min corresponded to 2-methylquinuclidine: nmr ($CDCl_3$), δ 1.15 doublet (J = 7 cps) (CH_3), 1.55 multiplet (CH_2), 2.90 multiplet (NCH_2); infrared spectrum (CCl_4), 3.45 (s), 6.9 (s), 7.3 (s), 7.5 (s), 7.7 (w), 8.35 (m), 9.1 (m), 9.3 (s), 9.5 (s). The picrate melted at 283–285° (lit.[6] 286°).

The fifth peak had a retention time of 99 min: nmr ($CDCl_3$), δ 7.0 multiplet (N=CH), 1.17 triplet (J = 5 cps), 2.17 multiplet; infrared (CCl_4), 3.35 (s), 6.3 (m), 6.6 (m), 6.82 μ (s). These data point to the presence of 3,4,5,6-tetrahydro-4-propylpiperidine.

D. N-Chloro-4-ethyl-3-methylpiperidine.—Irradiation at 0–5° for 8 hr gave a mixture of amines which gave only two peaks with a ratio of 48:52 under conditions of vpc used for the last two compounds. The first compound had a retention time of 41.5 min and from its nmr spectrum corresponded to 3,7-dimethyl-1-azabicyclo[2.2.1]heptane: nmr ($CDCl_3$), δ 0.90 doublet (J = 7.5 cps) (CH_3), 1.02 doublet (J = 7.0 cps) (CH_3), 1.8 multiplet (CH_2), multiplet centered at 2.7 (NCH_2); infrared spectrum (film), 3.35 (s), 3.42 (m), 6.89 (w), 7.21 (w), 10.05 (w), 10.85 (w), 12.35 μ (m). The amount isolated was too small to characterize further.

The second compound, 3-methylquinuclidine, had a retention time of 52.5 min and formed a picrate, mp 227–229° (lit.[6] 227°): nmr ($CDCl_3$), δ 0.95 doublet (J = 7.0 cps) (CH_3), 1.16 multiplet (CH_2), 2.70 multiplet (NCH_2); infrared (film), 3.35 (s), 3.45 (m), 6.89 (w), 7.59 (w), 9.40 (w), 9.55 (w), 10.20 (w), 12.60 (w).

E. N-Chloro-2-methyl- and N-Chloro-3-methylpiperidines.—Irradiation of these compounds at 0° for 24 hr gave no bicyclic amines.

Alumina: Catalyst and Support. XXIX.[1] Dehydration of the Four Isomers of 1-Decalol over Aluminas

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Dehydrations of the four isomers of 1-decalol were carried out over various catalysts in a micropulse reactor and in a conventional flow-type reactor. The results obtained from these two techniques were in good agreement. On alumina, which was prepared from aluminum isopropoxide, the *trans* elimination was the preferred mode of reaction for all isomers. This preference ranged from 24:1 for *cis,trans*-1-decalol, to 3:1 for *trans,trans*-1-decalol. These dehydrations were pictured mechanistically as occurring preferentially between two alumina surfaces, in submicroscopical crevices, or pores in the catalyst particles. A basic site of the catalyst abstracts a proton from one side of the molecular plane; an acidic site removes a hydroxyl group from the other side. This explanation is in support of the concept of alumina acting as a "pseudo-solvent." Catalysts prepared by impregnation of pure alumina with sodium carbonate solution, or by precipitation from sodium or potassium aluminate, were less active for dehydration than pure alumina. In the presence of these catalysts the dehydration of the decalols was accompanied by the formation of 1-decalones and by the epimerization of the alcohols.

The ability of alumina to catalyze the dehydration of alcohols has been recognized since the 18th century and numerous studies have been carried out to determine the nature of the catalytic activity of this material.[3] Recent investigations from this laboratory have led, however, to the realization that alumina contains Lewis and possibly Brønsted acidic sites of variable number and strength and that the nature of the acidity depends upon the alkali content of the catalyst and its mode of preparation.[4]

While the effect of molecular structure on reactivity has been a powerful tool in the elucidation of the mechanism of homogeneous elimination reactions, this technique has been applied to a lesser degree in the study of heterogeneous reactions. Indeed, with a few exceptions, the stereochemistry of the alumina-catalyzed dehydration reaction has been largely ignored.

Pines and Pillai[5] have reported that the dehydration of menthol over this catalyst produced 2-menthene while the dehydration of neomenthol yielded 2- and 3-menthene in a 1:3 ratio. Both reaction products were found to contain small amounts of 1-menthene, which occurred as a primary dehydration product. The preferred formation of 2-menthene from menthol was interpreted as a clear indication of *trans* elimination proceeding through the axial conformation of the alcohol. These results correspond closely to those obtained from the E2 elimination of hydrogen chloride from menthyl and neomenthyl chloride.[6,7]

One of the processes suggested by Pines and Pillai for the stereospecific elimination was that the hydroxyl group of the alcohol was attacked by an intrinsic acidic site on the catalyst; a basic site was then left to abstract a proton from the opposite side of the molecular plane. In this way a normal *trans*-diaxial elimination could be effected. Such a mechanism would require two alumina surfaces and thus the dehydration might occur in a crevice, pore, or fault in the alumina particle.

The formation of 1,4-epoxycyclohexene from *trans*-1,4-cyclohexanediol,[8] tricyclene from 2-*exo*-bornanol,[9] and nortricyclene from 2-*exo*-norbornanol[9] have been described as occurring by a similar process in which alumina behaves as a "pseudo-solvent."

Lippens[10] studied the texture of the catalytically active aluminas by means of diffraction and adsorption techniques. It was concluded that the structure of η-alumina formed from bayerite consisted of lamallae with an average thickness of about 15 A with a separa-

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(1) (a) For paper XXVIII, see C. T. Goetschel and H. Pines, *J. Org. Chem.*, **30**, 3548 (1965). (b) Paper 8 in the series on dehydration of alcohols. For previous papers, see ref 8; *Chem. Ind.* (London), 984 (1963); *J. Am. Chem. Soc.*, **84**, 3934 (1962); **83**, 3274 (1961); ref 5; ref. 18; *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(2) Taken from a Ph.D. dissertation submitted to the Graduate School, June 1965. Monsanto Co. Fellow, 1963–1964. This research was supported in part by the Atomic Energy Commission, Contract AT(11-1)-1096.

(3) M. E. Winfield in "Catalysis," Vol. VII, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp 93–182.

(4) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

(5) H. Pines and C. N. Pillai, *ibid.*, **83**, 3270 (1961).

(6) W. Huckel, W. Tappe, and G. Legutke, *Ann.*, **543**, 191 (1940).

(7) E. D. Hughes, C. K. Ingold, and J. B. Rose, *J. Chem. Soc.*, 3839 (1953).

(8) J. Manassen and H. Pines, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, **2**, 845 (1965).

(9) K. Watanabe, C. N. Pillai, and H. Pines, *J. Am. Chem. Soc.*, **84**, 3934 (1962).

(10) B. C. Lippens, Doctoral Thesis, University of Delft, 1961.

TABLE 1

COMPOSITION OF THE PRODUCTS FROM 1-DECALOL DEHYDRATIONS *vs.* TEMPERATURE STUDIES AT THE LOWEST CONVERSIONS

Conditions			% conversion to		Composition of octalins, mole %				
Alcohol[a]	Catalyst[b]	Temp, °C	Octalin	Others[c]	*trans*-1,2-	*trans*-2,3-	1,9-	*cis*-1,2-	9,10-
c,c-1-OH	Al_2O_3 A	225	43.5	0	0.9		89.2	4.8	5.1
c,c-1-OH	Al_2O_3 B	268	30.5	2.2	5.8		72.0	16.0	6.2
c,c-1-OH	Al_2O_3 H	310	4.1	15.3	12.7		63.9	23.4	
c,t-1-OH	Al_2O_3 A	243	40.3	0			3.8	91.5	4.4
c,t-1-OH	Al_2O_3 B	269	18.8	2.2			9.7	90.3	
c,t-1-OH	Al_2O_3 H	310	6.0	3.6	13.2		10.4	76.4	
t,c-1-OH	Al_2O_3 A	225	32.9	0	25.2	2.7	67.5		4.6
t,c-1-OH	Al_2O_3 B	262	10.0	0	22.1		67.8		10.1
t,c-1-OH	Al_2O_3 H	340	8.5	1.1	28.6		60.3		11.1
t,t-1-OH	Al_2O_3 A	263	35.5	0	64.8	8.1	22.7		4.4
t,t-1-OH	Al_2O_3 B	269	9.6	0	50.8		49.2		
t,t-1-OH	Al_2O_3 H	322	1.3	0	27.8		72.2		

[a] *c* = *cis*, *t* = *trans*. Decalols were 10% in *t*-BuOH. Structures of the decalols are given in Chart I. [b] See text. All were 20–40 mesh; 15 mg of catalyst was used. [c] Composed of decalones and isomeric decalols. For the distribution of these compounds see Figure 1–4.

tion of 25 A. γ-Alumina prepared from gelatinous boehemite was reported to be composed of fibrillar shaped particles of 30 × 30 A. Both of these structures could account for the "pseudo-solvent" effect of alumina.

Schwab and Schwab-Agallides[11] have studied the competitive dehydration and dehydrogenation of ethanol over α- and γ-alumina and proposed that dehydration occurs mostly in the pores of the catalyst, while dehydrogenation takes place on the surface of the alumina. These conclusions were based on the observation that the dehydrating activity of the catalyst diminished when heated to high temperatures where healing of the irregularities in the crystal lattice occurred.

