

## The Reaction of 5-Cyano- and 5-Methoxycarbonyl-7-oxabicyclo[2.2.1]hept-2-enes with Chlorotrimethylsilane/Sodium Iodide Reagent

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**Synopsis.** Reactions of 5-cyano- and 5-methoxycarbonyl-7-oxabicyclo[2.2.1]hept-2-enes with a chlorotrimethylsilane/sodium iodide reagent in acetonitrile gave 2-furanpropanenitrile and 5-methoxycarbonyl-1,3-cyclohexadiene in good yields, respectively.

In recent years, Olah<sup>1-4</sup>) has developed an equivalent of iodotrimethylsilane generated *in situ* from chlorotrimethylsilane and sodium iodide ( $\text{Me}_3\text{SiCl}/\text{NaI}$ ). Treatments of appropriate oxygen-containing compounds such as ethers, esters and lactones with this reagent afford a silicon-oxygen bonded intermediate which then can be converted to another product through a subsequent step.

Previously, we reported the synthesis of 7-oxabicyclo[2.2.1]hept-2-enes and their stereochemistries.<sup>5</sup>) These compounds were allowed to react with  $\text{Me}_3\text{SiCl}/\text{NaI}$  to induce the rearrangement and deoxygenation of oxabicyclo[2.2.1]heptene ring. We describe here the rearrangement of 5-cyano-7-oxabicyclo[2.2.1]hept-2-ene (**1**) to 2-furanpropanenitrile (**3**) and the deoxygenation of 5-methoxycarbonyl-7-oxabicyclo[2.2.1]hept-2-ene (**2**) to 5-methoxycarbonyl-1,3-cyclohexadiene (**4**). (Eq. 1)

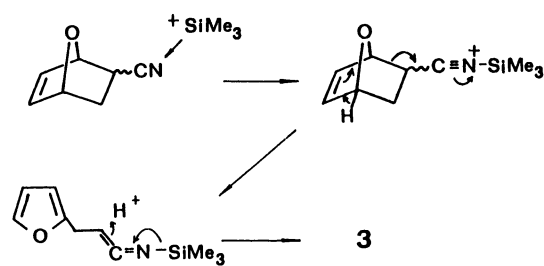
### Results and Discussion

**The Reaction of 1 with  $\text{Me}_3\text{SiCl}/\text{NaI}$ .** An isomeric mixture of **1** (*endo/exo* ≃ 1/1), derived from furan and acrylonitrile, was allowed to react with  $\text{Me}_3\text{SiCl}/\text{NaI}$  in acetonitrile at room temperature to give a rearranged product **3** in fairly good yield. (Table 1)

An approximately stoichiometric reaction of **1** with  $\text{Me}_3\text{SiCl}/\text{NaI}$  provided **3** in 91% yield. When  $\text{MeSiCl}_3$  was employed instead of  $\text{Me}_3\text{SiCl}$ , **1** was rearranged slowly to **3** in 81% yield. However, the same reaction using three equiv of NaI to  $\text{MeSiCl}_3$  took place rapidly giving **3** in good yield (94%). Conventionally, compound **3** has been prepared by a somewhat difficult method.<sup>6-8</sup>) Thus, the present method seems to be favorable for preparing **3**. This rearrangement was expected to proceed catalytically, but a reaction with 0.1 equiv of  $\text{Me}_3\text{SiCl}/\text{NaI}$  merely afforded **3** at a yield of 12%. Lengthening the reaction time, however, led to an

increase of **3** (46%).

The rearrangement of **1** to **3** may be illustrated by an attack by a cationic species,  $[\text{CH}_3\text{CN}^+-\text{SiMe}_3]\text{I}^-$ ,<sup>9</sup>) to a cyano group of **1**, followed by a cleavage of the C-C bond to form **3**. (Scheme 1)



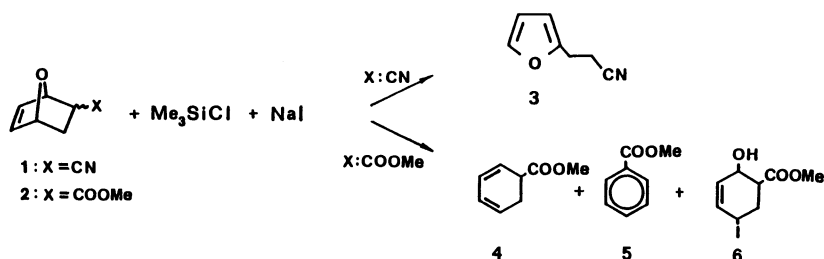
Scheme 1.

