

(*c*, 1.2), and its melting point and mixed melting point of 154–155°.

The mother liquor from the sedoheptulosan still would not crystallize when concentrated and inoculated with D-mannoheptulose. The 0.38 g. of sirup was acetylated with acetic anhydride and pyridine, to yield 0.57 g. of sirupy acetate. Using the technique of flowing chromatography which we had already found could be applied to the acetylated mother liquor of the *A. suboxydans* experiment, we dissolved the 570 mg. of this acetate in ether, poured it on a column containing 10 g. of alumina, and eluted it exhaustively with absolute ether to remove 363 mg. of levorotatory material. Further elution with mixtures of ether and ethyl acetate produced 152 mg., in five fractions, all of which were dextrorotatory, but none could be induced to crystallize when inoculated with hexaacetyl- α -D-mannoheptulose as did certain of the corresponding fractions from the *A. suboxydans* experiment. In this case the dextrorotatory material presumably consists of acetylated sedoheptulose which has not yet been obtained in crystalline form. The combined five fractions were deacetylated,

but the small amount of sirup still would not crystallize when inoculated with mannoheptulose.

Summary

The action of *Acetobacter suboxydans* upon volemitol proceeds readily and nearly quantitatively to produce both D-mannoheptulose and D-althroheptulose (=sedoheptulose). This result is in agreement with the specificity rule of Hann, Tilden and Hudson for the action of *A. suboxydans*.

The action of *Acetobacter xylinum* upon volemitol is slow and incomplete; only one end of the molecule appears to be oxidized, and the sirupy ketose, which was first obtained by Bertrand and named "volemulose," has been identified as D-althroheptulose (=sedoheptulose).

BETHESDA, MARYLAND

RECEIVED MAY 31, 1949

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

Hydrogen Transfer. III.¹ Reaction of *p*-Ethyltoluene and *p*-Propyltoluene with Methylcyclohexene. Synthesis of Diarylalkanes

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

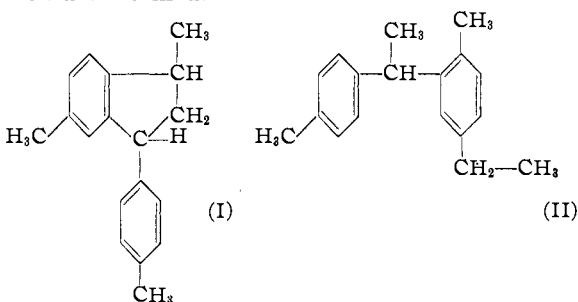
In a previous paper it has been shown that an abnormal reaction occurs when *p*-cymene is contacted with methylcyclohexene in the presence of either sulfuric acid or hydrogen fluoride.³ Instead of the expected cycloalkylation of *p*-cymene, a hydrogen transfer was the main reaction; the methylcyclohexene acted as a hydrogen acceptor, forming methylcyclohexane, while *p*-cymene acted as a hydrogen donor yielding as the main product 1,3,3,6-tetramethyl-1-*p*-tolylindan.

It was of interest to determine whether a para disubstituted benzene ring having an alkyl group containing more than one hydrogen atom on the carbon attached to the benzene ring would also yield products resulting from a hydrogen transfer reaction. For that reason *p*-xylene, *p*-ethyl- and *p*-propyltoluene reacted with methylcyclohexene in the presence of hydrogen fluoride and/or sulfuric acid.

p-Xylene, on reacting with methylcyclohexene in the presence of hydrogen fluoride, yielded only methylcyclohexyl-*p*-xylene. The formation of methylcyclohexane which serves as an indicator of a hydrogen transfer reaction was not observed.

Hydrogen transfer was the main reaction when *p*-ethyltoluene and methylcyclohexene in the molar ratio of two to one reacted in the presence of hydrogen fluoride. Forty-five per cent. of the methylcyclohexene was converted to methylcyclohexane and 20% to a compound corresponding to dimethylidicyclohexyl. Of the converted *p*-ethyl-

toluene 65% underwent a hydrogen transfer reaction to form a compound (Y) containing 18 carbon atoms boiling at 157° (6 mm.), n_D^{20} 1.5540; and 23% underwent condensation with methylcyclohexene, yielding probably 2-(1-methylcyclohexyl)-4-ethyltoluene^{3a}; and remainder of the reacted *p*-ethyltoluene corresponded to a condensation product of methylcyclohexene with compound (Y). It was thought at first that *p*-ethyltoluene reacted with methylcyclohexene in a manner similar to the reaction of *p*-cymene and methylcyclohexene, and that 3,6-dimethyl-1-*p*-tolylindan (I), would be formed.



It was found however that the physical constants, solid derivatives and infrared absorption spectra (Graph I) of synthetic (I) did not correspond to the compound (Y) (Graph II).

