Methyl 2,2-Diphenylethylenesulfonate (12).—To a solution containing 8.0 g (19.9 mmol) of 9 dissolved in 120 ml of tetrahydrofuran and 250 ml of methanol at −10° was added 15.0 g of sodium methoxide. This mixture stirred at −10° for 2 hr. The usual water work-up with ether extraction gave a solid which was recrystallized from hexane–carbon tetrachloride to give 3.8 g (70%) of 12, mp 95–96°.

Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 66.00; H, 5.11.

Registry No.—2, 16003-63-7; 9, 16003-62-6; 12, 16003-64-8; 13, 16003-65-9; phenyldibromomethyl sulfone, 16003-66-0.

Acknowledgment.—We are grateful to the National Science Foundation (NSF GP-4208) for support of this work.

Alumina: Catalyst and Support. XXXVII.[1] Mechanism of Dehydration of *cis*- and *trans*-2-Alkyl-, -2-Phenyl-, and -3-*t*-Butylcyclohexanols over Alumina Catalysts[2,3]

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The mechanism of dehydration of the stereoisomers of 2-alkyl-, 2-phenyl-, and 3-*t*-butylcyclohexanols over alumina, prepared from aluminum isopropoxide, was studied by the micropulse technique at atmospheric pressure and at temperatures of 200–350°. The preferred mode of dehydration was found to be *trans* elimination. The *cis*-2-substituted cyclohexanols gave the 1-substituted cyclohexenes as the major product, whereas the 3-substituted cyclohexenes were the major products from the *trans*-2-substituted cyclohexanols. This *trans* elimination may be pictured as taking place between two surfaces of alumina, such as in a crevice or pore. Thus a basic site could abstract a proton on one side of the alcohol molecule, while an acidic site was attacking a hydroxyl group on the opposite side. This explanation is consistent with the concept of alumina acting as a "pseudo-solvent." Treatment of the catalyst with pyridine and extrapolation of the plots of per cent composition *vs.* per cent conversion to zero conversion showed the 4- and the 1-substituted cyclohexenes from the *trans*-2-substituted cyclohexanols to be initial products. A 1,3 elimination and an E1 process, respectively, were proposed as the mechanistic pathways to these olefins. The dehydration of *cis*- and *trans*-2-methylcyclohexanol-2-*d* was consistent with the concept of concerted *trans* elimination as the preferred mode of dehydration. However, the results also suggested that 1-methylcyclohexene from *trans*-2-methylcyclohexanol was produced *via* an E1 process. Variances in product distribution with the position, size, and nature of the group suggested that steric and polar factors play a role in determining the product distribution.

Recently the concept of alumina acting as a "pseudo-solvent" has been proposed by Pines and Manassen.[4] This "solvating" action of alumina is considered to arise from an acidic site attacking the hydroxyl group of the alcohol while a basic site abstracts a proton from the opposite side of the molecule. Thus *trans* elimination, similar to E2 reaction in solution, is the preferred mode of dehydration.

This concept has been used to explain the results or dehydration of menthol and neomenthol,[5] 2-*exo*- and 2-*endo*-bornanol,[6] and the four stereoisomers of 1-decalol.[7] In all of these cases products other than those which arise from *trans* elimination were also found. These were products of *cis* and γ or 1,3 elimination.

In the present study the dehydration of a series of *cis*- and *trans*-substituted cyclohexanols was investigated in order to evaluate the effect of steric and polar factors on the product distribution. The alcohols studied were *cis*- and *trans*-2-methyl-, 2-isopropyl-, 2- and 3-*t*-butyl-, and 2-phenylcyclohexanol. The dehydration of *cis*- and *trans*-2-methylcyclohexanol-2-*d* was also studied in order to shed more light on the formation of the 1-R-cyclohexenes which cannot be formed by *trans* elimination of *trans*-2-R-cyclohexanols.

The alcohols were prepared by hydrogenation of the corresponding alkylphenols, and the isomers were separated by preparative gas chromatography or by chromatography over alumina.

The dehydrations were made using the micropulse technique, which was first applied by Emmett and coworkers[8] and modified by Steingaszner and Pines.[9] Schappell and Pines[7] showed that the micropulse technique used for dehydration over alumina gave results similar with those obtained in a flow system. The reactions were carried out at atmospheric pressure and at temperatures of 200–350°.

Alumina prepared from aluminum isopropoxide was used in amounts of 2–16 mg. The catalyst was of 20/40 mesh size and was supported between zones of glass beads of the same mesh.

To each of the alcohols a known amount of an internal standard was added. This standard, a hydrocarbon which was stable under the reaction conditions, was used to calculate the conversion into olefins and the relative retention times of the olefins. The solid alcohols were dissolved in cyclohexane to form a 10–20 mol % solution. The sample sizes were 5–10 μl.

The reaction products were analyzed by gas chromatography and identified by comparison of their relative retention times with those of known samples.

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[1] For paper XXXVI, see W. F. Fry and H. Pines, *J. Org. Chem.*, **33**, 602 (1968).

[2] Paper XIV of the series of Dehydration of Alcohols. For Paper XIII, see N. C. Sih and H. Pines, *ibid.*, **31**, 4092 (1966).

[3] (a) This research was supported in part by the Atomic Energy Commission Contract AT(11-1) 1096. (b) The following terminology was used in this paper: "2-R-cyclohexanols," "2-R-cyclohexenes," etc. R stands for the substituent groups methyl, isopropyl, *t*-butyl, and phenyl.

[4] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 49 (1966).

[5] H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.*, **83**, 3270 (1961).

[6] K. Watanabe, C. N. Pillai, and H. Pines, *ibid.*, **84**, 3934 (1962).

[7] F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

[8] R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *J. Amer. Chem. Soc.*, **77**, 5860 (1955).

[9] P. Steingaszner and H. Pines, *J. Catal.*, **5**, 356 (1966).

TABLE I

EFFECT OF TEMPERATURE UPON THE DEHYDRATION OF *cis*- AND *trans*-2-METHYLCYCLOHEXANOL[a]

Temp, °C	% conversion	Methylcyclohexenes 1-	3-	4-	Methylenecyclohexane	Ratio of methylcyclohexenes
			cis			
						1-/3-
250	38	76.8	22.0		1.2	3.5
300	58	72.3	24.2	0.7	2.8	3.0
350	69	70.3	23.0	2.3	4.4	3.1
			trans			
						1-/3-
250	33	12.3	86.0	1.7		7.0
300	51	18.3	78.3	3.4		4.3
350	62	25.0	67.6	7.4		2.7

[a] Catalyst, 10 mg; flow rate, 60 cc of helium/min.

TABLE II

EFFECT OF TEMPERATURE UPON THE DEHYDRATION OF *cis*- AND *trans*-2-ISOPROPYLCYCLOHEXANOL

Catalyst, mg	Temp, °C	Helium flow rate, cc/min	% conversion	Isopropylcyclohexenes 1-	3-	4-	Ratio of isopropylcyclohexenes
				cis			
							1-/3-
5	200	100	18	84.9	15.1	Trace	5.6
5	255	100	22	80.8	19.2	Trace	4.2
5	295	100	28	80.1	19.9	Trace	4.0
				trans			3-/1-
15	100	38	50	13.9	84.7	1.4	6.1
15	250	38	62	17.1	80.3	2.6	4.7
15	300	38	84	24.1	66.7	9.2	2.8

I. Effect of Temperature.—The results in Table I and II show the effect of temperature upon the dehydration of the *cis*- and *trans*-2-methyl- and 2-isopropylcyclohexanols. The *cis*-2-alkylcyclohexanols gave 1-alkylcyclohexenes as the major product, the 3-alkylcyclohexenes as minor product, and sometimes small amounts of the 4-alkylcyclohexenes. *cis*-2-Methylcyclohexanol also gave some of the exocyclic olefin, methylenecyclohexane. As the temperature increased, the 1-/3-methylcyclohexene ratio decreased (selectivity decreased).

