

For 2-substituted benzophenones the effect may be more pronounced and the molecule may, moreover, exist in two forms such as III and IV; however, essentially the same argument applies. This general hypothesis receives further support from the observation that the more intense ultraviolet *B*-band for 2- and 3-halogen-substituted benzophenones is most frequently the *B*-band associated with ring B (see Table II) as would be anticipated from predominant conformations of types III and IV. In 4-substituted benzophenones the above-mentioned short-range interactions are presumably of less importance and resonance-type interactions may predominate. These can adequately account for the ultraviolet spectral changes and also for the relatively higher intensities in the infrared

carbonyl band of 4- (and 2-) substituted benzophenones.

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## Alumina: Catalyst and Support. XV.<sup>1</sup> Dehydration of 2-endo- and 2-exo-Bornanol and of endo- and exo-Norbornanol over Alumina Catalyst<sup>2,3</sup>

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The dehydration of 2-endo- and 2-exo-bornanol, and endo- and exo-norbornanol over alumina catalysts were studied. The major primary products correspond to those expected from the removal of the hydroxyl group and the hydrogen on the third carbon atom with respect to the one which originally carried the hydroxyl. This process involves either rearrangement of the carbon skeleton (leading to camphene and 2-norbornene) or to the formation of a three-membered ring (leading to tricyclene and nortricyclene). The rate of dehydration of the *exo*-alcohols is faster than that of the corresponding *endo* isomers. The camphene obtained from active 2-endo-bornanol was found to retain optical activity. The norbornanols also underwent dehydrogenation to 2-norbornanone over the catalyst. These results are discussed from a mechanistic point of view. While confirming the earlier observation that amines modified the alumina, reducing its ability to bring about olefin isomerizations, it was also observed that the solvent itself may exert this effect to some extent. Thus benzene was capable of reducing the isomerizing ability of the catalyst to a greater extent than *n*-hexane. Equilibrium compositions of 2-bornene, camphene and tricyclene at 275° and of 2-norbornene and nortricyclene at 280° and 310° were established.

In previous papers of this series the differences in catalytic activity of aluminas prepared by various methods were discussed.<sup>5,6,7</sup> It was shown that the dehydration of certain aliphatic and cyclic alcohols may undergo secondary isomerizations accompanying dehydration, depending on the type of alumina used.<sup>8a,b</sup> These secondary isomerizations could be avoided by using aluminas containing only relatively weak acid sites or by modification of aluminas by the use of ammonia or organic bases.<sup>9-11</sup>

The present paper deals with the dehydration of 2-endo- and 2-exo-bornanol and of 2-endo- and 2-exo-norbornanol over an "acidic" alumina prepared from aluminum isopropoxide and over the same alumina but modified by the addition of piperidine to the alcohols.<sup>5</sup>

### Experimental Part

**Alcohols.** 1. *d*-2-endo-Bornanol was purchased from Smith-New York Co., Freeport, L. I., N.Y. It was purified by treating a boiling ethanolic solution of the borneol with activated charcoal, followed by recrystallization from ethanol. *d*-2-endo-Bornanol melted at 208° and had  $[\alpha]_D + 15.8^\circ$  in ethanol.

2. 2-*exo*-Bornanol was prepared by reducing optically pure *d*-camphor with lithium aluminum hydride in tetrahydrofuran solution.<sup>12</sup> The infrared spectrum showed the absence of carbonyl group. The alcohol was composed, according to gas chromatography, of 89% 2-*exo*- and 11% 2-*endo*-bornanol and the observed rotation was  $[\alpha]_D - 28^\circ$  in ethanol. The literature value of pure 2-*exo*-bornanol was reported<sup>13</sup> to be  $[\alpha]_D - 34.34^\circ$ .

3. 2-endo-Norbornanol was prepared from cyclopentadiene and vinyl acetate by the method of Winstein and Trifan<sup>14</sup>; the alcohol melted at 151–152° and was over 99% pure as determined by gas chromatography.

4. 2-*exo*-Norbornanol was prepared by the method of Walborsky and Loncrini,<sup>15</sup> which consisted in epoxidation of bicyclo[2.2.1]-2-heptene (2-norbornene) with peracetic acid and reduction of 2,3-epoxybicyclo[2.2.1]heptane with lithium aluminum hydride.<sup>16</sup>

(11) F. V. Rudloff, *Can. J. Chem.*, **39**, 1860 (1961).

(12) Prepared by C. Goetschel, University of Michigan.

(13) R. H. Pichard and W. O. Littlebury, *J. Chem. Soc.*, **91**, 1973 (1907).

(14) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952).

(15) H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954).

