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The Stereoselectivity of Catalysts in Hydrogenation. I.
The Catalytic Hydrogenation of 2-Cyclopentylidene-
cyclopentanol and 2-Benzylidene-1-tetralol

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2-Cyclopentylidenecyclopentanol (I) was hydrogenated over Raney Ni to produce a mixture of 95% of *trans*- and 5% of *cis*-2-cyclopentylcyclopentanol (III). However, over a Pd catalyst I gave a mixture of 2-cyclopentylcyclopentanone (IV), cyclopentylcyclopentane (V) and *trans*- and *cis*-III. In the hydrogenation of I over PtO₂, *trans*-III was a predominant product (93%) in ethanol, whereas in acetic acid a mixture of 2 parts of *trans*- and 1 part of *cis*-III was obtained, and in acetic acid with one drop of hydrochloric acid, the ratio of *trans* and *cis* was one to two. A large amount of V was also obtained in cases of both acetic acid. The hydrogenation of 2-benzylidene-1-tetralol (II) resulted in 2-benzyl-1-tetralols (VI), the yields of *trans*- and *cis*-VI being as follows: over Raney Ni, 78% and 19%; over Pd, 33% and 63%; and over PtO₂ in ethanol, 58% and 34%, respectively. From these results, it was found that, in the cases of Raney Ni and PtO₂ in ethanol, the directive effect of the hydroxyl group is very efficient, but that it is small over Pd, while in acetic acid, especially with hydrochloric acid, such an effect decreases over PtO₂.

Recent communications^{1,2)} reporting that the catalytic hydrogenation of 2-cyclopentylidenecyclopentanol and its methyl ether over Raney nickel gave *trans*-2-cyclopentylcyclopentanol and its methyl ether respectively, have prompted us to report our observations of stereoselectivity of the catalysts in the hydrogenation of some allyl-type alcohols.

We have investigated to see whether such a directive effect of the hydroxyl group may be found in the hydrogenation of allyl-type alcohols as has been observed in the hydrogenolysis of some optically-active benzyl-type alcohols.³⁻⁶⁾

2-Cyclopentylidenecyclopentanol (I) and 2-benzylidene-1-tetralol (II) have been hydrogenated over Raney nickel, palladium-charcoal and platinum oxide at room temperature and atmospheric pressure (Tables I and II). The Raney nickel hydrogenation of I had already been done by Howard,¹⁾ who obtained mainly a single entity, *trans*-2-cyclopentylcyclopentanol (III). Similar results were obtained in the present work. III was formed in a ratio of 95% *trans* and 5% *cis*. The palladium-charcoal hydrogenation of I gave a mixture containing *cis* and *trans* isomers of III, along with 2-cyclopentylcyclopentanone (IV) and cyclopentylcyclopentane (V). The products were analyzed by vapor phase chromatography (Hitachi model F-6, P. E. G. 45 m. Golay column).

2-Benzylidene-1-tetralol (II) (m. p. 72°C) was hydrogenated to give 78% *trans*-2-benzyl-1-tetralol (VI) (m. p. 119°C) over Raney nickel, but a 63% *cis* isomer (m. p. 72°C) over palladium-charcoal. The products were separated by fractional recrystallization from petroleum benzine and confirmed by elementary analysis. An authentic sample of the *trans* isomer of VI was synthesized by the hydroboration⁷⁾ of 3-benzyl-1,2-dihydronaphthalene, which had been prepared by the dehydration of VI with *p*-toluenesulfonic acid in benzene, followed by oxidation with alkaline hydrogen peroxide.

It may be considered from the results that, if it is accepted that hydrogen adds *cis* from the catalyst surface, the unsaturated alcohols are preferentially adsorbed with the hydroxyl group directed toward the surface of the Raney nickel catalyst by the interaction of the lone pair of oxygen as well as of the π -electrons of the double bond, with the catalyst, and that the addition of hydrogen to the compounds in these adsorbed states will give the *trans*

alcohols¹⁾ (Fig. 1). On the other hand, in the case of the palladium catalyst, the adsorbed states where the hydroxyl group is directed away from the catalyst surface are assumed to increase in the course of the reaction (Fig. 1).

