tinctly different from that of 3-chloro-1-phenyl-1-propanol. The yields from the cleavage were: 32% in acetone–water, accompanied by a 28% yield of cinnamyl alcohol, b.p. 53–57° (0.04 mm.) and correct infrared spectrum; 27% in dioxane–water, accompanied by a 7% yield of cinnamyl alcohol and a large amount of polymer; and 19% in acetonitrile–water, accompanied by 5% of cinnamyl alcohol.

3-Chloro-3-phenyl-1-propanol.—A solution of thionyl chloride (43 g.) in 30 ml. of chloroform was added to a solution of 60 g. of methyl 3-hydroxy-4-phenylpropionate[28] and 31 g. of pyridine at 0°, and the mixture was then warmed to 50° for one-half hour. After the usual processing, 45 g. (75%) of methyl 3-chloro-3-phenylpropionate, b.p. 80–85° (0.08 mm.), was obtained. This product was infrared-spectroscopically pure of hydroxyl impurities. It was reduced then with lithium aluminum hydride (4.95 g.) in ether, inverse addition being employed, to give 10 g. (26%) of 3-chloro-3-phenyl-1-propanol, b.p. 98° (0.08 mm.). The unstable character of this compound made it difficult to purify and impossible to keep. The instability to heat caused it to decompose during careful fractional distillation, so that little material could be obtained other than an unsaturated substance and polymer (mostly the latter). It was purified best by chromatography over activated alumina in benzene solution; removal of the benzene under vacuum at 50° from a freshly chromatographed solution gave a material which had no C=C, C=O or other unexpected infrared bonds. Unfortunately, it was not sufficiently stable to get a satisfactory elemental analysis. Its infrared differed from that of 3-chloro-1-phenyl-1-propanol in the presence of principal bands at 8.22, 9.04, 10.71 and 11.09μ and the absence of such at 8.38, 8.64 and 10.91 μ.

Reaction of Acetyl Chloride with 2-Phenyloxetane.—A solution of acetyl chloride (8.6 g., 0.11 mole) in 45 ml. of benzene was added dropwise to a stirred solution of 2-phenyloxetane (13.4 g., 0.1 mole) in 45 ml. of benzene at 5–10°. The stirring at this temperature was continued for 4 hours and then the mixture was allowed to stand overnight. The reaction mixture was washed with cold water and 5% sodium bicarbonate, dried and distilled, to give 15.9 g. (75%) of a chloroester, b.p. 82–87° (0.03 mm.). Since acid-catalyzed methanolysis of this material had been previously found to give only 17% yield of a chlorohydrin, it was cleaved with lithium aluminum hydride (1.06 g. for 9.5 g. of ester, inverse addition used). After the usual processing, distillation gave 4.8 g. of a mixture, b.p. 75–93° (0.08 mm.). Infrared spectral analysis showed this to be about 75% 3-phenyl-3-chloro-1-propanol and 25% hydrocinnamyl alcohol; there was no indication of the presence of any 3-chloro-1-phenyl-1-propanol.

MANHATTAN, KANSAS

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[28] C. R. Hauser and D. S. Breslow, *Org. Syntheses*, **21**, 51 (1941).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

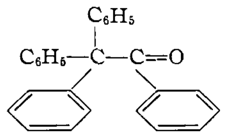
The Action of Phenylmagnesium Bromide on 10,10-Diphenyl-9,10-dihydro-9-phenanthrone[1]

BY REYNOLD C. FUSON AND PAUL TOMBOULIAN[2]

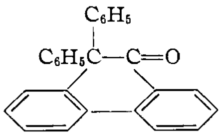
RECEIVED AUGUST 8, 1956

Treatment of 10,10-diphenyl-9,10-dihydro-9-phenanthrone (II) with phenylmagnesium bromide yields products formed by 1,2- and 1,4-addition. The 1,4-adduct undergoes rearrangement to form a phenanthrene derivative. Similar compounds are formed from the *p*-tolyl analog of the phenanthrone II by the action of the *p*-tolyl Grignard reagent.

o-Phenylation of hindered ketones by the action of phenylmagnesium bromide was first realized by Schmidlin and Wohl[3] with β-benzopinacolone (I); it remained, however, for Mosher and Huber,[4] 41 years later, to interpret the experiment correctly. In the meantime a number of similar reactions had been reported.[5] In the hope of finding a more vulnerable ketone we have studied 10,10-diphenyl-9,10-dihydro-9-phenanthrone (II), the closest cyclic analog of β-benzopinacolone. It was expected that the rigidity of the fused ring system might render the phenanthrone more susceptible to nucleophilic attack than the pinacolone.