The kinetic data obtained by Kochloefl, *et al.*,[12] on the rate constants and activation energies of dehydration of alkylcyclohexanols over γ-alumina can also be interpreted by a *trans*-elimination reaction.

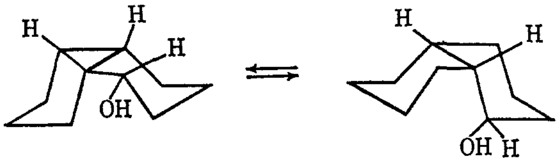
In order to clarify further the mechanism of dehydration over alumina, 1-decalol was allowed to react on a number of catalysts. This alcohol was chosen because it posesses four stereoisomers; thus, the catalyst could be presented with four different compounds differing only in their stereochemistry. In this way effects other than those imposed by the shape of the alcohols were minimized. It was hoped that in the dehydration process these stereochemical differences would direct the reaction in such a way that the concept of alumina behaving as a "pseudo-solvent" could either be supported or disproved. Furthermore, this system, unlike menthol, is well suited for the detection of 1,3-elimination products. In the menthol–neomenthol system 1-menthene was proposed to be such a product, but this compound is also a stable carbonium ion product which casts some doubt as to its origin. This need not be the case with the 1-decalol isomers. Also, the ridigidity of the *trans*-1-decalols eliminates some of the uncertainty as to the reactive conformation of the alcohol.

Results

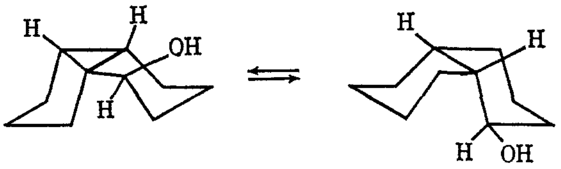
I. The Effect of Temperature on Dehydration of 1-Decalols over Alumina Catalysts.

—The alcohols used in this investigation and their respective structures are given in Chart I. The isomeric octalins are represented in Chart II. The following aluminas were used as catalysts: alumina A, prepared from aluminum isopropoxide; alumina B, impregnated with sodium carbonate and contained 0.4 wt % Na^+; and alumina H, obtained from Harshaw Co. and containing 0.37 wt % of Na^+. The relative catalytic intrinsic acidities of the aluminas which are A > B > H were determined by the extent

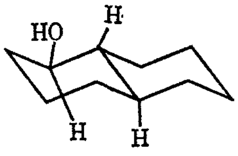
CHART I
STRUCTURES OF THE FOUR ISOMERS OF 1-DECALOL



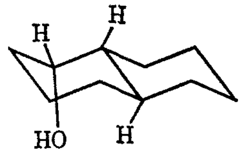
cis,cis-1-decalol (1)



cis,trans-1-decalol (2)

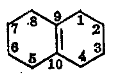


trans,cis-1-decalol (3)

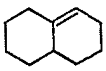


trans,trans-1-decalol (4)

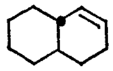
CHART II
STRUCTURES OF THE SIX ISOMERS OF OCTALIN



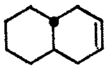
9,10-octalin (5)



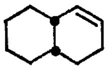
1,9-octalin (6)



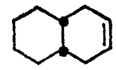
trans-1,2-octalin (7)



trans-2,3-octalin (8)



cis-1,2-octalin (9)



cis-2,3-octalin (10)

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(11) G. M. Schwab and E. Schwab-Agallides, *J. Am. Chem. Soc.*, **71**, 1806 (1949).

(12) K. Kochloefl, M. Kraus, C. Chin-Shen, L. Beranek, and V. Bazant, *Collection Czech. Chem. Commun.*, **27**, 1199 (1962).

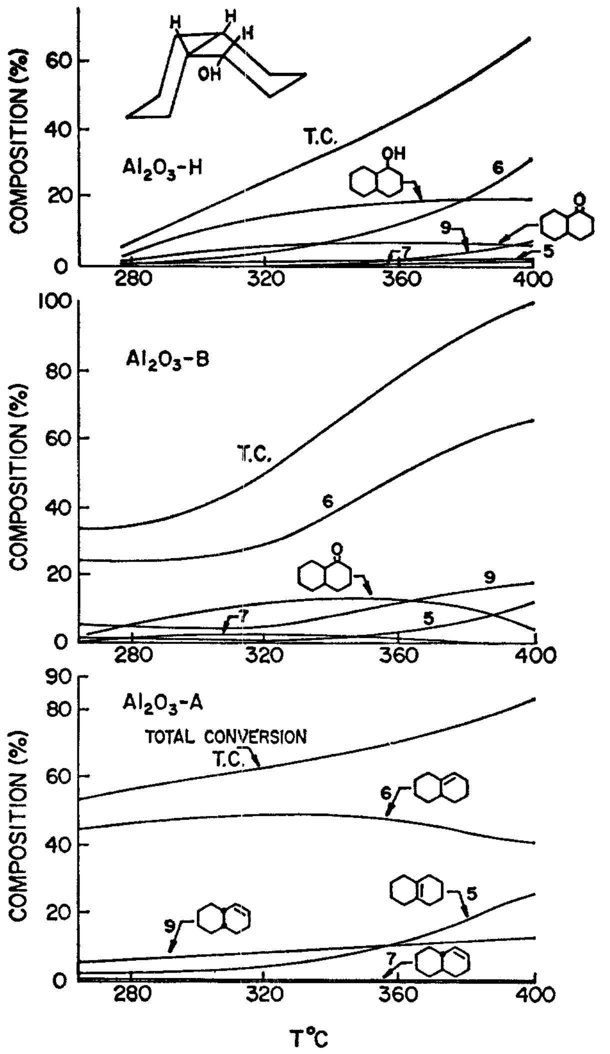

Figure 1.—The effect of temperature upon the dehydration of *cis,cis*-1-decalol.

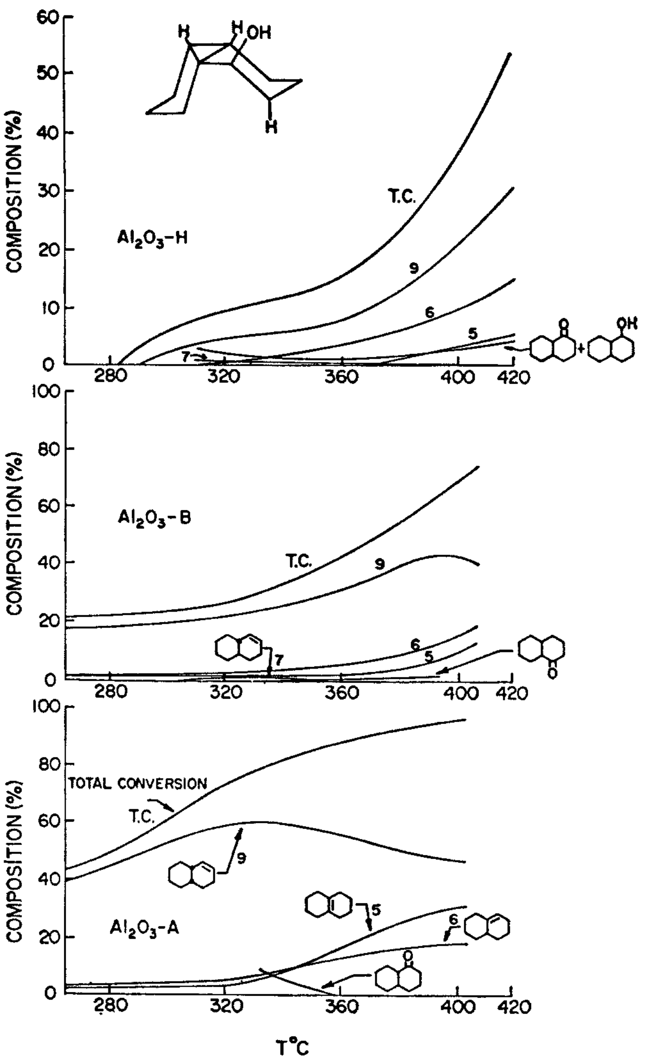

Figure 2.—The effect of temperature upon the dehydration of *cis,trans*-1-decalol.

and depth of the isomerization of 3,3-dimethylbutene when passed over these catalysts.[4]

The effect of temperature upon the dehydration of the 1-decalols over the various aluminas was studied in a pulse reactor at 20–40° temperature intervals and ranging from 225° to at least 400°. In this way changes in the catalyst caused by heating and usage could be observed. Fifteen milligrams of catalyst of 20–40 mesh size was used in most of the experiments.

The data given in Table I shows the product distribution for the dehydrations of all four decalols over the three catalysts at temperatures which caused low conversion and therefore minimum secondary reactions. It is apparent from a study of the temperature *vs.* per cent composition plots, Figures 1–4, that the most acidic catalyst A is the more active for dehydration. However, this catalyst caused the formation, at high temperature, of the more stable 9,10-octalin. This effect was not unexpected since the strong isomerization ability of this catalyst at high temperatures was noted previously.[4]

While isomerizations did not seriously complicate the reactions carried out over the less acidic catalysts, dehydrogenation processes resulting in the formation of decalones and epimerized alcohols were found to occur in the dehydrations of the *cis*-1-decalols over alumina B and H, which contain sodium ions.

