the dihydrofuran (V), m.p. 74–75° by isolation and mixed m.p., and a major fraction, b.p. 190–205° (2 mm.), which cooled to a glassy solid. This latter material was probably largely polymeric oxide.

Anal. Calcd. for $(C_{11}H_{14}O)_n$: C, 81.44; H, 8.70. Found: C, 81.57; H, 8.13.

The alkali-soluble fraction from the acid-catalyzed reaction of the oxide with phenol was processed in the same manner described for the alkali-soluble fraction of the oxide–phenoxide reaction. A small amount of the dihydrofuran V was isolated after the cyclization step. The ether solution from the bicarbonate extraction of the esterification mixture was freed of solvent, heated with dilute sodium hydroxide, and again extracted with ether. The aqueous layer was now treated with Dry Ice. This caused the separation of an oil which, after washing with water to remove residual phenol, was recrystallized from dilute ethanol, 0.8 g., m.p. 153–154°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.66; H, 7.94.

This compound is isomeric with the ether-alcohol I, it is phenolic, but it is not esterified under the conditions used. Its structure is not entirely clear to us.

Preparation of 2-Phenoxy-1-(2,4,6-trimethylphenyl)-ethanol (IV).—The preparation of 2,4,6-trimethylphenacyl bromide was readily accomplished by the bromination of acetomesitylene in glacial acetic acid, or by the method of Jacobs and Heidelberger[14] from mesitylene and bromoacetyl bromide.

A reaction mixture, consisting of 2,4,6-trimethylphenacyl bromide (24.1 g., 0.1 mole, m.p. 55–56°), phenol (10 g., 0.106 mole), sodium hydroxide (4 g., 0.1 mole), dioxane (50 cc.) and water (35 cc.), was held at reflux temperature with stirring for 4 hours. It was then poured into water and extracted twice with ether. The aqueous layer analyzed for 77% of the theoretical bromide ion. The ether layer was dried over anhydrous sodium sulfate and then distilled from a modified Claisen flask having 2 inches of $^1/_8$ inch glass helices. The **phenoxymethyl mesityl ketone** (12.3 g., 48.4%) boiled at 180–192° (4–7 mm.), $n^{20}\mathrm{D}$ 1.5655.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.80; H, 7.45.

Reduction of this ketone with lithium aluminum hydride gave the ether-alcohol IV (80%) as a viscous, colorless liquid, b.p. 185–191° (3–4 mm.), $n^{20}\mathrm{D}$ 1.5730.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.26; H, 7.64.

The **p-nitrobenzoate**,[13] from dilute ethanol, melted at 114.5–115.5°.

Anal. Calcd. for $C_{24}H_{23}NO_5$: C, 71.09; H, 5.72. Found: C, 70.85; H, 6.03.

The mixture of this *p*-nitrobenzoate with that obtained from the primary alcohol I melted at 95–113°.

The **3,5-dinitrobenzoate**, from ethanol, melted at 126–127°.[13]

Anal. Calcd. for $C_{24}H_{22}N_2O_7$: C, 64.00; H, 4.92. Found: C, 64.07; H, 4.97.

A mixture of the 3,5-dinitrobenzoates of IV and the oxide–phenol reaction product melted at 110–129°.

The **α-naphthylurethan** of IV melted at 138.5–139.5°.

Anal. Calcd. for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40. Found: C, 78.79; H, 6.68.

α-Naphthylurethans of IV and the oxide–phenol reaction product melted at 120–140° when mixed.

Preparation of 2-Phenoxy-2-(2,4,6-trimethylphenyl)-ethanol (I).—A preparation of α-bromo-2,4,6-trimethylphenylacetyl bromide,[15] not purified by distillation, was poured into excess phenol and the mixture warmed for a few minutes. This was then poured into water, extracted with ether, and finally distilled in vacuum to obtain a relatively poor yield of a compound presumed to be phenyl α-bromo-2,4,6-trimethylphenylacetate. This ester (6.3 g.) was added to a mixture of phenol–sodium phenoxide prepared from phenol (14 g.) and sodium (0.5 g.). After being heated 6 hours in a boiling water-bath, the mixture was poured into water, treated with Dry Ice, extracted with ether, and the aqueous layer acidified. The solid thus obtained weighed 1.8 g. after one recrystallization from dilute ethanol. The pure, white needles of **α-phenoxy-2,4,6-trimethylphenylacetic acid** melted at 139–140°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.46; H, 6.94.

This acid (0.5 g.) was reduced with lithium aluminum hydride, and the resulting clear, viscous oil was converted to its *p*-nitrobenzoate (93% yield from the substituted phenylacetic acid), m.p. 112–113.5° alone or when mixed with the *p*-nitrobenzoate derived from the oxide–phenoxide product.

