## [Contribution from the Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University]

# Studies in the Terpene Series. VIII.<sup>1</sup> Effect of Catalyst, Solvent and Temperature on the Dehydrogenation of Pinane and p-Menthane<sup>2</sup>

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Pinane has been reported to yield *p*-cymene and a small amount of *o*-cymene on dehydrogenation with such catalysts as platinized charcoal,<sup>4</sup> platinized asbestos<sup>5</sup> and nickel.<sup>6</sup>

In view of the fact that pinane on destructive hydrogenation<sup>1</sup> yielded a mixture of hydrocarbons consisting predominantly of 1,1,2,3-tetramethylcyclohexane and containing smaller amounts of 1,2-methylisopropylcyclohexane, 1,4-methylisopropylcyclohexane and 1,1,2,5tetramethylcyclohexane, and in the light of the close similarity between hydrogenation and dehydrogenation, it was decided to reinvestigate the dehydrogenation of pinane and to determine whether or not poly-

methylated benzenes might be formed along with the previously reported o- and p-cymene.

In the present study it was found that when pinane was passed over platinized alumina, platinized pumice or platinized charcoal at 240-300° and at an hourly liquid space velocity of 0.2, dehydrogenation took place to yield a complex mixture of liquid products and gases consisting of hydrogen and methane. In addition to o- and p-cymene the liquid product contained 1,2,4- and 1,2,3-trimethylbenzene in considerable quantity. The relative amounts of the various hydrocarbons produced depended upon the conditions employed. Based upon previous hydrogenolysis studies with pinane and nickel-kieselguhr catalyst1 in which 1,1,2,3-tetramethylcyclohexane was shown to be the principal hydrogenolysis product, the above results may be presumed to be obtained by the reactions.

It is believed that the hydrogen liberated in the formation of o- and p-cymene acts upon the unreacted portion of pinane to form 1,1,2,3- and 1,1,2,5-tetramethylcyclohexane which then, in part, may undergo dehydrogenation and demetha-

(1) For paper VII of this series, see V. N. Ipatieff, H. Pines and M. Savoy, THIS JOURNAL, 69, 1948 (1947).

nation to 1,2,3- and 1,2,4-trimethylbenzene, respectively. 1,2- and 1,4-methylisopropylcyclohexane may also be formed upon hydrogenolysis



which upon subsequent dehydrogenation yield oand p-cymene. However, at high temperatures or at conditions of low hydrogen concentration pinane gives increased yields of p-cymene suggesting that another reaction takes precedence. Therefore, the cleavage of the four-membered ring of pinane appears to take place by at least two different and concurrent reactions: (a) a hydrogenolysis to favor the formation of 1,1,2,5and 1,1,2,3-tetramethylcyclohexane in approximately 2:1 molal ratio and 1,2-methylisopropylcyclohexane; the two tetramethylated cyclohexanes on subsequent dehydrogenation and demethanation yield 1,2,4- and 1,2,3-trimethylbenzene while 1,2-methylisopropylcyclohexane on dehydrogenation yields o-cymene; and (b) a straightforward rupture favoring the formation of p-cymene.

A study was made of the factors influencing the relative ease of cleavage of the four bonds constituting the four-membered ring of pinane. The role of temperature, nature of diluent, catalyst support and added hydrogen were investigated. The temperature was varied between 175 and  $300^{\circ}$ . Three types of diluents were employed: (1) hydrogen acceptors, such as pentenes and benzene, (2) hydrogen donors, such as methyl-cyclohexane and (3) "neutral acting" diluents such as *n*- and isopentane. In order to facilitate the cleavage of the four-membered ring, hydrogen gas was added to the reactions carried out at 175° with platinized alumina catalyst and at 300° with the less active platinized pumice catalyst.

The effect of temperature on the rupture of the

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<sup>(4)</sup> R. P. Linstead, K. O. Michaelis and S. L. S. Thomas, J. Chem. Soc., 1139 (1940).

<sup>(5)</sup> N. D. Zelinsky and R. J. Lewina, Ann., 476, 60 (1929).

<sup>(6)</sup> P. Sabatier and G. Gaudion, Compl. rend., 168, 670 (1919).