It was observed previously that while the extent of dehydration decreases with a decrease in the "acidity" of the catalyst, the dehydrogenation reactions, as evidenced by ketone formation and epimerization, show no such dependence.[8] The data in Figures 2 and 3 clearly illustrate this phenomenon. On the "acidic" alumina A dehydrogenation could not compete successfully with dehydration. However, when 0.4% sodium ions were present in the catalyst as in alumina B, dehydrogenation became important; over alumina H this reaction acquired even more importance. The formation of *trans*-1,2-octalin from the *cis*-1-decalols, Figures 1 and 2, can be explained by the epimerization of the *cis*-1-decalols to *trans*-1-decalols, *via* a decalone intermediate,[8] followed by dehydration to form the *trans* olefin.

1. *cis,cis*-**1-Decalol.**—At all temperatures reactions of this alcohol over all three catalysts were found to produce 1,9-octalin in up to 20:1 preference over the *cis*-1,2-octalin (Figure 1, Table I).

2. *cis,trans*-**1-Decalol.**—The dehydrations of the title alcohol over the three aluminas studied gave results with regard to isomerization and dehydration similar to those observed for its epimer (Figure 2). However, in these reactions *cis*-1,2-octalin was the major product in up to a 24:1 excess over the more stable 1,9-octalin (Table I).

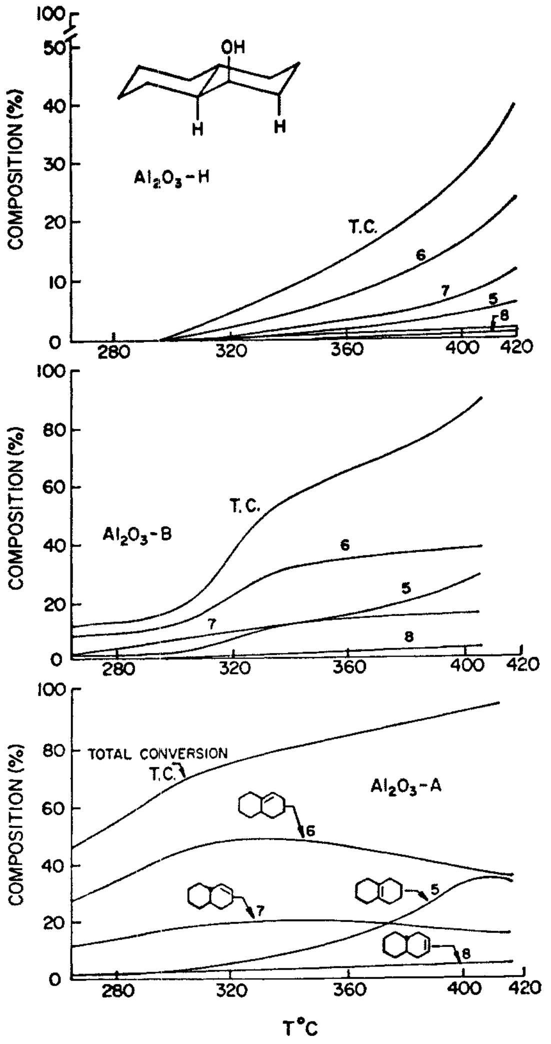

Figure 3.—The effect of temperature upon the dehydration of *trans,cis*-1-decalol.

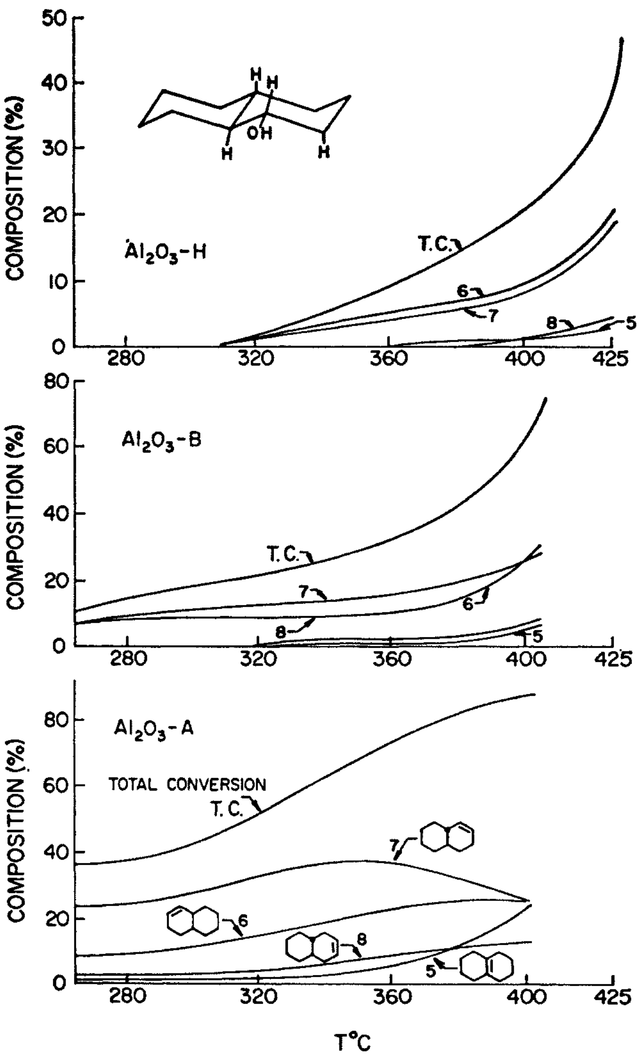

Figure 4.—The effect of temperature upon the dehydration of *trans,trans*-1-decalol.

3. ***trans,cis*-1-Decalol.**—Unlike any other 1-decalol, this isomer showed little tendency for a loss of specificity in the dehydration reaction with decreasing "acidity" of the catalysts. Rather, a 3:1 preference for elimination to the ring fusion carbon atom to produce 1,9-octalin was observed on all the aluminas (Figure 3, Table I).

The presence of *trans*-2,3-octalin was detected in the reaction products obtained over all the catalysts (Figure 3). This compound cannot result from a normal 1,2 elimination of water nor can its occurrence be ascribed to a carbonium ion rearrangement, especially on the less acidic catalysts, since there is little 9,10-octalin among the products. At equilibrium at 175° 9,10-octalin is favored over *trans*-2,3-octalin by a ratio of 25:1.[13]

4. ***trans,trans*-1-Decalol.**—This isomer was unique in that the same octalin was not the major product on all three catalysts. Dehydrations of *trans,trans*-1-decalol over the highly "acidic" alumina A produced the less substituted *trans*-1,2-octalin in a 3:1 preference over 1,9-octalin; this ratio is the opposite to that observed for the epimeric *trans,cis*-1-decalol. Upon reaction of the *trans,trans* alcohol over the moderately "acidic" sodium-impregnated alumina B, this ratio fell to about 1.5. Over the least "acidic" catalyst, Harshaw alumina, the formation of 1,9-octalin was preferred by up to 3:1 over *trans*-1,2 isomer (Figure 4). That no such trend was observed for any other alcohol is clearly shown by the data in Table I.

It was also observed that this alcohol produced about twice as much *trans*-2,3-octalin as did *trans,cis*-1-decalol.

5. **Catalyst Changes.**—In the study of the effect of temperature on the 1-decalol dehydration reactions it was noted that after use at high temperatures there were changes in the nature of the catalysts. With alumina prepared from aluminum isopropoxide these effects were minimal. After the catalyst had been used at 400° or higher, subsequent reactions at low temperatures showed that its dehydration activity increased about 5%. Also, the isomerization activity, as indicated by the 9,10-octalin formation, increased considerably. However, after prolonged use at 275° such effects were barely discernible.

The sodium-modified catalysts showed a much more marked change after use at high temperatures. The extent of dehydration of *cis,cis*-1-decalol over alumina B increased about 70% at 310°, after the catalyst had been used at 400°. On the other hand, the dehydrogenation ability of this material decreased tenfold at the same time. Similar effects were observed over alumina H.

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[13] A. W. Weitkamp, private communication.

TABLE II

COMPOSITION OF THE OCTALINS RESULTING FROM THE DEHYDRATION OF 1-DECALOLS OVER VARIABLE AMOUNTS OF ALUMINA[a] AT 275°

Alcohol[b]	Catalyst, mg	Octalins formed, mole % *trans*-1,2-	*trans*-2,3-	1,9-	*cis*-1,2-	9,10-	Conversion to octalin, %
c,c-1-OH	2			84.7	9.9	5.4	15.2
c,c-1-OH	5			83.8	10.8	5.4	23.7
c,c-1-OH	10	0.5		85.3	10.5	4.2	39.0
c,c-1-OH	100	0.8		78.2	8.6	12.2	97.6
c,c-1-OH	200	1.0		71.8	6.5	20.7	100
c,c-1-OH	1000	3.7	3.4	23.4	5.6	63.7	100
c,t-1-OH	2			5.2	94.8		8.2
c,t-1-OH	5	1.0		6.3	88.0	4.7	14.9
c,t-1-OH	10			5.8	89.1	5.0	27.3
c,t-1-OH	100			7.4	84.8	8.0	96.2
c,t-1-OH	200	0.1		6.2	79.6	14.1	100
c,t-1-OH	1000	4.0	3.8	18.2	5.8	68.2	100
t,c-1-OH	2	23.4	4.4	57.4		14.8	8.7
t,c-1-OH	5	22.6	2.7	60.7		14.0	17.0
t,c-1-OH	10	24.1	1.8	62.9		11.2	33.0
t,c-1-OH	100	26.1	2.3	60.8		10.8	98.5
t,c-1-OH	200	22.3	3.9	56.7		17.1	100
t,c-1-OH	10000	4.6	5.0	25.5		64.9	100
t,t-1-OH	2	63.1	12.1	24.8			4.3
t,t-1-OH	5	61.6	11.8	23.3		3.3	12.5
t,t-1-OH	10	60.3	11.1	24.4		4.2	21.1
t,t-1-OH	100	48.7	16.6	24.0		10.7	96.2
t,t-1-OH	200	38.2	21.0	22.7		18.1	100
t,t-1-OH	1000	4.1	3.7	25.2		66.9	100

[a] Al_2O_3 A prepared from aluminum isopropoxide, 20–40 mesh. [b] *c* = *cis*, *t* = *trans*. Structures are given in Chart I. The 1-decalols were 10% solutions in *t*-butyl alcohol.

