

for the other substances is made similarly. At the end of the process a series of final residuals is obtained by subtracting the optical densities due to all of the known components from the measured optical densities of the solution. These final residuals will approximate to zero if no interfering impurities are present. Interfering impurities show up as a series of final residuals which form a smooth curve when plotted, but obviously this curve must not show any tendency of being an absorption curve (positive or negative) for one of the known compounds already estimated. For the compounds listed in Table III this second method seems to be as reliable as the analytical method.

Decomposition of N-Nitrosoacetanilide in Methanol.—In a 50-ml. distilling flask were placed 20 ml. of reagent grade methanol and 174 mg. of N-nitrosoacetanilide. The mixture was allowed to stand for more than 12 hours. Then 0.20 ml. of 5 *N* NaOH solution was added to convert the liberated acetic acid into non-volatile sodium acetate and the reaction mixture was distilled on the steam-bath. The distillate was collected in a 50-ml. volumetric flask. When all of the methanol had distilled, methanol was run into the flask from a dropping funnel at the same rate as it distilled, the flask remaining nearly dry during the distillation. When the first volumetric flask was nearly full, a second one was put in place and the distillation continued. All of the benzene and at least 70% of the anisole came over in the first 50 ml. of distillate.

For the acetic acid and acetic anhydride solutions an extraction technique was developed. A 5-ml. aliquot of distillate was transferred to a 50-ml. volumetric flask, hydrolyzed with water, then the mixture was cooled and made alkaline with 5 *N* NaOH solution. Water was added to bring the liquid level just to the neck of the flask and the aqueous solution was extracted in the volumetric flask with four 2.5-ml. portions of 2,2,4-trimethylpentane of spectroscopic grade. The hydrocarbon layer was removed from the neck with a pipet and transferred to another volumetric flask for dilution with methanol. The extinction coefficients obtained in methanolic solution were used for estimating the concentration of benzene and of anisole. The errors introduced should not be very great since the solution used for determination of optical density contained only 20% of the isoöctane.

The phenyl acetate absorption spectrum has poorly defined maxima at 2590 and 2650 Å. and a slight minimum at 2640 Å. It is unsuitable for the determination of phenyl acetate in the presence of other materials. The phenyl acetate formed in acetic acid solution was isolated by neutralization of the acetic acid, extraction of the phenyl acetate with methylene chloride followed by drying and distillation, b.p. 77° at 9 mm., odor similar to that of an authentic sample, b.p. 76° at 8 mm.

ITHACA, NEW YORK

RECEIVED JUNE 7, 1950

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, U. S. BUREAU OF MINES.]

The Anomalous Reaction of 1-Tetralone with *o*-Tolylmagnesium Bromide¹

BY MILTON ORCHIN, LESLIE REGGEL AND R. A. FRIEDEL

The reaction of 1-tetralone with *o*-tolylmagnesium bromide gives, in addition to the expected 1-(*o*-tolyl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene (I) and 1-(*o*-tolyl)-3,4-dihydronaphthalene (II) a 19% yield of a substance which is believed to be 1-(*o*-tolyl)-1,1'-dihydroxy-1,2,3,4,1',2',3',4'-octahydro-2,1'-dinaphthyl (III). Dehydrogenation of III with palladium-on-charcoal gives 1-(*o*-tolyl)-2-(1'-naphthyl)-naphthalene (V). Treatment of III with formic acid gives two isomeric hydrocarbons; one of these is shown to be 1-(*o*-tolyl)-2-(3',4'-dihydro-1'-naphthyl)-3,4-dihydronaphthalene (IX). The second hydrocarbon is believed to have a spiro-3,4-benzfluorene structure (AII) arising from a cyclodehydration. 1-(*o*-Tolyl)-2-(1'-naphthyl)-naphthalene (V) has been synthesized from *o*-tolyllithium and 1-keto-2-(1',2',3',4'-tetrahydro-1'-naphthyl)-1,2,3,4-tetrahydronaphthalene (VI), followed by dehydration and dehydrogenation.

The most direct route to 1-(*o*-tolyl)-naphthalene would appear to be reaction of *o*-tolylmagnesium bromide with 1-tetralone, followed by dehydration and dehydrogenation of the intermediate tertiary carbinol. Although this series of reactions has been shown to provide some of the desired hydrocarbon,² the formation of an unusual product during the Grignard addition has prompted us to investigate the reaction in detail. We have found that four products are obtained: 1-(*o*-tolyl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene (I); 1-(*o*-tolyl)-3,4-dihydronaphthalene (II); a high-boiling, viscous gum, of unknown composition; and a colorless, crystalline compound, C₂₇H₂₈O₂, m.p. 173.5–176.0°, whose study constitutes the major portion of the present investigation.

The structure of I follows from its analysis, from the presence of a hydroxyl group (as shown by its infrared absorption spectrum) and from its conversion to the known 1-(*o*-tolyl)-naphthalene (IV). The structure of II is established by its analysis, by its conversion to IV, and by its ultraviolet absorption spectrum (Fig. 3), which is that of a substituted 1,2-dihydronaphthalene.

