3′,5,5-trimethylspiro[1,3]dioxane-2,2′(1′*H*)-pentalen-4′-ol methoxyacetate ester, 74609-35-1; cyclohex-2-en-1-ol methoxyacetate ester, 74563-39-6; cyclooct-2-en-1-ol methoxyacetate ester, 74563-40-9; α-methylcyclohex-1-enemethanol methoxyacetate ester, 74563-41-0; 1-ethenylcyclopentanol methoxyacetate ester, 74563-42-1; 2,3,4,4a,5,6,7,8-octahydronaphthalen-2-ol methoxyacetate ester, 74563-43-2; non-1-en-3-ol methoxyacetate ester, 74563-44-3; 3,7-dimethylocta-2,6-dien-1-ol methoxyacetate ester, 74563-45-4; 3,7-dimethylocta-1,6-dien-3-ol methoxyacetate ester, 74563-46-5; 2-furanmethanol methoxyacetate ester, 74563-47-6; 3-phenylprop-2-en-1-ol methoxyacetate ester, 74563-48-7; 1-phenylprop-2-en-1-ol methoxyacetate ester, 74563-49-8.

Mechanism of the Liquid-Phase Catalytic Hydrogenolysis on Palladium/Carbon of Cyclohexene Epoxides

Georges C. Accrombessi, Patrick Geneste,* and Jean-Louis Olivé

Laboratoire de Chimie Organique Physique Appliquée, Ecole Nationale Supérieure de Chimie de Montpellier, 34075 Montpellier, Cédex, France

André A. Pavia

Laboratoire de Chimie Organique, CSU, 84000 Avignon, France

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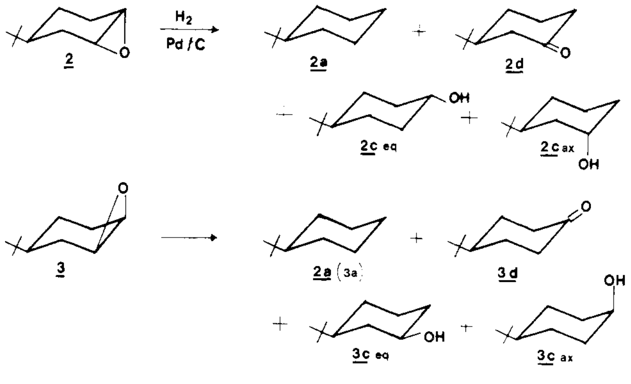
Heterogeneous catalytic hydrogenolysis of cyclohexene epoxides on 10% Pd/C was studied in different solvents. The principal products were found to be alcohols, formed by cleavage of one epoxide C–O bond. In addition, simultaneous cleavage of both C–O bonds gave hydrocarbons, and isomerization on the catalyst gave ketones as byproducts. The deuterolysis of *cis*- and *trans*-*tert*-butylcyclohexene epoxides and kinetic studies with cyclohexene epoxides carrying an axial methyl group in position 3 or 5 showed that hydrogenolysis gives preferentially axial alcohols and trans hydrogen addition, after a "roll over" on the catalyst. If one epoxide carbon carries a methyl group, conformational and steric factors come into play. C–O bond cleavage at the more substituted carbon, leading to equatorial alcohols, becomes competitive with preferential formation of axial alcohols, and steric hindrance to molecular reorientation on the catalyst causes cis as well as trans hydrogen addition.

Table I. Hydrogenolysis of 1,2-Epoxycyclohexane[a]

solvent	% 1a	% 1d	% 1c	% solvolysis
cyclohexane		18	82	
ether	20	12	68	
2-propanol	32	10	58	traces
ethanol[b]	15	5	65	15
methanol[b]	14	5	61	20

[a] P_{H_2} = 1 atm; T = 20 °C. [b] The use of these solvents leads to the trans 1,2-diaxial ether–alcohol.

