

melting point of 104°, which identified this product as dipentene.

The trimer fraction from the preliminary distillation with the Vigreux column had a b. p. of 235–245° and n_D^{20} of 1.4940 and was not further identified.

Discussion of Results

From the results presented in Table I, it can be seen that both sulfuric and phosphoric acids may be used as catalysts for the polymerization of isoprene to low polymers. Up to 92% of isoprene was polymerized by using sulfuric acid and up to 49% was polymerized by using phosphoric acid. By varying the concentration of the acid and the temperature of the reaction different ratios of the different polymers could be obtained. The increase of acid concentration and temperature promotes the formation of trimers and high polymers.

The best conditions for the formation of dimers with the acids investigated without simultaneous production of high polymers are as follows: for sulfuric acid, 48% acid, 20°, forty-minute stirring period, 3 to 1 acid to isoprene ratio; for phosphoric acid, 70% acid, 20°, sixty-minute stirring period, and 3 to 1 acid to isoprene ratio (experiments 5 and 15).

In the presence of lower acid concentrations, a decline in polymerization was noted (experiments 26 and 13). The dimers produced were composed of aliphatic and cyclic compounds. Phosphoric acid favored the formation of aliphatic dimer (ex-

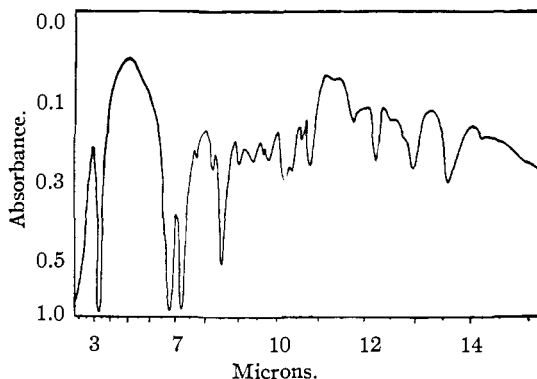


Fig. 1.—Infrared absorption spectra of 2,6-dimethyloctane.

periment 15 gave a ratio of 7 to 3) as compared with the mixture obtained from sulfuric acid reactions (experiment 5 gave a ratio of 2 to 3).

Summary

1. Isoprene was polymerized to low polymers by using either sulfuric or phosphoric acid as catalyst without the formation of high polymers.

2. The low polymers consisted of dimers and trimers. The dimers were identified as the mixture of dipentene and an aliphatic dimer, which when hydrogenated gave 2,6-dimethyloctane.

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

Hydrogen Transfer. IV.¹ Reaction of *p*-Isobutyltoluene and of *p*-*s*-Butyltoluene with Methylcyclohexene

BY HERMAN PINES, D. R. STREHLAU² AND V. N. IPATIEFF

It has been shown previously³ that a hydrogen transfer occurred when *p*-cymene was contacted with methylcyclohexene in the presence of either sulfuric acid or hydrogen fluoride. The main products of this reaction were methylcyclohexane and 1,3,3,6-tetramethyl-1-*p*-tolylindan; the methylcyclohexene acted as a hydrogen acceptor while *p*-cymene acted as a hydrogen donor. A hydrogen transfer reaction also occurred when *p*-ethyltoluene or *p*-propyltoluene was contacted with methylcyclohexene in the presence of the above-mentioned catalysts; the aromatic hydrocarbons were converted, respectively, to 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane and 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane.

Continuing this study, an investigation was made of the type of products which are formed

when a branched chain alkyltoluene such as *p*-isobutyltoluene is treated with 4-methylcyclohexene in the presence of hydrogen fluoride or sulfuric acid. It was found that hydrogen transfer was the main reaction. The methylcyclohexene was converted to the extent of 33 mole per cent. to methylcyclohexane, 10 mole per cent. to dimethyldicyclohexyl and only 28 mole per cent. reacted with *p*-isobutyltoluene to form methylcyclohexylisobutyltoluene. Of the reacted *p*-isobutyltoluene, 28% was cycloalkylated by 4-methylcyclohexene and 60% underwent a hydrogen transfer reaction to form 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane, compound I.

The cycloalkylated product corresponded to 4-isobutyl-2-(1-methylcyclohexyl)-toluene. This conclusion was based on the observations that during alkylation or cycloalkylation of *p*-cymene the carbon atom ortho to the methyl group was substituted⁴ and that the reaction between benzene

(1) For paper III of this series see H. Pines, D. R. Strehlau and V. N. Ipatieff, *THIS JOURNAL*, **71**, 3534 (1949).

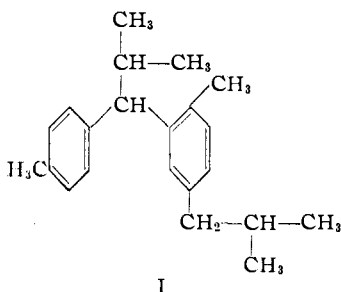
(2) Universal Oil Products Company Predoctorate Fellow (1945–1948).