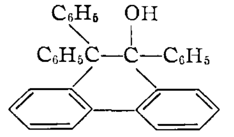


I

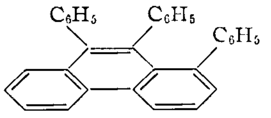


II

When the phenanthrone was treated with phenylmagnesium bromide in anisole at 100°, however, the reaction took an unexpected course. Chromatographic separation of the product furnished an alcohol (13% yield), which proved to be the 1,2-addition product, 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol (III), and a hydrocarbon (24% yield), which was eventually identified as 1,9,10-triphenylphenanthrene (IV).



III



IV

The identity of the alcohol, clearly indicated by its elementary composition and infrared spectrum, was confirmed by comparison with an authentic sample prepared by the condensation of phenyllithium with the phenanthrone according to the method of Mosher and Huber.[4] These authors obtained the alcohol in a yield of 50% by using a reaction time of 2 hr. We found that, by extending this time to 24 hr., the alcohol could be prepared in an 83% yield. This alcohol has been synthesized also by the action of sulfuric acid on *o*-biphenylyl triphenylmethyl ketone.[3,4]

The hydrocarbon had the composition of a triphenylphenanthrene, and only the 1,9,10-isomer IV seemed to be in full agreement with the infrared and ultraviolet spectral data. This structure was confirmed by an independent synthesis. The starting material was 1-phenylphenanthrene (V), prepared by the method of Bachmann and

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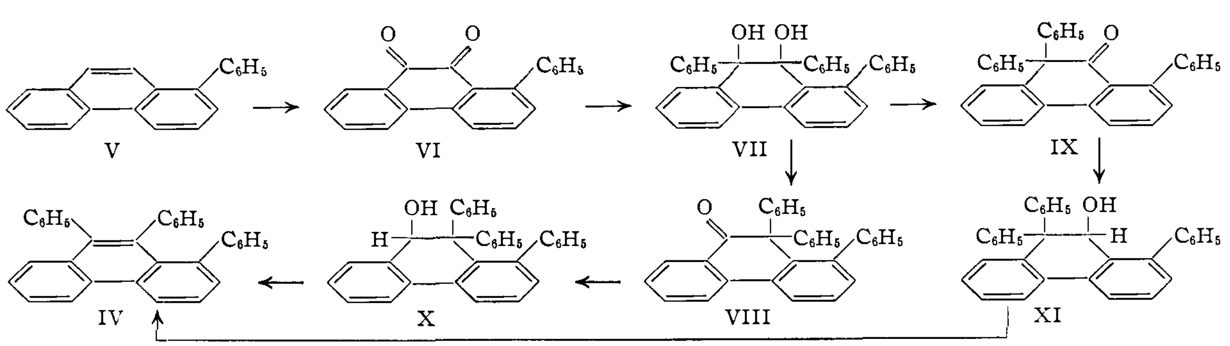
[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] Du Pont Postgraduate Teaching Assistant, 1955–1956.

[3] J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

[4] W. A. Mosher and M. L. Huber, THIS JOURNAL, **73**, 795 (1951).

[5] For references see R. C. Fuson and P. E. Wiegert, *ibid.*, **77**, 1138 (1955).



Wilds.[6] The series of reactions employed parallels that used by Bachmann in the synthesis of 9,10-diphenylphenanthrene from phenanthrene.[7]

1-Phenylphenanthrene was converted to 1-phenyl-9,10-phenanthrenequinone (VI) in 39% yield by the action of chromic acid. Treatment of the *o*-quinone with phenylmagnesium bromide furnished the diol VII, presumably the *trans* isomer. This pinacol, when treated with sulfuric acid in acetic acid, underwent rearrangement to form two isomeric ketones which are assigned the structures VIII and IX. Migration of the phenyl group in preference to the biphenylyl group is expected in the phenanthrenediol series, as demonstrated by the studies of Bachmann.[8,9] Although the two phenanthrones, formed in a ratio of ten to one, differ widely in their physical properties, it has not been established which is the 1,10,10-triphenylated ketone VIII and which the 8,10,10-isomer IX. Reduction of these pinacolones to the corresponding phenanthrols X and XI was effected in high yield by the action of lithium aluminum hydride. Both alcohols were converted to 1,9,10-triphenylphenanthrene (IV) by treatment with iodine in acetic acid.

Evidence that the benzene rings of 1,9,10-triphenylphenanthrene are not coplanar with the phenanthrene nucleus was obtained from the ultraviolet spectrum. The spectrum is very similar to those of 9,10-diphenylphenanthrene and 1-phenylphenanthrene (Fig. 1).

