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Stereochemical Aspects of Oxirane Ring Opening. Heterogeneous Catalytic Deuterolysis of cis and trans-1,2-Epoxy-4-t-butylcyclohexanes

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^{2}H NMR analysis of deuterolyzed products from cis- and trans-1,2-epoxy-4-t-butylcyclohexane indicated that the cleavage of the oxirane C-O bond proceeds with inversion of configuration over noble metal catalysts except for Ru, while with retention over Co. Both retention and inversion competitively occurs over Ni and Ru.

The deuterolysis of cis- and trans-1,2-epoxy-4-t-butylcyclohexanes (c-**1** and t-**1**) has been studied in a liquid phase and ordinary pressure over 10% Pd on charcoal catalyst by Accrombessi et al.[1)] They reported that the deuterium addition to c-**1** and t-**1** proceeds in a trans fashion to preferentially give axial alcohols, cis-4- (c-**4**) and trans-3-t-butylcyclohexanol (t-**3**), respectively (Scheme 1). These results are consistent with those that the hydrogenolysis of oxiranes proceeds with inversion of configuration over Pd.[2)]

To examine how other metals act as catalysts towards stereoselectivity of oxirane ring opening, the catalytic deuterolysis of **1** was performed over Co, Ni and Group VIII noble metal black catalysts at ordinary temperature under 20 kg/cm^2 of deuterium pressure. The Co and Ni catalysts were prepared from the corresponding metal oxides by the reduction at 350 °C in hydrogen flow. Noble metal catalysts were prepared according to the procedure described by Tanaka et al.[3)] These catalysts were presaturated with 20 kg/cm^2 of deuterium prior to use. The deuterolysis of **1** on the metal black catalysts gave predominantly the axial alcohols (c-**4** from c-**1** and t-**3** from t-**1**). The distribution of the products is given in Table 1.

The products were separated by silica gel-column chromatography and the axial alcohols, c-**4** and t-**3**, were subjected to IR, ^{13}C NMR and ^{2}H NMR analysis. The stereochemistry of the products was established by comparison with those of authentic samples prepared by the LiAlD$_4$ reduction of c-**1** and t-**1**. The IR, ^{13}C NMR,

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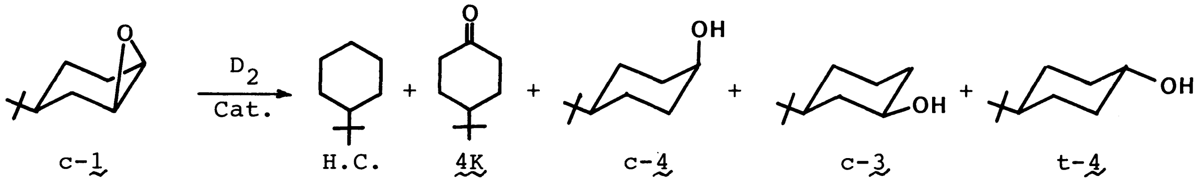
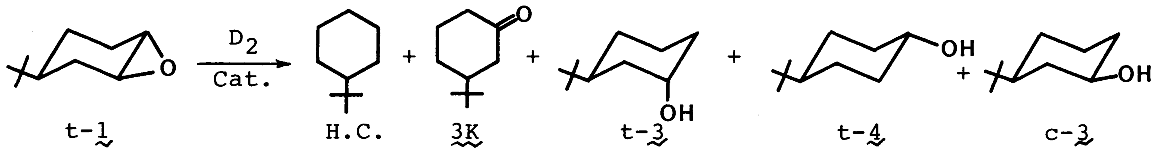
Table 1. Deuterolysis of cis- and trans-1,2-epoxy-4-t-butylcyclohexanes (c-1 and trans-1)[a)]





Cis-Isomer (c-1)

