

## Supporting Information

### Photolysis of 1-Alkylcycloalkanols in the Presence of (Diacetoxiodo)benzene and I<sub>2</sub>.

#### Intramolecular Selectivity in the $\beta$ -Scission Reactions of the Intermediate

#### 1-Alkylcycloalkoxyl Radicals

Carla S. Aureliano Antunes,<sup>a</sup> Massimo Bietti,<sup>\*:a</sup> Osvaldo Lanzalunga,<sup>b</sup> and Michela Salamone<sup>a</sup>

<sup>a</sup> *Dipartimento di Scienze e Tecnologie Chimiche, Università “Tor Vergata”, Via della Ricerca Scientifica, 1 I-00133 Rome, Italy,*

<sup>b</sup> *Dipartimento di Chimica, Università “La Sapienza”, P.le A. Moro, 5 I-00185 Rome, Italy*

<b>Synthesis of the substrates</b>	<b>S2</b>
1) <i>1-alkylcyclobutanols (1f-g)</i>	<b>S2</b>
2) <i>1-alkylcyclopentanols (2a-i)</i>	<b>S2</b>
3) <i>1-alkyl-cyclohexanols (3a-e, 3g-i)</i>	<b>S3</b>
4) <i>1-alkyl-cycloheptanols (4c-e, 4g, 4h)</i>	<b>S5</b>
5) <i>1-alkyl-cyclooctanols (5c-e, 5g, 5h)</i>	<b>S5</b>
<b><sup>1</sup>H NMR and GC-MS characterization of reaction products</b>	<b>S7</b>
1) <i>Products from 1-alkylcyclobutanols (1f-g)</i>	<b>S7</b>
2) <i>Products from 1-alkylcyclopentanols (2a-i)</i>	<b>S7</b>
3) <i>Products from 1-alkylcyclohexanols (3a-e, 3g-i)</i>	<b>S9</b>
4) <i>Products from 1-alkylcycloheptanols (4c-e, 4g, 4h)</i>	<b>S10</b>
5) <i>Products from 1-alkylcyclooctanols (5c-e, 5g, 5h)</i>	<b>S10</b>
<b>References</b>	<b>S12</b>

## Synthesis of the substrates

### 1) 1-alkylcyclobutanols (1f-g)

1-Allyl and 1-benzylcyclobutanol were prepared by reaction of cyclobutanone with the appropriate alkylmagnesium chloride in anhydrous tetrahydrofuran, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

#### 1-Allylcyclobutanol (1f):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.89-5.81 (m, 1H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ),  $\delta$  5.21-5.15 (m, 2H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ),  $\delta$  2.40-2.37 (m, 2H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ),  $\delta$  2.13-2.04 (m, 4H,  $\text{CH}_2$ ),  $\delta$  1.86-1.62 (m, 1H,  $\text{CH}_2$ ),  $\delta$  1.59-1.46 (m, 1H,  $\text{CH}_2$ ).

GC-MS m/z (relative abundance): 83, 71 (100), 56.

#### 1-Benzylcyclobutanol (1g):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.30-7.25 (m, 5H, ArH),  $\delta$  2.90 (s, 2H, Ar $\text{CH}_2$ ),  $\delta$  2.21-2.12 (m, 2H,  $\text{CH}_2$ ),  $\delta$  2.02-1.98 (m, 2H,  $\text{CH}_2$ ),  $\delta$  1.82-1.78 (m, 1H,  $\text{CH}_2$ ),  $\delta$  1.67-1.58 (m, 1H,  $\text{CH}_2$ ).<sup>S1</sup>

GC-MS m/z (relative abundance): 162 ( $\text{M}^+$ ), 134, 133, 116, 91 (100), 71, 51.

### 2) 1-alkylcyclopentanols (2a-i)

1-Ethyl, 1-propyl, 1-allyl, 1-benzyl and 1-phenylcyclopentanol were prepared by reaction of cyclopentanone with the appropriate alkylmagnesium chloride in anhydrous tetrahydrofuran, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

#### 1-Ethylcyclopentanol (2b):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.86-1.55 (m, 10H,  $(\text{CH}_2)_4$  and  $\text{CH}_2\text{CH}_3$ ),  $\delta$  0.97 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).<sup>S2</sup>

GC-MS m/z (relative abundance): 85 (100), 72, 67, 57.<sup>S3</sup>

#### 1-Propylcyclopentanol (2c):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.86-1.30 (m, 12H,  $(\text{CH}_2)_4$  and  $\text{CH}_2\text{CH}_2\text{CH}_3$ ),  $\delta$  0.94 (t, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ).