	EFFECT (	OF IE	MPERA	ATURE							
Experiment no.	1	2	3	4	5	6	7	8	9	10	11
Temperature, °C.		240	300	240	<b>24</b> 0	300	300	240	300	300	300
Diluent, kind	H2	None		Isopentane	<i>n</i> -Pentane		Benzene		Pentene		
Diluent: Pinane, molal ratio	1.5:1			4:1	4:1	4:1	1:1	4:1	4:1	4:1	1:1
Number of passes over catalyst	3	3	3	1	1	1	1	1	1	1	3
Aromatic, vol. %	0	35	59	34	49	56	66 <sup>.</sup>	35	68	0	50
Bond cleavage, vol. %											
$P_{\text{end}} \int p$ -Menthane	21	1	0	0	0	9	7	0	3	24	24
Bond I p-Cymene	0	<b>25</b>	41	24	<b>27</b>	54	26	29	44		42
$\mathbf{B}_{ond}$ II $\int \mathbf{o}$ -Menthane	7	1	0	0	0	0	0	0	0		0
boliu II ) o-Cymene	0	7	1	2	2	0	0	2	0		1
Bond III $\int 1,1,2,3$ -Tetramethylcyclohexane	30	20	14	17	13	9	9	20	6		10
Bond III ( 1,2,3-Trimethylbenzene	0	0	5	0	0	0	13	0	0		0
$B_{ond}$ IV $\int 1,1,2,5$ -Tetramethylcyclohexane	31	39	25	41	33	17	12	39	13		15
boliu IV ( 1,2,4-Trimethylbenzene	0	0	9	3	9	2	23	1	12		1
Unidentified	11	7	5	14	17	9	10	9	21		8

TABLE I

bonds constituting the four-membered ring of pinane is shown in Table I; platinized alumina was used as a catalyst.

Higher temperatures favor the formation of larger amounts of *p*-cymene; this is especially evident when a "neutral" diluent such as n-pentane is used. n-Pentane in 4:1 molal ratio appears to enhance the Bond I cleavage to form pcymene at 300° but has no effect at 240°. However, the extent of dehydrogenation appears to be increased at 240° when n-pentane is used as a diluent as evidenced by the fact that an equivalent or greater yield of aromatics is obtained in only one pass over the catalyst as compared to three passes when no diluent is used. Lower temperature and the absence of a diluent appears to favor the cleavage of Bond II to form 1,2-methylisopropylcyclohexane and o-cymene. At 300° small amounts of naphthalene were detected in the reaction product which may have been formed by the cyclodehydrogenation of o-cymene. When pure o-cymene was passed over platinum-alumina at 300° the reaction product contained 10-15%naphthalene, 50-60% unreacted o-cymene and 25-40% unidentified product, which may be 1methylindane, but owing to the unavailability of pure 1-methylindane as a reference sample for infrared spectra analysis no proof of its presence could be obtained. Naphthalene was separated, recrystallized and identified by its melting point



and mixed melting point with pure naphthalene. Its formation from *o*-cymene may be explained if one assumes the intermediate formation of 1methylindane followed by ring fission and cyclic dehydrogenation to naphthalene.

The formation of new rings under conditions of catalytic dehydrogenation is not new.<sup>7</sup> Moreover, the formation of naphthalene from 1-methylindane by catalytic dehydrogenation over palladized charcoal at 450°8 and from 1-methylindane and 1-methyloctahydroindene over platinized charcoal at 300° supports the above interpretation.

If, as postulated above, *p*-cymene formation is favored by the higher temperatures and conditions of low hydrogen concentration, it follows that the yield of *p*-cymene should be increased if the dehydrogenation is carried out in the presence of substances which would remove the hydrogen from the reaction zone as it is formed. Thus, the hydrogenolysis of the pinane should be minimized. The straight and branched chain pentenes and benzene were therefore used as hydrogen acceptors. It was thought that the pentenes should be particularly effective as hydrogen acceptors because of the ease with which they undergo hydrogenation of the pentanes.

The results obtained with both the branched and straight chain pentenes in the ratio of one mole of pentenes to one mole of pinane support the above advanced supposition. The pentenes act as true hydrogen acceptors and are completely converted to the pentanes. Bond I cleavage to form p-cymene is markedly facilitated since the hydrogen removed from the surface of the catalyst retards the hydrogenolysis of pinane. However, when the molal ratio of the pentenes to pinane

(7) (a) N. D. Zelinski, I. N. Titz and M. V. Gaverdowskaja, Ber.,
59, 2590 (1926); (b) N. D. Zelinski and I. N. Titz, *ibid.*, 62, 2869 (1929); 64, 183 (1931); (c) S. R. Sergienko, Doklady, U. S. S. R., 27, 960 (1940); (d) H. Pines, A. Edeleanu and V. N. Ipatieff, THIS JOURNAL, 67, 2193 (1945).

