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THE CATALYTIC HYDROGENOLYSIS OF 1-PHENYLBICYCLO[4.1.0]HEPTANE AND THE CORRESPONDING AZIRIDINE AND EPOXIDE

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Abstract—The hydrogenolysis of 1-phenylbicyclo[4.1.0]heptane (**1a**), *cis*-1-phenyl-2-methylbicyclo-[4.1.0]heptane (**1b**), 1-phenyl-7-azabicyclo[4.1.0]heptane (**2**) and 1-phenyl-7-oxabicyclo[4.1.0]heptane (**3**) was studied using Ni, Pd, Rh and Pt as catalysts. The hydrogenolysis of the C_1–C_7 bond of **1a** and **1b** led to the selective formation of *trans*-1-phenyl-2-methylcyclohexane (**4a**) with retention of configuration. Compound **1a** gave not only **4a** but also phenylcycloheptane (**6a**), which is the product of C_1–C_6 bond fission, and the ratio of **6a** to **4a** increased in the sequence: Ni ≪ Pd, Rh < Pt. No C_1–C_6 bond fission was observed in the hydrogenolysis of **1b**. These results can be explained by a mechanism involving the formation of the π-benzyl complex.

trans-2-Phenylcyclohexylamine (**8**) was obtained stereoselectively in the hydrogenolysis of **2** over Raney Ni. This selective formation can be ascribed to the competition of "SN i" and "radical" processes. The Pd catalysed hydrogenolysis gave *cis*-2-phenylcyclohexylamine (**9**) as the main product, while the presence of sodium hydroxide promoted the formation of **8**.

Raney Ni catalysed hydrogenolysis of **3** yielded a mixture of phenylcyclohexane (**13**) and 2-phenylcyclohexanols (**10** and **11**). *trans*-2-Phenylcyclohexanol (**10**) was the dominant isomer; the hydrogenolysis resulted in the predominant configurational retention. Compound **13** was confirmed to be produced *via* 1-phenylcyclohexene (**12**). This deoxygenation may be explained by a mechanism involving the radical cleavage reaction of **3**. The presence of sodium hydroxide led to the formation of *cis*-2-phenylcyclohexanol (**11**). The Pd catalysed hydrogenolysis also gave mainly **11**.

The differences in behaviour of cyclopropane, aziridine and epoxide we ascribe to the differences in the affinity for the catalyst and differences in the electronegativity between C, N and O atoms.

INTRODUCTION

Cyclopropane, aziridine and epoxide have high reactivities on ring-opening reactions because of their strains. The study of the hydrogenolysis of their derivatives is an important method to understand heterogeneous catalysis. The hydrogenolysis of substituted cyclopropanes has been investigated extensively.[1-8] The direction of ring-opening is a function of substituents: phenyl or vinylcyclopropanes ring-open mainly in the less-substituted or allylic positions,[5-8] while alkyl or aralkylcyclopropanes ring-open mainly in less-substituted bonds.[1-5] However, there are no reports on the stereochemistry of the hydrogenolysis of the phenylcyclopropanes.

On the other hand, the hydrogenolysis of styrene imines and oxides has been studied previously in this laboratory.[9-11] The stereospecificity varied with the kind of substrate, catalyst and solvent.

In this work, we present the first example of stereospecific hydrogenolysis of 1-phenylcyclopropanes: 1-phenylbicyclo[4.1.0]heptane and its 2-methyl derivative. The hydrogenolysis of the corresponding aziridine and epoxide is also studied in order to know the difference in behaviour of these 3-membered compounds with the catalyst.

RESULTS

The hydrogenolysis of 1-*phenylbicyclo*[4.1.0]*heptane* (**1a**) *and* cis-1-*phenyl*-2-*methylbicyclo*[4.1.0]*heptane* (**1b**). The results of hydrogenolysis of **1a** are shown in Table 1. The Raney Ni catalysed hydrogenolysis yielded exclusively *trans*-1-phenyl-2-methylcyclohexane (**4a**), which is the configurationally retained product of C_1–C_7 bond fission. Over Pd, Rh and Pt, **1a** gave not only **4a** but also phenylcycloheptane (**6a**), which is the product of C_1–C_6 bond fission. Over these metals, the ratio of **6a** to **4a** increased in the sequence: Ni ≪ Pd, Rh < Pt. *cis*-1-Phenyl-2-methylcyclohexane (**5a**) and 1-phenyl-1-methylcyclohexane were not obtained under our conditions; the hydrogenolysis of C_1–C_7 bond occurs with stereospecific retention of configuration. No significant effect of sodium hydroxide on the stereospecificity was observed over Raney Ni and Pd, though the

