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FRIEDEL-CRAFTS REACTION INVOLVING UNSATURATED KETONES AND ESTERS. I. NEW SYNTHESES OF 1-METHYL-1,4-DIMETHYL-, AND 9-METHYL-PHENANTHRENE[1]

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It has been recently demonstrated by Colonge and Pichat (1) that the aluminum chloride-catalyzed reaction between benzene and allylacetone leads to the formation of 2-phenylhexan-5-one in excellent yield. Similarly toluene reacts with allylacetone to give 2-*p*-tolylhexan-5-one. The proof of the structures of the products was obtained through hypobromite oxidation to the corresponding acids and through syntheses of naphthalene homologs from the Friedel-Crafts condensation products (2). Somewhat parallel observations were previously made by Brochet (3) who obtained a satisfactory yield of 2-phenylhexane by reacting benzene and 1-hexene in presence of sulphuric acid as the catalyst. It appears, therefore, that the +E ketonic group in allylacetone has no bearing on the course of the cationotropic reactions.

An examination of the structures of the above products obtained by Colonge and Pichat (1) would suggest a possibility of a development of a convenient and elegant method for the synthesis of polynuclear aromatic and hydroaromatic systems. Following this idea the synthesis of 1,4-dimethylnaphthalene (2) was fully corroborated in this laboratory (4).

This method was then extended to a synthesis of 1,4-dimethylphenanthrene with naphthalene as the starting material. Naphthalene in carbon disulphide solution reacted smoothly with allylacetone in the presence of aluminum chloride to give 2-(β-naphthyl)hexan-5-one. The formation of binaphthyl (6) which might arise due to the high reactivity of the aromatic substrate towards aluminum chloride was obviated by using a dilute solution of naphthalene in carbon disulphide. The product, 2-(β-naphthyl)hexan-5-one (I), was reduced to the corresponding carbinol (II) through the Pondorff method. The sodium and moist ether method was avoided, as nuclear reduction by dissolving metals may well be induced in this case. Cyclization of the above alcohol with concentrated sulphuric acid (5) followed by dehydrogenation by palladium-charcoal (30%) (7) gave 1,4-dimethylphenanthrene (IV).

Bardhan and Sengupta (8) claimed to have first synthesized 1,4-dimethylphenanthrene, but the structure of their synthetic product was invalidated by Bogert, *et al.* (9), who suggested that Bardhan and Sengupta's product should in all probability be 1,3-dimethylphenanthrene. Later Bachmann and Edgerton (10) confirmed the physical data for 1,4-dimethylphenanthrene as recorded by Bogert, *et al.* (9). Our results fully agree with the observations of the American workers (9, 10, 11).

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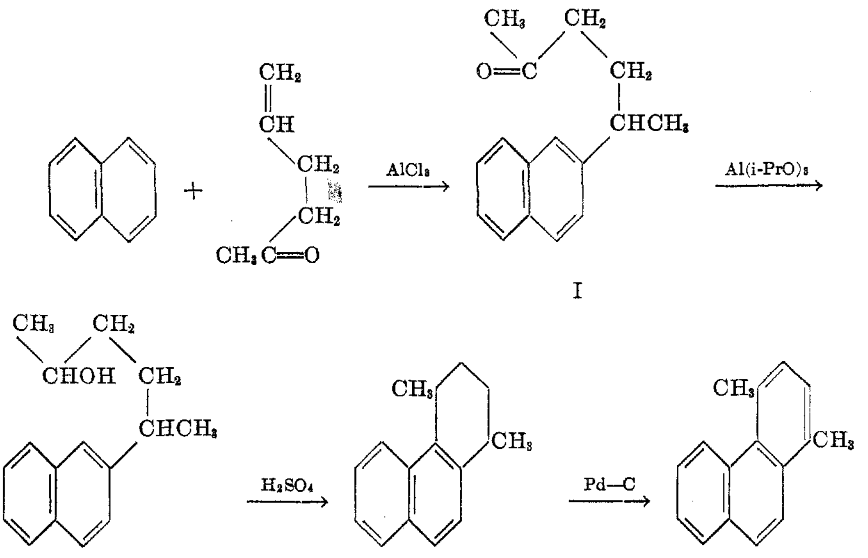


