this table hydrogenation methods were used which permitted distinction to be made between that hydrogenation entering the aromatic rings and that saturating the alkene double bond. Cuts IV and V obviously contaminated each other to a slight extent. The balance of Table II agrees reasonably well with the expected figures. Substantiation of the mechanism and the identification of the fragments seem satisfactory.

Oxidation Products

Figure 4 shows the oxidation products resulting when the cyclopentadiene structure is broken down to produce ketones or aldehydes. These hypothetical products are noted as II, III, IV, V, and VI. The presence of ketone, aldehyde, and acidic bodies is well established; separation has not yet been accomplished. Indene and coumarone are presumed to produce compounds of the types shown in II-A, V-A, II-B, and V-B. A and B represent indene and coumarone, re-

spectively, which may polymerize to give the formula of Staudinger shown in XI, and which is now believed to be inadequate in explaining indene polymer properties and reactions. XII is the more satisfactory representation which can give rise to XIII and XV. IX is the fulvenated structure which is the main product resulting from the oxidation reactions. Studies are in progress in this field which have brought new individuals to light, and which promise to have immediate industrial application. Oxidation of indene resins leads to the production of a complex mixture of organic acids whose separation should be of extreme interest. The present papers on hydrogenation and oxidation do not by any means exhaust the possibilities in the field of coal-tar-derived resins.

Literature Cited

- (1) Carmody, IND. ENG. CHEM., 32, 525 (1940).
- Hercules Powder Co., private communication.
 Neville Company, "Neville Resins", p. 39 (1938)
- (4) Thiele, Balhorn, and Albrecht, Ann., 1, 348 (1906).

Liquid-Phase Hydrogenation of *p*-Cymene

KENNETH A. KOBE AND ANTON VITTONE

University of Washington, Seattle, Wash.

The optimum conditions have been determined for the liquid-phase hydrogenation of p-cymene to p-menthane, with a nickel catalyst. The physical properties of *p*-menthane have been determined and tabulated.

THE chemical utilization of *p*-cymene prepared from spruce turpentine has presented an interesting problem because of the quantity of spruce turpentine potentially available which would be recovered if a sufficient market existed (6). Most of this work on *p*-cymene has been directed toward its oxidation, or a sequence of reactions to produce thymol or carvacrol. The purpose of this series of papers¹ has been to study the variable factors affecting the organic unit processes applied to *p*-cymene.

The formation of p-cymene in the pulp digester during the sulfite pulping of spruce wood is attributed to the dehydrogenation and rearrangement of various terpenic compounds present in the wood. This paper reports a study of the liquid-phase hydrogenation of p-cymene to p-menthane, which is the parent member of the *p*-menthane series of terpenic compounds (2). This product would be the cheapest starting material for synthesis in the *p*-menthane series.

The earliest work was the vapor-phase hydrogenation by Sabatier and Senderens in 1901 (10) and by Sabatier and Murat in 1913 (8). The hydrogenated product consisted of 66 per cent menthane with 16 per cent p-dimethylcyclohexane and p-methylethylcyclohexane (9). Skita and Schneck (12) studied the stereoisomerism of p-menthane prepared by both vapor-phase hydrogenation over nickel and

¹ p-Cymene Studies, V. Previous articles appeared in J. Am. Chem. Soc., 57, 1640 (1935), 62, 562 (1940), and in IND. ENG. CHEM., 31, 257, 264 (1939).

liquid-phase hydrogenation with platinum catalyst. They state that the former method yielded the trans form and the latter the cis form of p-menthane. Adams and Marshall (1) hydrogenated p-cymene in glacial acetic acid with platinum oxide catalyst at room temperature and reported quantitative reduction as measured by hydrogen absorption. Brown, Durand, and Marvel (3) found that reduction by this method is greatly accelerated by small amounts of hydrogen chloride. Shoorel, Tulleners, and Waterman (11) studied the liquid-phase hydrogenation of p-cymene over nickel on kieselguhr at about 140 atmospheres pressure. Their yield is not stated.