**The Reaction of 2 with  $\text{Me}_3\text{SiCl}/\text{NaI}$ .** A reaction of **2** with  $\text{Me}_3\text{SiCl}/\text{NaI}$ , followed by hydrolysis with water, gave deoxygenated products, **4** and **5**, as well as **6** in which the O-C bond was cleaved. However, their yields changed extremely due to the orientation of the methoxycarbonyl group of **2**. The isomeric **2** (*endo/exo* ≃ 3/2), derived from furan and methylacrylate, was treated with 1.2 equiv of  $\text{Me}_3\text{SiCl}/\text{NaI}$  to form about 30% of **4** and benzoic acid **5** (3%). (Table 2) The yield of **4** increased to 43% when an excess amount of  $\text{Me}_3\text{SiCl}/\text{NaI}$  was used (Run 2).

TABLE 1. RING CLEAVAGE OF 5-CYANO-7-OXABICYCLO[2.2.1]HEPT-2-ENE<sup>a)</sup>

| Run | <sup>b)</sup> $\text{Me}_3\text{SiCl}:\text{NaI}$ | Time<br>h | Yield <sup>c)</sup> of <b>3</b><br>% |
|-----|---|-----------|--------------------------------------|
|     | mmol  |           |                                      |
| 1   | 10: 12 : 12                                       | 3         | 91.3                                 |
| 2   | 10: 12 <sup>d)</sup> : 12                         | 20        | 81.1                                 |
| 3   | 10: 10 <sup>d)</sup> : 30                         | 3         | 93.6                                 |
| 4   | 10: 1 : 1   | 20        | 11.5                                 |
| 5   | 10: 1 : 1   | 70        | 46.0                                 |

a) Reactions were carried out in acetonitrile (10 ml) at room temperature. b) An isomeric mixture of *endo*- and *exo*-**1** (1:1) was used. c) Estimated by v.p.c. d)  $\text{MeSiCl}_3$  was used instead of  $\text{Me}_3\text{SiCl}$ .



Equation 1.

TABLE 2. RING CLEAVAGE OF 5-METHOXYCARBONYL-7-OXABICYCLO [2.2.1] HEPT-2-ENE<sup>a)</sup>

| Run             | 2<br>endo:exo | Time             | Yield/% <sup>b)</sup> |      |      |
|-----------------|---------------|------------------|-----------------------|------|------|
|                 |               | h                | 4                     | 5    | 6    |
| 1               | 3:2           | 20               | 29.3                  | 1.0  | —    |
| 2 <sup>c)</sup> | 3:2           | 20               | 43.0                  | 8.2  | —    |
| 3 <sup>d)</sup> | 3:2           | 20               | 11.4                  | 2.3  | —    |
| 4               | endo          | 20               | 42.8                  | 11.6 | 27.2 |
| 5 <sup>e)</sup> | endo          | 20               | 56.1                  | 7.0  | —    |
| 6 <sup>e)</sup> | endo          | 48 <sup>f)</sup> | 67.3                  | 13.4 | —    |
| 7 <sup>e)</sup> | endo          | 1 <sup>g)</sup>  | 62.6                  | 16.0 | —    |
| 8 <sup>h)</sup> | exo           | 20               | 9.2                   | 4.0  | —    |

a) **2** (10 mmol) was allowed to react with Me<sub>3</sub>SiCl (12 mmol) and NaI (12 mmol) in acetonitrile (10 ml) at room temperature. b) Isolated yield c) Me<sub>3</sub>SiCl (30 mmol) and NaI (30 mmol) were used. d) MeSiCl<sub>3</sub> was used instead of Me<sub>3</sub>SiCl. e) Me<sub>3</sub>SiCl (20 mmol) and NaI (20 mmol) were used. f) At 0°C. g) At 40°C. h) About 50% of *exo-2* was converted to furan and methyl acrylate.