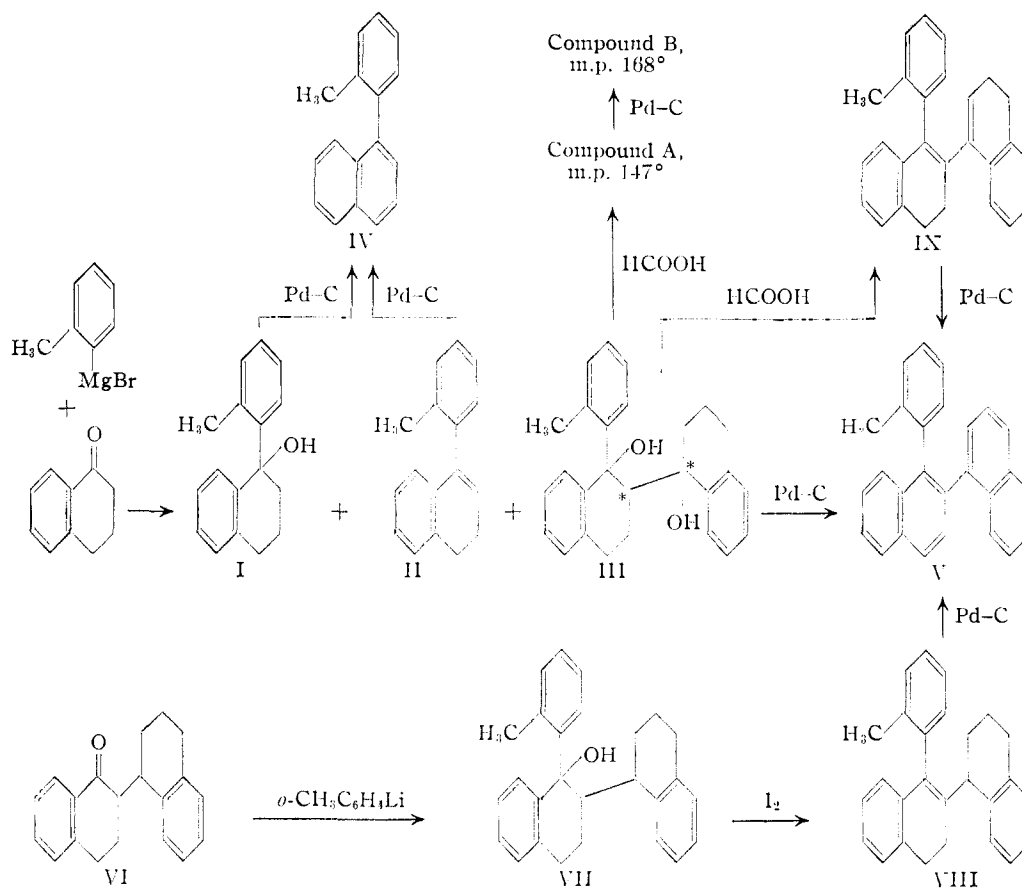
We have assigned the structure of 1-(*o*-tolyl)-1,1'-

dihydroxy - 1,2,3,4,1',2',3',4' - octahydro - 2,1'-dinaphthyl (III) to the crystalline compound C₂₇H₂₈O₂. Compound III, the "diol," is obtained in 19% yield when the Grignard reaction mixture is decomposed with ammonium chloride, the ether layer separated and the ether evaporated; the diol precipitates as a white solid and is obtained analytically pure by filtration and washing with petroleum ether. It melts, without obvious decomposition, over a fairly small temperature range, with some dependence upon the rate of heating. When it is recrystallized from ether, ethanol or petroleum ether, the melting point is lowered, extends over a wider range, and gas is evolved on melting; the analysis is unchanged. It is possible that the diol is not a stereochemically pure individual, but is a mixture of two or more of the four possible racemates having the structure III. If the diol is such a mixture, the change in melting point after recrystallization might be explicable, although the gas evolution on melting seems unusual.

The structure of the diol follows from its analysis; from the presence of two active hydrogen (hydroxyl) atoms in the Zerewitinoff determination; from the ultraviolet spectrum (Fig. 3), which indicates substituted phenyl groups only; and from catalytic dehydration-dehydrogenation to

(1) Not subject to copyright.

(2) R. A. Friedel, M. Orchin and L. Reggel, THIS JOURNAL, 70, 199 (1948).



1-(*o*-tolyl)-2-(1'-naphthyl)-naphthalene (V). For comparison, V was synthesized independently, as shown in Fig. 1, from *o*-tolylmagnesium bromide and 1-keto-2-(1',2',3',4'-tetrahydro-1'-naphthyl)-1,2,3,4-tetrahydronaphthalene (VI); dehydration of the carbinol, VII, followed by catalytic dehydrogenation of the resulting liquid hexahydro compound, VIII, gave V in high yield. The formation of III may be explained by the Grignard reagent acting as a base in the base-catalyzed aldol condensation between two molecules of 1-tetralone to give the hydroxy-ketone XII (Fig. 2) or its magnesiohalide salt, followed by the normal addition of *o*-tolylmagnesium bromide to XII to give the diol, III.³ The ultraviolet spectrum of V (Fig. 3) indicates the presence of naphthalene groups and is quite similar to the spectrum of 1,2'-dinaphthyl.²

The reactions of the diol, III, were studied further. When III, $C_{27}H_{28}O_2$, is refluxed with formic acid, two isomeric compounds are obtained. Both of these compounds have the formula $C_{27}H_{24}$ and result from the loss of two molecules of water from III. The lower melting (139.0 – 140.5°) dehydration product still contains the unrearranged carbon skeleton of III, since it gives V on catalytic dehydrogenation. Of the three possible structures,

(3) It has been shown that phenylmagnesium bromide and *o*-anisylmagnesium bromide react with 1-tetralone to give the products of normal addition, no compounds analogous to III being formed; see R. Weiss and K. Woidich, *Monatsh.*, **46**, 453 (1926); M. Orchin, *This Journal*, **70**, 495 (1948).

