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Catalytic Hydrogenolysis of 7-Chloro-7-fluorobicyclo[4.1.0]heptane in the Presence of Ethylenediamine

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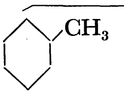
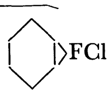
During the course of an investigation on the catalytic hydrogenolysis of *gem*-dichlorocyclopropanes to monochlorocyclopropanes,[1] it became desirable to confirm the stereochemical behavior of the substrates in the formation of *endo* and *exo* isomers of monochlorocyclopropanes. Ando *et al.*[2] reported that cyclopropyl radical is formed and partly inverted in the reduction of some *gem*-chlorofluorocyclopropanes with tri-*n*-butyltin hydride. The behavior of *gem*-halofluorocyclopropanes in their catalytic hydrogenolyses seemed of interest to investigate. This paper deals with the catalytic hydrogenolysis of 7-chloro-6-fluorobicyclo-[4.1.0]heptane (**1**) with Raney nickel catalyst (R–Ni) in the presence of various basic additives.

7-*exo*-Chloro-7-*endo*-fluorobicyclo[4.1.0]heptane (*exo*-Cl-**1**), 7-*endo*-chloro-7-*exo*-fluorobicyclo[4.1.0]heptane (*endo*-Cl-**1**), and a mixture of isomers (*mixture*-**1**, *exo*-Cl-**1**/*endo*-Cl-**1**=43/57) were catalytically hydrogenolyzed with R-Ni in a methanol solution in the presence of sodium hydroxide, potassium hydroxide, lithium hydroxide, ethylamine, diethylamine, triethylamine, piperidine, ethylenediamine, trimethylenediamine, hexamethylenediamine, benzylamine, and monoethanolamine under ordinary conditions. 7-Fluorobicyclo[4.1.0]heptane (**2**) was obtained predominantly without monochlorocyclopropane only in the presence of ethylenediamine as an additive, with considerable evolution of hydrogen. No reaction occurred in the presence of other basic additives.

The results of catalytic hydrogenolyses of *exo*-Cl-**1** and *endo*-Cl-**1** are shown in Table 1. Hydrogenolyses proceeded stereospecifically with retention of configuration and gave 7-*endo*-fluorobicyclo[4.1.0]heptane (*endo*-F-**2**) and 7-*exo*-fluorobicyclo[4.1.0]heptane (*exo*-F-**2**) from *exo*-Cl-**1** and *endo*-Cl-**1** respectively. *Exo*-Cl-**1** was hydrogenolyzed more easily than *endo*-Cl-**1**. The difference seems to be attributable to the effect of hindrance of condensed ring.

Table 1. Catalytic hydrogenolysis of *exo*-Cl-**1** and *endo*-Cl-**1**

Substrate: 0.005 mol, Catalyst: 2.5 g as Ni, Additive: $NH_2(CH_2)_2NH_2$ 0.03 mol, Reaction time: 24 hr

	Composition of product			
				
		endo-F	*exo*-F	
Substrate	%	%	%	%
exo-Cl-**1**	6	39	—	55
endo-Cl-**1**	5	—	17	78

Hydrogenolysis of *mixture*-**1** with various amount of R-Ni and ethylenediamine is shown in Table 2. Increase in the amounts of R-Ni and ethylenediamine gave rise to the increase of hydrogenolyzed products.

It is of interest that *gem*-dichlorocyclopropanes are hydrogenolyzed readily in the presence of common amines and alkali hydroxides[1], whereas **1** is hydrogenolyzed gradually only in the presence of ethylenediamine. Poor reactivity of **1** may be caused by the

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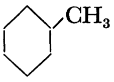
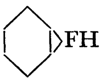
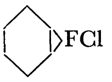
[1] K. Isogai, S. Kondo, K. Katsura, S. Sato, N. Yoshihara, Y. Kawamura, and T. Kazama, *Nippon Kagaku Zasshi*, **91**, 561 (1970).

[2] T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Amer. Chem. Soc.*, **89**, 5719 (1967), *J. Org. Chem.*, **35**, 33 (1970).

