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Studies on Hydrogenolysis. LVI.[1] The Effect of Solvent and Additive on the Stereochemistry of Catalytic Hydrogenolysis of 2-Methyl-2-phenylaziridine Derivatives*1

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In order to assess the effects of solvent and additive on the stereochemical course of the catalytic hydrogenolysis of styrene imine derivatives, the hydrogenolysis of optically active 2-methyl-2-phenylaziridine (Ia), 1,2-dimethyl-2-phenylaziridine (Ib), and 1-acetyl-2-methyl-2-phenylaziridine (Ic) was carried out under various conditions. The hydrogenolysis of Ia and Ib over palladium hydroxide occurred preferentially with an inversion of the configuration in ethanol, but with a retention in benzene. Moreover, Ia was hydrogenolysed with a predominant inversion of the configuration in *n*-hexane, and the inverted product increased with a decrease in the adsorption strength of the hydrocarbon solvent. The hydrogenolysis of Ic, however, occurred with a significant inversion of the configuration in both ethanol and benzene. The addition of sodium hydroxide to the reaction mixture strongly promoted a retention of the configuration in the hydrogenolysis of Ia over palladium hydroxide, and finally Ia was hydrogenolysed with a stereospecific retention. In contrast, no such variations could be observed in the cases of Ib and Ic. The stereoselectivity was not affected significantly by the addition of sodium hydroxide in the Raney nickel-catalyzed hydrogenolysis of Ia. However, the addition of sodium hydroxide prompted a retention of the configuration in the case of Ib. These results can be explained consistently by the previously-proposed mechanism.

The mechanism of the hydrogenolysis of benzyl-type compounds at heterogenuous catalytic surfaces has been a subject of discussion for more than a decade.[1-9] Mitsui and his co-workers have reported the stereochemical course of this reaction.[1-6]

It seems established that the configurations of the products are responsible for the free-energy difference at the transition states leading to the π-benzyl intermediates. In a previous paper,[2] the present authors reported the hydrogenolysis of optically active 2-methyl-2-phenylaziridine with palladium, platinum, nickel, and cobalt catalysts. However, ethanol was used as the reaction solvent

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[*1] A part of this work was presented at the 24th Symposium on Catalysis, Tokyo, March, 1969 (*cf. Shokubai*, **11**, 54 P. (1969)) and has already been reported in a preliminary form: S. Mitsui and Y. Sugi, *Tetrahedron Lett.*, **1969**, 1291.

1) Part LV, S. Mitsui, M. Fujimoto, T. Sukegawa and Y. Nagahisa, *Kogyo Kagaku Zasshi*, **73**, 97 (1970).

2) S. Mitsui and Y. Sugi, *Tetrahedron Lett.*, **1969**, 1287; Y. Sugi and S. Mitsui, This Bulletin, **42**, 2984 (1969).

3) S. Mitsui and S. Imaizumi, *Nippon Kagaku Zasshi*, **77**, 1516 (1956); This Bulletin, **34**, 774 (1961); **36**, 855 (1963).

4) S. Mitsui, M. Fujimoto, Y. Nagahisa and T. Sukegawa, *Chem. Ind.* (London), **1969**, 241.

5) S. Mitsui, Y. Kudo and M. Kobayashi, *Tetrahedron*, **25**, 1921 (1969).

6) S. Mitsui, S. Imaizumi and Y. Esashi, This Bulletin, in press.

7) W. A. Bonner, *J. Amer. Chem. Soc.*, **74**, 1033, 3218 (1952); W. A. Bonner, J. A. Zderic and G. A. Caseletto, *ibid.*, **74**, 5086 (1952).

8) A. M. Khan, F. J. McQuillin and I. Jardine, *J. Chem. Soc. C*, **1967**, 136.

9) E. W. Garbisch, Jr., L. Schreader and J. J. Frankel, *J. Amer. Chem. Soc.*, **89**, 4233 (1967).