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

Studies in the Terpene Series. XVI.[1] Hydrogenolysis of Pinane in a Flow Type Apparatus in the Presence of Hydrogenation Catalysts

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The hydrogenolysis of pinane was studied in a flow type apparatus in the presence of nickel–kieselguhr, nickel–alumina, copper–alumina and nickel catalysts. The hydrogenolysis was carried out under 56 atmospheres of pressure and at temperatures ranging from 225 to 295°, using a molar ratio of hydrogen to pinane varying from 2.1 to 11.7. From 35 to 67% of the reacted pinane consisted of alkylcyclopentanes admixed with small amounts of bicyclic dihydroterpenes, the remainder being alkylcyclohexanes. The presence of alkylcyclopentanes indicates that skeletal isomerization accompanied the hydrogenolysis of pinane.

In a previous paper[3] it was shown that pinane undergoes hydrogenolysis when reacting with hydrogen at 175° in the presence of a nickel–kieselguhr catalyst and at 100 atmospheres of hydrogen pressure. The reaction product contained 65% of 1,1,2,3-tetramethylcyclohexane and smaller amounts of 1-methyl-2-isopropyl-, 1-methyl-4-isopropyl- and 1,1,2,5-tetramethylcyclohexane. It was also observed[4] that by using Raney nickel or copper–alumina as catalysts the hydrogenolysis of pinane yielded, in addition to the above-mentioned alkylcyclohexanes, also alkylcyclopentanes. Owing to the difference in the results obtained it was

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[1] For Paper XV of this series see V. N. Ipatieff, G. Czajkowski and H. Pines, *J. Org. Chem.*, **17**, 1431 (1952); (a) Deceased November 29, 1952.

[2] Universal Oil Products Company Predoctorate Fellow 1949–1951.

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TABLE I

HYDROGENOLYSIS OF PINANE

Experiment	3	4	12	14	18
Catalyst,[a] kind	Ni(K)	Ni(K)	Ni	Ni–Al_2O_3	Cu–Al_2O_3
Catalyst, ml.	50	50	24[b]	50	50
H.L.S.V.[c]	0.44	0.54		0.26	0.20
Temp., °C.	225	260	280	295	265
Molar ratio, H_2/pinane	2.08	4.71	4.82	8.82	11.68
Pinane reacted, %	100	100	32	62	54
Composition of product based on reacted pinane, mole %					
Alkylcyclohexanes	65	57	33	54	44
"Alkylcyclopentanes"[d]	35	43	67	46	56
Composition of alkylcyclohexanes, %					
1-Methyl-2-isopropyl-	8	7	6	4	5
1-Methyl-4-isopropyl-	29	28	18	41	10
1,1,2,3-Tetramethyl-	41	46	57	33	32
1,1,2,5-Tetramethyl-	17	10	9	20	43
Unknown	5	0	10	2	10
"Alkylcyclopentanes"					
n^{20}_D	1.4426		1.4399		1.4404
Carbon %, found	85.95	86.00	86.06	86.51	85.94
Hydrogen %, found	13.90	14.15	14.29	13.50	14.37

Calculated: for alkylcyclopentanes, $C_{10}H_{20}$: C, 85.63; H, 14.37.
for bicyclic compounds, $C_{10}H_{18}$: C, 86.8; H, 13.13.

[a] All the catalysts were in the form of $^1/_8 \times {}^1/_8$ inch cylinders with the exception of nickel which was in the form of powder. [b] In grams. [c] H.L.S.V. = Volume of liquid per volume of catalyst per hour. [d] Composed of a mixture of alkylcyclopentanes and bicyclic hydrocarbons.

decided to reinvestigate the hydrogenolysis of pinane using a flow type apparatus which has the following advantages over an autoclave.

1. The reactants can be preheated to the temperatures at which the hydrogenolysis is to be carried out before coming into contact with the catalysts.
2. The ratios of hydrogen to pinane and the contact time can be controlled
3. More accurate control of the temperature can be obtained.
4. The ratio of the catalyst to pinane passed at any one time is large, which allows maximum opportunity for studying the effect of catalysts upon the reaction.