(16) Although the experimental conditions used in the epoxidation reaction apparently were similar to those described,<sup>15</sup> the epoxy-norbornene after distillation melted at 110–123° (literature,<sup>15</sup> m.p. 125–127°) and was composed of three isomers which on reduction with lithium aluminum hydride formed 2-*exo*-norbornanol admixed with a small amount of *endo*-norbornanol. The epoxides are probably 2,3-

(1) For paper XIV of these series see H. Pines and S. M. Csicsery, *J. Am. Chem. Soc.*, **84**, 292 (1962).

(2) Paper V of the series: Dehydration of Alcohols.

(3) For IV see C. N. Pillai and H. Pines, *J. Am. Chem. Soc.*, **83**, 3271 (1961).

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

(6) W. O. Haag and H. Pines, *ibid.*, **82**, 2488 (1960).

(7) H. Pines and J. Ravoire, *J. Phys. Chem.*, **65**, 1859 (1961).

(8) (a) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961); (b) H. Pines and C. N. Pillai, *ibid.*, **83**, 3270 (1961).

(9) H. Pines and C. N. Pillai, *ibid.*, **82**, 2401 (1960).

(10) L. Beranek, V. Bazant, M. Kraus and K. Kochloeff, "Proc. Intern. Congr. on Catalysis," 2nd Paris, 1960; **1**, 749 (1961).

The *exo*-norbornanol used in the dehydration studies melted at 124.5–125.5°, and according to the gas chromatographic analysis was of about 99% purity (lit.<sup>15,17–19</sup> m.p. 126–127°).

**Alumina.**—The alumina catalyst was prepared by hydrolyzing aluminum isopropoxide with water. The precipitate after being dried at 120° for 6 hours was compressed to 120,000 pounds per sq. inch, broken up to 10–14 mesh size and calcined at 700° for 4 hours in the presence of a stream of nitrogen.<sup>8</sup>

**Apparatus and Procedure.**—The apparatus and procedure were essentially the same as described previously.<sup>5,9</sup> Five cc. of 10–14 mesh size alumina was dispersed in twice its volume of Pyrex chips of the same mesh size and placed in a Pyrex reaction tube. The tube was inserted into an aluminum bronze block and heated electrically. The alcohols, 25 wt. % solution in either *n*-hexane or benzene, were passed over the catalyst at 280° and 310° and at variable space velocities. When a base-modified alumina was used, piperidine in the amount of 60 wt. % based on the alcohol used was added to the solution.

The products of the dehydration reactions were analyzed by gas chromatography with columns of Carbowax (600 and 1500), dinonyl phthalate, di-*n*-propyl tetrachlorophthalate and silicone. The retention times of the various compounds are given in Tables I and II.

TABLE I

## RETENTION TIME OF REACTION PRODUCTS FROM 2-BORNANOLS

Column: length, 30 ft.; 7% di-*n*-propyl tetrachloro-*o*-phthalate on 30–60 mesh Celite; conditions: temp. 110°; helium 68 ml. per min.

Component	Rel. retention time
Toluene	1.00
2-Bornene	1.49
Tricyclene	1.66
Camphene	2.23

Column: length, 6 ft.; 15% Carbowax 1500 on 30–60 mesh Celite; conditions: temp. 140°; helium 200 ml. per min.

Component	Rel. retention time
Camphor	1.00
2- <i>exo</i> -Bornanol	1.58
2- <i>endo</i> -Bornanol	1.87

**Dehydration of 2-*endo*- and 2-*exo*-Bornanol.**—The experimental conditions and the results obtained are summarized in Tables III and IV. The dehydration was made in the presence of hexane and benzene as solvents and using an "acidic" alumina and the same alumina but modified by the introduction of piperidine to the hydrocarbon solution of the bornanols. Under "non-acidic" conditions of dehydration, 2-*exo*-bornanol formed 4.3% of tricyclene (1,7,7-trimethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane), 95.2% camphene and 0.5% camphor (expt. 6c). 2-*endo*-Bornanol under similar conditions formed 12.5% tricyclene and 86.5% camphene (expt. 3c).

*endo*-epoxynorbornane, 2,3-*exo*-epoxynorbornane and 2,7-epoxynorbornane. The relative retention of the norbornane epoxides are 1.0, 1.2 and 1.7 and their relative volumes are 14, 50 and 36. The lowest retention is assigned to the *endo* isomer. The relative retention for 2-*exo*-norbornanol is 2.5 and that for 2-*endo*-norbornanol 3.0. The relative retention times were determined on a column of 15% Carbowax (1500) on Celite (ca. 30 mesh; length, 6 feet) and at 140° with helium flow of 45 ml. per minute.

