acids in high yields. The results of the PIDA and LTA oxidations are summarized in **Table 1**.



1 (R = TMS)
2 (R = H)

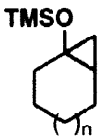
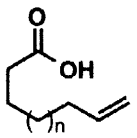
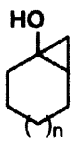
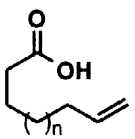
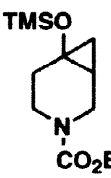
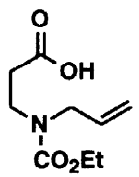
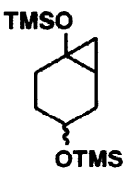
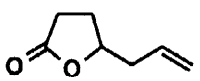
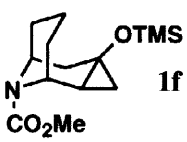
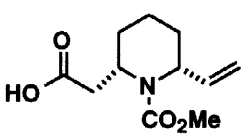
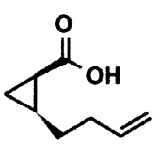
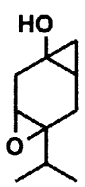
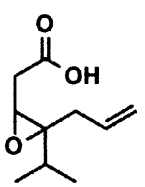
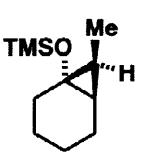
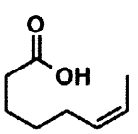
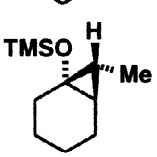
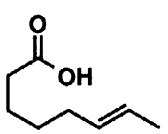
Scheme 3

The yields of the alkenoic acids in the PIDA oxidation were higher than those in the LTA oxidation in all cases. Particularly, in the case of the compound that has a nitrogen or an oxygen functionality (entries 3-5), the LTA oxidation gave **3** in low yield and was accompanied by several by-products while the PIDA oxidation gave **3** as the sole product in high yield. A cyclopropane without oxygen functionalities and an epoxide were inert toward PIDA under these reaction conditions (entries 6,7). As noted in entries 8 and 9, the *endo* compound (**1i**) gave only the (*Z*)-alkene (**3i**) while the *exo* compound (**1j**) gave only the (*E*)-alkene (**3j**). These results confirm that the PIDA-mediated fragmentation is a stereospecific reaction. Rubottom also observed a similar stereospecificity for the LTA oxidation.[22]

We also found that the PIDA oxidation of **1** in methanol or ethanol afforded the corresponding methyl- and ethyl esters. PIDA did not react with **1** in *i*-propanol (*i*-PrOH), *t*-butanol (*t*-BuOH), dichloromethane or acetonitrile (**Table 2**).

In an aqueous solvent, **1c** reacted with PIDA to give the alkenoic acid **3c**, and the results are summarized in **Table 3**. The best result was obtained in the case of aqueous acetone (acetone:H_2O = 3:1~ 10:1). The yields of the product were lower than that obtained from the reaction of PIDA in acetic acid.

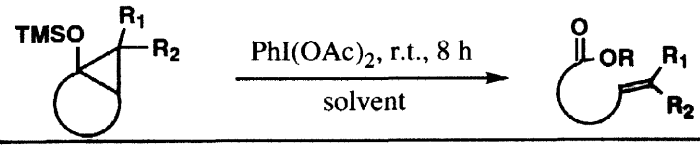
Table 1

Entry	Starting Material	Product	Yield (%) $PhI(OAc)_2$	Yield (%) $Pb(OAc)_4$
1	 **1a** (n=1) **1b** (n=2) **1c** (n=3)	 **3a** (n=1) **3b** (n=2) **3c** (n=3)	n =1 : 92 n =2 : 96 n =3 : 84[24]	n =1 : 83[21] n =2 : 92[21] n =3 : 70
2	 **2a** (n=1) **2b** (n=2) **2c** (n=3)	 **3a** (n=1) **3b** (n=2) **3c** (n=3)	n =1 : 64 n =2 : 73 n =3 : 65	n =1 : -* n =2 : -* n =3 : -*
3	 **1d**	 **3d**	84[24]	36
4	 **1e**	 **3e**	63	44
5	 **1f**	 **3f**	91#	67#
6	 **1g**	 **3g**	85	51
7	 **2h**	 **3h**	80#	38#
8	 **1i**	 **3i**	82	65[22]
9	 **1j**	 **3j**	74	73[22]

* Not examined. The ethers **1a-c** were found to be immediately hydrolyzed in acetic acid in the presence of $Pb(OAc)_4$ into **2a-c**, the actual species in the oxidation concerned in entry 1.