Scheme I



Heterogeneous catalytic hydrogenations are often accompanied by some degree of hydrogenolysis, depending on factors like the metal or solvent.[1] For example, catalytic hydrogenation of carbonyl derivatives (to alcohols) often leads to, besides the alcohols, the formation of hydrocarbons via hydrogenolysis of the alcoholic C–O bond. Epoxides show the same behavior and are particularly well suited for adsorption studies of the C–O bond. In this case, opening of one C–O bond gives alcohols, simultaneous cleavage of both C–O bonds leads to hydrocarbons,[2-5] and intramolecular rearrangements on the catalyst give rise to the formation of ketones.[6-8] While homogeneous acid- or base-catalized epoxide ring opening is well understood,[9] no model has yet been found which explains all stereochemical results of heterogeneous catalytic studies in the liquid[5-10] and gas phase.[2,3,8] We therefore decided to study the hydrogenolysis of some cyclohexene epoxides, since the conformations of both the initial and final products (alcohols, hydrocarbons, and ketones) are well-defined in these systems. Palladium on charcoal was chosen as the catalyst, since it proved to be more active in the liquid phase and at ordinary pressure than platinum, nickel, or rhodium.

Results and Discussion

Hydrogenolysis of cyclohexene epoxide (1) on palladium in various solvents (Table I) gives predominantly cyclo-

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(1) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, 1965, p 81.
(2) G. Senechal and D. Cornet, *Bull. Soc. Chim. Fr.*, 773 (1971).
(3) G. Senechal, J. C. Duchet and D. Cornet, *Bull. Soc. Chim. Fr.*, 783 (1971).
(4) S. Mitsui and S. Imaizumi, *Tetrahedron*, **29**, 4093 (1973).
(5) S. Mitsui, Y. Nagahisa, and Y. Sugi, *Chem. Ind. (London)*, 38 (1975).
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(10) E. J. McQuillin and W. O. Ord, *J. Chem. Soc.*, 3169 (1959).

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Table II. Hydrogenolysis of *trans*- and *cis*-1,2-Epoxy-4-*tert*-butylcyclohexanes (2 and 3)[a]

For *trans*-2

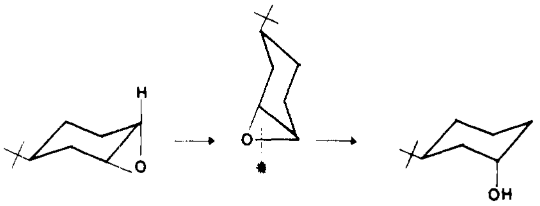
solvent	% 2a	% 2d	% $2c_{eq}$	% $2c_{ax}$	% solvolysis of 2e
cyclohexane	2	20	2.5	75.5	
ether	14	3	4	79	
2-propanol	20	0	5.5	74.5	
ethanol	14	1	5	70	10

For *cis*-3

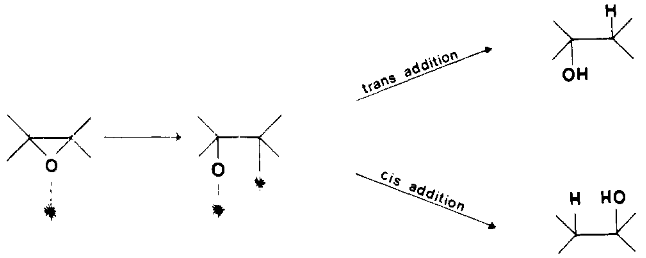
solvent	% 2a	% 3d	% $3c_{eq}$	% $3c_{ax}$
2-propanol	18	0	6	74
ethanol	12	1	10	71

[a] P_{H_2} = 1 atm; T = 20 °C.

