Catalytic Hydrogenolysis of 1,1-Difluoro-2-phenyl- and 1,1-Difluoro-3-methyl-2-phenylcyclopropane

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Synopsis. The title compounds were hydrogenolyzd over PdO or Raney nickel. The C_2–C_3 bond of the cyclopropane ring underwent cleavage exclusively over the both catalysts. The contribution of the fluorine substituent to the lengthening and weakening the C_2–C_3 bond of the cyclopropane ring seems to become a dominant factor in the regioselectivity.

In a previous paper[1] we reported that the palladium oxide (PdO)-catalyzed hydrogenolysis of 1,1-dichloro-3-methyl-2-phenylcyclopropane caused exclusive cleavage of the C_2–C_3 bond, whereas both the C_1–C_2 and C_2–C_3 bonds were cleaved competitively using Raney nickel (R-Ni) as a catalyst.

In this paper, we wish to report that the regioselective cyclopropane ring cleavage occurs in the catalytic hydrogenolysis of 1,1-difluoro-2-phenylcyclopropane(**1**) and its 3-methyl derivative(**2**) by the use of PdO and R-Ni. The products arising from the C_2–C_3 bond cleavage of the cyclopropane ring were obtained exclusively.

The results are given in Tables 1 and 2. PdO-catalyzed hydrogenolysis of **1** gave propylbenzene(**1a**), 2-fluoro-1-phenylpropane(**1b**), and 2,2-difluoro-1-phenylpropane(**1c**). The addition of a large amount of potassium hydroxide reduced the rate of hydrogenolysis of **1** and gave a substantial amount of (*Z*)-2-fluoro-1-phenylpropene(**1d**). **1d** was hydrogenated readily to give **1a** and **1b** in the absence of the additive. Hence **1d** seems to be a precursor of **1a** and **1b**. Using R-Ni as a catalyst, **1** gave mainly **1a** accompanied by **1b** and **1c** in the absence and the presence of a base such as triethylamine (TEA). The addition of ethylenediamine (EDA), however, inhibited effectively the hydrogenolysis of **1**.

The catalytic hydrogenolysis of **2** was slower than that of **1** and gave butylbenzene(**2a**), 2-fluoro-1-phenylbutane(**2b**), (*Z*)-2-fluoro-1-phenyl-1-butene(**2d**), and (*Z*)-2-fluoro-1-phenyl-2-butene(**2e**). 2,2-Difluoro-1-phenylbutane(**2c**) was detected only in the case of the PdO-catalyzed hydrogenolysis in the absence of the additive, although **2c** was identified only by use of GC-MS (H^+=170) because of the difficulty to isolate **2c** by VPC preparatively. The products show more clearly that the cyclopropane ring cleavage occurs selectively at the C_2–C_3 bond, and the olefins are the important intermediates as the precursors of the final products.

Table 1. Hydrogenolysis of **1**

Catalyst		Additive		Time	Composition of products(%)				
	(mg)		(mmol)	min	**1**	**1a**	**1b**	**1c**	**1d**
PdO	2	—		90	1.8	14.6	40.1	43.5	—
PdO	10	KOH	1.5	45	25.0	53.0	—	5.3	16.7
R-Ni	15	—		180	—	68.6	14.5	16.9	—
R-Ni	15	TEA	0.4	120	—	92.5	6.0	1.5	—
R-Ni	15	EDA	0.4	600	99.4	0.6	—	—	—

31 mg (0.2 mmol) of **1** was used for each hydrogenolysis.

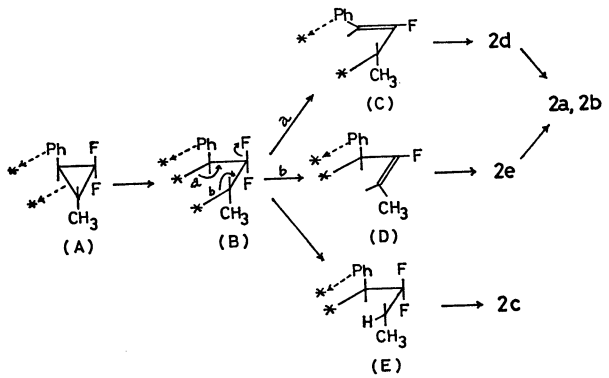
Table 2. Hydrogenolysis of **2**

Catalyst		Additive		Time	Composition of products(%)				
	(mg)		(mmol)	min	**2**	**2a**	**2b**	**2d**	**2e**
PdO	10	—		60	33.7	22.9	38.8	—	4.6
PdO	10	KOH	1.5	60	20.0	46.7	19.9	3.2	10.2
R-Ni	15	—		60	45.7	48.6	5.7	—	—
R-Ni	15	TEA	0.6	60	8.3	89.1	2.6	—	—
R-Ni	15	EDA	0.6	60	100	—	—	—	—

168 mg (1 mmol) of **2** was used for each PdO-catalyzed hydrogenolysis. 34 mg (0.2 mmol) of **2** was used for each R-Ni-catalyzed hydrogenolysis.

