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Catalytic Hydrogenolysis of 1,1-Dichloro-3-methyl-2-phenylcyclopropane

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Synopsis. The title compound was hydrogenolyzed over PdO or Raney nickel. The C_2–C_3 bond of the cyclopropane ring underwent cleavage exclusively over PdO. Cleavage of the C_1–C_2 and C_2–C_3 bonds occurred competitively over Raney nickel. A probable pathway is suggested.

The position of ring cleavage on the catalytic hydrogenolysis of cyclopropanes is determined by substituents.[1,2] However, little attention has been given to the role of negative substituents such as halogens in the regioselectivity of the ring cleavage. The hydrogenolysis of 1-bromo-1-fluoro-2-phenylcyclopropane over palladium oxide catalyst (PdO) has been investigated.[3] Cleavage of the C_2–C_3 bond of the cyclopropane ring occurred exclusively, two olefins being obtained as intermediates. In order to clarify the behavior of halogens in the regioselective hydrogenolysis of cyclopropane ring, we have studied the hydrogenolysis of 1,1-dichloro-3-methyl-2-phenylcyclopropane (**1**).

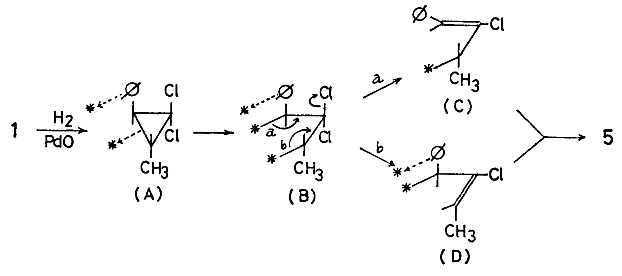
The results of catalytic hydrogenolysis of **1** are given in Table 1. When PdO was used as a catalyst, hydrogenolysis of **1** was reduced in the presence of potassium hydroxide, but proceeded smoothly in the absence of potassium hydroxide, giving butylbenzene (**5**) exclusively. On the other hand, with use of Raney nickel (R-Ni), only in the presence of potassium hydroxide, it gave a mixture of stereoisomeric 1-chloro-*r*-3-methyl-*t*-2-phenylcyclopropane (**2**) (*r*-1-chloro-*c*-3-methyl-*t*-2-phenylcyclopropane (**2t**) and *r*-1-chloro-*t*-3-methyl-*c*-2-phenylcyclopropane (**2c**)), *r*-2-methyl-*t*-1-phenylcyclopropane (**3**), isobutylbenzene (**4**) and **5**. In the presence of potassium hydroxide, the product composition for R-Ni catalyzed hydrogenolysis varied with the progress of reaction. The main products in the early stage of the hydrogenolysis were **2** and **4**. After **1** almost disappeared, **2** decreased gradually, **5** increasing in proportion to the decreased amount of **2**. **2** and **3** were hydrogenolyzed over R-Ni in a manner similar to that observed in the case of **1**. Hydrogenolysis of **2** gave **4** (15.2%) and **5** (64.2%); that of **3** gave predominantly **4** (83.0%) with a small amount of **5** (3.1%). PdO catalyzed hydrogenolysis of 1-bromo-1-fluoro-2-phenylcyclopropane (**6**) gave 2-fluoro-3-phenylpropene (**7**) and (*Z*)-2-fluoro-1-phenylpropene (**8**) as intermediates.[3] They were finally hydrogenolyzed to propylbenzene (**9**) and 2-fluoro-1-phenylpropane (**10**). The formation of these olefins can be explained by assuming that **6** adsorbed on the catalyst by C_2–C_3 bond undergoes cleavage accompanied by elimination of bromide ion. Hydrogenolysis of **1** over PdO seems to proceed in a similar manner to that above, a plausible pathway being shown in Scheme 1. Since palladium catalyst has greater affinity to carbon–carbon π-bond than to negative groups such as oxygen or nitrogen,[4,5] and the affinity to chlorine lone pairs is not very high,[6,7] the hydrogenolysis occurs selectively through the adsorption state (A) chemisorbed by the C_2–C_3 bond of the cyclopropane ring and phenylgroup followed by the formation of C_2,C_3-diadsorbed species (B). The elimination of chloride ion (or chlorine atom) from (B) is caused by the electron transfer from C_2–metal or C_3–metal bond to give (C) or (D). Since (D) forms π-benzyl complex with catalyst, elimination of the chlorine atom seems to prefer course (b). Absence of the expected olefins in the reaction mixture seems to be due to their rapid hydrogenation to the final product **5** under the experimental conditions.

The R-Ni catalyzed hydrogenolysis of **1** is complicated. Predominant formation of **2** and **4** at the

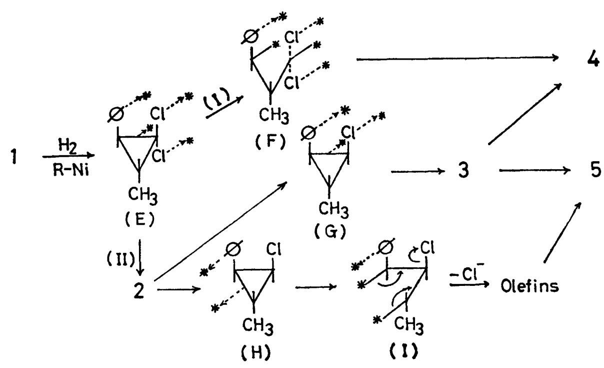
Table 1. Hydrogenolysis of 1

Catalyst	Additive	Composition of products/mol %				
		5	**4**	**3**	**2**	**1**
PdO	—	65.2	—	—	—	34.8
PdO	KOH	3.3	0.5	0.7	—	95.5
R-Ni	—	2.3	0.9	—	—	96.8
R-Ni	KOH	35.0	37.9	1.1	25.0[a]	—

a) **2t**/**2c** ratio is 39/61.