GC-MS m/z (relative abundance): 99, 85 (100), 72, 67, 57.

1-Isopropylcyclopentanol (2d) was prepared by reaction of isopropylmagnesium chloride with cyclopentanone in the presence of  $\text{CeCl}_3$  according to a procedure reported in the literature,<sup>S4</sup> purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.89-1.47 (m, 9H,  $(\text{CH}_2)_4$  and  $\text{CH}(\text{CH}_3)_2$ ),  $\delta$  1.05 (s, 1H, OH),  $\delta$  0.95 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

GC-MS m/z (relative abundance): 99, 85 (100), 72, 67, 57.

1-tert-Butylcyclopentanol (2e) was prepared by reaction of *tert*-butyllithium (solution 1.7 M in heptane) with cyclopentanone at  $-78$  °C according to a procedure reported in the literature,<sup>S5</sup> purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.83-1.42 (m, 8H,  $(\text{CH}_2)_4$ ),  $\delta$  0.97 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).<sup>S6</sup>

GC-MS m/z (relative abundance): 109, 85 (100), 67, 57.

1-Allylcyclopentanol (2f):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.97-5.83 (m, 1H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ),  $\delta$  5.17-5.12 (m, 2H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ),  $\delta$  2.35-2.33 (m, 2H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ),  $\delta$  1.82-1.78 (m, 2H,  $\text{CH}_2$ ),  $\delta$  1.72-1.51 (m, 6H,  $\text{CH}_2$ ).<sup>S7</sup>

GC-MS m/z (relative abundance): 97, 85 (100), 67, 55.

1-Benzylcyclopentanol (2g):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.35-7.18 (m, 5H, ArH),  $\delta$  2.90 (s, 2H, Ar $\text{CH}_2$ ),  $\delta$  1.90-1.75 (m, 2H,  $\text{CH}_2$ ),  $\delta$  1.74-1.51 (m, 6H,  $\text{CH}_2$ ).<sup>S8</sup>

GC-MS m/z (relative abundance): 92 (100), 85, 67, 57, 55.

1-Phenylcyclopentanol (2h):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.48-7.24 (m, 5H, ArH),  $\delta$  2.03-1.82 (m, 8H,  $(\text{CH}_2)_4$ ),  $\delta$  1.62 (s, 1H, OH).<sup>S9</sup>

GC-MS m/z (relative abundance): 162 ( $\text{M}^+$ ), 144, 133 (100), 128, 115, 105, 77, 55.

1-Neopentylcyclopentanol (2i) was prepared by reaction of neopentylmagnesium chloride with cyclopentanone in the presence of  $\text{CeCl}_3$  (powdered in a mortar and then heated to  $140$  °C under vacuum for 2 hours before use), purified by column chromatography (basic alumina, eluent hexane) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.77-1.59 (m, 10H,  $\text{CH}_2$ ),  $\delta$  1.21 (s, 1H, OH),  $\delta$  1.04-1.01 (m, 9H,  $\text{C}(\text{CH}_3)_3$ ).

GC-MS m/z (relative abundance): 141, 99, 85, 71, 57 (100).

### 3) 1-alkylcyclohexanols (3a-e, 3g-i)

1-Ethyl, 1-propyl, 1-benzyl, 1-phenyl and 1-neopentylcyclohexanol were prepared by reaction of cyclohexanone with the appropriate alkylmagnesium chloride in anhydrous tetrahydrofuran, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

1-Ethylcyclohexanol (3b):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.69-1.23 (m, 12H,  $(\text{CH}_2)_5$  and  $\text{CH}_2\text{CH}_3$ ),  $\delta$  0.90 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).<sup>S10</sup>

GC-MS m/z (relative abundance): 99 (100), 85, 81, 72, 57.

*1-Propylcyclohexanol (3c):*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.70-1.25 (m, 14H,  $(\text{CH}_2)_5$  and  $\text{CH}_2\text{CH}_2\text{CH}_3$ ),  $\delta$  1.21 (s, 1H, OH),  $\delta$  0.97 (t, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ).