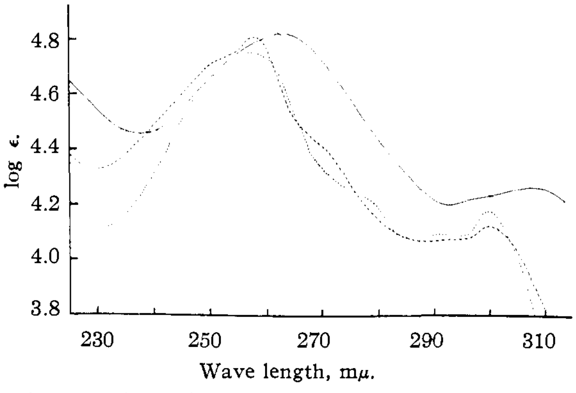


Fig. 1.—Ultraviolet spectra of three arylated phenanthrenes: 1,9,10-triphenylphenanthrene, ———; 9,10-diphenylphenanthrene, - - - -; 1-phenylphenanthrene, ...

Thus in these compounds, little conjugation exists between the aryl substituent and the aromatic nucleus. An examination of a molecular model of the triphenylated hydrocarbon reveals that the benzene rings are perpendicular to the nucleus and that the rings on the 1- and 10-positions are parallel (Fig. 2).

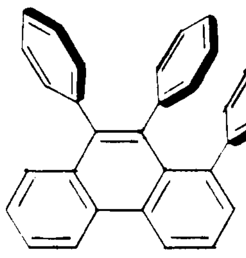
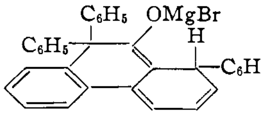
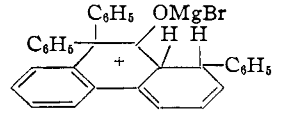


Fig. 2.

The formation of the phenanthrene derivative IV is assumed to occur during the course of the Grignard reaction since the hydrocarbon was isolated in experiments in which very mild hydrolysis and work-up conditions were used. An infrared analysis of a crude reaction product failed to indicate the presence of any components in addition to the phenanthrene IV and the phenanthrol III. Therefore, it is proposed that the initial 1,4 adduct XII may undergo a carbonium ion rearrangement *via* an intermediate such as XIII.



XII



XIII

When 10,10-di-*p*-tolyl-9,10-dihydro-9-phenanthrone was treated with *p*-tolylmagnesium bromide under forcing conditions, products were obtained which are analogous to those formed by the action of the phenyl Grignard reagent on the phenanthrone II. 9,10,10-Tri-*p*-tolyl-9,10-dihydro-9-phenanthrol was obtained in a yield of 11%, and 1,9,10-tri-*p*-tolylphenanthrene was found in 36% yield.

The action of two other Grignard reagents on the ketone II was investigated. A phenanthrene derivative was obtained from the reaction in which the *t*-butyl reagent was employed. On the basis of the combustion, infrared and ultraviolet analyses, as well as the tendency for 1,6-addition with this reagent,[5] the structure 3-*t*-butyl-9,10-diphenylphenanthrene (XIV) is proposed for the adduct. When the phenanthrone II was treated with benzyl-

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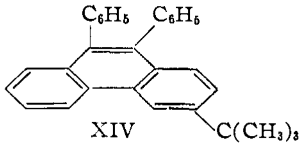
[6] W. E. Bachmann and A. L. Wilds, THIS JOURNAL, **60**, 624 (1938).

[7] W. E. Bachmann, *ibid.*, **55**, 3857 (1933).

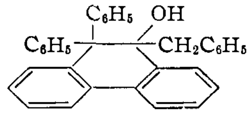
[8] W. E. Bachmann, *ibid.*, **54**, 1969 (1932).

[9] W. E. Bachmann and E. J.-H. Chu, *ibid.*, **57**, 1095 (1935).

magnesium chloride, an alcohol was produced. The spectral and analytical data are consistent with those to be expected for the 1,2-addition compound, 9-benzyl-10,10-diphenyl-9,10-dihydro-9-phenanthrol (XV).



XIV



XV

Experimental[10]

9,10-Phenanthrenequinone.—This method was developed by modification of an analytic procedure for the determination of phenanthrene.[11]

Ten grams (0.056 mole) of Eastman Kodak Co. White Label phenanthrene was dissolved in 350 ml. of warm acetic acid in a flask fitted with a distillation head. The solution was heated almost to the boiling point and a solution of 10 g. of iodic acid in 40 ml. of water was added slowly. The iodic acid precipitated and the mixture turned orange, then purple as iodine was liberated. The distillation set-up was found to be the most convenient for removal of the iodine. The mixture was heated at such a rate that 100 ml. of distillate was collected per hour. An additional 100 ml. of acetic acid was added during the course of the 2.5-hr. distillation. The yield of iodine corresponded to about 75% conversion of phenanthrene to the quinone. The hot mixture was poured into 400 ml. of water and allowed to stand for 0.5 hr. in the cold. The powdery orange product was collected on a filter and washed with sodium carbonate solution, sodium thiosulfate solution and water. The crude quinone was dried in an oven at 100°, dissolved in 100 ml. of chloroform and treated with Darco. The solution was taken to dryness, and the orange crystalline residue was washed with small portions of a cyclohexane–ether mixture; yield 7.40 g. (63%), m.p. 202–204°.

