Supporting Information

for

Iodine as a Catalyst for Efficient Conversion of Ketones to *gem*-Dihydroperoxides by Aqueous Hydrogen Peroxide

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General remarks:

Ketones and 30% aq H₂O₂ were obtained from commercial sources and were used as received. Silica gel 60 (70-230 mesh ASTM) was used for column chromatography.

¹H and ¹³C spectra were obtained with TMS and CDCl₃ as internal standards on a 300 MHz spectrometer.

Standard KBr pellet procedures were used to obtain IR spectra of solids, while a film of neat material was used for liquid products. Absorptions are reported in cm⁻¹ (ν_{max}). Active oxygen content was determined by iodometric titration.¹

Caution. Although we have encountered no difficulties in working with these peroxides, routine precautions (shields, fume hoods, avoidance of transition metal salts) should be observed whenever possible, as organic peroxides are potentially hazardous compounds.

Reaction procedure for synthesis of 4-*tert*-Butyl-1-methoxy-cyclohexyl-hydroperoxide **3**:

To the solution of 0.1 mmol of I₂ (25.4 mg) and 4 mmol of 30% aq H₂O₂ (0.45 mL) in 2 mL of methanol, 1 mmol (154 mg) of 4-*t*-Bu-cyclohexanone **1** was added and solution stirred at room temperature for 24 hours. The mixture was then poured into water, products were extracted by dichloromethane, organic phase was dried over Na₂SO₄ and solvent was partly evaporated under reduced pressure (cca. 20 mmHg). The product was separated from iodine and starting substrate by column chromatography on SiO₂. Elution with ethyl acetate-dichloromethane (1: 9) yielded 141 mg (70%) of monoperoxy ketal **3** as a 3: 2 mixture of diastereomers.

4-*tert*-Butyl-1-methoxy-cyclohexyl-hydroperoxide **3**:²

white solid, major diastereomer (from mixture): ¹H NMR (CDCl₃, ppm): 0.86 (s, 9H), 0.92-1.50 (m, 5H), 1.69 (m, 2H), 2.03-2.38 (m, 2H), 3.34 (s, 3H), 7.89 (s, 1H); ¹³C NMR (CDCl₃, ppm): 23.6, 27.6, 30.9, 32.3, 47.4, 48.5, 105.4.

minor diastereomer (from mixture): ¹H NMR (CDCl₃, ppm): 0.86 (s, 9H), 0.92-1.50 (m, 5H), 1.69 (m, 2H), 2.03-2.38 (m, 2H), 3.30 (s, 3H), 7.89 (s, 1H); ¹³C NMR (CDCl₃, ppm): 23.4, 27.6, 30.9, 31.4, 47.5, 48.2, 105.7.

Reaction procedure for synthesis of *gem*-dihydroperoxides:

The preparation of **2** is representative.

To the solution of 0.1 mmol of I₂ (25.4 mg) and 4 mmol of 30% aq H₂O₂ (0.45 mL) in 10 mL of acetonitrile, 1 mmol (154 mg) of 4-*t*-Bu-cyclohexanone **1** was added and solution stirred at room temperature for 5 hours. Reaction mixture was concentrated under reduced pressure (cca. 20 mmHg), dichloromethane (10 mL) added and solution dried over Na₂SO₄. The solvent was again partly evaporated and product was separated from H₂O₂, iodine and starting substrate by column chromatography on SiO₂. Elution with dichloromethane-ethyl acetate (8: 2) yielded 185 mg (91%) of dihydroperoxide **2**.

4-tert-butylcyclohexane-1,1-diyl dihydroperoxide 2 (91%):³

white solid, mp 79-81°C,

¹H NMR (CDCl₃, ppm): 0.87 (s, 9H), 1.06 (m, 1H), 1.25 (m, 2H), 1.46 (m, 2H), 1.72 (bd, 2H, *J*=12 Hz), 2.30 (bd, 2H, *J*=12 Hz), 9.38 (bs, 2H); ¹³C NMR (CDCl₃, ppm): 23.2, 27.6, 29.7, 32.3, 47.4, 111.0.