The 3-ene was the major product from the *trans*-2-alkylcyclohexanols. The minor products were the 1- and 4-enes. With increase in temperature the 1-/3-alkylcyclohexene ratio increased (selectivity decreased) and the amount of the 4-ene increased.

II. Determination of the Initial Products of Dehydration.—In order to determine if the observed products were those of dehydration and not of isomerization, plots of per cent composition of olefins *vs.* per cent conversion into olefins were made and extrapolated to zero conversion. As an example the plots of the dehydration of *cis*- and *trans*-2-isopropylcyclohexanol are given in Figures 1 and 2. The values at zero conversion are in Table III and they indicate that the initial products of dehydration from the *cis*-2-R-cyclohexanols were the 1- and 3-R-cyclohexenes. Besides these two olefins the *trans*-2-R-cyclohexanols also gave the 4-R-cyclohexenes.

A further check upon isomerization was performed by decreasing the helium flow rate (increasing the residence time) by a factor of 2. As the helium flow rate decreased the conversion increased, but there was little change in the 1-/3-R-cyclohexenes ratios from the various alcohols. This indicated that under the reaction conditions there was little, if any, isomerization taking place.

III. Epimerization.—From their studies with *cis*- and *trans*-1,4-cyclohexanediol, Manassen and Pines[10] found that on alumina these diols can epimerize *via* a ketone intermediate. In order to check for possible epimerization, the unreacted alcohols were analyzed in several runs. In all cases of the unreacted alcohols there was no detectable amount of the epimer. However, sometimes there was less than 2% of an unidentified product, which was presumed to be the ketone of the particular alcohol in question. Thus it seems that ketone formation and epimerization were not significant which is in accord with the findings of Schappell and Pines[7] in their study of the dehydration of stereoisomeric 2-decalols.

TABLE III

INITIAL PRODUCTS OF DEHYDRATION OF THE 2-R-CYCLOHEXANOLS[a]

R	R-Cyclohexenes 1-	3-	4-	Ratio of 1-/3-R-cyclohexenes
		At 250°		
cis-2-Methyl	84	16		5.3
cis-2-Isopropyl	83	17		4.9
cis-2-*t*-Butyl	73	27		2.7
cis-2-Phenyl	74	26		2.8
		At 300°		
cis-2-Methyl	80	19	1	4.1
cis-2-Isopropyl	81	19		4.3
cis-2-*t*-Butyl	75	25		3.0
cis-2-Phenyl	71	23	6	3.1
		At 250°		
trans-2-Methyl	15	83	2	0.18
trans-2-Isopropyl	19	79	2	0.24
trans-2-*t*-Butyl	21	77	2	0.27
trans-2-Phenyl	12	85	3	0.14
		At 300°		
trans-2-Methyl	20	77	3	0.26
trans-2-Isopropyl	23	67	10	0.34
trans-2-*t*-Butyl	29	64	7	0.45
trans-2-Phenyl	17	69	14	0.25

[a] These values were obtained by extrapolating the plots of % composition *vs.* % conversion to zero conversion. The values of phenyl at 300° and of methyl were single determinations.

IV. Effect of Catalyst Age.—As the catalyst was used it was found that the 1-/3-ene ratio from *cis*-2-*t*-butylcyclohexanol was not effected by catalyst age but the ratio from *cis*-2-phenylcyclohexanol decreased (Table IV). The 1-/3-ene ratios from *trans*-2-isopropyl-,

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[10] J. Mannassen and H. Pines, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, **2**, 845 (1965).

TABLE IV

EFFECT OF CATALYST AGE UPON THE PRODUCT DISTRIBUTION[a]

Cyclohexanol	Run no.	Catalyst, mg	Temp, °C	% conversion	R-Cyclohexenes, % 1-	3-	4-	Ratio of 1-/3-R-cyclohexenes
trans-2-*i*-Pr	4	5	200	13	13.7	85.0	1.3	0.16
trans-2-*i*-Pr	11	5	200	9	16.5	81.0	2.5	0.20
cis-2-*t*-Bu	2	10	250	47	69.3	30.7		2.3
cis-2-*t*-Bu	17	10	250	40	69.7	29.7	0.6	2.3
trans-2-*t*-Bu	1	10	250	43	19.2	77.7	3.0	0.25
trans-2-*t*-Bu	18	10	250	41	21.2	73.1	5.6	0.29
cis-2-Ph	3	10	250	84	76.0	22.8	1.2	3.3
cis-2-Ph	18	10	250	75	66.7	28.1	5.2	2.4
trans-2-Ph	1	10	250	53	14.2	83.0	2.8	0.17
trans-2-Ph	19	10	250	55	18.4	66.4	15.2	0.28

[a] The helium flow rate was 100 cc/min.

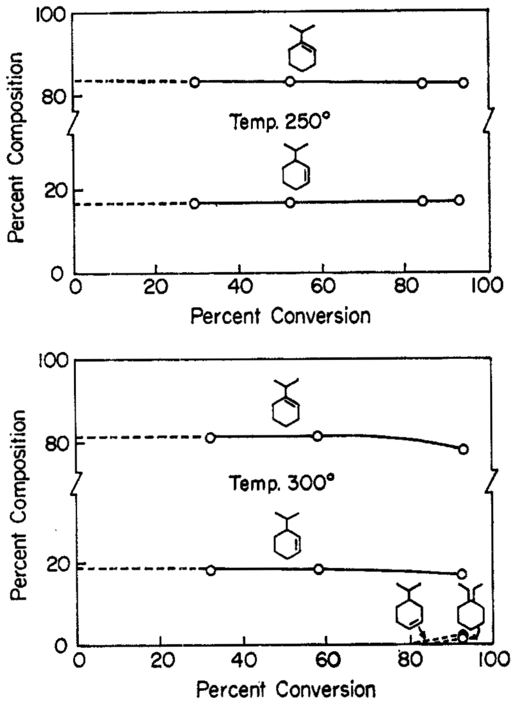

Figure 1.—Per cent composition of isopropylcyclohexenes against per cent conversion into isopropylcyclohexenes from the dehydration of *cis*-2-isopropylcyclohexanol.

