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Regioselectivity in the Catalytic Hydrogenolysis of 7-Fluoro-1-phenylbicyclo[4.1.0]heptanes

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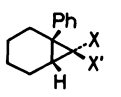
The palladium-catalyzed hydrogenolysis of 7-chloro-7-fluoro-1-phenyl-, 7-fluoro-1-phenyl-, and 7,7-difluoro-1-phenylbicyclo[4.1.0]heptane was investigated. The hydrogenolysis of the cyclopropane ring occurs at the C_1–C_6 bond selectively, accompanied by the elimination of the *endo*-halogen. The hydrogenolysis of *endo*-7-fluoro-1-phenylbicyclo[4.1.0]heptane proceeded rapidly to give phenylcycloheptane as a sole product, whereas *exo*-7-fluoro-1-phenylbicyclo[4.1.0]heptane reacted slowly to give *trans*-1-fluoro-2-phenylcycloheptane, accompanied by a small amount of the C_1–C_7 bond-cleaved product. The different reactivity between the endo and exo derivatives became more considerably by the introduction of a methyl group at the 2-position. Thus, with the compounds having 2-methyl group the *endo*-fluoro derivative was cleaved at the C_1–C_6 bond accompanied by the C_1–C_7 bond cleavage, whereas the *exo*-fluoro derivative was cleaved at the C_1–C_7 bond exclusively.

Although many studies on the catalytic hydrogenolysis of vinyl, aryl, allyl, and benzyl fluorides have been reported,[1] little attention has been given to the catalytic hydrogenolysis of cyclopropyl fluorides. In the previous paper,[2] we reported the regioselective hydrogenolysis of 1,1-difluoro-3-methyl-2-phenylcyclopropane. The cyclopropane ring was cleaved at the C_2–C_3 bond exclusively using both palladium oxide (PdO) and Raney nickel (R-Ni), accompanied by a considerable extent of the carbon–fluorine bond hydrogenolysis. Mitsui et al.[3] reported that 1-phenylbicyclo[4.1.0]heptane and its 2-methyl derivative were hydrogenolyzed at the C_1–C_7 bond preferentially because of the difference of the catalyst hindrance between the C_1–C_6 bond and the C_1–C_7 bond on the catalyst surface. It seems to be interesting to investigate the behavior of the fluorine for the regioselectivity in the catalytic hydrogenolysis of the cyclopropane ring contained in such condensed ring systems. Here, we wish to report the palladium-catalzed hydrogenolysis of several 7-fluoro-substituted -phenylbicyclo[4.1.0]heptanes.

Results and Discussion

exo-7-Chloro-*endo*-7-fluoro-1-phenyl- (1-endo-F), *endo*-7-chloro-*exo*-7-fluoro-1-phenyl- (1-exo-F), *endo*-7-fluoro-1-phenyl- (2-endo-F), *exo*-7-fluoro-1-phenyl- (2-exo-F) and 7,7-difluoro-1-phenylbicyclo[4.1.0]heptane (**3**) were hydrogenated over PdO in ethanol solution at room temperature under atmospheric pressure. The results are shown in Table 1. The hydrogenolysis of the cyclopropane ring of these fluorocyclopropanes occurred at the C_1–C_6 bond selectively although only 2-exo-F was accompanied by a small amount of the C_1–C_7 bond cleaved product. Characteristic differences between the endo isomer and the exo isomer were observed in the reactivity and in the ratio of the products. The reaction of 1-endo-F proceeded very slowly and gave phenylcycloheptane (**5**) as a sole product, whereas the reaction of 1-exo-F proceeded rapidly than that of 1-endo-F to give **5** (37%) and *cis*-1-fluoro-2-phenylcycloheptane (**6**) (63%). On the other hand, 2-endo-F reacted very rapidly to give **5** as a sole product, whereas 2-exo-F reacted slowly to give mainly *trans*-1-



