

The Nature of the Methylcyclohexane-Ferric Chloride Reaction¹

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The reaction of methylcyclohexane with ferric chloride produced a liquid product in low yield, solid polymer in major proportions, ferrous chloride, and hydrogen chloride. The evidence (elemental analyses, molecular weight, spectral data, oxidative degradation, and catalytic dehydrogenation) indicates that the liquid is predominantly *m*-(2-methylcyclohexyl)toluene. Treatment of 1-chloro-1-methylcyclohexane, a possible intermediate, with ferric chloride gave results similar to those obtained with methylcyclohexane. In an attempted synthesis of the authentic liquid, alkylation of toluene with 1-chloro-1-methylcyclohexane in the presence of aluminum chloride gave instead, *m*- and *p*-(4-methylcyclohexyl)toluene. When the methylcyclohexane-ferric chloride reaction was carried out in chlorobenzene, (methylcyclohexyl)chlorobenzene was formed, indicating entrapment of a labile intermediate. Interpretations of the results are provided.

Recently it was found that anhydrous ferric chloride reacts with alkanes under mild conditions, with the order of reactivity being tertiary > secondary.² In a related area, investigations of the alkylbenzene-ferric chloride system disclosed the existence of various competing reactions, including nuclear chlorination, disproportionation, conversion to biaryls, polymerization, and formation of di-, tri-, and tetraarylmethanes.^{3,4} Ferric chloride is reported to yield chlorine-containing derivatives with olefins,^{5,6} such as α -pinene. Our objective was to elucidate the mechanism of the ferric chloride-alkane reaction. The present paper reports on the first phase of this work dealing with the isolation and characterization of products formed from ferric chloride and methylcyclohexane.

Results and Discussion

The reaction of methylcyclohexane with ferric chloride produced a liquid product, C₁₄H₂₀, in low yield, solid polymer in major proportions, ferrous chloride (89%),² and hydrogen chloride (70–80%). Even though the C₁₄H₂₀ product was formed in low yield, we centered our attention on this material with the aim of obtaining information concerning the reaction pathway. A detailed investigation revealed that *m*-(2-methylcyclohexyl)toluene (V) comprised 70–80% of the oily fraction, with possibly some of the isomeric *o*-(1-methylcyclohexyl)toluene also present. In addition to the elemental analyses and molecular weight determination, information was provided by spectral data, oxidative degradation, and catalytic dehydrogenation.

The infrared and ultraviolet spectra compared favorably with those reported for *m*-cymene.^{7a,8a} From the n.m.r. spectrum, evidence was obtained for the presence of a *meta* substituted toluene having no quaternary carbon in the methylcyclohexyl portion.⁹ Of the isomeric benzenedicarboxylic acids, only isophthalic acid

was obtained from oxidative degradation. Catalytic dehydrogenation gave as the principal products, 2,3'-dimethylbiphenyl from V as precursor, and 3-methylfluorene from subsequent dehydrocyclization of 2,3'-dimethylbiphenyl. Furthermore, a small amount of fluorene (about 5% of the product) was shown to be present. This hydrocarbon is presumably generated from *o*-(1-methylcyclohexyl)toluene by demethanation and dehydrogenation, or perhaps by loss of a non-tertiary methyl group.^{10–12} The products from catalytic dehydrogenation were characterized by comparison with authentic materials.

In an attempt to synthesize the original liquid product by an alternative route, toluene was alkylated with 1-chloro-1-methylcyclohexane in the presence of aluminum chloride. The resulting C₁₄H₂₀ fraction, different from the corresponding methylcyclohexane-ferric chloride hydrocarbon, was identified by the same techniques as described earlier. On the basis of the experimental evidence, it was concluded that the alkylated aromatic consisted of approximately equal amounts of *m*- and *p*-(4-methylcyclohexyl)toluene, with possibly *m*-(1-methylcyclohexyl)toluene as a minor component.

The infrared and ultraviolet spectra were similar to those reported for *m*- and *p*-cymene.^{7,8} In addition, the n.m.r. spectrum suggested the presence of *meta* and *para* substituted toluenes having no quaternary carbon in the methylcyclohexyl group.⁹

High temperature oxidation with dilute nitric acid provided equivalent quantities of iso- and terephthalic acids. From catalytic dehydrogenation equal amounts of 3,4'- and 4,4'-dimethylbiphenyl were obtained, along with 3-methylbiphenyl as a minor component. *m*-(1-Methylcyclohexyl)toluene conceivably might function as a precursor of the 3-methylbiphenyl.