I

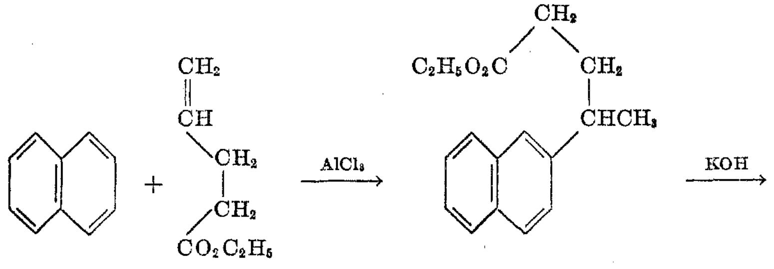
II

III

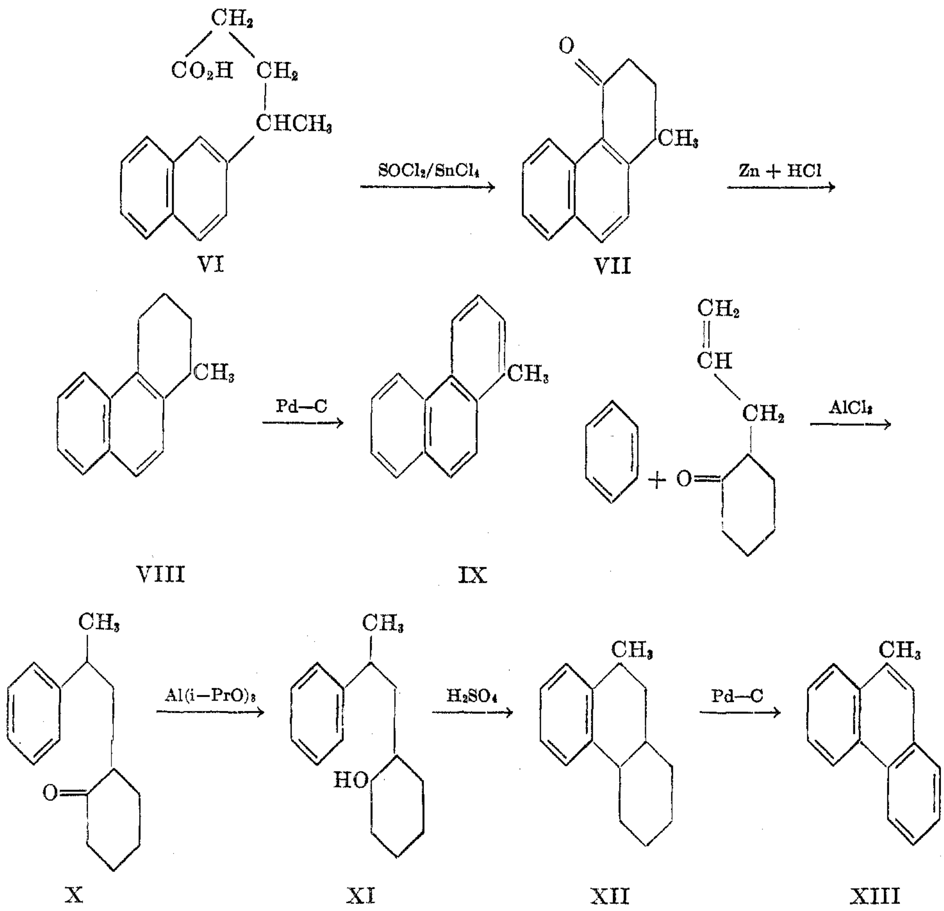
IV

The proof of the structure (I) for the condensation product from naphthalene and allylacetone is based on the following observations: A Friedel-Crafts reaction between naphthalene and ethyl allylacetate in carbon disulphide gave ethyl 4-(β-naphthyl)valerate (V). This ester on hydrolysis gave an acid (VI) which solidified after long standing (about eight weeks) and after crystallization was found to be 4-(β-naphthyl)valeric acid (11). Again, the condensation product (I) from naphthalene and allylacetone on hypoiodite oxidation gave an acid which was found to be identical with VI through the mixture melting point of these acids as well as of their amides.