(8) L. Ruzicka and E. Peyer, Helv. Chim. Acta, 18, 676 (1935).

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is increased to 4:1, the dehydrogenation reaction is completely inhibited even at 300°. Presumably, the pentenes in this concentration so completely saturate the surface of the catalyst that the adsorption of pinane is prevented and pinane is recovered unchanged. Even *p*-menthane, which undergoes dehydrogenation almost quantitatively at 300° in the absence of a solvent, yields only 8% *p*-cymene under the above conditions; this amount of dehydrogenation occurred at the beginning of the run before the catalyst surface was completely saturated.

Although benzene may also act as a hydrogen acceptor, only about 3% of it was converted to cyclohexane at  $300^{\circ}$  when used in a ratio of 4 moles of benzene to 1 mole of pinane. Presumably, benzene is not as strongly adsorbed to the surface of the catalyst as the pentenes and therefore does not inhibit the dehydrogenation. The

TABLE	I	Ι
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Тне	Effect	OF	Hydrogen	AND	AND HYDROGEN-DONOR		
			DILUENT	•			
Exper	riment no				1	12	
Temp	erature, '	°C.			175	<b>2</b> 40	
Dilue	nt, kind				$H_2$	Methylcyclo-	
						hexane	
Dilue	nt :Pinane	, mol	al ratio	1.	5:1	1:1	
Numl	per of pas	ses o	ver catalyst		3	1	
Per ce	ent. arom	atic			0	25	
$\mathbf{Bond}$	cleavage						
n	, - (p-N	Menti	hane		21	. 0	
Bond I (p-Cyn		Cyme	ne		0	15	
<b>D</b>	f o-:	Ment	hane		7	0	
Bond 11	10 II { o-1	Cym	ene		0	6	
	(1	,1,2,3	3-Tetramethy	1-			
Bor	ıd III {	cycl	lohexane		30	30	
	(1	,2,3-'	Trimethylben	izene	0	0	
	( 1,	,1,2,5	-Tetramethy	1-			
Bor	id IV {	cycl	ohexane		30	41	
	( 1,	,2,4-7	[rimethylben]	zene	0	0	
Unide	ntified				11	8	

extent of dehydrogenation under the above conditions is somewhat increased and the Bond I cleavage to yield *p*-cymene is slightly enhanced. At  $240^{\circ}$  benzene, like *n*- and isopentane, has little effect upon the ratio of products obtained except that the *o*-menthane and *o*-cymene resulting from Bond II cleavage is diminished.

Increasing the molal ratio of pentanes to pinane from 1:1 to 4:1 at  $300^{\circ}$  results in a greatly increased yield of *p*-cymene at the expense of 1,2,3- and 1,2,4-trimethylbenzene. There appears to be no difference in the action of *n*- and isopentane. These effects are shown in Table I.

In order to determine the effect of a hydrogen donor diluent, an equimolal mixture of methylcyclohexane and pinane was passed over platinized alumina at 240°. It was found that the methylcyclohexane underwent dehydrogenation and the hydrogen liberated facilitated the hydrogenolysis of Bonds II, III and IV. Only 15% of Bond I cleaved to form *p*-cymene. The same effect was experienced when hydrogen in 1.5:1 mole ratio was added to pinane at  $175^{\circ}$ , a temperature too low for dehydrogenation to occur. The hydrogenolysis of the four-membered ring of pinane was complete; bonds III and IV were predominantly cleaved. The effect of added hydrogen and hydrogen donor diluent is shown in Table II.

In order to determine whether the catalyst support influences the cleavage of the various bonds, platinized alumina, platinized charcoal and platinized pumice were used as catalysts. It was found that platinized alumina and platinized charcoal are of comparable high activity, but that platinized pumice has very low activity presumably because of its lower adsorptive capacity. The results obtained in the absence of a solvent at 300° are given in Table III.