10,10-Diphenyl-9,10-dihydro-9-phenanthrone (II).[9]—*trans*-9,10-Diphenyl-9,10-dihydro-9,10-phenanthrenediol was prepared from phenanthrenequinone by the action of phenylmagnesium bromide. Conversion of the diol to the ketone II was effected by a 0.2% acetic acid solution of iodine. The infrared spectrum[12] of the phenanthrone contains absorption bands attributed to an aromatic ketone (1687, 1265 cm.$^{-1}$), to monosubstituted benzene (752, 697 cm.$^{-1}$) and to *o*-disubstituted benzene (741 cm.$^{-1}$).

Treatment of 10,10-Diphenyl-9,10-dihydro-9-phenanthrone with Phenylmagnesium Bromide at 100°.—To a Grignard reagent prepared from 4.0 ml. (0.038 mole) of bromobenzene, 1.00 g. (0.042 g. atom) of magnesium and 30 ml. of ether was added a solution of 2.70 g. (0.0078 mole) of 10,10-diphenyl-9,10-dihydro-9-phenanthrone in 40 ml. of anisole. The temperature of the reaction mixture was gradually raised to 100° by allowing the ether to distil; anisole was added until the volume of the mixture was about 80 ml. After 14 hr. of reflux at 100°, the brown mixture was hydrolyzed with a saturated ammonium chloride solution. An infrared spectrum of the residue obtained after removal of the solvent exhibited weak alcohol absorption and no carbonyl absorption. Because purification of the reaction product could not be accomplished by crystallization, chromatography on alumina was employed. By combination and crystallization of fractions, two compounds were obtained. The first, 1,9,10-triphenylphenanthrene (IV), crystallized from ethanol in fluffy leaflets, yield 0.75 g. (24%), m.p. 184–186°. An analytical sample melted at 188–189°.

Anal.[13] Calcd. for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.42; H, 5.45.

The infrared spectrum of this phenanthrene contains absorption bands assignable to *o*-disubstituted (757 cm.$^{-1}$) and monosubstituted (749, 693 cm.$^{-1}$) benzene rings. The vicinal-trisubstituted benzene band also occurs at 757 cm.$^{-1}$, since no strong absorption bands above 757 cm.$^{-1}$ are present. No aliphatic C–H absorption bands are present. The ultraviolet spectrum[14] exhibits maxima at 263 mμ (log ε 4.82) and 307 mμ (log ε 4.26).

The second solid, 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol (III), obtained in the later fractions of the chromatography, was crystallized from a benzene–ethanol mixture; yield 0.42 g. (13%), m.p. 229–232°. A sample purified for analysis melted at 232–233°.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.69; H, 5.58.

The infrared spectrum exhibits tertiary alcohol absorption (3550, 1335, 1171, 1158 cm.$^{-1}$), *o*-disubstituted and monosubstituted benzene absorption bands. No aliphatic C–H absorption is present.

Variations of the reaction procedure such as hydrochloric acid hydrolysis or the use of a nitrogen atmosphere during the reaction and work-up had no effect on the nature of the products obtained from the reaction. No other crystalline compounds were obtained from the chromatographic analysis.

Treatment of 10,10-Diphenyl-9,10-dihydro-9-phenanthrone with Phenylmagnesium Bromide at 56°.—A Grignard reagent prepared from 5.2 ml. (0.050 mole) of bromobenzene and 1.20 g. (0.050 g. atom) of magnesium in 40 ml. of ether was heated under reflux for 1 hr. before a solution of 3.46 g. (0.0100 mole) of the ketone in 40 ml. of benzene was added. The temperature of the green mixture was raised to 56° and maintained there for 5 hr. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution. The solvent was evaporated from the organic layer, but because the red-brown residue (4.84 g.) could not be crystallized, it was subjected to chromatography. Elution with a cyclohexane–benzene mixture yielded 0.80 g. of solid, m.p. 225–231°, which was found to be 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol (III). One crystallization from benzene–ethanol furnished 0.58 g. (14%) of the pure phenanthrol, m.p. 232–234°. The orange oils obtained from the other fractions of the chromatography could not be crystallized from any of the common solvents. From the infrared analyses of two fractions, it is apparent that a number of compounds are present, but there are no absorption bands characteristic of the hydrocarbon obtained in the high-temperature experiment. There are at least two ketonic components present, with absorptions at 1707 and 1668 cm.$^{-1}$, but absorption characteristic of the starting material (1687 cm.$^{-1}$) is absent; a broad hydroxyl band is present.