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Table 1. The hydrogenation of 1-phenylbicyclo[4.1.0]-heptane (**1a**)

Catalyst	(mg)	Products distribution (%) **4a**	**5a**	**6a**	**7a**
Raney Ni	500[a]	100	—	—	—
Raney Ni	500[a,b]	100	—	—	—
Pd—C	50	90	trace	10	—
Pd—C	50[b]	90	trace	10	—
$Pd(OH)_2$	10	95	1	4	—
Rh—C	100	60	trace	10	30
PtO_2	40	15	—	5	80
Pt-Black	40[c]	40	trace	20	40

Substrate: 1/400 mol. Solvent: EtOH 10 ml. At 25° and 1 atm.
[a] Wet weight with EtOH.
[b] Additive: NaOH 5 mg.
[c] Weight as PtO_2.

rate slowed down. The relatively extensive reduction of the phenyl group was also observed during the hydrogenation over Rh and Pt, and yielded 1-cyclohexylbicyclo[4.1.0]heptane (**7a**). This was not hydrogenolysed under our conditions.

Table 2 summarizes the hydrogenolysis of **1b**. *trans*, *cis*-1-Phenyl-2,6-dimethylcyclohexane (**4b**) was the only product of the hydrogenolysis over all metals. The reduction of the phenyl group of **1b** was less pronounced than that of **1a**.

The hydrogenolysis of 1-*phenyl*-7-*azabicyclo*[4.1.0]*heptane* (**2**). The product distributions in the hydrogenolysis of **2** are listed in Table 3. The hydrogenolysis over Raney Ni gave selectively *trans*-2-phenylcyclohexylamine (**8**), which is the configurationally retained product. No variation of stereochemical results was observed by the addition of sodium hydroxide over Raney Ni. The Pd catalysed hydrogenolysis resulted in the formation of *cis*-2-phenylcyclohexylamine (**9**), which is the product of inverted configuration. However, the presence of sodium hydroxide in the mixture promoted the formation of **8**.

The hydrogenolysis of 1-*phenyl*-7-*oxabicyclo*-[4.1.0]*heptane* (**3**). Table 4 summarizes the results

Table 2. The hydrogenation of *cis*-1-phenyl-2-methylbicyclo[4.1.0]heptane (**1b**)

Catalyst	(mg)	Products distribution (%) **4b**	**7b**[a]
Raney Ni	200	100	—
Pd—C	50	100	—
Rh—C	20	89	11
Pt-Black	20	69	31

Substrate: 80 μl. Solvent: EtOH 2 ml. At 25° and 1 atm.
[a] *cis*-1-cyclohexyl-2-methylbicyclo[4.1.0]heptane.

Table 3. The hydrogenolysis of 1-phenyl-7-azabicyclo-[4.1.0]heptane (**2**)

Catalyst	(mg)	NaOH (mmol)	Products distribution (%) **8**	**9**	**13**
Raney Ni	500	—	99	1	trace
Raney Ni	500	1·0	98	1	1
Pd—C	50	—	17	83	trace
$Pd(OH)_2$	10	—	23	75	2[a]
$Pd(OH)_2$	10	0·1	67	37	trace
$Pd(OH)_2$	10	0·5	64	36	trace

Substrate: 1/800 mol. Solvent: EtOH 5 mol. At 25° and 1 atm.
[a] 1-Phenylcyclohexene (**12**).

