

To the dry residue distilled water was added. The water-insoluble material was filtered off and recrystallized three times from absolute alcohol; m. p. 187.5–188°.

Anal. Calcd. for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86. Found: C, 59.84; H, 5.79.

1-(3'-Methoxy-4'-acetoxyphenyl)-4-isonitroso-2,6-dicarbethoxycyclohexanedione-3,5.—To a solution of 3 g. of 1-(3'-methoxy-4'-acetoxyphenyl)-2,6-dicarbethoxycyclohexanedione-3,5 in absolute alcohol, 0.492 g. of sodium nitrite and 0.5 ml. of glacial acetic acid were added. The reaction mixture was kept in a refrigerator for five days. The straw-colored precipitate which formed was filtered, washed with distilled water and then dried in a desiccator, m. p. 198°, yield 85%. The yellow salt of the monoxime was dissolved in cold water and filtered. To the cold filtrate 0.1 *N* cold hydrochloric acid was added dropwise until the solution was slightly acidic to litmus. (Excess acid converts the oxime to the original compound.) A white precipitate formed and was filtered and recrystallized from absolute methanol, m. p. 184°, yield 80%.

Anal. Calcd. for $C_{21}H_{22}O_{10}N$: C, 56.12; H, 5.16. Found: C, 55.93; H, 5.23.

1-(3'-Methoxy-4'-hydroxyphenyl)-4-isonitroso-2,6-dicarbethoxycyclohexanedione-3,5.—The procedure for this preparation is similar to that above. The starting material was 1-(3-methoxy-4-hydroxyphenyl)-2,6-dicarbethoxycyclohexanedione-3,5 instead of 1-(3-methoxy-4-acetoxyphenyl)-2,6-, etc. This monoxime melts at 203°.

Anal. Calcd. for $C_{19}H_{21}O_9N$: C, 56.02; H, 5.19. Found: C, 56.38; H, 5.25.

1-(3'-Methoxy-4'-acetoxyphenyl)-4,5-dioxime-2,6-dicarbethoxycyclohexanetrione-3,4,5.—To 0.210 g. of hydroxylamine hydrochloride dissolved in a minimum amount of water, a solution of 0.070 g. of sodium in absolute alcohol was added. To the mixture, 1.5 g. of the sodium monoxime salt of 1-(3'-methoxy-4'-acetoxyphenyl)-4-oxime-2,6-dicarbethoxycyclohexanedione-3,4,5 was added and the solution allowed to stand for several days at room temperature. An intensely yellow precipitate was formed; m. p. 205–216°; yield 75%. The precipitate was dissolved in hot distilled water. The solution was cooled and treated with cold 0.1 *N* hydrochloric acid dropwise until it became faintly acid to litmus. The yellowish-white precipitate formed was filtered and

recrystallized from absolute methanol; m. p. 194°; yield 80%.

Anal. Calcd. for $C_{21}H_{24}O_{10}N_2$: C, 54.31; H, 5.29. Found: C, 54.68; H, 5.25.

The use of this dioxime of structure (I) in the determination of nickel, cobalt and other metallic ions is under investigation.

N,N'-Bis{4-[1-(3'-Methoxy-4'-hydroxyphenyl)-2,6-dicarbethoxycyclohexanedione-3,5]}-p,p'-disazo-diphenyl (II).—Benzidine tetrazonium dichloride, prepared by diazotizing 2.571 g. of benzidine dihydrochloride at 0°, was added to an alkaline cold water solution containing 8.40 g. of 1-(3-methoxy-4-acetoxyphenyl)-2,6-dicarbethoxycyclohexanedione-3,5 (I). The product of the coupling was soluble in the alkaline solution. The mixture was kept at 0°. After an hour, the solution was acidified with dilute hydrochloric acid and reddish-brown crystals were formed. The crystals were filtered, redissolved in alkali, reprecipitated by acid, washed with cold distilled water and dried in a vacuum desiccator. The melting point was too high to be determined by ordinary means.