None of the phenanthrene could be obtained from the ketonic residue by treatment with either magnesium bromide etherate or phenylmagnesium bromide in anisole at 110° for 14 hr. The alcohol III also was found to be unaffected by phenylmagnesium bromide in anisole at 110° for 9 hr.

9,10,10-Triphenyl-9,10-dihydro-9-phenanthrol (III).—This alcohol was prepared by treatment of the phenanthrone II with phenyllithium, according to a procedure adapted from that of Mosher and Huber.[4] A benzene solution of 1.00 g. (0.0029 mole) of the ketone was added to a ten-fold excess of the lithium reagent.[15] The dark gray reaction mixture was heated at the reflux temperature for 24 hr. in an atmosphere of nitrogen before hydrolysis was effected by use of dilute hydrochloric acid. After removal of the solvent, the yellow semi-solid was washed with a mixture of ether and petroleum ether; yield 1.15 g. (94%), m.p. 225–230°. Crystallization of the crude alcohol from benzene–ethanol afforded 1.02 g. (83%) of colorless square prisms, m.p. 232–233° (reported[4] 231.5–232.5°).

This alcohol (III) was shown to be identical with the alcohol obtained from the Grignard reactions by comparison of the infrared spectra and by the method of mixture melting points.

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[10] All melting points are corrected.

[11] A. G. Williams, THIS JOURNAL, **43**, 1911 (1921).

[12] The infrared spectra were determined by Mr. James Brader and Mrs. Louise Griffing. The spectra were obtained from a Perkin-Elmer model 21 spectrophotometer and were measured in carbon disulfide solution unless otherwise specified. All wave numbers are corrected.

[13] The microanalyses were performed by Mr. Joseph Nemeth, Mrs. R. Maria Benassi, Mrs. Lucy Chang, Mrs. Ruby Ju and Mr. Rollo Nesset.

[14] The ultraviolet spectra were obtained from a Cary model 11 recording spectrophotometer by Miss Gerardine Meerman. The spectra were measured in 1-cm. quartz cells at concentrations of about 2×10^{-5} *M* in cyclohexane.

[15] R. B. Woodward and E. C. Kornfeld, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. III, 1955, p. 413.

1-Phenylphenanthrene (V).—This hydrocarbon was prepared from 1,2,3,4-tetrahydro-1-phenanthrone[16] in the manner described by Bachmann and Wilds.[6] The compound melted at 80–81° (reported[6] 79–79.5°). The picrate derivative melted at 118–118.5° (reported[6] 117–117.5°).

The infrared spectrum contains absorption bands characteristic of four types of substituted benzene rings: 1,2,3,4-tetrasubstituted benzene (807 cm.$^{-1}$), vicinal-trisubstituted benzene (765 cm.$^{-1}$), *o*-disubstituted benzene (751 cm.$^{-1}$) and monosubstituted benzene (702 cm.$^{-1}$). The ultraviolet spectrum exhibits two absorption maxima: 257 mμ (log ϵ 4.74) and 299 mμ (log ϵ 4.15).

1-Phenyl-9,10-phenanthrenequinone (VI).—To a solution of 31.5 g. (0.124 mole) of crude 1-phenylphenanthrene dissolved in 250 ml. of acetic acid was added slowly a solution of 40 g. of chromic acid in 40 ml. of water. Boiling started spontaneously and the mixture was heated under reflux for 30 minutes. After addition of 120 ml. of water, the hot reaction mixture was allowed to cool before it was poured into an additional 300 ml. of water. The crude orange product weighed 28.5 g. and was crystallized from ethyl acetate to yield 13.8 g. (39%) of bright orange crystals, m.p. 229–232°. An analytical sample melted at 230.5–231.5°.

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25. Found: C, 84.36; H, 4.29.

The infrared spectrum (Nujol) of this compound shows an intense absorption band in the carbonyl region (1665 cm.$^{-1}$) as well as absorption characteristic of a monosubstituted benzene ring (698 cm.$^{-1}$).

The phenazine derivative was prepared by heating a solution of the *o*-quinone and *o*-phenylenediamine in acetic acid for a few minutes. The derivative crystallized from ethanol in pale yellow needles, m.p. 196.5–197°. After vacuum sublimation, the phenazine melted at 197–197.5°.

Anal. Calcd. for $C_{26}H_{16}N_2$: C, 87.61; H, 4.53; N, 7.86. Found: C, 87.78; H, 4.54; N, 7.91.

The infrared spectrum (Nujol) is consistent with the structure proposed for the derivative.