Table 2. The influence of quantities of R-Ni and ethylenediamine
Substrate: *mixture*-**1** 0.005 mol, Reaction time: 24 hr

		Composition of product						
								
R-Ni g as Ni	$NH_2(CH_2)_2NH_2$ mol	%	%	(*endo*-F :	*exo*-F)	%	(*exo*-Cl :	*endo*-Cl)
2.5	10 μl	—	—			100	(43	57)
2.5	0.015	4	20	(79	21)	76	(30	70)
2.5	0.03	4	28	(75	25)	68	(21	79)
2.5	0.10	6	39	(74	26)	55	(15	85)
2.5	0.30	3	55	(63	37)	42	(—	100)
5.0	0.03	9	35	(71	29)	56	(14	86)
7.5	0.03	12	48	(67	33)	40	(—	100)

polarizability of C-F bond and the weak affinity to the catalyst surface. By stirring the methanol solution of ethylenediamine with R–Ni, a colored complex was formed which dissolved into the solution with the evolution of hydrogen. The catalytic hydrogenolysis of **1** was retarded when ethylenediamine and R–Ni were stirred in the reaction medium for several hours before addition of **1**. The behavior of ethylenediamine is not clear, but it might be explained as follows: chlorine atom adsorbed on the catalyst is extracted by the complex formed from ethylenediamine and R–Ni, and concerted reduction takes place simultaneously by the transfer of electron to the substrate in the transition from Ni(0) to Ni(II).

Experimental[3)]

Preparation of 7-Chloro-7-fluorobicyclo[4.1.0]heptane (1). The compound was prepared by the method of Ando *et al.*[4)] To a mixture of cyclohexene, sodium hydride and methyl dichlorofluoroacetate, methanol was added gradually at 0°C. A mixture of *endo*-chloro and *exo*-chloro isomers of **1** (*mixture*-**1**; *exo*-Cl/*endo*-Cl=43/57) was obtained in 30% yield, bp 23.5—25°C/4 mmHg. Found: C, 57.02; H, 6.87%; Calcd for $C_7H_{10}ClF$: C, 56.98; H, 6.83%. Isomer ratio of **1** was identified by NMR and vpc. ^{19}F NMR of isomers; *exo*-Cl-**1** (R_t: 6.4 min): δ 80.0 (J=5 Hz); *endo*-Cl-**1** (R_t: 7.3 min): δ 45.1 (J=19 Hz). Isolation of two isomers of **1** was carried out by preparative vpc.

7-Fluorobicyclo[4.1.0]heptane (2). A mixture of *endo*- and *exo*-fluoro isomers of **2** isolated from hydrogenolyzed products of *mixture*-**1** by preparative vpc gave satisfactory ^1H NMR and data of elemental analysis. NMR; *exo*-F-**2** (R_t: 3.6 min); δ 4.12 (J=2 Hz); *endo*-F-2 (R_t: 4.0 min): δ 4.38 (J=7 Hz). Found: C, 73.58; H, 9.76%. Calcd for $C_7H_{11}F$: C, 73.65; H, 9.71%.

General Procedure of Catalytic Hydrogenation. A mixture of chlorofluorocyclopropane (0.005 mol), R–Ni (2.5 g as Ni), methanol (50 m*l*) and commercial amine or alkali hydroxide (0.03 mol) was stirred under ordinary pressure of hydrogen at 18—22°C for 24 hr. The solution was separated from catalyst, poured into 500 m*l* of water and extracted with ether. Ether solution was washed with dilute HCl and water, and then dried (Na_2SO_4). After removal of ether, the residue was identified and determined by vpc.

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3) ^1H NMR spectrum was obtained with a JEOLCO JNM-4H-100 spectrometer in CCl_4 with TMS as an internal reference. ^{19}F NMR spectrum was obtained with a JEOLCO JNM-4H-100 spectrometer (94 MHz) in CCl_4 with trifluoroacetic acid as an external reference. Vpc analyses and separations were performed with an OHKURA MODEL 6000 or an OHKURA MODEL 1200 gas chromatograph. For analytical purposes, a 3 mm × 2 m column with 15% TCP on 60—80 Celite 545 or a 3 mm × 3 m column with 15% HV grease on 60—80 Celite 545 was used. As carrier gas, hydrogen was used at a rate of 60 ml/min. For preparative purposes, a 8 mm × 5 m column was used with 30% HV grease or 30% TCP on 40—60 Celite 545.

4) T. Ando, H. Yamanaka, S. Terabe, A. Horike, and W. Funasaka, *Tetrahedron Lett.*, **1967**, 1123.