TABLE 1. EFFECT OF THE SOLVENT ON THE STEREOCHEMISTRY OF THE CATALYTIC HYDROGENOLYSIS OF 2-METHYL-2-PHENYLAZIRIDINE (Ia) AND ITS DERIVATIVES (Ib AND Ic)

Run	Reactant	Catalyst (g)	Solvent	Optical purity of I[b] (%)	Products (%)			II				
					II	III	IV	[α]D	Optical purity[b] (%)	Maintained optical activity (%)	Configuration	
											Retention (%)	Inversion (%)
1	Ia	Pd(OH)$_2$ 0.05	Benzene	R 43.6	100	—	trace	−4.48	15	35	68	32
2	Ia	Pd(OH)$_2$ 0.05	Toluene	S 91.0	100	—	trace	−6.09	21	23	38	62
3	Ia	Pd(OH)$_2$ 0.05	*o*-Xylene	S 91.0	100	—	trace	−6.20	21	23	38	62
4	Ia	Pd(OH)$_2$ 0.05	*m*-Xylene	S 91.0	100	—	trace	−8.90	30	33	33	67
5	Ia	Pd(OH)$_2$ 0.05	*p*-Xylene	R 43.6	100	—	trace	+5.34	18	41	29	71
6	Ia	Pd(OH)$_2$ 0.05	*t*-Butylbenzene	R 43.6	100	—	?	+6.19	21	48	26	74
7	Ia	Pd(OH)$_2$ 0.05	*n*-Hexane	R 43.6	100	—	trace	+9.70	33	75	12	88
8[a]	Ia	Pd(OH)$_2$ 0.05	Ethanol	R 43.6	100	—	trace	+9.28	31	72	14	86
9	Ib	Pd(OH)$_2$ 0.05	Benzene	R 44.3	100	—	trace	−0.99	4	9	55	45
10	Ib	Pd(OH)$_2$ 0.05	Ethanol	R 44.3	97	—	3	+8.01	32	72	14	86
11	Ic	Pd(OH)$_2$ 0.05	Benzene	R 37.3	100	—	?	+15.05	32	85	7	93
12	Ic	Pd(OH)$_2$ 0.05	Ethanol	R 37.3	100	—	?	+13.23	28	75	12	88
13	Ia	Ra-Ni 1[c]	Benzene	S 91.0	88	11	1	+5.65	19	21	61	39
14	Ia	Ra-Ni 1[c]	*n*-Hexane	S 91.0	85	13	2	+4.67	16	17	59	41
15[a]	Ia	Ra-Ni 1[c]	Ethanol	S 91.0	93	7	trace	+6.26	21	23	62	38

I: 0.01 mol, Solvent: 20 m*l*, Under ordinary pressure and at room temperature.

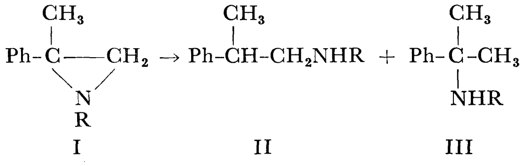
a, Ref. 2, *b*, 100% optical rotation: S(+)-Ia, [α]D +33.3°; S(+)-Ib, [α]D +49.5°; S(+)-Ic, [α]D +97.0°; R(+)-IIa, [α]D +29.5°; R(+)-IIb, [α]D +25.3°; R(+)-IIc, [α]D +47.2°. All rotations were measured in ethanol, *c*, wet weight with ethanol.

Table 2. Effect of sodium hydroxide and potassium iodide on the stereochemistry of the catalytic hydrogenolysis of 2-methyl-2-phenylaziridine (Ia) and its derivatives (Ib and Ic)