1,9,10-Triphenyl-9,10-dihydro-9,10-phenanthrenediol (VII).—To a Grignard reagent prepared from 42 ml. (0.40 mole) of bromobenzene, 9.6 g. (0.40 g. atom) of magnesium and 150 ml. of ether was added a solution of 10.6 g. (0.037 mole) of 1-phenyl-9,10-phenanthrenequinone in 250 ml. of benzene. The reaction mixture was heated at the reflux temperature (63°) for 4.5 hr. before hydrolysis was effected with a dilute hydrochloric acid–ice mixture. The organic layer was removed and concentrated. Treatment of the residue with ethanol–benzene yielded 8.8 g. (54%) of a crystalline substance (m.p. 226–236°). The red tarry residue was subjected to chromatography, but no additional product could be obtained. After crystallization from benzene, the glycol melted at 238–239°.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 87.16; H, 5.72.

The infrared spectrum contains bands characteristic of a tertiary alcohol (3650, 1340, 1188 cm.$^{-1}$) and a band at 765 cm.$^{-1}$ assigned to a vicinal-trisubstituted benzene ring.

1,10,10- (VIII) and 8,10,10-Triphenyl-9,10-dihydro-9-phenanthrone (IX).—The usual aryl pinacol rearrangement conditions (iodine in refluxing acetic acid) were ineffective in the transformation of 1,9,10-triphenyl-9,10-dihydro-9,10-phenanthrenediol (VII) to the pinacolones. More vigorous conditions, however, did cause rearrangement.

A solution of 7.1 g. (0.016 mole) of the crude glycol VII (m.p. 226–236°) in 2 ml. of sulfuric acid and 80 ml. of acetic acid was heated under reflux for 45 minutes. The cooled reaction mixture was poured into water and the precipitate was collected on a filter. A benzene solution of the product was treated with decolorizing charcoal and concentrated to furnish 6.4 g. of a pink solid. The amorphous solid was subjected to chromatography from which two crystalline substances were isolated. By combination of the early fractions, 5.48 g. (81%) of ketone XVI (m.p. 146–156°) was obtained. The later fractions yielded 0.52 g. (8.2%) of ketone XVII (m.p. 246–261°). After crystallization from ethanol, the compound XVI melted at 155–156°. The compound XVII was crystallized twice from benzene, since it is very insoluble in ethanol. The small prisms melted at 267.5–268°.

Anal. Calcd. for $C_{32}H_{22}O$: C, 90.96; H, 5.25. Found (XVI): C, 90.78; H, 5.32. Found (XVII): C, 90.64; H, 5.24.

The infrared spectrum (chloroform) of the low-melting phenanthrone XVI exhibits ketone absorption at 1695 cm.$^{-1}$. The corresponding absorption in the spectrum (chloroform) of the high-melting ketone XVII occurs at 1682 cm.$^{-1}$. The latter spectrum contains two absorption bands (1294, 1268 cm.$^{-1}$) which are absent from the spectrum of the ketone XVI.

1,10,10- (X) and 8,10,10-Triphenyl-9,10-dihydro-9-phenanthrol (XI).—A mixture of 0.20 g. (0.00047 mole) of phenanthrone XVI and 0.100 g. (0.0026 mole) of lithium aluminum hydride in 20 ml. of ether was heated at the reflux temperature for 1 hr. Ethyl acetate followed by dilute hydrochloric acid was added to decompose the reaction mixture. The hydrolysis mixture was extracted with benzene and the benzene extract was concentrated to furnish 0.19 g. (95%) of the phenanthrol. After crystallization of the crude alcohol (m.p. 188–193°) from ethanol–benzene, the melting point was 190–191°.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.69; H, 5.90.

The infrared spectrum contains absorption typical of a secondary alcohol: 3580, 2855, 1387 and 1185 cm.$^{-1}$.

The reduction of the isomeric high-melting ketone XVII was accomplished in the same manner. The yield was 93% and the product melted at 158–162°. A sample purified for combustion analysis by crystallization from ethanol and from benzene–cyclohexane melted at 163–164°.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.10, 90.00; H, 6.07, 5.86.

Secondary alcohol absorption is present in the infrared spectrum: 3660, 2840, 1392 and 1197 cm.$^{-1}$.

1,9,10-Triphenylphenanthrene (IV).—A solution of 0.19 g. (0.00045 mole) of the high-melting (m.p. 190–191°) alcohol in 10 ml. of a 0.3% acetic acid solution of iodine was heated under reflux for 1 hr. A few milliliters of an aqueous ethanolic solution of sodium bisulfite was added, and the mixture was allowed to stand. The crystalline precipitate was collected on a filter; yield 0.17 g. (94%), m.p. 187.5–188°.