Table 4. The hydrogenolysis of 1-phenyl-7-oxabicyclo-[4.1.0]heptane (**3**)

Catalyst	(g)	NaOH (mmol)	Products distribution (%) **10**	**11**	**13**
Raney Ni	1·0	—	30	11	59
Raney Ni	1·0	1·0	5	93	2
Pd—C	0·1	—	3	93	4
Pd—C	0·1	1·0	—	100	trace

Substrate: 1/200 mol. Solvent: EtOH 50 ml. At 25° and 1 atm.

of the hydrogenolysis of **3**. The Raney Ni catalysed hydrogenolysis gave the deoxygenated product, phenylcyclohexane (**13**) as well as normally hydrogenolysed ones, 2-phenylcyclohexanols (**10** and **11**). *trans*-2-Phenylcyclohexanol (**10**) was richer than the *cis*-isomer (**11**); this hydrogenolysis proceeds with predominant retention of configuration. As clearly seen in Table 5, **13** was produced *via*

Table 5. The dependence of the conversion on the deoxygenation in the Raney Ni catalysed hydrogenolysis of **3**

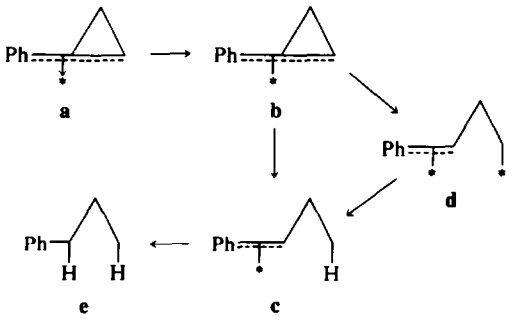
Conversion (%)	Products distribution (%) **10**	**11**	**12**	**13**
51	20	12	46	22
70	24	16	36	24
84	26	14	27	32
95	27	14	24	35
100	27	14	—	59

Substrate: 1/100 mol. Catalyst: 2 g (wet with EtOH).
Solvent: EtOH, 100 ml. At 25° and 1 atm.

1-phenylcyclohexene (**12**). No 1-phenylcyclohexanol was observed during the reaction and, moreover, was hydrogenolysed under our conditions. The presence of sodium hydroxide in the mixture led to the selective formation of **11** and to decreasing the deoxygenation. On the other hand, the hydrogenolysis over Pd yielded selectively **11**. The more selective formation of **11** was observed in the presence of sodium hydroxide.

DISCUSSION

The hydrogenolysis of 1-*phenylbicyclo*[4.1.0]-*heptane.* 1-Phenylcyclopropanes are known to undergo the facile hydrogenolyses at benzylic positions, whereas the alkyl or aralkylcyclopropanes are hydrogenolysed mainly in the less-substituted bonds.[1-6] The hydrogenolysis of C_1–C_7 bond of **1a** and **1b** occurred stereospecifically with retention of configuration as shown in Tables 1 and 2. These specificities in the hydrogenolysis of 1-phenylcyclopropanes can be explained by a mechanism involving the chemisorption of phenyl and cyclopropyl groups, followed by the formation of the π-benzyl complex (Scheme 1).* The cyclopropane has olefinic character. Therefore, the phenylcyclopropane, holding the conjugation of π-electrons in the phenyl group and cyclopropane ring, may form the π-complex **b** through the back-donation from the catalyst to the donative π-complex **a**. The hydrogen will attack nucleophilically the terminal carbon leading to the π-benzyl complex **c**,† or the cyclopropane will ring-open by the initial formation of the 1,3-diadsorbed alkanes



SCHEME 1

d. Either way, the hydrogenolysis is, then, accomplished by the hydrogen addition to the π-benzyl complex **c**, and results in overall retention of configuration. Scarcely any hydrogenolysis with inversion will occur because of low polarisation of the C–C bond at the transition state of the "SN 2" process.

As shown in Tables 1 and 2, the hydrogenolysis of the C_1–C_7 bond of **1a** and **1b** gave selectively **4a** and **4b**, respectively. These results indicate that the C_1–C_7 bond fissions occur through path 1 with retention of configuration. Some C_1–C_6 bond fissions were also observed in the hydrogenolysis of **1a** over Pd, Rh and Pt, but no such reaction occurred in the case of **1b**. This C_1–C_6 bond fission will occur through path 2 with retained configuration,‡ and the degree of C_1–C_6 bond fission may depend on the difference of the catalyst hindrance at the transition states **g** and **j**, because the transition state **j** has a larger catalyst hindrance than **g**. Therefore, path 2 is considered to be retarded by the catalyst hindrance of the C_2-Me group in the hydrogenolysis of **1b**.