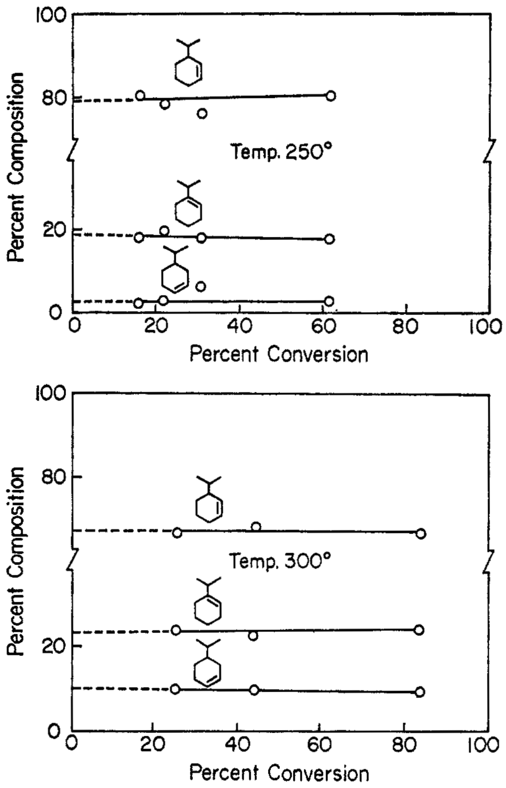

Figure 2.—Per cent composition of isopropylcyclohexenes against per cent conversion into isopropylcyclohexenes from the dehydration of *trans*-2-isopropylcyclohexanol.

trans-2-*t*-butyl-, and *trans*-2-phenylcyclohexanol increased with catalyst age.

V. Modified Catalyst.—It had been shown,[5,11] that pyridine can selectively deactivate alumina so that isomerization of olefins does not take place during dehydration. A 10-mg sample of alumina was treated with five 15-μl injections of pyridine. It was found that the pyridine treatment decreased the isomerization of 3-isopropylcyclohexene at 250° from 3 to 0%.

The results of dehydration over this treated catalyst are compared with the results over untreated catalyst (Table V). The per cent conversion to olefins was decreased over the treated catalyst. In all cases there was an increase in the 1-/3-substituted cyclohexenes ratio, indicating that the rate of formation of 3-R-cyclohexene is decreased preferentially to that of the 1-R-cyclohexene.

The *trans*-2 alcohols gave all three isomeric R-cyclohexenes on this nonisomerizing catalyst. The products from the *cis*-2 alcohols were essentially the 1- and 3-enes.

VI. Dehydration of *cis*- and *trans*-3-*t*-Butylcyclohexanol.—The ratio of 4-/3-ene (*t*-butylcyclohexene) from *cis*-3-*t*-butylcyclohexanol was smaller than that from the *trans* isomer (Table VI).

VII. Dehydration of *cis*- and *trans*-2-Methylcyclohexanol-2-*d*.—Samples of *cis*- and *trans*-2-methylcyclohexanol and *cis*- and *trans*-2-methylcyclohexanol-2-*d* were dehydrated over 13 mg of alumina and the products analyzed on column C (Table VII) at 50°. On this column 1-methylcyclohexene could be separated from 3- and 4-methylcyclohexene, but a mixture of the latter two gave only one peak. The results (Table VIII) showed that 1-methylcyclohexene was formed with an isotope effect from *cis*-2-methylcyclohexanol-2-*d* and without an isotope effect from *trans*-2-methylcyclohexanol-2-*d*.

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[11] L. Beranek, M. Kraus, K. Kochloefl, and V. Bazant, *Collect. Czech. Chem. Commun.*, **25**, 2531 (1960).

TABLE V

EFFECT OF PYRIDINE TREATMENT UPON THE DEHYDRATION OF 2-ALKYLCYCLOHEXANOLS[a]

Cyclohexanol	Catalyst	Temp, °C	% conversion	Cyclohexenes, % 1-	3-	4-	Ratio of 1-/3-R-cyclohexene
cis-2-*i*-Pr	Untreated	250	47	83.2	16.8		5.0
cis-2-*i*-Pr	Treated	250	22	85.6	14.4		5.9
cis-2-*i*-Pr	Untreated	300	58	81.8	18.2		4.5
cis-2-*i*-Pr	Treated	300	31	83.3	16.3	0.4	5.1
trans-2-*i*-Pr	Untreated	300	44	22.6	68.0	9.4	0.33
trans-2-*i*-Pr	Treated	300	17	26.5	68.0	5.5	0.39
cis-2-*t*-Bu	Untreated	250	46	69.2	30.7	0.1	2.3
cis-2-*t*-Bu	Treated	250	21	77.6	22.4		3.5
cis-2-*t*-Bu	Untreated	300	56	69.2	28.9	1.9	1.4
cis-2-*t*-Bu	Treated	300	26	79.3	20.4	0.4	3.9
trans-2-*t*-Bu	Untreated	250	54	19.3	76.8	3.9	0.25
trans-2-*t*-Bu	Treated	250	22	28.7	68.1	3.2	0.42
trans-2-*t*-Bu	Untreated	300	52	25.8	65.6	8.6	0.39
trans-2-*t*-Bu	Treated	300	34	34.1	57.8	8.1	0.59

[a] Catalyst, 10 mg, treated with five 15-μl injections of pyridine; the helium flow rate was 100 cc/min.

If the observed isotope effect were a secondary rather than a primary effect, both alcohols would be expected to exhibit an isotope effect. The fact that only one had an isotope effect suggests that this effect is primary. The isotope effect was calculated according to the method of Zavada, *et al.*[12]

A second batch of labeled alcohols was made and the products of dehydration were separated by preparative gas chromatography and analyzed by mass spectroscopy (Table IX). The 1-methyl-cyclohexene from *cis*-2-methylcyclohexanol-2-*d* was formed with almost total loss of deuterium, whereas it was formed with retention of 27% deuterium (after correction for 16% d_0 species in the *trans* alcohol) from *trans*-2-methyl cyclohexanol-2-*d*.

The 3- and 4-methylcyclohexenes from the *trans* alcohol retained all of the deuterium.

TABLE VI

DEHYDRATION OF *cis*- AND *trans*-3-*t*-BUTYLCYCLOHEXANOL[a]

Catalyst, mg	Temp, °C	% conversion	*t*-Butylcyclohexenes, % 3-	4-	Ratio of 4-/3-*t*-butylcyclohexene
			cis		
5	250	35	34.7	65.3	1.9
15	250	67	34.8	65.2	1.9
15	350	81	42.8	57.2	1.3
			trans		
5	250	54	21.2	78.8	3.7
15	250	67	26.2	73.8	2.8
15	350	76	25.5	74.5	2.9

[a] The helium flow rate was 100 cc/min.

TABLE VII

GAS CHROMATOGRAPHIC COLUMNS

Column	% substrate	Solid support[a] (mesh)	Length, m	Outer diameter,[b] in.
A	20% diglycerol	Gas Pack W (80/100)	2	0.25
B	20% diglycerol	Gas Pack W (80/100)	4	0.375
C	17% β,β′-oxydipropionitrile	Gas Pack W (80/100)	3	0.25
D	10% $AgNO_3$-diethylene glycol	Firebrick (100/120)	2	0.25
E	8% Bentone 34[c]–8% Apiezon L	Gas Pack W (80/100)	4	0.25
F	8% Bentone 34–12% Apiezon L	Gas Pack W (80/100)	4	0.375
G	15% GE SE-52[d]	WAB White Celite	1.5	0.375

[a] Gas Pack W and Celite are diatomaceous earth. [b] Columns A, C, and E were copper; columns B, F, and G were aluminum; and column D was Pyrex glass. [c] Bentone 34 is dimethyldioctadecyl ammonium bentonite. [d] GE SE-52 is a silicone gum.