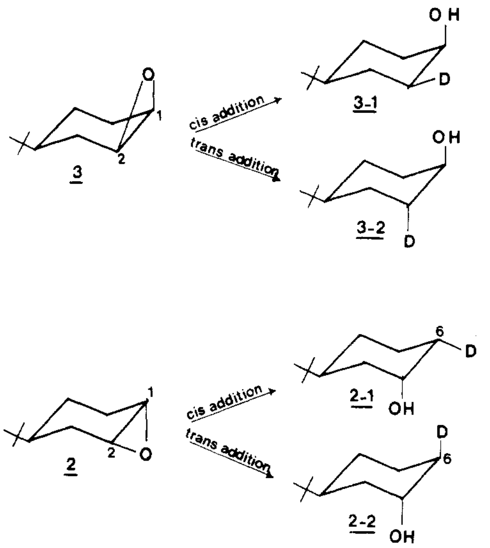
Scheme II



Scheme III



Scheme IV



hexanol (**1c**). On addition, varying amounts of cyclohexane (**1a**) and cyclohexanone (**1d**) are produced, depending on the choice of solvent.

The stereochemistry of the epoxide ring-opening reaction may be studied with the conformationally fixed *trans*- and *cis*-4-*tert*-butrylcyclohexene epoxides (**2** and **3**).

The distribution of the products shown in Scheme I is given in Table II. Hydrogenolysis of **2** and **3** preferentially forms the axial alcohol, which means that the epoxide ring must approach the catalyst from the less hindered side, the outside of the cyclohexane ring, as shown for **2** in Scheme II.

Epoxide ring opening leads to intermediates, to which hydrogen may add cis or trans, giving the same alcohol in both cases. The breakage of the C–O bond leads to 90% of axial alcohol. The formation of alcohols, hydrocarbons, and ketones during the heterogeneous reaction is due to different processes. The alcohol formation will be considered first and the formation of the secondary products then discussed.

It is known from the work of Mitsui[5] and Cornet[8] that the first step in the formation of alcohol is the fixation of the oxygen atom on the catalyst, since it is more strongly attracted than the carbon atom.[11] If the molecule is diadsorbed after C–O bond cleavage, hydrogen then adds cis (Scheme III). If there is a possibility for a "roll over" of the molecule[12,13] on the catalytic surface without desorption the addition of hydrogen can take place in a trans manner. For precise determination of the distribution between cis and trans addition the use of deuterium labeling is required. The deuterium atom will be found in the equatorial position in the cis addition and in the axial position after a trans addition. In the case of the *trans*- and *cis*-4-*tert*-butylcyclohexene oxides the corresponding labeled products would be **2-1**, **2-2** and **3-1**, **3-2** (see Scheme IV).

Table III. Hydrogenolysis of *trans*- and *cis*-1,2-Epoxy-1-methyl-4-*tert*-butylcyclohexanes (4 and 5)[a,b]

For *trans*-4

solvent	% 4a	% 4d	% 5d	% 4f	% 4g
2-propanol	72	traces	10	6	12
ether	54	4	15	15.5	11.5
cyclohexane	8.5	24	28	32	7.5

For *cis*-5

solvent	% 4a	% 4d	% 5d	% 5f	% 5g	% 5c
2-propanol	20	11	9	25	9	26
ether	8.5	9.5	8.5	34.5	10	29
cyclohexane	traces	20	14	16	12	38

[a] P_{H_2} = 1 atm; T = 20 °C. [b] Traces of 4b found in each case.

Deuterolysis of **3** gives essentially only **3-2**, the product of trans addition. The stereochemistry is established by comparison with the IR and ^{13}C NMR spectra of an authentic sample of **3-2**, prepared by $LiAlD_4$ reduction of **3**,[14] which proceeds by trans ring opening (>92% trans). The IR and ^{13}C NMR spectra of the deuterolysis and $LiAlD_4$ reduction products are superimposable. The ^{13}C NMR spectrum shows the C_2 triplet at 32.4 ppm, upfield from 32.6 ppm in the undeuterated alcohol.[15] The IR spectrum shows bands at 2140 and 2155 cm^{-1} typical of the axial C_2–D bond of 4-*tert*-butylcyclohexanol.[16] The equatorial

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(11) G. C. Bond, "Catalysis by Metals", Academic Press, London, 1962.