It is evident that the methylcyclohexyl side chain has undergone isomerization during the course of the reactions leading to the (methylcyclohexyl)toluenes. Similar transformations have been observed previously by various investigators, *e.g.*, the formation of 3- and 4-(methylcyclohexyl)benzene from benzene and 1-chloro-1-methylcyclohexane with aluminum chloride

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(7) (a) Infrared Spectral Data, American Petroleum Institute, 1956, serial no. 1586; (b) serial no. 1587.

(8) (a) Ultraviolet Spectral Data, American Petroleum Institute, 1959, serial no. 74; (b) serial no. 75.

(9) We are grateful to Dr. Eugene A. Pier of Varian Associates, Palo Alto, Calif., for obtaining and interpreting the n.m.r. spectrum.

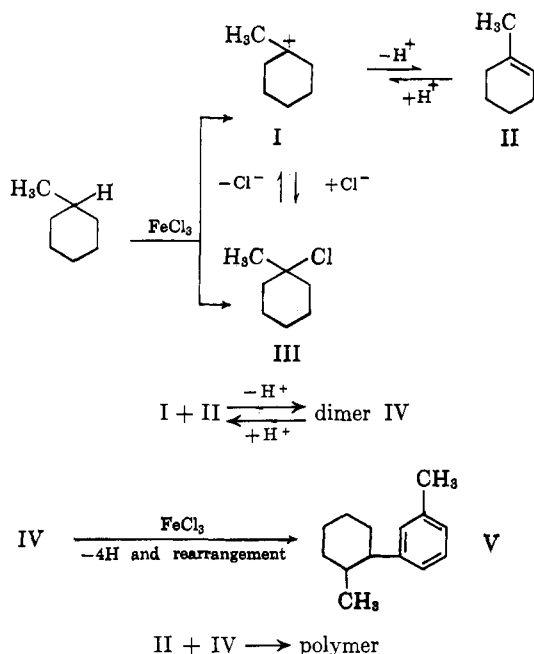
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catalyst.^{13,14} Alkylation of benzene with 1-methylcyclohexene in the presence of aluminum chloride was reported to give a mixture of all possible isomeric (methylcyclohexyl)benzenes.¹⁵ The rearrangements may involve bridged phenonium ions,¹³ 1,2-shifts, and/or dealkylation-alkylation. Furthermore, the predominance of the *meta* isomer of (2-methylcyclohexyl)toluene from the methylcyclohexane-ferrous chloride reaction can be rationalized on the basis of the relative stabilities of the corresponding σ -complexes formed during isomerization.¹⁶

A plausible sequence for the methylcyclohexane-ferrous chloride reaction is indicated.



Support for the proposed scheme was obtained by carrying out the methylcyclohexane-ferrous chloride reaction in chlorobenzene. Our objective was to trap intermediates such as I, II, or III. Indeed, (methylcyclohexyl)chlorobenzene, mainly *meta* and *para*, was isolated from the reaction mixture. Identification was accomplished by elemental analysis and infrared spectroscopy, and confirmed by Friedel-Crafts synthesis from 1-chloro-1-methylcyclohexane and chlorobenzene. Although the precise structure of the product was not ascertained, the results do indicate intermediate formation from methylcyclohexane of a species, *e.g.*, a carbonium ion, capable of effecting aromatic substitution. A similar type of participation involving methylcyclohexane was observed previously in Friedel-Crafts alkylations of benzene with dichloroalkanes.^{13,17}

In order to test further the proposed mechanism, II, III, and IV were subjected to simulated reaction conditions. With 1-chloro-1-methylcyclohexane (III) and ferrous chloride, a product was isolated by distilla-

tion which appeared to be essentially identical to the liquid formed from methylcyclohexane-ferrous chloride on the basis of infrared, ultraviolet, and gas chromatographic analysis. The volatile product from the dimer IV and ferrous chloride was very similar, but not identical, to the reference $\text{C}_{14}\text{H}_{20}$ hydrocarbon. In addition, polymer was formed in both cases. 1-Methylcyclohexene and ferrous chloride gave polymer, compound III, and a complex mixture which was not characterized.