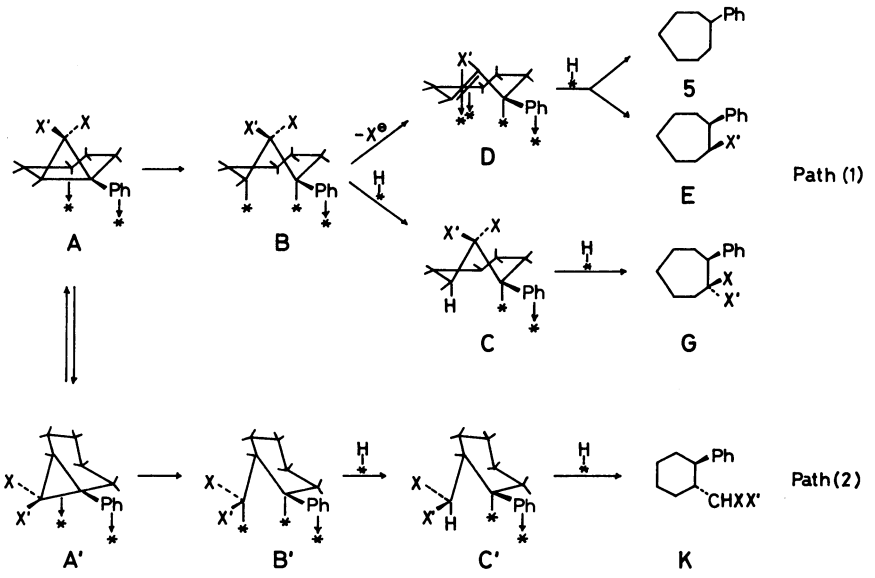
1-endo-F: X=F, X'=Cl
1-exo-F : X=Cl, X'=F
2-endo-F: X=F, X'=H
2-exo-F : X=H, X'=F
3 : X=F, X'=F

Fig. 1.

Table 1. Hydrogenolysis of 7-Fluoro-1-phenylbicyclo[4.1.0]heptanes

Substrate	Reaction time/h	Conversion %	Composition of products (%)				
			C_1–C_6 Fission				C_1–C_7 Fission
			5	**6**	**7**	**8**	**9**
1-endo-F	24	47	100	—	—	—	—
1-exo-F	4	95	37	63	—	—	—
2-endo-F	1	97	100	—	—	—	—
2-exo-F	24	96	10	—	78	—	12
3	0.5	100	20	27	—	53	—

Substrate: 20 mg, PdO: 20 mg.



Scheme 1.

fluoro-2-phenylcycloheptane (**7**) (78%) with **5** (10%), accompanying a small amount of *trans*-1-fluoromethyl-2-phenylcyclohexane (**9**) formed by the C_1–C_7 bond cleavage. The hydrogenolysis of **3** proceeded more easily and gave **5**, **6**, and 1,1-difluoro-2-phenylcycloheptane (**8**) of the C_1–C_6 bond cleaved products.

It has been known that the bond lengths of cyclopropane are changed markedly by the fluorine substitution. The available data of ring bond length (Å) for C_1–C_2 and C_2–C_3 bonds in cyclopropane,[4] 1,1-dichloro-,[5] chloro,[6] fluoro,[7] and 1,1-difluorocyclopropane[8] are reported, respectively, as follows; 1.514, 1.514; 1.532, 1.534; 1.513, 1.515; 1.494, 1.527; 1.464, 1.552. In the case of 7-fluoro derivatives of 1-phenylbicyclo[4.1.0]heptane, analogous lengthening of the C_1–C_6 bond and shortening of the C_1–C_7 and C_6–C_7 bonds are expected which may cause an additional strain in the condensed ring system. In this hydrogenation, these effects may overcome the steric effect which is a dominant factor in the case of the parent compound and the C_1–C_6 bond hydrogenolysis occurs preferentially.

Additionally, the ease of hydrogenolysis of the cyclopropane ring and the carbon–fluorine bond seems to depend markedly upon whether the fluorine binds to endo- or exo-side. A similar stereochemical behavior was reported in the case of the ring-enlargement of 7-chlorobicyclo[4.1.0]heptanes by means of a thermal[9] and a solvolysis[10] reaction. The *endo*-chloro isomer reacts more easily than the *exo*-chloro isomer with the elimination of the chlorine as chloride ion. This stereospecific reaction is explained by a "concerted disrotatory process."[11] Similar fast progress of the ring-enlargement was observed in the hydrogenolysis of 1-exo-F, 2-endo-F, and **3**. Therefore, the elimination of the *endo*-halogen seems to contribute as one of fators to make easy the C_1–C_6 bond hydrogenolysis.