(3) V. N. Ipatieff, H. Pines and R. C. Olberg, *THIS JOURNAL*, **70**, 2123 (1948);

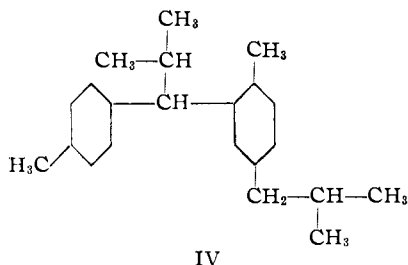
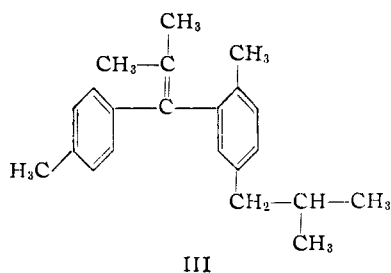
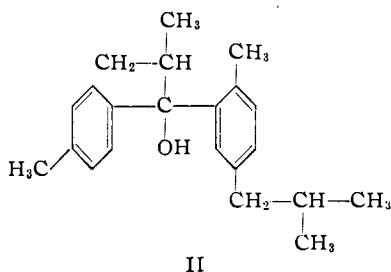
(4) H. Pines, A. Weizmann and V. N. Ipatieff, *ibid.*, **70**, 3850 (1948).

and isomeric methylcyclohexenes, including 4-methylcyclohexene, results in the formation of 1-methyl-1-phenylcyclohexane.⁵

A mixture of higher boiling hydrocarbons corresponding to products of interaction of methylcyclohexene with compound I was also formed.



The structure of I was proved by an independent synthesis which consisted in treating the Grignard of 2-bromo-4-isobutyltoluene with *p*-isobutyryltoluene; the alcohol thus formed (II) was dehydrated by means of alumina to the corresponding unsaturated hydrocarbon III which on hydrogenation in the presence of platinum and acetic acid yielded compound I, and which on complete hydrogenation yielded compound IV.



The infrared spectra, physical constants and derivatives of compound I obtained from the hy-

drogen transfer reaction and by the synthesis showed they were identical (Fig. 1). The infrared spectra of compound IV and the product resulting from the complete hydrogenation of the hydrogen transfer reaction product were also identical (Fig. 2).

It was of interest to note that the olefinic bond in 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropene (III) showed no tendency to add bromine in carbon tetrachloride solution and did not reduce 2% potassium permanganate in alcoholic solution, a reagent usually sensitive to double bonds.⁶

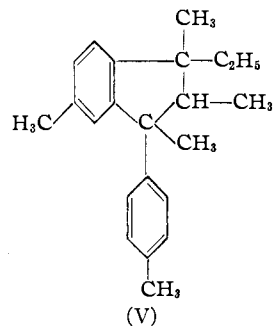
Hydrogenation procedures usually effective for olefinic bonds failed with III; thus no hydrogen was absorbed at 55° and 100 atm. pressure over a nickel-kieselguhr catalyst nor at 160° and 100 atm. pressure in alcoholic solution in the presence of platinum oxide.

Reduction of III was accomplished by means of a platinum catalyst at 25° and atmospheric pressure with glacial acetic acid as a solvent, conditions drastic enough to reduce aromatic bonds at a slow rate. The rate of hydrogenation of the olefinic bond was rapid enough under these conditions to produce an almost selective hydrogenation.

In order to determine the course which the reaction would take when the carbon atom attached to the para position of the toluene ring is bound to a primary and a secondary carbon atom, *p*-*s*-butyltoluene was treated with 4-methylcyclohexene in the presence of hydrogen fluoride.

It was found that hydrogen transfer was again the main reaction. Of the methylcyclohexene charged, 56 mole per cent. was converted to methylcyclohexane and 9% to a compound corresponding to 4-*s*-butyl-2-(1-methylcyclohexyl)-toluene. Of the *p*-*s*-butyltoluene which reacted, 12 mole per cent. was alkylated and 76% was converted to 1,2,3,6-tetramethyl-3-ethyl-1-*p*-tolylindan (V); the reaction is similar to that which occurs when *p*-cymene or substituted *p*-cymene⁴ react with 4-methylcyclohexene.

Hydrogen transfer was also the main reaction when *p*-*s*-butyltoluene was contacted with 4-methylcyclohexene in the presence of sulfuric acid. The yield of cycloalkylated product formed



(5) V. N. Ipatieff, E. E. Meisinger and H. Pines, *THIS JOURNAL*, **72**, in press (1950).

(6) V. N. Ipatieff, W. W. Thompson and H. Pines, *ibid.*, **70**, 1658 (1948).