A solution of 85 mg. (0.00020 mole) of the low-melting (m.p. 163–164°) alcohol in 3 ml. of a 0.3% acetic acid solution of iodine was heated at the reflux temperature for 1.5 hr. The iodine color was discharged by the addition of a few milligrams of sodium bisulfite, and 2 ml. of ethanol was added to precipitate the product, which was collected on a filter; yield 75 mg. (92%), m.p. 187–188°.

The infrared spectra of these two products are identical and may be superimposed on the spectrum of the phenanthrene IV obtained from the reaction of the phenanthrone II with phenylmagnesium bromide at 100° (see above). A number of mixture melting point determinations were made with the Grignard reaction product; in every case the melting point was 187–188°.

Treatment of 10,10-Di-*p*-tolyl-9,10-dihydro-9-phenanthrone with *p*-Tolylmagnesium Bromide at 100°.—*p*-Tolylmagnesium bromide was prepared from 8.6 ml. (0.070 mole) of *p*-bromotoluene, 1.68 g. (0.070 g. atom) of magnesium and 30 ml. of ether. To this reagent a solution of 3.74 g. (0.0100 mole) of the phenanthrone[8] in 60 ml. of anisole was added. The temperature of the red reaction mixture was raised to 100° and maintained there throughout the reaction period of 15 hr. The cooled contents of the flask were added to a saturated solution of ammonium chloride. Evaporation of the solvent from the organic layer yielded 5.26 g. of yellow-brown semi-solid. The only functional group indicated by the infrared analysis of this semi-solid was the hydroxyl group. The amount present, however, was estimated at less than 20%. Separation of the mixture was attempted by crystallization, but little purification of the crude reaction product could be effected. All the solids and mother liquors were combined and the mixture was subjected to chromatography. The first of the two solid products isolated appeared in the early fractions. Crystallization from ethanol–benzene furnished 1.33 g. (30%) of fluffy leaflets, m.p. 195–197°. A sample of the 1,9,10-tri-*p*-tolylphenanthrene purified for analysis melted at 196.5–197°.

Anal. Calcd. for $C_{35}H_{28}$: C, 93.71; H, 6.29. Found: C, 93.28, 93.60; H, 6.36, 6.16.

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[16] W. E. Bachmann, W. Cole and A. L. Wilds, THIS JOURNAL, **62**, 824 (1940).

Two maxima are found in the ultraviolet spectrum: 264 mμ (log ε 4.74) and 308 mμ (log ε 4.19). The infrared spectrum exhibits *p*-disubstituted benzene absorption bands at 824 and 811 cm.$^{-1}$. Other aromatic bands occur at 798, 762, 757 and 748 cm.$^{-1}$. Absorption associated with the methyl group is found at 2905, 2845, 1386 and 1376 cm.$^{-1}$, but no functional group absorption is present.

The second solid isolated from the chromatographic separation was crystallized twice from ethanol–benzene; yield 0.43 g. (11%), m.p. 256–259°. Two additional crystallizations furnished an analytical sample of 9,10,10-tri-*p*-tolyl-9,10-dihydro-9-phenanthrol, m.p. 260–261°.

Anal. Calcd. for $C_{35}H_{30}O$: C, 90.09; H, 6.48. Found: C, 90.08; H, 6.77.

The infrared spectrum contains absorption assigned to a tertiary alcohol (3560, 1334, 1173, 1159 cm.$^{-1}$). The spectrum is very similar to that of the phenanthrol III except for bands attributable to the methyl groups.

Treatment of 10,10-Diphenyl-9,10-dihydro-9-phenanthrone with *t*-Butylmagnesium Chloride at 110°.—To the Grignard reagent prepared from 10.0 ml. (0.092 mole) of *t*-butyl chloride, 2.00 g. (0.083 g. atom) of magnesium and 50 ml. of ether was added a suspension of 3.46 g. (0.0100 mole) of the phenanthrone II in 40 ml. of anisole. The temperature of the mixture was adjusted to 110° and the volume to 80 ml. by distillation of the ether and addition of anisole. The green reaction mixture was heated at 110° for 24 hr. A stream of dry air then was passed over the hot mixture for 0.5 hr.; this reduced the volume in the reaction flask to 40 ml. A saturated ammonium chloride solution was introduced into the flask to effect hydrolysis. Following the addition of benzene to this mixture, the organic layer was removed, dried over sodium carbonate and concentrated. The infrared analysis of the red-brown semisolid residue (4.92 g.) indicated that less than 10% of any ketonic material was present. Treatment of this residue with 15 ml. of ethanol caused separation of a white solid (1.62 g., m.p. 233–239°) from the red oil. After crystallization from ethanol–benzene, the compound melted at 238–243°, yield 1.40 g. (36%). An analytical sample of the 3-*t*-butyl-9,10-diphenylphenanthrene (XIV) in the form of fine needles, m.p. 242–243°, was obtained by two additional crystallizations.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.63; H, 6.86.