The procedure of Bloomfield,¹⁸ entailing treatment of 1-methylcyclohexene with perchloric acid-formic acid, was used for the synthesis of 1-methylcyclohexene dimer. Dimerization was also investigated with 65% sulfuric acid as the catalyst. It appears that the reaction course with sulfuric acid is quite sensitive to supposedly minor alterations in the conditions. In certain cases, the product was essentially identical to the Bloomfield dimer, whereas in other instances, a complex mixture resulted with accompanying formation of sulfur dioxide. The gross mixture apparently contained *m*- and *p*-(2-methylcyclohexyl)toluene as major components as evidenced by infrared, ultraviolet, and gas chromatographic analysis. The formation of V in this system further strengthens the designation of 1-methylcyclohexene and its dimer as intermediates in the principal reaction under study. It is significant that fuming sulfuric acid and methylcyclohexene interact in a manner somewhat similar to the ferrous chloride-methylcyclohexane transformation. The reaction is characterized by reduction of the Brønsted acid to sulfur dioxide, and conversion of the alicyclic to a complex mixture containing unsaturated components.¹⁹

We also have considered, as an alternative reaction pathway in the over-all mechanism, initial dehydrogenation of 1-methylcyclohexane to toluene, followed by alkylation with the methylcyclohexyl cation. However, there was no evidence from gas chromatography for the presence of toluene or chlorotoluene which might possibly arise from chlorination by ferrous chloride; nor, on the other hand, were there indications of I, II, or III in the reaction mixture by this same analytical technique.

The principal product from the methylcyclohexane-ferrous chloride reaction consisted of a brown, insoluble, chlorine-containing polymer. The C/(H + Cl) atomic ratio (0.9) is equal to the C/H ratio for the parent hydrocarbon polymer. Since the theoretical ratios are lower for the saturated polymer (0.58) of methylcyclohexene and for the polymer containing one double bond per monomer unit (0.70), the material obtained probably contains some aromatic structure. On the assumption that the polymer is formed by polar polymerization of 1-methylcyclohexene,^{20,21} the reaction would then be analogous to the cationic polymerization of isobutylene.

Although the volatile product constitutes a small percentage of the total, its identification provides valuable clues concerning the nature of precursors and the

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mode of polymer formation. However, the nature of the initial attack of methylcyclohexane by ferric chloride remains to be elucidated. We have formulated several reasonable working hypotheses. The methylcyclohexyl carbonium ion may be formed by hydride abstraction with concomitant reduction of ferric chloride. Methylcyclohexane is known to be a good hydride donor in systems containing strong Lewis acids.^{13,17} Alternatively, 1-chloro-1-methylcyclohexane might conceivably arise through a free radical sequence.

Experimental²²

Materials.—Methylcyclohexane (Phillips Petroleum Co., 99% minimum purity) was washed with concentrated sulfuric acid and distilled, b.p. 99–100°. 1-Methylcyclohexene (Aldrich Chemical Co.) was distilled, b.p. 108–111°. Anhydrous, sublimed ferric chloride powder, was from Matheson Coleman and Bell and Fisher Scientific Co.

Analytical Procedures.—The ultraviolet spectra were obtained with 95% ethanol as the solvent. Unless otherwise specified, the samples for infrared spectroscopy were run neat. The indicated gas chromatography columns were used: (A) 20 ft. by 0.25 in., 0.5% Carbowax 20 M and 15% silicone on Chromosorb P, 200°, 75 ml./min. flow rate at 30 p.s.i.; (B) 9 ft. by 0.25 in., 30% Apiezon M on Chromosorb P, 250°, 100 ml./min. flow rate at 30 p.s.i.

Methylcyclohexane and Ferric Chloride.—On heating a mixture of methylcyclohexane (196.3 g., 2 moles) and ferric chloride (162.2 g., 1 mole) under nitrogen with stirring, hydrogen chloride was evolved rapidly at 71°. The acid gas was produced in 70–80% of the theoretical amount from the dark colored reaction mixture during 3 hr. Filtration yielded a gray-black residue which was washed with ether. The combined filtrate was washed first with dilute hydrochloric acid and then with a saturated sodium chloride solution. Distillation of the dried organic solution at atmospheric pressure effected removal of the ether and unchanged methylcyclohexane. The residue on vacuum distillation through a short Vigreux column gave 5.1 g. of yellow oil, b.p. 45–100° (1 mm.), with the major portion distilling at 82° (0.75 mm.). Gas chromatography indicated the presence of a complex mixture, of which one component comprised 70–80% of the total.