A probable pathway is shown in Scheme 1. The substrate adsorbs on the catalyst by the C_1–C_6 bond (adsorbed species A) or the C_1–C_7 bond (adsorbed species A′). In the case of the parent compound 1-phenylbicyclo[4.1.0]heptane (X=H, X′=H in A and A′), A has a larger catalyst hindrance than A′. Therefore, the C_1–C_7 bond cleaves preferentially.[3] In the hydrogenolysis of the fluorocyclopropanes, however, the weakening effect of the C_1–C_6 bond seems to overcome the catalyst hindrance and the hydrogenolysis proceeds easily through Path (1). Releasing the strain of the condensed ring by the ring-enlargement makes easy the formation of the C_1,C_6-diadsorbed species B from A. Additionally, in the case of 1-exo-F (X=Cl, X′=F) and 2-endo-F (X=F, X′=H), the elimination of the *endo*-halogen accelerates the C_1–C_6 bond cleavage to give cycloolefin intermediate D. Subsequent cis addition of hydrogen forms **5** and **6** (X′=F in E) competitively.

In this hydrogenation, 1-endo-F was ring-enlarged and gave **5**. The hydrogenolysis of 1-endo-F, therefore, seems to proceed via A, B, and D similarly to that of 1-exo-F and 2-endo-F. However, the reaction of 1-endo-F proceeded more slowly than that of 2-endo-F. Although the cause of the difference in the reactivity between 1-endo-F and 2-endo-F is not clear, it appears that the chlorine probably plays a role in the adsorption step. The role may be explained as one of examples of self-poisoning effects.[12] Because of the affinity of the chlorine to the catalyst is relatively stronger than that of the fluorine, the contribution of A′ in the adsorption state of 1-endo-F seems to be expected to some extent.

Table 2. Hydrogenolysis of 7-Fluoro-2-methyl-1-phenylbicyclo[4.1.0]heptanes

Substrate	Reaction time/h	Conversion %	Composition of products/%	
			C_1–C_6 Fission **10**	C_1–C_7 Fission **11**
4-endo-F	2	100	83	17
4-exo-F	8	86	—	100

Substrate: 20 mg, PdO: 100 mg.

The adsorption of the chlorine in A′ causes the lowering of the activity of catalyst. This effect makes difficult the hydrogenolysis of 1-endo-F from A′ which hinders the adsorption of 1-endo-F by the C_1–C_6 bond. By these factors, the lowering the activity of catalyst and the hindrance of adsorption by the C_1–C_6 bond, the hydrogenolysis of 1-endo-F seems to be retarded considerably. Although this self-poisoning effect affects in the case of 1-exo-F, the reaction seems to proceed smoothly by the assistance of the ready elimination of the *endo*-chlorine.

On the other hand, 2-exo-F reacted slowly than 2-endo-F and gave **7** (X=H, X′=F in G). The formation of **7** is explained by an alternative pathway in Path (1). Because the elimination of the *exo*-fluorine from B is disadvantageous stereoelectronically,[11] the cleavage of the C_1–C_6 bond of 2-exo-F proceeds more slowly than that of 2-endo-F and forms the half-hydrogenated state C (X=H, X′=F) without the elimination of the *exo*-fluorine. The half-hydrogenated state C receives hydrogen from the catalyst to give **7**. Furthermore, 2-exo-F gave a small amount of the C_1–C_7 bond cleaved product 9 (X=H, X′=F in K). The pathway of the C_1–C_7 bond cleavage may be explained by Path (2). Because the cleavage of the C_1–C_6 bond from A is relatively slow, the sterically less-hindered adsorption species A′ participated to some extent in this hydrogenation and causes the contamination of the C_1–C_7 bond cleaved product formed via B′ and C′.

In the case of the hydrogenolysis of **3** (X=F, X′=F), it was expected that **3** reacted in analogy with 1-exo-F to give **5** and **6**. However, **8** (X=F, X′=F in G) was obtained in an about 50% yield with **5** and **6**. It seems to be that the 7,7-difluoro-substitution weakens the C_1–C_6 bond more strongly and the C_1–C_6 bond cleaves easily without the assistance of the elimination of the *endo*-fluoine followed by the competitive formation of D (X′=F) and C (X=F, X′=F).