The increased dehydration and isomerization activity of the catalysts can be attributed to the formation of new or stronger acidic sites by the effect of heating or by the formation of carbonaceous deposits. The decreased dehydrogenation ability of the sodium modified catalysts could indicate that the sites responsible for decalone formation are destroyed by heating to 400°. An alternative explanation would be that these sites are selectively deactivated by the formation of carbonaceous deposits at high temperatures.

II. Determination of the Initial Reaction Products.—While the study of the effect of temperature upon the dehydration of the 1-decalols gave strong indications as to the nature of the initial reaction products, it was deemed necessary to carry out a series of reactions in which the amount of catalyst was the only variable (Table II). In this way plots of the olefin composition *vs.* per cent conversion could be made. Extrapolation of plots to zero conversion yielded the composition of the initial reaction products (Table III). These reactions were carried out over alumina A at 275° with amounts of catalyst ranging from 2 to 100 mg. The primary reaction products under these conditions were similar to those obtained at the temperature of lowest conversion (Table I). The increase in the amount of catalyst used from 2 to 100 mg caused the conversion to rise from less than 10 to 95% there was little variation in the product distribution. Only when 200 mg of catalyst was used did extensive readsorption and isomerization take place. With 1.0 g of catalyst nearly identical products were obtained from each decalol, indicating that equilibrium was reached (Table II).

TABLE III

COMPOSITION OF OCTALINS AT ZERO CONVERSION FROM THE DEHYDRATION OF 1-DECALOLS OVER ALUMINA A AT 275°

Alcohol[a]	Composition of octalins,[b] % **5**	**6**	**7**	**8**	**9**
c,c-1-OH (**1**)	6.4	85.5			8.1
c,t-1-OH (**2**)	3.1	5.6			91.3
t,c-1-OH (**3**)	16.5	53.6	24.4	5.5	
t,t-1-OH$_6$ (**4**)		24.8	63.1	12.1	

[a] Structures of the alcohols are given in Chart I. [b] The nomenclature of the octalins is given in Chart II. [c] At 4.3% conversion.

The data in Tables II and III indicate that both 9,10- and *trans*-2,3-octalin are initial dehydration products of *trans,cis*-1-decalol. The same seems to be true for the formation of *trans*-2,3-octalin from *trans,trans*-1-decalol.

III. Flow-Type Reactions.—Since nearly all of the data in the literature on the dehydrations of alcohols over alumina have been obtained through the use of flow reactions, several reactions of this type were carried out for comparison with the micropulse reactions. It was found that the data obtained from the reactions of 10% *t*-butyl alcohol solutions of the 1-decalols in a vertical flow reactor employing 100 mg of alumina H at 270° closely approximated those obtained with the microreactor at similar conditions (Table IV).

IV. Decalone Formation.—It was shown previously[3] that in the presence of ketones alumina-catalyzed epimerizations of alcohols can occur under dehydration conditions. The epimerization process was described as proceeding *via* a ketone intermediate.

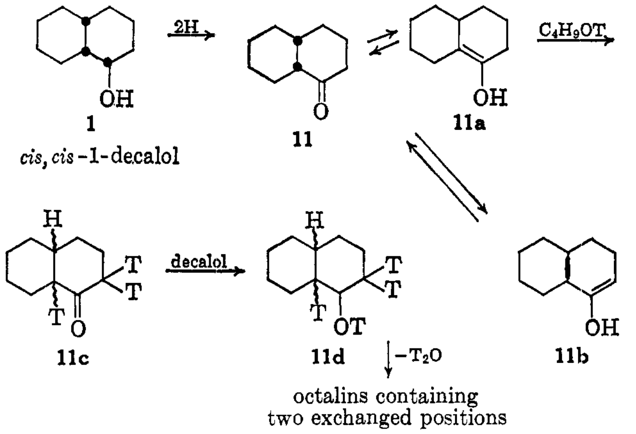
The extent to which such an epimerization accompanied the normal dehydration reaction was tested by carrying out flow-type reactions in which the *t*-butyl alcohol solvent was marked with tritium on the hy-

TABLE IV

COMPOSITION OF THE PRODUCTS OF DEHYDRATIONS OF 1-DECALOLS OVER 100 MG OF ALUMINA[a] IN A FLOW-TYPE REACTOR AT 270°

	c,c-1-OH (**1**)[b]		*c,t*-1-OH[c] (**2**)[b]		*t,c*-1-OH (**3**)[b]	*t,t*-1-OH (**4**)[b]	
	Hlsv[d]						
Products	100	185	50	100	100	50	100
Octalins,[e] mole %							
trans-1,2 (**7**)			0.9	0.6	13.6	26.6	10.8
trans-2,3 (**8**)					2.4	5.0	1.8
1,9 (**6**)	86.0	25.1	10.3	9.9	43.3	14.3	5.6
cis-1,2 (**9**)		5.7	46.4	40.5			
9,10 (**5**)	4.7	3.9	11.5	4.7	14.1	0.9	
Alcohols,[b] mole %							
c,c-1-OH	9.2	59.7	1.2				
c,t-1-OH		2.9	28.6	42.2			
t,c-1-OH					26.6		
t,t-1-OH		2.6	1.1	2.1		53.2	81.7
Conversion to octalins, %	90.8	34.7	69.1	55.7	73.4	46.8	18.2

[a] Al_2O_3 A, prepared from aluminum isopropoxide, 20–40 mesh. [b] *c* = *cis*, *t* = *trans*. Structural formulas are given in Chart I. [c] Contained 10% *cis,cis*-1-decalol. [d] All decalols were 10% solutions in *t*-BuOH. Hourly liquid space velocity (hlsv) = volume of liquid passed per volume of catalyst per hour. [e] Structures are given in Chart II.



droxyl group. Hence, if a decalone was present, through its enol form it would exchange protons for tritium from the solvent. Following reduction to the 1-decalol and subsequent dehydration, the resulting octalin would contain at least two atoms of tritium.

A comparison of the specific activity of the product and the solvent gave the extent of decalone participation in the dehydration (Table V). It was assumed that the exchange reaction proceeded much faster than the dehydration. Also, the dilution of the solvent with protons was ignored since 10% solutions of the decalols were used.

V. Relative Reactivity of the 1-Decalols. 1. Competitive Reactions.—A 10% *t*-butyl alcohol solution containing equal amounts of all four 1-decalol isomers reacted over alumina A and alumina B at various temperatures in the microreactor. Analysis of the distribution of the unreacted alcohols indicated the reactivity order: *cis,cis* > *trans,cis* > *cis,trans* > *trans,trans*. The data in Table VI for temperatures near 400° best illustrate this effect.

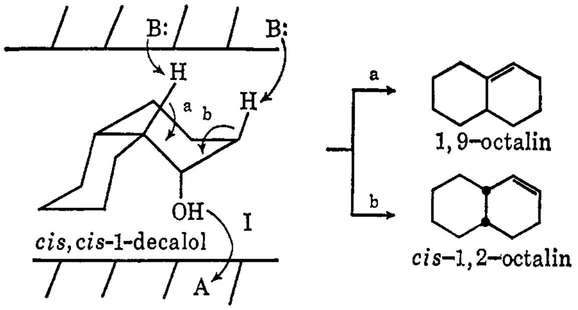
2. Variation of the Amount of Catalyst in the Microreactor.—Catalytic dehydrations of all four 1-decalol isomers were carried out over 2, 5, 10, and 15 mg of alumina A at three temperatures: 250, 275, and 350°. It was found that plots of per cent conversion *vs.* the amount of catalyst frequently produced straight lines. The slopes of these lines appear in Table VII.

Discussion

I. 1,2 Eliminations over Alumina Prepared from Aluminum Isopropoxide.—The 19:1 preponderance of 1,9-octalin over *cis*-1,2-octalin found upon the dehydration of *cis,cis*-1-decalol over alumina A at 225° is a clear indication of the preference for *trans* elimination in this system (Table I, Figure 1).

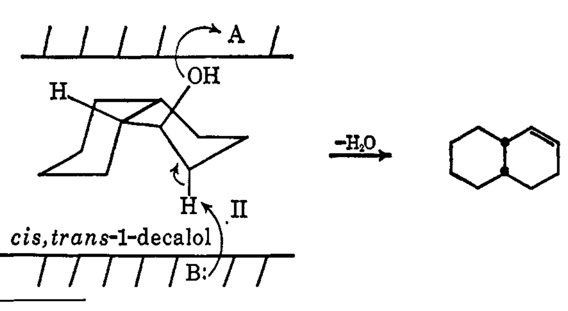
A similar preponderance of the more substituted olefin was reported in the dehydration of neomenthol,[5] the E2 dehydrochlorination of neomenthyl chloride,[6] and the Hofmann elimination of neomenthyl trimethylammonium hydroxide.[14] In all these reactions the less acidic tertiary hydrogen atom was removed.

Pines and co-workers[5,9] have proposed that *trans* eliminations on alumina can be explained by the removal of the hydroxyl group from one side of the molecule by an acidic site; a basic site then must abstract a proton from the opposite side of the molecular plane. It was also suggested that such a process could occur between two catalyst surfaces, possibly in a pore or crevice of molecular dimensions in the alumina particle. Following this idea the elimination reactions of *cis,cis*-1-decalol can be pictured by structure I.



