for the cyclohexyl group that is five times greater than that of the phenyl group. A possible interpretation of this point has been discussed in terms of rearrangement in an intermediate possessing cationic oxygen.

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

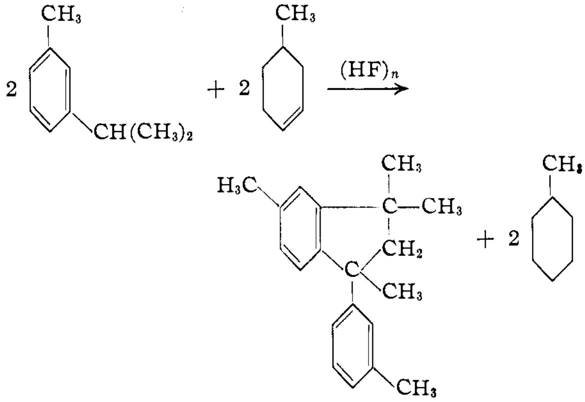
Hydrogen Transfer. V.[1] Reaction of *m*-Cymene and *o*-Cymene with Methylcyclohexene in the Presence of Hydrogen Fluoride

BY HERMAN PINES, D. R. STREHLAU[2] AND V. N. IPATIEFF

In previous studies of this series[3,4,5] it was shown that *p*-alkyl substituted toluenes reacted with 4-methylcyclohexene in the presence of either hydrogen fluoride or sulfuric acid to give mainly products resulting from hydrogen transfer.

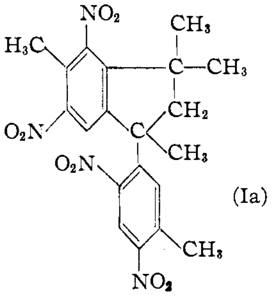
It was of interest to determine whether this type of reaction was limited only to the *p*-alkyl substituted toluenes; therefore *meta*- and *ortho*-cymene were prepared and treated with 4-methylcyclohexene at 0° in the presence of anhydrous hydrogen fluoride.

It was found that the reaction of *m*-cymene with methylcyclohexene also gave products resulting from hydrogen transfer. Of the methylcyclohexene charged, 26 mole per cent. was converted to methylcyclohexane, 7% to dimethyldicyclohexyl and 43% condensed with *m*-cymene to form an alkylated product probably 2-(1-methylcyclohexyl)-5-isopropyltoluene. Of the *m*-cymene reacted, 42 mole per cent. was isolated as the cycloalkylated product and 25% underwent a hydrogen transfer type reaction to form a compound whose elementary analysis corresponded to $C_{20}H_{24}$. In accordance with the mechanism proposed for the hydrogen transfer reactions described previously,[3,5] it was assumed that the $C_{20}H_{24}$ hydrocarbon corresponds to 1,3,3,5-tetramethyl-1-*m*-tolylindan (Compound I) formed according to the first equation shown.

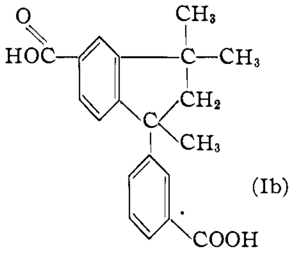


(I)

Compound I on nitration yielded a tetranitro derivative, melting at 202–203° and corresponding probably to 1,3,3,5-tetramethyl-1-(3-methyl-4,6-dinitrophenyl)-4,6-dinitroindan (Compound Ia).



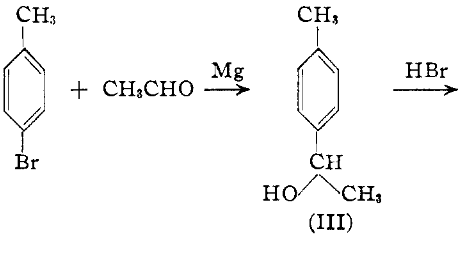
(Ia)



(Ib)