Run	Reactant	Catalyst (g)	NaOH (1×10^{-4} mol)	Optical purity of I (%)	Products (%)			II				
					II	III	IV	$[\alpha]_D$	Optical purity (%)	Maintained optical activity (%)	Configuration	
											Retention (%)	Inversion (%)
8	Ia	Pd(OH)$_2$ 0.05	—	R 43.6	100	—	trace	+9.28	31	72	14	86
16	Ia	Pd(OH)$_2$ 0.05	1.0	R 43.6	100	—	trace	+5.98	20	46	27	73
17	Ia	Pd(OH)$_2$ 0.05	2.0	R 43.6	100	—	trace	−7.35	25	57	79	21
18	Ia	Pd(OH)$_2$ 0.05	5.0	R 43.6	100	—	trace	−10.10	34	79	90	10
19	Ia	Pd(OH)$_2$ 0.05	10	S 91.0	100	—	trace	+26.80	91	100	100	0
20	Ia	Pd(OH)$_2$ 0.05	KI 0.1	R 43.6	100	—	trace	+4.38	15	34	33	67
21	Ia	Pd(OH)$_2$ 0.05	KI 0.2	S 91.0	100	—	trace	−9.35	32	35	32	68
10	Ib	Pd(OH)$_2$ 0.05	—	R 44.3	97	—	3	+8.01	32	72	14	86
22	Ib	Pd(OH)$_2$ 0.05	5.0	R 44.3	100	—	trace	+7.26	29	65	17	83
23	Ib	Pd(OH)$_2$ 0.05	10	R 44.3	100	—	trace	+7.13	28	64	18	82
12	Ic	Pd(OH)$_2$ 0.05	—	R 37.3	100	—	?	+13.23	28	75	12	88
24	Ic	Pd(OH)$_2$ 0.05	5.0	R 37.3	100	—	?	+16.62	35	94	3	97
15	Ia	Ra-Ni 1	—	S 91.0	93	7	trace	+6·26	21	23	62	38
25	Ia	Ra-Ni 1	10	S 91.0	93	7	trace	+5.81	20	22	61	39
26	Ia	Ra-Ni 1	100	S 91.0	92	8	trace	+5.14	17	19	60	40
27	Ia	Ra-Ni 1	KI 10	S 91.0	90	10	trace	+4.27	15	16	58	42
28	Ib	Ra-Ni 1	—	S 89.0	78	—	22	+2.47	10	11	56	44
29	Ib	Ra-Ni 1	10	S 89.0	100	—	—	+10.22	40	45	73	27

I: 0.01 mol, Solvent: ethanol, 20 m*l*, Under ordinary pressure and at room temperature.

in all cases. In this work, we will attempt to assess the possible effects of solvent and additive on the stereochemical course of the catalytic hydrogenolysis of optically active 2-methyl-2-phenylaziridine (Ia), 1,2-dimethyl-2-phenylaziridine (Ib), and 1-acetyl-2-methyl-2-phenylaziridine (Ic) under ordinary pressure and at room temperature.



a) R=H, b) R=CH_3, c) R=$COCH_3$

Results

Effect of the Solvent on the Stereochemistry. The hydrogenolysis of Ia with palladium hydroxide was investigated in several kinds of solvents. The results are summarized in Table 1 (Runs 1—8). The hydrogenolysis in ethanol occurred preferentially with an inversion of the configuration, while the hydrogenolysis in benzene was accompanied by a retention. The inversion of the configuration occurred in several aromatic hydrocarbons other than benzene. In these cases, the inverted products increased in the order: benzene < toluene ≒ *o*-xylene < *m*-xylene < *p*-xylene < *t*-butylbenzene; this order is associated with the adsorption strengths of these hydrocarbons under hydrogenation conditions.[10-12] The hydrogenolysis also proceeded with a significant inversion of the configuration in *n*-hexane. The stereochemical results of similar experiments on Ib and Ic are also summarized in Table 1 (Runs 9—12).[*2] The hydrogenolysis of Ib occurred predominantly with an inversion of the configuration in ethanol, but with a retention in benzene; these results are in agreement with those in the case of Ia. The hydrogenolysis of Ic, however, proceeded with a significant inversion of the configuration in both ethanol and benzene.

On the other hand, no significant effect of the solvent on the stereochemical course was observed in the Raney nickel-catalyzed hydrogenolysis of Ia, in contrast with the case of palladium hydroxide (Runs 13—15).

Effects of Sodium Hydroxide and Potassium Iodide on the Stereochemistry. Table 2 shows the influence of sodium hydroxide on the stereochemical results in the hydrogenolysis of Ia, Ib, and Ic. The hydrogenolysis of Ia over palladium hydroxide occurred with a predominant inversion of the configuration in ethanol, as has been described previously.[2] However, the addition of sodium hydroxide to the reaction mixture strongly promoted a retention of the configuration, and finally Ia was hydrogenolysed with a stereospecific retention (Runs 8, 16—19). No such variations in the stereochemical results could be observed in the hydrogenolysis of Ib (Runs 10 and 23), and the stereoselectivity increases in the case of Ic (Runs 11 and 24).