IX, X and XI, for this tetrahydro compound, the ultraviolet spectrum (Fig. 4) favors structure IX, with two dihydronaphthalene chromophores, because of the single broad absorption band at 2700 \AA . Both structures X and XI, which contain naphthalene systems, would produce two or more absorption bands, one of which would be at a wave length longer than 2700 \AA . The spectrum of VIII (Fig. 4) resembles that of IX; however, the intensity of VIII is approximately half that of IX, because VIII has only one dihydronaphthalene group. The tolyl groups in both VIII and IX are conjugated with the dihydronaphthalene groups, but can contribute very little to the absorption intensities because of steric hindrance.²

The second substance isolated from the dehydration of III, "Compound A," m.p. 146.4 – 147.8° , apparently arises from a rearrangement of the carbonium ion intermediate which is produced by the attack of the formic acid on the diol. On catalytic dehydrogenation, Compound A, $C_{27}H_{24}$, in contrast to its isomer, loses only two (rather than four) atoms of hydrogen to give "Compound B," $C_{27}H_{22}$, m.p. 166.6 – 168.0° . This failure to produce a completely aromatic system isomeric with V ($C_{27}H_{20}$) suggests that Compound A contains a quaternary carbon atom; such a compound, on dehydrogenation, would give a dihydro compound resistant to further dehydrogenation. A possible rearranged product of the diol, III, is shown as AI in Fig. 2. Such a structure might arise during the dehydration of III by migration of

the tolyl group from the 1-position to the 1'-position. Dehydrogenation of AI could result in the loss of two hydrogen atoms, giving BI. This series of reactions accounts for the stoichiometry of the transformations of III to Compound A and Compound B.⁴

The ultraviolet absorption spectrum of Compound B (Fig. 5) is not, however, consistent with its formulation as the dinaphthyl derivative BI; absorption bands in the 3000–3500 Å. region are not characteristic of dinaphthyl or naphthalene structures.² Further, there is little reason to suppose that a structure such as AI would tend to dehydrogenate, since the product, BI, is still a hydroaromatic compound. A structure for Compound A, more consistent with the non-naphthalenic ultraviolet spectrum (Fig. 4), is the spiran AII, which could arise from a cyclodehydration during the treatment with formic acid. Dehydrogenation of the spiran, AII, should result in the loss of two atoms of hydrogen, with the formation of the spiro-3,4-benzfluorene, BII. The ultraviolet spectrum of a spiro-3,4-benzfluorene⁵ is presented in Fig. 5 for comparison. The spectrum of Compound B is shifted to longer wave lengths than the other spectrum, probably because of the presence of a methyl group in B.

The structure BII is not supported by the failure of Compound B to form complexes with picric acid, *s*-trinitrobenzene and 2,4,7-trinitrofluorenone⁶; such failure would be expected for a naphthalenic structure such as BI, but since 3,4-benzfluorene forms stable complexes,⁷ BII might also be expected to form complexes. It is quite possible, however, that a methyl group in the 5-position of the 3,4-benzfluorene ring system, as in BII, would inhibit complex formation, because of its inter-

(4) Several other rearrangements can be written which would result in a compound containing a quaternary carbon atom; migration of the tolyl group from the 1-position to the 2-position; migration of the 1',2',3',4'-tetrahydro-1'-naphthyl group from the 2-position to the 1-position; migration of the tetrahydro-1'-naphthyl group from the 2-position to the 1-position with its simultaneous rearrangement to a tetrahydro-2'-naphthyl structure, which would lead to AI; and migration of the tolyl group with simultaneous rearrangement. The choice between structures AI and AII and (BI and BII) would not be altered by consideration of these other rearrangement products, however.

(5) R. N. Jones, *THIS JOURNAL*, **66**, 185 (1944).

(6) M. Orchin and E. O. Woolfolk, *ibid.*, **68**, 1727 (1946); M. Orchin, L. Reggel and E. O. Woolfolk, *ibid.*, **69**, 1225 (1947); E. O. Woolfolk and M. Orchin, "Organic Syntheses," Vol. 28, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 91.

(7) M. Orchin and R. A. Friedel, *ibid.*, **71**, 3002 (1949).