GC-MS m/z (relative abundance): 99 (100), 81, 71, 57.

*1-Isopropylcyclohexanol (3d)* was prepared by reaction of isopropylmagnesium chloride with cyclohexanone in the presence of  $\text{CeCl}_3$  according to a procedure reported in the literature,<sup>S4</sup> purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.65-1.47 (m, 8H,  $(\text{CH}_2)_4$ ),  $\delta$  1.43-1.32 (m, 2H,  $\text{CH}_2$ ),  $\delta$  1.25-1.12 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ),  $\delta$  1.08 (s, 1H, OH),  $\delta$  0.91 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).<sup>S10</sup>

GC-MS m/z (relative abundance): 99 (100), 81, 71, 55.

*1-tert-Butylcyclohexanol (3e)* was prepared by reaction of *tert*-butyllithium (solution 1.7 M in heptane) with cyclohexanone at  $-78$  °C according to a procedure reported in the literature,<sup>S5</sup> purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.67-1.32 (m, 10H,  $(\text{CH}_2)_5$ ),  $\delta$  0.92 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).<sup>S11</sup>

GC-MS m/z (relative abundance): 123, 99 (100), 81, 67, 57.

*1-Benzylcyclohexanol (3g):*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.32-7.15 (m, 5H, ArH),  $\delta$  2.75 (s, 2H, Ar $\text{CH}_2$ ),  $\delta$  1.68-1.40 (m, 10H,  $(\text{CH}_2)_5$ ).<sup>S12</sup>

GC-MS m/z (relative abundance): 99, 92 (100), 91, 81, 65, 55.

*1-Phenylcyclohexanol (3h):*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.25-7.21 (m, 5H, ArH),  $\delta$  1.82-1.58 (m, 10H,  $(\text{CH}_2)_5$ ),  $\delta$  1.33-1.28 (m, 1H, OH).<sup>S13</sup>

GC-MS m/z (relative abundance): 176 ( $\text{M}^+$ ), 158, 143, 133, 120, 115, 105, 91, 77, 55 (100).

*1-Neopentylcyclohexanol (3i):*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.63-1.41 (m, 12H,  $\text{CH}_2$ ),  $\delta$  1.23 (s, 1H, OH),  $\delta$  1.04 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).

GC-MS m/z (relative abundance): 170 ( $\text{M}^+$ ), 155, 137, 127, 114, 99 (100), 96, 81, 71, 67, 57.

#### 4) 1-alkylcycloheptanols (4c-e, 4g, 4h)

1-Propyl, 1-benzyl and 1-phenylcycloheptanol were prepared by reaction of cycloheptanone with the appropriate alkylmagnesium chloride in anhydrous tetrahydrofuran, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

##### 1-Propylcycloheptanol (4c):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.65-1.36 (m, 16H,  $(\text{CH}_2)_6$  and  $\text{CH}_2\text{CH}_2$ ),  $\delta$  0.94-0.90 (t, 3H,  $\text{CH}_3$ ).

GC-MS m/z (relative abundance): 156 ( $\text{M}^+$ ), 141, 138, 127, 123, 113 (100), 99, 95, 86, 81, 67, 57, 55.

1-Isopropylcycloheptanol (4d): was prepared by reaction of isopropyllithium (solution 0.7 M in pentane) with cycloheptanone at  $-78$  °C, purified by column chromatography (basic alumina, eluent hexane/ethyl acetate 50:1) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.72-1.47 (m, 13H,  $(\text{CH}_2)_6$ ,  $\text{CH}(\text{CH}_3)_2$ ),  $\delta$  0.91 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

GC-MS m/z (relative abundance): 113 (100), 99, 95, 86, 67, 55.

1-tert-butylcycloheptanol (4e) was prepared by reaction of *tert*-butyllithium (solution 1.7 M in heptane) with cycloheptanone at  $-78$  °C according to a procedure reported in the literature,<sup>S5</sup> purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.81-1.43 (m, 12H,  $(\text{CH}_2)_6$ ),  $\delta$  0.94 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).<sup>S14</sup>

GC-MS m/z (relative abundance): 152, 137, 123, 113 (100), 95, 81, 79, 67, 57, 55.