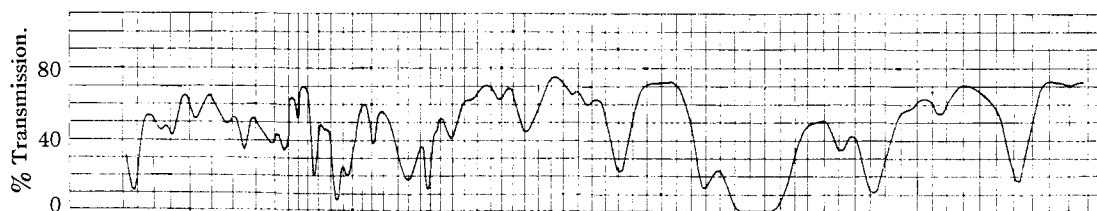
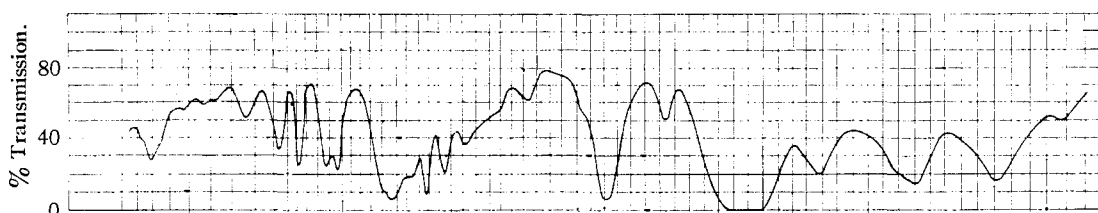
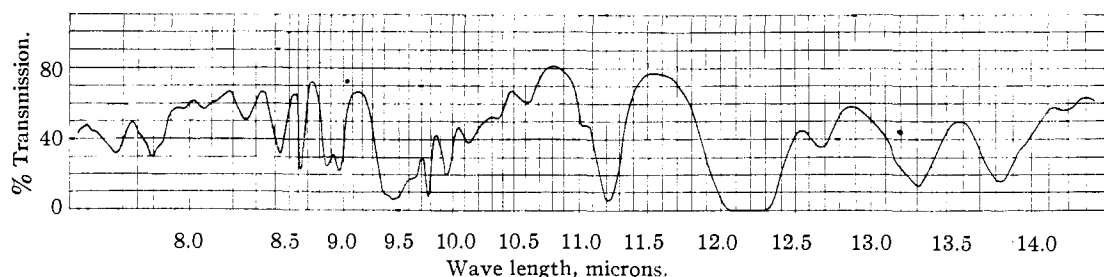
In line with the mechanism proposed for the hydrogen transfer reactions described previously,¹ it

(1) For paper II of this series see H. Pines, A. Weizmann and V. N. Ipatieff, *THIS JOURNAL*, **70**, 3859 (1948).

(2) Universal Oil Products Company Predoctorate Fellow (1945–1947).

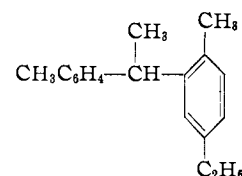
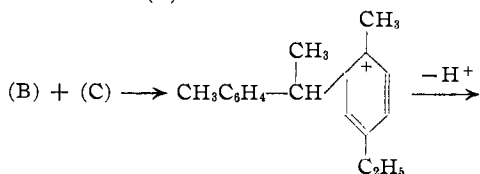
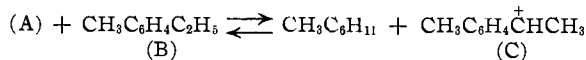
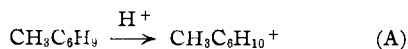
(3) V. N. Ipatieff, H. Pines and R. C. Olberg, *THIS JOURNAL*, **70**, 2123 (1948)

(3a) This conclusion is based on the observation that during the reaction of *p*-cymene with cyclohexene the carbon atom ortho to the methyl group is substituted¹ and that the reaction between benzene and isomeric methylcyclohexenes, including 4-methylcyclohexene results in the formation of 1-methyl-1-phenylcyclohexane (V. N. Ipatieff, E. E. Meisinger and H. Pines, unpublished work).

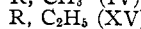
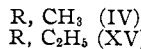
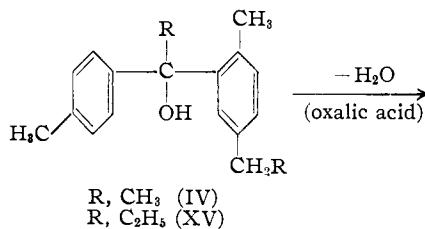
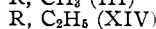
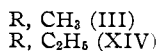
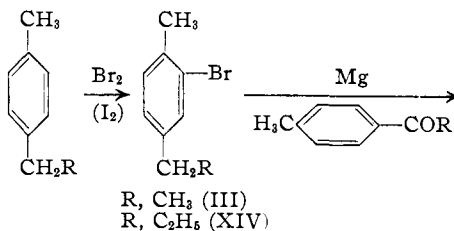
Fig. 1.—Synthetic 3,6-dimethyl-1-*p*-tolylindan.Fig. 2.—1-*p*-Tolyl-1-(2-methyl-ethylphenyl)-ethane obtained from hydrogen transfer reaction.Fig. 3.—Synthetic 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane.