Scheme 1.



Scheme 2.

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early stage of the hydrogenolysis of **1** is ascribed to the adsorption by the chlorine atom which has high affinity to nickel catalyst,[6,7] phenyl group and C_1–C_2 bond of **1**, followed by competitive hydrogenolysis of C_1–C_2 bond (path I) and C–Cl bond (path II) as shown in Scheme 2. The hydrogenolysis of C–Cl bond from the adsorbed species (F) seems to occur readily, giving **4**. The formation of **5** is mainly due to the hydrogenolysis of **2** *via* adsorbed species (H) since the stepwise hydrogenolysis of **2** *via* adsorbed species (G) gives predominantly **4**.

The adverse effect of potassium hydroxide in the PdO and R-Ni catalyzed hydrogenolysis of **1** might be explained in terms of the adsorption states of substrate. When PdO is used as a catalyst, the presence of potassium hydroxide prevents adsorption of the phenyl group and cyclopropane (adsorption state (A)) as in the case of carbon–carbon π-bond. The accelerating effect of potassium hydroxide in the case of R-Ni catalyzed hydrogenolysis is due to the inhibition of the production of Ni^{2+} ion, *viz.* poison of nickel catalyst, caused by removal of chloride ion as a salt.

Experimental

*1,1-Dichloro-*r*-3-methyl-*t*-2-phenylcyclopropane (1).* To a mixture of petroleum ether (200 ml), β-methylstyrene (29.5 g, 0.25 mol) and potassium *t*-butoxide prepared from 10 g of potassium metal was added dropwise 30 g (0.25 mol) of chloroform at −10 °C over a period of 3 h. **1**: bp 86.5—88 °C/3.5 mmHg, 19.5 g (39% yield) was obtained. R_t: 29.0 min, MS *m/e*: 200 (M^+). Found: C, 59.76; H, 4.90%. Calcd for $C_{10}H_{10}Cl_2$: C, 59.72; H, 5.01%.

Catalysts. Palladium oxide (Nippon Engelhard Co.) and Raney nickel alloy NDH (Kawaken Fine Chemical Co.) were used. The alloy was treated according to the W-5 method[8] and washed with water until the washings showed no coloration with phenolphthalein.

Catalytic Hydrogenolysis of 1. **1** (5 mmol) was hydrogenated for 24 h over R-Ni (1 g, as Ni) or PdO (0.2 g) in methanol (25 ml) at room temperature under atmospheric pressure in the presence or absence of potassium hydroxide (10 mmol). The composition of products was determined by VPC (TCP 2 m: 130 °C) at appropriate time intervals.

Identification of Products. **1** was hydrogenolyzed over R-Ni under similar conditions to those described above. Hydrogenation was stopped after 1 h, 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.

r*-1-Chloro-*c*-3-methyl-*t*-2-phenylcyclopropane (2t)*: R_t: 17.3 min, MS *m/e*: 166 (M^+), NMR (CCl_4): δ=1.86 (1H, dd, $\underline{H}_a$-C-Ph), 3.30 (1H, dd, $\underline{H}_x$-C-Cl, $J(H_a-H_x)=3.8$ Hz). Found: C, 72.27; H, 6.80%. Calcd for $C_{10}H_{11}Cl$; C, 72.09; H, 6.66%.

r*-1-Chloro-*t*-3-methyl-*c*-2-phenylcyclopropane (2c)*: R_t: 19.8 min, MS *m/e*: 166 (M^+), NMR (CCl_4): δ=2.04 (1H, dd, $\underline{H}_a$-C-Ph), 3.08 (1H, dd, $\underline{H}_x$-C-Cl, J $(H_a-H_x)=7.8$ Hz). Found: C, 72.18: H, 6.67%. Calcd for $C_{10}H_{11}Cl$: C, 72.09; H, 6.60%.

r*-2-Methyl-*t*-1-phenylcyclopropane (3)*: R_t: 4.2 min, MS *m/e*: 132 (M^+). Found: C, 90.16; H, 9.3%. Calcd for $C_{10}H_{12}$: C, 90.58; H, 9.15%.

Isobutylbenzene (4): R_t: 2.2 min, MS *m/e*: 134 (M^+), NMR (CCl_4): δ=0.91 (6H, d, $-CH(C\underline{H}_3)_2$), 1.84 (1H, m, $-C\underline{H}(CH_3)_2$).

Butylbenzene (5): R_t: 3.0 min, MS *m/e*: 134 (M^+), NMR (CCl_4): δ=0.90 (3H, t, $-C\underline{H}_3$), 1.4 (4H, m, $-C\underline{H}_2-C\underline{H}_2-$).

Catalytic Hydrogenolysis of 2 and 3. **2** (**2t**/**2c**=44/56) and **3** were hydrogenolyzed in a similar manner to that for hydrogenolysis of **1**, respectively.

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