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THE STEREOSELECTIVITY OF THE CATALYSTS ON THE HYDROGENOLYSIS OF OPTICALLY ACTIVE 2-METHYL-2-PHENYLAZIRIDINE

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Mitsui and his co-workers reported that the stereoselectivity on the hydrogenolysis of benzyl-type compounds is effected by many factors, such as structures of compounds (1), natures of catalysts (2), solvents (3), additives (4,5) and others. There are, however, only a few works on that of benzylamine derivatives (6). We now wish to report the stereoselectivity of several Group VIII transition metal catalysts on the hydrogenolysis of optically active 2-methyl-2-phenylaziridine (I) under ordinary pressure and temperature.

The results are summarized in Table I. 2-Phenylpropylamine (II) was obtained mainly in every case. The configuration of II was predominantly inverted over palladium catalyst. However, the hydrogenolysis of I over platinum catalyst occured with significant retention of configuration in contrast with that of styrene oxide derivatives (4). Further, in the case of Raney nickel and Raney cobalt, a small amount of 2-phenyl-2-propylamine (III) was obtained in addition to

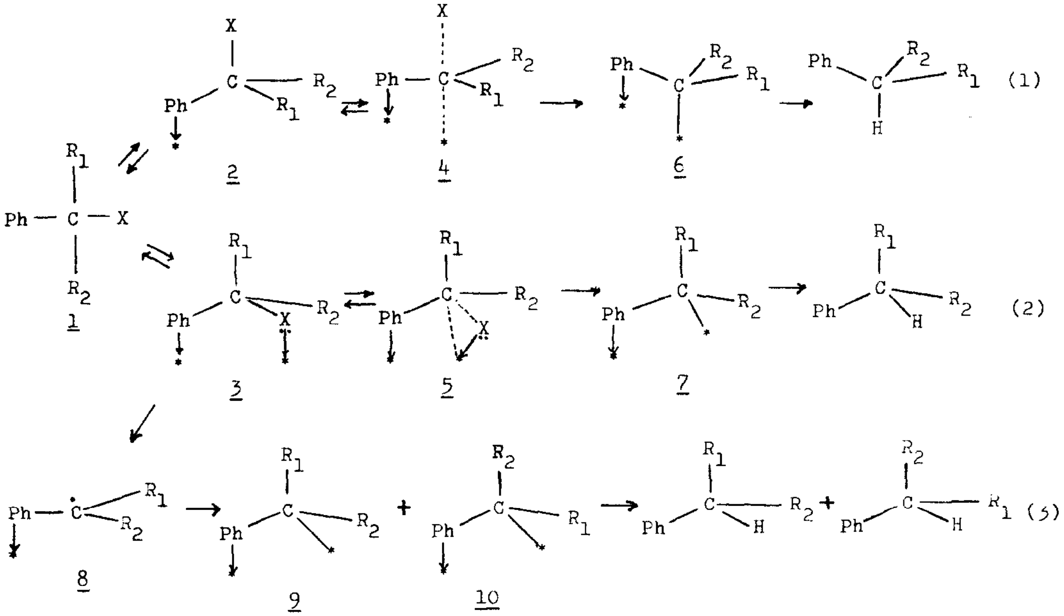
Table I. The Catalytic Hydrogenolysis of 2-Methyl-2-phenylaziridine (I).
I, 0.01 mol.; Solvent, Ethanol: 20 ml.

Exp. No.	Catalyst (g.)		Product			II	
			II	III	H.C.[*1]	Maintained optical activity	Configuration
1	$Pd(OH)_2$	0.05	100	-	trace	72	Inversion
2	PtO_2	0.10	92	4[*2]	4	95	Retention
3	Pt-Black	0.10	94	3[*2]	3	73	Retention
4	Ra-Ni	1(wet)	93	7	trace	23	Retention
5	Ra-Co	4(alloy)	92	3	5	14	Retention

*1, 2-phenylpropene or 2-phenylpropane; *2, 2-cyclohexylpropylamine.