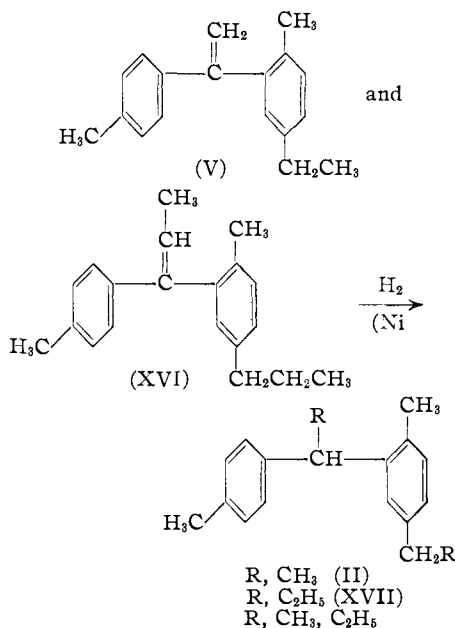
was reasoned that the reaction between *p*-ethyltoluene and methylcyclohexene might have yielded 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane (II). Compound II was synthesized, and it was found to be identical with the compound (Y) obtained from the hydrogen transfer reaction (Graphs I and III). Sulfuric acid used as the catalyst caused a similar type of reaction to occur as did hydrogen fluoride; 60% of the olefins used was converted to methylcyclohexane. The higher boiling hydrocarbons obtained from the reaction catalyzed by sulfuric acid were identical with the corresponding fraction obtained from the reaction in the presence of hydrogen fluoride.

To explain these findings, it is assumed that the proton from sulfuric acid or hydrogen fluoride adds to the methylcyclohexene to form a carbenium ion which then acts with *p*-ethyltoluene

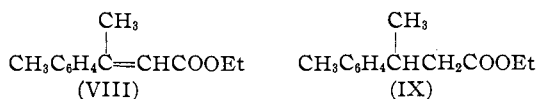


The synthesis of compound II and of a similar compound XVII was carried out according to the equations

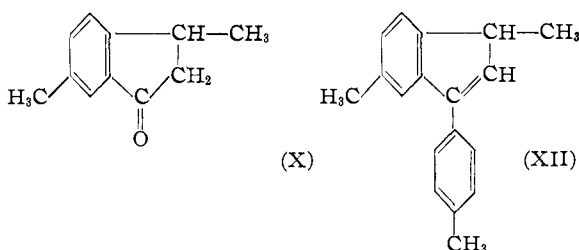




To synthesize (I) these steps were followed: *p*-methylacetophenone and ethyl bromoacetate were condensed in a Reformatsky reaction into ethyl 3-*p*-tolyl-3-hydroxybutyrate (VII); after dehydration of this compound to VIII, hydrogenation to IX and ring closure to 3,6-dimethyl-1-indanone



(X) using hydrogen fluoride, the indanone was treated with *p*-tolylmagnesium bromide; the intermediary tertiary alcohol (XI) was not isolated but was dehydrated to the substituted indene (XII) which was hydrogenated to (I).



p-Propyltoluene on treatment with 4-methylcyclohexene in the presence of hydrogen fluoride under experimental conditions indicated for *p*-ethyltoluene, yielded also as main reaction products compounds resulting from a hydrogen transfer reaction. Of the methylcyclohexene reacted, 40% was converted to methylcyclohexane and 15% to a compound corresponding to a dimethyldicyclohexyl and only 24% was condensed with *p*-propyltoluene to form methylcyclohexyl-*p*-propyltoluene. Of the *p*-propyltoluene reacted, 50% was converted to 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane; the structure of this compound

was proved by comparing its infrared spectra (Graph IV) with that of the corresponding compound prepared by synthesis (Graph V).

The synthesis of 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane was made according to the outline presented above.

The *p*-ethyl- and *p*-propyltoluene used in this reaction were prepared by hydrogenation of the appropriate ketones.⁴

In attempting to prepare acetyl derivatives of compounds II and XVII which could be converted to solid 2,4-dinitrophenylhydrazones, it was found that acetylation causes a split at the aliphatic bridge at the para position of the tolyl and gives rise to *p*-methylacetophenone and tarry products from either II or XVII.