Precise fractionation of the combined product from several runs was accomplished with a 36-in., semimicro spinning band column at a 10:1 reflux ratio. The center cut consisted of colorless (methylcyclohexyl)toluene, n_D^{20} 1.5140.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.51; H, 10.42; mol. wt., 187 (Rast), 188 (parent peak in mass spectrum).

The infrared spectrum possessed absorption maxima at 1640, 1466, 1400, 790, and 705 cm^{-1} ; ultraviolet spectrum, λ_{max} 264.5 and 271.5 $m\mu$. Gas chromatography (column A) revealed one principal peak in the chromatogram.

Repeated trituration of the residue from the reaction mixture with hot concentrated hydrochloric acid gave a light brown solid.

Anal. Found: C, 78.02; H, 6.90; Cl, 4.36; residue, 1.56. These data indicate a C/(H + Cl) molar ratio of 0.93.

Oxidation of (Methylcyclohexyl)toluene from Ferric Chloride-Methylcyclohexane.—A mixture of the (methylcyclohexyl)toluene (0.5 ml.) and 15% nitric acid (25 ml.) was heated in a stainless steel bomb for 63 hr. at 160–176° (furnace temperature).²³ After the product was removed with the aid of acetone, the solvent was evaporated, and the residue then treated with 50 ml. of hot 1 N sodium hydroxide. Decantation, followed by acidification of the solution with hydrochloric acid, yielded a curdy yellow solid, wt. 0.16 g. The acid was then esterified with diazomethane in the presence of ether. After removal of the ether, steam distillation of the residue gave fine white needles of dimethyl isophthalate in the distillate, m.p. 64.5°; authentic material, m.p. 64–65°; m.m.p. 65–66°. Gas chromatography (column A) of the product revealed a single peak as did the mixture with authentic dimethyl isophthalate. The authentic

dimethyl phthalate isomers were shown to be separable by means of the column used.

Catalytic Dehydrogenation of (Methylcyclohexyl)toluene from Ferric Chloride-Methylcyclohexane.—The (methylcyclohexyl)toluene (0.5 ml.) was vaporized by gentle heating under a nitrogen stream during 6.5 hr. into a glass column (28.5 by 1.5 cm.) containing platinum on alumina at 307–318°. The product, which was condensed in two consecutive U-tubes cooled in liquid nitrogen, was dissolved in ether and subjected to gas chromatography (column B). Collection of the components present yielded 2,3'-dimethylbiphenyl; ultraviolet spectrum, λ_{max} 239 $m\mu$; fluorene, ultraviolet spectrum, λ_{max} 300 and 260 $m\mu$; 3-methylfluorene, m.p. 86–88°, m.m.p. with authentic material, 85–86°, ultraviolet spectrum, λ_{max} 303 and 262 $m\mu$, infrared spectrum, identical to that of authentic material. The products were present in the ratio 10:1:15 with retention times relative to biphenyl of 1.26, 2.27, and 3.18, respectively. The relative retention times of various alkylbiphenyls with a similar column are reported by Johnson.²⁴

2,3'-Dimethylbiphenyl.—The Grignard reagent from *o*-bromotoluene (24 g., 0.14 mole) and magnesium (3.6 g., 0.15 g.-atom) was allowed to react with 3-methylcyclohexanone (15.7 g., 0.14 mole). Subsequently, the hydrolyzed product was heated with 2 g. of 5% palladium on charcoal at 245° for 6 hr. in an "Ace Glass Minilab" distillation apparatus. During this time, gas was evolved and water distilled from the reaction mixture. After removal of the catalyst by filtration, distillation of the product gave 2,3'-dimethylbiphenyl, 6 g. (24%), b.p. 100–106° (2 mm.), lit.²⁴ b.p. 135° (13.5 mm.); n_D^{20} 1.5756, lit.²⁴ n_D^{20} 1.5810; ultraviolet spectrum, λ_{max} 238 $m\mu$. The gas chromatography retention time relative to biphenyl was 1.24.