Experimental Procedure

p-CYMENE. A technical grade of p-cymene was purified by successive shaking with 25-ml. portions of concentrated sulfuric acid per liter of p-cymene until the acid layer remained practically colorless, and then washing with dilute sodium carbonate solution and with water. After being dried over calcium chloride, the p-cymene was refluxed over sodium for 2 hours and fractionally distilled through a Young and Thomas column having 14 disks, 2 cm. in diameter, spaced over a length of 30 cm. The purified product distilled between 175° and 176° C. $(d_4^{25} = 0.8534, n_D^{25} = 1.4878)$. This p-cymene was used in runs 1 to 6; for runs 7 to 15 it was refluxed over the catalyst (2 grams catalyst per 300 ml.) for

2 hours to remove poisons possibly present, and was then filtered.

RANEY NICKEL CATALYST was prepared from Raney nickelaluminum alloy (4, 7).

HYDROGENATION. The hydrogenation apparatus was described previously (5). In runs 1 to 6 (Table I) 26.8 grams (0.2 mole) of *p*-cymene were placed in the bomb with the catalyst and heated without agitation until the temperature was within 15° to 20° of the desired temperature. The initial

hydrogen pressure was about half of the final, and when the maximum temperature was reached, the pressure was increased to the desired value and kept there by addition of hydrogen at intervals. In runs 7 to 15 the original hydrogen pressure was either 1000 or 1500 pounds per square inch (70.3 or 105.5 kg. per sq. cm.), and no further hydrogen was added during the run. Agitation and heating were started together. Temperature and pressure data were taken at 5-minute intervals and plotted. Figure 1 shows typical data

from run 9, showing temperature, actual pressure, and pressure calculated to 220° C.





ISOLATION OF *p*-MENTHANE. The hydrogenated product was removed from the bomb with a pipet, and the nickel catalyst was removed by settling. In runs 1 to 7 any unhydrogenated cymene was removed by conversion to nitrocymene. To the hydrogenated product were added 15 ml. of concentrated sulfuric acid, and the mixture was cooled to 0-5° C. To this mixture was slowly added, with shaking, a nitrating acid (15 ml. concentrated sulfuric and 7 ml. concentrated nitric acid). After shaking for 15 minutes, the product was separated from the acid layer, and washed with sodium carbonate solution and with water. The product was fractionated in a Vigreux flask. In runs 8 to 14 the p-menthane was not isolated, but the yield was determined from the refractive index of the hydrogenated product after simple distillation. The refractive index-composition diagram is given in Figure 2.

YIELDS. Two bases are used for calculating yield. Yield per cent input signifies the yield of p-menthane calculated on the quantity of p-cymene introduced into the bomb. Per cent p-menthane in the product signifies the percentage of p-menthane in the hydrogenated product removed from the bomb or the yield calculated on the recovered product. This latter percentage represents the yield of p-menthane on hydrogenation, for it leaves from consideration the product lost when the hydrogen pressure is relieved. The per cent pmenthane determined from the refractive index is but slightly greater than that obtained by nitration and fractionation (92.2 and 90.7 per cent on identical runs).

Optimum Conditions

TEMPERATURE. The first series of runs was made at 240° C. using various amounts of catalyst. The data are given in Table I.

TABLE I.HYDROG(0.2 mole p-cymene, 1000	ENATION pounds p	OF p-C	YMENE inch hyd	AT 240° rogen pre	C.	
Run No.	1	2	3	4	5	6
Catalyst, gram Hydrogenation time, min. Yield, % input p-Menthane in product, % Low-boiling fractions, % recovery	$0.88 \\ 185 \\ 77.7 \\ 82.8 \\ 12.6 \end{cases}$	$0.86 \\ 180 \\ 83.3 \\ 88.0 \\ 5.4$	$0.73 \\ 145 \\ 69.6 \\ 74.2 \\ 7.9 \\$	$0.42 \\ 145 \\ 79.5 \\ 83.5 \\ 12.1 \\$	0.26 130 83.5 89.4 2.7	$0.12 \\ 195 \\ 92.8 \\ 97.5 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.12 \\ 0.0 \\ $

The boiling range of the product varied from 166.5° to 171.5° C., which indicated the presence of intermediate products of hydrogenation, decomposition products, or a stereoisomer of lower boiling point. The low-boiling fractions, 166.5° to 168.5° C., from the five runs were added together and a further hydrogenation was attempted. No hydrogenation occurred. Runs at lower temperatures gave no low-boiling fraction. The experiment of Shoorel, Tulleners, and Waterman (11) on the hydrogenolysis of *p*-menthane over nickel on kieselguhr at 470° C. for 60 minutes yielded methane, propane, and liquid products boiling from 35° to 160° . From these facts it seemed probable that the low-boiling products in runs 1 to 5 were products of decomposition.