C_1–C_6 Bond fission in the hydrogenolysis of **1a** varied with the kind of metal: Ni $\ll$ Pd, Rh $<$ Pt. Similar trends are noticed in the hydrogenation of substituted 1-phenylcyclohexenes.[14] These results may be reasonable in reflecting the sensitivity to the catalyst hindrance at the transition state to form the π-benzyl complex; the benzyl carbon-metal bond length in the π-benzyl complex will increase, as the atomic radius increases. For these reasons, Pt is less sensitive to the catalyst hindrance than Ni, and C_1–C_6 bond fission is considered to increase in the sequence: Ni $\ll$ Pd, Rh $<$ Pt.

In conclusion, the catalytic hydrogenolysis of 1-phenylcyclopropanes proceeds *via* the π-benzyl complex with retained configuration, and hydrogen attacks from less-hindered side.

Recently, Roth[7] presented similar benzyl adsorbed species in the catalytic hydrogenolysis of 1-phenylcyclopropanes over Pd. This author considered that this species would be formed *via* corner attack, and therefore, that the initial attack must occur on the cyclopropyl C atom and not on the ring itself or any of its bonds. If this corner attack should occur in our findings over Pd, then a similar C_1–C_6 bond fission should be observed in both hydrogenolyses of **1a** and **1b**. However, this is not the case; **1a** gave 10% of **5a**, while **1b** was hydrogenolysed selectively to **4b**. Therefore, such corner attack is probably less important in the hydrogenolysis of **1a** and **1b**.

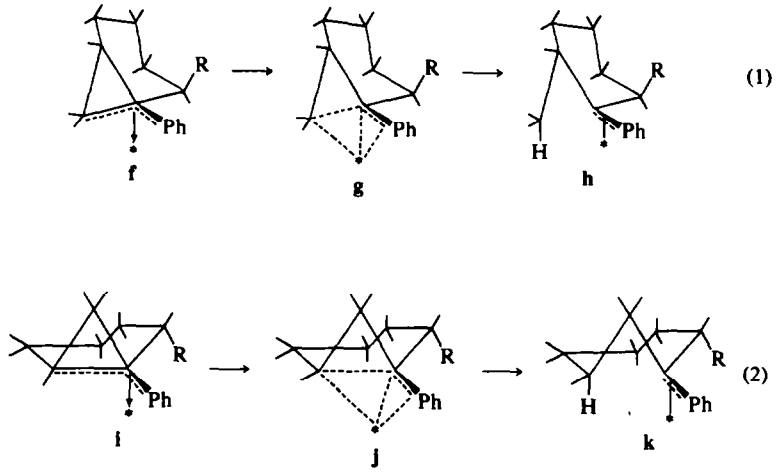
Poulter and Heathcock[8] reported that the catalytic reduction of vinylcyclopropanes occurred in the ring hydrogenolysis as well as the double bond saturation. This hydrogenolysis can be explained by the above mechanism, if we assume a π-allyl complex in place of a π-benzyl complex.

The hydrogenolysis of 1-*phenyl*-7-*azabicyclo*-

*We have previously proposed similar π-benzyl complexes in the hydrogenolysis of benzyl derivatives[9-13] and in the hydrogenation of 1-phenylcycloalkenes.[14]

†It is considered that the hydrogen addition to the conjugated system occurred mostly in the terminal carbon to yield π-allyl or π-benzyl complex.[14,15]