On oxidation with chromic anhydride in acetic acid, a dicarboxylic acid was obtained melting at 210° and corresponding to 1,3,3-trimethyl-1-(3-carboxylphenyl)-5 carboxyindan (Compound Ib). Compound I yielded, on destructive hydrogenation at 230° under pressure in the presence of a copper oxide–alumina catalyst, toluene and a bicyclic aromatic hydrocarbon corresponding to $C_{13}H_{18}$ which was believed to be 1,3,3,6-tetramethylindan (II). The reaction is similar to that reported previously.[3]

The bicyclic hydrocarbon obtained from the destructive hydrogenation was identical, according to its physical constants, solid derivatives and infrared absorption spectra with a synthetic sample of II prepared as shown



(III)

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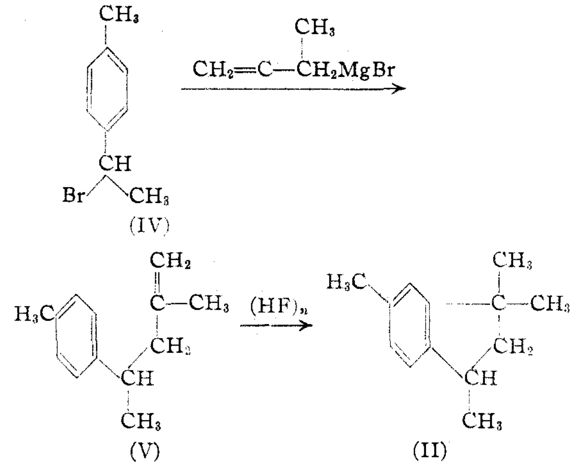
(1) For paper IV of this series see H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, **72**, 1463 (1950).

(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**, 3859 (1948).

(5) H. Pines, D. R. Strehlau and V. N. Ipatieff, *ibid.*, **71**, 3534 (1949).



Attempts to synthesize V by a Wurtz type coupling between IV and methylallylmagnesium chloride gave only 2,3-di-*p*-tolylbutane.

o-Cymene on treatment with 4-methylcyclohexene in the presence of hydrogen fluoride under the experimental conditions indicated for *m*-cymene, gave only methylcyclohexyl-*o*-cymene. No products resulting from hydrogen transfer were observed.

The *m*- and *o*-cymene used in this work were prepared from *m*- and *o*-tolylmagnesium bromide by a sequence involving reaction with acetone, dehydration and hydrogenation.

Experimental

I. **Synthesis of *m*-Cymene.**—(a) 2-*m*-Tolyl-2-propanol[6] was prepared by means of the Grignard reaction using 544 g. (3.18 moles) of *m*-bromotoluene, 77.8 g. (3.2 moles) of magnesium, 190 g. (3.5 moles) of acetone and a total of 2100 ml. of ether. The carbinol, amounting to 416 g. (85.5% yield), distilled at 98–100° (9 mm.), n^{20}D 1.5185.

(b) 2-*m*-Tolylpropene[7] was prepared by dehydrating the carbinol over activated alumina at 290°. The olefin distilled at 86–89° at 25 mm., n^{20}D 1.5335; yield 96%.

(c) *m*-Cymene: 2-*m*-tolylpropene (165 g.) dissolved in 150 ml. of *n*-pentane was hydrogenated at 55° in the presence of a nickel–kieselguhr catalyst at an initial hydrogen pressure of 110 atmospheres. The *m*-cymene formed (140 g., 96% yield) distilled at 174–176°. Redistillation over sodium metal through a 20-plate column gave a product, b. p. 172–173°, n^{20}D 1.4925.