The yields of the corresponding methyl esters that were obtained from diazomethane treatment of **3**.

Table 2



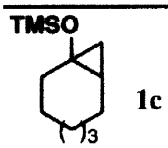
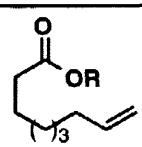
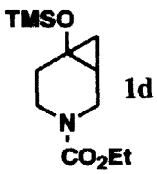
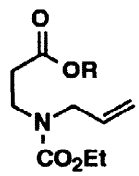
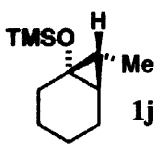
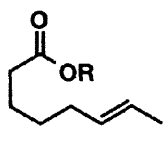
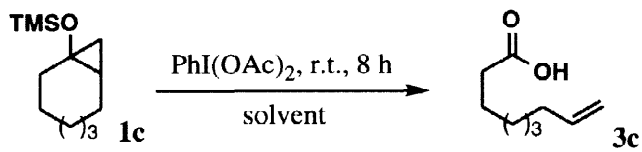
Starting Material	Product	Solvents					
		CH_2Cl_2	CH_3CN	MeOH	EtOH	*i*-PrOH	*t*-BuOH
 **1c**		N. R.	N. R.	76%[24] **6** (R=Me)	56%[24] **7** (R=Et)	N. R.[24]	N. R.[24]
 **1d**		N. R.	N. R.	68%[24] **8** (R=Me)	56%[24] **9** (R=Et)	N. R.[24]	N. R.[24]
 **1j**		N. R.	N. R.	42% **10** (R=Me)	68% **11** (R=Et)	N. R.	N. R.

Table 3



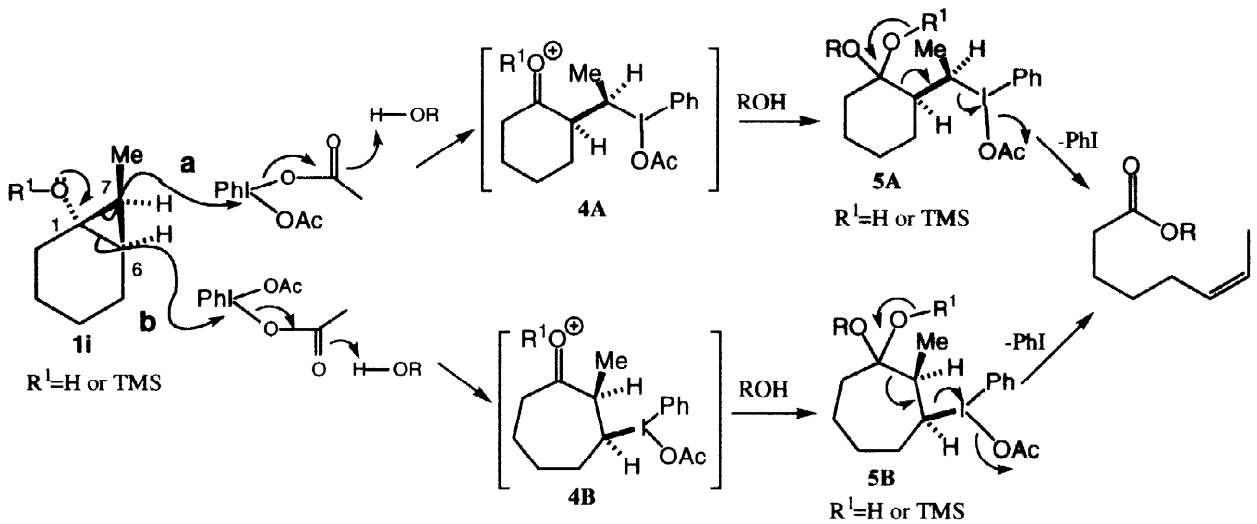
1c **3c**

n	acetone : H_2O = n : 1	CH_3CN : H_2O = n : 1	THF : H_2O = n : 1
1	66%	69%	-*
3	79%[24]	62%	56%
5	79%	61%	-*
10	81%	59%	-*
30	70%	-#	-*

* Not examined.
\# The reaction was not completed.