The formation of IV and V on the palladium catalyst may also be explained from the adsorbed state shown in Fig. 1 (see Figs. 2 and 3). 2-Cyclopentyl-1-cyclopentene-1-ol, the enol form of IV, may be obtained by the same kind of isomerization as was observed in the isomerization reported by Henbest et al.⁸⁾ (Fig. 2). Since it was reported that the hydrogenolysis of the optically-active benzyl-type alcohols over the palladium catalyst proceeds with an inversion of the configuration,³⁻⁶⁾ the allylic alcohol such as I may also be hydrogenolized with inversion to give cyclopentylidenecyclopentane, which is then hydrogenated to V (Fig. 3). It may be argued from these considerations that the favored adsorbed state on the palladium catalyst is the one in which the hydroxyl group is directed away from the catalyst surface, especially on palladium-charcoal-A.⁹⁾

On the hydrogenation of II over palladium-charcoal, the *cis* isomer of VI was obtained preferably.

Since it has been reported that the hydrogenolysis of the C-O bonds of benzyl-type alcohols and alkyl ethers takes different courses of reaction according to the kind of catalyst used,³⁻⁶⁾ it may be suggested that the difference in the affinity of nickel and palladium for the oxygen atom controls not only the stereochemistry of the hydrogenolysis of benzyl-type alcohols, but also that of the hydrogenation of the double bond of allyl-type alcohols. Therefore, the composition of the products is affected by the difference in this affinity with the kind of catalyst. The platinum oxide hydrogenation of I in ethanol gave the *trans* isomer as the predominant product (*trans* : *cis* = 23 : 1). It may be presumed that this is because of the directive effect of the hydroxyl group, as was observed in the Raney nickel hydrogenation. In acetic acid, I was hydrogenated to give a mixture containing 22% *trans*- and 10% *cis*-III (*trans* : *cis* = 2 : 1), 3% IV and 50% V. The hydrogenation in acetic acid containing one micro drop of concentrated hydrochloric acid gave more than 90% hydrocarbon (V), 3% *trans*- and 6% *cis*-III (*trans* : *cis* = 1 : 2). These results show that the presence of acid increases the percentage of the *cis* product.

On the hydrogenolysis of optically-active 2-phenyl-2-butanol in ethanol over platinum oxide, which usually contains a trace of alkaline substances,

* A part of this study was presented at the 18th Annual Meeting of the Chemical Society of Japan, Suita, Osaka, April, 1965.

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a slight excess of a configurationally inverted product (55%) was obtained, but upon the addition of two micro drops of concentrated hydrochloric acid to the solvent, the reaction proceeded predominantly with an inversion of the configuration (80%).⁵⁾ Consequently, it may be assumed that, in an acidic solvent, the hydrogenolysis of a benzyl- or allyl-type alcohol such as I takes place mainly, with an inversion of the original configuration over platinum oxide. These results are in line with the present observations that, on platinum oxide which contains a trace of basic substances, the directive effect of the hydroxyl group is observed in ethanol to be as on Raney nickel,¹⁰⁾ while in acetic acid this effect decreases,¹¹⁾ that the attack of hydrogen on the double bond or the carbon atom to which the hydroxyl group is attached, occurs from the less hindered side, and that it seems that this trend is promoted by the presence of hydrochloric acid.

As III was not acetylated by letting it stand with acetic acid, the III-acetate obtained (in Experimental Runs 5 and 6 in Table I) seems to be the hydrogenated product of I-acetate formed by the acetylation of I during the course of the reaction.