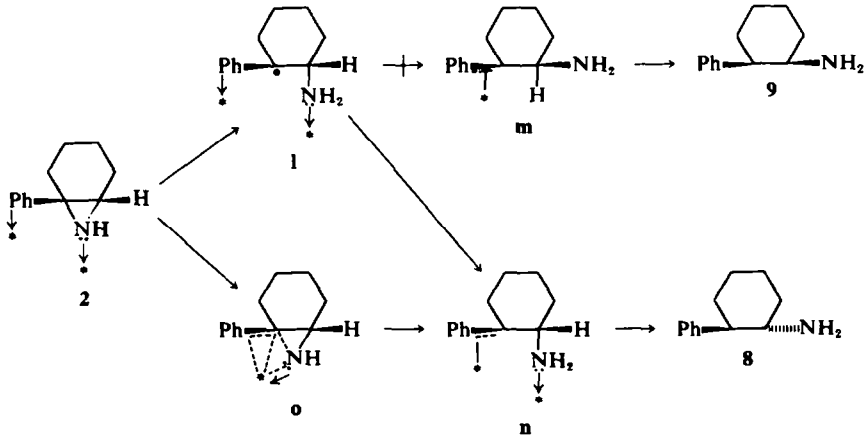
‡There is also a possibility that **6a** is formed by C_1–C_6 bond fission with inversion of configuration. However, this possibility can be eliminated for the reason that, if this is the case, C_1–C_6 bond fissions should be observed in both cases of **1a** and **1b** since **1a** and **1b** would have similar steric situations at the adsorption states **f**.



SCHEME 2

[4.1.0]*heptane*. The Raney Ni catalysed hydrogenolysis of **2** gave stereoselectively **8**. However, we previously reported that the hydrogenolysis of optically active 2-methyl-2-phenylaziridine (**14**) over Raney Ni occurred with slightly-predominant retention of configuration, and ascribed this low stereospecificity to the competition of "SN i" and "radical" processes.[9] The differences between **2** and **14** are explained on the basis of the differences in the structure of the substrate. The radical formed from **14** yields the racemic product because it has only a chiral center; this is the reason of the low stereospecificity. On the other hand, there is the possibility that the radical **l** formed from **2** yields diastereomeric π-benzyl complexes **m** and **n**, since **2** has two chiral centers. In this case, the complex **n** leading to **8** may be formed more significantly than the alternative complex **m**, because the desorption of the radical **l** is required for the formation of **m** and the adsorption of NH_2 stabilises **n**. Moreover, an alternative "SN i" process will also give **8** *via* the transition state **o** and the complex **n** with retention of configuration. Therefore, **2** is considered to be hydrogenolysed competitively *via* "SN i" and "-radical" processes. Either way, the Raney Ni catalysed hydrogenolysis of **2** can be expected to give **8** selectively, and supports the mechanism as previously proposed.[9]

The Pd catalysed hydrogenolysis of **2** gave mainly **9**, whereas the presence of sodium hydroxide promoted the formation of **8**. These results agree with those of **14** as previously described.[9] Since Pd has not as high an affinity for the nitrogen lone pair, the stereoelectronic factor is operative, so the hydrogenolysis of **2** will occur through "SN 2" process. The variation of the stereochemistry in the presence of sodium hydroxide is due to the participation of $\rangle N^- Na^+$ to the hydrogenolysis as previously discussed.[9]