##### 1-Benzylcycloheptanol (4g):

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.26-7.19 (m, 5H, ArH),  $\delta$  2.75 (m, 2H, ArCH<sub>2</sub>),  $\delta$  2.04-1.25 (m, 12H,  $(\text{CH}_2)_6$ ).<sup>S15</sup>

GC-MS m/z (relative abundance): 186, 129, 113 (100), 95, 92, 91, 67, 55.

##### 1-Phenylcycloheptanol (4h)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.48-7.23 (m, 5H, ArH),  $\delta$  2.11-1.59 (m, 13H,  $(\text{CH}_2)_6$  and OH).<sup>S16</sup>

GC-MS m/z (relative abundance): 190 ( $\text{M}^+$ ), 172, 157, 144, 133 (100), 124, 115, 104, 91, 77, 55.

#### 5) 1-alkylcyclooctanols (5c-e, 5g, 5h)

1-Propyl, 1-benzyl and 1-phenylcyclooctanol were prepared by reaction of cyclooctanone with the appropriate alkylmagnesium chloride in anhydrous tetrahydrofuran, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H}$  NMR.

*1-Propylcyclooctanol (5c):*

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.75-1.34 (m, 18H,  $(\text{CH}_2)_7$  and  $\text{CH}_2\text{CH}_2$ ),  $\delta$  0.95-0.90 (t, 3H,  $\text{CH}_3$ ).

GC-MS  $m/z$  (relative abundance): 170 ( $\text{M}^+$ ), 152, 141, 127 (100), 123, 109, 99, 87, 86, 71, 67, 58.

*1-Isopropylcyclooctanol (5d):* was prepared by reaction of isopropyllithium (solution 0.7 M in pentane) with cyclooctanone at  $-78\text{ }^\circ\text{C}$ , purified by column chromatography (basic alumina, eluent hexane/ethyl acetate 50:1) and identified by GC-MS and  $^1\text{H NMR}$ .

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.80-1.32 (m, 15H,  $(\text{CH}_2)_7$  and  $\text{CH}(\text{CH}_3)_2$ ),  $\delta$  0.91 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

GC-MS  $m/z$  (relative abundance): 127 (100), 109, 99, 86, 81, 71, 67, 57, 55.

*1-tert-Butylcyclooctanol (5e):* was prepared by reaction of *tert*-butyllithium (solution 1.7 M in heptane) with cyclooctanone at  $-78\text{ }^\circ\text{C}$  according to a procedure reported in the literature,<sup>S5</sup> purified by column chromatography (silica gel, eluent hexane/ethyl acetate 10:1) and identified by GC-MS and  $^1\text{H NMR}$ .

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.78-1.45 (m, 14H,  $(\text{CH}_2)_7$ ),  $\delta$  0.96 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).

GC-MS  $m/z$  (relative abundance): 166, 151, 138, 127, 122, 109, 95, 83, 81, 69, 67, 57 (100).

*1-Benzylcyclooctanol (5g):*

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.26-7.20 (m, 5H,  $\text{ArH}$ ),  $\delta$  2.75 (m, 2H,  $\text{ArCH}_2$ ),  $\delta$  1.69-1.48 (m, 14H,  $(\text{CH}_2)_7$ ).<sup>S15</sup>

GC-MS  $m/z$  (relative abundance): 200, 172, 143, 127, 109, 104, 91, 81, 67 (100), 55.

*1-Phenylcyclooctanol (5h):*

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.53-7.25 (m, 5H,  $\text{ArH}$ ),  $\delta$  2.09-1.56 (m, 14H,  $(\text{CH}_2)_7$ ).<sup>S17</sup>

GC-MS  $m/z$  (relative abundance): 204 ( $\text{M}^+$ ), 186, 171, 158, 143, 129, 118 (100), 105, 91, 77, 55.