TABLE I. CATALYTIC HYDROGENATION OF 2-CYCLOPENTYLIDENECYCLOPENTANOL^{a)}

Catalyst	Products, %			
	Compound III Trans	Cis	IV	V
1 Raney nickel	95	5	—	—
2 5% Palladium Charcoal-A ^{b)} (contains a trace of acid)	14	10	11	65
3 5% Palladium charcoal-B ^{b)} (contains a trace of base)	71	23	5	1
4 Platinum oxide	92	4	3	1
5 Platinum oxide ^{c)}	22	10	3	50
6 Platinum oxide ^{d,e)}	3	6	—	90

a) Runs 1—4: in ethanol, Runs 5 and 6: in acetic acid. b) Reference 9. c) In addition to these products, 9% *cis*-III-acetate and 6% *trans*-III-acetate were also obtained. d) With one micro drop of concentrated hydrochloric acid. e) In addition to these products, III-acetate was also obtained.

TABLE II. CATALYTIC HYDROGENATION OF 2-BENZYLIDENE-1-TETRALOL IN ETHANOL

Catalyst	Products (%)		
	Compound VI Trans	Cis	Unidentified component
7 Raney nickel	78	19	3
8 5% Palladium charcoal-B (contains a trace of base)	33	63	4
9 Platinum oxide	58	34	8

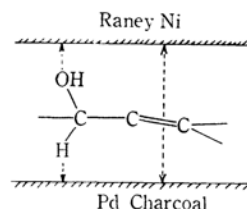


Fig. 1

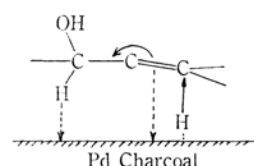


Fig. 2

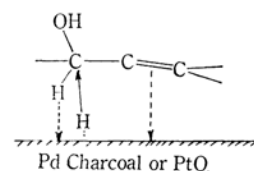


Fig. 3

Experimental

2 - Cyclopentylidenecyclopentanone.—2 - Cyclopentylidenecyclopentanone was prepared by the method of Hückel et al.,¹²⁾ by the self-condensation of cyclopentanone. From 84 g. of cyclopentanone and 4 g. of sodium hydroxide in 250 ml. of 30% aqueous ethanol, there was obtained 30.4 g. (40%) of the product, b. p. 96—101°C/5.0 mmHg.

2-Cyclopentylidenecyclopentanol (I).—I was prepared by the method of Le Guillanton¹³⁾ by the reduction of 2-cyclopentylidenecyclopentanone with lithium aluminum hydride in ether at 0—10°C. The distilled substance (b. p. 91—101°C/1.0 mmHg) was partly solidified, and the oily part, which was expected to be the saturated alcohol, was removed by absorption on a porous plate. The solid was recrystallized from petroleum ether to give pure I, m. p. 57—59°C; yield 12 g. (39%).

The Catalytic Hydrogenation of I.—I (1.5 g.), a catalyst and 50 ml. of solvent were stirred with hydrogen at an ordinary temperature and at atmospheric pressure. After the hydrogenation was over, the catalyst was filtered and the products were analyzed by V. P. C. The experimental data are summarized in Table III.

2-Benzylidene-1-tetralone.—Benzaldehyde (17 g.) was added drop by drop to a mixture of 20 g. of 1-tetralone in 300 ml. of 60% aqueous ethanol and 9.5 g. of sodium hydroxide. The reaction mixture was stirred at room temperature for 4 hr., and then 250 ml. of water was added. The yellow solid which separated was filtered, washed with water, and recrystallized from ethanol, m. p. 107°C; yield 27.5 g. (85%).

Found: C, 87.04; H, 5.78. Calcd. for C₁₇H₁₄O: C, 87.15; H, 6.02%.

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TABLE III. EXPERIMENTAL DATA OF CATALYTIC HYDROGENATION

1) 2-Cyclopentylidenecyclopentanol (1.5 g.)			
Catalyst	Weight of catalyst, g.	Hydrogen Uptake ml. (mol.)	Solvent
Raney nickel	0.4	220 (1.0)	Ethanol
5% Palladium charcoal-A	0.1	380 (1.7)	Ethanol
5% Palladium charcoal-B	0.1	225 (1.0)	Ethanol
Platinum oxide	0.1	273 (1.2)	Ethanol
Platinum oxide	0.1	295 (1.3)	Acetic acid
Platinum oxide	0.1	477 (2.1)	Acetic acid with one micro drop of HCl
2) Benzylidene-1-tetralol (1.4 g.)			
Catalyst	Weight of catalyst, g.	Hydrogen Uptake ml. (mol.)	Solvent
Raney nickel	0.5	146 (1.1)	Ethanol
5% Palladium charcoal-B	0.2	139 (1.0)	Ethanol
Platinum oxide	0.04	160 (1.2)	Ethanol