The difference observed in the hydrogenolysis of 2-endo-F and 2-exo-F appeared more strongly in the case of 2-methyl derivatives of 2-endo-F and 2-exo-F. The results of the hydrogenolysis of *t*-7-fluoro-*c*-2-methyl-*r*-1-phenylbicyclo[4.1.0]heptane (4-endo-F) and *c*-7-fluoro-c-2-methyl-*r*-1-phenylbicyclo[4.1.0]heptane (4-exo-F) are shown in Table 2. Since the rate of

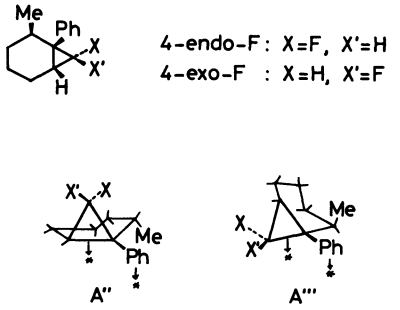


Fig. 2.

hydrogenolysis of 4-endo-F and 4-exo-F was considerably slower than that of 2-endo-F and 2-exo-F, PdO was used in the amount five times that for the other compounds. Although the hydrogenolysis of 4-endo-F proceeded more easily than 4-exo-F to give mainly *cis*-1-methyl-2-phenylcycloheptane (**10**), it was accompanied by *r*-1-fluoromethyl-*t*-3-methyl-*t*-2-phenylcyclohexane (**11**) which was arose by the C_1–C_7 bond cleavage. On the other hand, 4-exo-F was cleaved at the C_1–C_7 bond exclusively to give **11** as a sole product.

As can be seen from Fig. 2, the 2-methyl group increases the catalyst hindrance against the adsorption of the C_1–C_6 bond in the adsorbed species A.″ This steric effect seems to be large enough to retard the C_1–C_6 bond cleavage and 4-exo-F prefers the adsorbed species A‴ to give the C_1–C_7 bond cleaved product exclusively. This steric effect seems to affect even in the hydrogenolysis of 4-endo-F and causes the contamination of the C_1–C_7 bond cleaved product.

Experimental

^{1}H NMR spectra were recorded on a JNM-PMX 60 spectrometer with $Si(CH_3)_4$ as the internal standard. ^{19}F NMR spectra were recorded on a JNM-FX 90Q spectrometer with CF_3COOH as the external standard. Mass spectra were obtained with a HITACHI M-60 GC-MS spectrometer.

***exo*-7-Chloro-*endo*-7-fluoro-1-phenylbicyclo[4.1.0]heptane (1-endo-F) and *endo*-7-Chloro-*exo*-7-fluoro-1-phenylbicyclo-[4.1.0]heptane (1-exo-F).** According to the procedure of Ando et al.,[13] to a mixture of 1-phenylcyclohexene (20.5 g, 0.13 mol) and sodium hydride (3.1 g, 0.13 mol) was added

methyl dichlorofluoroacetate (30 g 0.13 mol) at 0—5 °C. After 2 h, methanol (4.2 ml) was added to the reaction mixture. A mixture of 1-endo-F and 1-exo-F (1:2) was obtained in a 24% yield; bp 110—113 °C/6 mmHg (1 mmHg=133.322 Pa). ^{19}F NMR ($CDCl_3$) δ=45.8 (d, J_{HFvic}= 19.5 Hz, cis), 68.8 (d, J_{HFvic}=3.0 Hz, trans). Found: C, 69.64; H, 6.33%. Calcd for $C_{13}H_{14}FCl$: C, 69.49; H,6.28%.

Isomers 1-endo-F and 1-exo-F were separated by preparative VPC. **1-endo-F:** MS *m/z* 224(M^+). ^{19}F NMR ($CDCl_3$): δ=68.8 (d, J_{HFvic}=3.0 Hz). **1-exo-F:** MS *m/z*: 224 (M^+). ^{19}F NMR ($CDCl_3$): δ=45.8 (d, J_{HFvic}=19.5 Hz). The value of ^{19}F NMR is comparable to that of each isomer of 7-chloro-7-fluorobicyclo[4.1.0]heptane.[9]

***endo*-7-Fluoro-1-phenylbicyclo[4.1.0]heptane (2-endo-F) and *exo*-7-Fluoro-1-phenylbicyclo[4.1.0]heptane (2-exo-F).** A mixture of 1-endo-F and 1-exo-F (0.5 g) was hydrogenated by use of Raney nickel (2 g) in ethanol in the presence of ethylenediamine (0.8 g) at room temperature under atmospheric pressure. The carbon-chlorine bond was hydrogenolyzed selectively with retention of configuration to give 2-endo-F and 2-exo-F, respectively, with a small amount of cyclopropane ring cleaved products. From the reaction mixture, the two isomers were separated by preparative VPC.