II whose configuration was retained with only low maintained optical activity.

It has previously been proposed that the catalytic hydrogenolysis of benzyl-type compounds proceeds *via* paths 1 and 2 unless the substituent X has very strong affinity for the catalyst (1-7). The configuration of the product is determined by the free energy difference between the transition states 4 and 5.



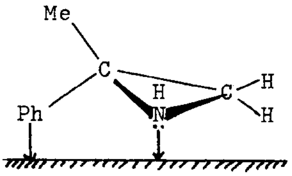
When X is an electron-withdrawing group and has relatively weak affinity for the catalyst, the stereoelectronic factor is so operative that path 1 becomes more favorable than path 2. Consequently, the hydrogenolysis would proceed with predominant inversion of configuration.

When X is not so bulky and has relatively strong affinity for the catalyst, strong chemisorption of X would make it so prone to the hydrogenolysis as to overcome the unfavorable stereoelectronic situation. Therefore, the free energy of the transition state 5 becomes lower than that of 4, and the configuration of the product would be retained predominantly.

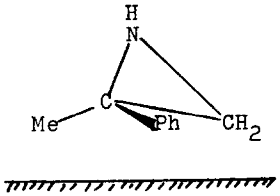
Further, when X has very strong affinity for the catalyst, path 3 as well as path 2 would participate in this reaction. The benzylic carbon - X bond cleaves into the radical 8 on the catalyst because of strong chemisorption of X and the phenyl group, and the racemic product would be obtained.

The mechanism on the hydrogenolysis of I is discussed on the basis of above-mentioned considerations.

In spite of the low reactivity of benzylamine derivatives, not only 2-phenylaziridines as reported in this paper, but 2-alkylaziridines undergo the hydrogenolysis even under ordinary pressure and temperature (8). This high reactivity may be attributable to the high strain of aziridine ring.



A



B

Because of the tetrahedral character of the nitrogen of aziridine, I would be favorably adsorbed edgewise on the catalyst as A, which corresponds to 3. Since palladium has not so strong affinity for the nitrogen, the benzyl carbon of A would not bear sufficiently large positive charge and be so approachable to the catalyst as that of B, which corresponds to 2. Moreover, the stereoelectronic requirement of the transition state is filfilled in the latter state. Therefore, the hydrogenolysis *via* B would be more favorable than that *via* A, and the configuration of II would be inverted predominantly over palladium catalyst.

Several workers reported the anchor effect of the nitrogen lone-pair for platinum catalyst (9). Platinum is less sensible for catalyst hindrance than nickel and palladium (10). Therefore, path 2 would be more favorable than path 1, and the configuration of II would be retained predominantly over platinum catalyst. The maintained optical activity with platinum oxide was higher than that with platinum black, which was prepared by hydrogen reduction of platinum oxide and washing with water. This would depend on the effect of alkali containing in platinum oxide (11). The hydrogenolysis of styrene oxide derivatives occured, however, with predominant inversion of configuration over platinum catalyst (4). This difference would be attributed to the differences of the electronegativity and the affinity for platinum between nitrogen and oxygen.

Nickel and cobalt have stronger affinity for the nitrogen lone-pair than platinum, palladium and others. Therefore, the hydrogenolysis of I would occur *via A*. Both benzyl and homobenzyl carbons would closely approach to the catalyst and bear positive charges because of strong chemisorption of the phenyl group and the nitrogen. Hydrogen would attack nucleophilically not only the benzyl but the homobenzyl carbons, and, consequently, II and a small amount of III would be obtained. However, the maintained optical activity was only 10 - 20 per cent. This would depend on the participation of path 3 as well as path 2 because of strong chemisorption of the phenyl group and the nitrogen.

In conclusion, the variations of configuration and maintained optical activity of II on the hydrogenolysis of I would be attributable to the free energy difference of the transition states to form the carbon metal bond, which would depend on the affinity of catalysts for the nitrogen, catalyst hindrance and others.

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