Other reaction schemes and the question of concerted *vs.* stepwise elimination will be discussed later.

The dehydration of *cis,trans*-1-decalol supports the *trans*-diaxial elimination scheme proposed above. Unlike its epimer, this alcohol offers only one path for *trans* elimination, and that will lead to the formation of *cis*-1,2-octalin. The more stable 1,9 isomer can only form by a *cis* elimination. The observation that the *cis*-1,2 isomer is formed in up to 24-fold excess over the more thermodynamically stable 1,9-octalin clearly shows the preference of the dehydration to proceed *via* a *trans* elimination (Table I, Figure 2). Structure II, which illustrates this process being carried out between two alumina surfaces, could readily explain the observed data.



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[14] N. L. McNivean and J. Read, *J. Chem. Soc.*, 158 (1952).

TABLE V

DETERMINATION OF THE EXTENT OF THE PARTICIPATION OF KETONE INTERMEDIATES IN THE DEHYDRATION OF 1-DECALOL ON ALUMINA

Alcohol[a]	*c,c*-1-OH (**1**)	*t,c*-1-OH (**3**)	*t,t*-1-OH (**4**)	*c,c*-1-OH (**1**)	*t,t*-1-OH[b] (**4**)	*t,t*-1-OH[c] (**4**)
Alumina	A	A	A	H	H	H
Temp, °C	270	270	270	354	354	354
Hlsv[d]	185	100	50	20	10	10
Conversion to octalin, mole %	66.4	85.2	76.8	74.5	69.4	61.0
Composition of octalins, %[e]						
trans-1,2- (**7**)		27.3	69.4	0.6	53.7	49.2
trans-2,3- (**8**)			4.7	1.4	8.1	9.2
1,9- (**6**)	91.6	68.7	25.0	72.5	33.7	36.6
cis-1,2- (**9**)	6.0		0.9	21.4		
9,10- (**5**)	2.4	4.0		4.1	4.5	5.0
Activity of BuOH, counts/min per mole	80,030	80,030	80,030	72,250	72,250	72,250
Activity of octalin, counts/min per mole	425	726	1033	5214	10,447	15,882
Extent of ketone participation, %[f]	0.27	0.48	0.64	3.6	7.3	10.9

[a] The structures of the alcohols are given in Chart I. [b] The product contained 1.8% *trans*-1-decalone. [c] Feed contained 92% *trans,-trans*-1-decalol and 8% *trans*-1-decalone. The recovered product contained 8.5% *cis*- and *trans*-1-decalone in a 1:3 ratio plus 1.5% *trans,cis*-1-decalol. [d] Hlsv = hourly liquid space velocity, volume of feed per hour per volume of catalyst. [e] The structures are given in Chart II. [f] Calculated on the basis of two exchangeable positions per octalin molecule.

TABLE VI

COMPOSITION OF THE UNREACTED ALCOHOLS OBTAINED FROM THE COMPETITIVE DEHYDRATION OF AN EQUAL MOLAR SOLUTION OF ALL FOUR 1-DECALOL ISOMERS OVER 15 MG OF ALUMINA

	Temp, °C	
	402	408
	Catalyst	
	Alumina A	Alumina B
Unreacted 1-decalols,[a] mole %		
trans,trans- (**4**)	47.0	45.1
cis,trans- (**2**)	26.6	22.8
trans,cis- (**3**)	17.9	22.0
cis,cis- (**1**)	8.6	10.1
Conversion to octalins, %	81.0	72.6

[a] The structures of 1-decalols are given in Chart I.

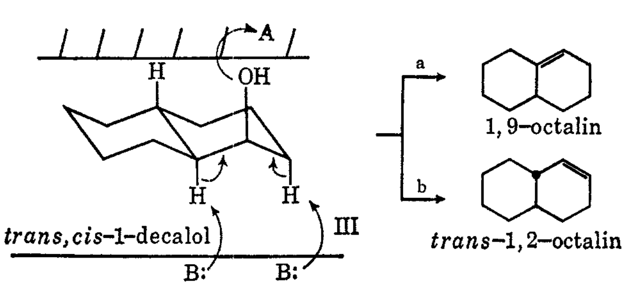
TABLE VII

SLOPES OF THE PLOTS OF 1-DECALOL CONVERSION TO OCTALIN *vs.* AMOUNT OF ALUMINA A USED

	Slopes, % conversion *vs.* amounts of catalyst[b]		
	Temp, °C		
1-Decalol[a]	250	275	350
cis,cis- (**4**)	1.34 (1.88)	1.33 (1.88)	2.12 (2.90)
trans-cis- (**3**)	0.80 (1.13)	1.00 (1.41)	1.70 (2.40)
cis,trans- (**2**)	0.80 (1.13)	0.90 (1.27)	1.66 (2.34)
trans,trans- (**4**)	0.71 (1.00)	0.65 (0.92)	1.38 (1.94)

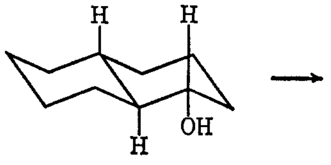
[a] The structures of 1-decalols are given in Chart I. [b] Data in parantheses are normalized on the basis of the slope of the *trans,trans*-1-decalol dehydration at 250°.

As with the *cis,cis* isomer, *trans,cis*-1-decalol with its hydroxyl group locked in an axial configuration presents the catalyst with two paths for *trans*-diaxial elimination. In agreement with the previous observations the production of the more substituted olefin, 1,9-octalin, was favored over the *trans*-1,2 isomer although in this reaction over alumina A the ratio was only 2.7:1 at 225° (Table I, Figure 3).

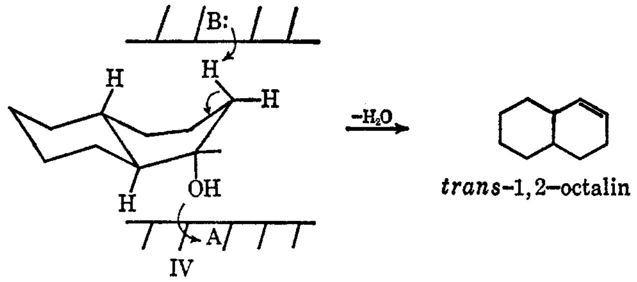


Comparison of structures I and III does not reveal any large stereochemical differences which might explain why the formation of 1,9-octalin is favored more from the *cis,cis*- than the *trans,cis*-1-decalol. This observation can probably be better explained by the energetics of the *cis*- and *trans*-decalin system. It has been reported that *cis*-decalin is 0.52–8.23 kcal less stable than *trans*-decalin.[15] A similar situation should exist for the *cis*- and *trans*-1-decalols. Since the *cis* isomer has the highest ground-state energy, any process which destroys the ring-fusion isomerism and results in a common product should be more favored for the *cis* compound.

Dehydration of *trans,trans*-1-decalol over the "acidic" alumina A produced *trans*-,2-octalin and 1,9-octalin in about a 3:1 proportion (Table I, Figure 4). Unlike any other 1-decalol, this isomer offers no conventional route for *trans* elimination because its hydroxyl group is locked in an equatorial position. While ring "flips" with interconversion of axial and equatorial positions are not possible in the *trans*-decalin system, either one or both of the cyclohexane chair forms may be distorted to a boat form.[15] If such a distortion is carried out on *trans,trans*-1-decalol, as in structure IV, the "masthead" hydrogen on carbon 2 and the "gunwale" hydroxyl group become well oriented for *trans* elimi-



trans,trans-1-decalol



IV

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[15] W. G. Dauben, and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 23–30.

nation leading to the formation of *trans*-1,2-octalin. As before, structure IV illustrates how this reaction might proceed between two alumina surfaces.

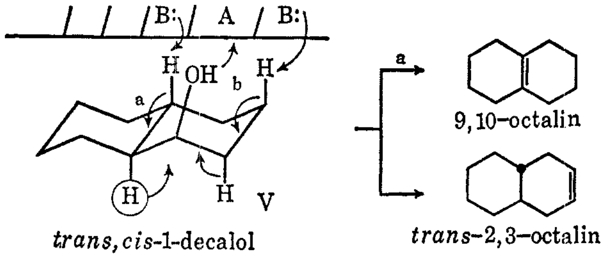
The formation of 1,9-octalin cannot be so easily rationalized. Imposing boat and twist boat forms on one or both of the cyclohexane rings does little to improve the orientation of the hydrogen atom on carbon 9 and the hydroxyl group for *trans* elimination. From the runs in tritiated *t*-butyl alcohol it is known that this compound does not arise from the epimeric *trans,cis*-1-decalol. The experimental data indicate that this compound is definitely a primary reaction product and as such its formation cannot be ascribed to a readsorption–isomerization process. It is thus probable that 1,9-octalin was produced by E1 elimination.

II. 1,3 Eliminations over Alumina Prepared from Aluminum Isopropoxide.—Unlike 1,2 eliminations which can only cause the formation of 1,9- and 1,2-octalins, 1,3 elimination can give rise to 9,10- and 2,3-octalins as primary reaction products.

Unfortunately, 9,10- and *cis*-2,3-octalin could not be completely resolved by gas chromatography. Inspection of Table III, however, shows that for dehydrations of the *cis*-1-decalol the combined peak of these compounds comprises only a few per cent of the primary products at 275°.