Cyclopentane-1,1-diyl dihydroperoxide 7 (70%):⁴

colorless oil,

¹H NMR (CDCl₃, ppm): 1.63-1.82 (m, 4H), 1.88-2.06 (m, 4H), 9.69 (bs, 2H); ¹³C NMR (CDCl₃, ppm): 24.5, 33.1, 122.2.

2-Methylcyclohexane-1,1-diyl dihydroperoxide 9 (80%):⁵

colorless oil,

¹H NMR (CDCl₃, ppm): 1.07 (d, 3H, *J*=7.2 Hz), 1.37-1.80 (m, 7H), 1.89-2.01 (m, 1H), 2.20-2.34 (m, 1H), 8.83 (s, 1H), 8.89 (s, 1H); ¹³C NMR (CDCl₃): 14.4, 20.2, 22.4, 24.8, 29.5, 32.0, 113.2.

3-Methylcyclohexane-1,1-diyl dihydroperoxide 11 (93%):

colorless oil,

¹H NMR (CDCl₃, ppm): 0.81-1.01 (m, 4H), 1.12 (t, 1H, *J*=13 Hz), 1.26-1.79 (m, 5H), 2.23 (bd, 2H, *J*=13 Hz), 9.28 (bs, 2H); ¹³C NMR (CDCl₃, ppm): 21.9, 22.0, 29.0, 29.0, 34.0, 37.4, 111.4; IR: 3440, 1155 1005. Anal.

Calcd. for C₇H₁₄O₄ x 0.15H₂O: C, 50.99; H, 8.74. Found C, 50.92; H, 8.70.

MS-ESI (NH₄⁺): 185 (MNa⁺)

4-Methylcyclohexane-1,1-diyl dihydroperoxide 13 (98%):⁶

white solid, mp 135°C with decomposition,

¹H NMR (CDCl₃, ppm): 0.95 (d, 6.4 Hz, 3H), 1.1-1.80 (m, 7H), 2.2 (m, 2H), 9.25 (bs, 2H); ¹³C NMR (CDCl₃, ppm): 21.4, 29.0, 30.6, 31.6, 110.9

MS-ESI (NH₄⁺): 180 (MNH₄⁺)

Cycloheptane-1,1-diyl dihydroperoxide 15 (90%):³

white solid, mp 60-61°C

¹H NMR (CDCl₃, ppm): 1.50 (s, 8H), 1.87-2.11 (m, 4H), 9.64 (s, 2H); ¹³C NMR (CDCl₃, ppm): 22.6, 22.7, 29.8, 30.0, 32.4, 33.0, 116.2.

Cyclododecane-1,1-diyl dihydroperoxide 17 (60%):³

white solid, mp 137-138°C with decomposition

¹H NMR (DMSO-d₆, ppm): 1.20-1.60 (m, 22H), 10.81 (s, 2H); ¹³C NMR (DMSO-d₆, ppm): 18.9, 21.5, 21.8, 25.6, 25.8, 25.9, 112.3.

Adamantane-2,2-diyl dihydroperoxide 19 (92%):³

mp 147-148°C

¹H NMR (CDCl₃, ppm): 1.64-2.39 (m, 14H), 8.80 (s, 2H); ¹³C NMR (CDCl₃, ppm): 27.0, 31.2, 33.7, 37.0, 112.7.

3,3-Dihydroperoxyandrostane-17-on 21 (77%)

white solid, mp 161-161.5°C with decomposition

¹H NMR (CDCl₃, ppm): 0.76-2.50 (m, 22H), 0.84 (s, 3H), 0.87 (s, 3H), 8.35 (s, 1H), 8.53 (s, 1H); ¹³C NMR (CD₃CN, ppm): 11.9, 14.2, 21.3, 22.4, 26.5, 28.8, 31.7, 32.6, 32.7, 35.8, 35.9, 36.3, 36.8, 43.2, 48.5, 52.2, 55.2, 110.4, 221.4; IR: 3400, 3280, 1700, 1060, 1030, 980.