## **<sup>1</sup>H NMR and GC-MS characterization of reaction products**

### **1) Products from 1-alkylcyclobutanols (1f-g):**

#### **a) Products from 1-allylcyclobutanol (1f):**

##### 7-iodo-1-hepten-4-one

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.99-5.85 (m, 1H, CH<sub>2</sub>=CHCH<sub>2</sub>), δ 5.22-5.13 (m, 2H, CH<sub>2</sub>=CHCH<sub>2</sub>), δ 3.24-3.18 (m, 4H, CH<sub>2</sub>=CHCH<sub>2</sub> and CH<sub>2</sub>I), δ 2.61 (t, 2H, C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I), δ 2.15-2.03 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I).

GC-MS m/z (relative abundance): 197 (100), 169, 161, 127, 118, 104, 91, 65, 63.

#### **b) Products from 1-benzylcyclobutanol (1g):**

##### 5-iodo-1-phenylpentan-2-one

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.43-7.33 (m, 5H, ArH), δ 3.70 (s, 2H, ArCH<sub>2</sub>), δ 3.17 (t, 2H, CH<sub>2</sub>I), δ 2.61 (t, 2H, C(O)CH<sub>2</sub>), δ 2.02-1.95 (m, 2H, C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I).

GC-MS m/z (relative abundance): 197 (100), 169, 155, 141, 127, 111, 69, 68.

### **2) Products from 1-alkylcyclopentanols (2a-i):**

#### **a) Products from 1-methylcyclopentanol (2a):**

##### 6-iodohexan-2-one

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.18 (t, 2H, CH<sub>2</sub>I), δ 2.46 (t, 2H, C(O)CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>I), δ 2.11 (s, 3H, CH<sub>3</sub>C(O)), δ 1.85-1.80 (m, 2H, C(O)(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I), δ 1.73-1.65 (m, 2H, C(O)CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>I).<sup>S18</sup>

GC-MS m/z (relative abundance): 155, 127, 99 (100), 71, 55.

#### **b) Products from 1-ethylcyclopentanol (2b):**

##### 7-iodoheptan-3-one

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.18 (t, 2H, CH<sub>2</sub>I), δ 2.46-2.39 (m, 4H, CH<sub>3</sub>CH<sub>2</sub>C(O) and C(O)CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>I), δ 1.84-1.78 (m, 2H, C(O)(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I), δ 1.71-1.63 (m, 2H, C(O)CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>I), δ 1.06 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>C(O)).

GC-MS m/z (relative abundance): 183, 155, 127, 113, 85, 57 (100), 54.

#### **c) Products from 1-propylcyclopentanol (2c):**

##### 8-iodooctan-4-one

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.19 (t, 2H, CH<sub>2</sub>I), δ 2.46-2.35 (m, 4H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(O) and C(O)CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>I), δ 1.90-1.55 (m, 4H, C(O)CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>I), δ 0.89 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)).

GC-MS m/z (relative abundance): 183, 127, 71 (100), 55.

**d) Products from 1-isopropylcyclopentanol (2d):**

7-iodo-2-methylheptan-3-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.18 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.63-2.53 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ),  $\delta$  2.46 (t, 2H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  1.97-1.55 (m, 4H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{I}$ ),  $\delta$  1.1 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

GC-MS m/z (relative abundance): 183, 127, 71, 55 (100).

**e) Products from 1-tert-butylcyclopentanol (2e):**

7-iodo-2,2-dimethylheptan-3-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.18 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.51 (t, 2H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  2.08-1.92 (m, 2H,  $\text{C}(\text{O})(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.62-1.50 (m, 2H,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ),  $\delta$  0.96 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).

GC-MS m/z (relative abundance): 183, 141, 125, 83, 69, 57 (100), 55.

**f) Products from 1-allylcyclopentanol (2f):**

8-iodo-1-octen-4-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.99-5.85 (m, 1H,  $\text{CH}_2=\text{CHCH}_2$ ),  $\delta$  5.22-5.11 (m, 2H,  $\text{CH}_2=\text{CHCH}_2$ ),  $\delta$  3.20-3.15 (m, 4H,  $\text{CH}_2\text{I}$  and  $\text{CH}_2=\text{CHCH}_2$ ),  $\delta$  2.48 (t, 2H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  1.95-1.90 (m, 2H,  $\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.53-1.45 (m, 2H,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ).

GC-MS m/z (relative abundance): 211, 183, 155, 125, 69, 55 (100).