This analytical difficulty posed no problem in the analysis of the *trans*-1-decalol dehydration products. Table III shows that at 275° about 16% of the primary product of the dehydration of *trans,cis*-1-decalol was 9,10-octalin. While smaller amounts of this compound were found in the reactions at variable temperatures (Figure 3), it nevertheless seems that this compound is a primary dehydration product of this alcohol. Smaller amounts of *trans*-2,3-octalin, 2–5%, were also detected among the primary products of this reaction.

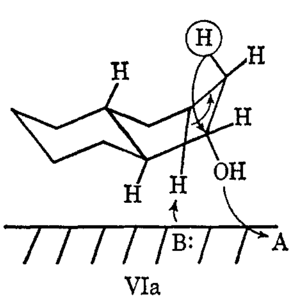
The formation of both of these olefins could be explained by the processes shown in structure V. In these reactions a basic site on the catalyst abstracts a γ-proton and an acidic site removes the hydroxyl group. The electron pair released from the carbon–hydrogen bond can perform a *trans* backside attack on the β-carbon and cause the *trans* migration on a hydride ion which aids in the displacement of the hydroxyl group. Such reactions could also proceed through hydronium ion bridged intermediates.



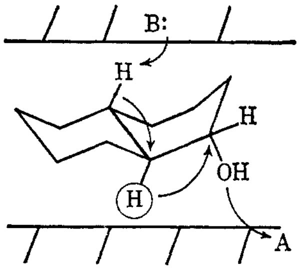
V

The formation of 1% 1-menthene as a primary product of the dehydration of menthol was explained by a similar argument.[5]

The dehydration of *trans,trans*-1-decalol at 275° supports this line of thought. The data in Tables II and III show that the dehydration of this alcohol produces little, if any, 9,10-octalin as a primary product. However, the other 1,3 elimination product, *trans*-2,3-octalin, comprises about 18% of the primary product. As shown in structure VIa, the formation of the *trans*-2,3 olefin can result from two favorable *trans* displacements. On the other hand, 9,10-octalin can form only by a *trans* displacement of a hydride ion followed by an unfavorable *cis* displacement of the "gunwale" hydroxyl group Xb.



VIa



VIb

III. Reactivity of the 1-Decalols.—It was observed that the competitive reactions (Table VI), studies of conversion *vs.* amount of catalyst (Table II), and flow reactions (Table IV) all gave the same qualitative trend for reactivities of the 1-decalols.

The results obtained from the competitive reactions suffer from complications imposed by the difference of adsorption of the various 1-decalol isomers upon the active sites on the catalyst. However, at 400°, where such effects should be minimal, a distinct trend in the reactivities of the alcohols became apparent. The decreasing order of reactivity was *cis,cis*- > *trans,cis*- > *cis, trans*- > *trans,trans*-1-decalol.

Unlike flow reactions, the kinetics of pulse-type reactions are difficult to interpret since equilibrium conditions between catalyst and substrate may not be established with the latter technique. Furthermore, the direct linkage of the reactor and analytical instrument forbids large variations in the flow rate of the alcohol feed over the catalyst. In this study variations in the amount of catalyst were made while holding the temperature constant. However, such a procedure is not identical with changing the reaction time. In spite of these objections, the slopes of conversion *vs.* amount of catalyst plots are of some value as they indicate a small but definite trend, the 1-decalol reactivities being identical with that observed by other methods (Table VII).

The flow reactions run at 270° at the same contact time show a clear difference in the reactivities of the 1-decalol isomers (Table IV). The order of reactivity was clearly that found previously.

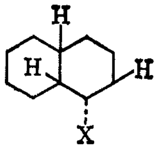
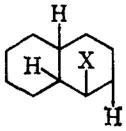
In order to undergo *trans*-diaxial elimination, *cis,*-*cis*-1-decalol must flip to its least stable conformation with its hydroxyl group in an axial position. In spite of this, the highly preferential formation of 1,9-octalin with subsequent loss of the *cis* ring fusion may provide sufficient driving force to make this alcohol the most reactive 1-decalol isomer.

The position of *trans,cis*-1-decalol as the second most reactive alcohol in this series may be associated with its less preferential formation of the 1,9-octalin and the smaller energy difference between the *trans* ring structure and this olefin.

Unlike *cis,cis* and the *trans,cis* isomer, *cis,trans*-1-decalol upon dehydration produces almost exclusively *cis*-1,2-octalin. Formation of this compound can do little to remove any interactions associated with the

Table VIII

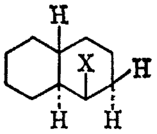
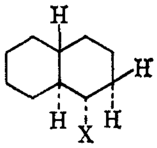
Comparison of the Products Obtained from the Dehydrations of *cis*-1-Decalols over Alumina with Those Received from the Homogeneous Eliminations of Their Derivatives

Radical	Substituent X	Conditions of reaction (kinetic order)	Product composition, mole %			
			Octalins			
			1,9-	*cis*-1,2-	9,10-	*trans*-1,2-
cis,cis-1-Decalyl	Xanthate[a]	Pyrolysis	10	90		
	OTs[a]	EtOH-NaOEt (E2)	100			
	OTs[b]	MeOH (E1)	88		12	
	OTs[b]	EtOH (E1)	75	25		
	OH	Al_2O_3, 225°	89	5	5	1
cis,trans-1-Decalyl						
	OH	Al_2O_3, 243°	4	92	4	

[a] Reference 6. [b] Reference 16.

Table IX

Comparison of the Products Obtained from the Dehydration of *trans*-1-Decalols over Alumina with Those Received from the Homogeneous Eliminations of Their Derivatives

Radical	Substituent X	Conditions of reaction (kinetic order)	Product composition, mole %			
			Octalins			
			1,9-	*trans*-1,2-	*trans*-2,3-	9,10-
trans,cis-1-Decalyl						
	Xanthate[a]	Pyrolysis	20	80		
	OTs[a]	EtOH-NaOEt (E2)	10	90		
	OTs[b]	MeOH (E1)	57	1		18
	OTs[b]	EtOH (E1)	75	25		
	OH	Al_2O_3, 275°	54	24	6	16
trans,trans-1-Decalyl						
	Xanthate[a]	Pyrolysis	80	20		
	OTs[b]	EtOH-NaOEt (E2)		100		
	OTs[b]	MeOH (E1)	29	61		10
	OH	Al_2O_3, 275°	24	63	12	

[a] Reference 6. [b] Reference 16.

ring fusion and the olefinic product is less stable thermodynamically than the 1,9 isomer.

The low relative reactivity of *trans,trans*-1-decalol can be rationalized in light of the unfavorable geometry of this compound for *trans* elimination.

IV. Comparison with Homogeneous Reactions.—The pyrolysis of xanthates has been established as proceeding *via* a concerted *cis* elimination.[6] The data in Tables VIII and IX for the pyrolysis of the methyl xanthates of the 1-decalols are what would be expected if such a mechanism were in effect. Because of the wide differences between these results and those obtained by alumina-catalyzed dehydrations, it is obvious that a *trans* elimination occurred over alumina.

As shown in Table VIII, the dehydration of *cis,cis*-1-decalol could be interpreted as occurring by either an E1- or E2-type mechanism because the solvolysis of the *p*-toluenesulfonate of this compound gives roughly the same products under E1 or E2 conditions.

We were unable to find any report of the solvolyses of derivatives of *cis,trans*-1-decalol. Possibly the best models for this system are the derivatives of menthol since they too have an alkyl substituent adjacent to the functional group in a *trans* orientation. It is shown in Table X that the E1 reactions of these compounds produce predominantly the more substituted olefin, 3-menthene, while the concerted eliminations form the less substituted 2-menthene. The dehydration of *cis,trans*-1-decalol clearly resembles more closely the concerted process.

trans,cis-1-Decalol resembles both *cis,cis*-1-decalol and neomenthyl compounds in that it offers two routes for *trans* elimination. However, unlike these materials the concerted elimination of *trans,cis*-1-decalyl *p*-toluenesulfonate produced the less substituted olefin, *trans*-1,2-octalin, in 9:1 preference over 1,9-octalin[16] (Table IX). Hückel, *et al.*,[16] have explained this result by a steric argument in which they claim the more acidic secondary hydrogen atom is more accessible to attack by an alkoxide ion than the hydrogen atom at the bridgehead. If this steric argument is valid, the effect of the subtle differences between this system and the neomenthyl and *cis,cis*-1-decalyl systems is remarkable inasmuch as in the former system the less acidic hydrogen is also sterically hindered owing to the interaction of the two methyl groups.

Although the ratios of 1,9- and 1,2-octalins produced from the dehydration of *trans,cis*- and *trans,trans*-1-decalol resemble more the products of E1 elimination (Table IX), nevertheless the formation of 9,10- and 2,3-octalins as primary products of dehydration, and not

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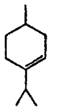
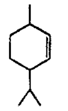
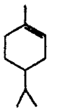
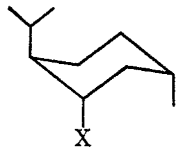
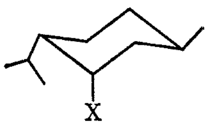
(16) W. Hückel, D. Maucher, O. Fechtig, J. Kurz, M. Heinzel, and A. Hubele, *Ann.*, **645**, 115 (1961).