The data on runs made at lower temperatures are given in Table II. No lower boiling fraction was found in the product at 220° C. Since the *p*-menthane in the recovered products at 220° and 200° are almost identical and the rate of reaction at 220° is greater, the latter was adopted for all further runs as being the optimum temperature of hydrogenation.



FIGURE 2. REFRACTIVE INDEX-COMPOSITION DIAGRAM FOR *p*-CYMENE IN *p*-MENTHANE (PER CENT BY WEIGHT)

TABLE	II.	EFFECT OF	VARIABLE	TEMPERATURE	ON	Hydro-
		GEN	ATION OF p -	Cymene		

(0.2 mole *p*-cymene, 0.26 gram Raney catalyst, 1000 pounds per square inch initial hydrogen pressure)

Run No.	9	12	13
Temp., ° C. Time, min,	220 115	200 120	180 180
Yield, % input p-Menthane in product, %	90.6 97.6	$\begin{array}{c} 93.4\\ 97.9\end{array}$	$\begin{array}{c} 84.5\\ 93.6\end{array}$

TABLE III. EFFECT OF VARIABLE CATALYST AT 220° C. (0.2 mole p-cymene, 1000 pounds per square inch initial hydrogen pressure)

Run No. 7 8 9 10 11 Catalyst, gram 0.33 0.33 0.26 0.20 0.11 Time, min. 120 115 115 115 130 Yield, % input 83.3 88.2 90.6 88.5 86.5 p.Menthane in 90.7 92.2 97.6 93.2 90.8	ora more p-oymene,	rooo boanas	per square	/ mod minia	L H S GL O BOH	pressure
Catalyst, gram 0.33 0.33 0.26 0.20 0.13 Time, min. 120 115 115 115 130 Yield, % input 83.3 88.2 90.6 88.5 86.5 p-Menthane in 90.7 92.2 97.6 93.2 90.8 product, % 90.8	Run No.	7	8	9	10	11
	Catalyst, gram Time, min. Yield, % input p-Menthane in product, %	0.33 120 83.3 90.7	$\begin{array}{c} 0.33\\ 115\\ 88.2\\ 92.2 \end{array}$	0.26 115 90.6 97.6	0.20 115 88.5 93.2	0.13 130 86.5 90.8

TABLE IV. EF	FECT OF VARIABLE	PRESSURE AND	QUANTITY AT
Run No.	9 220 4	14	15
<i>p</i> -Cymene, m Catalyst, gra:	ole 0.2 m 0.26	$\substack{\textbf{0.2}\\\textbf{0.26}}$	$\substack{\textbf{0.4}\\\textbf{0.52}}$
lb./sq. in. Time, min. Yield, % inpu	1000 115 ut 90.6	$\begin{array}{c}1500\\90\\82.2\end{array}$	$1500 \\ 115 \\ 90.2$
p-Menthane i product, %	in 97.6	91.6	93.2

CATALYST. Table I shows that the time required for hydrogenation decreased with decreasing catalyst concentration until a minimum time was obtained. Another series

of runs was made at the optimum temperature of 220° C. The data are shown in Table III. The time of hydrogenation is practically constant except in run 11, where it increased noticeably. The yield was a maximum in run 9, so that 0.26 gram of catalyst is considered optimum.

PRESSURE AND QUANTITY. The effect of pressure and quantity of reactants is shown in Table IV. Although the increased pressure (runs 9 and 14) decreases the time of hydrogenation, the yield is also decreased somewhat. Doubling the quantity of *p*-cymene and catalyst used at the higher pressure (runs 14 and 15) increased the time required to that of the usual charge at the lower pressure.