**g) Products from 1-benzylcyclopentanol (2g):**

6-iodo-1-phenylhexan-2-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.43-7.33 (m, 5H, ArH),  $\delta$  3.68 (s, 2H,  $\text{ArCH}_2\text{C}(\text{O})$ ),  $\delta$  3.11 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.47 (t, 2H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  1.85-1.61 (m, 4H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{I}$ ).

GC-MS m/z (relative abundance): 211, 183, 175, 91, 65, 55 (100).

**h) Products from 1-phenylcyclopentanol (2h):**

5-iodo-1-phenylpentan-1-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.97-7.94 (m, 2H, ArH),  $\delta$  7.55-7.50 (m, 3H, ArH),  $\delta$  3.23 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  3.01 (t, 2H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  2.08-2.03 (m, 2H,  $\text{C}(\text{O})(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.71-1.66 (m, 2H,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ).<sup>S19</sup>

GC-MS m/z (relative abundance): 160, 145, 131, 115, 105 (100), 91, 77, 63, 51.

**i) Products from 1-(2,2-dimethyl)propylcyclopentanol (2i):**

2,2-dimethyl-8-iodooctan-4-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.17 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.41 (t, 2H,  $\text{C}(\text{O})\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  2.29 (s, 2H,  $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{O})$ ),  $\delta$  1.84-1.76 (m, 2H,  $\text{C}(\text{O})(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.68-1.60 (m, 2H,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ),  $\delta$  1.01 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).

GC-MS m/z (relative abundance): 226, 211, 183, 155, 141, 127, 111, 99, 81, 71, 57 (100), 51.

**3) Products from 1-alkylcyclohexanols (3a-e, 3g-i):**

**a) Products from 1-methylcyclohexanol (3a):**

7-iodoheptan-2-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.19 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.45 (t, 2H,  $\text{C(O)CH}_2(\text{CH}_2)_4\text{I}$ ),  $\delta$  2.15 (s, 3H,  $\text{CH}_3\text{C(O)}$ ),  $\delta$  1.87-1.78 (m, 2H,  $\text{C(O)(CH}_2)_3\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.66-1.31 (m, 4H,  $\text{C(O)CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{I}$ ).<sup>S18</sup>

GC-MS m/z (relative abundance): 155, 141, 127, 113 (100), 95, 71, 58, 55.

**b) Products from 1-ethylcyclohexanol (3b):**

8-iodooctan-3-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.19 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.46-2.36 (m, 4H,  $\text{CH}_3\text{CH}_2\text{C(O)}$  and  $\text{C(O)CH}_2(\text{CH}_2)_4\text{I}$ ),  $\delta$  1.88-1.78 (m, 2H,  $\text{C(O)(CH}_2)_3\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.65-1.36 (m, 4H,  $\text{C(O)CH}_2\text{CH}_2(\text{CH}_2)_3\text{I}$  and  $\text{C(O)(CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ),  $\delta$  1.06 (t, 3H,  $\text{CH}_3\text{CH}_2\text{C(O)}$ ).

GC-MS m/z (relative abundance): 155, 141, 127, 113 (100), 95, 71, 58, 55.

**c) Products from 1-propylcyclohexanol (3c):**

9-iodononan-4-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.19 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.43-2.35 (m, 4H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)}$  and  $\text{C(O)CH}_2(\text{CH}_2)_4\text{I}$ ),  $\delta$  1.88-1.78 (m, 2H,  $\text{C(O)(CH}_2)_3\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.63-1.36 (m, 4H,  $\text{C(O)CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{I}$  and  $\text{C(O)CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ),  $\delta$  0.91 (t, 3H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ).

GC-MS m/z (relative abundance): 268 ( $\text{M}^+$ ), 253, 225, 213, 197, 169, 141, 127, 113, 86, 71 (100), 58.

**d) Products from 1-isopropylcyclohexanol (3d):**

8-iodo-2-methyloctan-3-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.19 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.61-2.57 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ),  $\delta$  2.46 (t, 2H,  $\text{C(O)CH}_2\text{CH}_2$ ),  $\delta$  1.77-1.67 (m, 2H,  $\text{C(O)(CH}_2)_3\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.43-1.38 (m, 4H,  $\text{C(O)CH}_2\text{CH}_2(\text{CH}_2)_3\text{I}$  and  $\text{C(O)(CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ),  $\delta$  1.09 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

GC-MS m/z (relative abundance): 223, 168, 139, 127, 95, 81, 69, 55 (100).