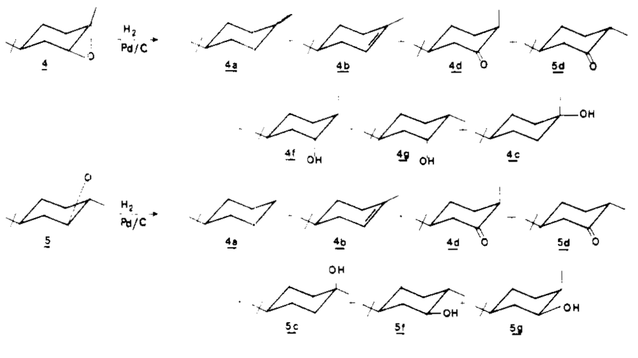
(12) R. L. Burwell, *Acc. Chem. Res.*, **2**, 289 (1969); W. R. Patterson, R. L. Burwell, and J. A. Roth, *J. Am. Chem. Soc.*, **93**, 839 (1971).

(13) M. A. McKervey, J. J. Rooney, and N. G. Samman, *J. Chem. Soc., Chem. Commun.*, 1185 (1972).

(14) G. Lamaty, C. Tapiero, and R. Wylde, *Bull. Soc. Chim. Fr.*, 4010 (1966).

(15) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 163.

Scheme V



Scheme VI

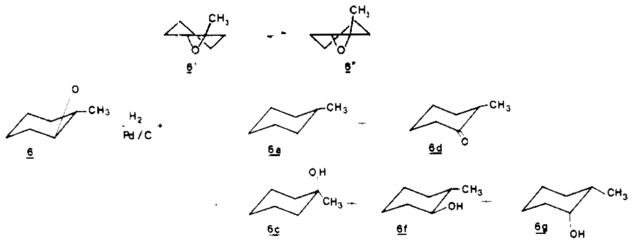


Table IV. Hydrogenolysis of 1,2-Epoxy-1-methylcyclohexane (6)[a, b]

solvent	t, h	% 6a	% 6c	% *trans*-6f	% *cis*-6g	% 6d
2-propanol	4	35	13	32.5	12.5	7
ether	15	20	13.5	41	14.5	11
cyclohexane	25	5	19	30.5	13	32.5

[a] P_{H_2} = 1 atm; T = 20 °C. [b] No epoxide 6 found in any case.

C_2–D bond would only give a single band at 2155 cm^{-1}. Deuterolysis of *trans*-4-*tert*-butylcyclohexene oxide (**2**) also gives only the trans addition product **2-2**, since this gives superimposable spectra with the $LiAlD_4$ reduction product as described.[17] The C_6–D triplet in the ^{13}C NMR spectrum appears at 32.3 ppm, upfield from 32.7 ppm in undeuterated 3-*tert*-butylcyclohexanol. The IR spectrum shows two bands as 2160 and 2120 cm^{-1}, corresponding to the axial C–D bond.

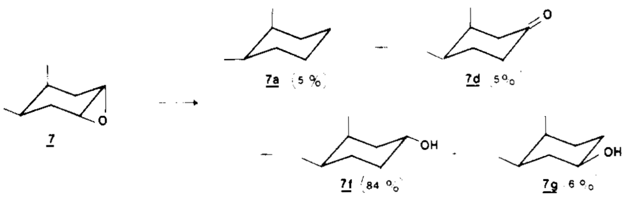
Thus both *cis*- and *trans*-4-*tert*-butylcyclohexene oxides give trans deuterium addition.

Trans addition probably means that nothing prevents the roll over of the molecule on the catalyst. In order to test this hypothesis, we studied substrates with a methyl group at one epoxide carbon, namely, the *trans*- and *cis*-1-methyl-4-*tert*-butylcyclohexene epoxides **4** and **5**.