2-endo-F: MS *m/z* 190(M^+). ^{1}H NMR (CCl_4) δ=7.13 (5H, s, C_6H_5), 4.47 (1H, dd, J_{HFgem}=66.6 Hz, J_{HHvic}=7.0 Hz), 2.5—1.0 (9H, broad, ring). Found: C, 82.14; H, 8.09%. Calcd for $C_{13}H_{15}F$: C, 82.07; H, 7.95%.

2-exo-F: MS *m/z*: 190(M^+). ^{1}H NMR (CCl_4) δ=7.16 (5H, s, C_6H_5), 4.30 (1H, dd, J_{HFgem}=66.6 Hz, J_{HHvic}=2.5 Hz), 2.5—1.0 (9H, broad, ring). Found: C, 82.06; H, 8.16%. Calcd for $C_{13}H_{15}F$: C, 82.07; H, 7.95%. The values of ^{1}H NMR are comparable to those of each isomer of 7-fluoro-bicyclo[4.1.0]heptane.[9]

7,7-Difluoro-1-phenylbicyclo[4.1.0]heptane (3). A mixture of 1-phenylcyclohexene (9.0 g, 0.057 mol), chlorodifluoromethane (12 g, 0.4 mol), epichlorohydrin (28.3 g, 0.31 mol) and tetrabutylammonium chloride (1.1 g) was heated at 130 °C, 19 h, in an autoclave according to the procedure of Kamel.[14] The fraction, bp 93—96 °C/7 mmHg, 4.0 g, was purified by preparative VPC to give **3**. MS *m/z*: 208(M^+). ^{1}H NMR (CCl_4) δ=7.19 (5H, s, C_6H_5), 2.66—0.85 (9H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=49.2 (dd, J_{FF}=148.4 Hz, J_{HFvic}=15.6 Hz), 64.6 (dd, J_{FF}=148.4 Hz, J_{HFvic}=3.0 Hz). Found: C, 74.78; H, 6.83%. Calcd for $C_{13}H_{14}F_2$: C, 74.97; H, 6.78%.

***t*-7-Fluoro-*c*-2-methyl-*r*-1-phenylbicyclo[4.1.0]heptane (4-endo-F) and *c*-7-Fluoro-*c*-2-methyl-*r*-1-phenylbicyclo[4.1.0]-heptane (4-exo-F).** To a mixture of 3-methyl-2-phenylcyclohexene (22.5 g, 0.13 mol) and sodium hydride (3.1 g, 0.13 mol) was added methyl dichlorofluoroacetate (30 g, 0.13 mol) at 0—5 °C followed by addition of methanol (4 ml) as described above. A mixture of endo and exo isomers of 7-chloro-7-fluoro-*c*-2-methyl-*r*-1-phenylbicyclo-[4.1.0]heptane (endo-F/exo-F=3/7) was obtained in a 20% yield, bp 115—120 °C/4 mmHg. MS *m/z*: 238(M^+). ^{19}F NMR ($CDCl_3$) δ=71.7 (d, J_{HFvic}=3.0 Hz) 48.0 (d, J_{HFvic}=22.4 Hz). Found: C, 70.24; H, 6.99%. Calcd for $C_{14}H_{16}FCl$: C, 70.43; H, 6.76%.

The chlorofluorocyclopropane was hydrogenated over Raney nickel according to the preceding procedure to give a mixture of 4-endo-F and 4-exo-F and the isomers were separated by preparative VPC, respectively.