II. **Reaction of *m*-Cymene with 4-Methylcyclohexene in the Presence of Hydrogen Fluoride.**—One hundred thirty-four grams (1 mole) of *m*-cymene and 48 g. (0.5 mole) of 4-methylcyclohexene reacted in the presence of hydrogen fluoride at 0° according to the procedure previously described.[3] The product resulting from the reaction weighed 160 g. It was fractionated on a 20-plate column to give 12.2 g. of methylcyclohexane, 64 g. of *m*-cymene, 3.5 g. of dimethyldicyclohexyl, 49 g. of 2-(1-methylcyclohexyl)-5-isopropyltoluene and 17.5 g. of 1,3,3,5-tetramethyl-1-*m*-tolylindan (I). The following data were observed for 2-(1-methylcyclohexyl)-5-isopropyltoluene, b. p. 120–121° at 4 mm., n^{20}D 1.5170; d^{20}_4 0.9213; *MR*D calcd. 74.9, obs. 75.5. *Anal.* Calcd. for $C_{16}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.92; H, 11.38. A **dinitro derivative** was prepared by treating 0.2 g. of the hydrocarbon with 3 ml. of a solution of 2 vol. 96% sulfuric acid and 1 vol. 72% nitric acid. Colorless needles were obtained from benzene–pentane solvent, m. p. 87–88°, probably 2-(1-methylcyclohexyl)-5-isopropyl-4,6-dinitrotoluene. *Anal.* Calcd. for $C_{17}H_{24}N_2O_4$: C, 63.80; H, 7.52; N, 8.75. Found: C, 63.89; H, 7.69; N, 8.56.

Oxidation of 1 g. of the hydrocarbon by refluxing with a solution of 10 g. of chromic anhydride in 30 ml. of glacial acetic acid, 30 ml. of water and 10 ml. of concentrated sulfuric acid for 24 hours gave a solid acid which after three crystallizations from dilute alcohol melted at 305–307°; neutral equivalent 130. *Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.75; H, 6.88. Found: C, 69.07; H, 6.79. The dibasic acid corresponds to 1-(1-methylcyclohexyl)-2,4-benzenedicarboxylic acid. The following data were observed for (I), b. p. 140–145° at 4 mm., n^{20}D 1.5535; d^{20}_4 0.9723; *MR*D calcd. 85.2, obs. 86.9. *Anal.* Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.68; H, 9.43. **Nitration** according to the procedure described above gave a tetranitro derivative. Pale yellow needles were obtained from an ethanol–chloroform solution, m. p. 202–203° (Compound Ia). *Anal.* Calcd. for $C_{20}H_{20}N_4O_8$: C, 54.05; H, 4.50; N, 12.61. Found: C, 53.70; H, 4.56; N, 12.8.

Oxidation of 1 g. of the hydrocarbon by refluxing with a solution of 7 g. of chromic anhydride in 30 ml. of glacial acetic acid, 30 ml. of water and 5 ml. of 96% sulfuric acid for six hours resulted in a solid acid which precipitated out when the solution was cooled and diluted. After crystallization from dilute alcohol it melted at 210°. Neutral equivalent was 160. *Anal.* Calcd. for $C_{20}H_{20}O_4$: C, 74.08; H, 6.17. Found: C, 73.61; H, 6.42. The dibasic acid corresponds to compound Ib.

Destructive Hydrogenation.—Ten grams of fraction 5 was destructively hydrogenated in the presence of 2 g. of a copper oxide–alumina catalyst (67% CuO, 33% Al_2O_3). At 230° for six hours, the maximum pressure at 230° was 240 atm. The gases were collected and analyzed; they consisted of 99% hydrogen. Fractionation of the reaction products resulted in the isolation of 4.1 g. of unreacted starting material, 1.5 g. of toluene and 2.6 g. of a hydrocarbon (b. p. 95–99 at 15 mm., n^{20}D 1.5080, d^{20}_4 0.9065) corresponding to 1,3,3,5-tetramethylindan. *Anal.* Calcd. for $C_{13}H_{18}$: C, 89.66; H, 10.34; *MR*D, 56.43. Found: C, 89.87; H, 10.19; *MR*D, obs. 57.26.

Acetylation of the latter according to the method described previously[3,4] gave a liquid ketone the 2,4-dinitrophenylhydrazone of which melted at 170–171° and showed no depression in m. p. when mixed with the corresponding derivative of the synthetic sample of 1,3,3,5-tetramethylindan.