The infrared spectrum exhibits no absorption assignable to a functional group. Absorption characteristic of the *t*-butyl group occurs at 2950, 1407 and 1358 cm.$^{-1}$. Absorption assignable to a 1,2,4-trisubstituted benzene ring is found at 878 cm.$^{-1}$ (weak) and 829 cm.$^{-1}$ (strong). In addition, bands associated with *o*-disubstituted and monosubstituted benzene rings are present. Two maxima appear in the ultraviolet spectrum: 260 and 305 mμ, for which the log ε values are 4.82 and 4.17, respectively.

When this Grignard reaction was carried out at 60°, no solid product was obtained, even after an attempted chromatographic separation of the reaction mixture.

Treatment of 10,10-Diphenyl-9,10-dihydro-9-phenanthrone with Benzylmagnesium Chloride.—A solution of 3.46 g. (0.0100 mole) of 10,10-diphenyl-9,10-dihydro-9-phenanthrone (II) in 50 ml. of benzene was added to the Grignard reagent prepared from 5.7 ml. (0.050 mole) of benzyl chloride and 1.20 g. (0.050 g. atom) of magnesium in 50 ml. of ether. The pale gray-green mixture was stirred and heated for 14 hr. at 70° before being hydrolyzed with a saturated ammonium chloride solution. Following addition of chloroform to the hydrolysis mixture, the organic layer was removed, dried over sodium carbonate and concentrated. Bibenzyl was sublimed from the crude yellow solid by heating on a steam-plate. The product weighed 4.33 g., m.p. 226–236°, with previous sintering. After crystallization from benzene, the 9-benzyl-9,10-diphenyl-9,10-dihydro-9-phenanthrol (XV) melted at 236–237°, yield 4.06 g. (94%).

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.37; H, 5.97. Found: C, 90.47; H, 6.29.

The infrared spectrum exhibits absorption assigned to a tertiary alcohol (3565, 1368, 1195 cm.$^{-1}$) and a methylene group (2955, 2935 cm.$^{-1}$). The characteristic 2840 cm.$^{-1}$ C–H absorption associated with a secondary alcohol is absent.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. I. 1,4-Pentadiene, 3-Phenylpropene and 3-Phenylcylohexene by Amine Oxide Pyrolysis[1]

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Thermal decomposition of the oxides of penten-5-yldimethylamine and 3-phenylpropyldimethylamine has been found to give 1,4-pentadiene (61%) and 3-phenylpropene (91%), respectively. Application of the Hofmann exhaustive methylation procedure to 3-phenylpropyldimethylamine yielded a mixture of olefins which vapor-phase chromatography indicated was *trans*-1-phenylpropene containing small amounts of *cis*-1-phenylpropene and 3-phenylpropene. *trans*-2-Phenylcyclohexyldimethylamine oxide on heating yielded a mixture (96%) consisting of 85% 1-phenylcyclohexene and 15% 3-phenylcyclohexene. The isomeric *cis*-amine oxide gave a mixture (72%) composed of 98% 3-phenylcyclohexene and 2% 1-phenylcyclohexene. *cis*-2-Phenylcyclohexyldimethylamine has been prepared from *cis*-2-phenylcyclohexylamine by a procedure that is more stereospecific than methylation with formic acid and formaldehyde. The primary amine was methylated with methyl iodide to form *cis*-2-phenylcyclohexyltrimethylammonium iodide, which on treatment with lithium aluminum hydride formed the tertiary amine.

Thermal decomposition of a number of alkyldimethylamine oxides previously has been shown to yield olefins by intramolecular *cis* elimination of N,N-dimethylhydroxylamine.[3,4] Although this reaction resembles the Hofmann exhaustive methylation,[5] pyrolysis of amine oxides also may be compared with ester and xanthate pyrolyses.[6] Application of the Hofmann exhaustive methylation procedure to certain amines, for example, to N-methylpiperidine[7] and to 3-phenylpropyldimethylamine[8,9] has been reported to yield conjugated olefins resulting from base-catalyzed isomerization of

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[2] United States Rubber Co. Fellow, 1954–1955.

[3] A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

[4] D. J. Cram and J. E. McCarty, *ibid.*, **76**, 5740 (1954).

[5] W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

[6] E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810 (1950).

[7] A. W. Hofmann, *Ber.*, **14**, 659 (1881).

[8] L. Senfter and J. Tafel, *ibid.*, **27**, 2309 (1894).

[9] J. Weinstock, *J. Org. Chem.*, **21**, 540 (1956).