Fluorene.—The authentic material gave a retention time of 2.22 relative to biphenyl in gas chromatography; ultraviolet spectrum, λ_{max} 300 and 261 $m\mu$.

3-Methylfluorene. **A. From 3-Methylfluorenone.**—3-Methylfluorenone was prepared according to the procedure of Ullmann and Mallet,²⁵ yellow crystals from ethanol, m.p. 66–67°; lit.²⁵ m.p. 66.5°.

A mixture of 3-methylfluorenone (3 g., 0.02 mole), hydrazine (60 g., 1.88 moles), sodium hydroxide (60 g.), and ethylene glycol (500 ml.) was refluxed for 2 hr. A mixture of the product and solvent was collected by distillation. Dilution of the distillate with water provided white solid, 2.9 g., m.p. 90–91°, lit.²⁶ m.p. 91–92°.

The infrared spectrum possessed absorption maxima at 1620, 1390, 955, 800, 765, and 735 cm^{-1} ; ultraviolet spectrum, λ_{max} 303 and 262 $m\mu$. The gas chromatogram (column B) exhibited a single peak with a retention time of 3.18 relative to biphenyl.

B. From 2,3'-Dimethylbiphenyl.—2,3'-Dimethylbiphenyl was passed over the platinum-alumina catalyst according to the procedure previously described. The 3-methylfluorene, m.p. 86–87°, was separated from unchanged starting material by gas chromatography. The ultraviolet spectrum and retention time in gas chromatography were essentially identical to those of the authentic material.

(Methylcyclohexyl)chlorobenzene from Methylcyclohexane-Ferric Chloride-Chlorobenzene.—Methylcyclohexane (2 moles) and ferric chloride (1 mole) were allowed to react in the presence of chlorobenzene as described in Table I. The product obtained with 1 mole of chlorobenzene gave, on refractionation, 4 g. of (methylcyclohexyl)chlorobenzene, b.p. 114° (1.1 mm.), n_D^{20} 1.5352.

Anal. Calcd. for $C_{13}H_{17}Cl$: C, 74.80; H, 8.21; Cl, 16.99. Found: C, 75.01; H, 8.65; Cl, 16.72.

The infrared spectrum possessed absorption maxima at 820 (s), 780 (s), 725 (w), and 695 (s) cm^{-1} .

TABLE I
(METHYLCYCLOHEXYL)CHLOROBENZENE FROM
METHYLCYCLOHEXANE-FERRIC CHLORIDE-CHLOROBENZENE

C_6H_5Cl , moles	Temp., °C.	Time, hr.	HCl, %	Yield, g.	B.p., °C. (mm.)	n_D^{20}
1	63–80	2.5	80.5	10	122–124/2	1.5282
5	68–70	3	77.5	19.2	132–140/4–5	1.5330

(22) Boiling points and melting points are uncorrected. Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England.

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(Methylcyclohexyl)chlorobenzene from 1-Chloro-1-methylcyclohexane-Chlorobenzene-Aluminum Chloride.—A solution of 1-methylcyclohexene (20 g., 0.21 mole) in 200 ml. of chlorobenzene was saturated with dry hydrogen chloride and then added during 1.5 hr. to a mixture of 400 ml. of chlorobenzene and 2.8 g. (0.021 mole) of aluminum chloride at 69–70°. The temperature was kept at 70° for another 5 hr. Work-up provided 25.2 g. (58%) of isomeric (methylcyclohexyl)chlorobenzenes, b.p. 103–104° (0.7 mm.), n_D^{20} 1.5339. Except for relative band intensities, the infrared spectrum was essentially identical to that of the (methylcyclohexyl)chlorobenzene from methylcyclohexane-chlorobenzene-ferric chloride.