That the product from naphthalene and ethyl allylacetate is the β-isomer was conclusively proved by converting VI through its acid chloride into 4-keto-1-methyl-1,2,3,4-tetrahydrophenanthrene (VII) (11) in 73% yield. We have not yet been able to isolate any α-isomer of I and V, nor the α-isomers of the compounds obtained in subsequent reactions with our Friedel-Crafts products. This is indeed very important in view of the early findings that the α-isomer is



V



ordinarily the major product in the Friedel-Crafts alkylation of naphthalene in carbon disulphide (18).

The ketone (VII) was smoothly reduced by the Clemmensen method and subsequently dehydrogenated to 1-methylphenanthrene (IX) (11, 12, 13).

By an extension of the above method to benzene and 2-allylcyclohexanone, 2-(β-methyl-β-phenylethyl)cyclohexanone (X) was obtained in excellent yield. This was reduced by aluminum isopropoxide in isopropyl alcohol to yield the corresponding carbinol (XI) which was cyclized with concentrated sulphuric acid (5) and the cyclized product (XII) dehydrogenated with palladium-charcoal (30%) (7) to give 9-methylphenanthrene, whose properties are in full agreement with the hydrocarbon obtained by other authors (16).

Similarly, a number of polycyclic aromatic hydrocarbons (17) and their derivatives which are expected to show carcinogenic activity have been synthesized in this laboratory, and efforts are being made to further extend this method to heterocyclic systems as well.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Analyses marked with an asterisk (*) were by Drs. G. Weiler & F. B. Strauss, Micro-analytical laboratory, Oxford; the others were by one of the authors (N. K. B.).

2-(β-Naphthyl)hexan-5-one (I). Finely powdered commercial naphthalene (26 g.) was placed in a three-necked flask (500 cc.) fitted with a dropping-funnel, a calcium chloride guard tube, a thermometer, and a stirrer. The flask was cooled in an ice water-bath. Carbon disulphide (50 cc., dried over calcium chloride) was poured in the flask and the stirrer started. When the naphthalene dissolved completely, about 10 to 12 g. of finely powdered aluminum chloride, out of the total required quantity of 36 g., was added. As soon as the temperature of the resulting mixture came down to 5°, 20 cc. of allylacetone (prepared by condensing allyl iodide with ethylacetoacetate in the presence of sodium ethoxide in dry benzene and hydrolyzing the product with 10% sodium carbonate solution) dissolved in 10 cc. of carbon disulphide was added dropwise to the cold contents of the flask. The temperature of the mixture increased gradually and a brown color slowly developed. When about one-third of the allylacetone had been added the temperature went up to 12–13°. Addition of allylacetone was stopped at this stage. When the temperature came down to 8° about 6 g. of aluminum chloride was again added, followed by the dropwise addition of allylacetone, maintaining the temperature between 10–15°. The rest of the aluminum chloride was added in portions with controlled temperatures. The contents of the flask slowly turned deep red. The stirring was continued for another 1½ hours and the water was allowed to attain room temperature. The reaction mixture was hydrolyzed with ice-cold hydrochloric acid. The red-colored carbon disulphide layer was separated and the aqueous part was extracted with three 70-cc. portions of ether. The combined extracts in carbon disulphide were washed well once with dilute hydrochloric acid, twice with water, and finally with 5% sodium bicarbonate solution, dried over sodium sulphate, and the solvents were removed. The distillation of the residue afforded 20 g. of a deep red viscous oil (I) boiling at 160–175°/5 mm. This oil was redistilled *in vacuo* when 18 g. (40%) of a light yellow liquid boiling at 168°/5 mm. was obtained. The *semicarbazone*, prepared in the usual way, was crystallized from 90% ethanol, m.p. 166–67°.