When the reduction of the epoxides with lithium aluminum hydride in *N*-ethylmorpholine at 95° was carried out in such a way that only 80% of the epoxides was reduced, the product thus obtained consisted of almost pure 2-*exo*-norbornanol.

The Referee of this manuscript repeated the preparation of norbornane epoxide by the method of Walborsky and Loncrini with results exactly as they reported. The reasons for the discrepancy between the present results, which were repeated by us twice, and those of the previous workers will be a subject of another investigation.

(17) L. Schmerling, J. P. Luvisi and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

(18) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(19) D. C. Kleinfelter and P. v. R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

TABLE II

RETENTION TIME OF REACTION PRODUCTS FROM *endo*- AND *exo*-NORBORNANOL

Column: length, 10 ft.; 20% dinonyl *o*-phthalate on 30–60 mesh Celite; conditions: temp., 130°; helium 80 ml. per min.

Component	Rel. retention time
2-Norbornene	1.00
Nortricyclene	1.16

Column: length, 14 ft.; 15% Carbowax 600 on 80–100 mesh Chromosorb P; conditions: temp., 140°; helium 80 ml. per min.

Component	Rel. retention time
2-Norbornanone	1.00
Condensation prod. of 2-norbornanone	1.32
2- <i>exo</i> -Norbornanol	1.66
2- <i>endo</i> -Norbornanol	1.77

Gas chromatograph apparatus: linear programmed temperature gas chromatograph, F and M Scientific Corp., Avondale, Penna.; column: 2 ft. length, Chromosorb P-silicone gum rubber; conditions: programmed at 4.6° per min. from 70°; helium 40 ml. per min.

Component	Rel. retention time
2-Norbornene	1.00
Nortricyclene	1.15
2- <i>endo</i> -Norbornanol	3.06
2- <i>exo</i> -Norbornanol	3.14
2-Norbornanone	3.34
Condensation prod. of 2-norbornanone	5.55

The relative rate of dehydration of 2-*endo*- and 2-*exo*-bornanol was determined by passing a mixture of the two alcohols over alumina catalyst modified by piperidine. In order to facilitate the gas chromatographic analysis, camphor was used as an internal standard. The dehydration was carried out at 275° and at an hourly liquid space velocity of 8 and by passing an equimolar mixture of the bornanols dissolved in two parts by weight of benzene and 0.6 part of piperidine. The relative dehydration of 2-*exo*-bornanol/2-*endo*-bornanol was 7.2 as 79.3% of the *exo*-bornanol and 11% of the *endo*-bornanol underwent dehydration. The greater ease of dehydration of 2-*exo*-bornanol over 2-*endo*-bornanol can also be seen from the data given in Table IV.

The optical rotation of camphene produced from the dehydration of bornanols was determined and the results are given in Table V.

**Dehydration of 2-*endo*- and 2-*exo*-Norbornanol.**—The dehydration reactions of norbornanols were carried out at 280° and 310° in benzene solution. In order to determine the effect of the solvent upon the reaction, the dehydration of the *endo*-norbornanol was also made in *n*-hexane (Table VI). The principal products of dehydration were nortricyclene (tricyclo[2.2.1.0<sup>2,6</sup>]heptane) and 2-norbornene. In the presence of the modified catalyst a substantial amount of 2-norbornanone and of dimeric condensation product of 2-norbornanone was also obtained. When 2-norbornanone as such was passed over a modified alumina, under conditions of experiments 6 and 11 (Table VIII), the dimeric condensation product was obtained in amounts increasing with the contact time; e.g., at 0.65 hourly liquid space velocity the yield was 21.7%; at 1.5 H.L.S.V., 10.8%; at 5 H.L.S.V. 5%; at 10 H.L.S.V., 3%.

## Discussion

**a. 2-*endo*- and 2-*cis*-Bornanol.**—The product distribution under non-acidic conditions, namely, expt. 6c for 2-*exo*-bornanol and expt. 3c for 2-*endo*-bornanol, seems to represent the primary dehydration results which correspond to 12.5% tricyclene and 87.5% camphene for 2-*endo*-bornanol and 4.3% tricyclene and 95.2% camphene for 2-*exo*-bornanol. There is no conversion of 2-*exo*-bornanol to 2-*endo*-bornanol. If any 2-*endo*-bornanol was formed it would have been detected. There was a small

TABLE III

## DEHYDRATION OF 2-endo-BORNANOL OVER ALUMINA AT 275°

Solutions of 25% by weight of the alcohol in the respective solvents were used. When piperidine was used as a modifier (Catalyst M) the solution was composed of 1 part by weight of alcohol, 4 parts solvent and 0.6 part piperidine.