Discussion

The fact that the *cis* and the *trans* isomers of the 2-R-cyclohexanols did not give the same products ruled out the possibility that the two isomers reacted through a common intermediate, such as a carbonium ion. From the *cis*-2-R-cyclohexanols, the major product was the 1-R-cyclohexene. The pyrolysis of *cis*-2-R-cyclohexyl esters,[13] which went through a *cis* elimination, gave the 3-ene as the major, if not exclusive, product. Solution reactions, both E1 and E2, of

TABLE VIII

DEHYDRATION OF *cis*- AND *trans*-2-METHYLCYCLOHEXANOL-2-*d*[a]

	Alcohol	Temp, °C	Methylcyclohexenes, % 1-	3- and 4-	k_H/k_D[b]
I	*cis*-2	205	80.1	19.9	
II	*cis*-2-*d*	205	75.1	24.9	1.4
III	*trans*-2	205	12.3	87.7	
IV	*trans*-2-*d*	205	12.6	87.4	1.0
I	*cis*-2	240	79.0	21.0	
II	*cis*-2-*d*	240	72.6	27.4	1.5
III	*trans*-2	240	15.7	84.3	
IV	*trans*-2-*d*	240	15.8	84.2	1.0

[a] Catalyst, 13 mg; helium flow rate, 100 cc/min. [b] The k_H/k_D values were calculated from following formula[12] as shown for the *cis* alcohol. These values were corrected for the deuterium content of the alcohols; *i.e.*, the labeled *cis* alcohol contained 20% d_0 species and the labeled *trans* alcohol contained 16% d_0.

$$k_H/k_D = \frac{(\%\ \text{1-ene from I})/(\%\ \text{3- and 4-enes from I})}{(\%\ \text{1-ene from II})/(\%\ \text{3- and 4 enes from II})}$$

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[12] J. Zavada, M. Svoboda, and J. Sicher, *Tetrahedron Lett.*, 1627 (1966).

[13] (a) W. Hückel and D. Rucker, *Ann.*, **666**, 30 (1963); (b) E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

TABLE IX

DEUTERIUM CONTENT OF *cis*- AND *trans*-2-METHYLCYCLOHEXANOL-2-*d* AND THE PRODUCTS OF DEHYDRATION AT 300°

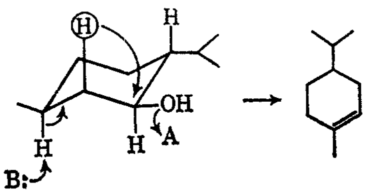
Species	2-Methylcyclohexanol, %	Methylcyclohexenes,[b] %	
		1-	3- and 4-
	cis		
D_0	14	90	
D_1	84	5	
D_2	2	5	
	trans		
D_0	16	77	14
D_1	84	22	84
D_2		1	2

[a] Catalyst, 15 mg; helium flow rate, 100 cc/min. [b] The *cis* alcohol gave 77% 1-methylcyclohexene and 23% 3- and 4-methylcyclohexenes, and the *trans* alcohol gave 21% 1-methylcyclohexene and 79% 3- and 4-methylcyclohexenes.

cis-2-R-cyclohexyl derivatives[13b,14] gave the 1-R-cyclohexene in preference over the 3-R-cyclohexene. In the case of *trans*-2-R-cyclohexanols the 3-R-cyclohexene was the major product. The 1-R-cyclohexene was the major product from the pyrolysis of *trans*-2-R-cyclohexyl esters[11d,14c] whereas E2 solution reactions[13b,14] gave the 3-R-cyclohexene as the major, if not the only, product. Large amounts of 1-R-cyclohexenes formed under E1 conditions in solution, and many times the 1-R-cyclohexene is the major product.

These facts indicated that dehydration over alumina is more like E2 *trans* elimination, rather than a *cis* or an E1 reaction. Thus *trans* elimination can explain the formation of 1- and 3-R-cyclohexenes from the *cis*-2-R-alcohols and the formation of 3- and 4-*t*-butylcyclohexenes from the 3-*t*-butylcyclohexanols. However, it cannot explain the formation of the 1- and 4-R-cyclohexenes from the *trans*-2-R-cyclohexanol.

Dehydration of menthol and neomenthol[5] and the stereoisomers of 1-decalol[7] gave products which were not 1,2-elimination products. It was proposed that these products might arise from a concerted 1,3-elimination process (eq 1) in which the β hydrogen migrates to

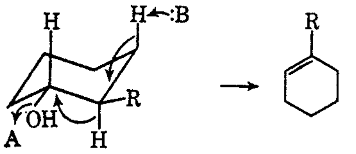


(1)

the α carbon as an acidic site of the alumina removes the hydroxyl group and a basic site abstracts the γ hydrogen.

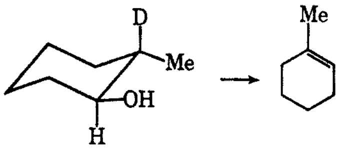
This type of 1,3 elimination can explain the formation of the 4-R-cyclohexenes from the *trans*-2-R-cyclohexanols as well as the formation of methylenecyclohexane from *cis*-2-methylcyclohexanol.[15]

In the cases of menthol and *trans,trans*- and *cis,-trans*-1-decalol, products of *cis* elimination were observed. It was suggested that these products might arise from an E1 process, although a concerted *cis* elimination could not be ruled out. The formation of the 1-ene from the *trans*-2-alcohols is a *cis* elimination. It may be formed by an E1 mechanism or a concerted *cis* elimination. It could also be formed by a 1,3 elimination[5] (eq 2).

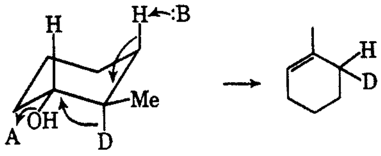


(2)

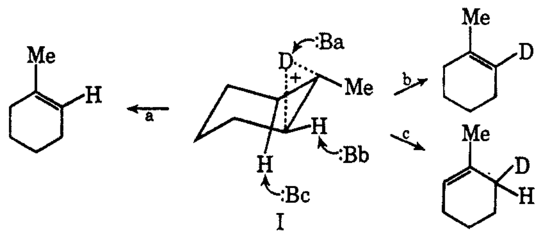
In order to investigate the mechanism for the formation of 1-R-cyclohexenes from the *trans*-2-cyclohexanols, the dehydration of *cis*- and *trans*-2-methylcyclohexanol-2-*d* was studied. From *trans*-2-methylcyclohexanol-2-*d*, 1-methylcyclohexene was formed without an isotope effect and with the retention of 27% deuterium. An exclusive concerted *cis* elimination (eq 3) would have been expected to exhibit an isotope effect and to lose 100% deuterium. Total retention of deuterium would have been expected for a 1,3 elimination (eq 4). The intermediate I seemed to best fit the data. Intermediate I (eq 5) can be formed in



(3)



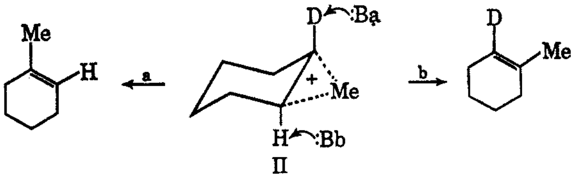
(4)



(5)

the rate-determining step without an isotope effect, and then can undergo three types of attack which would result in partial retention of deuterium. The preferred pathway is a; path c is a stepwise 1,3 elimination.[4]

Intermediate II (eq 6) could not be ruled out as participating in the reaction.