The effect of hydrogen in causing the hydrogenolysis reaction to occur is clearly shown when platinum-pumice is used as the catalyst. In the absence of added hydrogen no noticeable reaction takes place, while in the presence of hydrogen

	EFFECT OF	CATALYST SUPPO	rt at 300°		
Experiment	. 110.	3	13	14	15
Catalyst		Pt-Al <sub>2</sub> O <sub>3</sub>	Pt-C	Pt-Pumice	Pt-Pumice <sup>e</sup>
Number of	passes over catalyst	3	1	1	2
% Aromati	c	59	70	Trace	42
Bond cleave	age on dehydrogenation, vol. %				
Bond 1	f p-Menthane	0	0		8
	p-Cymenc	41	34		28
Bond II	ø-Menthane	0	0	••	0
	o-Cymene	1	1		11
Bond III	1,1,2,3-Tetramethylcyclohexane	14	9	••	17
	1,2,3-Trimethylbenzene	5	4		0
Bond 1V	1,1,2,5-Tetramethylcyclohexane	25	18	• •	29
	1,2,4-Trimethylbenzene	9	18		2
Unidentified	i	5	16	• •	6

TABLE III

• Small amount of hydrogen was passed over the catalyst.

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42% of aromatic hydrocarbons are formed and the reaction product did not contain any unreacted pinane. Also, when platinized alumina is flushed with nitrogen before pinane is passed very little dehydrogenation occurs until the concentration of hydrogen has increased to the point where the hydrogenolysis reaction can readily take place. The above experiments indicate that the products of hydrogenolysis of pinane undergo dehydrogenation more readily than pinane itself.

In order to gain a better insight into the effect of temperature, solvents and catalyst support on the dehydrogenation activity of the catalyst toward pinane, a comparative study of the same variables on the dehydrogenation of p-menthane (1-methyl-4-isopropylcyclohexane) was made.

The dehydrogenation of p-menthane was carried out at 240° and 300° using platinized alumina catalyst. At 300° without solvent or in the presence of either pentane or benzene in 4:1 molal ratio dehydrogenation is virtually complete and p-cymene is obtained in 95–100% yield. The use of pentene as a solvent in 1:1 molal ratio likewise favors the complete conversion to p-cymene and pentane is obtained in the product. However, when the mole ratio of pentenes is increased to 4:1, p-cymene is obtained in only 8% yield at 240°, 270° or 300°. The dehydrogenation which does take place occurs at the beginning of the experiment before the catalyst surface has been completely covered with adsorbed pentenes.

The effect of various diluents upon the dehydrogenation of p-menthane in the presence of platinized alumina has been studied. The reaction has been carried out at 240° using a molal ratio of diluents to p-menthane of 4:1. The results are given in Table IV.

## TABLE IV

EFFECT OF DILUENTS AT 240° ON DEHYDROGENATION OF p-

WIENTHANE	
Solvent, molal ratio 4:1	p-Cymene, %
None	55
<i>n</i> -Pentane	78
Isopentane	80
Benzene	95
Pentenes	8

*n*-Pentane, isopentane and benzene used as diluents increase the extent of dehydrogenation; there is no difference in the effect of *n*- and isopentane. Benzene has the most beneficial effect, the dehydrogenation of p-menthane being virtually complete at 240°. Pentenes, however, in 4:1 molal ratio inhibit the dehydrogenation.

### **Experimental Part**

Apparatus and Procedure.—The apparatus consisted of a graduated buret and a pump connected to a Pyrex glass reaction tube containing the catalyst bed, a water-cooled receiver-condenser, a Dry Ice-acetone cooled trap, and a calibrated gas-collecting bottle containing saturated salt solution. The reaction tube was heated in a thermostatically controlled vertical furnace, brought to the desired temperature, ranging from 175 to 300°, in a slow stream

of hydrogen. The pinane of p-menthane, with or without diluent, was added at an hourly rate approximately equal to two-tenths the volume of the catalyst bed. The liquid product was collected in the water-cooled condenser-receiver and the dehydrogenation gas was freed of entrapped solvent by passing it through a Dry Ice-acetone cooled trap and collected in a gas bottle over saturated salt solution. The temperature and barometric pressure were recorded along with the volume of the gas obtained. In some instances the liquid product was repassed through the catalyst tube until no further reaction occurred. In the absence of solvents the extent of dehydrogenation could also be followed from the change in the refractive index with each successive pass. If a solvent was present it was removed by distillation through a distilling column of an efficiency of seven theoretical plates.