The hydrogenolysis of Ia with Raney nickel was not seriously affected when sodium hydroxide was

TABLE 3. THE CATALYTIC HYDROGENOLYSIS OF 2-METHYL-2-PHENYLAZIRIDINE (Ia) AND 1,2-DIMETHYL-2-PHENYLAZIRIDINE (Ib) OVER PLATINUM CATALYSTS

Run	Reactant	Catalyst (g)	Optical purity of I (%)	Products (%)		II				
				II	IV	$[\alpha]_D$	Optical purity (%)	Maintained optical activity (%)	Configuration	
									Retention (%)	Inversion (%)
30[a]	Ia	PtO_2 0.1	R 37.3	92(4[b])	4	−10.36	35	94	97	3
31[a]	Ia	Pt-black 0.1[c]	S 91.0	94(3[b])	3	+19.60	67	73	87	13
32	Ia	Pt-black[d] 0.5[c]	S 91.0	93(5[b])	2	+13.78	47	51	76	24
33	Ib	PtO_2 0.1	S 89.0	94(4[e])	2	+19.30	78	87	94	6
34	Ib	Pt-black 0.1[c]	S 89.0	88(4[e])	8	+18.12	72	80	90	10

I: 0.01 mol, Solvent: ethanol, 20 m*l*, Under ordinary pressure and at room temperature.
a, Ref. 2, *b*, 2-cyclohexylpropylamine, *c*, weight as PtO_2, *d*, treated with concentrated nitric acid, see Experimental section, *e*, *N*-methyl-2-cyclohexylpropylamine.

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10) C. P. Rader and H. A. Smith, *ibid.*, **84**, 1443 (1962).

11) H. A. Smith and W. E. Campbell, *Proc. Intern. Congr. Catalysis, 3rd., Amsterdam, 1964*, North Holland Publ. Co., Amsterdam, 1965, p. 1373.

12) J. L. Garnett and W. A. Sollich-Baumgartner, "Advances in Catalysis," Vol. 16, p. 95, Academic Press, London and New York (1966).

[*2] The configurational relationships between the reactants and the products were established as has been described elsewhere.[13] (+)-Ia, (+)-Ib, and (+)Ic all have S configurations. However, (+)-IIa, (+)-IIb, and (+)-IIc all have R configurations.

13) Y. Sugi and S. Mitsui, This Bulletin, **43**, 564 (1970).

added to the reaction mixture (Runs 15, 25, and 26). A retention of the configuration occurred in the Raney nickel-catalyzed hydrogenolysis of Ib, although the maintained optical activity was only 10% (Run 28). However, the addition of sodium hydroxide to the reaction mixture prompted a retention of the configuration of IIb (Runs 28 and 29). Moreover, the following interesting results were also observed in the Raney nickel-catalyzed hydrogenolysis of Ib. *N*-Methyl-2-phenyl-2-propylamine (IIIb) was not obtained. 2-Phenylpropane (IV) was produced in the absence of sodium hydroxide, whereas IV was not formed in the presence of sodium hydroxide. These results are dissimilar to those in the case of Ia.[2]