(6)

Path b which leads to retention of deuterium also leads to alkyl migration. It is unlikely that this intermediate plays a role in the dehydration of *trans*-2-R-cyclohexanols because no migration of the isopropyl group was noted in the dehydration of menthol.[5]

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(14) (a) W. H. Saunders and T. H. Brownlee, *Proc. Chem. Soc.* (London), 314 (1961); (b) W. Hückel, *et al., Ann.*, **624**, 140 (1959); (c) H. L. Goering and R. L. Reeves, *J. Amer. Chem. Soc.*, **78**, 4931 (1956).

(15) W. Hückel and M. Hanack, *Angew. Chem. Intern. Ed. Engl.*, **6**, 534 (1967). This type of hydride shift was recognized to occur in homogeneous system only with a tertiary β hydrogen, and was recognized by the formation of a tertiary substitution product. The evidence for a hydride shift was provided by the formation of 3,8- and *rac*-3,4-*p*-menthene from the methanolysis of optically active *p*-toluenesulfonates of menthols.

Steric and Polar Factors.—The four *cis*-2-R-cyclohexanols all gave the 1-R-cyclohexenes as the major product over the 3-R-cyclohexenes because the R-group imparts more stability to the double bond (Table III). This is in agreement with the data of Herling, *et al.*[16] that the I-R-cyclohexenes are the most stable isomers of alkylcyclohexenes at equilibrium. At 250° the equilibrium ratio of 1-/3-methylcyclohexene was 3.8. Dehydration of *cis*-2-methylcyclohexanol at 250° produces these olefins in a ratio of 5.3.

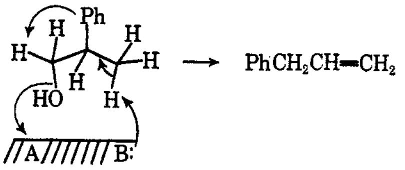
Considering only the alkyl groups, it can be seen that the methyl and isopropyl groups have a similar effect. The *t*-butyl group, however, caused a notable drop in the ratio, *i.e.*, the 3-*t*-butylcyclohexene increased. The order for olefin stabilization by alkyl groups is Me > *i*-Pr > *t*-Bu. In keeping with this idea Benkeser[17] found in equilibration studies that the methyl group imparts greater thermodynamic stability to the double bond than does the *t*-butyl group. At equilibrium in glacial acetic acid with catalytic amounts of *p*-toluenesulfonic acid there was 91–99% 1-methylcyclohexene and 76–79% 1-*t*-butylcyclohexene relative to the corresponding total amount of olefin.

The phenyl group, owing to its polarity, would be expected to have a larger stabilizing effect than the alkyl groups, and thus a higher ratio. However, the effect of the phenyl group was similar to that of the *t*-butyl group. Thus it seemed that as branching at the β carbon increased there was steric hindrance to the abstraction of the hydrogen on the β carbon, the phenyl group in this case being as bulky as the *t*-butyl group.

The effect of the R group in the 2 position of the *trans*-cyclohexanols on the ratio of the 1-R-cyclohexenes to the 3-R-cyclohexenes can be seen in Table III. Considering only the alkyl groups, the ratio increases as the size of the group increases.

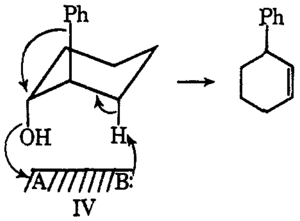
In order for the *trans*-2-R-cyclohexanols to undergo *trans* elimination, they must assume a conformation in which the R-group as well as the hydroxyl group is in an axial position. In separate studies Winstein[18] and Eliel[19] concluded from conformational analysis that the preference for the equatorial position for the alkyl groups is in the order *t*-Bu > *i*-Pr > Et > Me. This means as the group gets larger it is more difficult to assume an axial position, and consequently more difficult for that alcohol to undergo *trans* elimination. Of course as concerted *trans* elimination becomes more difficult, the process leading to the 1-R-cyclohexenes becomes more competitive and the ratio of 1-/3-R-cyclohexenes increases.

In another study Eliel[20] concluded from conformational analysis that the phenyl group should lie between the ethyl and isopropyl groups in its preference for the equatorial position. However, the ratio of 1-ene to 3-ene from *trans*-2-phenylcyclohexanol is smaller than that from *trans*-2-methylcyclohexanol. This seemingly low ratio for the phenyl group may be a reflection of the ability of the phenyl group to migrate during dehydration over alumina as in the case of 2-phenyl-1-propanol (III) (eq 7). It was found that the ratio of phenyl/methyl migration was 7.3:1 to 9.0:1, depending on the alumina used.[21] It would be helpful to study by the use of C-14 the extent of phenyl migration during the dehydration of *trans*-2-phenylcyclohexanol (IV) (eq 8) before attempting to explain the low ratio.



III

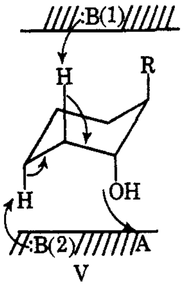
(7)



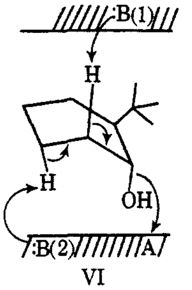
IV

(8)

At 250° and lower the amount of 4-R-cyclohexenes produced was too small to be measured with any high degree of accuracy; thus no meaningful trend could be seen. However, at 300° there was the following trend: Me, 3; *t*-Bu, 7; *i*-Pr, 10; and Ph, 14. This trend may be explained by considering the fact that for favorable 1,3 elimination to take place two hydrogens and the hydroxyl group involved must all be *trans* to each other. Thus the alcohol must attain the diaxial conformation (V).



V



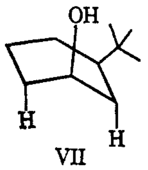
VI

As the R group becomes larger and longer, it is more difficult for :B(1) to approach the β hydrogen, thus the approach of :B(2) becomes relatively easier and extraction of the γ hydrogen becomes more competitive with the abstraction of the β hydrogen.

The bulky *t*-butyl group probably does not attain the axial position; thus *trans*-2-*t*-butylcyclohexanol might dehydrate through a boat form (VI). Apparently in the boat form the *t*-butyl group offers less hindrance than the isopropyl group in the axial position of the chair form.

In an attempt to investigate further steric effects during dehydration over alumina, the isomeric 3-*t*-butylcyclohexanols (VII and VIII) were dehydrated.

In the *cis* alcohol, which may dehydrate through a skew boat form, the *t*-butyl group would not be expected



VII

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[16] J. Herling, J. Shabtai, and E. Gil-Av, *J. Amer. Chem. Soc.*, **87**, 4107 (1965).

[17] R. A. Benkeser, *et al.*, *J. Org. Chem.*, **29**, 1313 (1964).

[18] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

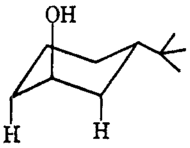
[19] E. L. Eliel and T. J. Brett, *ibid.*, **87**, 5039 (1965).

[20] E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1367 (1960).