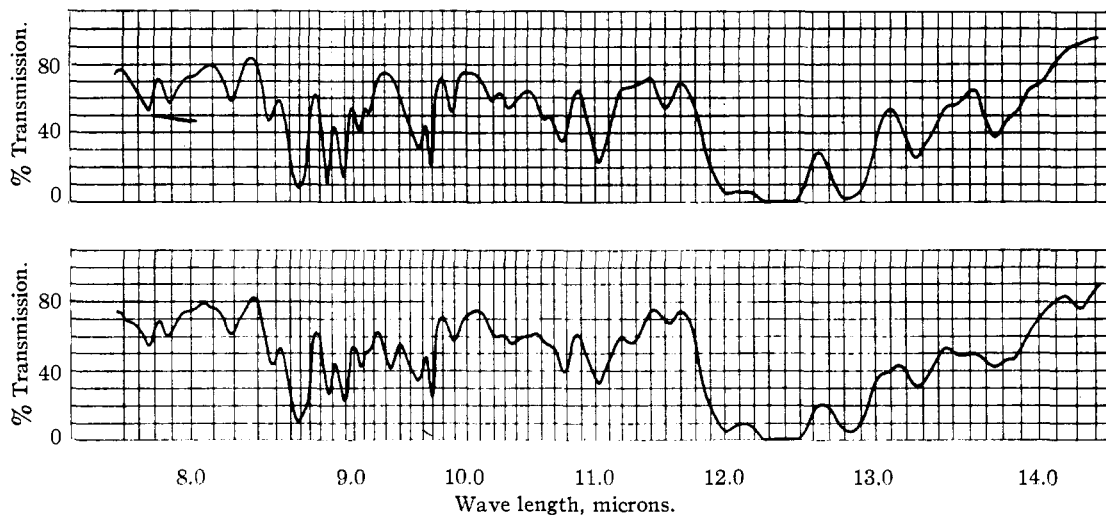


Fig. 1.—Infrared absorption spectra (cell thickness, 0.1 mm.): upper, 1,2-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane obtained from hydrogen transfer reaction; lower, synthetic 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane.

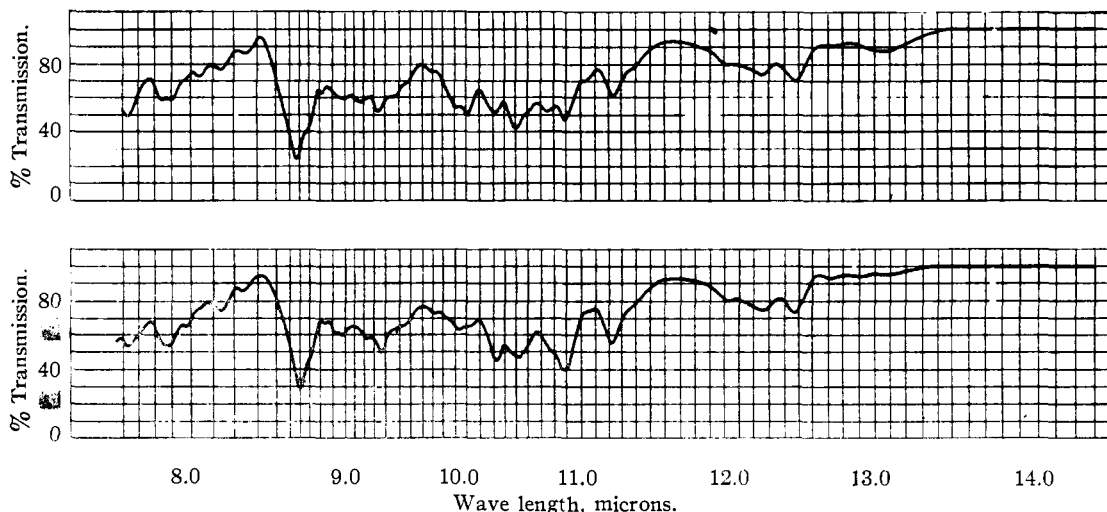
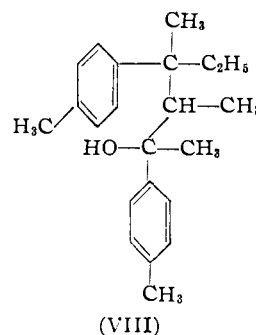
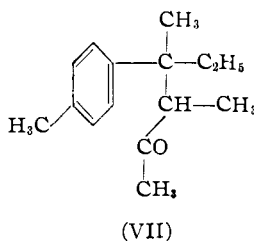
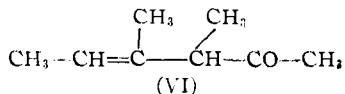


Fig. 2.—Infrared absorption spectra (cell thickness, 0.1 mm.): upper, synthetic 1-(4-methylcyclohexyl)-1-(2-methyl-5-isobutylcyclohexyl)-2-methylpropane; lower, 1-(4-methylcyclohexyl)-1-(2-methyl-5-isobutylcyclohexyl)-2-methylpropane from hydrogen transfer reaction.

was however larger than in the case of hydrogen fluoride catalyzed reaction. Compound V was prepared and found to be identical, according to the infrared absorption spectra (Fig. 3) and solid derivatives, with the compound V from hydrogen transfer.