III. **Synthesis of 1,3,3,5-Tetramethylindan (II).** (a) **Methallyl Bromide.**[8]—One mole (271 g.) of freshly distilled phosphorus tribromide was added dropwise to 3 moles of redistilled methallyl alcohol at 5°. After being allowed to stand overnight at room temperature the batch was distilled from a Claisen flask at 205 mm. The distillate, collected at 60–65°, was shaken with anhydrous potassium carbonate to remove dissolved hydrogen bromide and redistilled at atmospheric pressure through a 10-plate column. One hundred sixty-four grams (42% yield) distilled at 92.5–93°; n^{20}D 1.4698.

(b) 1-*p*-Tolylethanol (III)[9] was prepared by means of the Grignard reaction using 105 g. (0.61 mole) of *p*-bromotoluene, 14.6 g. (0.6 mole) of acetaldehyde, and 14.6 g. (0.6 mole) of magnesium. The carbinol (60 g.) distilled at 105–106° at 15 mm., n^{20}D 1.5245; yield 74%.

(c) **1-Bromo-1-*p*-tolylethane (IV).**—The replacement of the hydroxyl group of (III) by a bromine atom was accomplished according to the procedure of Conant and Blatt[10] with anhydrous hydrogen bromide at 0–5°. A 79% yield of the desired product (b. p. 94–95° (10 mm.), n^{20}D 1.5560) was realized.

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(6) F. Eisenlohr and L. Schultz, *Ber.*, **57**, 1818 (1924).

(7) W. H. Perkins and G. Tattersall, *J. Chem. Soc.*, **87**, 1106 (1905).

(8) A. Wohl, *Bull. soc. chim.*, [4] **37**, 712 (1925).

(9) A. K. v. Auwers and H. Kolligs, *Ber.*, **55**, 42 (1922).

(10) J. B. Conant and A. H. Blatt, THIS JOURNAL, **50**, 544 (1928).

(d) **2-Methyl-4-*p*-tolylpentene** (V) was prepared by condensing methallylmagnesium bromide and 1-bromo-1-*p*-tolylethane. Methallylmagnesium bromide was prepared by the procedure of Gilman[11] using 87.5 g. (3.6 mole) of magnesium, 81 g. (0.6 mole) of methallyl bromide and a total of 600 ml. of ether. The Grignard solution was pumped off the excess magnesium through a glass wool filter by means of nitrogen pressure into a dry reaction flask. A solution of 84 g. (0.42 mole) of 1-bromo-1-*p*-tolylethane in 100 ml. of ether was added dropwise in the course of 3.5 hours. Steady reflux was maintained by the heat of reaction; after the reaction was completed the product was cooled and poured over ice. Dilute hydrochloric acid was added to dissolve the small amount of precipitate formed. The organic layer was washed with alkali, and fractionated at reduced pressure. The main fraction, comprising 43 g. (60% yield) distilled at 121–122° at 30 mm.; n^{20}D 1.5038; d^{20}_4 0.8785; MR_D calcd. 58.17, obs. 58.66. *Anal.* Calcd. for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.31; H, 10.40.

(e) **1,3,3,5-Tetramethylindan** (II).—A solution of 20 g. of (V) in 20 ml. of cyclohexane was added dropwise with stirring to 25 g. of anhydrous hydrogen fluoride at 0°. Stirring was continued for 30 minutes. The batch was then poured onto ice. The organic layer was separated, washed with 5% potassium hydroxide and water and dried. Distillation yielded 17 g. of the cyclized product boiling at 97% (12 mm.); n^{20}D 1.5086, d^{20}_4 0.9022; MR_D calcd. 56.43, obs. 57.6. *Anal.* Calcd. for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.29; H, 10.50. Acetylation gave a product whose 2,4-dinitrophenylhydrazone melted at 170–171°. *Anal.* Calcd. for $C_{21}H_{24}N_4O_4$: C, 63.64; H, 6.11; N, 14.14. Found: C, 62.92; H, 5.888; N, 14.37.