Anal. Calcd. for $C_{66}H_{60}O_{18}N_4$: C, 62.36; H, 5.23. Found: C, 62.47; H, 5.11.

Acknowledgment.—The authors appreciate the interest which Dr. Christopher L. Kenny has shown in this research.

Summary

The syntheses of the following compounds are described:

- 1-(3'-Methoxy-4'-acetoxyphenyl)-2,6-dicarbethoxycyclohexanedione-3,5 (I) and its deacetylated product.
- 1-(3'-Methoxy-4'-hydroxyphenyl)-4-oxime-2,6-dicarbethoxycyclohexanedione-3,5.
- 1-(3'-Methoxy-4'-hydroxy)-4,5-dioxime-2,6-dicarbethoxycyclohexanetrione-3,4,5.
- N,N'-Bis{4-[1-(3'-methoxy-4'-hydroxy)-phenyl-2,6-dicarbethoxycyclohexanedione-3,5]}-p,p'-disazodiphenyl (II).

OMAHA, NEBR.

RECEIVED OCTOBER 27, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL CO. (INDIANA)]

Rearrangement of 4-Methylcyclohexene during Sulfuric Acid-catalyzed Reaction with Benzene

BY JACK LINSK

Under suitable conditions a carbonium ion can remove a hydride ion from another hydrocarbon.¹ This intermolecular transfer of hydrogen takes place readily between tertiary carbonium ions and tertiary hydrocarbons, and occurs frequently under the acid conditions of the olefin-isoparaffin alkylation reaction.^{2,3,4} It was recently reported⁵ that 4-methylcyclohexene in the presence of *p*-cymene and sulfuric acid is readily reduced to

(1) Whitmore, *THIS JOURNAL* **54**, 3274 (1932); *Chem. Eng. News*, **26**, 668 (1948).

(2) Bartlett, Condon and Schneider, *THIS JOURNAL*, **66**, 1531 (1944).

(3) Schmerling, *ibid.*, **67**, 1778 (1945).

(4) Pines and Ipatieff, *ibid.*, **67**, 1631 (1945).

(5) Ipatieff, Pines and Olberg, *ibid.*, **70**, 2123 (1948).

methylcyclohexane, but neither cyclohexene nor octene-1 is reduced to saturated hydrocarbons. This suggested that 4-methylcyclohexene must have rearranged prior to hydrogen transfer. The rearrangement probably yields the same tertiary carbonium ion intermediate as that obtained directly from 1-methylcyclohexene in the presence of the acid catalyst. Reaction by intermolecular transfer of a hydride ion from *p*-cymene or another suitable donor then gives methylcyclohexane.

The present work confirmed the ready rearrangement of methylcyclohexenes through a study of the sulfuric acid-catalyzed reaction of benzene with various methylcyclohexenes. The same

products resulted from 1- and 4-methylcyclohexene, and from 2- and 4-methylcyclohexanol.⁶ One of these products was a liquid which was shown by synthesis to be 1-methyl-1-phenylcyclohexane.⁷ Its identity was proved through the acetyl derivatives, whose 2,4-dinitrophenylhydrazones showed the same melting point either alone or when mixed. The liquid reaction product was also shown to be different from 2-, 3- and 4-methyl-1-phenylcyclohexane by comparison of the 2,4-dinitrophenylhydrazones of the respective acetyl derivatives.

The second reaction product was a solid which corresponded by analysis to a compound resulting from the interaction of one molecule of benzene with two molecules of methylcyclohexene. This is believed to be 1,4-di-(1'-methylcyclohexyl)-benzene. Partial evidence for this structure was the selenium dehydrogenation of the solid in low yield to *p*-terphenyl.