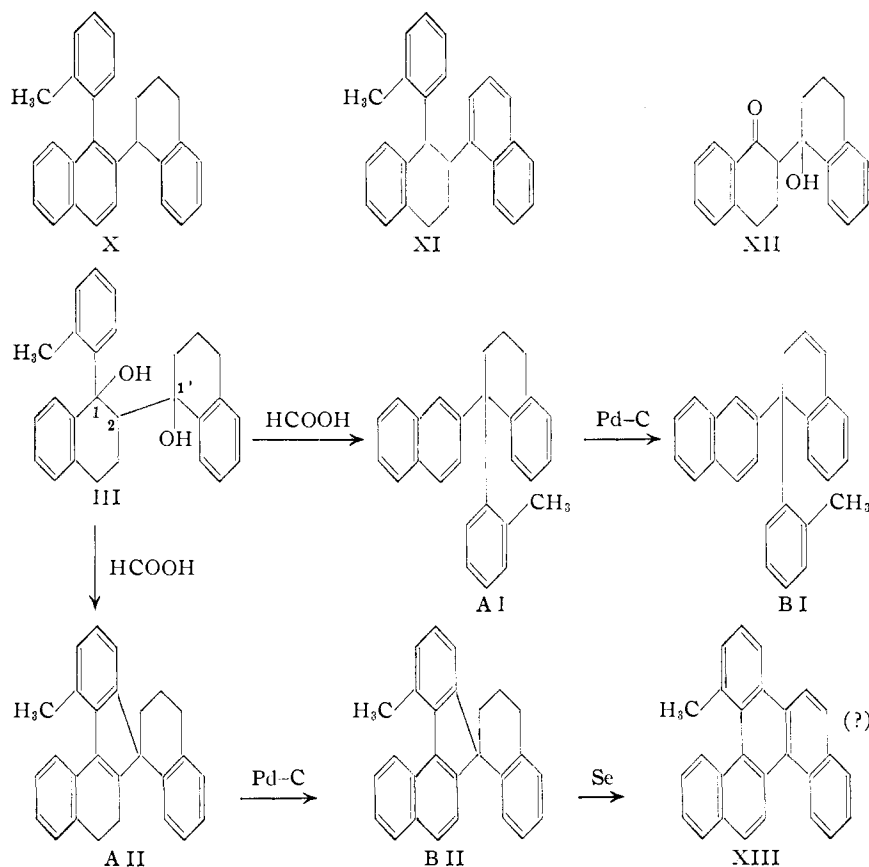


Fig. 2.

ference with the planarity of the ring system. The effect of such steric factors in complex compound formation has been amply demonstrated.⁸

An attempt to synthesize BI, although productive of interesting results,⁹ was not successful. Attempts were then made to determine the correct structure for Compound B by treatment with selenium and by oxidation. It is known that selenium dehydrogenation of compounds with an angular group sometimes results in elimination of the angular substituent, and that this elimination is less likely to take place with platinum or palladium catalysts.¹⁰ Selenium treatment of Compound B at 350–460° gave neither 1,2'-dinaphthyl nor 1-(*o*-tolyl)-naphthalene; about 37% of starting material was recovered and a small amount of an incompletely identified transformation product was isolated.¹¹

Finally, oxidation of Compound B with sodium dichromate in acetic acid led to the formation of a red compound, C₂₇H₂₀O₂, which is apparently a quinone. Under similar conditions, V was largely

(8) M. Orchin, paper presented before the Organic Division at the Atlantic City Meeting of the American Chemical Society, April, 1949.

(9) M. Orchin and L. Reggel, *THIS JOURNAL*, in press.

(10) J. W. Cook, *Chem. and Ind.*, 315 (1935); P. A. Plattner and E. C. Armstrong, in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 21–59.

(11) The ultraviolet absorption spectrum of this material (see experimental) indicated a highly conjugated fused ring system, possibly a dibenzchrysenes. It is conceivable that Compound B, represented by the structure BII, partly rearranged under the dehydrogenation conditions to 5-methylbenzo[*c,p*]chrysenes (XIII) perhaps with partial loss or migration of the methyl group.

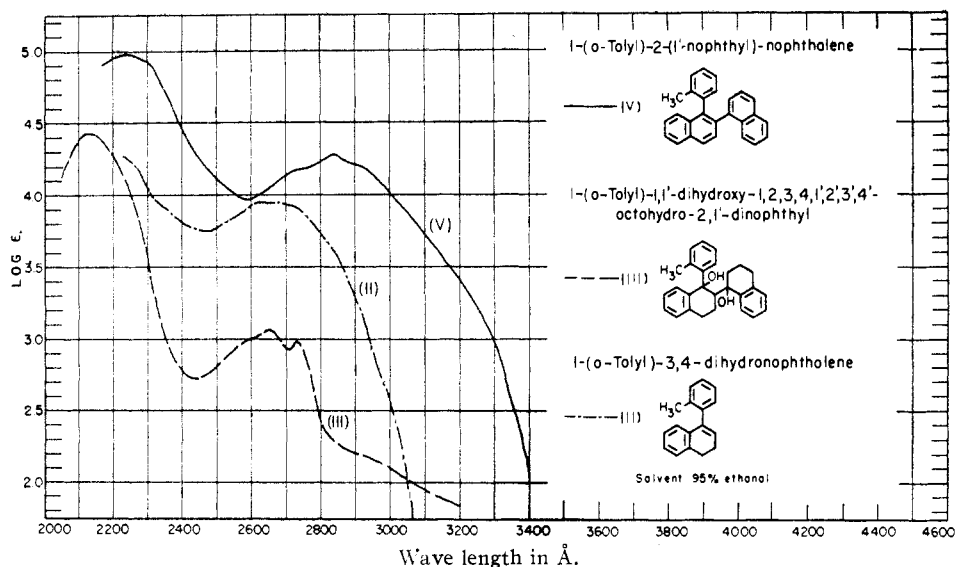


Fig. 3.