Compound V was synthesized as follows: 3,4-dimethylhexene-4-one-2 (VI) reacted with toluene in the presence of aluminum chloride and hydrogen chloride; the ketone produced (VII) was condensed with *p*-tolylmagnesium bromide to form a tertiary carbinol (VIII) which on cyclo-



dehydration by means of hydrogen fluoride yielded V.

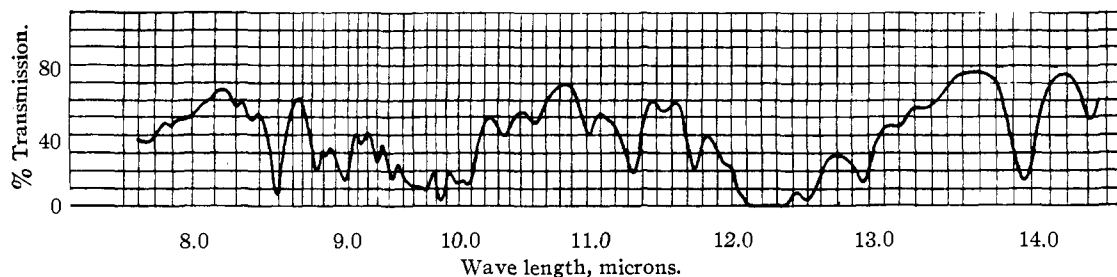


Fig. 3.—Infrared absorption spectra (cell thickness, 0.1 mm.): 1,2,3,6-tetramethyl-3-ethyl-1-2-tolylindan.

Experimental Part

I. Synthesis of *p*-Isobutyltoluene

(a) Isobutyryl chloride was prepared according to the method for *n*-butyryl chloride.⁷ From 715 g. of isobutyric acid and 1071 g. of thionyl chloride, 600 g. of isobutyryl chloride was obtained boiling at 91–92°; yield 70%.

(b) *p*-Isobutyryltoluene which was synthesized from 586 g. of isobutyryl chloride according to the procedure described previously¹ distilled at 128–130° (25 mm.), n_D^{20} 1.5147; yield 95%. Derivatives⁸: oxime, m. p. 92°; semicarbazone, m. p. 101°. The 2,4-dinitrophenylhydrazone (not previously prepared) melted at 111.5–112.5°.

Anal. Calcd. for $C_{17}H_{18}N_4O_4$: N, 16.35. Found: N, 16.26.

(c) *p*-Isobutyltoluene was prepared by hydrogenating *p*-isobutyryltoluene under pressure and in the presence of a copper oxide–alumina catalyst (94% CuO, 6% Al_2O_3) at 190°. After redistillation over sodium the *p*-isobutyltoluene boiled at 191–192° (752 mm.), n_D^{20} 1.4888, d_4^{20} 0.8509; yield 74%.

The sulfonamide of *p*-isobutyltoluene was prepared according to the procedure described in the literature¹⁰; after recrystallization from a mixture of benzene and pentane it melted at 89–90° (new compound). *Anal.* Calcd. for $C_{11}H_{17}O_2NS$: C, 58.20; H, 7.50; N, 6.17. Found: C, 58.20; H, 7.52; N, 6.99.

The acetyl derivative of *p*-isobutyltoluene was prepared by treating one gram of the hydrocarbon in 5 ml. of carbon disulfide with a solution composed of 0.5 g. of acetyl chloride, 0.8 g. of aluminum chloride and 5 ml. of carbon disulfide. The semicarbazone of this ketone melted at 141–142° (new compound). *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 68.02; H, 8.52. Found: C, 67.82; H, 8.73.

II. Reaction of *p*-Isobutyltoluene and Methylcyclohexene in the Presence of Hydrogen Fluoride.—*p*-Isobutyltoluene, 296 g. (2 moles) and 96 g. (1 mole) of 4-methylcyclohexene reacted at 0–5° in the presence of 200 g. of hydrogen fluoride according to the procedure described previously.^{1,3} The following cuts were separated on distillation on a 15–20 plate column at a reflux ratio of 10 to 1: (1) b. p. 102°, n_D^{20} 1.4247, 31 g. (methylcyclohexane); (2) 96–97° (32 mm.), n_D^{20} 1.4880, 158 g. (*p*-isobutyltoluene); (3) 96–105° (4 mm.), n_D^{20} 1.4840, 10 g.; (4) 128–131° (3 mm.), n_D^{20} 1.5200, 64 g.; (5) 148–150° (3 mm.), n_D^{20} 1.5360, 83 g.; (6) 150–200° (3 mm.), n_D^{20} 1.5310, 11 g.; (7) residue, 5 g.

Fraction 3 corresponded to dimethylcyclohexyl; d_4^{20} 0.8855, *MRD* calcd. 62.4, obsd. 63.1. *Anal.* Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 87.17; H, 13.17.