Expt.	Catalyst <sup>a</sup>	Solvent	H.L.S.V. <sup>b</sup>	Bornanol reacted, %	Composition of products, mole %			
					Bornene	Tricyclene	Camphene	Camphor
1a	A	Benzene	1.5	100	4.8	20.8	73.9	0.5
1b	A	Benzene	4.5	100	2.4	21.3	75.8	.5
1c	A	Benzene	10	95	0	22.9	76.6	.5
2a	A	Hexane	1.6	100	4.2	21.4	74.5	Trace
2b	A	Hexane	4.5	100	3.8	21.4	74.8	Trace
2c	A	Hexane	10.3	100	2.0	23.4	74.5	Trace
3a	M	Benzene	1.4	27	1.4	25.1	71	2.5
3b	M	Benzene	4.8	18.7	0	18.1	81.6	0.3
3c	M	Benzene	12	11.6	0	12.5	87.5	0
4a	M	Hexane	1.5	47	2.0	21.6	69.7	6.5
4b	M	Hexane	5	26.5	0	13.4	84.6	2.0
4c	M	Hexane	10	15	0	12.8	86.4	0.8
Equilibrium <sup>c</sup>					3.0	24.3 ± 0.4	72.7 ± 0.4	

<sup>a</sup> Catalyst: A, alumina, M, alumina modified with piperidine. <sup>b</sup> Hourly liquid space velocity = volume of liquid passed per volume of catalyst per hour. <sup>c</sup> The equilibria were established starting from tricyclene and camphene enriched mixtures. Literature data: G. Swann and F. J. Cripwell, *Ind. Chemist*, 24, 573 (1948), reported 17% of tricyclene and small amounts of bornene to be present with camphene at boiling point. Kitajima, *et al.*, *Reports Assoc. Camphor Ind. Eng., Japan*, No. 20, 140 (1955); *C. A.*, 53, 18975 (1959), reported equilibria at boiling point: bornene, 2.5%, tricyclene 15.6% and camphene 81.8%.

TABLE IV

## DEHYDRATION OF 2-exo-BORNANOL OVER ALUMINA AT 275°

Expt.	Catalyst	Solvent	H.L.S.V. <sup>b</sup>	Reaction, % <sup>a</sup> bornanol		Composition of products, mole %			
				2-exo-	2-endo-	Tricyclene	Camphene	Camphor	
5a	A	Benzene	1.6	100	100	1.9	22.6	73.5	2.0
5b	A	Benzene	6	100	100	0.2	21.5	76.7	1.6
5c	A	Benzene	12	100	100	.2	8.4	89.8	1.6
6a	M	Benzene	1.6	99.9	46.3	.3	4.2	94.0	1.5
6b	M	Benzene	5.1	90.2	30.6	.3	4.2	94.8	0.7
6c	M	Benzene	10	52.8	1.8	0	4.3	95.2	0.5
7a	M	Hexane	1.5	100	67.5	0.4	5.1	93.4	1.1
7b	M	Hexane	5.2	76	28.4	0.4	4.8	94.3	0.5
7c	M	Hexane	10	52.8	5.0	0	5.2	94.5	0.3

<sup>a</sup> The alcohol used for dehydration was composed of 89% isoborneol and 11% borneol. The experimental conditions were similar to those indicated in the footnote to Table V. <sup>b</sup> See footnote b, Table III.

TABLE V

OPTICAL ACTIVITY OF *d*-CAMPHENE PRODUCED FROM THE DEHYDRATION OF BORNANOLS

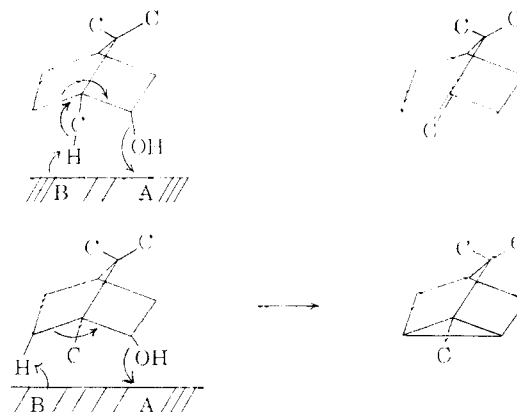
Bornanol <sup>a</sup>	Catalyst <sup>b</sup>	Temp., °C.	H.L.S.V. <sup>c</sup>	Dehydration, %	[α] <sub>D</sub> <sup>d</sup>	Reten-
						tion, <sup>e</sup> %
<i>d</i> -2-endo-	M	330	1.3	100	+30°	77
<i>d</i> -2-endo-	A	280	1	100	+1.4	4
<i>d</i> -2-endo-	A	280	8	97	+31.0	79
<i>l</i> -2- <i>exo</i> -	M	275	1.4	80	+80	80