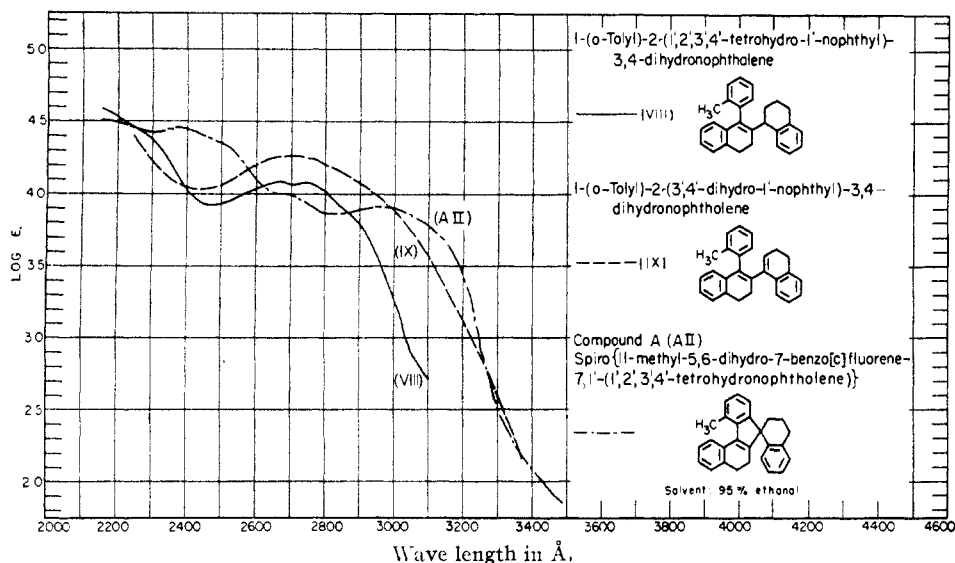


Fig. 4.

unattacked. When V was oxidized under somewhat more vigorous conditions, several products were obtained; a considerable acidic fraction was formed, but the only substance isolated was apparently a quinone, $C_{27}H_{18}O_2$. It is obvious that oxidative attack on V and on Compound B is quite different; this is perhaps further evidence that the structure of Compound B is not that of a substituted naphthalene system. We believe that the structure BII is probably correct for Compound B.

Experimental¹²

Reaction between 1-Tetralone and *o*-Tolylmagnesium Bromide.—To the Grignard reagent prepared from 188 g.

(12) All melting points corrected. Microanalyses marked *a* are by Arlington Laboratories, Fairfax, Virginia; microanalyses marked *b* are by Mr. G. L. Stragand, University of Pittsburgh; macroanalyses marked *c* are by the Bureau of Mines. Unless otherwise specified, "petroleum ether" refers to material of b.p. 90–100°. Gas volumes are reduced to standard conditions. Ultraviolet absorption spectra were determined with a Cary Recording Spectrophotometer.

(1.10 moles) of *o*-bromotoluene, 29.4 g. (1.21 moles) of magnesium and 725 ml. of ether there was added a solution of 146 g. (1.00 mole) of 1-tetralone¹³ in 150 ml. of ether. The mixture was refluxed with stirring for 20 hours and then decomposed with ammonium chloride solution. The aqueous layer was extracted with ether and the combined ether layers washed three times with saturated sodium chloride solution and dried over calcium chloride. Most of the ether was distilled off; the resulting mixture of oil and solid was left in the refrigerator overnight, filtered, and the white solid washed with cold 60–68° petroleum ether. There was obtained 36.59 g. of 1-(*o*-tolyl)-1,1'-dihydroxy-1,2,3,4,1',2',3',4'-octahydro-2,1'-dinaphthyl (III). The mother liquor and the petroleum ether washings were combined and distilled. There was obtained about 80 ml. of toluene; 58.12 g. of liquid, b.p. 82–121° (0.4–0.6 mm.) which gave naphthalene and 1-naphthol on dehydrogenation and was apparently mostly 1-tetralone; 37.05 g., b.p. 120–145° (0.4 mm.); 16.49 g., b.p. 145–165° (0.4 mm.); and 18.52 g. of a viscous residue.

The material of boiling point 120–145° was distilled from sodium and then redistilled in a two-foot Podbielniak col-

(13) This compound was the generous gift of Dr. Gilbert Thiessen and the Koppers Company. It was stated to be 95% pure and was redistilled just prior to use.

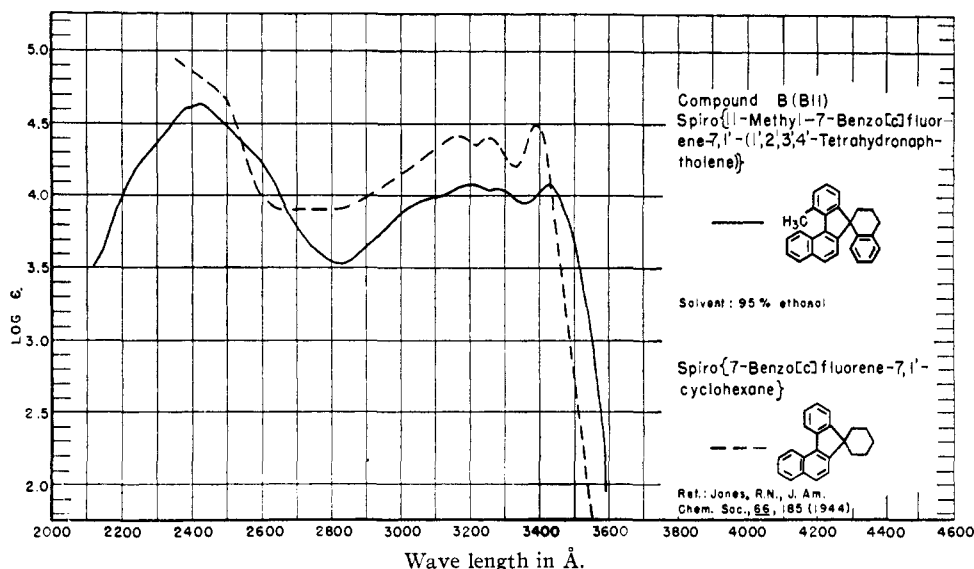


Fig. 5.