Fraction 4 corresponded to methylcyclohexyl-*p*-isobutyltoluene, d_4^{20} 0.9334; *MRD* calcd. 79.5, obsd. 79.9. *Anal.* Calcd. for $C_{18}H_{28}$: C, 88.44; H, 11.56. Found: C, 89.09; H, 11.23.

(7) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 194, p. 147.

(8) K. V. Auwers, *Ber.*, **49**, 2406 (1916).

(9) V. N. Ipatieff and V. Haensel, *THIS JOURNAL*, **64**, 520 (1942).

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

Acetyl derivative was prepared as described above. The 2,4-dinitrophenylhydrazone of this ketone melted at 220–222°. *Anal.* Calcd. for $C_{26}H_{34}N_4O_4$: C, 66.9; H, 7.3; N, 12.0. Found: C, 66.7; H, 7.1; N, 12.5.

Fraction 5 corresponded to 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane, d_4^{20} 0.9322, *MRD* calcd. 97.6, obsd. 98.3. *Anal.* Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.89; H, 10.10.

Nitro Derivative.—Nitration with a nitrating mixture composed of 2 vol. of 96% sulfuric acid and 1 vol. 72% nitric acid gave a tetranitro derivative m. p. 173–175°. *Anal.* Calcd. for $C_{22}H_{28}N_4O_8$: C, 55.70; H, 5.48; N, 11.80. Found: C, 55.62; H, 5.54; N, 11.26. On acetylation a ketone was produced which formed a 2,4-dinitrophenylhydrazone melting at 265–266° and corresponding to that of *p*-acetyltoluene; a split of the molecule during acetylation occurred. *Anal.* Calcd. for $C_{15}H_{14}N_4O_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 57.20; H, 4.49; N, 17.83.

A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of *p*-acetyltoluene showed no depression.

Hydrogenation of 10 g. (0.034 mole) of fraction 5 at 180° in the presence of 1 g. of nickel-kieselguhr catalyst and an initial pressure of 123 atm. consumed 0.214 mole of hydrogen. The product distilled at 140–144° at 3 mm.; n_D^{20} 1.4795, d_4^{20} 0.8749; *MRD* calcd. 99.8, obsd. 99.5. *Anal.* Calcd. for $C_{22}H_{42}$: C, 86.18; H, 13.82. Found: C, 86.17; H, 13.67.

III. Synthesis of 1-*p*-Tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane.—(a) 2-Methyl-5-isobutyl-bromobenzene was prepared by the bromination of 49 g. (0.33 mole) of *p*-isobutyltoluene with 53 g. (0.33 mole) of bromine containing iodine at 0° according to the procedure described in the literature.¹¹

The bromide distilled at 119–121° (12 mm.), n_D^{20} 1.5308, d_4^{20} 1.2057; yield 85%; *MRD* calcd. 57.2, obsd. 58.8 (new compound). *Anal.* Calcd. for $C_{11}H_{15}Br$: C, 58.14; H, 6.62; Br, 35.20. Found: C, 58.80; H, 6.77; Br, 34.68.

The position of the entering bromine atom was proved to be ortho to the methyl group by oxidation with nitric acid; 2 g. was refluxed for forty-eight hours with 10 ml. of nitric acid (1 vol. water, 4 vol. 72% nitric acid). One gram of 3-bromo-4-methylbenzoic acid was formed, melting at 203–204° which agrees with the melting point previously reported.¹¹

(b) 1-*p*-Tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropanol (II) was prepared by means of a Grignard reaction from 43 g. (0.19 mole) of 2-methyl-5-isobutylbromobenzene, 4.6 g. (0.19 mole) of magnesium, 31 g. (0.20 mole) of *p*-isobutyryltoluene and 120 ml. of ether. Fractionation of the reaction mixture at 5 mm. gave *p*-isobutyltoluene (10.3 g.); *p*-isobutyryltoluene (16 g.) and a principal fraction distilling at 153–160° (4 mm.) (25.5 g.) which corresponded to a mixture of the desired tertiary carbinol and the corresponding olefin. The carbon-hydrogen analysis showed that partial dehydration of the carbinol occurred during distillation. *Anal.* Calcd. for $C_{22}H_{30}O$: C, 85.16; H, 9.68. Calcd. for $C_{22}H_{28}$: C, 90.34; H, 9.66. Found: C, 88.47; H, 10.02.

(11) H. N. Morse and I. Remsen, *Ber.*, **11**, 225 (1878).

(c) 1-*p*-Tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropene (III) was prepared by dehydrating the carbinol dissolved in equal volume of cyclohexane by passing it over activated alumina at 290°. The olefin distilled at 145° (3 mm.), n_D^{20} 1.5550, d_4^{20} 0.9402, yield 85%; *MRD* Calcd. 96.1, obsd. 99.7. *Anal.* Calcd. for $C_{22}H_{28}$: C, 90.34; H, 9.66. Found: C, 89.90; H, 9.87.