[21] J. Herling and H. Pines, *J. Org. Chem.*, **31**, 4088 (1966).

to offer steric hindrance to the abstraction of the β hydrogen which leads to the formation of the 3-*t*-butylcyclohexene. Thus if the controlling factor is the relative product stability we would expect the 4-*t*-butylcyclohexene to form in a slight preference over the 3 isomer, because in the cases of the methyl and ethylcyclohexenes the 4-R-cyclohexenes are slightly more stable than the 3-R-cyclohexenes.[16] A ratio of 1.9 was obtained for 4- to 3-R-cyclohexenes.

The hydroxyl group in the *trans*-3-butylcyclohexanol would be in the axial position in the more stable conformation, *i.e.*, the one with the *t*-butyl group in the equatorial position (VIII). The *t*-butyl group on the γ-carbon atom might offer steric hindrance to the abstraction of the β-hydrogen which leads to the formation of 3-*t*-butylcyclohexene. Thus the *trans*-*t*-butylcyclohexanol should give a larger ratio of 4- to 3-*t*-butylcyclohexene than the *cis* alcohol. The ratio from the *trans* alcohol was found to be about 3.3, suggesting that there is a steric effect.



VIII

The evidence seems to be very strong that steric factors play an important role in determining the product distribution from dehydration of alcohols over alumina. For the *cis*-2- and *trans*-3-*t*-butylcyclohexanol the steric factor appears to be a hindrance to the approach of the alcohol to the catalyst surface. In the case of the *trans*-2-*t*-butylcyclohexanol the steric factor is one of steric compression within the alcohol molecule itself. The relative product stability (polar effect) also seems to play a role in the case of the *cis*-2-R-cyclohexanols.

The Effect of Catalyst Aging and Modification.—It has been shown[5,11] that pyridine can selectively poison alumina toward isomerization of olefins compared to dehydration of alcohol. The pyridine treated catalyst also decreased the conversion of the alcohols into olefins, which means that some of the dehydrating as well as the isomerizing sites were destroyed by the pyridine.

In the case of the *trans*-2-alkylcyclohexanols the pyridine treatment caused an increase in the 1-/3-R-cyclohexenes ratios. Since the total conversion into olefins was lowered, assuming that isomerization did not take place, it may be that the 1-ene and the 3-alkylcyclohexenes were formed by different pathways and perhaps even on different types of sites.

Aging of the catalyst was similar to the effect of catalyst modification by "basic" compounds. This suggests that aging is caused by the deactivation of some of the sites by the "basic" olefinic products of the reaction. In the case of the phenylcyclohexenes the aging is more pronounced than in the case of alkylcyclohexenes.

The preferred mode of dehydration over alumina is *trans* elimination. For it to occur it is necessary for an acidic site to attack the hydroxyl group on one side of the molecule while a base abstracts a hydrogen from the other side. This base may be a basic site on the alumina, in which case the alcohol molecule can be in a pore, crevice, or fault of the catalyst, or the base may be another alcohol molecule.

Owing to this ability to cause *trans* elimination similar to that of E2 solution reactions, alumina may be considered a "pseudo-solvent." The modification of alumina with "basic" compounds may analogously be called a "pseudo-solvent effect."

Experimental Section

A. Preparation of the Alcohols. 1. Hydrogenation of Alkylphenols.—The alkylphenols (Aldrich Chemical Co., Milwaukee, Wis.) were quantitatively hydrogenated to the corresponding alkylcyclohexanols over 4 g of finely ground nickel-kieselguhr (Ni-0101 T, 44% Ni; Harshaw Chemical Co., Cleveland, Ohio) in a 450-ml capacity rotating autoclave. The experimental conditions and the composition of the alcohols are given in Table X.

A mixture of the 2-phenylcyclohexanols was obtained from Aldrich Chemical Co.

2. Separation of the Isomeric Pairs.—The isomeric pairs of the alkylcyclohexanols were separated by preparative gas chromatography over column B (see analytical procedure) at 100–120° and a helium gas flow of 100–120 cc/min. Alcohols of 99% purity were obtained.

The isomers of 2-phenylcyclohexanol were separated by passing a 2-ml mixture over 100 g of alumina (80/200 mesh, Cat. No. A-540, Fisher Scientific, Fairlawn, N. J.). A 15% solution of benzene in pentane was used to elute the *cis* isomer, and then ether was used in order to elute the *trans* isomer. Recrystallization of the respective fractions gave 175 mg of the *cis* and 400 mg of the *trans* isomers.

Identification of each isomer was based upon its infrared spectrum and a physical constant (Table XI). It has been reported[18] that axial –OH groups give a band in the infrared region at *ca.* 955 (10.5 μ) and equatorial –OH groups give a band at *ca.* 1062 cm^{-1} (9.4 μ).

B. Preparation of the Olefins. 1. 1-Isopropylcyclohexene, Isopropylidenecyclohexane, and Isopropenylcyclohexane.—1-Isopropylcyclohexanol was prepared in a yield of about 40% from isopropyl bromide (73.8 g, 0.6 mol), magnesium (17 g, 0.63 g-atom), and cyclohexanone (49 g, 0.5 mol) *via* a Grignard reaction. Iodine[22] was added to the crude mixture after stripping off the ether and heated to 180°. Analysis of the product on column C (Table VII) showed one large peak (90%) followed by two smaller peaks. Samples of the three were collected by preparative gas chromatography on column C, and their infrared spectra were taken.

The first compound gave an infrared spectrum consistent with 1-isopropylcyclohexene, the significant bands being 7.23 and 7.33 (*gem*-dimethyl group) and 12.43 μ (trisubstituted alkene). A band at 11.27 μ in the spectrum of the second compound indicated a *gem*-disubstituted alkene as in isopropenylcyclohexane. The third compound had no strong bands at 10.3–1.4 (*trans*-disubstituted alkene), 14.5 (*cis*-disubstituted alkene), 11.2–11.3 (*gem*-disubstituted), or 11.9–12.7 μ (trisubstituted alkene); so it was assumed to be isopropylidenecyclohexane. The interpretation of the infrared bands was based on the data given by Dyer.[23]

2. 3-Isopropylcyclohexene.—Cyclohexene (120 g, 1.47 mol) was brominated with N-bromosuccinimide (91 g, 0.51 mol) in 360 ml of carbon tetrachloride according to the method of Dauben and McCoys.[24] Upon distillation 30 g (37% yield) of material was obtained: bp 49–50 (10 mm).

Isopropyl bromide (0.2 mol) was treated with magnesium (0.19 g-atom) in absolute ether in order to couple it with 3-bromocyclohexene[25] (30 g, 0.186 mol). Pure 3-isopropylcyclohexene was separated from the crude product by preparative gas chromatography over column G (Table VII) at 85°.

3. 4-Isopropylcyclohexene and Mixtures of the *t*-Butylcyclohexenes.—The acetates were prepared by the procedure of

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[22] W. A. Mosher, *J. Amer. Chem. Soc.*, **62**, 552 (1940).

[23] J. R. Dyer, "Applications of Adsorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 33.

[24] H. J. Dauben and L. L. McCoy, *J. Amer. Chem. Soc.*, **81**, 4863 (1959).

[25] W. R. Biggerstaff, A. P. Menditto, and I. Yokoyama, *J. Org. Chem.*, **19**, 934 (1954).