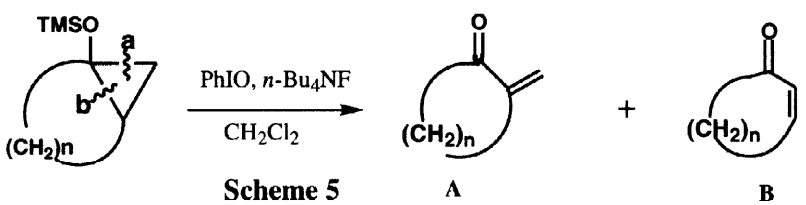
There are two plausible mechanisms based on the observed stereochemistry. These are shown in **Scheme 4** with **1i** as an example of the general reaction.[25] For path (a), attack of PIDA occurs at C7 behind the C1-C7 bond, resulting in the formation of the oxonium cation **4A**, where the stereochemistry at C7 is inverted.[26] The activation of PIDA by acidic protons in this step is essential, because the reaction did not proceed in aprotic solvents (dichloromethane and acetonitrile) or lower acidic solvents (*i*-PrOH and *t*-BuOH).

A protic solvent attacks **4A** to afford **5A**. Elimination of iodobenzene from **5A** then causes the C1-C6 cleavage to give the alkenoic acid anhydride (R=Ac),[27] the alkenoic ester (R=Me or Et), or the alkenoic acid (R=H). The *anti*-periplanar relationship between the C_1-C_6 and C_7-I bonds in **5A** is ideal for this fragmentation. In the LTA oxidation, Rubottom[22] proposed a mechanism similar to path (a). For path (b), PIDA attacks at C_6, and the C_1-C_6 bond is cleaved to give **5B**, where the stereochemistry at C_6 is inverted. The *anti*-periplanar relationship between the C_1-C_7 and C_6-I bonds in **5B** is ideal for the next fragmentation at C_1-C_7.



Scheme 4

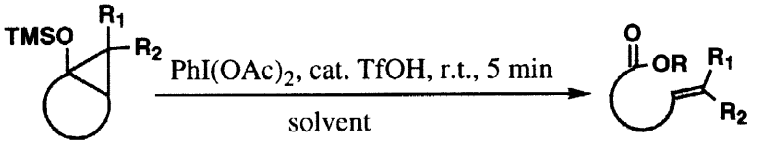
Moriarty *et al.* reported that the reaction of 1-(trimethylsiloxy)bicyclo[n.1.0]alkanes (n=4-7) with iodosobenzene in the presence of tetrabutylammonium fluoride in dichloromethane afforded a mixture of compound **A**, obtained through the "a" bond cleavage, and compound **B**, obtained through the "b" bond cleavage.[28] According to this result, we postulate that this PIDA oxidation proceeds through both paths (a) and (b).

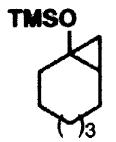
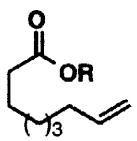
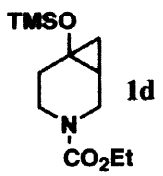
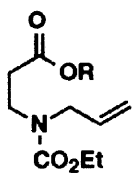
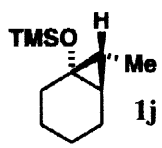
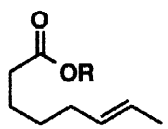


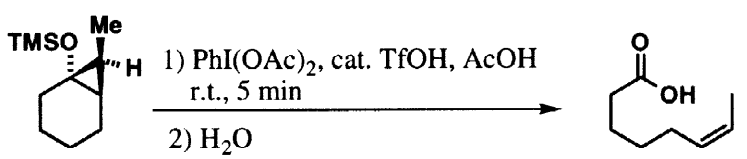
Scheme 5 **A** **B**

According to this reaction mechanism, it is assumed that strong acids enhance this fragmentation. We found that trifluoromethanesulfonic acid (TfOH) is an effective catalyst.[24,29] The results are shown in **Table 4**. With a catalytic amount of TfOH, the reaction terminated within a few minutes and the yields of the products were improved in all cases. Even in *i*-PrOH or *t*-BuOH, the reaction smoothly proceeded to afford the corresponding esters.[30] It is notable that the same stereospecificity was observed in the cases of **1i** and **1j** (**Table 4** and **Scheme 6**).