(d) 1-*p*-Tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane (I) was prepared by hydrogenation of III. The olefin, 5.1 g., was dissolved in 15 ml. of glacial acetic acid and 0.34 g. of platinum oxide was added. The hydrogenation was carried out at room temperature and at atmospheric pressure until 615 cc. of hydrogen was absorbed and the rate of absorption dropped off sharply. The theoretical amount of hydrogen calculated for reduction of the olefinic double bond and of the catalyst was 560 cc. The reduced product distilled at 156–157° (3 mm.), n_D^{20} 1.5385, d_4^{20} 0.9366; *MRD* calcd. 97.6, obsd. 98.2. *Anal.* Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.71; H, 10.31.

(e) 1-(4-Methylcyclohexyl)-1-(2-methyl-5-isobutylcyclohexyl)-2-methylpropane (IV) was prepared by hydrogenating 5 g. of 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane using nickel-kieselguhr as a catalyst¹² at 200° and 100 atmospheres pressure. The saturated product formed distilled at 140–142° (3 mm.), n_D^{20} 1.4825, d_4^{20} 0.8833; *MRD* calcd. 99.8, obsd. 98.9. *Anal.* Calcd. for $C_{22}H_{42}$: C, 86.18; H, 13.82; Found: C, 86.17; H, 13.67.

IV. Synthesis of *p*-*s*-Butyltoluene. (a) Methyl ethyl-*p*-tolylcarbinol¹³ was prepared by means of the Grignard reaction using 48.6 g. (2 moles) of magnesium, 342 g. (2 moles) of *p*-bromotoluene and 144 g. (2 moles) of methyl ethyl ketone. An 80% yield of the carbinol (261 g.) was realized, b. p. 90–91° (4 mm.), n_D^{20} 1.5180. In addition to the carbinol 36 g. of *p*-ditolyl melting at 121–122° was obtained.

(b) *p*-*s*-Butyltoluene was prepared by dehydrating the carbinol over activated alumina at 335° and reducing the resulting olefin at 50° at an initial hydrogen pressure of 130 atm. in the presence of nickel-kieselguhr catalyst.¹² Two hundred ml. of pentane was used as a solvent. Upon distillation the bulk of the material (193 g.) came over at 96–97° (32 mm.), comprising a yield of 82% from the carbinol. Redistillation from sodium metal at atmospheric pressure through a 20-plate column gave a pure product boiling at 189.5°, n_D^{20} 1.4900.

V. Reaction of *p*-*s*-Butyltoluene and 4-Methylcyclohexene in Presence of Hydrogen Fluoride.—*p*-*s*-Butyltoluene, 164 g. (1.1 moles) and 54 g. (0.56 mole) of 4-methylcyclohexene were contacted in the presence of 80 g. of hydrogen fluoride according to the procedure previously described.¹ The product resulting from this reaction weighed 201 g. from which the following cuts were separated by distillation from a 20-plate column: (1) b. p. 101° (750 mm.), n_D^{20} 1.4238, 30 g. (methylcyclohexane); (2) b. p. 187–192° (750 mm.), n_D^{20} 1.4915, 105 g. (*p*-*s*-butyltoluene); (3) b. p. 128–131° (4 mm.), n_D^{20} 1.5214, 11.5 g.; (4) b. p. 163–169° (4 mm.), n_D^{20} 1.5565, 45.5 g.; (5) residue 7.4 g.

Fraction 3 corresponded to 4-*s*-butyl-2-(1-methylcyclohexyl)-toluene; d_4^{20} 0.9365; *MRD* calcd. 79.5, obsd. 79.5. *Anal.* Calcd. for $C_{18}H_{28}$: C, 88.44; H, 11.56. Found: C, 88.47; H, 11.25.

Fraction 4 corresponded to 1,2,3,6-tetramethyl-3-ethyl-1-*p*-tolylindan. Infrared absorption spectrum is given in Fig. 1. *Anal.* Calcd. for $C_{22}H_{28}$: C, 90.40; H, 9.60. Found: C, 90.56; H, 9.75.

The tetranitro derivative was prepared by nitration with a mixture of 2 vol. of 96% sulfuric acid and 1 vol. of 72% nitric acid. Crystallization from an alcohol-chloroform mixture gave needles melting at 183–184°. *Anal.* Calcd. for $C_{22}H_{24}N_4O_8$: C, 55.93; H, 5.12; N, 11.86. Found: C, 56.18; H, 5.13; N, 11.84.

Oxidation of 1 g. of the hydrocarbon by boiling with a solution of 7 g. of chromic anhydride in 30 ml. of acetic acid, 30 ml. of water and 5 ml. of sulfuric acid gave an acid of m. p. 309–312° having a neutral equivalent of 175 and corresponding to 1,2,3-trimethyl-3-ethyl-1-(4-carboxyphenyl)-6-carboxyindan.

Acetylation yielded a ketone whose 2,4-dinitrophenylhydrazone melted at 265°. A mixed melting point with the 2,4-dinitrophenylhydrazone of *p*-methylacetophenone showed no depression. During acetylation a rupture of the molecule occurred. *Anal.* Calcd. for $C_{15}H_{14}N_4O_4$: N, 17.8. Found: N, 17.9.