TABLE X

HYDROGENATION OF ALKYLPHENOLS OVER NICKEL–KIESELGUHR

Alkylphenol (g, mol)	Solvent (ml)	Initial pressure,[a] atm	Temp, °C	Alcohol composition[b] % *cis*	% *trans*
2-Methyl (43.2, 0.40)	None	110	170	27	73
2-Isopropyl (20.4, 0.15)	Ethanol (20)	110	150	56	44
2-*t*-Butyl (21.0, 0.14)	Ethanol (15)	136	120	80	20
3-*t*-Butyl (30.0, 0.20)	Ethanol (25)	117	170	68	32

[a] At 25°. [b] Analyzed on a chromatographic column A, see Table VII.

TABLE XI

PHYSICAL PROPERTIES OF THE SUBSTITUTED CYCLOHEXANOLS

Cyclohexanol	Physical constants Found	Reported	Ref	Significant ir bands, μ	
2-Methyl					
cis-	n^{20}D 1.4645	1.4641	*a*, *b*	2.97	10.2
trans-	n^{20}D 1.4618	1.4611		3.0	9.6
2-Isopropyl					
cis-	Mp 49–50°	50.2–50.5°	*c*	2.9	10.3
trans-	Mp 62–63°	64.4°		3.0	9.5
2-*t*-Butyl					
cis-	Mp 54–55°	56.8–57.7°	*d*	2.97	10.3
trans-	Mp 83–84°	84.4–85.0°		2.98	9.4
2-Phenyl					
cis-	Mp 43–44°	42–44°	*e*	2.85	10.3
trans-	Mp 55–56°	56–57°		3.0	9.4
3-*t*-Butyl					
cis-	Mp 38–40°	40–41°	*f*	3.03	9.45
trans-	Mp 58–60°	62.5–63°		2.97	10.3

[a] See ref 20. [b] W. Hückel and A. Hubele, *Ann.*, **613,** 27 (1958). [c] W. Hückel and R. Neidlein, *Chem. Ber.*, **91,** 1991 (1958). [d] See ref 14c. [e] H. J. Schaeffer and C. J. Collins, *J. Amer. Chem. Soc.*, **78,** 124 (1956). [f] W. Hückel and K. Thiele, *Chem. Ber.*, **94,** 2027 (1961).

Vaughn and coworkers[26] from the corresponding alcohols and acetyl chloride in the presence of pyridine. The yields are given in Table XII.

TABLE XII

YIELD OF ACETATES FROM SUBSTITUTED CYCLOHEXANOLS

Cyclohexanol (g, mol)	Acetyl chloride, g, mol	Crude yield, %
4-Isopropyl (43, 0.3)	27, 0.35	90
2-*t*-Butyl (9, 0.058)	6.3, 0.8	81
3-*t*-Butyl (22, 0.14)	16, 0.2	85
4-*t*-Butyl (3.2, 0.02)	4.3, 0.055	75

The acetates were pyrolyzed over pyrex glass beads at 490° in a manner similar to that of Baily and King.[27] Column G (Table VII) was used to separate samples of the olefins from the reaction mixtures. The 4-isopropyl- and 4-*t*-butylcyclohexyl acetates gave the pure 4-enes. The 2-*t*-butylcyclohexyl acetate gave the 1- and 3-*t*-butylcyclohexenes and the 3-*t*-butylcyclohexyl acetate gave the 3- and 4-*t*-butylcyclohexenes. The relative retention times of butylcyclohexenes obtained from the pyrolysis of the *t*-butylcyclohexyl acetates is given in Table XIII.

TABLE XIII

RELATIVE RETENTION TIMES[a] OF THE PRODUCTS FROM PYROLYSIS OF THE *t*-BUTYLCYCLOHEXYL ACETATES

Structural assignment	Acetates 2-	3-	4-
Isopropylcyclohexane[b]	1.00	1.00	1.00
1-*t*-Butylcyclohexene	2.06		
3-*t*-Butylcyclohexene	2.59	2.55	
4-*t*-Butylcyclohexene		3.10	3.13

[a] Column C; 50°; helium flow rate, 100 cc/min. [b] Internal standard.

4. **Phenylcyclohexenes.**—2-Phenylcyclohexanol (4 ml of a mixture of *cis* and *trans* isomers) was mixed with 5 ml of *t*-butyl alcohol, and the mixture was dehydrated over alumina (Al-014T, Harshaw Chemical Co.) at 270–280° at a rate of 15–20 drops/min.

Three olefinic products were separated by preparative chromatography on column F (Table VII) and their infrared spectra were taken. Two of the olefins were identified as the 1- and 3-phenylcyclohexenes by comparison of their spectra with reported spectra.[13b] The third olefin, whose spectrum was not consistent with that of benzalcyclopentane or 1-benzylcyclopentene,[13b] was assumed to be 4-phenylcyclohexene.

C. **Preparation of *cis*- and *trans*-2-Methylcyclohexanol-2-*d*.** 1. **2-Methyl-1-cyclohexenyl Acetate.**—This compound was produced in 47% yield from 0.5 mol of 2-methylcyclohexanone by the method of House, *et al.*[28] It distilled at 70–75° (12–14 mm) [lit.[29] 82–84° (18 mm)] and nmr spectra showed no peak at τ 4.8 (vinyl hydrogen[29]), indicating very little, if any of the 6-methyl-1-cyclohexenyl acetate.

2. **Lithium 2-Methyl-1-cyclohexene Oxide.**—To 2-methyl-1-cyclohexenyl acetate (10 g, 0.065 mol) in 20 ml of anhydrous ether cooled by an ice bath, 65 ml of 2.3 *M* methyllithium (Alfa Inorganics, Inc., Beverly, Mass.) in ether was added dropwise while stirring.[30] The mixture was stirred while being allowed to warm to room temperature.

3. **2-Methylcyclohexanone-2-*d*.**—The solution of the lithium 2-methyl-1-cyclohexenoxide in ether was added dropwise to a mixture of 100 g of deuterium oxide (99.84 mol % D_2O, Bio-Rad Laboratories, Richmond, Calif.) and 10 ml of acetic anhydride while being stirred.[29] The mixture was stirred overnight, then the ether layer was separated off and dried over anhydrous potassium carbonate.

4. ***cis*- and *trans*-2-Methylcyclohexanol-2-*d*.**—The dried solution of the 2-methylcyclohexanone-2-*d* was added dropwise to lithium aluminum hydride (2 g) in anhydrous ether (50 ml) while being stirred. The mixture was stirred for 3 hr and the excess lithium aluminum hydride destroyed by 10% sodium hydroxide. After being separated off and concentrated the ether layer was analyzed on column A. The alcohol produced was 40% *cis* and 60% *trans*. This crude mixture gave on preparative gas chromatography on column B pure *cis*- and pure *trans*-2-methylcyclohexanol-2-*d*.

Two batches of the alcohols were made and mass spectral analysis showed that in the first batch the *cis* and *trans* each had 84% d_1.

The infrared spectra of the alcohols had a peak at ~4.7 μ indicating a C–D bond. In the nmr spectra the labeled alcohols gave an unsplit methyl peak (τ ~9.0) indicating that the deuterium was mostly if not exclusively on carbon 2. As a further check on the position of the deuterium the nmr spectrum of the 3-methylcyclohexene from *trans*-2-methylcyclohexanol-2-*d* was taken and found to have an unsplit methyl group (τ ~9.0).