Experimental

Preparation of Olefins.—1-Methylcyclohexene was obtained in 85% yield by condensing cyclohexanone with methylmagnesium iodide and dehydrating the resulting carbinol with iodine; it boiled at 108–109°, and had n_{20}^D 1.4500, in agreement with reported values.⁸

To prepare 4-methylcyclohexene, 980 g. of Eastman Kodak Co. 4-methylcyclohexanol was dehydrated over 400 g. of phosphoric acid (85%) at 175°. The olefin was removed as formed through a short column and the dried product was distilled from 5 g. of sodium. Fractionation through a column having about 10 theoretical plates gave 104 g. of 4-methylcyclohexene (b. p. 102°, n_{20}^D 1.4405,⁹ a large fraction) containing isomeric methylcyclohexenes, and 200 g. of 1-methylcyclohexene.

Hydrogen Transfer from *p*-Cymene to 1- and 4-Methylcyclohexene.—In a typical run 28.9 g. (0.3 mole) of 1-methylcyclohexene was added over a period of one hour to a vigorously stirred mixture of 161 g. of *p*-cymene and 56 g. of 96% sulfuric acid at 0–2°, and stirring was continued for 0.5 hour. The mixture was transferred to a separatory funnel; the upper phase was separated, washed with water and aqueous sodium chloride, dried over anhydrous calcium chloride, and fractionated. The fraction corresponding to methylcyclohexane (16.5 g.) was collected at 100.1–1.4°, n_{20}^D 1.4229. The additional methylcyclohexane (3.8 g.) present in cuts boiling to 175° was estimated by refractive index. The total amount of methylcyclohexane (20.3 g.) represented a yield of 69% based on olefin. From the residue, 1,3,3,6-tetramethyl-1-*p*-tolylindan⁶ was obtained; b. p. 146° (1.2 mm.), n_{20}^D 1.5580, m. p. 37.6–39.8° (from ethanol). In an analogous

reaction using 4-methylcyclohexene as the olefin acceptor, the yield of methylcyclohexane was 72%.

Cycloalkylation of Benzene.—The experimental data for the reactions are given in Table I. Each experiment was performed by adding the appropriate reagent dissolved in a little of the benzene to a stirred mixture of benzene and sulfuric acid. When addition was complete, the mixture was stirred, the hydrocarbon phase was separated from the acid phase, washed with dilute sodium hydroxide and with water, and concentrated. By careful distillation in a Stedman column 25 cm. long, the liquid product in each case was completely distilled from a higher boiling residue, which crystallized on cooling. Data given for the solid products in Table I are for material recrystallized once from acetone.

TABLE I

SULFURIC ACID CATALYZED REACTION OF BENZENE WITH: 1-METHYLCYCLOHEXENE (A), 4-METHYLCYCLOHEXENE (B), 2-METHYLCYCLOHEXANOL (C), AND 4-METHYLCYCLOHEXANOL (D)

	A	B	C	D
Alkylation agent, g.	31.6	46.0	41.2	82.1
Benzene, g.	156	160	156	312
H ₂ SO ₄ (96%), g.	60	50	81	200
Time, hr., 10–13°	1.5	1.5	2.5	3
Products:				
Liquid, g.				
(% yield)	31.7 (51)	33.2 (40)	31.6 (50)	49.1 (39)
B. p., °C.	129.0–129.5 (26)	77–78 (1.2)	131–133 (26)	133–134 (28)
(mm.)				
n_{20}^D	1.5275	1.5274	1.5269	1.5272
Solid, g. (% yield)	15.7 (32)	21 (32)	12.6 (26)	30.2 (31)
M. p., °C.	70–73	71–73.5	71–73.5	73–75

Characterization of the Liquid Product.—The liquid reaction product from A, Table I, corresponded to the compound resulting from the interaction of one molecule of methylcyclohexene with one molecule of benzene. *Anal.* Calcd. for C₁₃H₁₈: C, 89.6; H, 10.4. Found: C, 89.5; H, 10.4.