Again, the MeSiCl<sub>3</sub>/NaI reagent was milder than the Me<sub>3</sub>SiCl/NaI one (Run 3). The reaction of *endo-2* with Me<sub>3</sub>SiCl/NaI led to **4**(43%), **5**(12%), and **6**(27%). The yield of **4** increased to 67% upon using 2.0 equiv of Me<sub>3</sub>SiCl/NaI at 0°C for 48 h (Run 6). When the same reaction was carried out at 40°C, the reaction was completed within 1 h to give **4** in 63% yield. **4** was prepared from 3,6-dihydrobenzoic acid by Boeckman,<sup>10</sup> but the procedure is somewhat difficult.

In contrast to the case of *endo-2*, *exo-2* reacted with Me<sub>3</sub>SiCl/NaI under similar conditions yielding **4** in poor yield (9%), and most of *exo-2* was converted to furan and methyl acrylate, corresponding to retro-Diels-Alder products. Although the differences in the reactivity of *endo-* and *exo-2* with Me<sub>3</sub>SiCl/NaI is still unclear, we believe that a cationic species, [CH<sub>3</sub>CN<sup>+</sup>-SiMe<sub>3</sub>]<sup>-</sup>,<sup>9</sup> has difficulty in attacking the bridge-oxygen atom of *exo-2* in which a methoxycarbonyl group is oriented in the same direction as the bridge-oxygen atom.

### Experimental

All of the starting materials were commercially available and were used without further purification except for the solvents. 7-Oxabicyclo[2.2.1]heptenes, **1** and **2**, were prepared according to procedures described in the literature.<sup>5,11</sup> IR spectra were taken with a JASCO-A202 spectrometer, and the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a JEOL PMX-60 spectrometer and a Hitachi R-90H, respectively. GLC

analyses were performed on a Yanaco-G1800 instrument.

*General Method for Ring Cleavage of 7-Oxabicyclo[2.2.1]hept-2-enes.* Reactions were normally conducted at a 10-mmol scale in a 25-ml flask fitted with a condenser under a nitrogen atmosphere. To a solution of chlorotrimethylsilane (12 mmol) and sodium iodide (12 mmol) in acetonitrile (10 ml) was added 7-oxabicyclo[2.2.1]hept-2-ene (10 mmol). The mixture was stirred for 20 h at room temperature and was then quenched by water. After washing with a solution of sodium thiosulfate, products were extracted with ether. The extract was washed again with water and dried over anhydrous sodium sulfate. After evaporation of the ether, the products were isolated by chromatography on silica gel (hexane:ethyl acetate=10:1 eluent) and were identified by their spectral data.

*2-Furanpropanenitrile (3):* <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ=151.4(s), 141.8(d), 118.7(s), 110.3(d), 106.6(d), 24.2(t), 16.5(t); <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ=7.31 (d, 1H), 6.29 (t, 1H), 6.16 (d, 1H), 2.96 (t, 2H), 2.62 (t, 2H); IR (neat) 2950 cm<sup>-1</sup>, 2250 cm<sup>-1</sup>, 1420 cm<sup>-1</sup>, 1110 cm<sup>-1</sup>, 740 cm<sup>-1</sup>; MS *m/z* 121.0 (M<sup>+</sup>).

*5-Methoxycarbonyl-1,3-cyclohexadiene (4):* <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ=174.2(s), 125.5(d), 125.0(d), 123.7(d), 123.1(d), 51.9(q), 39.1(d), 24.8(t); <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ=5.76 (d, 4H), 3.36 (s, 3H), 3.21 (t, 1H), 2.40 (d, 2H); MS *m/z* 138.1 (M<sup>+</sup>).

*4-Iodo-6-methoxycarbonyl-2-cyclohexen-1-ol (6):* <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ=174.1(s), 128.9(d), 126.1(d), 68.4(d), 52.1(q), 45.1(d), 38.8(d), 28.9(t); <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ=6.2—5.5 (m, 2H), 5.12 (s, 1H), 3.80 (s, 3H), 3.1—2.4 (m, 5H); IR (KBr) 3500 cm<sup>-1</sup>, 1740 cm<sup>-1</sup>, 1430 cm<sup>-1</sup>, 1165 cm<sup>-1</sup>; mp 75—76°C; MS *m/z* 282.2 (M<sup>+</sup>); Found: C, 34.10%, H, 3.81%. Calcd for C<sub>8</sub>H<sub>11</sub>O<sub>3</sub>I: C, 34.05%, H, 3.82%.

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