um, giving 16.0 g. of 1-(*o*-tolyl)-3,4-dihydronaphthalene (II), n_D^{20} 1.6157, n_D^{20} 1.6505, d_4^{20} 1.0174. An accurate boiling point could not be obtained. *Anal.* Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found^a: C, 92.7; H, 7.2. Dehydrogenation of a sample of crude II as previously described² gave 1-(*o*-tolyl)-naphthalene (IV) m.p. 68.9–70.4° (reported, 67.5–68.5°, 14a 63^{14b}). *Anal.* Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46; mol. wt., 218. Found^c: C, 93.22; H, 6.51; mol. wt. (ebulliometric in benzene), 210.

The material of boiling point 145–165° was redistilled; a fraction (6.40 g., b.p. 155° at 1–2 mm.) was obtained which was apparently crude 1-(*o*-tolyl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene (I). *Anal.* Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found^c: C, 87.71; H, 7.77. The infrared spectrum of I showed bands at 2.78 and 2.87 μ but no band at 5.8 μ . This behavior indicates the presence of an hydroxyl group and the absence of a carbonyl group. Dehydrogenation of I with 30% palladium-on-charcoal¹⁵ at 300–350° gave 1-(*o*-tolyl)-naphthalene (IV).

In one experiment the Grignard reaction gave, in addition to II and III, 30.14 g. of a red-brown, very viscous liquid, b.p. 130–230° (0.3–0.4 mm.); treatment with formic acid, followed by distillation, did not give any pure material. The infrared spectrum of one fraction (b.p. 230–248° (1 mm.)). *Anal.* Found^c: C, 90.73, 90.43; H, 7.28, 7.22 indicated the presence of a carbonyl group; however, a 2,4-dinitrophenylhydrazone could not be prepared. It is thought possible that this high-boiling material may contain the hydroxy-ketone XII, or its dehydration product.

1-(*o*-Tolyl)-1,1'-dihydroxy-1,2,3,4,1',1',3',4'-octahydro-2,1'-dinaphthyl (III).—The diol, III, as obtained above was a white crystalline solid, m.p. 173.5–176.0°; the melting point varied somewhat with the rate of heating. *Anal.* Calcd. for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34. Found^c: C, 84.27; H, 7.38. A sample recrystallized from alcohol and then from benzene–petroleum ether had m.p. 166.5–169.0° (gas). *Anal.* Found^c: C, 83.81; H, 7.36. A sample recrystallized four times from petroleum ether had melting point 164.5–167.2° (gas). *Anal.* Found^c: C, 84.33; H, 7.38. A sample recrystallized twice from ether melted at 150.0–151.8° (gas) after softening from 140°.

The diol gave a red color when treated with sulfuric acid, or with aluminum chloride and benzene. The presence of a hydroxyl group was shown by the infrared absorption spectrum. A Zerewitinoff determination¹⁶ gave 100.5% of the theoretical value for two hydroxyl groups; III was recovered unchanged from the reaction.

The diol, III, was not easily dehydrated by heating. A sample was heated at 190° and 3–4 mm. pressure for 2

hours; the resulting viscous material crystallized to a pasty mass, m.p. 70–155°. Several recrystallizations from petroleum ether gave unchanged III, m.p. 172.3–174.4°, mixed m.p. 169.6–174.2°. *Anal.* Found^a: C, 84.6; H, 7.5. Mol. wt. calcd. for $C_{27}H_{28}O_2$: 384. Found^a (micro Rast, camphor): 341, 317.

When III was treated with benzoyl chloride in pyridine solution, it was recovered unchanged, m.p. 166.8–167.8° (gas) (from petroleum ether), mixed m.p. 166.2–169.0° (gas). *Anal.* Found^a: C, 84.5; H, 7.5.

Treatment of III with 1-naphthyl isocyanate and pyridine gave a cream colored solid, m.p. 141.5–144.8° (from petroleum ether). The analysis did not correspond to either a monourethan or a diurethan of III. *Anal.* Calcd. for $C_{38}H_{38}NO_2$: C, 82.43; H, 6.37; N, 2.53. Calcd. for $C_{49}H_{42}N_2O_4$: C, 81.41; H, 5.86; N, 3.88. Found: C,^b 78.8, 79.0; H,^b 4.8, 5.0; N,^c 4.12, 4.41.