TABLE X

COMPARISON OF THE MENTHENE PRODUCTS OBTAINED FROM THE DEHYDRATIONS OF MENTHOL AND NEOMENTHAOL OVER ALUMINA WITH HOMOGENEOUS ELIMINATIONS OF THEIR DERIVATIVES

Radical	Substituent X	Conditions of reaction (kinetic order)	Menthenes, mole %		
					
			3-	2-	1-
Menthyl 	Cl[a]	EtOH-H_2O, NaOAc (pseudo E1)	47	22	
	OTs[b]	HOAc (E1)	Major	Minor	
	OTs[c]	EtOH (E1)	70	30	
	Cl[c]	EtOH-NaOEt (E2)		100	
	OH[d]	Al_2O_3	10	90	<2
Neomenthyl 	Cl[a]	EtOH-H_2O, NaOAc (E1)	99	1	
	OTs[b]	HOAc (E1)	100		
	OTs[c]	EtOH (E1)	100		
	Cl[c]	EtOH-NaOEt (E2)	80	20	
	OH[d]	Al_2O_3	75	25	<1

[a] Reference 7. [b] S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952). [c] Reference 6. [d] Reference 5.

as products resulting from isomerization of octalins, would have to be interpreted by a γ-participation reaction. The formation of 1,2-octalin could be explained by E2 reaction; however, the presence of 1,9-octalin from *trans,trans*-1-decalol would have to be interpreted by E1 elimination.

Strong evidence for a concerted *trans* elimination on aluminas in the formation of 1,4-epoxycyclohexane from 1,4-*trans*-cyclohexanediol[8] and of menthenes from menthols.[5] *trans* elimination is also the preferred mode of dehydration of 1-decalols on aluminas. In summary, it could be stated that a great bulk of evidence supports the concept of alumina acting as a "pseudo-solvent" with two catalyst surfaces involved in the reaction.

V. Participation of Ketones.—It was observed previously in this laboratory that dehydration of alcohols is often accompanied by ketone formation.[8,9] The extent of ketone formation depends on the structure of the alcohols, on the type of alumina, and on the temperature of the reaction. In the presence of alumina containing potassium or sodium ions (Table I) or in the presence of an organic base such as pyridine[9] the extent of ketone formation increases (Figure 1–4). The experimental evidence points out that a ketone intermediate is involved in the epimerization of cyclic alcohols and that a ketone usually promotes a ketonic intermediate through a hydrogen-transfer reaction.[8] Since decalones were formed in the present reaction (Figures 1–4), it was important to establish that the octalins formed were the products of the original decalols and not of the epimerized alcohols.

The experimental results (Table V), using tritium-labeling technique, have demonstrated that at 270° over alumina A the extent of ketone participation in the formation of octalins is less than 0.64%. However, at 354° in the presence of alumina H the participation of ketone as an intermediate in the formation of octalins is greater and amounted to 3.6%. In the presence of added decalone the ketone participation amounted to 10.9%. On the basis of these data it can be concluded that at temperatures below 350° in the absence of added ketones the octalins produced were almost all derived from the original decalols and not from their epimers. The mechanism of ketone formation and epimerization over aluminas will be a subject of a separate investigation.

Experimental Section

I. Preparation of the 1-Decalol Isomers (Procedure A). 1. 1-Decalol.—The four isomers of 1-decalol were prepared by the hydrogenation of 200 g of 1-naphthol using 100 ml of methanol as a solvent and 15 g of Raney nickel catalyst.[16] The reaction was carried out in a 1350-ml rocking autoclave at 150° and 120 atm of hydrogen pressure. A 55% yield of mixed 1-decalols was received which distilled at 90–105° (8 mm). Fractionation of this mixture on a Hypereal distillation column (Podbielniak Inc., Franklin Park, Ill.) produced samples of each alcohol in at least 60% purity.

2. **95% *trans*-5% *cis*-1-Decalone (Procedure B).**—An approximately equal molar mixture of *cis*- and *trans*-1-decalone was prepared by the oxidation of 32.4 g (0.21 mole) of mixed *cis*- and *trans*-1-decalol fractions obtained in procedure A. The oxidation was accomplished with 51.4 ml of a 2.7 *M* solution of chromium trioxide in water–sulfuric acid (Jones reagent)[17] following the procedure of Djerassi, *et al.*[18] The yield of the ketones was 98%

This product was added to 300 ml of a 0.75 *M* solution of sodium ethoxide in ethanol. After a brief period of stirring and standing overnight, the reaction mixture was decomposed by the addition of 500 ml of water and extracted three times with 100-ml portions of a 1:1 ether–hexane solution. After the removal of the solvent, distillation of the product produced a fraction boiling 74–75° (2 mm) which was composed of 95% *trans*- and 5% *cis*-1-decalones. The over-all yield of the synthesis was 82%.

3. ***trans,trans*-1-Decalol (Procedure C).**—The title alcohol was obtained by the addition of 20 g (0.8 g-atom) of sodium to a stirred solution of 31 g (0.21 mole) of the 1-decalone mixture, produced in procedure B, in 400 ml of absolute ethanol.[19] Sodium addition was carried out over a period of 8 hr, after which 750 ml of water was added, and the mixture was extracted three times

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[17] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[18] D. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

[19] W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

with 200-ml portions of an ether–hexane solution. Following the removal of the solvents, the crude alcohol mixture was dissolved in pentane and recrystallized. The pure *trans,trans*-1-decalol melted at 63°.

4. ***trans,cis*-1-Decalol (Procedure D).**—The *trans*-1-decalol, which was obtained from the fractional distillation of the product prepared by procedure A, was oxidized to pure *trans*-1-decalone with Jones reagent as described in procedure B.

A mixture of 15 g of *trans*-1-decalone, 30 ml of glacial acetic acid, and 0.3 g of platinum oxide were treated with hydrogen at 25 atm in a 250-ml Magne-Dash autoclave at 25° for 12 hr.[19] An 88.5% yield of 1-decalols was received which was composed of 73% *trans,cis* 1-decalol and 27% *trans,trans*-1-decalol. This product was purified by distillation on a spinning-band column, followed by chromatography over alumina.[20] The resulting *trans,cis*-1-decalol melted at 51–52°.

5. ***cis,trans*-1-Decalol.**—The crystalline fractions which were derived from the distillation of the decalols obtained by procedure A and containing about 60% of the title alcohol were recrystallized from pentane to 90% purity. Because of the large losses involved in the crystallization, the *cis,trans*-1-decalol was further purified by preparitive gas chromatography on a 20 ft × $^3/_8$ in. Ucon 75H 90,000 Polar column. The pure alcohol melted at 55°.

6. ***cis,cis*-1-Decalol.**—The fractions obtained from the distillation of decalols prepared by procedure A and which contained over 70% of *cis,cis*-1-decalol were solidified and recrystallized from pentane. The resulting *cis,cis*-1-decalol melted at 91–93°.

II. Preparation of Known Mixtures of the Octalin Isomers. 1. **9,10- and 1,9-Octalin.**—A mixture of all the octalin isomers, containing 85% 9,10-octalin, was prepared by treating 6 g of 1-decalol with 40 ml of phosphoric acid at 100° for 4 hr. Following pentane extraction, neutralization, and drying, the reaction product was chromatographed over alumina to remove unreacted alcohol. The resulting olefins were then hydrogenated with platinum oxide in ethanol at room temperature and atmospheric pressure. The unhydrogenated olefins were composed of 93.5% 9,10-octalin and 6.5% 1,9-octalin.

2. **1,9- and *trans*-1,2-Octalin.**—The acetate of *trans,trans*-1-decalol was prepared by the reaction of 2.2 g (0.014 mole) of the alcohol with 1.18 g (0.115 mole) of acetyl chloride in 5.75 ml of pyridine, according to the procedure of Vaughn, *et al.*[21] The acetate was diluted with a threefold excess of hexane and pyrolyzed over glass beads in a vertical furnace at 480°. A 92% conversion of acetate to olefins was achieved. The product composition was 1,9-octalin, 57.8%; *trans*-1,2-octalin, 40.4%; and 9,10-octalin, 1.8%.

3. ***cis*-1,2- and 1,9-Octalin.**—A mixture of 91.3% *cis*-1,2-octalin and 8.7% 1,9-octalin was obtained by the pyrolysis of *cis,cis*-1-decalyl acetate which was prepared and pyrolyzed according to procedure described above (II, 2).

4. ***cis*-2,3-, *trans*-2,3-, *cis*-1,2-, and *trans*-1,2-Octalin.**—The pyrolysis of a commercial mixture of 2-decalyl acetates (Aldrich Chemical Co.) produced the title compounds in the following composition: *cis*-2,3-octalin, 36.8%; *trans*-2,3-octalin, 10.2%; *cis*-1,2-octalin, 43.5%; and *trans*-1,2-octalin, 9.6%.

III. Catalysts. 1. **Alumina A.**—Alumina free from alkali metal ions was prepared by the hydrolysis of 125 g of distilled aluminum isopropoxide with 1 l. of distilled water. 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 sized to 20–40 mesh.

2. **Alumina B.**—This catalyst was prepared in a manner similar to alumina A, except that prior to the drying step the aluminum hydroxide was dispersed in 500 ml of a 0.019 *M* sodium carbonate solution, and stirred for 5 hr. The mixture was then filtered and the filtrate was diluted to 500 ml and titrated with 0.05 *N* hydrochloric acid. From the change in the base concentration, the amount of sodium carbonate in the filter cake was calculated. This material was then dried and calcined as above (III, 1). The resulting alumina contained 0.4 wt % sodium ion.