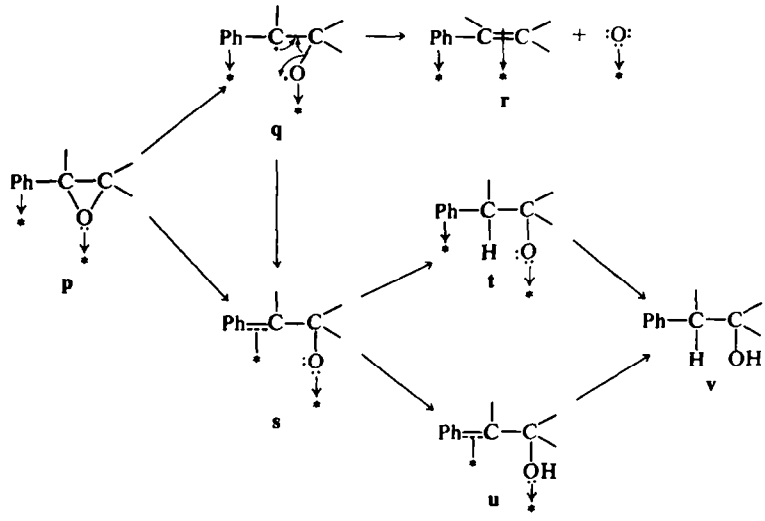
SCHEME 3

The hydrogenolysis of 1-*phenyl*-7-*oxabicyclo*-[4.1.0]*heptane.* **10** was more predominant than **11** in the Raney Ni catalysed hydrogenolysis of **3**. This is in agreement with α-alkylstyrene oxides and α,α'-dimethylstilbene oxides.[10,11] The adsorption of epoxy-oxygen helps to overcome the unfavourable stereoelectronic situation, and these hydrogenolyses may proceed predominantly through "SN i" process to give the retained product. However, the presence of sodium hydroxide in the reaction mixture increased the inverted product **11** in the hydrogenolysis of **3**. Similar results were also obtained in α-alkylstyrene oxides and α,α'-dimethylstilbene oxides.[10,11] The "SN i" process will be retarded since the adsorptivity of epoxy-oxygen will be decreased by the adsorption of sodium hydroxide. Consequently, the hydrogenolysis will be governed by the stereoelectronic factor, and give the inverted product through "SN 2" process.

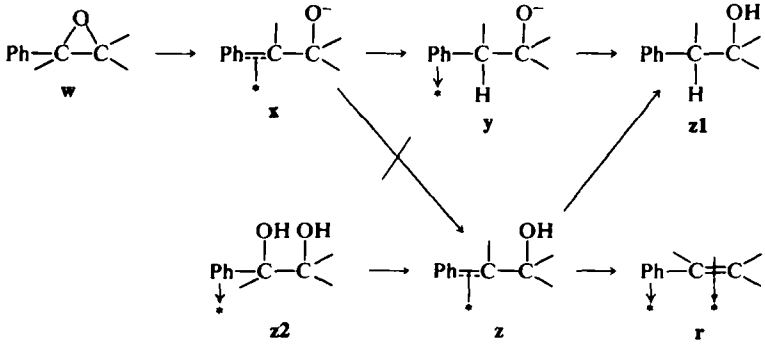
The hydrogenolysis of **3** over Raney Ni gave the deoxygenated product **13** as well as **10** and **11**. **13** was produced *via* the olefin **12** (Table 5). We can exclude the possibility that 1-phenylcyclohexanol is an intermediate of **13**, because it is not hydrogenolysed under our conditions. One possible mechanism for the deoxygenation of styrene oxides is shown in Scheme 4.

The strong adsorptions of oxygen and the phenyl group will increase the strain in the epoxy-ring, and styrene oxides will yield the radical **q** as well as the π-benzyl complex **s**. A part of **q** gives the olefin **r** by the elimination of an O atom. There is also a possibility that **r** will be formed *via* the π-benzyl complex **u** by *cis*-elimination. However, this possibility can be eliminated because *cis*-1-phenylcyclohexane-1,2-diol, which is expected to give the same π-benzyl complex **u**, produced **13** in only 5% yield.[12] The formation of **13** decreased by the addition of sodium hydroxide, and **3** was hydrogenolysed selectively to **11**. This is due to the reason that the chemisorption of sodium hydroxide hinders the radical cleavage reaction and "SN i" process.

The Pd catalysed hydrogenolysis of **3** gave selec-



SCHEME 4



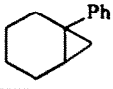
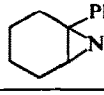
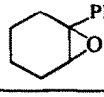
SCHEME 5

tively **11**. This is in agreement with α-alkylstyrene oxides and α,α'-dimethylstilbene oxides.[10,11] Because O has not as high an affinity for Pd, the hydrogenolysis of these compounds will be governed by the stereoelectronic factor, and will proceed *via* the π-benzyl complex **x** with configurational inversion. The deoxygenation in the case of **3** was less than 5%, whereas the hydrogenolysis of *cis*-1-phenylcyclohexane-1,2-diol, which proceeds *via* the π-benzyl complex **z**, gave **13** in 55% yield.[12] These results indicate that the hydrogenolysis of **3** proceeds *via* **y**. Smith and Roth[16] considered that the benzyl carbon-metal bond will not achieve the maximum overlap because of π-complexing of phenyl group to the surface, and the result of this effect is to increase the rate of hydrogen addition to the complex. Therefore, the π-benzyl complex **x** will give **y** rather than **z**.