Experimental Part

I. Synthesis of *p*-Ethyltoluene

(a) *p*-Acetyltoluene (VI).—This compound was prepared from 275 g. (3.5 moles) of acetyl chloride, 276 g. (3 moles) toluene and 467 g. (3.5 moles) of aluminum chloride in 1800 ml. of carbon disulfide; yield 88%, b. p. 108° (18 mm.), n_D^{20} 1.5348. The oxime of this ketone melted at 87–88°.⁵

(b) *p*-Ethyltoluene.—*p*-Acetyltoluene was hydrogenated under 100 atmospheres of initial hydrogen pressure and at 180° in the presence of a copper oxide-alumina catalyst⁴ (94% CuO, 6% Al₂O₃). The *p*-ethyltoluene which was obtained in a yield of 95% distilled at 161–162°, n_D^{20} 1.4943.⁶

II. Reaction of *p*-Ethyltoluene with 4-Methylcyclohexene in the Presence of Hydrogen Fluoride

The reaction was carried out according to a procedure described previously.³ The following reagents were used: 240 g. (2 moles) of *p*-ethyltoluene, 96 g. (1 mole) of 4-methylcyclohexene and 250 g. of hydrogen fluoride. The hydrocarbon, 310 g. obtained from this reaction, was distilled through a 20–25 plate column at a reflux ratio of 10 to 1 and the following fractions were separated: (1) b. p. 102° (752 mm.), n_D^{20} 1.4250, 43 g. (methylcyclohexane); (2) b. p. 160–161° (752 mm.), n_D^{20} 1.4944, 99 g. (*p*-ethyltoluene); (3) b. p. 96–98° (5 mm.), n_D^{20} 1.4860, 19 g.; (4) b. p. 114–115° (4 mm.), n_D^{20} 1.5310, 21 g.; (5) b. p. 142–143° (4 mm.), n_D^{20} 1.5560, 100 g.; (6) b. p. 150–230° (4 mm.), n_D^{20} 1.5505, 16 g.; (7) residue 10 g.

Fraction 3 was stable toward a nitrating mixture; it corresponds to dimethyldicyclohexyl, d_4^{20} 0.8858; MR_D calcd. 62.4, obsd. 62.8.

Anal. Calcd. for C₁₄H₂₆: C, 86.51; H, 13.49. Found: C, 86.23; H, 13.17.

Fraction 4 corresponds to a (methylcyclohexyl)-*p*-ethyltoluene, d_4^{20} 0.9478; MR_D calcd. 70.3; obsd. 70.5.

Anal. Calcd. for C₁₆H₂₄: C, 88.82; H, 11.18. Found: C, 88.91; H, 10.70.

Acetyl derivative was prepared according to the method described previously.¹ The 2,4-dinitrophenylhydrazone of the ketone melted at 179–181°.

Anal. Calcd. for C₂₄H₃₀N₄O₄: C, 65.72; H, 6.57; N, 12.77. Found: C, 65.75; H, 6.42; N, 12.99.

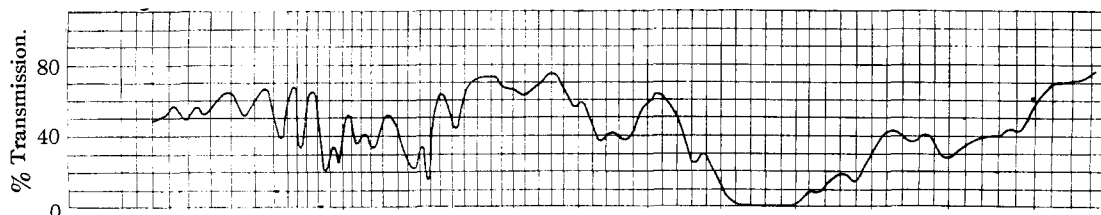
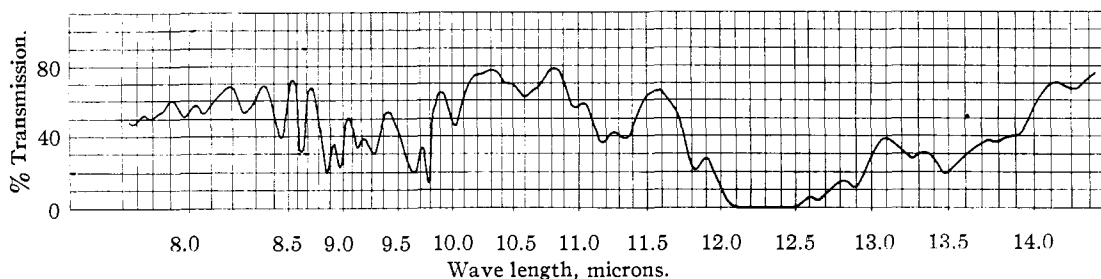
Fraction 5 corresponds to 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane, d_4^{20} 0.9617; MR_D calcd. 78.1, obsd. 79.5.

Anal. Calcd. for C₁₈H₂₂: C, 90.75; H, 9.25. Found: C, 91.23; H, 9.19.

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

(5) O. Widman and J. A. Bladin, *Ber.*, **19**, 587 (1886).

(6) Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corporation, New York, N. Y., 1946, p. 84.

Fig. 4.—1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-propane obtained from hydrogen transfer reaction.Fig. 5.—Synthetic 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane.

Infrared absorption spectra are given in Graph II.