<sup>a</sup> Optical purity of *d*-2-endo-bornanol used in the experiments was 39%, and that of *l*-2-*exo*-bornanol, 100%. pure *d*-2-endo-bornanol: [α]<sub>D</sub> 38° in toluene [W. Huckel, *et al.*, *Ann.*, 549, 186 (1941)]; [α]<sub>D</sub> + 36.4° in ethanol [R. M. Pickard, *et al.*, *J. Chem. Soc.*, 1973 (1907)]; pure *l*-2-*exo*-bornanol: [α]<sub>D</sub> - 34.4° in ethyl alcohol [R. H. Pickard *et al.*, *J. Chem. Soc.*, 1973 (1907)]. <sup>b</sup> M alumina modified by piperidine (Table III and Experimental Part); A "acidic" alumina prepared from aluminum isopropoxide. <sup>c</sup> The solution of the bornanols in benzene were of the same composition as in Table III, see footnote; see also Table III, footnote b. <sup>d</sup> A 10% solution in camphene in absolute ethanol was used. <sup>e</sup> Based on the value of *d*-camphene being [α]<sub>D</sub> + 99.6° [W. Huckel, *et al.*, *Ann.*, 549, 186 (1941)].

amount of 2-endo-bornanol present in the 2-*exo*-bornanol used. Its amount, relative to the internal standard, camphor, which was added to the mixture,

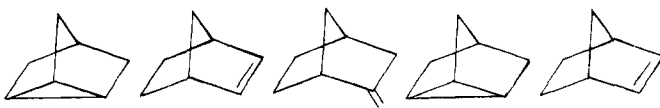
remained unchanged. However if some 2-endo-bornanol was converted to 2-*exo*-bornanol, it would not have been detected because of the faster rate of dehydration of 2-*exo*-bornanol.

The function of piperidine is to neutralize the relatively "strong acidic" sites of the alumina and still leave the "weak" acid sites free to act catalyti-



cally. This type of catalyst might act in a concerted way whereby the acidic sites would be attracting the

TABLE VI  
 DEHYDRATION OF *endo*- AND *exo*-NORBORNANOL OVER ALUMINA CATALYSTS



Expt.	Catalyst	Solvent	Temp., °C.	H.L.S.V. <sup>a</sup>	Alcohol reacted, %	Composition of products, %			D <sup>b</sup>	Composition of C <sub>7</sub> H <sub>10</sub> , %			
						2- <i>endo</i> -Norbornanol	2- <i>exo</i> -Norbornanol	norbornene		norbornene	norbornadiene		
8a	A	H	280	1.6	100	80	19	1	T <sup>c</sup>	81	19		
8b	A	H	277	5	90	83	14	3	T	85.2	14.8		
8c	A	H	278	12	78	86	13	?	..	86.5	13.5		
9a	M	B	284	1.6	9	69	3	13	15	95	5		
9b	M	B	284	4.5	3	56	..	38	6	100	0		
9c	M	B	284	9.0	2	52	..	40	8	100	0		
10a	M	H	280	1.5	20	45	10	20	25	81	19		
10b	M	H	280	2.4	7	48	10	26	16	83	17		
10c	M	H	280	6.2	3	48	9	31	12	85	15		
11a	M	B	310	1.5	34	74	4	4	18	95	5		
11b	M	B	310	6	20	85	8	1	6	90	10		
11c	M	B	310	12	10	86	..	8	6	100	0		
12a	M	H	310	1.4	83	76	14	4	6	85	15		
12b	M	H	313	5.4	38	76	17	4	3	82	18		
12c	M	H	313	12.0	18	77	15	5	3	84	16		
Equilibrium composition <sup>e</sup>													
			280							58.8 ± 0.2	41.2 ± 0.2		
			310							55.0	45.0		

The experimental conditions used were similar to the ones indicated in the footnote of Table III. <sup>a</sup> See Table III, footnote *b*. <sup>b</sup> Dimeric condensation product of norcamphor. <sup>c</sup> T = trace. <sup>d</sup> Under the conditions of experiment 15c, about 8% of norbornene isomerizes to norbornylene. <sup>e</sup> The equilibrium was determined starting with tricyclene and norbornene enriched mixtures. The following equilibrium data were reported: 23% norbornene and 77% norbornylene at about 105° [P. v. R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958)].