A diagrammatic sketch of the procedure for the determination of the composition of product obtained on the dehydrogenation of pinane is given below.

DIAGRAMMATIC SKETCH: DEHYDROGENATION OF PINANE PINANE



The aromatic hydrocarbons which were produced during the dehydrogenation were separated chromatographically according to the method of Mair and Forziati.<sup>9</sup> This was accomplished by diluting the solvent freed reaction product with four or five parts of pentane and by passing the mixture through a five-foot column containing 200-300 mesh silica gel. An almost quantitative separation of the aromatics and naphthenes was effected in this man-The aromatic and naphthene portions were each ner. distilled, and the aromatic portion was analyzed. The naphthene portion was again dehydrogenated and the aromatics formed were separated chromatographically and analyzed. This procedure was repeated until very little naphthene remained which was assumed to have the same composition as the naphthenes from which the last portion of aromatics was obtained.

#### Analytical Part

The naphthenic product obtained from the dehydrogenation of pinane, according to infrared spectral analysis, contained no pinane and corresponded to the monocyclic hydrocarbons  $C_{10}H_{20}$ .

Anal. Calcd. for C<sub>10</sub>H<sub>20</sub>: C, 85.63; H, 14.37. Found: C, 85.70; H, 14.27.

(9) B. J. Mair and A. F. Forziati, J. Research Natl. Bureau Stand., 32, 151, 165 (1944). The mixture of o- and p-cymene were separated by fractional crystallization of their sulfonamide derivatives<sup>10,11</sup> from hot benzene. The less soluble o-cymene sulfonamide crystallized out in fine needle crystals, m.p. 152.5-153.5°, and gave no depression in melting point when mixed with a known sample of o-cymene sulfonamide.

Anal. Calcd. for  $C_{10}H_{15}NO_{2}S$ : C, 56.31; H, 7.09; N, 6.57. Found: C, 56.56; H, 6.77; N, 6.64.

p-Cymene sulfonamide crystallized out from benzene in irregular plates, m.p.  $115-116^{\circ}$ .<sup>10,11</sup> p-Cymene was further characterized by chromic acid oxidation to terephthalic acid, the dimethyl ester of which melted at 141– 141.5°.

1,2,4-Trimethylbenzene was characterized by conversion to the trinitro derivative,<sup>12</sup> m.p. 184–185°. It showed no depression in melting point when mixed with a trinitroderivative of a known sample of 1,2,4-trimethylbenzene.

1,2,3-Trimethylbenzene was identified by conversion to the tribromo derivative, m.p. 242-243°, which gave no depression in melting point when mixed with a synthetic sample of tribromo-1,2,3-trimethylbenzene.

Naphthalene was identified by its melting point 79.5– 80°; it did not depress the melting point of a known sample of naphthalene.

Gaseous Product.—The gas was analyzed by absorption and combustion using a Goeckel type<sup>18</sup> gas analysis apparatus.

Infrared Spectral Analysis (by W. S. Gallaway).<sup>14</sup>— The analyses were made according to the procedure described previously.<sup>1</sup> The wave lengths used for calculating the composition of the various samples are given in Table V.

#### TABLE V

WAVE LENGTHS OF CHARACTERISTIC INFRARED ABSORPTIONS.  $\mu$ 

1,2,3-Trimethyl- benzene	1,2,4-Trimethyl- benzene	p-Cymene	o-Cymene
9.14	8.88	9.45	9.20
9.31	8.79	9.80	9.63
9.91	10.01	12.23	13.19
10.13	12,41		13.78
13.05			

#### Materials

Pinane was prepared by the hydrogenation of  $\alpha$ -pinene which was obtained from the Hercules Company as Pinene 111 and is reported to contain less than 2% of camphene. The  $\alpha$ -pinene was further purified by distillation through a column of twelve-plate efficiency using a reflux ratio of twelve to one. The middle portion boiling at 155-156°,  $n^{20}_D$  1.4660, was dissolved in an equal volume of pentane and hydrogenated in a rotating autoclave at 50°, using nickel-kieselguhr catalyst<sup>15</sup> (10% by weight of  $\alpha$ -pinene charged) and 100 atm. initial hydrogen pressure. The pinane distilled at 165-166°,  $n^{20}_D$  1.4605, and did not contain any olefins.