Table 4



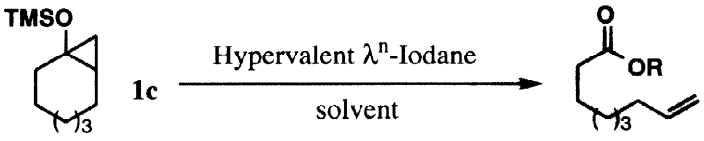
Starting Material	Product	Solvents					
		AcOH	H_2O:acetone = 1:3	MeOH	EtOH	*i*-PrOH	*t*-BuOH
 **1c**		88%[24] **3c** (R=H)	89%[24] **3c** (R=H)	88%[24] **6** (R=Me)	86%[24] **7** (R=Et)	89%[24] **12** (R=*i*-Pr)	57%[24] **13** (R=*t*-Bu)
 **1d**		87%[24] **3d** (R=H)	86%[24] **3d** (R=H)	92%[24] **8** (R=Me)	92%[24] **9** (R=Et)	81%[24] **14** (R=*i*-Pr)	77%[24] **15** (R=*t*-Bu)
 **1j**		86% **3j** (R=H)	90% **3j** (R=H)	90% **10** (R=Me)	76% **11** (R=Et)	65% **16** (R=*i*-Pr)	69% **17** (R=*t*-Bu)



1i **Scheme 6** **3i** (90%)

Other hypervalent λ^n-iodanes [phenyliodine bistrifluoroacetate (PIFA), iodosobenzene (PhIO) and iodoxybenzene ($PhIO_2$)] were also effective for the cleavage of **1**. All reagents efficiently gave an olefinic carboxylic acid in acetic acid. In the case of PIFA, the reactions were completed within 5 minutes. In the case of $PhIO_2$, 55 mol% of the reagent was enough to complete the reaction, because $PhIO_2$ is a λ^5-iodane (pentavalent iodine). Unfortunately, PhIO and $PhIO_2$ did not react with **1** in alcohol. PIFA turned out to be a highly effective reagent because it efficiently gave the desired products in alcohols (even in *i*-PrOH and *t*-BuOH). A catalytic amount of TfOH is also effective for the cleavage of **1** with PhIO or $PhIO_2$. With the catalyst, PhIO and $PhIO_2$ reacted with **1** in an alcohol to give the products (**Table 5**).

Table 5



	AcOH	MeOH	*i*-PrOH	*t*-BuOH
$PhI(OCOCF_3)_2$	**3c** (92%) (5 min)	**6** (64%)[a] (5 min)	**12** (81%) (5 min)	**13** (67%) (5 min)
PhIO	**3c** (96%) (8 h)	N. R.	N. R.	N. R.
PhIO + cat. TfOH	**3c** (97%) (5 min)	**6** (90%) (5 min)	**12** (67%) (4 h)	**13** (33%) (75 h)
$PhIO_2$[b]	**3c** (90%) (8 h)	N. R.	N. R.	N. R.
$PhIO_2$[b] + cat. TfOH	**3c** (95%) (5 min)	**6** (77%) (5 min)	**12** (77%) (16 h)	**13** (46%) (75 h)

a) With a catalytic amount of TfOH, **6** was obtained in 79% yield.

b) 55 mol% of reagent was used.

CONCLUSION

Hypervalent λⁿ-iodanes reacted with **1** and **2** to give alkenoic acids (or corresponding esters) in high yields. This oxidative ring cleavage had high chemoselectivity and stereospecificity. Acidity of the solvents is impotant to proceed the reaction and a catalytic amount of TfOH enhanced the reaction. Among the hypervalent λⁿ-iodanes, PIFA gave better results than the others. It is notable that $PhIO_2$, the reagent which has been seldom utilized in organic syntheses due to its insolubility in common solvents,[31-33] can be used for this oxidative fragmentation.

ACKNOWLEDGMENT

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EXPERIMENTAL SECTION

General: IR spectra were measured on a Perkin-Elmer 1600 Series FT-IR. NMR spectra were recorded on either a Varian Gemini 300 or a Varian UNITY plus 500 spectrometer. All the NMR spectra were taken using $CDCl_3$ solutions with tetramethylsilane as internal standard, and coupling constants (J) are given in hertz (Hz). Low-resolution and high-resolution mass spectra (electron impact) were recorded on either a JEOL D-200 or a JEOL AX505 spectrometer. Column chromatography was performed on silica gel (Merck Kieselger 60).