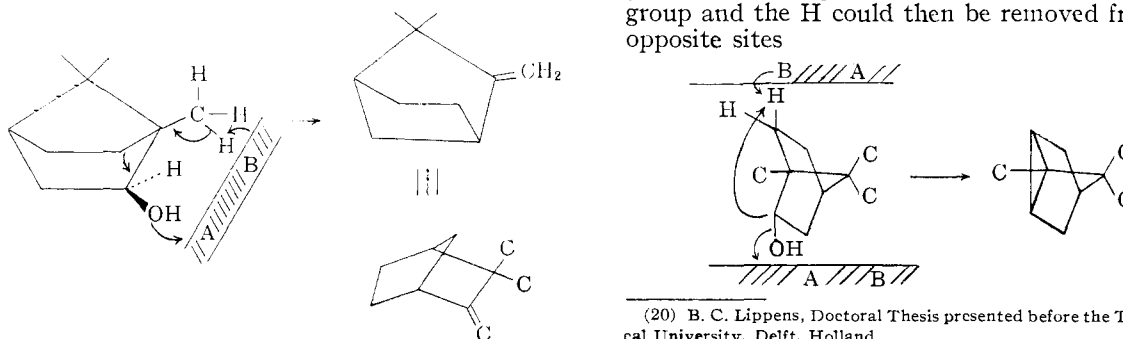
hydroxyl group from the alcohol while the basic sites of the catalyst were removing the proton.

The formation of tricyclene and camphene from 2-*endo*-bornanol on the modified catalyst could be explained by a mechanism previously suggested in which there is a concerted participation of the acidic and basic sites of the catalyst<sup>9</sup> (formulas, p. 3936).

The faster rate of dehydration of 2-*exo*-bornanol over that of 2-*endo*-bornanol can be attributed in part to the anchimeric assistance of the C<sub>1</sub>-C<sub>6</sub>

bonding electrons which are *trans* to the electrons bonding the OH group to C<sub>2</sub> carbon.<sup>14</sup> The adsorption of the hydroxyl group by the acid sites of the catalyst will thus be greatly enhanced. The formation of camphene from 2-*exo*-bornanol could be interpreted by a concerted mechanism as shown.

The occurrence of tricyclene as the primary product of dehydration of 2-*exo*-bornanol can best be explained by an elimination reaction which takes place within the pores of the aluminas.<sup>20</sup> The OH group and the H could then be removed from two opposite sites



(20) B. C. Lippens, Doctoral Thesis presented before the Technological University, Delft, Holland.

Benzene and *n*-hexane were used as solvents in the dehydration reactions of 2-bornanols. These solvents did not affect the product distribution obtained from the dehydration; in the case of 2-norbornanol some effect was noticeable.

The retention of optical activity of camphene (Table VII) rules out the occurrence of methyl migration (Nametkin rearrangement)<sup>21</sup> or symmetrical intermediates. On the acidic alumina at low contact time the retention of optical activity was high, at longer contact time, however, there was essentially complete racemization. Hence the dehydration mechanism seems to be the same on the acidic and on the base-modified alumina. The acidic alumina causes, however, the readsorption of the dehydration products leading to the isomerization and equilibration reaction. That the isomerization reaction succeeds the dehydration reaction was observed previously.<sup>2,8,9</sup>

The modified alumina catalyst caused skeletal isomerization of the products obtained from the dehydration of 2-*endo*-bornanol but not that of 2-*exo*-bornanol (expt. 3, 4, 6 and 7). This can be interpreted that the ease of adsorption of 2-*exo*-bornanol by the catalytic sites is not much greater than that of its dehydration products.

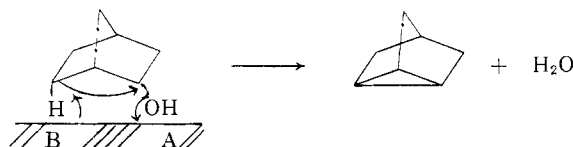
**b. 2-*endo*- and 2-*exo*-Norbornanol.**—The rate of dehydration of norbornanols is about three to six times slower than that of the corresponding bornanols (Table V, VI and VIII). The rate of dehydration of 2-*exo*-norbornanol is about six times greater than that of 2-*endo*-norbornanol (Table VII, expt. 11 vs. 6c). These results are in agreement with results obtained from the solvolysis studies of the corresponding tosylates and chlorides.<sup>14</sup>

The dehydration of norbornanols is complicated by the formation of 2-norbornanone and its condensation products. 2-Norbornanone is the major reaction product, especially when the experiments were carried out at milder conditions, 280°, and in the presence of piperidine-modified alumina. The mechanism of ketone formation from alcohols over alumina catalysts is being presently investigated.