Catalyst[b)]		Reaction time	Conv.[c)]	Product/%				
	mg	h	%	H.C.	4K	c-4	c-3	t-4
Co	500[d)]	72	100	28	0	70	2	0
Ni	250[d)]	72	100	2	0	95	3	0
Ru	50	48	100	10	0	85	4	1
Rh	10	24	100	2	0	92	6	0
Pd	10	24	100	18	5	70	7	0
Os	10	24	100	9	0	86	5	0
Ir	30	48	73	1	0	95	4	0
Pt	100	72	50	10	1	85	4	0

Trans-Isomer (t-1)

Catalyst[b)]		Reaction time	Conv.[c)]	Product/%				
	mg	h	%	H.C.	3K	t-3	t-4	c-3
Co	1000[d)]	80	88	30	0	64	6	0
Ni	1000[d)]	24	90	7	0	83	7	3
Ru	20	48	55	30	0	64	5	1
Rh	20	24	100	3	1	91	4	1
Pd	20	24	100	10	3	83	4	0
Os	20	24	100	8	0	88	4	0
Ir	20	48	89	4	0	92	4	0
Pt	100	192	83	8	5	81	5	1

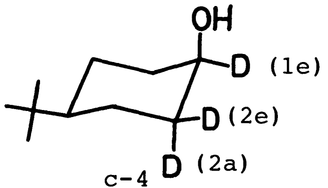
a) Substrate; 0.3 g, Solvent (cyclohexane); 3 cm^3, Ambient temperature under 20 kg/cm^2 of deuterium. b) Black metal catalyst. c) Conversion. d) Weight of the oxides of Co or Ni.

and ^{2}H NMR spectra of the deuterolyzed products over Pd, Ir, and Pt black were superimposable on those of the $\mathrm{LiAlD_4}$ reduction products, respectively. The ^{13}C NMR spectra showed the signals of C2 for c-4 and C6 for t-3 as a triplet at δ 32.0 (c-4) and 32.4 (t-3), respectively. These signals appeared at a higher field than the corresponding peaks of the undeuterated alcohols (δ 32.4 and 32.8, respectively). The IR spectrum of c-4 showed the bands at 2140 and 2155 cm^{-1}, and that of t-3 at 2120 and 2160 cm^{-1} corresponding to the axial C-D bond. The ^{2}H spectra exhibited two peaks at δ -5.8 and -5.9 as the deuterium in an axial position (see 2a and 6a in Table 2). The IR spectrum of the deuterolyzed product over the Co catalyst gave bands at 2155 and 2160 cm^{-1}, which correspond to the equatorial C2-D and C6-D of 4- and 3-t-butylcyclohexanols, respectively. The ^{2}H NMR spectra had peaks at δ -5.4 and -5.5 signifying the deuterium in an equatorial position (2e and 6e). The ^{2}H NMR spectra of the deuterolyzed products over Ni and Ru showed a 1e signal at δ -3.2 - -3.1 as well as 2a, 2e, 6a, and 6e signals. The ^{2}H NMR spectra of the products from c-1 over Os and from t-1 over Os and Rh showed the signal of 1e as well as those of 2a and 6a. These chemical shifts and the proportion (%) of the integrated peak areas are tabulated in Table 2.

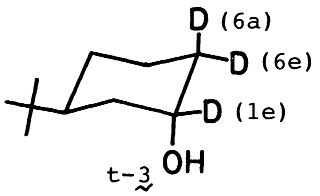
The results obtained from the spectroscopic survey of the products indicate that the addition of deuterium on the oxirane ring occurs stereospecifically with inversion of configuration over the noble metal catalysts except in the case of Ru.