**e) Products from 1-phenylcyclohexanol (3h):**

6-iodo-1-phenylhexan-1-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.97-7.95 (m, 2H, ArH),  $\delta$  7.49-7.46 (m, 3H, ArH),  $\delta$  3.21 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.99 (t, 2H,  $\text{C(O)CH}_2(\text{CH}_2)_4\text{I}$ ),  $\delta$  1.93-1.86 (m, 2H,  $\text{C(O)(CH}_2)_3\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.69-1.64 (m, 2H,  $\text{C(O)CH}_2\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  1.54-1.47 (m, 2H,  $\text{C(O)(CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ).<sup>S20</sup>

GC-MS m/z (relative abundance): 302 ( $\text{M}^+$ ), 231, 203, 175, 155, 133, 120, 105 (100), 77, 51.

**f) Products from 1-(2,2-dimethyl)propylcyclohexanol (3i):**

2,2-dimethyl-9-iodononan-4-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.19 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.40 (t, 2H,  $\text{C(O)CH}_2(\text{CH}_2)_4\text{I}$ ),  $\delta$  2.29 (s, 2H,  $(\text{CH}_3)_3\text{CCH}_2$ ),  $\delta$  1.88-1.73 (m, 2H,  $\text{C(O)(CH}_2)_3\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.62-1.52 (m, 2H,  $\text{C(O)(CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{I}$ ),  $\delta$  1.43-1.33 (m, 2H,  $\text{C(O)CH}_2\text{CH}_2(\text{CH}_2)_3\text{I}$ ),  $\delta$  1.01 (s, 9H,  $\text{C(CH}_3)_3$ ).

GC-MS m/z (relative abundance): 225, 197, 169, 155, 141, 127, 113, 99, 83, 69, 57 (100), 55.

**4) Products from 1-alkylcycloheptanols (4c-e, 4g, 4h):**

**a) Products from 1-propylcycloheptanol (4c):**

The reaction of 1-propylcycloheptanol (**4c**) led to the formation of comparable amounts of 10-iododecan-4-one, cycloheptanone and 1-iodopropane as major products accompanied by smaller amounts (together accounting for  $\approx$  23% of the detected products) of products identified as 1-propyl-3-cyclohepten-1-ol, 1-propyl-4-cyclohepten-1-ol and 4-iodo-1-propylcycloheptanol.

10-iododecan-4-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.18 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.50 (t, 2H,  $\text{C(O)CH}_2(\text{CH}_2)_5\text{I}$ ),  $\delta$  2.37 (t, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)}$ ),  $\delta$  1.88-1.76 (m, 2H,  $\text{C(O)(CH}_2)_4\text{CH}_2\text{CH}_2\text{I}$ ),  $\delta$  1.47-1.38 (m, 8H,  $\text{C(O)CH}_2(\text{CH}_2)_3\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)}$ ),  $\delta$  0.87 (t, 3H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ).

GC-MS m/z (relative abundance): 239, 196, 183, 169, 155, 141, 127, 111, 99, 86, 71 (100), 58, 53.

**b) Products from 1-phenylcycloheptanol (4h):**

7-iodo-1-phenylheptan-1-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.97-7.94 (m, 2H, ArH),  $\delta$  7.62-7.46 (m, 3H, ArH),  $\delta$  3.19 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.98 (t, 2H,  $\text{ArC(O)CH}_2$ ),  $\delta$  1.86-1.40 (m, 8H,  $\text{ArC(O)CH}_2(\text{CH}_2)_4\text{CH}_2\text{I}$ ).

GC-MS m/z (relative abundance): 316 ( $\text{M}^+$ ), 189, 171, 155, 120, 105 (100), 91, 77, 51.

**5) Products from 1-alkylcyclooctanols (5c-e, 5g, 5h):**

**a) Products from 1-propylcyclooctanol (5c):**

The reaction of 1-propylcyclooctanol (**5c**) led to the formation of 11-iodoundecan-4-one, cyclooctanone and 1-iodopropane (together accounting only for  $\approx$  19% of the detected products), accompanied by significant amounts of products identified as 1-propyl-3-cycloocten-1-ol, 1-propyl-4-cycloocten-1-ol, 4-iodo-1-propylcyclooctanol, and by a smaller amount of 6-iodo-1-propyl-4-cycloocten-1-ol.