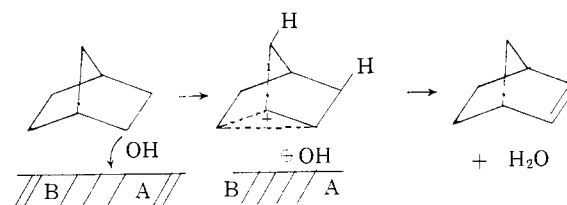
Nortricyclene is the only product of dehydration of 2-*endo*-norbornanol over modified alumina and in the presence of benzene as solvent (Table VIII, expt. 9b, 9c and 11c); with longer contact time, especially at higher temperature, the nortricyclene isomerizes to 2-norbornene. In the presence of acidic alumina or in the presence of modified alumina, but in hexane as solvent, the dehydration product consisted of nortricyclene and of 2-norbornene. The rate of 2-*endo*-norbornanol dehydration was greater in hexane than in benzene. This selectivity of dehydration, as far as the formation of nortricyclene is concerned, was also greater when benzene rather than hexane was used as solvent. This could be interpreted by the greater basicity of benzene than hexane. The concentration of nortricyclene, even in the reactions made over the acidic alumina, was greater than that of the established equilibrium mixture; the latter is composed of 59% and 55% tricyclene and of 41% and 45% norbornene at 280° and 310°, respectively.

(21) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **75**, 3165 (1953).

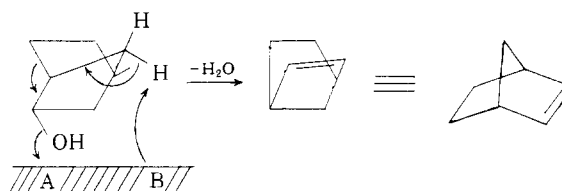
The formation of nortricyclene as the sole dehydration product of 2-*endo*-norbornanol in the presence of modified alumina is in agreement with the proposed mechanism.<sup>9</sup> Norbornanol, unlike bornanol, does not contain a methyl group on carbon in position and therefore the competition for the removal of hydrogen is eliminated and therefore the yield for the formation of tricyclic compounds is greatly increased. The dehydration seems to proceed on the alumina surface as



The formation of norbornene over the acidic alumina can be interpreted by a cationic mechanism, the proton being eliminated either from carbon atom 2 or 7.

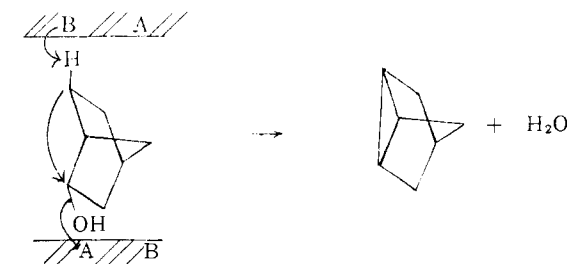


The formation of norbornene from *exo*-norbornanol can be explained by a concerted mechanism



The greater rate of dehydration of 2-*exo*-norbornanol over 2-*endo*-norbornanol can be interpreted by an anchimeric assistance which involves the delocalization of C<sub>1</sub>-C<sub>6</sub> bonding electron pair; this helps in the removal of a hydroxy ion and facilitates the dehydration reaction. This delocalization is probably responsible for the formation of norbornene as one of the primary products of the dehydration reaction.

It is more difficult to explain the formation of nortricyclene, unless one assumes a "back side" attack on the hydrogen attached to C<sub>6</sub>. The general problem here is similar to the one of *trans* elimination reaction involving the dehydration of



menthol and neomenthol to form menthenes over alumina catalyst.<sup>9</sup> It is very probable that the formation of nortricyclene over alumina occurs

within the pores of alumina so that the hydroxyl group is lost to a surface below the plane of the molecule and the hydrogen to the surface above.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

## Alumina: Catalyst and Support. XVIII.<sup>1</sup> Aromatization of 2,2-Dimethyl-3-methyl-C<sup>14</sup>-pentane over "Non-acidic" Chromia-Alumina Catalyst. Contribution to the Mechanism of Aromatization<sup>2</sup>

BY SIGMUND M. CSICSERY<sup>3</sup> AND HERMAN PINES

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2,2-Dimethyl-3-methyl-C<sup>14</sup>-pentane was allowed to react at 532–542° over "non-acidic" chromia-alumina catalyst in which the alumina was obtained from potassium aluminate. The aromatic fractions, amounting to about 7 mole % of the reacted trimethylpentane, contained mostly *m*-xylene and toluene. From 71 to 84% of the radioactivity in *m*-xylene was located in the methyl groups, while in toluene 77 to 82% of the radioactivity was in the ring. The radioactivity distribution in *m*-xylene suggests that adsorbed cyclopropane-type intermediates play a major role in the aromatization reaction. Recombination of the products of cracking also contributed to the formation of *m*-xylene. Toluene seems to be formed mostly from 1,1-dimethylcyclohexane-type intermediates through a demethanation reaction.