Nitro Derivative.—Nitration with a nitrating mixture composed of 2 volumes of 96% sulfuric acid and 1 volume of 72% nitric acid gave a tetranitro derivative, m. p. 160–163°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: C, 51.67; H, 4.36; N, 13.46. Found: C, 51.80; H, 4.25; N, 13.65.

Acetylation followed by the preparation of the 2,4-dinitrophenylhydrazone resulted in a small yield of solid product, m. p. 263–265°. A mixed melting point with the 2,4-dinitrophenylhydrazone of an authentic sample of *p*-methylacetophenone showed no depression.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 17.9. Found: N, 17.5.

III. Reaction of *p*-Ethyltoluene with 4-Methylcyclohexene in the Presence of Sulfuric Acid

The reaction was made according to the procedure described previously³; 48 g. (0.4 mole) of *p*-ethyltoluene, 20 g. (0.2 mole) of 4-methylcyclohexene and 35 g. of 96% sulfuric acid were used. Fifty-seven grams of product was obtained from which the following cuts were separated: (1) b. p. 102° (751 mm.), n_D^{20} 1.4230, 11.8 g., methylcyclohexane; (2) b. p. 159–160° (751 mm.), n_D^{20} 1.4943, 16.7 g., *p*-ethyltoluene; (3) b. p. 114–115° (4 mm.), n_D^{20} 1.5330, 2-(1-methylcyclohexyl)-4-ethyltoluene; (4) b. p. 136–137° (3 mm.), n_D^{20} 1.5562, 11 g. (compound II); (5) residue 10 g.

Cut 3 was identified by the dinitrophenylhydrazone of the acetyl derivative and cut 4 by the infrared absorption spectra and nitro derivative.

IV. Synthesis of 1-*p*-Tolyl-1-(2-methyl-5-ethylphenyl)-ethane

(a) 1-Bromo-2-methyl-5-ethylbenzene (III).—Prepared by the bromination of *p*-ethyltoluene at 0° with bromine in the presence of a small amount of iodine,^{7,8} 49 g. of the bromo-compound (83% yield), b. p. 99–101° (14 mm.), n_D^{20} 1.5440, was realized from 40 g. of the hydrocarbon.

Compound III on oxidation with a solution of chromic acid, sulfuric acid and water yielded 3-bromo-*p*-toluic acid melting at 203–204°; this agrees with the published data.⁷

(b) 1-*p*-Tolyl-1-(2-methyl-5-ethylphenyl)-ethanol (IV).—This was prepared by the Grignard method using 40 g. of 2-methyl-5-ethylbromobenzene, 4.8 g. of magnesium

and 26.8 g. of *p*-methylacetophenone. The carbinol which was obtained and which amounted to 20.6 g. boiled at 162–164° (5 mm.), (64% yield), n_D^{20} 1.5655, d_4^{20} 1.0307; MR_D calcd. 79.6, obsd. 79.8.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.04; H, 8.66. Found: C, 84.88; H, 8.43.

(c) 1-*p*-Tolyl-1-(2-methyl-5-ethylphenyl)-ethane (V).—A solution of 13 g. of compound (IV) in 40 cc. of benzene was refluxed for one hour with 2 g. of oxalic acid to effect the dehydration. The olefins, 12 g., had the following physical constants: b. p. 146–146.5° (4 mm.), n_D^{20} 1.5770, d_4^{20} 0.9745; MR_D calcd. 77.7, obsd. 80.2.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.50; H, 8.50. Found: C, 91.20; H, 8.52.

(d) 1-*p*-Tolyl-1-(2-methyl-5-ethylphenyl)-ethane (II) which was prepared by the hydrogenation of compound V in the presence of a nickel-kieselguhr catalyst at 100 atm. and 45° distilled at 148–150° (4 mm.), n_D^{20} 1.5540, d_4^{20} 0.9625; MR_D calcd. 78.1, obsd. 79.2. Infrared absorption spectra are given in Graph III. A tetranitro derivative, m. p. 160–162° was obtained by treating compound II with a nitrating mixture consisting of 2 volumes of 96% sulfuric acid and 1 volume of 72% nitric acid.

Anal. Calcd. for $C_{18}H_{18}N_4O_8$: C, 51.67; H, 4.36, N, 13.46. Found: C, 51.80; H, 4.31; N, 13.55.

The nitro compound did not show any depression in melting point when mixed with the corresponding nitro compound obtained from the hydrogen transfer reaction.

VI. Synthesis of 3,6-Dimethyl-1-*p*-tolylindan

(a) 3-*p*-Tolyl-3-hydroxybutyrate (VII) was prepared in 61% yield from 84 g. of *p*-methylacetophenone according to the procedure of Lindenbaum.⁹ Compound VII thus prepared was colorless, boiling at 116–117° (4 mm.), n_D^{20} 1.5000, d_4^{20} 0.9381; the same compound was reported⁷ as being a light yellow oil, boiling at 156–157° (16 mm.).