The hydrogenolysis of pinane was studied in the presence of the following catalysts: nickel–kieselguhr, reduced precipitated nickel oxide, nickel–alumina and copper–alumina. The reactions were made at temperatures ranging from 225 to 290°, at a pressure of 56 atmospheres and using a molar ratio of hydrogen to pinane varying from 2.1 to 11.7. The experimental results obtained which are summarized in Table I indicate that from 35–67% of the product resulting from hydrogenolysis consisted of alkylcyclopentanes admixed with small amounts of bicyclic hydrocarbons, the remainder being alkylcyclohexanes. The presence of alkylcyclopentanes and bicyclic compounds was demonstrated by the fact that only part of the hydrocarbons obtained from the hydrogenolysis of pinane underwent dehydrogenation to aromatics when passed over platinized alumina at 330°. Studies in this Laboratory showed that alkylcyclopentanes and bicyclic dihydroterpenes which do not contain either three- or four-membered rings do not undergo dehydrogenation even at 330°. At this temperature alkylcyclohexanes which contain a geminal carbon atom, as in 1,1,3-trimethylcyclohexane,[5] undergo both demethanation and dehydrogenation to form *m*-xylene; non-geminal alkylcyclohexanes form the corresponding aromatic hydrocarbons at lower temperatures, namely, 260–280°. By selective dehydrogenation followed by chromatography it was thus possible to separate the various types of hydrocarbons.[3,6] The "alkylcyclopentane" fraction does not seem to contain, according to elementary analysis and index of refraction, any appreciable amounts of paraffinic hydrocarbons, thus indicating that the hydrogenolysis of monocyclic naphthenes most probably did not occur to any great extent.

The formation of cyclopentanes could be explained by either skeletal isomerization of the primary products obtained from the hydrogenolysis of pinane or by isomerization of pinane to a bicyclic compound containing a five-membered ring with subsequent hydrogenolysis of one of the rings. A systematic study of hydrogenation reaction of simple model compounds would be necessary before the elucidation of the mechanism of the isomerization of pinane will be possible.

Experimental Part

Apparatus and Procedure.—The apparatus consisted of a calibrated buret containing the pinane, a proportioning pressure pump with a variable rate adjustment, a vertical constant temperature furnace,[7] a reaction tube, an automatic pressure regulator, a calibrated pressure receiver, a Dry Ice–acetone trap to collect condensable gases, a wet test meter to measure exit gases, a gas collecting bottle for taking samples for analysis and a thermoelectric flow meter to measure the rate of hydrogen gas input.

The reactor, which was similar to the one described pre-

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(5) V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **68**, 1709 (1946).

(6) H. Pines, R. C. Olberg and V. N. Ipatieff, *ibid.*, **74**, 4872 (1952).

(7) C. L. Thomas and G. Egloff, "A High Temperature Thermostat," in the treatise "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 617.

viously,[8] consisted of a stainless steel tube of 0.625 inch inside diameter, 32 inches long. The upper part of the tube contained a spiral, 8 inches long, which acted as a preheater. The bottom part contained a supporting rod (spacer), 8 inches long. The catalyst was contained between the spacer and the preheater. A thermocouple well containing four thermocouple wires was inserted through the center of the reaction tube. The thermocouple wires were spaced to permit the measurement of the temperature of the preheater and of the various sections of the catalyst bed.

For nickel catalyst, which could not be made up in pill form, a catalyst tray assembly was constructed. Each tray was filled with catalyst and the assembly was inserted in the reaction tube.

Pinane and hydrogen in the desired molar ratios were passed under pressure through the catalyst. The gaseous product was submitted to a mass spectrographic analysis. The liquid material was distilled and analyzed.

Analytical Procedure.—The procedure used for the determination of the various hydrocarbons obtained from one hydrogenolysis of pinane was similar to the one described previously.[6] The diagrammatic sketch of the procedure used is given in Fig. 1. Prior to the dehydrogenation the product was submitted to pyrolysis. This was done in order to convert the unreacted pinane to diolefins and cyclic monoölefins, which could then be removed chromatographically from the products resulting from hydrogenolysis. The pyrolysis was made by passing the hydrocarbons at 500° over copper pellets.[9] The composition of the aromatic hydrocarbons obtained from the dehydrogenation reaction at 260 and 330°, respectively, was determined by means of infrared spectral analysis,[10] using the wave lengths given previously[8] for calculating the composition of the various samples.

The presence of the various aromatic hydrocarbons formed from the dehydrogenation was also determined by chemical means. The mixture of *o*- and *p*-cymene, obtained from the dehydrogenation at 260°, was separated from hot benzene by fractional crystallization of their sulfonamide derivatives.[11,12] The less soluble *o*-cymene sulfonamide crystallized out in needle-like crystals, m.p. 152–154°. The *p*-cymene sulfonamide crystallized out from benzene in plate-like crystals, m.p. 114–116°. There was no depression in the mixed melting points of the above sulfonamides with the respective sulfonamides obtained from known samples of *o*- and *p*-cymene.

1,2,4-Trimethylbenzene was characterized by the trinitro derivative,[13] melting at 184–185°; it did not depress the melting point of a known sample of trinitro-1,2,4-trimethylbenzene.