### 1. Introduction

Extensive study of the aromatization of alkanes over chromia-alumina catalysts has been carried out in our laboratory during the last few years. Since alumina *per se* has intrinsic acidic properties,<sup>4</sup> we were concerned with the influence of the alumina upon the catalytic activity of chromia-alumina catalyst. It was found that a chromia-alumina catalyst which contains alumina prepared from aluminum isopropoxide has relatively strong acidic sites and that this catalyst may cause extensive cationic skeletal isomerization of the dehydrogenated product.<sup>5–7</sup> Dehydrogenation and aromatization proceed, however, without appreciable isomerization over chromia-alumina catalyst where the alumina was obtained from potassium aluminate; to this type of catalyst the name "non-acidic" chromia-alumina was assigned.

The study of the aromatization of *n*-heptane-1-C-14<sup>8,9</sup> and *n*-octane-1-C-14<sup>10</sup> over a "non-acidic" chromia-alumina has suggested that in the transition state adsorbed five-, six-, seven- and, in the case of *n*-octane, also eight-membered ring intermediates were involved.

In order to gain additional insight of the mechanism of aromatization, a systematic study of the behavior of branched C<sub>6</sub>–C<sub>8</sub>-hydrocarbons over non-acidic chromia-alumina catalyst was under-

taken<sup>6,7</sup>. It was found that 2,2-dimethylpentene dehydroisomerized mainly to 2-methylpentenes and 2-methylpentadienes; a small amount of 1,1,2-trimethylcyclopropane was also found in the reaction product. The aromatized product from 2,2,4-trimethylpentane over the "non-acidic" catalyst consisted only of *p*-xylene, while 2,3,4-trimethylpentane yielded all the three xylenes and ethylbenzene. 2,2,3-Trimethylpentane on aromatization produced mainly *m*-xylene and toluene, amounting to about 6 mole per cent. based on the reacted alkane. The aromatization of 2,2,4- and 2,2,3-trimethylpentane was accompanied by an extensive cleavage reaction resulting in the formation of butenes. In the case of 2,2,3-trimethylpentane almost equal amounts of *n*-butenes and isobutylene were produced.<sup>7</sup>

In order to explain skeletal isomerization accompanying the formation of *m*-xylene and toluene from 2,2,3-trimethylpentane, without the participation of a cationic intermediate, it was proposed that the aromatization reaction of branched hydrocarbons may involve adsorbed cyclopropane and cyclobutane-type intermediates.<sup>7</sup> This interpretation was based on the study of many model compounds.

In order to distinguish between these various mechanisms, 2,2-dimethyl-3-methyl-C<sup>14</sup>-pentane was synthesized and aromatized under conditions described previously.<sup>7</sup> The mechanism involving an adsorbed cyclopropane-type intermediate would predict 100% methyl-labeled *m*-xylene and 100% ring-labeled toluene from 2,2-dimethyl-3-methyl-C<sup>14</sup>-pentane (Fig. 1). All the radioactivity will be in the ring if the reaction should proceed through an adsorbed cyclobutane-type transition state (Fig. 2). Recombination of isobutylene and *n*-butene-1-C<sup>14</sup> will predict 50% radioactivity in the side chains of *m*-xylene (Fig. 3b).

Toluene could be produced either from 1,1-dimethylcyclohexane or from the corresponding olefins.<sup>5</sup> These hydrocarbons can be formed from 2,2,3-trimethylpentane through either adsorbed cyclopropane- (Fig. 1) or cyclobutane-type inter-

(1) For paper XVII of this series see S. M. Csicsery and H. Pines, *J. Catalysis*, in press (1962).

(2) Paper X of the series "Aromatization of Hydrocarbons," for paper 1X see ref. 1.

(3) This research was supported in part by the Atomic Energy Commission, Contract AT(11-1)-1046, and by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of the fund. Taken in part from the Doctoral Thesis of S.M.C., Northwestern University, December, 1961.

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

(5) H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

(6) H. Pines and S. M. Csicsery, *ibid.*, **84**, 292 (1962).

(7) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, in press (1962).

(8) H. Pines and C. T. Chen, *J. Org. Chem.*, **26**, 1057 (1961).

(9) C. T. Chen, W. O. Haag and H. Pines, *Chemistry & Industry*, 1379 (1959).

(10) H. Pines and C. T. Chen, "Proceedings of the 2nd International Congress in Catalysis," Paris, 1960, Vol. 1, pp. 367–384, published by Editions Technip, Paris, 1961.