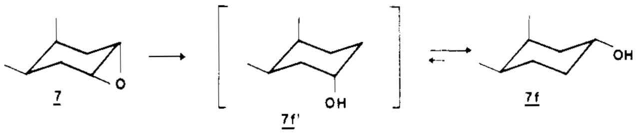
Scheme V and Table III show the product distribution of the hydrogenolysis of **4** and **5** in 2-propanol, ether, and cyclohexane. Both epoxides give a mixture of hydrocarbon **4a**, with the trans isomer predominating by about 70%, and variable amounts of cis and trans methyl ketones **4d** and **5d**, depending on the epoxide and the solvent. In addition, epoxide **4** gave the two secondary axial alcohols **4f** and **4g**, but no tertiary alcohol was found.

Epoxide **5**, on the other hand, gave a significant amount (25-40%) of tertiary axial alcohol **5c**, in addition to the two equatorial secondary alcohols **5f** and **5g**. The hydrogenolysis of 1-methylcyclohexene epoxide (**6**) under the conditions indicated in Table I gave the same product distribution (Scheme VI), with a large amount of tertiary alcohol **6c**, as in the case of hydrogenolysis of **5**, due to the conformational equilibrium between **6′** and **6″**; the conformation of **6′** is quite analogous to that of **5**, and so, as we checked it, the hydrogenolysis of these two epoxides occurs at the same rate (Table IV).

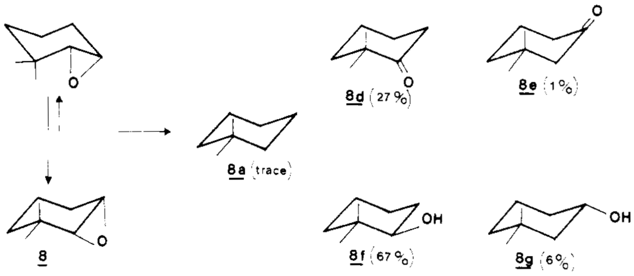
Scheme VII



Scheme VIII



Scheme IX



So, the opening of the epoxide ring in the 4-*tert*-butylcyclohexene oxide series is determined by two factors, namely, preferential formation of the axial aclohol and greater ease of cleavage of the C–O bond at the more substituted carbon. The two factors reinforce each other in the case of epoxide **4**, where both processes favor formation of the secondary axial alcohols **4f** and **4g** with **4f** coming from a preferential cis addition.

They work against each other in the case of epoxide **5**, where **5f** and **5g** result from the greater ease of cleavage of the more substituted bond, and product **5c** results from preferential formation of axial hydroxyl groups.

In the case of **5**, there is also competition between cis and trans addition. The predominant isomer **5f** is the result of cis addition, and isomer **5g** is obtained by trans addition. The fact that the cis opening mechanism competes with the trans mechanism is probably due to the steric effect of the methyl group acting during the roll over, consequently slowing down the trans addition.

If this hypothesis is correct, cyclohexene oxides with axial methyl groups in positions 3 or 5 should show the same behavior. We chose to study the 4,5- and 3,3-dimethylcyclohexene epoxides (**7** and **8**). Ring opening of **7** on palladium gave a large yield of a mixture of *cis*- and *trans*-3,4-dimethylcyclohexanols (**7b** and **7f**) as shown in Scheme VII. For the alcohols the more thermodynamically stable conformation is indicated.

In both alcohols the hydroxyl group is preferentially equatorial,[18] and in the corresponding ketone the methyl group at C_3 is axial.[19] Isomer **7f** is possibly formed in the

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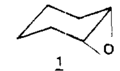
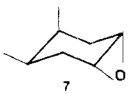
[16] G. Lamaty, C. Tapiero, and R. Wylde, *Bull. Soc. Chim. Fr.*, 2039 (1968).

[17] B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 3185 (1964).

[18] R. Granger, J. P. Chapat, F. Simon, J. P. Girard, and J. Crassous, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **270**, 869 (1970).

[19] R. Granger, J. P. Chapat, F. Simon, J. P. Girard, and P. Joyeux, *C. R. Hebd. Seances Acad. Sci, Ser. C*, **272**, 337 (1971).

Table V. Relative Rate Constants for Epoxides

compd	10^3k, min^{-1} g^{-1}	compd	10^3k, min^{-1} g^{-1}
 1	1300	 8	2
 7	14		

conformation with the hydroxyl group axial (Scheme VIII).