1-(*o*-Tolyl)-2-(1'-naphthyl)-naphthalene (V) from the Diol, III.—Two grams of the diol, III, and 0.20 g. of 30% palladium-on-charcoal were heated at 340–360° for one-half hour; 187 ml. (S.T.P.) of hydrogen was evolved (80% of theory). The product was distilled at 2–3 mm. (bath 320°) and the resulting gum (1.04 g.) recrystallized three times from petroleum ether giving 0.21 g. of V, white needles, m.p. 158.5–160.8° (constant). A mixture with 1,1'-dinaphthyl melted at 123–136°. *Anal.* Calcd. for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found^a: C, 94.2; H, 6.0. Subsequently, when V was obtained as a higher melting form, the above analytical sample was again recrystallized and then melted at 172.7–173.8°; the ultraviolet absorption spectra of both forms were identical.¹⁷

In another experiment, the diol, III, was heated at 160–180° and 0.15 mm. pressure for 4 hours. The product (2.45 g.) was heated at 340–360° with 0.20 g. of palladium-on-charcoal for 30 minutes; 161 ml. of hydrogen was evolved (56%). The product was distilled and recrystallized twice from petroleum ether, giving white rosettes, m.p. 170.6–173.4°. Three more recrystallizations raised the melting point to 172.8–174.0°. *Anal.* Found^a: C, 94.0; H, 6.4. A mixture of this sample of V with the above sample of V melted at 172.0–174.0°; a mixture with an authentic sample of V (m.p. 169.2–171.5°) melted at 169.2–173.5°.

1-(*o*-Tolyl)-2-(3',4'-dihydro-1'-naphthyl)-3,4-dihydroxynaphthalene (IX) and Compound A from the Diol, III.—A mixture of 5.00 g. of the diol, III, and 150 ml. of formic acid was refluxed for 2.5 hours. The product was taken up in benzene, washed with water, sodium carbonate solution, water, and saturated sodium chloride, dried with so-

(14) (a) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1431 (1936); (b) F. Mayer and R. Schiffner, *Ber.*, 65B, 1337 (1932).

(15) The catalyst-d of R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940), was used throughout this work.

(16) M. Orchin and I. Wender, *Anal. Chem.*, 21, 875 (1949).

(17) Compound A, Compound B and V crystallize slowly; it was found desirable to allow crystallizations to proceed overnight. Seeding was helpful, but not necessary. In a few instances, a solution of V which was seeded with the high-melting form deposited crystals of the low-melting form.

dium sulfate, and the benzene removed. The oily residue was taken up in petroleum ether and allowed to crystallize, giving 1.30 g. of crude Compound A (in two crops), m.p. 142.5–147.0 with previous softening. Recrystallization from petroleum ether gave 1.21 g. (27%) of Compound A, m.p. 145.5–147.2°. The analytical sample was recrystallized from methanol and then twice from petroleum ether, giving white crystals, m.p. 146.4–147.8°. *Anal.* Calcd. for $C_{27}H_{24}$: C, 93.1; H, 6.9. Found^a: C, 93.1; H, 6.8. The petroleum ether mother liquors of the crude Compound A on standing about 10 days deposited 0.78 g. of large prismatic crystals, m.p. 137.0–142.0°. Two recrystallizations from petroleum ether gave 0.61 g. (13%) of IX, m.p. 139.0–140.5°. *Anal.* Found^b: C, 93.1; H, 7.1. A mixture of IX and Compound A melted at 130–142°.

In another experiment, the diol, III, was heated at 160–180° and 0.15 mm. pressure for 4 hours and the product then refluxed with formic acid for 2 hours; two crystallizations from methanol gave Compound A in 38% yield. Fractional crystallization of the mother liquors from methanol and from petroleum ether did not lead to the isolation of any other pure substance.

Dehydrogenation of 1-(*o*-Tolyl)-2-(3',4'-dihydro-1'-naphthyl)-3,4-dihydronaphthalene (IX).—A mixture of 0.22 g. of IX and 0.05 g. of palladium-on-charcoal was heated for 30 minutes at 305–315° and for 30 minutes at 340–355°. There was evolved 31 ml. of hydrogen (110% of theory¹⁸). The product was dissolved in benzene and chromatographed on alumina; the blue-fluorescent band gave 0.17 g. of oil which was crystallized from petroleum ether, giving 0.09 g. of 1-(*o*-tolyl)-2-(1'-naphthyl)-naphthalene (V) identified by mixed melting point.

Dehydrogenation of Compound A.—A mixture of 1.03 g. of Compound A and 0.10 g. of palladium-on-charcoal was heated for 15 minutes at 320–330° and for 35 minutes at 350–360°; there was evolved 67 ml. of hydrogen (102% of theory¹⁸). The product was taken up in benzene, chromatographed on alumina-supercel (1:1), the purple-fluorescent band eluted with benzene, and the material crystallized from petroleum ether. There was obtained 0.64 g. of Compound B, white crystals, m.p. 165.8–167.0°. An additional 0.09 g. was obtained from the mother liquors; total yield 72%. The analytical sample had m.p. 167.2–168.5°. *Anal.* Calcd. for $C_{27}H_{22}$: C, 93.6; H, 6.4. Found^a: C, 93.4; H, 6.5. A mixture of Compound B and V melted at 142–160°. Compound B did not form complexes with picric acid, *s*-trinitrobenzene or 2,4,7-trinitrofluorenone.