Tertiary cyclopropyl silyl ethers (**1a**,[34] **1b**,[34] **1c**,[9] **1d**,[24] **1g**,[35] **1i**,[22] and **1j**[22]) and tertiary cyclopropanols (**2a**,[36] **2b**,[36], and **2c**[36]) were prepared according to the literature. Hypervalent λ^3-iodanes (PIDA, PIFA, PhIO) were purchased from Tokyo Kasei Kogyo Co. Iodoxybenzene ($PhIO_2$) was prepared according to the literature.[32]

Representative procedure for the preparation of tertiary cyclopropyl silyl ethers (1e and 1f)

Lithium diisopropylamide (LDA) was prepared at 0°C from diisopropylamine (1.40 ml, 10.0 mmol) and *n*-butyllithium (1.6 M in hexane, 5.80 ml, 9.2 mmol) in tetrahydrofuran (THF)(30 ml) under an inert atmosphere. To this LDA solution, 4-hydroxycyclohexanone (519 mg, 4.2 mmol) was added at -78 °C, and the resulting mixture was stirred for 1 hr. Chlorotrimethylsilane (1.60 ml, 12.6 mmol) was added at -78 °C and the mixture was stirred at room temperature for 1 hr. The reaction mixture was quenched with water (10 ml) and extracted with ether (30 ml x 2). The combined extract was washed with brine and dried over anhydrous magnesium sulfate ($MgSO_4$). The solvent was evaporated to afford the crude enol silyl ether. The crude enol silyl ether was dissolved in dry dichloromethane (30 ml) and diethylzinc (0.99 M in hexane, 9.90 ml, 9.8 mmol) was added to the solution under an inert atmosphere. Diiodomethane (1.08 ml, 13.4 mmol) was added dropwise over 15 min at 0 °C, and the resulting mixture was stirred at room temperature for 1 hr. The reaction mixture was quenched with saturated ammonium chloride (10 ml) and filtered using Celite. The organic layer was separated and dried over $MgSO_4$. The solvent was evaporated to afford the crude product. The crude product was purified using column chromatography (*n*-hexane:ethyl acetate = 40:1) to afford **1e** (808 mg, 71% in two steps, an 1:1 mixture of *cis*- and *trans*-isomers) as a colorless oil.

1,4-Bis(trimethylsilyloxy)bicyclo[4.1.0]heptane (1e)

IR (neat) cm^{-1} : 2956, 1251, 1082, 839; ^1H-NMR ($CDCl_3$) δ: 0.07 (9H, s, CH_3 x3), 0.11 (4.5H, s, CH_3 x1.5), 0.13 (4.5H, s, CH_3 x1.5), 0.20 (0.5H, t, J=5.6 Hz, CH x0.5), 0.41 (0.5H, t, J=5.6 Hz, CH x0.5), 0.75-1.26 (5H, m, CH_2 x2 +CH), 1.47-1.65 (1H, m, CH), 1.83-2.04 (1H, m, CH), 2.20-2.28 (1H, m, CH), 3.50-3.57 (0.5H, m, CH x0.5), 3.58-3.70 (0.5H, m, CH x0.5); MS (m/z): 272 (M^+); HRMS calcd for $C_{13}H_{28}O_2Si_2$: 272.1627, found: 272.1646.

Methyl 4-(Trimethylsilyloxy)-10-azatricyclo[4.3.1.0^{2,4}]decane-10-carboxylate (1f)

A pale yellow oil (**1f**) (304 mg, 89% in two steps) was obtained from methyl 9-aza-3-oxo-bicyclo[3.3.1]nonane-9-carboxylate (238 mg, 1.21 mmol) as a mixture of rotamers.

IR (neat) cm^{-1} : 2853, 1703, 1449; ^1H-NMR ($CDCl_3$) δ: 0.13 (9H, s, CH_3 x3), 0.84-1.01 (2H, m, CH_2), 1.49-1.78 (7H, m, CH_2 x3 +CH), 2.04-2.19 (1H, m, CH), 2.42-2.56 (1H, m, CH), 3.65 (3H, s, $OCOCH_3$), 4.02-4.07 (0.5H, m, CHx1/2), 4.14-4.21 (0.5H, m, CHx1/2), 4.22-4.27 (0.5H, br, CHx1/2), 4.35-4.40 (0.5H, br, CHx1/2); HRMS calcd for $C_{14}H_{25}NO_3Si$ 283.4429, found: 283.4457.

3,4-Epoxy-1-hydroxy-4-(1-methylethyl)bicyclo[4.1.0]heptane (2h)