Treatment of the above hydrocarbon with acetyl chloride and aluminum chloride in carbon disulfide gave a good yield of the acetyl compound, b. p. 125–126° (0.8 mm.), n_{20}^D 1.5465. *Anal.* Calcd. for C₁₅H₂₀O: C, 83.3; H, 9.3. Found: C, 83.5; H, 9.3. This material formed a 2,4-dinitrophenylhydrazone, red micro-crystals from chloroform-hexane, m. p. 188.0–189.2°. *Anal.* Calcd. for C₂₁H₂₄O₄N₄: N, 14.1. Found: N, 14.1. The liquid reaction products obtained from B, C and D were likewise converted to acetyl derivatives. Each gave a dinitrophenylhydrazone whose melting point (and mixed melting point) was the same as that obtained from A.

Passage of 26 g. of the liquid reaction product over 5% platinumized alumina¹⁰ at 340° gave a 6-g. fraction, b. p. 245–249° (740 mm.), n_{20}^D 1.5744. Infrared analysis of this fraction indicated the presence of aromatics, but showed little biphenyl or starting material. The coincidence of the infrared spectrum with that of 2-methylbiphenyl, especially the presence of a strong absorption maximum at 13.4 μ in both, indicates that the dehydrogenation product consists largely of 2-methylbiphenyl.

Characterization of the Solid Product.—The crystalline solid obtained from A was again recrystallized from acetone (m. p. 74.8–5.4°). Analysis corresponded to the compound resulting from the interaction of two molecules of methylcyclohexene with one molecule of benzene. *Anal.* Calcd. for C₂₀H₃₀: C, 88.9; H, 11.1. Found: C, 89.0; H, 11.2. Nitration of the solid with mixed nitric and sulfuric acids (1:2) gave a dinitro derivative, needles from ethanol, m. p. 197.0–198.2°. *Anal.* Calcd. for C₂₀H₂₈N₂O₄:

(6) The reaction between phenol and the isomeric methylcyclohexenes or 4-methylcyclohexanol gives the same product, probably 1-methyl-1-(*p*-hydroxyphenyl)-cyclohexane. Price in Adams, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 61.

(7) After this work was complete, a footnote in a paper by Pines, Strehlau and Ipatieff, *THIS JOURNAL*, **71**, 3534 (1949), indicated that they also have observed the formation of 1-methyl-1-phenylcyclohexane in the reaction between benzene and isomeric methylcyclohexenes. The identity of the product obtained by Ipatieff, Meisinger and Pines, *ibid.*, **72**, 2772 (1950), with our synthetic 1-methyl-1-phenylcyclohexane, is shown by the complete coincidence of the infrared spectra. Thirty bands between 7.5 and 15.0 μ have the same frequency, shape and relative intensity. We are indebted to P. J. Lauer for the infrared analysis.

(8) Signaigo and Cramer, *THIS JOURNAL*, **55**, 2326 (1933).

(9) Nametkin and Brussoff, *Ber.*, **56**, 1807 (1929), report b. p. 102.5–102.7°, n_{20}^D 1.4419.

(10) Ipatieff and Pines, *THIS JOURNAL*, **58**, 1056 (1936).