Selenium Dehydrogenation of Compound B.—A mixture of 0.40 g. of Compound B and 0.80 g. of selenium was heated for 7.5 hours at 350–460° in an open vessel.¹⁹ The product was taken up in benzene and chromatographed on alumina. The blue-fluorescent band gave 0.15 g. (38%) of crude starting material. A more strongly adsorbed fraction gave 0.06 g. of a yellow oil which was treated with 0.06 g. of *s*-trinitrobenzene in benzene-ethanol. The brick-red crystals (m.p. 191.0–201°) were recrystallized to give 0.03 g., m.p. 197.1–203° (softening from 195°). The complex was chromatographed on alumina and the recovered hydrocarbon crystallized from ethanol, giving a few mg. of a pale yellow solid, m.p. 145–151°. The ultraviolet absorption spectrum of this material in 95% ethanol gave the following maxima and extinction coefficients:

A	E	A	E
3945	1680	3010	44,700
3730	5200	2880	27,800

(18) This experiment was done in an apparatus¹⁸ which enabled the gas evolved to be measured with greater accuracy than in most of the dehydrogenations described here.

(19) J. W. Cook, N. A. McGinnis and S. Mitchell, *J. Chem. Soc.*, 286 (1944), have shown that selenium is sometimes a more effective dehydrogenating agent when it is used in an open vessel than when it is used in a closed tube.

3635	16,800	2775	21,600
3465	17,500	2540	28,200
3325	12,300	2390	27,100
3120	44,700	2220	80,200

The spectrum is consistent with the possibility that the compound is 5-methyldibenzo[*c,p*]chrysene (XIII) but insufficient material was available for further characterization.

Synthesis of 1-(*o*-Tolyl)-2-(1'-naphthyl)-naphthalene (V).—To a solution of *o*-tolyllithium (prepared from 17.1 g. of *o*-bromotoluene, 1.45 g. of lithium and 85 ml. of ether) there was added a solution of 11.21 g. of 1-keto-2-(1',2',3',4'-tetrahydro-1'-naphthyl)-1,2,3,4-tetrahydronaphthalene (VI) (non-crystalline material)²⁰ in 65 ml. of benzene. The solution was refluxed with stirring for 19 hours, decomposed with ammonium chloride solution, the organic layer washed with saturated sodium chloride, and the solvents removed (water-pump). The residual carbinol, VII, was dehydrated by heating at 160–190° with a crystal of iodine for one-half hour, the water formed distilled out (water-pump, bath at 180°) and the product distilled. There was obtained 13.58 g. of 1-(*o*-tolyl)-2-(1',2',3',4'-tetrahydro-1'-naphthyl)-3,4-dihydronaphthalene (VIII) as a viscous, pale yellow gum, b.p. 233–240° at 1–2 mm. (bath 280–310°) which could not be induced to crystallize. A portion was redistilled for analysis. *Anal.* Calcd. for $C_{27}H_{26}$: C, 92.52; H, 7.48. Found^c: C, 92.21; H, 7.51.

Dehydrogenation of 2.02 g. of VIII in the presence of 0.20 g. of palladium-on-charcoal gave 350 ml. of hydrogen (90%). The product was taken up in benzene, filtered, and the benzene replaced by petroleum ether. There was obtained 0.84 g. of V, m.p. 169.2–171.5°, and a second crop, 0.52 g., m.p. 168.5–170.5°; total yield 69%. A sample recrystallized from petroleum ether formed pale yellow clumps, m.p. 171.5–172.7°.

V did not form complexes with picric acid, *s*-trinitrobenzene or 2,4,7-trinitrofluorenone.

Oxidation of Compound B.—A solution of 0.20 g. of Compound B and 1.00 g. of sodium dichromate dihydrate in 20 ml. of acetic acid was heated on a steam-bath for 1 hour. The mixture was poured into water, the product taken up in benzene, and the benzene solution washed with water and saturated sodium chloride, dried over sodium sulfate, and chromatographed on silicic acid-celite (2:3 by weight).²¹ The less strongly adsorbed of the two red bands was eluted with benzene-chloroform and the resulting material (105 mg. of red gum) was recrystallized twice from methanol. There was obtained 44 mg. (20%) of deep red prisms, m.p. 192.8–194.8° (softening from 189°). *Anal.* Calcd. for $C_{27}H_{20}O_2$: C, 86.1; H, 5.4. Found: C, 86.0; H, 5.4.

Oxidation of V.—A solution of 0.50 g. of V and 1.50 g. of sodium dichromate dihydrate in 25 ml. of acetic acid was refluxed for 3 hours. The product was separated into neutral and acid fractions by extraction with sodium carbonate. The acidic material (0.31 g.) was chromatographed on silicic acid-celite, but no pure material was isolated. The neutral fraction, when chromatographed on silicic acid-celite, gave evidence for the presence of at least four materials. The less strongly adsorbed of two orange bands gave 108 mg. of orange solid, which was crystallized from ethanol. The product (m.p. 296.5–300.5°) was recrystallized from ethanol to give 14 mg. of orange crystals, m.p. 304.0–305.0°. *Anal.* Calcd. for $C_{27}H_{18}O_2$: C, 86.6; H, 4.8. Found^b: C, 86.0; H, 4.3.

Acknowledgments.—We wish to thank Lois Pierce, Lois Harnack and Marion Springer for the spectral measurements.

BRUCETON, PENNA.

RECEIVED SEPTEMBER 5, 1950

(20) M. Orchin, L. Reggel and R. A. Friedel, *THIS JOURNAL*, **71**, 2743 (1949).

(21) We have found that phenanthrenequinone is decomposed by chromatography on alumina.