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 70.22; H, 8.17. Found: C, 69.82; H, 7.91.

(b) Ethyl β -*p*-Tolylcrotonate (VIII).—Sixty-seven grams of compound (VII) was dehydrated in the presence of 12 g. of oxalic acid and 150 ml. of benzene. The following main two fractions were separated: (1) b. p. 116.5–120° (3–4 mm.), 39.6 g., n_D^{20} 1.5335; (2) b. p. 120–125° (3–4 mm.), 15.8 g., n_D^{20} 1.5455. The yield of VIII amounted to 89%. The dehydrated ester corresponded to a mixture of the two expected isomers.⁹

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

(8) G. Defren, *ibid.*, **23**, 2651 (1895).

(9) S. Lindenbaum, *Berg-techn.*, **50**, 1270 (1917).

(c) *β-p*-Tolylbutyric Acid (IX).—Compound VIII, 55 g. was hydrogenated in the presence of 69 g. of *n*-pentane and 6 g. of a nickel-kieselguhr catalyst at 48° and under 115 atm. of hydrogen pressure.

The saturated ester was saponified by heating it at a reflux temperature with a solution of alcoholic potassium hydroxide. An 82% yield of the acid was obtained, m. p. 91–92°. It yielded the known *p*-toluidide¹⁰ m. p. 112–113°.

(d) 3,6-Dimethylindanone (X).—Twenty grams of compound IX was stirred into 200 g. of anhydrous hydrogen fluoride in a copper beaker at 0°. After standing two hours at 0° the hydrogen fluoride was evaporated and the remaining oil was washed with 2% potassium hydroxide. Distillation yielded 15 g. (88.5%) of the cyclic ketone b. p. at 100–102° (5 mm.), n_D^{20} 1.5518. The semicarbazone melted at 225° with decomposition.¹¹

The following data on the ketone were not previously published: d_4^{20} , 1.0454; dinitrophenylhydrazone m. p. 271–273°.

Anal. Calcd. for $C_{17}H_{17}O_4N_4$: C, 59.82; H, 4.99; N, 16.42. Found: C, 59.80; H, 4.92; N, 16.20.

A study of the various methods for cyclization was made with the following results:

Cyclization agent	Yield of ketone, %
Hydrogen fluoride	88.5 (Acid was used directly)
Aluminum chloride	67.0 (Acid chloride was used)
Stannic chloride	48.0 (Acid chloride was used)

(e) 3,6-Dimethyl-1-*p*-tolylindene (XII).—3,6-Dimethyl-1-*p*-tolyl-1-indanol (XI) was prepared by the Grignard reaction using 2.68 g. of magnesium, 18.8 g. (0.11 mole) of *p*-bromotoluene and 13.0 g. (0.1 mole) of the 3,6-dimethyl-1-indanone (X). Because tertiary alcohol tends to dehydrate, it could not be isolated; 12.6 g. of the olefin (54% yield) was obtained distilling at 157° (5 mm.), n_D^{20} 1.6022, d_4^{20} 1.0307; MR_D calcd. 74.7, obsd. 74.4.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.31; H, 7.67. Found: C, 91.75; H, 7.97.

(f) 3,6-Dimethyl-1-*p*-tolylindan (I).—Twelve grams of the compound XII was hydrogenated under pressure in the presence of a nickel-kieselguhr catalyst at 50°. Distillation gave a colorless fluorescent oil boiling at 144–146° (5 mm.), n_D^{20} 1.5700, d_4^{20} 0.9998; MR_D calcd. 75.2, obsd. 77.4.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.53; H, 8.47. Found: C, 91.37; H, 8.46.

The infrared absorption spectra of this compound are given in Graph I.

VII. Synthesis of *p*-Propyltoluene (XIII)

(a) *p*-Methylpropiofenone.—This ketone boiled at 114.5° (18 mm.), n_D^{20} 1.5287. The semicarbazone of this ketone melted at 187–188° and the oxime melted at 87.5–88° which is identical with the data given in the literature.^{12,13} A dinitrophenylhydrazone (not previously reported) melted at 200–202°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: N, 17.1. Found: N, 17.0.

(b) *p*-Propyltoluene, which was obtained by hydrogenation⁴ of *p*-methylpropiofenone distilled at 179–180° (750 mm.), n_D^{20} 1.4934, d_4^{20} 0.8588; the physical constants agree with those reported in the literature.^{13a} A sulfonamide derivative¹⁴ (not previously reported) melted at 79–80°.

Anal. Calcd. for $C_{10}H_{16}O_2NS$: C, 56.34; H, 7.04; N, 6.57. Found: C, 56.53; H, 7.14; N, 6.48.

(10) H. Rupe and Fr. Wiederkehr, *Helv. Chim. Acta*, **7**, 654 (1924).

(11) Th. Wagner-Jauregg and H. Hippchen, *Ber.*, **76B**, 694 (1943).

(12) A. Klage, *Berg-techn.*, **35**, 2245 (1902).