TABLE II
 PROPERTIES OF SYNTHETIC METHYLPHENYLCYCLOHEXANES AND DERIVATIVES

Compound	Boiling point (uncor.)		Yield, %	n_D^{20}	Empirical formula	Analyses, %			
	°C.	mm.				Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1-Methyl-1-phenylcyclohexane	103	9.5		1.5278	C ₁₃ H ₁₈	89.6	89.3	10.4	10.5
Acetyl derivative	125-126	0.8		1.5465	C ₁₆ H ₂₀ O	83.3	83.4	9.3	9.4
2,4-Dinitrophenylhydrazone	M. p. 188.0-189.2°				C ₂₁ H ₂₄ O ₄ N ₄	63.6	63.8	6.1	6.2
2-Methyl-1-phenylcyclohexane ^a	86-87	2.5	65	1.5539	C ₁₃ H ₁₈	90.6	90.6	9.4	9.3
2-Methyl-1-phenylcyclohexane ^a	62-63	0.4	77	1.5285	C ₁₃ H ₁₈	89.6	89.8	10.4	10.4
Acetyl derivative	143-144	1.7		1.5475	C ₁₆ H ₂₀ O	83.3	82.8	9.3	9.3
2,4-Dinitrophenylhydrazone ^b	M. p. 191.8-192.8°				C ₂₁ H ₂₄ O ₄ N ₄	63.6	63.7	6.1	6.1
	Mixed m. p. 179-182.2°								
3-Methyl-1-phenylcyclohexane	87-88	1.5	91	1.5581	C ₁₃ H ₁₈	90.6	91.1	9.4	8.9
3-Methyl-1-phenylcyclohexane ^d	78-79	1.3	94	1.5232	C ₁₃ H ₁₈	89.6	89.7	10.4	10.3
Acetyl derivative	140-141	1.4		1.5418	C ₁₆ H ₂₀ O	83.3	83.3	9.3	9.3
2,4-Dinitrophenylhydrazone ^e	M. p. 182.2-182.9°				C ₂₁ H ₂₄ O ₄ N ₄	63.6	63.9	6.1	6.0
	Mixed m. p. 180.2-185.2°								
4-Methyl-1-phenylcyclohexane	86-88	0.8	85	1.5578	C ₁₃ H ₁₈	90.6	90.7	9.4	9.2
4-Methyl-1-phenylcyclohexane ^{d,f}	71-72	0.8	87	1.5201	C ₁₃ H ₁₈	89.6	89.5	10.4	10.5
Acetyl derivative ^g	132-134	0.8		1.5395	C ₁₆ H ₂₀ O	83.3	83.3	9.3	9.2
2,4-Dinitrophenylhydrazone ^{h,i}	M. p. 182.0-183.8°				C ₂₁ H ₂₄ O ₄ N ₄	63.6	63.4	6.1	6.1
	Mixed m. p. 168.8-175.4°								

^a Sidorova and Tsukervanik, *J. Gen. Chem. (U. S. S. R.)*, **10**, 2073 (1941); *C. A.*, **35**, 3979 (1941). ^b Golden orange needles from chloroform-ethanol. ^c Mixed m. p. with the 2,4-dinitrophenylhydrazone prepared from the acetyl derivative of 1-methyl-1-phenylcyclohexane. ^d Kursanov, *J. Russ. Phys.-Chem. Soc.*, **38**, 1304 (1906); *C. A.*, **1**, 2093 (1907). ^e Orange-red micro-crystals from chloroform-ethanol. ^f Pines, Edeleanu and Ipatieff, *THIS JOURNAL*, **67**, 2193 (1945). ^g Crystallized on standing. A sample was recrystallized from methanol, m. p. 55-56°. ^h Orange micro-crystals from chloroform-ethanol. ⁱ Mixed m. p. with previous 2,4-dinitrophenylhydrazone, 173.8-179.0°.

O₄N₂: N, 7.9. Found: N, 7.8. The solids obtained from A, B, C and D were recrystallized until the m. p. of each reached 74°. None of the melting points were depressed by admixture.

Two grams of the solid was heated for 70 hours with 3 g. of selenium in a salt-bath at 300-330°. The product was taken up in ether and crystallized from that solvent. A small yield of material, m. p. 210-212°, was obtained. The m. p. of an authentic sample of *p*-terphenyl (214°) was not depressed.