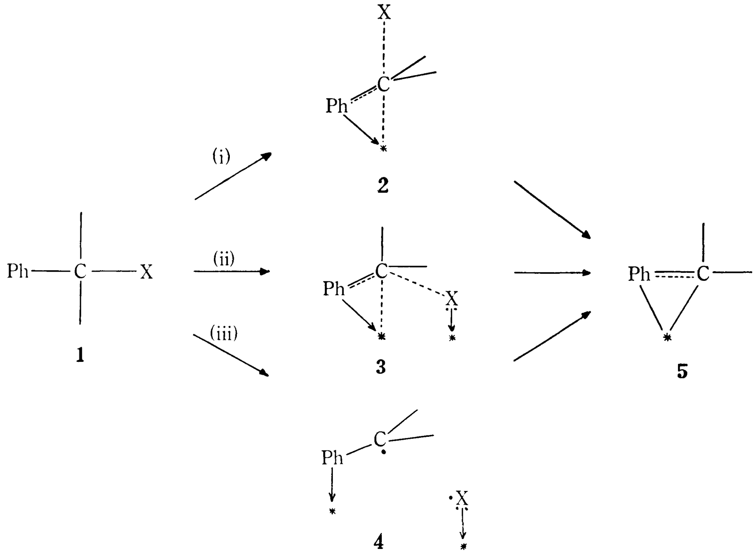
The influence of potassium iodide on the stereochemistry in the hydrogenolysis of Ia is also shown in Table 2. The stereoselectivity decreased over palladium hydroxide (Runs 8, 20, and 21), but no significant variation was observed over Raney nickel (Runs 16 and 27).

Variation in the Stereoselectivity with Platinum Catalysts. Table 3 summarizes the influences of the alkaline substances present in platinum catalysts. The stereoselectivity with platinum black (Run 31) was lower than that with platinum oxide (Run 30) in the hydrogenolysis of Ia.[2] It is well known that platinum oxide contains a trace of alkaline substances. To remove them, platinum black, which had been prepared by the reduction of platinum oxide, was treated with concentrated nitric acid, as will be described in the Experimental Section. The maintained optical activity with this catalyst (Run 32) was lower than those with platinum oxide and platinum black (Runs 30 and 31). The hydrogenolysis of Ib occurred with a significant retention of the configuration with both platinum oxide and platinum black; no serious difference in the stereoselectivity was observed (Runs 33 and 34).

Discussion

It is generally considered[1-6] that the catalytic hydrogenolysis of benzyl-type compounds proceeds to form the π-benzyl intermediate, **5**, *via* different transition states, **2** and **3**, and that the π-benzyl intermediate, **5**, suffers an electrophilic substitution with *s*-type adsorbed hydrogen.[14] In this case, the configurations of the products are responsible for the free-energy difference at the transition states, **2** and **3**; this difference depends on the structure of the compound, the catalyst, the solvent, the additive, and other factors. If the substituent X has a very strong affinity for the catalyst, the radical cleavage reaction (iii) as well as the S_N*i*-type reaction (ii) participates in this hydrogenolysis.[2]

We have previously reported that the hydrogenolysis of Ia in ethanol occurred with a predominant inversion of the configuration over palladium catalysts, but with a predominant retention over platinum, Raney nickel, and Raney cobalt catalysts, although low stereoselectivities were observed over the latter two catalysts.[2] These results may depend on the affinity for the nitrogen lone-pair and the catalyst hindrance.[2] Since palladium does not have so strong affinity for the nitrogen lone-pair, Ia is more probably hydrogenolysed *via* **6** over the palladium catalyst. However, the hydrogenolysis over the platinum catalyst favors the path *via* **7**,



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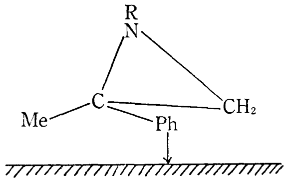
[14] T. Toya, *J. Research Inst. Catalysis, Hokkaido Univ.*, **6**, 308 (1958), **8**, 209 (1960), **10**, 236 (1962); *Kinzoku Butsuri*, **10**, 147 (1964).

because platinum is less sensitive to the catalyst hindrance than are nickel and palladium. Nickel and cobalt have stronger affinities for the nitrogen lone-pair than have palladium and platinum. Therefore, the S_Ni-type reaction and the radical cleavage reaction occur competitively *via* **7** over Raney nickel and Raney cobalt catalysts.