D. **Preparation of the Catalyst.**—Alumina free from alkali metal ions was prepared by the hydrolysis of 125 g of distilled aluminum isopropoxide with 1 l. of distilled water.[7,31] After filtration, the resulting aluminum hydroxide was redispersed in 500 ml of water and filtered, and the filter cake was dried at 120° for 24 hr. This material was then calcined at 650° for 4 hr in a stream of nitrogen, crushed, and sieved to 20/40 mesh.

A. **Apparatus.**—The apparatus used was similar with that described by Steingaszner and Pines[9] and consisted of (a) microreactor heated by a furnace, (b) gas chromatograph attached directly to the microreactor, and (c) temperature control panel.

The microreactor tube was constructed of a 5.75-in. length of 0.25-in. o.d. stainless steel tubing with stainless steel Swagelock

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(26) W. R. Vaughn, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Amer. Chem. Soc.*, **85,** 2282 (1963).

(27) W. J. Baily and C. J. King, *J. Org. Chem.*, **21,** 858 (1956).

(28) H. O. House and H. W. Thompson, *ibid.*, **26,** 3729 (1961).

(29) H. O. House and V. Kramer, *ibid.*, **28,** 3362 (1963).

(30) H. O. House and B. M. Troost, *ibid.*, **30,** 3141 (1965).

(31) H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82,** 247 (1960).

fittings on both ends. On the side of the reactor was welded a 0.125-in. thermocouple tube.

The microreactor was connected directly to the chromatograph so that a stream of helium gas swept the injected samples through the reactor and then through the chromatographic column for analysis. The system contained a bypass so that the flow through the reactor could be varied, yet the sum of the two paths, which passed through the chromatographic column, could be kept constant.

B. Analytical Procedures. 1. Gas Chromatographic Columns.—A list of the gas chromatographic columns used in this study is in Table VII. Columns A, C, D, and E were used on the F & M Model 300 gas chromatograph, while columns F and G were used on an F & M Model 720. Column B was used on an Aerograph Model A-700 (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.), which was manually operated.

The alkylcyclohexanols were analyzed and separated, respectively, on columns A and B at temperatures of 80–100° and a helium flow rate of 100 cc/min, while the 2-phenylcyclohexanols were analyzed on column E at 175° and a helium flow rate of 100 cc/min.

Analysis of the methylcyclohexenes was done on column D at room temperature and a helium flow rate of 60 cc/min. The areas of the peaks were calculated by an electronic integrator (Model CRS-11HSB, Infotronics Corp., Houston, Tex.). Owing to tailing of the peaks simple triangulation was less accurate. Simple triangulation was used for the other columns and olefins because the results were nearly identical with those obtained when the integrator was used as a check. In the case of the labeled 2-methylcyclohexanols the olefins were analyzed on column C at 50° and a flow rate of 100 cc of helium/min.

Column C had a vertical coil at the beginning hf the column which could be immersed in a liquid nitrogen bath.[9] This allowed the products from twenty 5-μl injections of the labeled alcohols to be trapped in the column. The bath was removed and the column was heated to room temperature resulting in the separation of the products, which could be individually collected in receivers cooled in liquid nitrogen. These products were then analyzed by mass spectroscopy.

Column C at 50° and a helium flow rate of 100 cc/min was used to analyze the isopropyl- and *t*-butylcyclohexenes. The phenylcyclohexenes were analyzed on Column E at 175° and a helium flow rate of 100 cc/min.

2. Identification of the Olefinic Reaction Products.—The olefinic products were identified by comparison of their relative retention times with those of known samples (Table XIV).

Authentic samples of the 1-, 3-, and 4-methylcyclohexenes were obtained from Professor A. S. Hussey (Northwestern University, Evanston, Ill.). The relative retention times of methylenecyclohexane on columns C and D were found by dehydration of samples of 1-methylcyclohexanol in the microreactor and taking the relative retention times of the products on the columns. Since a pure sample of the 1-methylcyclohexene was available, it could be identified and the other product formed was assumed to be methylenecyclohexene.

3. Spectra.—The infrared spectra of all the compounds were taken as a film between sodium chloride disks except for the 2-*t*-butyl- and 2-phenylcyclohexanols which were taken in potassium bromide disks and the 2-isopropyl- and 3-*t*-butylcyclohexanols which were dissolved in carbon tetrachloride and placed in a 0.94-mm sodium chloride cell. A Baird 4-55 spectrophotometer was used.

The mass-spectral analyses were performed by Seymour Meyerson of the American Oil Co., Whiting, Ind., to whom the authors are greatly indebted.

TABLE XIV

RELATIVE RETENTION TIMES OF SYNTHETIC R-CYCLOHEXENE ISOMERS AND OF THE R-CYCLOHEXENE FROM THE 2-R-CYCLOHEXANOLS

Compound	Known	Product from alcohols	
		cis	*trans*
2-Methylcyclohexanols			
Column C; temperature, 50°; helium flow rate, 100 cc/min			
Methylcyclohexane[a]	1.00	1.00	1.00
3-Methylcyclohexene	2.41	2.43	2.47
4-Methylcyclohexene	2.53		
Methylenecyclohexane	2.73	2.70	
1-Methylcyclohexene	3.46	3.57	3.54
Column D; room temperature; helium flow rate, 60 cc/min			
1-Methylcyclohexene	1.00	1.00	1.00
4-Methylcyclohexene	3.01	3.05	3.13
3-Methylcyclohexene	3.36	3.34	3.45
Methylenecyclohexane	6.03	5.97	
2-Isopropylcyclohexanols			
Column C; temperature, 50°; helium flow rate, 100 cc/min			
n-Propylcyclohexane[a]	1.00	1.00	1.00
1-Isopropylcyclohexene	1.57	1.57	1.57
3-Isopropylcyclohexene	1.90	1.88	1.90
4-Isopropylcyclohexene	2.21	2.19	2.20
Isopropylidenecyclohexane	2.39	2.43	
2- and (3-)-*t*-Butylcyclohexanols			
Column C; temperature, 50°; helium flow rate, 100 cc/min			
Isopropylcyclohexane[a]	1.00	1.00 (1.00)	1.00 (1.00)
1-*t*-Butylcyclohexene	2.06	2.10	2.09
3-*t*-Butylcyclohexene	2.57	2.60 (2.56)	2.62 (2.59)
4-*t*-Butylcyclohexene	3.12	3.13 (3.13)	3.14 (3.15)
2-Phenylcyclohexanols			
Column E; temperature, 175°; helium flow rate, 100 cc/min			
1-Propyl-4-isopropylbenzene[a]	1.00	1.00	1.00
3-Phenylcyclohexene	2.14	2.18	2.18
4-Phenylcyclohexene	2.31	2.36	2.32
1-Phenylcyclohexene	3.34	3.41	3.39

[a] Internal standard.

Registry No.—*cis*-2-Methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; *cis*-2-isopropylcyclohexanol, 10488-25-2; *trans*-2-isopropylcyclohexanol, 10488-23-0; *cis*-2-*t*-butylcyclohexanol, 7214-18-8; VI, 16201-62-0; *cis*-2-phenylcyclohexanol, 16201-63-1; IV, 16201-64-2; VII, 16201-65-3; VIII, 16201-66-4; *cis*-2-methylcyclohexanol-2-*d*, 16201-94-8; *trans*-2-methylcyclohexanol-2-*d*, 16201-95-9.