Synthesis of 1-Methyl-1-phenylcyclohexane.—The starting material was 2-methyl-2-phenylcyclohexanone—b. p. 123-124° (6 mm.); n_D^{20} 1.5367—synthesized by the methylation procedure of Newinan and Farbman.¹¹ Although Clemmensen reduction gave a negligible yield of the desired hydrocarbon, it was obtained in good yield by the Huang-Minlon modification¹² of the Wolff-Kishner reaction. A mixture of the ketone (68.2 g.), 85% hydrazine hydrate (90 g.), acetic acid (4 ml.), and triethylene glycol (400 ml.) was slowly distilled with reflux until the reaction temperature reached 180°. The reaction mixture was cooled, 40 g. of sodium hydroxide and an additional 30 g. of hydrazine hydrate were added, and distillation with reflux was repeated until the liquid temperature reached 195°. After refluxing gently for five hours, the cooled mixture was poured into iced hydrochloric acid and the product was thoroughly extracted with ether. The ether solution was washed successively with water, with dilute sodium hydroxide, and again with water; it was then dried and concentrated. The concentrate was distilled through the Stedman Column to give 46.0 g. (78% yield) of distillate fractions b. p. 102.5-103° (9.5 mm.), n_D^{20} 1.5273-83, and 8 g. of residue, n_D^{20} 1.5408. Table II gives physical properties and analytical data for the heart fraction of 1-methyl-1-phenylcyclohexane, its acetyl derivative, and the dinitrophenylhydrazone of the ketone. The melting point of the latter showed no depression when mixed with the corresponding derivative of the liquid alkylation product.

An incomplete Wolff-Kishner reduction provided, in addition to the desired hydrocarbon, a crystalline material melting at 144.6-5.6° from acetone. The analytical data correspond to the hydrazone of the unsaturated ketone resulting from aldol condensation of two molecules of 2-methyl-2-phenylcyclohexanone. *Anal.* Calcd. for C₂₆H₃₂N₂: C, 82.8; H, 8.7; N, 7.5. Found: C, 83.9; H, 8.7; N, 7.7.

Synthesis of 2-, 3- and 4-Methylphenylcyclohexanes.—These hydrocarbons were prepared from the isomeric methylcyclohexanones. The 3-methylcyclohexanone was Eastman Kodak Co. material carefully fractionated, whereas the 2- and 4-isomers were prepared by oxidation of the corresponding alcohols with potassium dichromate. The refractive index of each ketone agreed with the value reported.⁸ The reaction between phenylmagnesium bromide and the appropriate ketone, followed by dehydration of the resulting carbinol with iodine, gave the appropriate methylphenylcyclohexene in good yield. Each olefin was hydrogenated in ethanol with Raney nickel catalyst, the methylphenylcyclohexane was acetylated, and the ketone was converted to the 2,4-dinitrophenylhydrazone. The physical properties and analyses of the compounds prepared are given in Table II. The mixed melting point of each of the 2,4-dinitrophenylhydrazones with the one prepared from the acetyl derivative of 1-methyl-1-phenylcyclohexane was depressed. These data are also shown in Table II.

Acknowledgments.—The author wishes to thank Drs. B. L. Evering and R. F. Marschner for helpful advice and suggestions, and Miss Lydia Kotarski for the carbon and hydrogen analyses.

Summary

4-Methylcyclohexene is easily rearranged by concentrated sulfuric acid. The alkylation of benzene with 4-methylcyclohexene, 2-methylcyclohexanol or 4-methylcyclohexanol yields the

(11) Newman and Farbman, *THIS JOURNAL*, **66**, 1550 (1944).

(12) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

same two compounds as are obtained with 1-methylcyclohexene. The monoalkylation product is 1-methyl-1-phenylcyclohexane, and the dialkyla-

tion product is believed to be 1,4-di-(1'-methylcyclohexyl)-benzene.

WHITING, INDIANA

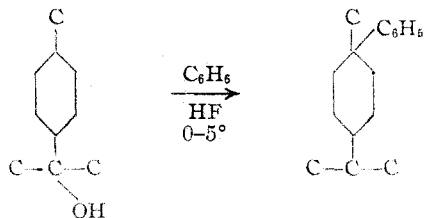
RECEIVED MARCH 3, 1950

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

Studies in the Terpene Series. IX.¹ Isomerization Accompanying Cycloalkylation of Benzene²

BY V. N. IPATIEFF, H. R. APPELL^{3,4} AND HERMAN PINES

It was observed that the products from the reaction of benzene with dihydrolimonene (1-methyl-4-isopropylcyclohexene) and a mixture of *p*-menthenes, in the presence of hydrogen fluoride at 0–5°, consisted of the same compound, 1-methyl-1-phenyl-4-isopropylcyclohexane.⁵ A hydrogen shift had occurred so that reaction always took place at the carbon atom holding the methyl group.⁶ Further work showed that the reaction of benzene with menthol (2-isopropyl-5-methylcyclohexanol) and dihydroterpineol [dimethyl-(4-methylcyclohexyl)-carbinol] under the same conditions also yielded the same product as formed previously (Equation I).