To a solution of 1-(triethylsilyloxy)-4-(1-methylethyl)cyclohexa-1,4-diene (1.00 g, 4.0 mmol) in dichloromethane (40 ml) was added diethylzinc (1.00 M, in hexane, 7.20 ml, 7.20 mmol) under an inert

atmosphere. Diiodomethane (0.384 ml, 4.8 mmol) was added dropwise over 15 min at 0 °C, and the resulting mixture was stirred at room temperature for 1 hr. The reaction mixture was quenched with saturated ammonium chloride (20 ml) and filtered using Celite. The organic layer was separated and dried over $MgSO_4$. The solvent was evaporated to afford the crude product of 4-(1-methylethyl)-1-(trimethylsilyloxy)bicyclo[4.1.0]hept-3-ene. The crude product was purified using column chromatography (*n*-hexane: ethyl acetate = 20:1) to afford the pure product (851 mg, 80%) as a colorless oil. To a solution of 4-(1-methylethyl)-1-(triethylsilyloxy)bicyclo[4.1.0]hept-3-ene (355 mg, 1.3 mmol) in methanol (10 ml) was added chlorotrimethylsilane (1 drop, ca. 12 mg) under an inert atmosphere and the mixture was stirred for 10 min. The reaction mixture was quenched with water (10 ml) and extracted with dichloromethane (60 ml x2), dried over magnesium sulfate and evaporated to afford the crude product of 1-hydroxy-4-(1-methylethyl)bicyclo[4.1.0]hept-3-ene. The crude product was dissolved in dry dichloromethane (10 ml) and *m*-chloroperbenzoic acid was added to the solution. The reaction mixture was stirred at room temperature for 2 hr, and then quenched with 5% aqueous sodium bicarbonate (50 ml). The mixture was extracted with ether (70 ml x2) and the combined organic layer was washed with 10% aqueous sodium bicarbonate (40 ml), water (40 ml) and brine (40 ml). The extract was dried over anhydrous magnesium sulfate and evaporated. The residue was purified using column chromatography (*n*-hexane: ethyl acetate = 5:2) to afford the pure product of **2h** (151 mg, 67%) as a colorless oil.

4-(1-methylethyl)-1-(triethylsilyloxy)bicyclo[4.1.0]hept-3-ene

A colorless oil. IR (neat) cm^{-1}: 2957, 2876, 1458, 1228, 1182, 998; ^{1}H-NMR ($CDCl_3$) δ: 0.48-0.52 (1H, m, CH), 0.58-0.80 (7H, m, CH_2x3 + CH), 0.89-0.98 (15H, m, CH_3 x5), 1.10-1.14 (1H, m, CH), 2.03-2.17 (2H, m, CH_2), 2.40-2.69 (3H, m, CH_2+CH), 5.18-5.20 (1H, m, CH); HRMS calcd for $C_{16}H_{30}OSi$ 266.2066, found: 266.2043.

3,4-Epoxy-1-hydroxy-4-(1-methylethyl)bicyclo[4.1.0]heptane (2h)

IR (neat) cm^{-1} : 3384, 2963, 1186; ^{1}H-NMR ($CDCl_3$) δ: 0.83 (3H, d, *J*=6.6 Hz, CH_3), 0.92 (3H, d, *J*=6.6 Hz, CH_3),0.99-1.02 (1H, m, CH), 1.39-1.43 (1H, m, CH), 1.71 (1H, dd, *J*=15.9 and 1.6 Hz, CH), 2.13-2.87 (6H, m, CH_2x2 + CHx2); HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found: 168.1143.

Representative procedure for the hypervalent λ^n-iodane oxidation of 1 or 2 in acetic acid

To a solution of **1a** (85.4 mg, 0.46 mmol) in glacial acetic acid (5 ml) was added PIDA (164 mg, 0.51 mmol), and the reaction mixture was then stirred for 8 hr at room temperature. The mixture was diluted with 5 ml of water and extracted with 2 x 20 ml of dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The residue was purified using chromatography on silica gel (*n*-hexane: ethyl acetate: formic acid = 6:1:0.01) gave **3a** (54.5 mg, 92%) as a colorless oil.

6-Heptenoic Acid (3a)

The sample obtained from **1a** (or **2a**) was identical with the authentic sample.[37]

7-Octenoic Acid (3b)

The sample obtained from **1b** (or **2b**) was identical with the authentic sample.[38]

γ-(Prop-2-enyl)-γ-butyrolactone (3e)

A colorless oil. The spectral data of this sample (obtained from **1e**) were identical with those of the literature.[39]

Methyl *cis*-6-Ethenyl-1-(methoxycarbonyl)-2-piperidinethanoate (Methyl ester of 3f)

The crude product of **3f** was treated with the ether solution of diazomethane [prepared from 50% aqueous potassium hydroxide (4 ml), ether (4 ml), and *N*-methyl-*N*-nitrosourea (276 mg)] to afford the methyl ester of **3f** as a pale yellow oil.