Anal. Calcd. for C₁₉H₃₀O₅ x 1/10 H₂O: C, 67.07; H, 8.95. Found C, 66.84; H, 9.00.

5α-Cholestane-3α,3β-dihydroperoxide 24:⁷

white solid: ¹H NMR (CDCl₃, ppm): 0.65 (s, 3H), 0.81 (s, 3H), 0.86 and 0.87 (both d, *J*= 6 Hz, 3H), 0.90 (d, *J*= 6 Hz, 3H), 8.0 (bs, 1H), 8.08 (bs, 1H).

Decane-3,3-diyl dihydroperoxide 5 (91%):

white solid, mp 30.1-30.5°C,

¹H NMR (CDCl₃, ppm): 0.88 (t, 3H, *J*=7 Hz), 0.96 (t, 3H, *J*=7 Hz), 1.21-1.46 (m, 10H), 1.60-1.80 (m, 4H), 8.50 (s, 2H); ¹³C NMR (CDCl₃, ppm): 8.0, 14.1, 22.3, 22.6, 23.5, 28.7, 29.1, 29.7, 31.7, 114.7; IR: 3440, 1150, 1130.

Anal. Calcd. for C₁₀H₂₂O₄: C, 58.23; H, 10.75. Found C, 58.12; H, 10.73.

MS-ESI (NH_4^+): 224 (MNH_4^+)

Nonane-2,2-diyl dihydroperoxide 26 (96%):

colorless oil,

^1H NMR (CDCl_3 , ppm): 0.88 (t, 3H, $J=7$ Hz), 1.17-1.50 (m, 13H), 1.70-1.80 (m, 2H), 8.97 (s, 2H); ^{13}C NMR (CDCl_3 , ppm): 14.1, 17.8, 22.6, 23.9, 29.1, 29.7, 31.7, 33.0, 112.7; IR: 3440, 1130, 1095.

Anal. Calcd. for $\text{C}_9\text{H}_{20}\text{O}_4 \times 0.1\text{H}_2\text{O}$: C, 55.70; H, 10.49. Found C, 55.52; H, 10.79.

MS-ESI (NH_4^+): 210 (MNH_4^+)

Nonane-5,5-diyl dihydroperoxide 28 (78%):³

colorless oil,

^1H NMR (CDCl_3 , ppm): 0.92 (t, 6H, $J=7$ Hz), 1.27-1.43 (m, 8H), 1.61-1.75 (m, 4H), 9.12 (bs, 2H); ^{13}C NMR (CDCl_3 , ppm): 13.9, 22.8, 25.7, 28.9, 114.3

5-Methylheptane-3,3-diyl dihydroperoxide 30 (50%):

colorless oil,

^1H NMR (CDCl_3 , ppm): 0.89 (t, 3H, $J=7$ Hz), 0.97 (t, 6H, $J=7$ Hz), 1.14-1.32 (m, 1H), 1.32-1.92 (m, 6H), 8.82 (s, 2H); ^{13}C NMR (CDCl_3 , ppm): 8.1, 11.3, 19.9, 22.6, 30.2, 30.5, 34.7, 115.1; IR: 3330, 1150, 1130.

Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{O}_4$: C, 53.91; H, 10.18. Found C, 53.83; H, 10.39.

MS-ESI (NH_4^+): 201 (MNa^+)

1-Phenylethane-1,1-diyl dihydroperoxide 32 (16%):

white solid, mp 76.8-77.4°C

^1H NMR (CDCl_3 , ppm): 1.70 (s, 3H), 7.31-7.41 (m, 3H), 7.46-7.58 (m, 2H), 9.31 (s, 2H); ^{13}C NMR (CDCl_3 , ppm): 23.1, 111.4, 125.7, 128.4, 128.6, 138.2; IR: 3348, 3219, 1142, 1123, 855.