Hydrogenolysis of epoxide **8** gave (Scheme IX; for the alcohols the more thermodynamically stable conformation is indicated) mainly 2,2-dimethylcyclohexanol (**8f**) and the corresponding ketone **8d**. The hydrocarbon, as well as the alcohol and ketone in position 3, was only found in small amounts.

These results do not verify the preferential formation of the axial alcohol and do not indicate whether there is cis or trans addition due to the mixture of conformers or enantiomers in the case of **7**. We therefore undertook a comparative kinetic study of the hydrogenolysis of these epoxides. The influence of the axial methyl group should be particularly marked in the case of trans addition, which requires the roll over of the molecule on the catalyst. In this case the hydrogen being added to the epoxide carbon will end up on the same side of the molecule as the axial methyl group, which should affect the rate of hydrogenolysis. The results reported in Table V show the influence of the methyl groups situated on the cycle. The rate is indeed found to decrease by a factor of 100 with increasing proximity of the axial methyl group and the oxirane ring, which confirms the preference for trans addition. We could compare this effect with the effect, steric in origin, previously reported for the hydrogenation of the carbonyl group in cyclohexanone and methylcyclohexanones. For all the catalysts it may be seen that as the substituted methyl group is located further away from the carbonyl linkage (in the order of the carbon positions 2–4), the effect of methyl substitution which hinders the adsorption process decreases:[20] the order of magnitude varies, depending upon the nature of the catalyst, between only 20 and 4 when the CH_3 group is in the 2-position and to a lesser extent when it is in the 3- or 4-position.

The secondary products of the hydrogenolysis of the cyclohexene epoxides, hydrocarbons, and ketones are obtained by similar processes. Hydrocarbons result from the simultaneous cleavage of both C–O bonds on the catalyst,[2,3] giving the corresponding olefins, which then may either be desorbed or hydrogenated. Alcohols are not hydrogenolized under these conditions. Ketones result from intramolecular rearrangements of the epoxides on the catalyst.[8] The kinetic study of the hydrogenolysis shows that the ketones are not the precursors of the alcohols (Figures 1 and 2). Furthermore, under the present conditions, we observed that ketones are not hydrogenated.[21]

In the hydrogenolysis of the epoxides studied the reaction rates increase as one goes from the aprotic solvents (ether and cyclohexane) to the protic solvent 2-propanol. For the *trans*-**2** derivative the rate is enhanced by a factor of 6 from cyclohexane to 2-propanol. In the same way the proportions of ketones and hydrocarbons change significantly (Tables I–IV).

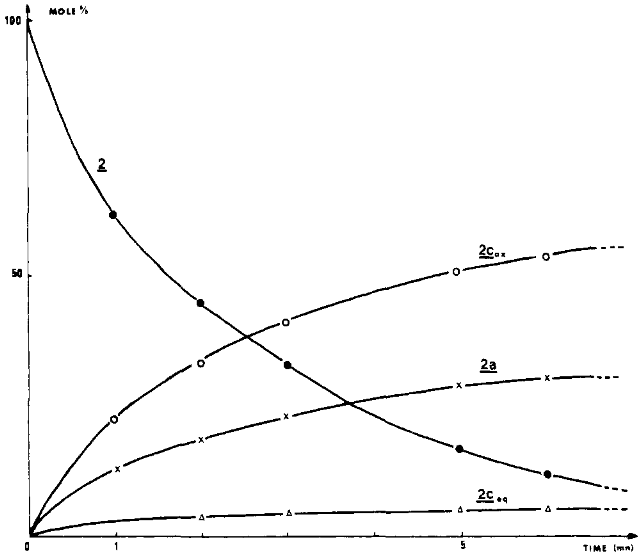


Figure 1. Hydrogenolysis of *trans*-1,2-epoxy-4-*tert*-butylcyclohexane (**2**) in 2-propanol: epoxide **2**, ●; axial alcohol **2c**, ○; hydrocarbon **2a**, x; equatorial alcohol **2c**, △.