VI. Reaction of *p*-*s*-Butyltoluene with 4-Methylcyclohexene in the Presence of 96% Sulfuric Acid.—Thirty grams (0.2 mole) of *p*-*s*-butyltoluene and 10 g. (0.1 mole) of 4-methylcyclohexene reacted in the presence of 18 g. of 96% sulfuric acid according to the procedure described previously.¹ Thirty-three grams of product was obtained from which the following cuts were separated by distillation from a 20-plate column: (1) b. p. 100–105° (754 mm.), n_D^{20} 1.4240, 4.2 g. (methylcyclohexane); (2) b. p. 191–193° (754 mm.), n_D^{20} 1.4912, 21.7 g. (*p*-*s*-butyltoluene); (3) b. p. 122–126° (4 mm.), n_D^{20} 1.5287, 3.3 g. (4-*s*-butyl-2-(1-methylcyclohexyl)-toluene); (4) 150–170° (4 mm.), n_D^{20} 1.5560, 2.6 g. (compound V). Cut 4 was identified by infrared absorption spectra and nitro derivative: (5) residue 1.0 g.

VII. Synthesis of 1,2,3,6-Tetramethyl-3-ethyl-1-*p*-tolylindan (V). (a) 3,4-Dimethylcyclohexane-4-one-2 (VI) was prepared by the condensation of methyl ethyl ketone at 0° in the presence of 96% sulfuric acid.¹⁴ The reaction mixture was worked up according to the procedure of Ekeley and Howe.¹⁵ From 500 ml. of methyl ethyl ketone, 65 g. of the desired product (10% yield) boiling at 64–67° (24 mm.), n_D^{20} 1.4520–1.4535 was obtained. The semicarbazone was prepared and recrystallized several times from methyl alcohol; m. p. 204–205. An iodoform test on the ketone was positive.

(b) 3,4-Dimethyl-4-*p*-tolyl-2-hexanone (VII) was prepared by the reaction of toluene with 65 g. (0.5 mole) of compound VI according to a procedure described previously.³ After distilling off 120 g. of toluene and 28 g. of unreacted starting ketone the following cuts were separated at 3 mm. pressure: (1) 97–110°, n_D^{20} 1.4955, 9.0 g.; (2) 110–113°, n_D^{20} 1.5045, 19 g.; (3) 113–165°, n_D^{20} 1.5170–1.5240, 9.4 g.; (4) residue, 16 g., glass-like solid.

Fraction 2, representing a 17% yield, corresponded to the desired product, d_4^{20} 0.9536; *MRD* calcd. 67.9, obsd. 67.8. *Anal.* Calcd. for $C_{18}H_{22}O$: C, 82.49; H, 10.16. Found: C, 82.53; H, 10.28.

The 2,4-dinitrophenylhydrazone was an oil which resisted all attempts at crystallization.

Oxidation with chromic acid solution gave terephthalic acid (dimethyl ester m. p. 140–142°).

(c) 3,4-Dimethyl-2,4-di-*p*-tolylhexanol-2 (VIII) was prepared by means of the Grignard synthesis using 24 g. (0.14 mole) of redistilled *p*-bromotoluene, 3.4 g. (0.14 mole) of magnesium and 24 g. (0.11 mole) of VII. The main fraction, 16 g. (47% yield), distilled at 180–183° (4 mm.), n_D^{20} 1.5465, d_4^{20} 0.9921; *MRD* calcd. 98.1, obsd. 99.1. *Anal.* Calcd. for $C_{22}H_{30}O$: C, 85.16; H, 9.68. Found: C, 85.4; H, 9.7.

(d) 1,2,3,6-Tetramethyl-3-ethyl-1-*p*-tolylindan (V) was prepared by the dehydrocyclization of 10 g. of the carbinol (VIII) by a method described previously.⁸ Six grams of the desired hydrocarbon (V) was obtained, boiling at 170° (14 mm.), n_D^{20} 1.5600. *Anal.* Calcd. for $C_{22}H_{28}$: C, 90.40; H, 9.6. Found: C, 90.15; H, 9.62.

Nitration by the usual procedure gave a product melting at 180–183° which showed no depression when mixed with the corresponding tetranitro derivative of the hydrogen transfer product.

The infrared absorption spectrum was identical with

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

(13) O. Wallach, *Ann.*, **414**, 195 (1917–1918).

(14) A. E. Abbott, G. H. R. Kon and R. D. Satchell, *J. Chem. Soc.*, 2514 (1928).

(15) J. B. Ekeley and W. W. Howe, *This Journal*, **45**, 1923 (1917).

that of the product formed from the hydrogen transfer reaction (Fig. 3).

Summary

The reaction of 4-methylcyclohexene with *p*-isobutyltoluene or with *p-s*-butyltoluene in the presence of hydrogen fluoride or of sulfuric acid yielded main products resulting from a hydrogen transfer in which the aromatic hydrocarbon acted as donor and 4-methylcyclohexene as acceptor.