(Methylcyclohexyl)toluene from 1-Chloro-1-methylcyclohexane-Toluene-Aluminum Chloride.—Hydrogen chloride was passed slowly during 6.5 hr. into a stirred solution of 1-methylcyclohexene (20 g., 0.22 mole) in toluene (300 ml.). During 6 hr., the solution of 1-chloro-1-methylcyclohexane was added at 68–71° to a stirred mixture of toluene (255 ml.) and aluminum chloride (5.46 g.) under nitrogen. After 2 hr. at 70°, the reaction mixture was diluted with ether and extracted first with dilute hydrochloric acid and then with saturated sodium chloride solution. Removal of ether from the dried organic solution by distillation gave a residue which on distillation through an "Ace Minilab" apparatus yielded a yellow oily fraction boiling at 89–109° (4 mm.). In a subsequent fractionation with a 36-in. semimicro spinning band column (8:1 reflux ratio), a center cut of colorless liquid was collected, b.p. 84–88° (1 mm.), n_D^{20} 1.5132.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.10; H, 10.77; mol. wt., 199 (vapor phase osmometry).²⁷

The infrared spectrum displayed absorption maxima at 1630, 1476, 1400, 816, 782, and 706 cm^{-1} , and the ultraviolet spectrum gave λ_{max} 264.5 and 272 $m\mu$. The gas chromatogram (column A) revealed an equivalent doublet with no shoulders.

Oxidation of (Methylcyclohexyl)toluene from 1-Chloro-1-methylcyclohexane-Toluene-Aluminum Chloride.—The (methylcyclohexyl)toluene (1 ml.) was oxidized with 15% nitric acid (25 ml.) in a stainless steel bomb for 50.5 hr. at 150° (furnace temperature).²³ Isolation and esterification of the product acids were carried out as previously described. The elution times and peak areas of the major components were identical to those for a 1:1 mixture of authentic dimethyl iso- and terephthalates.

Catalytic Dehydrogenation of (Methylcyclohexyl)toluene from 1-Chloro-1-methylcyclohexane-Toluene-Aluminum Chloride.—The (methylcyclohexyl)toluene (0.5 ml.) was dehydrogenated over platinum on alumina at 280–300° as previously described.¹¹ Gas chromatography of the product in ether yielded 3-methylbiphenyl; ultraviolet spectrum, λ_{max} 250 $m\mu$; infrared spectrum essentially identical to that of authentic material, 3,4'-dimethylbiphenyl; ultraviolet spectrum, λ_{max} 251 $m\mu$; and 4,4'-dimethylbiphenyl, ultraviolet spectrum, λ_{max} 255 $m\mu$. The three components were present in the ratio 1:6:6, and the retention times relative to biphenyl were 1.38, 1.94, and 2.03, respectively.²⁴

3-Methylbiphenyl.—This compound was synthesized by a modification of the procedure of Gomberg and Pernert.²⁸ After reaction of the diazohydroxide from *m*-toluidine (25 g., 0.23 mole) with benzene, ether extraction of the steam distillate, followed by removal of solvent, yielded a residue which on distillation through a short-path Vigreux column gave a yellow oil, 2 ml., b.p. 273°, lit.²⁹ b.p. 273°; n_D^{20} 1.6009, lit.²⁹ n_D^{20} 1.6016; ultraviolet spectrum, λ_{max} 250 $m\mu$ (material from gas chromatography). Gas chromatography revealed a minor amount of contaminant. The retention time of the principal product relative to biphenyl was 1.39.

3,4'-Dimethylbiphenyl.—The procedure used for 2,3'-dimethylbiphenyl was followed with *p*-bromotoluene (24 g., 0.14 mole), 3-methylcyclohexanone (15.1 g., 0.13 mole), magnesium turnings (3.6 g., 0.15 g.-atom), and 5% palladium on charcoal (3 g.). The product boiled at 104–110° (2.5 mm.); lit.²⁴ b.p. 153° (15 mm.); n_D^{21} 1.5925, lit.²⁴ n_D^{20} 1.5968; ultraviolet spectrum, λ_{max} : 253 $m\mu$; retention time (gas chromatography) relative to biphenyl, 1.95.

(27) We are grateful to Mrs. Nance Browdie of the Sohio Research Laboratory for this analysis.

(28) A. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.*, **48**, 1372 (1926).

(29) American Petroleum Institute, "Selected Values of Properties of Hydrocarbons," Vol. 1, 1958, Table 35a.

4,4'-Dimethylbiphenyl.—The retention time in gas chromatography relative to biphenyl was 2.05, ultraviolet spectrum λ_{max} 254.5 $m\mu$.