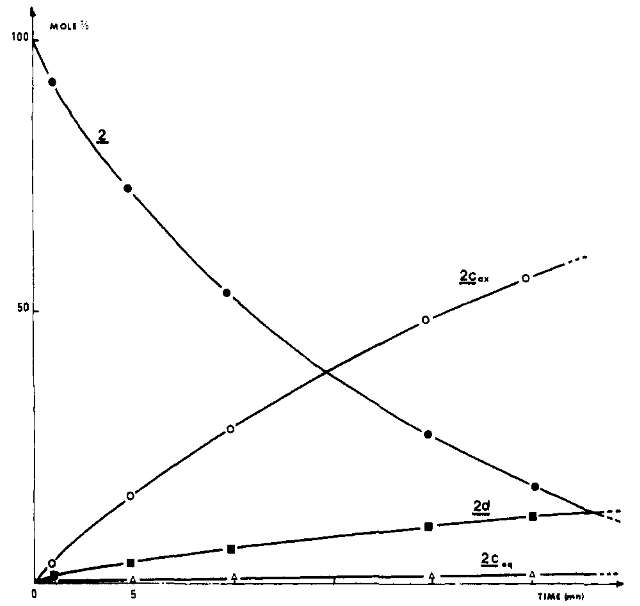


Figure 2. Hydrogenolysis of *trans*-1,2-epoxy-4-*tert*-butylcyclohexane (**2**) in cyclohexane: epoxide **2**, ●; axial alcohol **2c**, ○; equatorial alcohol **2c**, △; ketone **2d**, ■.

Formation of hydrocarbons is undoubtedly favored in 2-propanol because of the possibility of solvent interactions with reaction intermediates. In aprotic solvents such solvent–intermediate interactions are absent. Consequently, ketone formation by rearrangement is competitive, and the reaction rate decreases. The regioselectivity and selective formation of axial alcohols is high, regardless of the solvent.

Experimental Section

The majority of the epoxides and reaction products have already been described. The purity was verified in all cases by physical and spectroscopic measurements.

Product distributions were determined by gas chromatographic measurements, carried out on a Girdel 3000 gas chromatograph equipped with a 10% Carbowax 20M or 5% DEGS column. The retention times and percentages were obtained with a Hewlett-Packard 3380A integrator–calculator.

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[20] K. Tanaka, Y. Takazi, O. Nomura, and I. Kobayashi, *J. Catal.*, 35, 24 (1974).

[21] P. N. Rylander, "Catalytic Hydrogenation in Organic Synthesis", Academic Press, New York, 1979, p 82.

IR spectra were taken on a Perkin-Elmer spectrometer, NMR spectra on Varian A60 or HR-100 and Bruker HX 90 FT spectrometers, and mass spectra on a CEC 21-1100C spectrograph (ionization energy 70 eV).

The hydrogenolyses were carried out in a gas-flow reaction vessel thermostated at 20 °C which allowed experiments at 1 atm or below. The commercial catalyst Pd/C (10%, Merck) was placed in a reaction vessel flushed three times with nitrogen and then kept under reduced pressure for 1 h. Hydrogen was introduced and its pressure kept constant throughout the reaction. Solvent (25 mL) was added with a syringe, and the catalyst–solvent mixture was stirred for 1 h under a hydrogen atmosphere. The substrate disappearance was followed by gas chromatography.

Compounds **1**, **1a**,**c**,**d**, **2a**, **6**, and **6a**,**c**,**d**,**f**,**g** were commercial products. The epoxides were obtained by *m*-chloroperbenzoic acid oxidation of the corresponding olefins.[22]

***trans*- and *cis*-4-*tert*-Butylcyclohexene Epoxides (2 and 3).** The mixture of isomers was obtained by dehydration of 4-*tert*-butylcyclohexanol[23] to the olefin, followed by oxidation. The two isomers **2** and **3** were separated in several steps.[24,25]