3. **Harshaw Alumina.**—This alumina which was prepared by precipitation of aluminum hydroxide from an alkali metal aluminate solution was obtained from the Harshaw Chemical Co., Cleveland, Ohio. It contained 0.37% of sodium. Its properties and catalytic behavior were determined.[4]

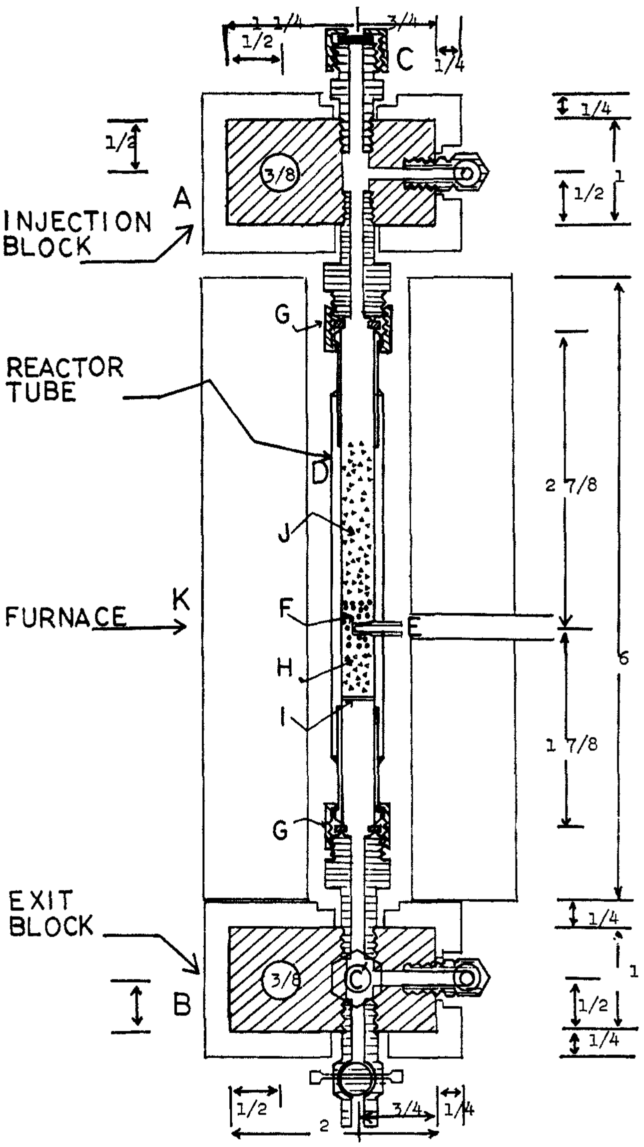

Figure 5.—Microreactor apparatus (dimensions are in inches).

IV. Apparatus. 1. **Microreactor.**—A micropulse reactor similar to that of Emmett[22] and Hall[23] was used for all microreactions described in this work. This apparatus is shown in Figure 5. The injection and exit blocks (A and B) were machined from 1 × 2 × 3 in. blocks of stainless steel and were heated by 120-w cartridge heaters. These parts were insulated with a 0.25-in. Transite jacket. Both blocks were fitted with injection ports (C and C). The $^5/_{16}$-in.-i.d. stainless steel reactor tube was attached to the blocks by means of a knife edge and gasket closure (G). A ground quartz preheater (J), the catalyst bed (F), and a quartz spacer (H) were supported by an 80 mesh screen (I) inside the reactor tube. A thermocouple well (E) was located in the catalyst bed. Heating of the reactor tube was accomplished by a split oven wound with nichrome wire.

2. **Procedure.**—All reactions were carried out at a helium flow of 120 cc/min. The catalysts of 20–40 mesh size were supported between zones of ground quartz of the same size. The samples for reaction were 10% *t*-butyl alcohol solutions of a 1-decalol isomer into which had been added known amounts of *t*-butylbenzene and naphthalene as internal standards. A trace of tetralin was also added as a marker for the calculation of relative retention times. A typical sample composition was (in mole per cent) naphthalene, 24.3; *t*-butylbenzene, 20.1; and *cis,cis*-1-decalol, 55.6. *t*-Butyl alcohol added was 3.4 ml,

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(20) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(21) W. R. Vaughn, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *ibid.*, **85**, 2282 (1963).

(22) R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *ibid.*, **77**, 5860 (1955).

(23) W. K. Hall, D. S. MacIver, and H. P. Weber, *Ind. Eng. Chem.*, **52**, 421 (1960).

sufficient to produce a 10% solution of the decalol. Twenty-microliter samples were used for reactions.

3. **Flow-Type Reactor.**—This apparatus has been described previously.[4]

V. Analytical Procedures. 1. Gas Chromatography.—All analyses were carried out on an F and M Model 300 gas chromatograph employing a composite column made up of three segments. Details of the analysis and the column composition are given in Table XI along with the relative retention times of the octalins, the 1-decalol, and 1-decalone isomers. On this column all of the above compounds except 9,10- and *cis*-2,3-octalin were sufficiently resolved so that the peak areas could be calculated using the "σ method" of Bartlett and Smith[24] or by simple triangulation. Analysis of the dehydration products of the 1-decalols required that the octalins be eluted at 125°; the unreacted 1-decalol was then eluted at 200°. This was carried out by a step-wise increase in the column temperature. The effect of the decreased flow rate upon the detector response at 200° was accounted for by determining a correction factor from the analysis of samples of known composition. This factor also corrected any thermoconductivity differences between the olefins and the alcohols.

TABLE XI

RELATIVE RETENTION TIMES OF THE OCTALIN ISOMERS, 1-DECALOL ISOMERS, AND 1-DECALONE ISOMERS[a]

Compound	Method of analysis		
	Individual[b]	15-Component mixtures[c]	
	Microreactor		
	Absent	Absent	Present
	Relative retention times		
t-Butylbenzene	1.00	1.00	1.00
trans-1,2-Octalin	1.16	1.17	1.17
trans-2,3-Octalin	1.22	1.23	1.23
1,9-Octalin	1.33	1.36	1.34
cis-1,2-Octalin	1.41	1.41	1.41
9,10-Octalin	1.52	1.49	1.49
cis-2,3-Octalin	1.55	1.52	1.52
Tetralin[d]	0.00	0.00	0.00
Naphthalene	1.00	1.00	1.00
trans,cis-1-Decalol	1.43	1.44	1.44
trans,trans-1-Decalol	1.72	1.72	1.72
trans-1-Decalone	1.91	1.84	1.85
cis-1-Decalone	2.12	2.03	2.02
cis,trans-1-Decalol	2.44	2.38	2.38
cis,cis-1-Decalol	2.79	2.64	2.65

[a] A composite column was employed; all liquid phases were 10% on 80–100 mesh Gas Pack W. The components of this column were, respectively, 3-m G.E. XF1150, 2-m G.E. XF1105, and 4-m Carbowax 20M; carrier gas He. [b] Octalins were analyzed at 125°, flow rate 120 cc/min; decalols and decalones were analyzed at 200°, flow rate 84 cc/min. [c] After the octalins eluted, the temperature was increased from 125 to 200° in a step-wise manner. Flow rates were the same as in *b*. [d] Tetralin was analogous to the air peak for the calculation of the relative retention times of the decalols and decalones.

2. **Radioactive Assay.**—The reaction products obtained from the flow reactor dehydrations employing 10% 1-decalol solutions in *t*-butyl alcohol which had been tritiated on the hydroxyl group were washed with water several times and chromatographed over alumina to remove unreacted alcohol. The pentane eluate was removed by evaporation with a nitrogen stream. Samples ranging from 15 to 75 mg were counted on a Packard Tri Carb Model 314EX liquid scintillation counter using 15 ml of a 3-g/l. solution of POPOP (1,4-bis[2-(5-phenegloxazolyl)]benzene) in toluene. A 24.6% counting efficiency was attained.

3. **Identification of the Octalins.**—The correlation of the octalin peaks obtained from gas chromatography with the correct octalin isomer was accomplished by the analysis of mixtures of these compounds similar to the method of Powell and Whiting.[25]

The major product of the phosphoric acid dehydration of 1-decalol is present to a significant extent in no other reaction.[26] The only isomer which would not be expected to be formed in at least one of these reactions is 9,10-octalin. Furthermore, since this isomer has been prepared by the reaction of 2-decalol with phosphoric acid and phosphorus pentoxide,[27,28] a similar reaction would be expected with 1-decalol and phosphoric acid.

The minor product of the above reaction can be identified as 1,9-octalin.[29] This compound was also observed as a minor product in the pyrolysis of *cis,cis*-1-decalyl acetate and as the major product of the *trans,trans*-1-decalyl acetate pyrolysis.[30] The stereochemistry of the acetates and the nature of the *cis* elimination during the pyrolysis establishes the identity of 1,9-octalin. The absence of this compound in the pyrolysate of 2-decalyl acetate confirms this assignment of structure. Knowing the relative retention time of 1,9-octalin, the other products of the pyrolyses of *trans,trans*- and *cis,cis*-1-decalyl acetate can be identified, respectively, as *trans*-1,2-octalin and *cis*-1,2-octalin. The yields of these compounds and their presence in the pyrolysis product of 2-decalyl acetate support these conclusions.

The two remaining unidentified octalin isomers obtained from 2-decalyl acetate must be *trans*-2,3- and *cis*-2,3-octalin. It is known that the following order of elution is generally observed: *trans*-1,2-, *trans*-2,3-, *cis*-1,2-, and *cis*-2,3-octalin.[13] This distinctive elution pattern was frequently observed in this work. On this basis the relative identities of *trans*-2,3- and *cis*-2,3-octalin were established.

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[24] J. C. Bartlett and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960).

[25] J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 163 (1961).

[26] F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1965 (1966).

[27] R. P. Linstead, A. B. Wang, J. H. Williams, and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

[28] W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).

[29] J. F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Am. Chem. Soc.*, **82**, 6090 (1960).

[30] J. F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **83**, 3874 (1961).