2-Benzylidene-1-tetralol (II).—Sodium borohydride (0.4 g.) was added gradually to a solution of 4.5 g. of 2-benzylidene-1-tetralone in 150 ml. of methanol at room temperature. The reaction mixture was then stirred at room temperature for 4 hr.; about 100 ml. of methanol was removed by distillation, and then an equal volume of water was added. The white solid which separated was filtered, washed with water, and recrystallized from petroleum benzene, m. p. 71–72°C; yield 3.9 g. (85%).

Found: C, 86.59; H, 6.99. Calcd. for $C_{17}H_{18}O$: C, 86.40; H, 6.83%.

3-Benzyl-1, 2-dihydronaphthalene.—2-Benzyl-1-tetralol (1.5 g.) was heated with 0.5 g. of *p*-toluenesulfonic acid in 200 ml. of benzene for 15 hr. Water was successively removed by azeotropic distillation; the benzene layer was washed with a sodium bicarbonate solution and water, and the benzene was distilled off under reduced pressure. 1.2 g. of 3-benzyl-1, 2-dihydronaphthalene was thus obtained. This compound was checked by a study of its infrared spectrum and V. P. C.

The Hydroboration¹⁴ of 3-Benzyl-1, 2-dihydronaphthalene.¹²—To a solution of 0.4 g. of sodium borohydride in 10 ml. of diglyme containing 1.1 g. of 3-benzyl-1, 2-dihydronaphthalene, there was added 0.76 ml. of boron trifluoride etherate at room temperature. The mixture was stirred for 3 hr. before the excess hydride was decomposed with water. The organoborane was oxidized at room temperature by the addition of 4 ml. of a 3 N solution of sodium hydroxide, followed by the drop-by-drop addition of 4 ml. of 30% hydrogen peroxide. The reaction mixture was extracted with ether, and the extract was washed five times with equal volumes of a saturated salt solution in order to remove the diglyme. The extract was then dried over anhydrous sodium sulfate. The residue left after the solvent had been removed, was recrystallized from

petroleum benzene. The yield of *trans*-2-benzyl-1-tetralol was 0.95 g. (80%), m. p. 119°C.

Found: C, 85.95; H, 7.82. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

The Catalytic Hydrogenation of II.—The following general procedure was used. 1.4 g. of II, a catalyst, and 50 ml. of ethanol were stirred with hydrogen at an ordinary temperature and at atmospheric pressure. The hydrogen uptake ceased after one mole of hydrogen had been absorbed; the catalyst was then filtered and, the ethanol distilled off.

Over Raney Nickel.—The residue was recrystallized from petroleum benzene to give the *trans* isomer of VI, m. p. 119°C. The yield was 1.09 g., 78%.

Found: C, 85.23; H, 7.71. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

When the mother liquor was concentrated, the *cis* isomer of VI was obtained, 0.27 g.; 19%. The melting point was 72°C.

Found: C, 85.37; H, 7.78. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

Over Palladium Charcoal-B.—The residue was recrystallized from petroleum benzene to give *trans*-VI, m. p. 119°C. The yield was 0.47 g., 33%. When the mother liquor was concentrated, *cis*-VI was obtained, m. p. 72°C. The yield was 0.88 g., 63%.

Over Platinum Oxide.—The residue was recrystallized from petroleum benzene to give *trans*-VI, m. p. 119°C. The yield was 0.81 g., 58%. When the mother liquor was concentrated, *cis*-VI was obtained, m. p. 72°C. The yield was 0.48 g., 34%. The products of the hydrogenation over palladium charcoal-B and platinum oxide were, by means of a mixed fusion and a comparison of the infrared spectra, identified with the samples obtained by the hydrogenation of II over Raney nickel.

The experimental details are summarized in Table III.