The difference in behaviour of cyclopropane, aziridine and epoxide on hydrogenolysis. Table 6 summarises the proportions of *trans*-isomer in the hydrogenolysis of C_1–C_7 bond of **1a**, and of corresponding bonds of **2** and **3**. Although these compounds have similar steric situations, the stereospecificities of hydrogenolysis vary with the kind of substrate and catalyst. The differences we may ascribe to the differences in the affinity for the catalyst and in the electronegativity between C, N and O atoms. **2** and **3** can undergo hydrogenolysis *via* "SN 2", "SN i" and/or "radical" processes, though the main path varies with the kind of catalyst and substrate as discussed above. However, **1a** was hydrogenolysed with stereospecific retention of configuration over every catalyst. Because the 1-phenylcyclopropane has a π-electron, its behaviour is expected to resemble that of the styrene. The hydrogenolysis of the phenylcyclopropane will lead to the formation of the π-complex **b** through back-donation to the π-complex **a** from the catalyst, followed by the formation of π-benzyl complex **c** as discussed above. The "SN 2" process will not be favoured because of the low electronegativity of the C atom. Since the phenylcyclopropane has not a group like $\diagdown\!\!>\!\!\diagup$NH or $\diagdown\!\!>\!\!\diagup$O, we can neglect the participation of "radical" process.

The hydrogenolysis of **3** over Raney Ni accompanied the considerable deoxygenation, while **2** gave scarcely any **13**. These results suggest that Ni can not stabilise :NH and/or ·NH_2, which will be produced through corresponding path: **q**→**r**, in the case of styrene oxides. The radical **l** produced from **2** will not yield **12**, but **8**.

Table 6. The stereospecificity in the hydrogenolysis of 1-phenylbicyclo[4.1.0]heptane, and the corresponding aziridine and epoxide (*trans* %)

Catalyst			
Raney Ni	100	98	73
Pd—C	100	17	3
Pt-Black	100	—	—

EXPERIMENTAL

Compound **1a** was prepared by the method in the lit,[17] and **1b** was synthesised from 2-phenyl-3-methylcyclohexene in a similar manner. **3** was obtained by the epoxidation of **12** with perbenzoic acid according to the procedure of Curtin and Schmukler.[18]

1-*Phenyl-7-azabicyclo*[4.1.0]*heptane* (**2**). Methyl N-(1-phenyl-*trans*-2-iodocyclohexane)carbamate was obtained by the procedure of Hassner *et al.*[19] The soln of the carbamate (6·2g) and KOH (10·0g) in MeOH (300 ml) was heated under reflux for 3 hr. After the evaporation of MeOH *in vacuo*, water (200 ml) was added to the oily residue, the imine product was extracted with ether, and dried over KOH pellets. The elimination of ether, and subsequent distillation afforded **2**; b.p. 103–104°/0·3 mmHg, 2·2g (Found: C, 82·91; H, 8·90; N, 7·91. Calcd. for $C_{12}H_{15}N$: C, 83·19; H, 8·73; N, 8·09%).

Catalysts. W-4 Raney Ni was prepared by the Adkins's method.[20] Pd, 5% on charcoal, and $Pd(OH)_2$ were obtained according to the lit.[21,22] Rh, 5% on charcoal, was purchased from Kawaken Fine Chemicals Co. Ltd., Tokyo. PtO_2 was obtained from Wako Junyaku Co. Ltd., Osaka. Pt-black was prepared by the reduction of PtO_2 with H_2, and by subsequent washing with H_2O.

Hydrogenolyses. **1a**(1/400 mol), **1b**(80 μl), **2**(1/800 mol) or **3**(1/100 or 1/200 mol) was hydrogenated in EtOH at 25° and 1 atm. After the absorption of H_2 had ceased, the mixture was submitted for gas chromatographic analysis. Each compoenent was identified by the authentic sample. Analysis in the case of **1a**, **1b** and **3** was carried out by Hitachi K-53 or F-6 gas chromatograph equipped with a Golay Column (0·25 mm × 45 m; liquid phase, Apieson grease L or Carbowax 4000). Analysis in the case of **2** was conducted by Shimadzu 5 AP gas chromatograph equipped with Carbowax 4000 or Silicone oil DC 710 on Celite 545 packed in stainless steel tube (3 mm × 4 m).

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