The main product was always accompanied by a small amount of crystalline material, melting at 145°, which corresponded to the dicycloalkylated benzene, presumably *p*-di-(1-methyl-4-isopropylcyclohexyl)-benzene.

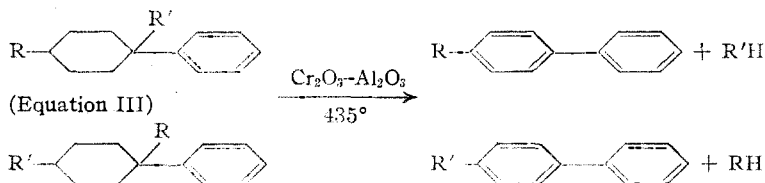
In order to gain additional evidence regarding the scope of the reaction, cyclohexanols with an ethyl and methyl group and with an ethyl and isopropyl group were used to cycloalkylate benzene.

The results obtained from the reactions of benzene with 1-ethyl-4-methylcyclohexanol, 1-ethyl-4-methylcyclohexene and 1-methyl-4-ethylcyclo-

hexanol produced a mixture of isomers. The greater amount of reaction had occurred at the carbon atom holding the methyl group, but a substantial amount had also occurred at the carbon atom holding the ethyl group.

The results from the reactions of benzene with 1-ethyl-4-isopropylcyclohexanol and 1-isopropyl-4-ethylcyclohexanol were somewhat inconclusive because of the difficulty of analyzing the reaction product. It appeared, however, that the greater amount of reaction had occurred at the carbon atom holding the ethyl group.

The structures of the cycloalkylated benzenes were determined by means of dehydrogenation. Naphthenes having a geminal alkyl group may be dehydrogenated under suitable conditions to yield aromatics with the elimination of alkyl groups.⁷ The gaseous product obtained from the dehydrogenation was analyzed on a mass spectrometer.⁸ Identification of the gaseous products thus produced made it possible to determine the position of the quaternary carbon atom. From the ratio of alkanes RH and R'H, produced from the dehydrogenation it was possible to establish the amount of each isomer, as exemplified by the following equations:



Dehydrogenation of known mixtures, given in Table II indicate the reliability of the method. Ethyl groups are cleaved more readily than methyl, making it imperative to have dehydrogenation as complete as possible. Dehydrogenation of hydrocarbons which may have an isopropyl group attached to the quaternary carbon atom, given in Table III, give inconclusive results, probably due to side reactions occurring during dehydrogenation.

In order to determine the behavior of hydrocarbons containing an isopropyl group attached to a

(1) For paper VIII of this series see H. Pines, R. C. Olberg and V. N. Ipatieff, *THIS JOURNAL*, **70**, 533 (1948).

(2) Taken from the dissertation submitted by H. R. Appell to the Graduate Faculty of Northwestern University in partial fulfillment of the requirements for the Ph.D. degree.

(3) Universal Oil Products Company Predoctorate Fellow (1947–1949).

(4) Universal Oil Products Company, Riverside, Illinois.

(5) This compound was also obtained by W. W. Thompson of our laboratories from the sulfuric acid catalyzed reaction of benzene with dihydrolimonene (unpublished work).

(6) It has previously been shown that if a tertiary carbon atom is part of the ring, reaction will occur at that position; V. N. Ipatieff, E. E. Meisinger and H. Pines, *THIS JOURNAL*, **72**, 2772 (1950).

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

(8) Mass spectrometer analyses were made by J. B. Grutka, Universal Oil Products Company, Riverside, Illinois.