OOH: calculated: 38.8%; by iodometric titration: 37.8%

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{O}_4$: C, 56.47; H, 5.92. Found C, 56.67; H, 6.16.

Phenylmethylene dihydroperoxide 36a (55%):⁸

colorless oil

^1H NMR (CDCl_3 , ppm): 6.32 (s, 1H), 7.20-7.52 (m, 5H), 9.60 (s, 2H); ^{13}C NMR (CDCl_3 , ppm): 109.9, 127.0, 128.4, 129.7, 132.3.

(4-Methoxyphenyl)methylene dihydroperoxide 36b (76%):

light yellow oil (non-stable compound, partial decomposition at 4°C after few hours)

^1H NMR (CDCl_3 , ppm): 3.80 (s, 3H), 6.27 (s, 1H), 6.88 (d, 2H, $J=9$ Hz), 7.34 (d, 2H, $J=9$ Hz), 9.41 (s, 2H); ^{13}C NMR (CDCl_3 , ppm): 55.3, 110.1, 113.9, 124.4, 128.5, 160.5. IR: 3360, 1230, 1170, 1040, 830, 730.

OOH: calculated: 35.48%; by iodometric titration: 34.95%

Literature:

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Comment	K429-1	Date	Aug 23 2005	Date Stamp	Aug 23 2005
File Name	C:\NMR\Katja\K400_499\K429_1_h	Frequency (MHz)	302.98	Nucleus	¹ H
Number of Transients	10	Pulse Sequence	s2pul	Receiver Gain	20.00
Temperature (degree C)	35.000	Solvent	CHLOROFORM-d		

—8.93

11:

—2.25
—2.21

—1.68

—1.11
—0.94
—0.92

Comment	K429-1	Date	Aug 23 2005	Date Stamp	Aug 23 2005	File Name	C:\NMR\Katja\K400_499\K429_1_c
Frequency (MHz)	76.19	Nucleus	13C	Number of Transients	2000	Pulse Sequence	s2pul
Receiver Gain	60.00	Solvent	CHLOROFORM-d	Temperature (degree C) 35.000			

11:

—111.39

—37.36

—34.02

—29.04

—28.99

—22.03

—21.94

Comment	K52a-3	Date	Feb 23 2006	Date Stamp	Feb 23 2006
File Name	C:\NMR\Katja\K500_599\k529_3_cdcl3_1h	Frequency (MHz)	302.98	Nucleus	¹ H
Number of Transients	2000	Pulse Sequence	s2pul	Receiver Gain	20.00
Temperature (degree C)	35.000	Solvent	CHLOROFORM-d		

—8.53
—8.35

21:

—0.87
—0.84

Comment	K529-3	Date	Feb 23 2006	Date Stamp	Feb 23 2006
File Name	C:\NMR\Katja\K500_599\k529_3_cd3cn_13c	Frequency (MHz)	76.19	Nucleus	13C
Pulse Sequence	s2pul	Receiver Gain	60.00	Solvent	ACETONITRILE-d3
Temperature (degree C)	35.000

Comment	K456-1	Date	Oct 11 2005	Date Stamp	Oct 11 2005	File Name	C:\NMR\Katja\K400_499\K456_1_h
Frequency (MHz)	297.80	Nucleus	1H	Number of Transients	8	Pulse Sequence	s2pul
Receiver Gain	20.00	Solvent	CHLOROFORM-d	Temperature (degree C) 22.000

Comment	K456-1	Date	Oct 11 2005	Date Stamp	Oct 11 2005	File Name	C:\NMR\Katja\K400_499\K456_1_C
Frequency (MHz)	74.89	Nucleus	13C	Number of Transients	2000	Pulse Sequence	s2pul
Receiver Gain	60.00	Solvent	CHLOROFORM-d	Temperature (degree C) 35.000			

-114.72

5:

-77.43
-77.00
-76.57

-31.74
-29.69
-29.10
-28.67

-23.47
-22.62
-22.28

-14.07

-7.95

Comment	K457-1	Date	Oct 11 2005	Date Stamp	Oct 11 2005	File Name	C:\NMR\Katja\K400_499\K457_1_H
Frequency (MHz)	297.80	Nucleus	1H	Number of Transients	8	Pulse Sequence	s2pul
Receiver Gain	20.00	Solvent	CHLOROFORM-d	Temperature (degree C) 22.000

Comment	K457-1	Date	Oct 11 2005	Date Stamp	Oct 11 2005	File Name	C:\NMR\Katja\K400_499\K457_1_C
Frequency (MHz)	74.89	Nucleus	13C	Number of Transients	2000	Pulse Sequence	s2pul
Receiver Gain	60.00	Solvent	CHLOROFORM-d	Temperature (degree C) 35.000

Comment	K459-1	Date	Oct 11 2005	Date Stamp	Oct 11 2005	File Name	C:\NMR\Katja\K400_499\K459_1_h
Frequency (MHz)	297.80	Nucleus	1H	Number of Transients	8	Pulse Sequence	s2pul
Receiver Gain	20.00	Solvent	CHLOROFORM-d	Temperature (degree C) 22.000			

-8.82

30:

-0.97
-0.89

Comment	K459-1	Date	Oct 11 2005	Date Stamp	Oct 11 2005	File Name	C:\NMR\Katja\K400_499\K459_1_C
Frequency (MHz)	74.89	Nucleus	13C	Number of Transients	2000	Pulse Sequence	s2pul
Receiver Gain	60.00	Solvent	CHLOROFORM-d	Temperature (degree C) 35.000			

30:

-115.08

-34.72

-30.48

-30.16

-22.66

-19.87

-11.30

-8.08

CHLOROFORM-d

Comment	K501-1	Date	Nov 24 2005	Date Stamp	Nov 24 2005
File Name	C:\NMR\Katja\K500_599\K501_1_h	Frequency (MHz)	297.80	Nucleus	¹ H
Number of Transients	8	Pulse Sequence	s2pul	Receiver Gain	40.00
Temperature (degree C)	25.000	Solvent	CHLOROFORM-d

Comment	K501-1	Date	Nov 24 2005	Date Stamp	Nov 24 2005	File Name	C:\NMR\Katja\K500_599\K501_1_c
Frequency (MHz)	74.89	Nucleus	13C	Number of Transients	2000	Pulse Sequence	s2pul
Receiver Gain	60.00	Solvent	CHLOROFORM-d	Temperature (degree C) 25.000

Comment	K478	Date	Nov 10 2005	Date Stamp	Nov 10 2005
File Name	C:\NMR\Katja\K400_499\K478_h	Frequency (MHz)	302.98	Nucleus	¹ H
Number of Transients	8	Pulse Sequence	s2pul	Receiver Gain	20.00
Temperature (degree C)	25.000	Solvent	CHLOROFORM-d

Comment	K478	Date	Nov 10 2005	Date Stamp	Nov 10 2005
File Name	C:\NMR\Katja\K400_499\K478_c	Frequency (MHz)	76.19	Nucleus	13C
Number of Transients	2000	Pulse Sequence	s2pul	Receiver Gain	60.00
Temperature (degree C)	35.000	Solvent	CHLOROFORM-d		

36a:

Comment	K492-1	Date	Nov 17 2005	Date Stamp	Nov 17 2005	File Name	C:\NMR\Katja\K400_499\K492_1_h
Frequency (MHz)	297.80	Nucleus	1H	Number of Transients	10	Pulse Sequence	s2pul
Receiver Gain	40.00	Solvent	CHLOROFORM-d	Temperature (degree C) 25.000

Comment	K492-1	Date	Nov 17 2005	Date Stamp	Nov 17 2005	File Name	C:\NMR\Katja\K400_499\K492_1_C
Frequency (MHz)	74.89	Nucleus	13C	Number of Transients	2000	Pulse Sequence	s2pul
Receiver Gain	60.00	Solvent	CHLOROFORM-d	Temperature (degree C) 25.000