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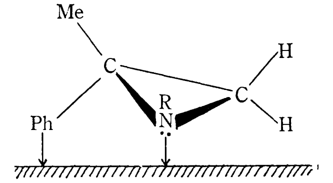

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-R : a) -H, b) $-CH_3$, c) $-COCH_3$, d) Na

Effect of the Solvent on the Stereochemistry. The hydrogenolysis of Ia over palladium hydroxide in benzene occurred preferentially with a retention of the configuration, but with an inversion in several aromatic hydrocarbons other than benzene. In these cases, the inverted product increased with a decrease in the adsorption strengths of these hydrocarbons under hydrogenation conditions.[10-12] Furthermore, the hydrogenolysis proceeded with a significant inversion of the configuration in *n*-hexane and ethanol, which are considered not to be adsorbed so strongly on the catalyst. Similar variations were observed in the hydrogenolysis of Ib. However, the hydrogenolysis of Ic occurred with a significant inversion of the configuration in both ethanol and benzene.

This characteristic behavior of Ia and Ib in benzene suggests the following considerations. The adsorptions of the reactant and hydrogen decrease in benzene since benzene acts as a weak catalytic poison. It is known that the mobility of an electron in platinum foil diminishes upon the adsorption of benzene.[15] From these two reasons, we are led to consider that the nucleophilicity of the catalyst decreases when benzene is used as the reaction solvent. Therefore, the hydrogenolysis of Ia and Ib in benzene is retarded because the adsorption of the reactant and the nucleophilicity of the catalyst decrease as has been mentioned above. In this case, the hydrogenolysis *via* **7** is less inhibited than that *via* **6**, for the nitrogen is adsorbed on the catalyst in the former state, but directed away in the latter. Consequently, when benzene is used as the reaction solvent, the free-energy level of the transition state leading to the π-benzyl intermediate *via* **7** is lower than that *via* **6**, and the configuration of the product will be retained predominantly. However, in solvents other than benzene the free-energy level of the transition state *via* **6** becomes lower than that *via* **7** with a decrease in the adsorption strength of the solvent. Since potassium iodide acts as a catalytic poison, the decrease in the stereoselectivity in the hydrogenolysis of Ia upon the addition of potassium iodide may be explained consistently by the above arguments.

The nitrogen of Ic will be adsorbed less strongly on the catalyst than those of Ia and Ib, for the electron density of Ic becomes lower upon the withdrawal of the acetyl group. It seems, therefore, that the activation free-energy leading to the π-benzyl intermediate *via* **7** increases upon the adsorption of benzene. However, since the acetyl group withdraws the electrons of the benzylic-carbon-nitrogen bond of Ic, the stereoelectronic requirement of the transition state is fulfilled *via* **6** ; the hydrogenolysis *via* this state is less inhibited by the adsorption of benzene. Consequently, the free-energy level of the transition state *via* **6** becomes lower than that *via* **7** in both ethanol and benzene ; this is in contrast with the cases of Ia and Ib.

On the other hand, no such effect of the solvent and potsssium idodide was observed in the Raney nickel-catalyzed hydrogenolysis of Ia ; this is in contrast with the case over palladium hydroxide. Since nickel has a very strong affinity for the nitrogen lone-pair, Ia will be hydrogenolysed without large inhibitions by the adsorption of benzene or potassium iodide.

Iijima and Mitsui[16] have reported similar solvent effects on the hydrogenolysis of 2-phenyl-2-butanol over a palladium catalyst. The retention of the configuration occurred preferentially in benzene, whereas the hydrogenolysis in ethanol, *n*-hexane, and toluene proceeded with a predominant inversion. Thus, these results are in accord with our present findings. Recently, Grimm and Bonner[17] have presented similar variations in the stereochemistry of the Raney nickel-catalyzed desulfuration of 2-phenyl-2-benzenesulfonylpropionamide. These authors have shown that this sulfone was hydrogenolysed with a predominant inversion of the configuration in ethanol, while the acetone treatment of the catalyst and the acetone solvent strongly prompted a retention of the configuration. However, they have not discussed the mechanistic details. These interesting observations can be interpreted consistently by the above arguments, for

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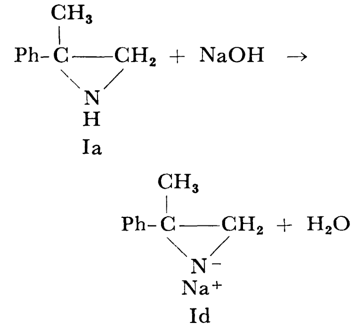
[15] V. M. Gryazow and V. I. Shimulis, *Kineti. Katal.*, **2**, 534 (1961).