IR (neat) cm^{-1}: 2951, 1737, 1700, 1443, 1309; ^{1}H-NMR ($CDCl_3$) δ: 1.47-1.52 (1H, m, CH), 1.60-1.69 (4H, m, CH_2x2), 1.91-1.97 (1H, m, CH), 2.51-2.65 (2H, m, CH_2), 3.66 (3H, s, CH_3), 3.71 (3H, s, CH_3), 4.65-4.70 (1H, br, CH), 4.76-4.81 (1H, br, CH), 5.11-5.19 (2H, m, CH_2), 5.85-5.93 (1H, m, CH); ^{13}C-NMR ($CDCl_3$) δ: 14.4, 27.2, 28.1, 38.5, 47.9, 51.5, 51.8, 52.9, 115.5, 139.5, 156.5, 172.1; HRMS calcd for $C_{12}H_{19}NO_4$ 241.1314, found 241.1317.

***cis*-2-(But-3-enyl)cyclopropanecarboxylic Acid (3g)**

A colorless oil. IR (neat) cm^{-1}: 3500-2500, 1700, 1438, 1234; ^{1}H-NMR ($CDCl_3$) δ: 0.94-1.01 (1H, m, CH), 1.05-1.14 (1H, m, CH), 1.30-1.42 (1H, m, CH), 1.60-1.74 (3H, m, CH_2+CH), 2.06-2.18 (2H, m, CH_2), 4.92-5.07 (2H, m, CH_2), 5.74-5.89 (1H, m, CH), 10.20-12.25 (1H, br, COOH); ^{13}C-NMR ($CDCl_3$) δ: 14.5, 18.2, 22.7, 26.5, 33.8, 115.0, 138.2, 180.0; HRMS calcd for $C_8H_{12}O_2$ 140.0837, found 140.0858.

Methyl 3,4-Epoxy-4-(1-methylethyl)-6-heptenoate (Methyl ester of 3h)

The crude product of **3h** was treated with the ether solution of diazomethane [prepared from 50% aqueous potassium hydroxide (4 ml), ether (4 ml), and *N*-methyl-*N*-nitrosourea (276 mg)] to afford the methyl ester of **3h** as a pale yellow oil.

IR (neat) cm^{-1} : 2964, 1741, 1437, 1336, 1174; ^{1}H-NMR ($CDCl_3$) δ: 0.92 (3H, d, *J*=7.1 Hz, CH_3), 0.97 (3H, d, *J*=7.1 Hz, CH_3), 1.78-1.89 (1H, m, CH), 2.24-2.47 (2H, m, CH_2), 2.55-2.74 (2H, m, CH_2), 3.21 (1H, t, *J*=6.3 Hz, CH), 3.72 (3H, s, CH_3), 5.05-5.15 (2H, m, CH_2), 5.72-5.87 (1H, m, CH) ; ^{13}C-NMR ($CDCl_3$) δ: 17.6, 18.3, 32.5, 34.1, 34.3, 52.0, 56.5, 65.2, 117.6, 133.8, 171.2; HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1289.

(*Z*)-6-Octenoic Acid (3i)

A colorless oil. The sample obtained from **1i** was identical with the authentic sample.[22]

(*E*)-6-Octenoic Acid (3j)

A colorless oil. The sample obtained from **1j** was identical with the authentic sample.[22]

Representative procedure for the hypervalent iodine oxidation of 1 in an alcohol

To a solution of **1j** (95.0 mg, 0.48 mmol) in methanol (3.0 ml) was added PIDA (186 mg, 0.58 mmol), and the reaction mixture was stirred for 8 hr under an inert atmosphere at room temperature. The mixture was diluted with water and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate and then evaporated. Chromatography of the residue gave 31.1 mg (42%) of **10** as a colorless oil.

Methyl (*E*)-6-Octenoate (10)

A colorless oil; IR (neat) 2932, 1741, 967 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.30-1.42 (2H, m, CH_2),1.55-1.66 (5H, m, CH_3+CH_2), 1.93-2.03 (2H, m, CH_2), 2.29 (2H, t, *J*=7.4 Hz, CH_2), 3.66 (3H, s, CH_3), 5.37-5.44 (2H, m, CHx2); ^{13}C-NMR ($CDCl_3$) δ: 18.1, 24.6, 29.2, 32.3, 34.1, 51.6, 125.3, 131.0, 174.4; Anal. calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.21; H, 10.19.