Physical Properties of *p*-Menthane

From the various experiments about 500 ml. of p-menthane had been accumulated. It was desired to purify this p-menthane further in order that the physical constants might be accurately determined. The p-menthane was successively treated with a mixture of 30 ml. concentrated sulfuric acid and 7 ml. concentrated nitric acid until the mixed acid was no longer yellow. It was washed with sodium carbonate solution, dilute alcohol solution, and finally with water. After drying over calcium chloride, it was fractionated through the Young and Thomas column previously used. The middle fraction, which distilled over the range 171.0° to 171.7° C. at 760 mm., was used for the determination of the physical properties.

VAPOR PRESSURE. The vapor pressure of *p*-menthane was determined by the isoteniscope method over the range 75 to 760 mm. From the straight line resulting from the data plotted as log p against 1/T, the boiling point was found to be 171.0° at 760 mm. The equation for the vapor pressure line is:

where
$$P = -(2143/T) + 6.706$$

where $P =$ vapor pressure at 0° C., cm. Hg
 $T =$ temp., °K.

From this equation the following boiling points are calculated:

Pressure	в. Р.	Pressure	В. Р.
Mm.	° C.	Mm.	° C.
15	55.0	300	136.6
25	66.5	400	146.6
50	83.5	500	154.8
75	94.7	600	161.6
100	102.3	700	167.5
200	123.3	760	171.0

REFRACTIVE INDEX. The refractive index was determined with both the Abbé and dipping refractometer. At 25° the Abbé gave 1.4383, and the data shown in Figure 2 were obtained in this way. The dipping refractometer was used to determine the refractive index-temperature line. The data are given in Table V. A straight line was obtained, whose equation is:

$$n_D^t = 1.44924 - 0.000417 t$$

where $t = \text{temp.}$, ° C.

DENSITY. Data for density are given in Table V. All data obtained in this work are given and compared with those of previous workers.

		TABLE	V. PHYS	ICAL CON	STANTS O	F p-ME	NTHANE		
Citation	(10)	(8)	trans (12)	(1)	(3)	(11)	(13)	This work
B. P., • C.	169-70	167-8	161.0	168.5	63 (22 mm.)	168-9	168-9 (769 mm.)	170-2 (755 mm.)	171.0
Density					(22 mm.)		(100 mm)	(100 mm.)	(100 mm.)
dg	• • • •	0.8134		• • • • • •		• • • •	••••	••••	
d ₀ 25	• • • •	0.8025							• • • • •
d°	0.8132								
d10		••••							0.8089
d10			0.792	0.816		0.8038	0.8026	0.7974	0.8008
d ^{§5}		• • • •	• • • • • •		0.8061				0.7973
Refractive									
n ¹⁰ _D			•••••	• • • • •					1.44507
n_D^{15}									1.44296
$n_{\rm D}^{20}$			1.43931	1.45149		1.4395	1.4416	1.4380	1.44092
n_{D}^{25}			• • • • •	• • • • •	1.4370				1.43876
n_{D}^{so}									1.43673
$n^{20}C$							1.4392		
n ²⁰							1.4470		
n_{G}^{20}	• • • •	••••	••••		• • • •	• • • •	1.4517	••••	••••

Literature Cited

- Adams and Marshall, J. Am. Chem. Soc., 50, 1970-3 (1928).
 Brooks, "Non-Benzenoid Hydrocarbons", Chap. 9, New York,
- McGraw-Hill Book Co., 1922. (3) Brown, Durand, and Marvel, J. Am. Chem. Soc. 58 1594-6
- (1936).(4)
- Covert and Adkins, Ibid., 54, 4116 (1932). (5)
- Goss and Kobe, J. Chem. Education, 11, 250-1 (1934). Groggins, Chem. & Met. Eng., 34, 291-3 (1927). (6)
- (7) Raney, U. S. Patents 1,628,190 (May 10, 1927), 1,915,473 (June 27, 1933).
- (8) Sabatier and Murat, Compt. rend., 156, 184-7 (1913).
 (9) Sabatier and Reid, "Catalysis in Organic Chemistry", p. 447, New York, D. Van Nostrand Co., 1922.
- Sabatier and Senderens, Compt. rend., 132, 1254-7 (1901).
 Shoorel, Tulleners, and Waterman, J. Inst. Petroleum Tech.,
- 18, 179-82 (1932)
- (12) Skita and Schneck, Ber., 55, 144-52 (1922).
- (13) Smirnov, J. Russ. Phys. Chem. Soc., 41, 1374 (1910).