1,2,3-Trimethylbenzene was identified by infrared spectral analysis which showed the sample to consist of 93% of 1,2,3-trimethylbenzene. This was confirmed by bromination at 0° of 0.3 ml. of the sample. Crystallization of the brominated product from ethanol yielded a solid melting at 242–244°, which did not depress the melting point of an authentic sample prepared from 1,2,3-trimethylbenzene. A mixed melting point with an authentic sample was 241–242°.

Materials. Pinane was prepared by hydrogenation of α-pinene.[8] It distilled at 165–166° at 750 mm., $n^{20}{}_{\mathrm{D}}$ 1.4616.

Nickel-Kieselguhr[14] was obtained from Universal Oil Products Company in $^1/_8$ inch cylindrical pills.

Nickel-Alumina.—To a solution of 75 g. (0.2 mole) of $Al(NO_3)_3 \cdot 9H_2O$ in two liters of water was added 296 g. (1 mole) of $Ni(NO_3)_2 \cdot 6H_2O$. One liter of solution containing 200 g. of $(NH_4)_2CO_3$ was added in small portions over a period of 35 minutes to the above solution. A sample of approximately 5 ml. of the clear solution was tested for unreacted nickel nitrate by warming it to 70° and adding an ammonium carbonate solution. If a precipitate was noted, more $(NH_4)_2CO_3$ was added in 25-ml. portions till the precipitation was completed. The beaker was then heated slowly until the temperature reached 70°. The precipitate was allowed to settle and the liquid siphoned off. The precipitate was washed twice by decantation and filtered on a buchner funnel. The precipitate was removed, homogenized with water and filtered again; this was repeated twice. The precipitate was then dried, pilled into $^1/_8 \times {}^1/_8$ inch cylinders and reduced according to the method described previously.[15] The catalyst consisted of approximately 75% nickel and 25% alumina.

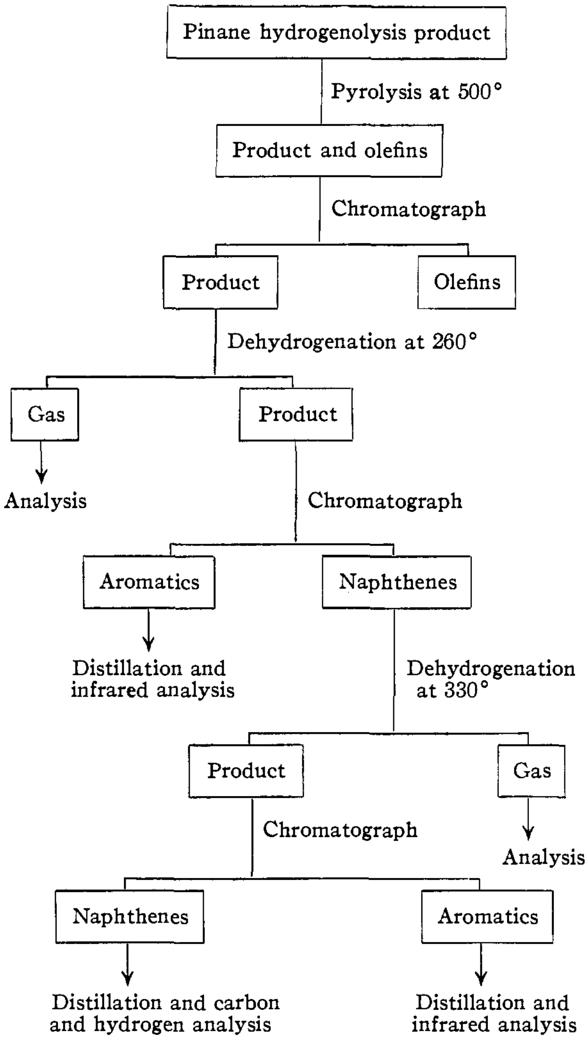

Fig. 1.—Diagrammatic sketch of the analytical procedure.

Copper-Alumina.—The catalyst, which was prepared from 19 g. (0.05 mole) of $Al(NO_3)_3 \cdot 9H_2O$ and 120 g. (0.5 mole) of $Cu(NO_3)_2 \cdot 3H_2O$ according to the method described for nickel-alumina, contained 13 parts of copper oxide per 100 parts of alumina.

Nickel.—To a solution of 437 g. (1.5 moles) of $Ni(NO_3)_2 \cdot 6H_2O$ in 2 liters of water there was added 2.85 g. (2.5 moles) of $(NH_4)_2CO_3 \cdot H_2O$ in 1.5 liters of water at 70°. The nickel carbonate formed was washed, dried and decomposed at 350–400° in a muffle furnace. The nickel oxide was reduced at 325° in a Pyrex tube which was placed in a horizontal furnace.

Platinum-alumina (dehydrogenation catalyst) was prepared according to the procedure described previously.[16]

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