Ethyl (*E*)-6-Octenoate (11)

A colorless oil; IR (neat) 2927, 1737, 1458, 1160, 966 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, *J*=7.1 Hz, CH_3), 1.29-1.41 (2H, m, CH_2), 1.54-1.66 (5H, m, CH_3+CH_2), 1.93-2.02 (2H, m, CH_2), 2.27 (2H, t, *J*=7.4 Hz, CH_2), 4.10 (2H, q, *J*=7.1 Hz, CH_2), 5.36-5.42 (2H, CHx2); ^{13}C-NMR ($CDCl_3$) δ: 14.5, 18.2, 24.7, 29.3, 32.4, 34.5, 60.4, 125.2, 131.0, 173.8; MS m/z 170 (M^+); HRMS calcd for $C_{10}H_{18}O_2$ 170.1307, found: 170.1295.

Representative procedure for the hypervalent iodine oxidation of 1 in an aqueous solvent
To a solution of **1c** (113 mg, 0.53 mmol) in water (0.4 ml) and acetone (4.0 ml) was added PIDA (187 mg, 0.58 mmol), and the mixture was stirred for 8 hr under an inert atmosphere at room temperature. The mixture was diluted with water and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, and evaporated. Chromatography of the residue gave 67 mg (81%) of **3c** as a colorless oil.

Representative procedure for the hypervalent iodine oxidation of 1 in the presence of TfOH
To a solution of **1j** (108 mg, 0.55 mmol) and PIDA (211 mg, 0.66 mmol) in *i*-propanol (3.0 ml) was added one drop of TfOH, and the reaction mixture was stirred for 5 min under an inert atmosphere at room temperature. The mixture was diluted with water and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, and evaporated. Chromatography of the residue gave 65.4 mg (65%) of **16** as a colorless oil.

(1-Methyl)ethyl (*E*)-6-Octenoate (16)
A colorless oil; IR (neat) 2980, 2935, 1732, 1374, 1180, 1110, 967 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.21 (6H, d, *J*=6.0 Hz, CH_3x2), 1.25-1.41 (2H, m, CH_2), 1.53-1.71 (5H, m, CH_3+CH_2), 1.92-2.02 (2H, m, CH_2), 2.24 (2H, t, *J*=7.4 Hz, CH_2), 4.39-5.03 (1H, m, CH), 5.35-5.46 (2H, m, CHx2); ^{13}C-NMR ($CDCl_3$) δ: 18.2, 22.1, 24.8, 29.3, 32.4, 34.8, 67.5, 125.2, 131.0, 173.3; MS m/z 184 (M^+); HRMS calcd for $C_{11}H_{20}O_2$: 184.1463, found: 184.1490.

(1,1-Dimethyl)ethyl (*E*)-6-Octenoate (17)
A colorless oil; IR (neat) 2933, 1734, 1367, 1152, 966 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.28-1.70 (7H, m, CH_3+CH_2x2), 1.43 (9H, s, CH_3x3), 1.92-2.02 (2H, m, CH_2), 2.19 (2H, t, *J*=7.4 Hz, CH_2), 5.36-5.47 (2H, m, CHx2); ^{13}C-NMR ($CDCl_3$) δ: 18.2, 24.9, 28.4, 29.2, 32.5, 35.7, 80.1, 125.1, 131.1, 173.2; MS m/z 198 (M^+); HRMS calcd for $C_{12}H_{22}O_2$: 198.1620, found: 198.1611.

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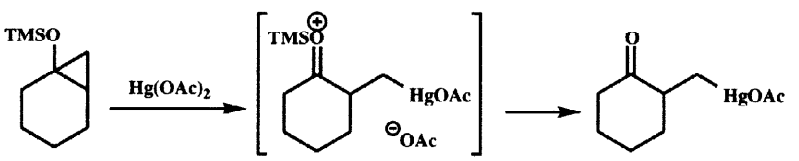
25. Rubottom reported that a small quantity of lead(II) acetate promoted the rapid conversion of **1** to **2**, and the fragmentation process was actually an oxidation reaction involving **2**. However, **1** was not hydrolyzed immediately in acetic acid in the presence of PIDA. It is not sure that PIDA reacts with **1** directly, or reacts with a hydrolyzed compound **2**.
26. The reaction of **1** with mercury(II) acetate gives β-mercurio ketones,[6] and resembles the first step of the PIDA reaction in reaction mechanism. A similar feature has been reported with ZnI_2,[2] $Cu(BF_4)_2$,[7,8] $AgBF_4$,[7,8] or $SnCl_4$.[9]



27. Infrared spectra of the PIDA oxidation psroduct from **1** showed, prior to treatment with water, bands at 1820 and 1750 cm^{-1}, those consistent with a postulated anhydride.
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