Table 2. Distribution of deuterium in isolated axial alcohols (c-4 and t-3)

Isolated
axial
alcohol



c-4



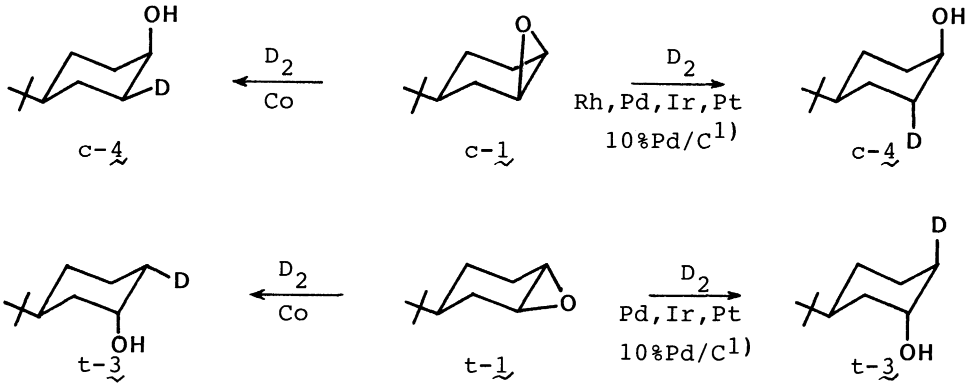
t-3

Position of deuteriu (δ)$^{a)}$

Catalyst	2a (-5.8)	2e (-5.4)	1e (-3.2)	6a (-5.9)	6e (-5.5)	1e (-3.1)
Co	0	100	0	0	100	0
Ni	38	54	0	47	39	14
Ru	54	6	40	45	30	25
Rh	100	0	0	96	0	4
Pd	100	0	0	100	0	0
Os	50	0	50	66	0	34
Ir	100	0	0	100	0	0
Pt	100	0	0	100	0	0
$\mathrm{LiAlD_4}$	100	0	0	100	0	0

a) δ: the ^{2}H shifts are presented in parts per million upfield from deuterochloroform.

The Co catalyst exhibited a sharp contrast with the noble metal catalysts and the reaction proceeds exclusively with retention of configuration. Both retention and inversion of configuration seems to occur competitively over the Ni and Ru catalysts. Such a difference in the stereochemistry of the hydrogenolysis is dependent on the affinity of the metal for the negative elements such as oxygen. Incorporation of an appreciable amount of deuterium at the carbinyl carbon of the products during the deuterolysis, together with the formation of a ketone suggests that the deuterolysis of the C-O bond is accompanied by the isomerization of oxirane to the ketone except over Co and Ir catalysts.[4)] It is of significant interest from the viewpoint of stereoselective synthesis that an oxirane ring is hydrogenolyzed in a different manner depending on the catalyst metal.



Scheme 1.

References

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2) S. Mitsui and Y. Nagahisa, Chem. Ind. (London), 1965, 1975 ; S. Mitsui and S. Imaizumi, Nippon Kagaku Zasshi, 86, 219 (1965); S. Mitsui, S. Imaizumi, and Y. Esashi, Bull. Chem. Soc. Jpn., 43, 2143 (1969); and the references cited therein.

3) K. Tanaka, Y. Takagi, O. Nomura, and I. Kobayashi, J. Catal., 35, 24 (1974).

4) *Incorporation of an appreciable amount of deuterium into the carbinyl carbons of* the axial alcohols, t-3 and c-4, over Ni, Ru, and Os suggested that the corresponding amounts of epoxide isomerized to ketone during the hydrogenation over these catalysts. Both axial and equatorial alcohols are usually produced in the hydrogenation of 3K and 4K over Ni, Ru, and Os [axial alcohol/equatorial alcohol; 52/48 (Ni), 71/29 (Ru), 52/48 (Os) for 3K and 68/32 (Ni), 84/16 (Ru), 71/29 (Os) for 4K]. However, only a very small amount or no equatorial alcohols (c-3 and t-4) were detected here. For example, if 34% (distribution of deuterium at the carbinyl carbon in t-3, see Table 2) of t-1 isomerized to a ketone over Os during the reaction, 34% x 48/52 c-3 should have appeared in the hydrogenation product of t-1. This indicates that the ketone formed over the catalysts may be successively deuterated without desorption from the catalyst surface during the reaction.

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