4-endo-F: MS *m/z*: 204(M^+). ^{1}H NMR (CCl_4) δ=7.13 (5H, s, C_6H_5), 4.50 (1H, dd, J_{HFgem}=66.6 Hz, J_{HHvic}=6.6 Hz) 2.4—0.9 (8H, broad, ring), 0.67 (3H, d, J=7.0 Hz, CH_3). Found: C, 82.55; H, 8.55%. Calcd for $C_{14}H_{17}F$: C, 82.31; H, 8.39%.

4-exo-F: MS *m/z*: 204(M^+). ^{1}H NMR (CCl_4) δ=7.16 (5H, s, C_6H_5), 4.35 (1H, dd, J_{HFgem}=66.6 Hz, J_{HHvic}=2.4 Hz), 2.2—0.8 (8H, broad, ring), 0.67 (3H, d, J=6.4 Hz, CH_3). Found: C, 82.47; H, 8.43%. Calcd for $C_{14}H_{17}F$: C, 82.31; H, 8.39%.

General Procedure of Hydrogenation. Substrates (20 mg) were hydrogenated over PdO (20 mg, Kawaken Fine Chemical Co.) in ethanol (2 ml) at room temperature under atmospheric pressure. The composition of the products was determined by VPC at appropriate time intervals.

Identification of Products. After the hydrogenolysis proceeded appropriately, the reaction mixture was subjected to measurement of GC-MS. For measurement of NMR and elementary analysis, each component of products was separated by preparative VPC.

Phenylcycloheptane (5): Ms *m/z*: 174(M^+), which was identical with that of an authentic sample, bp 113—114 °C/10 mmHg, lit,[15] bp 114.5 °C/10 mmHg, prepared by the hydrogenation of 1-phenylcycloheptene over Pd-C.

***cis*-1-Fluoro-2-phenylcycloheptane (6):** MS *m/z*: 192(M^+). ^{1}H NMR (CCl_4) δ=7.14 (5H, s, C_6H_5), 4.88 (1H, mm, J_{HFgem}=48.0 Hz), 2.6—1.0 (12H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=112.13 (m). Found: C, 81.37; H, 8.89%. Calcd for $C_{13}H_{17}F$: C, 81.21; H, 8.91%.

Compound **6** was identical with an authentic sample which was prepared as follows; hydrogenation of 1-phenyl-8-oxabicylo[5.1.0]octane (3.9 g) over Raney nickel (2 g) in hexane at room temperature under atmospheric pressure gave phenylcycloheptane (41%) and a mixture of *cis*- and *trans*-2-phenylcycloheptanol (51%, trans/cis=9/1). The fractional distillation of the reaction mixture gave *trans*-2-phenylcycloheptanol, 1.7 g, bp 130—137 °C/4 mmHg, lit,[16] bp 113—114 °C/0.5 mmHg, *p*-nitrobenzoate, mp 83—84 °C, lit,[16] mp 84—85 °C. To a methylene dichloride soluion (5 ml) of *trans*-2-phenylcycloheptanol (0.95 g, 5 mmol) was added a methylene chloride solution (5 ml) of hexafluoropropene-diethylamine (1.35 g, 6 mmol) at 0—5 °C and allowed to stand overnight. After removal of low boiling products, the residue was purified by a column chromatography to obtain **6** (70 mg). The values of NMR and elementary analysis were in agreement with those of **6** obtained by the hydrogenolysis of 1-exo-F and **3**. ^{1}H NMR (CCl_4) δ=7.14 (5H, s, C_6H_5), 4.85 (1H, mm, J_{HFgem}=48.0 Hz), 2.6—1.0 (12H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=112.13 (m). Found: C, 80.86; H, 8.87%. Calcd for $C_{13}H_{17}F$: C, 81.21; H, 8.91%.

***trans*-1-Fluoro-2-phenylcycloheptane (7):** MS *m/z*: 192(M^+). ^{1}H NMR (CCl_4) δ=7.15 (5H, s, C_6H_5), 4.54 (1H, mm, J_{HFgem}=46.0 Hz), 2.4—1.2 (12H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=86.38 (m). Found: C, 81.40; H, 9.05%. Calcd for $C_{13}H_{17}F$: C, 81.21; H, 8.91%.