According to Hoffmann's proposal,[2] using the Walsh model as a basis, the π-electron donating groups raise the electron density of antibonding LUMO to cause weakening of ring bonds together with an increase in their length. The available data of ring bond lengths (Å) for C_1–C_2 and C_2–$C_{2'}$ bonds in cyclopropane,[3] dichloro-,[4] fluoro-,[5] and difluorocyclopropanes[6] are reported, respectively, as follows; 1.514, 1.514; 1.532, 1.534; 1.494, 1.527; 1.464, 1.553. Analogous deformation of the cyclopropane ring is expected for **1** and **2**. Therefore, the affinity of fluorine to the catalysts seems to become a minor factor even when R-Ni is used, and the cleavage of the cyclopropane ring of **1** and **2** occurs at the weakened C_2–C_3 bond exclusively.

A plausible pathway of hydrogenolysis of **2** is shown in Scheme 1. From species (B), the elimination of fluoride ion (or fluorine atom) is caused by the electron transfer from C_2– or C_3–metal bond to give (C) and (D). In competition with the elimination, unlike dichloro derivatives, the combination of *s*-type adsorbed hydrogen[7] at the C_2– and C_3–metal bonds occurs to give **2c** *via* (E). As the adsorption of EDA to the nickel catalyst is more stronger than that of monoamines, the adsorption by C_1–C_2 or C_2–C_3 bond of cyclopropane ring seems to be not strong enough to promote the hydrogenolysis.



Scheme 1.

Experimental

*1,1-Difluoro-2-phenylcyclopropane (**1**).* **1** was prepared according to the method described in the literature.[8] The fraction, bp 55—65 °C/25 mmHg (1 mmHg = 133.322 Pa) was purified preparatively by VPC. MS *m/e*: 154(M^+) ^{1}H NMR(CCl_4): δ = 1.70 (2H, m, C(H)—C(H)—H), 2.67 (1H, m, C_6H_5-C(H)—C), 7.17 (5H, s, $C_6\underline{H}_5$-). Found: C, 70.17; H, 5.31%. Calcd for $C_9H_8F_2$: C, 70.12; H, 5.23%.

*1,1-Difluoro-3-methyl-2-phenylcyclopropane (**2**).* **2** was prepared in a similar manner as **1** and the fraction, bp 45—50 °C/19 mmHg, was purified preparatively by VPC. MS *m/e*: 168(M^+), ^{1}H NMR(CCl_4): δ = 1.36 (3H, m, $C\underline{H}_3$-), 1.76 (1H, m, C(H)—C-CH_3), 2.16 (1H, m, C_6H_5-C—C), 7.16 (5H, s, $C_6\underline{H}_5$-). Found: C, 71.54; H, 6.05%. Calcd for $C_{10}H_{10}F_2$: C, 71.42; H, 5.99%.

General Procedure of Catalytic Hydrogenolysis. Substrates were hydrogenated over prescribed amount of PdO (Nippon Engelhard Co.) or R-Ni (alloy NDH, Kawaken Fine Chemical Co., was treated according to the W-5 method[9] and washed with water until free from the alkaline solution) catalyst in the presence or absence of additives, such as potassium hydroxide or amines, in methanol at room temperature under atmospheric pressure. The composition of products was determined by VPC (DOS, 2 m, 100 and 130 °C) at appropreate 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 the products was separated preparatively by VPC.

*Propylbenzene (**1a**)*: MS *m/e*: 120(M^+), which was identical with that of an authentic sample.

*2-Fluoro-1-phenylpropane (**1b**)*: MS *m/e*: 138(M^+), ^{1}H NMR (CCl_4): δ = 1.24 (3H, dd, -$C\underline{H}_3$, $J(CH_3\text{-H})$ = 6.0 Hz, $J(CH_3\text{-F})$ = 23 Hz), 2.65 (1H, dd, C_6H_5-C($\underline{H}_a$)—C($\underline{H}_b$)-F, $J(H_a\text{-}H_c)$ = 6.0 Hz, $J(H_a\text{-F})$ = 6.0 Hz), 2.98 (1H, dd, C_6H_5-C($\underline{H}_b$)—C-, $J(H_b\text{-}H_c)$ = 6.0 Hz, $J(H_b\text{-F})$ = 2.5 Hz), 4.73 (1H, mm, $\underline{H}_c$-C(F)-CH_3, $J(H_c\text{-F})$ = 48 Hz), 7.15 (5H, s, $C_6\underline{H}_5$). Found: C, 77.68; H, 7.98%. Calcd for $C_9H_{11}F$: C, 78.23; H, 8.02%.