(13) K. Auwers, *Ann.*, **408**, 243 (1915).

(13a) Reference 6, p. 99.

(14) E. H. Huntress and J. S. Autenrieth, *This Journal*, **63**, 3446 (1941).

VIII. Reaction of *n*-Propyltoluene with 4-Methylcyclohexene in the Presence of Hydrogen Fluoride

The reaction was carried out as described above, using the following reagents: *p*-propyltoluene, 240 g. (1.86 moles), 89 g. (0.93 mole) of 4-methylcyclohexene and 250 g. of hydrogen fluoride. The product resulting from this reaction weighed 304 g. The following fractions were separated by distillation: (1) b. p. 102° (750 mm.), n_D^{20} 1.4260, 40.5 g., methylcyclohexane; (2) b. p. 179–180° (750 mm.), n_D^{20} 1.4930, 109 g., *n*-propyltoluene; (3) b. p. 84–87° (3 mm.), n_D^{20} 1.4833, 13 g.; (4) b. p. 116–120° (3 mm.), n_D^{20} 1.5300, 34 g.; (5) b. p. 151–153° (3 mm.), n_D^{20} 1.5450, 86 g.; (6) b. p. 155–180° (3 mm.), n_D^{20} 1.5418, 10.0 g.; (7) residue 9.6 g.

Fraction 3 corresponds to a dimethyldicyclohexyl; it was stable toward a nitrating mixture consisting of 2 volumes of 96% sulfuric acid and 1 volume of 72% nitric acid; d_4^{20} 0.8850; MR_D calcd. 62.4, obsd., 62.6.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.19; H, 13.13.

Fraction 4 corresponds to 2-(1-methylcyclohexyl)-4-propyltoluene d_4^{20} 0.9502; MR_D calcd. 74.9; obsd. 74.8.

Anal. Calcd. for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 89.12; H, 10.90.

The 2,4-dinitrophenylhydrazone of the acetyl derivative melted at 230–233°.

Anal. Calcd. for $C_{25}H_{32}N_4O_4$: C, 66.30; H, 7.13; N, 12.38. Found: C, 66.35; H, 7.05; N, 12.50.

Fraction 5 corresponds to 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane, d_4^{20} 0.9478; MR_D calcd. 89.1, obsd. 88.7.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.31; H, 9.93.

The infrared absorption spectra are given in Graph IV.

Nitration yielded a gummy product which could not be crystallized.

Acetylation followed by treatment with 2,4-dinitrophenylhydrazone gave a solid derivative, m. p. 263–265°. A mixed melting point with the dinitrophenylhydrazone of synthetic *p*-methylacetophenone showed no depression.

Anal. Calcd. for $C_{15}H_{14}N_4O_4$: C, 57.32; H, 4.46; N, 17.83. Found: C, 57.50; H, 4.89; N, 17.40.

IX. Reaction of *n*-Propyltoluene with 4-Methylcyclohexene in the Presence of Sulfuric Acid

p-Propyltoluene, 26.8 g. (0.2 mole), 4-methylcyclohexene, 10 g. (0.1 mole) and 10 g. of 96% sulfuric acid were used for the reaction. The following cuts were separated from 33.6 g. of the hydrocarbon layer: (1) b. p. 103° (750 mm.), n_D^{20} 1.4215, 3.6 g.; (2) b. p. 179° (750 mm.), n_D^{20} 1.4938, 15.8 g.; (3) b. p. 122–129° (5 mm.), n_D^{20} 1.5318, 6.5 g.; (4) b. p. 144–150° (5 mm.), n_D^{20} 1.5440, 4.2 g.; (5) residue 2 g.

The distillation data and the physical constants show that the results obtained from sulfuric acid catalyzed reaction are comparable to the hydrogen fluoride catalyzed reaction except that no dimethyldicyclohexyl fraction is detectable and more cycloalkylation seems to occur.

X. Synthesis of 1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-propane

(a) 1-Bromo-2-methyl-5-propylbenzene (XIV).—The same procedure was used as for bromination of *p*-ethyltoluene. Forty-eight grams (95% yield) of compound XIV was obtained (not previously reported), boiling at 119–120° (20 mm.), n_D^{20} 1.5388, d_4^{20} 1.2470; MR_D calcd. 52.4, obsd. 53.5.

Anal. Calcd. for $C_{10}H_{12}Br$: Br, 37.52. Found: Br, 37.48.

The position of the entering bromine atom was proved to be ortho to the methyl group by oxidation with dilute nitric acid to 3-bromo-*p*-toluic acid, m. p. 203–204°, which agrees with the data reported.⁷

(b) 1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-1-propanol (XV).—Prepared by means of a Grignard reaction using

4.1 g. of magnesium, 40 g. of the bromide XIV and 28 g. of *p*-propionyltoluene. Distillation gave 26.2 g. of the tertiary alcohol boiling at 160–163° (3 mm.), n_D^{20} 1.5540, d_4^{20} 1.0025; MR_D calcd. 88.9, obsd. 90.2.