Compound **7** was identical with an authentic sample which was prepared as follows; hydrogenation of 1-phenyl-8-oxabicyclo[5.1.0]octane (3.2 g) over Pd-C (0.36 g) in hexane solution in the presence of diethylamine (0.67 g) gave phenylcycloheptane (3%) and 2-phenylcycloheptanol (96%, cis/trans=95/5). The fractional distillation gave *cis*-2-phenylcycloheptanol, 2.5 g, bp 124—132 °C/3.5 mmHg,

lit,[16] bp 98.5—102.5 °C/0.25 mmHg, *p*-nitrobenzoate, mp 90—92 °C, lit,[16] mp 92—93 °C. Fluorination of the *cis*-alcohol (0.95 g) was carried out in a similar manner as described above to obtain **7** (0.45 g). The values of NMR and elementary analysis were in agreement with those of **7** obtained by the hydrogenolysis of 2-exo-F. ^{1}H NMR (CCl_4) δ=7.16 (5H, s, C_6H_5), 4.56 (1H, mm, J_{HFgem}=46.0 Hz), 2.4—1.2 (12H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=86.38 (m). Found: C, 80.89; H, 8.91%. Calcd for $C_{13}H_{17}F$: C, 81.21; H, 8.91%.

1,1-Difluoro-2-phenylcycloheptane (8): MS *m/z*: 210(M^+). ^{1}H NMR (CCl_4) δ=7.17 (5H, s, C_6H_5), 2.7—0.8 (11H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=4.80 (mm, J_{FFgem}=243.2 Hz), 23.27 (mm, J_{FFgem}=243.2 Hz). Found: C, 74.09; H, 7.80%. Calcd for $C_{13}H_{16}F_2$: C, 74.26; H, 7.67%.

***trans*-1-Fluoromethyl-2-phenylcyclohexane (9):** MS *m/z*: 192(M^+). ^{1}H NMR (CCl_4) δ=7.17 (5H, s, C_6H_5), 4.00 (2H, dd, J_{HFgem}=48.0 Hz, J_{HHvic}=3.0 Hz, CH_2F), 2.6—1.2 (10H, broad, ring). ^{19}F NMR ($CDCl_3$) δ=153.68 (m). Found: C, 80.92; H, 8.77%. Calcd for $C_{13}H_{17}F$: C, 81.21; H, 8.77%.

Compound **9** was identical with an authentic sample which was prepared as follows; to a methylene dichloride solution (5 ml) of *trans*-2-phenylhexahydrobenzyl alcohol (0.95g, 5 mmol), mp 46—48 °C, lit,[17] mp 46—48 °C, was added a methylene chloride solution (5 ml) of hexafluoropropene-diethylamine (1.35 g, 6 mmol) at 0—5 °C and the reaction mixture was allowed to stand overnight. The fraction, bp 107—110 °C/5 mmHg, 0.55 g, was purified by TLC and 0.17 g of **9** was obtained. The values of NMR and elementary analysis were in agreement with those of **9** obtained by the hydrogenolysis of 2-exo-F. ^{1}H NMR (CCl_4) δ=7.15 (5H, s, C_6H_5), 3.96 (2H, dd, J_{HFgem}=48.0 Hz, J_{HHvic}=2.8 Hz, CH_2F). ^{19}F NMR ($CDCl_3$) δ=153.68 (m). Found: C, 81.17; H, 8.97%. Calcd for $C_{13}H_{17}F$: C, 81.21; H, 8.91%.

***cis*-1-Methyl-2-phenylcycloheptane (10):** MS *m/z*: 188(M^+). ^{1}H NMR (CCl_4) δ=7.11 (5H, s, C_6H_5), 2.6—1.2 (12H, broad, ring), 0.73 (3H, d, *J*=6.0 Hz, CH_3). Found: C, 89.16; H, 10.73%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%.

***r*-1-Fluoromethyl-*t*-3-methyl-*t*-2-phenylcyclohexane (11):** MS *m/z*: 206(M^+). ^{1}H NMR (CCl_4) δ=7.17 (5H, s, C_6H_5), 4.13 (2H, dd, J_{HFgem}=48.0 Hz, J_{HHvic}=3.0 Hz, CH_2F), 2.6—1.2 (9H, broad, ring), 0.78 (3H, d, *J*=7.0 Hz, CH_3). ^{19}F NMR ($CDCl_3$) δ=153.08 (m). Found: C, 81.74; H, 9.16%. Calcd for $C_{14}H_{19}F$: C, 81.51; H, 9.28%.

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