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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[1–4] has developed an equivalent of iodotrimethylsilane generated *in situ* from chlorotrimethysilane and sodium iodide (Me$_3$SiCl/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.

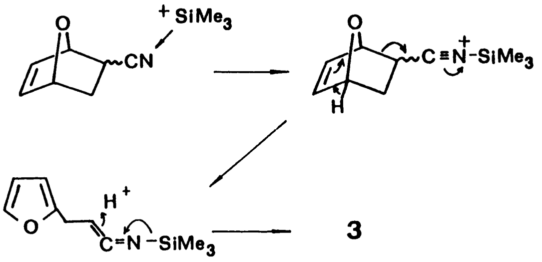
Previously, we reported the synthesis of 7-oxabicyclo[2.2.1]hept-2-enes and their stereochemistries.[5] These compounds were allowed to react with Me$_3$SiCl/NaI to induce the rearrangement and deoxygenation of oxabicyclo[2.2.1]heptene ring. We describe here the rearrangement of 5-cyano-7-oxabicyclo[2.2.1]hept-2-ene (**1**) to 2-furanpropanenitrile (**3**) and the deoxgenation 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 Me$_3$SiCl/NaI. An isomeric mixture of **1** (endo/exo≑1/1), derived from furan and acrylonitrile, was allowed to react with Me$_3$SiCl/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 Me$_3$SiCl/NaI provided **3** in 91% yield. When MeSiCl$_3$ was employed instead of Me$_3$SiCl, **1** was rearranged slowly to **3** in 81% yield. However, the same reaction using three equiv of NaI to MeSiCl$_3$ took place rapidly giving **3** in good yield (94%). Conventionally, compound **3** has been prepared by a somewhat difficult method.[6–8] 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 Me$_3$SiCl/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, [CH$_3$CN$^+$–SiMe$_3$]I$^-$,[9] to a cyano group of **1**, followed by a cleavage of the C–C bond to form **3**. (Scheme 1)



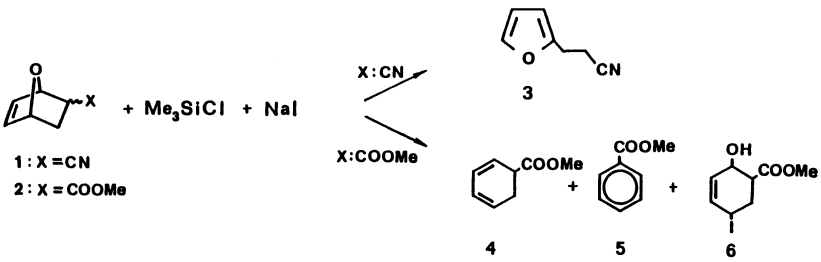
Scheme 1.

The Reaction of 2 with Me$_3$SiCl/NaI. A reaction of **2** with Me$_3$SiCl/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 Me$_3$SiCl/NaI to form about 30% of **4** and benzoic acid **5** (3%). (Table 2) The yield of **4** incresed to 43% when an excess amount of Me$_3$SiCl/NaI was used (Run 2).

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

Run	1[b)]:Me$_3$SiCl:NaI	Time	Yield[c)] of 3
	mmol	h	%
1	10: 12 : 12	3	91.3
2	10: 12[d)]: 12	20	81.1
3	10: 10[d)]: 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) MeSiCl$_3$ was used instead of Me$_3$SiCl.



Equation 1.

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

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

a) **2** (10 mmol) was allowed to react with $\mathrm{Me_3SiCl}$ (12 mmol) and NaI (12 mmol) in acetonitrile (10 ml) at room temperature. b) Isolated yield c) $\mathrm{Me_3SiCl}$ (30 mmol) and NaI (30 mmol) were used. d) $\mathrm{MeSiCl_3}$ was used instead of $\mathrm{Me_3SiCl}$. e) $\mathrm{Me_3SiCl}$ (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 $\mathrm{MeSiCl_3/NaI}$ reagent was milder than the $\mathrm{Me_3SiCl/NaI}$ one (Run 3). The reaction of *endo*-**2** with $\mathrm{Me_3SiCl/NaI}$ led to **4**(43%), **5**(12%), and **6**(27%). The yield of **4** increased to 67% upon using 2.0 equiv of $\mathrm{Me_3SiCl/NaI}$ 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,[10)] but the procedure is somewhat difficult.

In contrast to the case of *endo*-**2**, *exo*-**2** reacted with $\mathrm{Me_3SiCl/NaI}$ 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 $\mathrm{Me_3SiCl/NaI}$ is still unclear, we believe that a cationic species, $[\mathrm{CH_3CN^+\text{-}SiMe_3}]\mathrm{I^-}$,[9)] has difficulty in attacking the bridge-oxgen 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.[5,11)] IR spectra were taken with a JASCO-A202 spectrometer, and the ^{1}H- and ^{13}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 anhyd 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): ^{13}C-NMR ($\mathrm{CDCl_3}$) δ=151.4(s), 141.8(d), 118.7(s), 110.3(d), 106.6(d), 24.2(t), 16.5(t); ^{1}H NMR($\mathrm{CCl_4}$) 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^{-1}, 2250 cm^{-1}, 1420 cm^{-1}, 1110 cm^{-1}, 740 cm^{-1}; MS *m/z* 121.0 (M$^+$).

5-Methoxycarbonyl-1,3-cyclohexadiene (4): ^{13}C-NMR($\mathrm{CDCl_3}$) 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); ^{1}H-NMR($\mathrm{CCl_4}$) δ=5.76 (d, 4H), 3.36 (s, 3H), 3.21 (t, 1H), 2.40 (d, 2H); MS *m/z* 138.1 (M$^+$).

4-Iodo-6-methoxycarbonyl-2-cyclohexen-1-ol (6): ^{13}C-NMR ($\mathrm{CDCl_3}$) 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); ^{1}H-NMR ($\mathrm{CCl_4}$) 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^{-1}, 1740 cm^{-1}, 1430 cm^{-1}, 1165 cm^{-1}; mp 75—76 °C; MS *m/z* 282.2 (M$^+$); Found: C, 34.10%, H, 3.81%. Calcd for $\mathrm{C_8H_{11}O_3I}$: C, 34.05%, H, 3.82%.

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