Ring Opened Products. 4-*tert*-Butylcyclohexanone (**3d**) was purchased and purified by recrystallization from pentane at −20 °C. The synthesis of the remaining products has already been described: **2c**$_{\mathrm{eq}}$ and **3c**$_{\mathrm{ax}}$,[26-28] **2d**,[29] **2c**$_{\mathrm{ax}}$ and **3c**$_{\mathrm{eq}}$.[30]

***trans*- and *cis*-1-Methyl-4-*tert*-butylcyclohexene Epoxides (4 and 5).** Oxidation of 1-methyl-4-*tert*-butylcyclohexene (**4b**), obtained from the corresponding alcohols,[31,32] gave a mixture of **4** and **5**, which was separated via the *p*-nitrobenzoates.[33]

Ring-Opened Products. A mixture of 1-methyl-4-*tert*-butylcyclohexanes (**4a**) was obtained by hydrogenation of **4b**. The other products are all known: **4c** and **5c**,[31-34] **4d** and **5d**,[32] **4f**, **4g**, **5f**, and **5g**.[32]

***cis*-4,5-Dimethylcyclohexene Epoxide (7).** Epoxide **7** was prepared by *m*-chloroperbenzoic acid oxidation of *cis*-4,5-dimethylcyclohexene obtained from *cis*-1,1,2,2,3,3,6,6-octahydrophthalic anhydride:[35] NMR ($CDCl_3$) δ 3.13 (CHO), 0.78 and 0.88 (2 CH_3).

Ring-Opened Products. The *cis*-3,4-dimethylcyclohexanols **7f** and **7g** were obtained by hydrogenation of 3,4-dimethylphenol[18,19] or by $LiAlH_4$ reduction of **7**.[35] Jones oxidation of the mixture of **7f** and **7g** gave ketone **7d**[36] in good yield. A mixture of dimethylcyclohexanes containing **7a** was commercially available.

3,3-Dimethylcyclohexene Epoxide (8). This epoxide was prepared by *m*-chloroperbenzoic acid oxidation of 3,3-dimethylcyclohexene,[35] which was obtained by methylation of 2-methylcyclohexanone to give **8d**,[37] followed by elimination of the corresponding tosylhydrazone with *n*-butyllithium:[38] NMR ($CDCl_3$) δ 3.15 (CHO), 0.93 (CH_3).

Ring-Opened Products. Hydrocarbon **8a** was commercially available, and the synthesis of **8d** has already been described. $LiAlH_4$ reduction of **8d** gave **8f**.[39] 3,3-Dimethylcyclohexanol (**8g**) was obtained by hydrogenation of dimedone over PtO_2.[40] Jones oxidation of **8g** gave **8e**.[41]

Registry No. 1, 286-20-4; **1a**, 110-82-7; **1c**, 108-93-0; **1d**, 108-94-1; **2**, 14753-40-3; **2a**, 3178-22-1; **2c** (equatorial), 21862-63-5; **2c** (axial), 16201-66-4; **2d**, 936-99-2; **3**, 14753-39-0; **3c** (equatorial), 10488-10-5; **3c** (axial), 937-05-3; **3d**, 98-53-3; **4**, 22823-71-8; **4a** (isomer 1), 3325-80-2; **4a** (isomer 2), 4001-94-9; **4b**, 3419-74-7; **4d**, 5951-22-4; **4f**, 17388-13-5; **4g**, 17388-14-6; **5**, 5951-21-3; **5c**, 16980-55-5; **5d**, 5937-40-6; **5f**, 5937-42-8; **5g**, 18952-28-8; **6**, 1713-33-3; **6a**, 108-87-2; **6c**, 590-67-0; **6d**, 583-60-8; **6f**, 7443-52-9; **6g**, 7443-70-1; **7**, 74806-54-5; **7a**, 2207-01-4; **7d**, 27922-05-0; **7f**, 31527-84-1; **7g**, 31527-80-7; **8**, 74752-30-0; **8d**, 1193-47-1; **8e**, 2979-19-3; **8f**, 1193-46-0; **8g**, 767-12-4.

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