[16] K. Iijima and S. Mitsui, *Nippon Kagaku Zasshi*, **85**, 686 (1964).

[17] R. A. Grimm and W. A. Bonner, *J. Org. Chem.*, **32**, 3470 (1967).

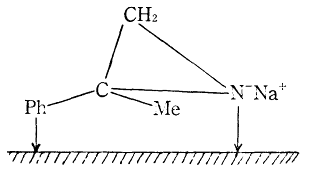
the nucleophilicity of the catalyst decreases upon treatment with acetone.

Effect of Sodium Hydroxide on the Stereochemistry. The hydrogenolysis of Ia in ethanol over palladium hydroxide occurred with a predominant inversion of the configuration in the absence of sodium hydroxide. However, the addition of sodium hydroxide promoted a retention of the configuration, and finally the hydrogenolysis proceeded with a stereospecific retention. On the other hand, no such variations in the stereochemistry were observed in the hydrogenolysis of Ib and Ic. These observations can be explained as follows. Ia and Id will establish an equilibirum as in Equation (1) in the presence of sodium hydroxide. It is difficult for Id to undergo hydrogenolysis *via* **6**, because the nitrogen of Id acts as an electron-donor. However, the hydrogenolysis *via* **7** or **8** is less inhibited than that *via* **6**, since the nitrogen of **7** or **8** is absorbed on the catalyst. Therefore, Id participates in the hydrogenolysis of Ia in the presence of sodium hydroxide; consequently, the retained product will increase when sodium hydroxide is added to the reaction mixture. No such influences are observed in the hydrogenolysis of Ib and Ic, thus eliminating an equilibrium like that of Equation (1) and supporting the participation of Id in the hydrogenolysis of Ia in the presence of sodium hydroxide. The stereoselectivity in the hydrogenolysis of Ic over palladium hydroxide increased when sodium hydroxide was added to the reaction mixture; this variation is in accord with the hydrogenolysis of α-methylstyrene oxide with Raney nickel and palladium catalysts.[18] Adsorbed sodium hydroxide will retard the adsorption of the nitrogen lone-pair of Ic. Moreover, the stereoelectronic requirement of the transition state leading to the π-benzyl intermediate is fulfilled *via* the state **6**, since the acetyl group withdraws the electrons of the carbon-nitrogen bond. Therefore, the difference in the free-energies of the transition states *via* **6** and **7** becomes larger upon the adsorption of sodium hydroxide. The variation in the stereoselectivity with platinum catalysts can be explained similarly to that in the case with palladium hydroxide.



(1)

The hydrogenolysis of Ib over Raney nickel occurred with a predominant retention of the configuration, and the stereoselectivity increased when sodium hydroxide was added to the reaction mixture. This variation suggests that the radical-cleavage reaction decreases in the presence of sodium hydroxide because adsorbed sodium hdyroxide retards the adsorption of the nitrogen lone-pair of Ib. On the other hand, the hydrogenolysis of Ia with Raney nickel was not significantly affected by the addition of sodium hydroxide; this may be the result of alkaline substances present in the catalyst. We have previously reported the formation of 2-phenyl-2-propylamine (IIIa), in addition to IIa, in the Raney nickel-catalyzed hydrogenolysis of Ia, and have postulated that IIIa forms *via* the state **7**.[2] However, *N*-methyl-2-phenyl-2-propylamine (IIIb) was not formed in the case of Ib. This may be attributed to the inductomeric effect of the *N*-methyl group. Further, a considerable amount of 2-phenylpropane (IV) was produced in the Raney nickel-catalyzed hydrogenolysis of Ib, in contrast with the case of Ia.[2] It seems that the stability of $\cdot\underset{\cdot\cdot}{\dot{N}}CH_3$ and/or $\cdot\underset{\cdot\cdot}{N}HCH_3$, which are formed according to the radical-cleavage reaction of Ib, is larger than that of $\cdot\underset{\cdot\cdot}{\dot{N}}H$ and/or $\cdot\underset{\cdot\cdot}{N}H_2$, which are formed from Ia. However, IV was not obtained in the presence of sodium hydroxide. This is consistent with the decrease in the radical-cleavage reaction.