The products obtained from the respective aromatic hydrocarbons through a hydrogen transfer were 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane and 1,2,3,6-tetramethyl-3-ethyl-1-*p*-tolylindan.

The following new compounds and some of their derivatives were prepared: 2-methyl-5-isobutyl-1-bromobenzene, 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methyl-1-propene, 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane, 1-(4-methylcyclohexyl)-1-(2-methyl-5-isobutylcyclohexyl)-2-methylpropane, 2-acetyl-4-isobutyltoluene, 3,4-dimethyl-4-*p*-tolylhexanone, 3,4-dimethyl-2,4-di-*p*-tolylhexanol-2, 1,2,3,6-tetramethyl-3-ethyl-1-*p*-tolylindan and 1,2,3-trimethyl-3-ethyl-1-(4-carboxyphenyl)-6-carboxyindan.

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Reaction of Thiophene with Olefinic Compounds¹

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The present paper describes the alkylation of thiophene and 2-bromothiophene with olefins in the presence of various catalysts.

Boron Fluoride.—Contrary to the statement made by Kutz and Corson^{1a} and in agreement with the recent paper by Caesar,² it was found that either boron fluoride-ethyl ether complex or boron fluoride is an efficient catalyst for the interaction of thiophene with propene, 2-butene, 1-octene, 2,2,4-trimethylpentenes, cyclohexene, bicycloheptene, cyclopropane, α -methylstyrene, and methallyl chloride. The reaction proceeded at temperatures varying from 30 to 90° in an autoclave or at atmospheric pressure. The product consisted of mono- and disubstituted thiophene (Table I). The position of the substituents on the thiophene ring was shown in a few cases to be predominantly on the two carbon atom. In the case of disubstituted thiophene it was assumed that the two and five carbon atoms were substituted inasmuch as the products gave a negative test with ceric nitrate-alcohol reagent.³

In the experiments in which the structure of the compound was not proved it was assumed that the substitution was also in the 2 and 5 positions of the thiophene ring.

The monosubstituted product obtained by treating cyclopropane with thiophene was a mixture consisting of 47% of 2-*n*-propyl- and 52% of isopropylthiophene, as determined by comparing the infrared spectra of the pure 2-*n*-propylthiophene (Fig. 1) and isopropylthiophenes; the latter were obtained from the interaction of propylene with thiophene. The 2-*n*-propylthiophene was obtained by the Clemmensen reduction of 2-pro-

pionylthiophene. The wave lengths used for the calculation of 2-*n*-propylthiophene were 8.6 and 11.2 microns and for isopropylthiophene 7.7 and 10.7 microns. The strong bands beyond 11.5 microns could not be used for calculation since the spectra of isomers were similar in this region.

In the presence of boron fluoride-ethyl ether complex methallyl chloride reacted with thiophene forming predominantly 2- and some 3-(chloro-*t*-butyl)-thiophene. The structure of this compound was determined by converting it to *t*-butylthiophenes, which was accomplished by reaction of the (chloro-*t*-butyl)-thiophene with magnesium and decomposing the resulting organomagnesium compound with water. The *t*-butylthiophenes produced were characterized by means of infrared analysis; they consisted of about 70% of 2- and 30% of 3-*t*-butylthiophene. This was determined by comparing the infrared absorption spectra with those of the pure *t*-butylthiophenes described by Appleby and co-workers.^{4a,b} The organomagnesium compound was also treated with air and hydrolyzed. This resulted in the production of a primary alcohol, (hydroxy-*t*-butyl)-thiophene.

Stannic Chloride.—It was observed that olefinic hydrocarbons, in which the double bond was attached to a completely substituted carbon atom, reacted with thiophene in the presence of stannic chloride at 38 to 50° at atmospheric pressure. Isobutylene yielded *t*-butyl- and 2,5-di-*t*-butylthiophene, and trimethylethylene formed *t*-amyl- and 2,5-di-*t*-amylthiophene. The *t*-butylthiophene was found, according to infrared spectra, to consist of about 70% of 2- and 30% of 3-*t*-butylthiophene. Olefinic hydrocarbons such as propene, 2-butene, isopropylethylene, cyclohexene, or 4-methylcyclohexene did not react

(1) Presented before the Sulfur Symposium, Division of Petroleum Chemistry, San Francisco meeting of the American Chemical Society, April, 1949.

(1a) W. Kutz and B. B. Corson, *THIS JOURNAL*, **68**, 1477 (1946).

(2) P. D. Caesar, *ibid.*, **70**, 3623 (1948).

(3) H. D. Hartough, *Anal. Chem.*, **20**, 860 (1948).

(4) (a) W. G. Appleby, A. F. Sartor, S. H. Lee, Jr., and S. W. Kapranos, *THIS JOURNAL*, **70**, 1552 (1948); (b) W. M. Kutz and B. B. Corson, *ibid.*, **71**, 1503 (1949).