1-Chloro-1-methylcyclohexane.—Dry hydrogen chloride was passed through a gas dispersion tube into a 1-methylcyclohexene (30.4 g., 0.32 mole) during 6 hr. at ice bath temperatures. Distillation produced a colorless liquid, 34.6 g. (81%), b.p. 69–71° (54 mm.), lit.³⁰ b.p. 53–55° (40 mm.); n_D^{20} 1.4570, lit.³⁰ n_D^{20} 1.4565.

Anal. Calcd. for $C_7H_{13}Cl$: C, 63.38; H, 9.88. Found: C, 63.89; H, 10.10.

1-Chloro-1-methylcyclohexane and Ferric Chloride.—A mixture of 1-chloro-1-methylcyclohexane (30 g., 0.23 mole) and ferric chloride (20.2 g., 0.12 mole) evolved acid gas at 5°. A total of 0.13 mole of hydrogen chloride was obtained while the reaction mixture was heated to 70° during 1.5 hr. Work-up gave two fractions from distillation, b.p. 45–130° (34 mm.) and b.p. 80–120° (4 mm.), which were shown to contain the same major component, total yield, 2.8 g. of yellow oil. The principal component, isolated by gas chromatography (column A) was very similar in its properties to the (methylcyclohexyl)toluene from methylcyclohexane-ferric chloride; identical retention volumes in gas chromatography; absorption bands in the infrared spectrum at 1640, 1475, 1400, 790, and 705 cm^{-1} , ultraviolet spectrum, λ_{max} 271.5, 262.5 $m\mu$.

The reaction also gave brown polymer, 4 g.

Anal. Found: C, 84.74; H, 9.30; Cl, 2.31.

The results correspond to a C/(H + Cl) molar ratio of 0.76.

1-Methylcyclohexene Dimer and Ferric Chloride.—A mixture of the dimer¹⁸ (6.4 g., 0.033 mole), ferric chloride (21.6 g., 0.13 mole), and cyclohexane (250 ml.) was heated under nitrogen to 70° during 1 hr., and then allowed to cool to room temperature during 2.5 hr. Hydrogen chloride (48% of theory) was first evolved at 54°. Filtration yielded a black residue which was washed with ether. The combined filtrate, washed first with acid and then with salt solution, was freed of low boiling material by distillation. Fractionation of the residue through a short Vigreux column gave a dark brown liquid, 1.5 ml., b.p. 45–130° (3 mm.). The infrared and ultraviolet spectra of the main component (separated by gas chromatography) were very similar to those of the (methylcyclohexyl)toluenes. However, the retention time in gas chromatography was different. The presence of several components in the crude product was indicated.

Dimerization of 1-Methylcyclohexene. A. With Perchloric Acid-Formic Acid.—The procedure of Bloomfield¹⁸ gave 1-methylcyclohexene dimer, b.p. 125–129° (14 mm.), n_D^{20} 1.4978; lit.¹⁸ b.p. 90–92° (2 mm.), n_D^{20} 1.5000.

B. With Sulfuric Acid.—A modification of the method of Whitmore and Wrenn³¹ was used. 1-Methylcyclohexene (20 g., 0.21 mole) was allowed to react with 65% sulfuric acid (40 ml.) for 2.5 hr. at reflux. The reaction mixture was then dissolved in ether and washed well with cold saturated sodium chloride solution. After distillation of the ether from the dried ether solution, the product was obtained as a colorless oil, 14.7 g. (74%), b.p. 88–90° (0.8 mm.), n_D^{20} 1.4950. The infrared spectrum was essentially identical to that of the Bloomfield dimer.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.42; H, 12.58; Found: C, 87.43; H, 12.68.

The product from a similar reaction carried out for 0.5 hr. showed at least six components by gas chromatography.

When the 0.5-hr. run was doubled in scale, the odor of sulfur dioxide was detected during reaction. Work-up yielded a fraction, 9 g., b.p. 98–132° at 5 mm., which contained at least six components by gas chromatographic analysis. The principal one, about 50% of the total, was very similar in its properties to the (methylcyclohexyl)toluene obtained from ferric chloride-methylcyclohexane: the same retention volume in gas chromatography; absorption bands in the infrared spectrum at 1396, 780, 704 cm^{-1} (in CS_2); ultraviolet spectrum, λ_{max} 271.5 and 264 $m\mu$.

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