Anal. Calcd. for $C_{20}H_{26}O$: C, 85.1; H, 9.2. Found: C, 84.3; H, 9.4.

(c) 1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-propene (XVI).—Prepared by dehydration of compound XV in benzene solution in presence of oxalic acid. The olefin was obtained in 87% yield, b. p. 149–150° (3 mm.), n_D^{20} 1.5695, d_4^{20} 0.9616; MR_D calcd. 86.9, obsd. 89.9.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.84; H, 9.16. Found: C, 90.80; H, 9.20.

(d) 1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-propane (XVII).—The olefin, compound XVI, was hydrogenated under pressure in the presence of a nickel-kieselguhr catalyst at 45°. The hydrocarbon obtained (XVII) boiled at 143–144° (3 mm.), n_D^{20} 1.5455, d_4^{20} 0.9480; MR_D calcd. 87.3, obsd. 86.6.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.29; H, 9.80.

The infrared absorption spectra are given in Graph V.

Acetylation followed by treatment with 2,4-dinitrophenylhydrazine gave a solid derivative m. p. 263–265°. A mixed melting point with the dinitrophenylhydrazone of synthetic *p*-methylacetophenone showed no depression.

XI. Reaction of *p*-Xylene with 4-Methylcyclohexene

Forty-two grams (0.4 mole) of *p*-xylene was treated with 19.2 g. (0.2 mole) of 4-methylcyclohexene in the presence of 50 g. of hydrogen fluoride by the usual procedure described above. The hydrocarbon layer after washing and drying weighed 52 g. The following products were separated by fractional distillation through a 20-plate column: (1) 135–137° (750 mm.), 22 g., n_D^{20} 1.4960 (*p*-xylene); (2) 131–134° (10 mm.), 18 g., n_D^{20} 1.5260; (3) > 135° (4 mm.), 9 g., n_D^{20} 1.5310.

Fraction 2 corresponded to (1-methylcyclohexyl)-*p*-xylene, d_4^{20} 0.9363; MR_D calcd. 65.7, obsd. 66.2 (new compound).

Anal. Calcd. for $C_{15}H_{22}$: C, 89.11; H, 10.89. Found: C, 89.05; H, 10.77.

Acetylation yielded a ketone from which 2,4-dinitrophenylhydrazone was prepared. Crystallization from the chloroform-ethanol solution produced orange needles m. p. 172–174° (new compound).

Anal. Calcd. for $C_{23}H_{28}N_4O_4$: N, 13.21. Found: N, 13.70.

Nitration of the hydrocarbon with a solution of 2 volumes of 96% sulfuric acid gave a sirupy product which could not be crystallized.

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Summary

When *p*-ethyltoluene and *p*-propyltoluene react with methylcyclohexene in the presence of hydrogen fluoride and sulfuric acid, the main products formed result from a hydrogen transfer in which the aromatic hydrocarbons acted as a hydrogen donor and methylcyclohexene as a hydrogen acceptor.

The products obtained from the respective aromatic hydrocarbons through a hydrogen transfer were: 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane and 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane.

A mechanism for the hydrogen transfer reaction has been proposed; *p*-xylene on reaction with methylcyclohexene yields the expected cycloalkylation products.

The following new compounds and their derivatives were prepared; 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethanol, 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethene, 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane, 3,6-dimethyl-1-*p*-tolylindene, 3,6-dimethyl-1-*p*-tolylindan, 1-bromo-2-methyl-5-propylbenzene, 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propanol, 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propene, 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane and (1-methylcyclohexyl)-*p*-xylene.

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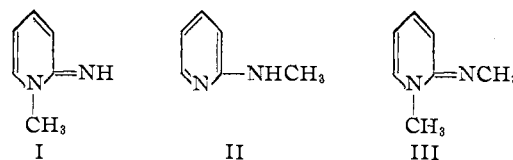
NOTES

2-Triphenylmethylaminopyridine

BY ROGER ADAMS AND JOHN B. CAMPBELL

The direct interaction of 2-aminopyridine and methyl iodide yields almost entirely the hydroiodide of N-methyl-2-pyridoneimide (I).¹ The reaction of the sodio derivative of 2-aminopyridine and methyl iodide yields principally 2-methylaminopyridine (II). The reaction of I or II with methyl iodide gives the dimethyl derivative (III). The same general behavior occurs when benzyl chloride is used rather than methyl iodide.

(1) Chichibabin, Konovalova and Konovalova, *Ber.*, **54**, 814 (1921).



Triphenylcarbinol was condensed with 2-aminopyridine in the presence of a trace of acid in an attempt to obtain 5-triphenylmethyl-2-aminopyridine. Diazotization of the product in an effort to get the known 5-triphenylmethyl-2-hydroxypyridine (IV) resulted in cleavage of the molecule to yield triphenylcarbinol. Cleavage was also readily effected by means of concentrated