(f) **2,3-Di-*p*-tolylbutane.**—Preliminary attempts to synthesize 2-methyl-4-*p*-tolylpentene-1 by a Wurtz type coupling between the Grignard compound of 1-bromo-1-*p*-tolylethane and methallyl chloride resulted in failure. The sole product resulting corresponded to 2,3-di-*p*-tolylbutane, b. p. 149° (5 mm.) m. p. 120–120.5° formed from the condensation of 2 molecules of 1-bromo-1-*p*-tolylethane. *Anal.* Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.80; H, 9.45.

IV. Synthesis of *o*-Cymene.—(a) 2-*o*-Tolylpropene[12] was prepared by means of the Grignard reaction, using 171 g. (1.0 mole) of *o*-bromotoluene, 24.3 g. (1.1 mole) of magnesium, 60 g. (1.1 mole) of acetone and 600 ml. of ether. The tertiary alcohol was not isolated. The crude product was dissolved in 250 ml. of toluene and refluxed for two hours in the presence of 10 g. of oxalic acid to effect the dehydration; water was taken off as formed, and washed free of oxalic acid with 5% sodium carbonate. Eighty-seven grams of olefin, b. p. 120–122° (110 mm.), was obtained. Redistillation through a 20-plate column at atmospheric pressure gave 60% yield (78.5 g.) of the olefin boiling at 168–169°; n^{20}D 1.5149.

(b) **o-Cymene.**—75 g. of 2-*o*-tolylpropene dissolved in 100 ml. of *n*-pentane was hydrogenated at 50° under 100 atm. of initial hydrogen pressure in the presence of 7 g. of nickel–kieselguhr. The *o*-cymene formed in 98% yield (73 g.) was distilled over sodium; b. p. 177–177.5°; n^{20}D 1.5002.

V. Reaction of *o*-Cymene with 4-Methylcyclohexene in the Presence of Hydrogen Fluoride.—Sixty-seven grams (0.5 mole) of *o*-cymene and 24 g. (0.25 mole) of 4-methylcyclohexene were contacted in the presence of 50 g. of anhydrous hydrogen fluoride at 0° and worked up in the usual way. The product from the reaction weighed 81 g. Distillation through a 20-plate column gave 32 g. of *o*-cymene, 43 g. of a hydrocarbon corresponding to 2-isopropyl-4- or 5-(1-methylcyclohexyl)-toluene, b. p. 113–115° at 1 mm., n^{20}D 1.5230, d^{20}_4 0.9318. *Anal.* Calcd. for $C_{17}H_{26}$: C, 88.63; H, 11.37; MR_D, 74.9. Found: C, 88.86; H, 11.19; MR_D, 75.4.

Acetylation by the usual procedure gave a liquid ketone from which the 2,4-dinitrophenylhydrazone was prepared. Orange needles, m. p. 185–187°, were obtained from a chloroform–ethanol solution. In view of the observation that a tertiary carbon group in para position to an alkyl group on a benzene ring was susceptible to replacement,[1] it was assumed that the dinitrophenylhydrazone was a derivative of 2-isopropyl-4- or 5-acetyltoluene. The analysis was in agreement. *Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.66; N, 15.73. Found: C, 60.52; H, 5.44; N, 15.41.

Summary

m-Cymene on treatment with methylcyclohexene in the presence of hydrogen fluoride underwent a hydrogen transfer and a cycloalkylation reaction; the latter predominated. 1,3,3,5-Tetramethyl 1-*m*-tolylindan was produced through the hydrogen transfer reaction.

When *o*-cymene reacted with methylcyclohexene in the presence of hydrogen fluoride no hydrogen transfer was observed, only cycloalkylation occurred.

The following new compounds and their derivatives were prepared: 1,3,3,5-tetramethylindan, 2-methyl-4-*p*-tolylpentene, 2,3-di-*p*-tolylbutane, 3-isopropyl-4 or 6-(1-methylcyclohexyl)-toluene, 2-isopropyl-4 or 5-(1-methylcyclohexyl)-toluene, 1,3,3,5-tetramethyl-1-*m*-tolylindan.

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[11] H. Gilman and C. McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[12] P. Sabatier and M. Murat, *Ann. chim.*, [9] **4**, 253 (1915).