*2,2-Difluoro-1-phenylpropane (**1c**)*: MS *m/e*: 156(M^+), ^{1}H NMR(CCl_4): δ = 1.46 (3H, t, -CF_2-$C\underline{H}_3$, $J(CH_3\text{-F})$ = 18 Hz), 3.08 (2H, t, C_6H_5-$C\underline{H}_2$-CF_2-, $J(CH_2\text{-F})$ = 15 Hz), 7.20 (5H, s, $C_6\underline{H}_5$). Found: C, 69.12; H, 6.57%. Calcd for $C_9H_{10}F_2$: C, 69.21; H, 6.45%.

(Z)-*2-Fluoro-1-phenylpropene (**1d**)*: MS *m/e*: 136(M^+), ^{1}H NMR(CCl_4): δ = 2.05 (3H, d, C(F)=C(F)-$C\underline{H}_3$, $J(CH_3\text{-F})$ = 15 Hz), 5.35 (1H, d, C_6H_5-C(F)=C(H)-, $J(H\text{-F})$ = 36.5 Hz), 7.24 (5H, m, $C_6\underline{H}_5$), IR(CCl_4): 1695 cm^{-1} (C=C). Found: C, 79.27; H, 6.98%. Calcd for C_9H_9F: C, 79.38; H, 6.66%.

*Butylbenzene (**2a**)*: MS *m/e*: 134(M^+), which was identical with that of an authentic sample.

*2-Fluoro-1-phenylbutane (**2b**)*: MS *m/e*: 152(M^+), ^{1}H NMR (CCl_4): δ = 0.97 (3H, t, -$C\underline{H}_3$), 1.15—1.94 (2H, m, -CHF-$C\underline{H}_2$-CH_3), 2.67 (1H, dd, C_6H_5-C($\underline{H}_a$)—C($\underline{H}_b$)-F, $J(H_a\text{-}H_c)$ = 6.0 Hz, $J(H_a\text{-F})$ = 3.0 Hz), 3.01 (1H, ss, C_6H_5-C($\underline{H}_a$)—C($\underline{H}_b$)-F, $J(H_b\text{-}H_c)$ = 6.0 Hz, $J(H_b\text{-F})$ = 0 Hz), 4.50 (1H, mm, $\underline{H}_c$-C(F)-, $J(H_c\text{-F})$ = 52 Hz), 7.15 (5H, s, $C_6\underline{H}_5$). Found: C, 78.30; H, 8.49%. Calcd for $C_{10}H_{13}F$: C, 78.91; H, 8.61%.

(Z)-*2-Fluoro-1-phenyl-1-butene (**2d**)*: MS *m/e*: 150(M^+), ^{1}H NMR(CCl_4): δ = 1.15 (3H, t, -CH_2-$C\underline{H}_3$), 2.28 (2H, m, C=C(F)-$C\underline{H}_2$-, $J(H\text{-F})$ = 14 Hz), 5.30 (1H, ss, C_6H_5-C(H)=C(F)-, $J(H\text{-F})$ = 37 Hz), 7.27 (5H, m, $C_6\underline{H}_5$), IR(CCl_4): 1685 cm^{-1} (C=C). Found: C, 79.86; H, 7.48%. Calcd for $C_{10}H_{11}F$: C, 79.79; H, 7.38%.

(Z)-*2-Fluoro-1-phenyl-2-butene (**2e**)*: MS *m/e*: 150(M^+), ^{1}H NMR(CCl_4): δ = 1.60 (3H, mm, -CF=CH-$C\underline{H}_3$, $J(CH_3\text{-H})$ = 7.0 Hz), 3.42 (2H, ss, C_6H_5-$C\underline{H}_2$-CF=C(H)-, $J(H\text{-F})$ = 15 Hz), 4.48 (1H, mm, -C(F)=C(H)-CH_3, $J(H\text{-F})$ = 35 Hz), 7.18 (1H, s, $C_6\underline{H}_5$), IR(CCl_4): 1700 cm^{-1} (C=C). Found: C, 79.82; H, 7.47%. Calcd for $C_{10}H_{11}F$: C, 79.97; H, 7.38%.

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References

1) K. Isogai and S. Hirabayashi, *Bull. Chem. Soc. Jpn.*, **52**, 3757 (1979).
2) R. Hoffmann, *Tetrahedron Lett.*, **1970**, 2907.
3) W. J. Jones and B. P. Stoicheff, *Can. J. Phys.*, **42**, 2259 (1964).
4) W. Flygare, A. Narath, and W. Gwinn, *J. Chem. Phys.*, **36**, 200 (1962).
5) S. Durmaz and H. Kollmar, *J. Am. Chem. Soc.*, **102**, 6942 (1980).
6) A. T. Perretta and V. W. Laurie, *J. Chem. Phys.*, **62**, 2469 (1975).
7) T. Toya, *J. Res. Inst. Catal. Hokkaido Univ.*, **6**, 308 (1958); **8**, 209 (1961); *Kinzoku Butsuri*, **10**, 147 (1964).
8) K. Kamel, W. Kimpenhaus, and J. Buddrus, *Chem. Ber.*, **109**, 2351 (1976).
9) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).