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Experimental

Materials. S(+)- and R(−)-2-Methyl-2-phenylaziridines (Ia), S(+)- and R(−)-1,2-dimethyl-2-phenylaziridines (Ib), and R(−)-1-acetyl-2-methyl-2-phenylaziridine (Ic) were prepared by methods described previously.[2,14]

Catalysts. Palladium hydroxide ($Pd(OH)_2$) was prepared according to the literature.[19] Raney nickel (Ra–Ni) was prepared by the method used for W-4,[20] stored in ethanol, and used within a week. Except when ethanol was used as the reaction solvent, Raney nickel was dried in a hydrogen stream at 15—20 mmHg below 60°C just before use. Platinum oxide (PtO_2) was purchased from the Wako Pure Chem Co., Ltd., Osaka. Platinum black used in Runs 31 and 34 was obtained

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[18] S. Mitsui and S. Imaizumi, *Nippon Kagaku Zasshi*, **86**, 219 (1965).

[19] Y. Takagi, T. Naito and S. Nishimura, This Bulletin, **38**, 2119 (1965).

[20] H. Adkins and A. A. Pavlic, *J. Amer. Chem. Soc.*, **69**, 3039 (1947).

by the reduction of platinum oxide with hydrogen and was washed with water. However, platinum black used in Run 32 was prepared as follows. Platinum black which had been prepared from platinum oxide was boiled with concentrated nitric acid for 2 hr and then washed well with water. The resulting catalyst was reduced with hydrogen and washed with water. To remove any nitric acid present in the catalyst, this reduction-washing procedure was repeated three times.

Solvents. The aromatic solvent was purified by treatment with concentrated sulfuric acid and by subsequent distillation over sodium. *n*-Hexane was purified by treatment with Raney nickel under a hydrogen atmosphere and by subsequent distillation over sodium. Ethanol was obtained commercially.

Additives. Sodium hydroxide and potassium iodide were obtained commercially.

Catalytic Hydrogenolysis of Ia. The following general procedure was used.[2] After a definite amount of a catalyst and an additive in an solvent (10 *ml*) had been agitated under a hydrogen atmosphere for 1 hr, 0.01 mol (1. 33 g) of Ia in the solvent (10 *ml*) was added; the resulting suspension was agitated with hydrogen under ordinary pressure and at room temperature. After the theoretical amount of hydrogen had been absorbed, the catalyst was filtered off, and the reaction mixture was analyzed by gas chromatography (PEG 4000 dispersed on fire-brick at 150—180°C using helium as the carrier gas). It was then worked-up as has previously been described, ethanol, benzene, toluene, or *n*-hexane being used as the reaction solvent. However, when *o*-xylene, *m*-xlyene, *p*-xylene, or *t*-butylbenzene was used as the reaction solvent, the filtrate was treated with dilute hydrochloric acid, and the product IIa was obtained from the aqueous layer by treatment with aqueous ammonia. IIa was separated in the usual manner.

Catalytic Hydrogenolysis of Ib. The hydrogenolysis of Ib was carried out by a procedure similar to that used for Ia. However, Ib and IIb were unseparable under our gas-chromatographic conditions. After the evaporation of the solvent, the oily product was treatep with dilute hydrochloric acid and IIb was obtained from the apueous layer by treatment with aqueous ammonia. For the rotation of optically-pure IIb, we adopted $[\alpha]_D$ 25.3° (ethanol), a value calculated from the purity of IIa, as has been described elsewhere.[13]

Catalytic Hydrogenolysis of Ic. The hydrogenolysis of Ic was carried out by a procedure similar to that used for Ia. The reaction mixture was analyzed by gas chromatography (PEG 4000, Golay column (0.5 mm × 15 m), 180°C, using nitrogen as the carrier gas). In this case, Ic was decomposed during the gas-chromatographic analysis. Therefore, we considered the reaction to be complete when the decomposed product became undetectable. IIc was separated in the usual manner. For the rotation of optically-pure IIc, we adopted $[\alpha]_D$ 47.2° (ethanol), a value calculated from the purity of IIa.[13]

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