*p*-Menthane was prepared by the hydrogenation of *p*-cymene. The *p*-cymene was purified by washing repeatedly with sulfuric acid and distilling through a twelve-plate column. The portion boiling at  $176.5^{\circ}$ ,  $n^{20}$ <sub>D</sub> 1.4998, was hydrogenated in a rotating autoclave at 115° with nickelkieselguhr catalyst and 100 atm. initial hydrogen pressure. The *p*-menthane produced contained no aromatics and distilled at  $167^{\circ}$ ,  $n^{20}$ <sub>D</sub> 1.4398.

(10) E. H. Huntress and F. H. Carten, THIS JOURNAL, 52, 511 (1940).

(11) E. H. Huntress and J. S. Autenrieth, ibid., 63, 3446 (1941).

(12) Huntress and Mulliken, "Identification of Pure Organic Compounds," Order 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 530.

1941, p. 530. (13) "U. O. P. Laboratory Test Methods for Petroleum and Its Products"-g-84-40, Universal Oil Products Company, Chicago, Illinois (1940).

(14) Research Laboratories, Universal Oil Products Company,

(15) V. N. Ipatieff and B. B. Corson, Ind. Eng. Chem., 30, 1039 (1938).

o-Cymene was prepared from o-bromotoluene and acetone via the Grignard reaction. The o-tolyldimethylcarbinol produced from this reaction was dehydrated by passing it over activated alumina at  $320^{\circ}$ . o-Isopropenyltoluene boiling at  $171-173^{\circ}$ ,  $n^{20}$ p 1.5253, was obtained in an over-all yield of 48% based upon the bromotoluene. o-Isopropenyltoluene was hydrogenated to o-cymene in a rotating autoclave at 40° with nickel-kieselguhr catalyst and an initial hydrogen pressure of 61 atm. The theoretical amount of hydrogen was absorbed. The o-cymene distilled at  $174^{\circ}$ ,  $n^{20}$ p 1.4994.

Platinum-Alumina Catalyst was prepared by heating platinum, 12.0 g., on a steam-bath with aqua regia, until solution was complete. The excess acid was removed by evaporating the solution almost to dryness and then adding a 100-cc. portion of water and again evaporating down; this procedure was repeated ten times. The chloroplatinic acid was dissolved in 200 cc. of distilled water and suction filtered to remove any contaminants. The clear filtrate was added to 150 cc., 120 g., of alumina (Alorco 10-12 mesh). The liquid completely covered the alumina. The solution was evaporated on a steam-bath with thorough stirring. When dry the catalyst has a uniform yellow-orange color. It was heated in a vertical furnace at 100° in an atmosphere of hydrogen for several hours. The temperature was then raised to 200° and the heating continued for several more hours. Finally, it was heated at 254° for two hours prior to use for dehydrogenation. The reduced catalyst has a uniform gray color.

**Platinum-pumice catalyst** was prepared according to the same method described for platinum-alumina catalyst, using 10.1 g. of platinum to 125 cc., 54.5 g. of pumice.

**Platinum charcoal catalyst** was prepared according to the method described by Linstead and co-workers<sup>4</sup> except that activated Burrell cocoanut charcoal (10-14 mesh) was used in place of norit charcoal in order to facilitate its use in a vertical catalyst tube.

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#### Summary

Pinane on dehydrogenation yields in addition to the previously reported p- and o-cymene also a large amount of 1,2,4- and 1,2,3-trimethylbenzene, the ratio of products obtained depending upon the temperature, solvent and catalyst support employed.

The cleavage of the four-membered ring of pinane appears to occur by two different reactions; a thermal cleavage to favor the formation of p-cymene and a hydrogenolysis which favors the formation of 1,1,2,3- and 1,1,2,5-tetramethyl-cyclohexane and o-menthane. The hydrogen liberated from the former reaction causes the latter reaction to occur. At high temperatures the tetramethylcyclohexanes undergo demethanation and dehydrogenation to the corresponding trimethylbenzenes.

The dehydrogenation of pinane is inhibited when it is diluted with four moles of pentenes. Pentane and benzene enhance the extent of dehydrogenation of pinane.

A comparative study of the dehydrogenation of *p*-menthane using the same variables was made. EVANSTON. ILLINOIS RECEIVED AUGUST 2, 1947