11-iodoundecan-4-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.18 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.43-2.35 (m, 2H,  $\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2$ ),  $\delta$  2.31-2.27 (m, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})$ ),  $\delta$  1.79-1.25 (m, 12H,  $\text{CH}_2$ ),  $\delta$  0.94-0.90 (t, 3H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ).

GC-MS m/z (relative abundance): 253, 183, 169, 155, 127, 99, 86, 71 (100), 58.

***b) Products from 1-phenylcyclooctanol (5h):***

The reaction of 1-phenylcyclooctanol (**5h**) led to the formation of 1-phenyl-8-iodooctan-1-one, accompanied by significant amounts of products identified as 1-phenyl-3-cycloocten-1-ol, 1-phenyl-4-cycloocten-1-ol, 4-iodo-1-phenylcyclooctanol (together accounting for  $\approx$  43% of the detected products).

*8-iodo-1-phenyloctan-1-one*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.98-7.92 (m, 2H, ArH),  $\delta$  7.54-7.49 (m, 3H, ArH),  $\delta$  3.18 (t, 2H,  $\text{CH}_2\text{I}$ ),  $\delta$  2.97 (t, 2H,  $\text{ArC}(\text{O})\text{CH}_2$ ),  $\delta$  1.85-1.38 (m, 10H,  $\text{ArC}(\text{O})\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{I}$ ).

GC-MS m/z (relative abundance): 330 ( $\text{M}^+$ ), 254, 231, 203, 185, 169, 155, 120, 105 (100), 91, 77, 55.

## References

- S1. Bernardon, C.; Deberly, A. *J. Org. Chem.* **1982**, *47*, 463-468.
- S2. Laurent, A.; Laurent, E.; Locher, P.; Mison, P. *Bull. Soc. Chim. Fr.* **1972**, 1369-1374.
- S3. McAdoo, D. J.; Farr, W.; Hudson, C. E. *J. Am. Chem. Soc.* **1980**, *102*, 5165-5169.
- S4. Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392-4398.
- S5. Buhler, J. *J. Org. Chem.* **1973**, *38*, 904-906.
- S6. Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T. *J. Org. Chem.* **1984**, *49*, 3904-3912.
- S7. a) Katzenellenbogen, J. A.; Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326-335; b) Brady, W. T.; Giang, Y. F.; Weng, L.; Dad, M. M. *J. Org. Chem.* **1987**, *52*, 2216-2220.
- S8. Janes, N. F.; Khambay, B. P. S. *Magn. Res. Chem.* **1989**, *27*, 197-200.
- S9. Celebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8613-8620.
- S10. Guijarro, D.; Guillena, G.; Mancheno, B.; Yus, M. *Tetrahedron* **1994**, *50*, 3427-3436.
- S11. Ranganayukulu, K.; Devi, M. V.; Rao, R. B.; Rageswari, K. *Can. J. Chem.* **1980**, *58*, 1484-1489.
- S12. Katritzky, A. R.; Qi, M. *J. Org. Chem.* **1997**, *62*, 4116-4120.
- S13. Wu T.; Xiong, H.; Rieke R. D. *J. Org. Chem.* **1990**, *55*, 5045-5051.
- S14. Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1975**, *97*, 2892-2895.
- S15. a) Komatsu, K.; Fujimori, M.; Okamoto, K. *Tetrahedron* **1977**, *33*, 2791-2797; b) Sisti, A. J. *J. Org. Chem.* **1968**, *33*, 453-454.
- S16. de Costa, B. R.; Clifford, G.; Guiying, L.; Xiao-shu, H. *J. Org. Chem.* **1994**, *59*, 482-485.
- S17. Strickland, A. D.; Caldwell, R. A. *J. Phys. Chem.* **1993**, *97*, 13394-13402.
- S18. House, H. O.; Riehl, J.; Pitt, C. G. *J. Org. Chem.* **1965**, *30*, 650-653.
- S19. Molander, G. A.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 1135-1138.
- S20. Wagner, P. J.; Lindstrom, M. J.; Sedon, J. H.; Ward, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 3842-3849.