*Anal.** Calc'd for $C_{17}H_{21}N_3O$: N, 14.84. Found: N, 14.7.

For analysis of I a small part was redistilled, b.p. 168–169°/5 mm., giving an almost colorless liquid (n_D^{27} 1.5763).

Anal. Calc'd for $C_{16}H_{18}O$: C, 84.96; H, 7.96.
Found: C, 85.10; H, 8.27.

Oxidation of I *with sodium hypoiodite.* The ketone (I; 2 g.) was dissolved in 40 cc. of dioxane; 30 cc. of 10% NaOH solution was added. The mixture was stirred and an iodine solution (prepared in the ratio $KI:I_2:H_2O::2:1:4$) was added with shaking until a dark red color persisted even after warming the mixture on a water-bath at 60° for 2–3 minutes (about 100 cc. of the iodine solution required). The excess of iodine was discharged by a few drops of sodium hydroxide solution, when iodoform separated at the bottom. It was allowed to settle and the aqueous layer was decanted. The residual portion of iodoform and the unconverted ketone were removed by washing the aqueous layer with ether. The aqueous layer was acidified with dilute sulphuric acid and the liberated iodine was reacted with sodium bisulphite. The liberated oil settled at the bottom and it was taken up with ether, once washed with water, and dried over sodium sulphate. After removal of the solvent the residue was sublimed at 200–220° under 4 mm. when a thick liquid was obtained; yield, 1.0 g. It solidified on cooling for a long time (about five weeks) and was crystallized from benzene-petroleum ether (40–60°), m.p. 72°, mixture m.p. with VI (*vide infra*) 71.5°. The *amide* was prepared in the same manner as in the case of VI and crystallized from a large volume of water, m.p. 98°, mixture m.p. with the amide of VI, 97–98°.

2-(β-Naphthyl)hexan-5-ol (II). The ketone (I) (4.62 g.) in 35 cc. of isopropyl alcohol was reduced with aluminum isopropoxide prepared from aluminum (1.62 g.), isopropyl alcohol

(35 cc.), $HgCl_2$ (0.09 g.), and carbon tetrachloride (0.3 cc.) in the usual manner. Distillation of the product at 170° at 3 mm. gave 2-(β-naphthyl)hexan-5-ol (II), a colorless, highly viscous liquid; n_D^{25} 1.5809. Yield, 4.2 g. (93%).

Anal. Calc'd for $C_{16}H_{20}O$: C, 84.21; H, 8.77.
Found: C, 84.73; H, 9.01.

1,4-Dimethyl-1,2,3,4-tetrahydrophenanthrene (III). The alcohol (II) was then cyclized by the method of Bogert, *et al.* (5). Treatment of the alcohol (II, 4 g.) with 4 cc. of conc'd H_2SO_4 (*d.* 1.80) in the cold (5–12°) for 2½ hours gave 1,4-dimethyl-1,2,3,4-tetrahydrophenanthrene (III), a colorless, mobile liquid, b.p. 150°/4 mm.; $n_D^{26.5}$ 1.5926. Yield, 2.5 g. (71%).

Anal. Calc'd for $C_{16}H_{18}$: C, 91.43; H, 8.57.
Found: C, 91.72, H, 9.13.

The *picrate* was prepared in the usual manner and crystallized from ethanol as orange-yellow needles, m.p. 116°.

*Anal.** Calc'd for $C_{16}H_{18}{\cdot}C_6H_3N_3O_7$: N, 9.64. Found: N, 9.95.

1,4-Dimethylphenanthrene (IV). The above product (III) (1 g.) was smoothly dehydrogenated by heating with Pd-C (30%) catalyst (0.1 g.) at 280–290° for 1½ hours and finally at 310° for one hour more. The solid product, thus obtained, after sublimation at 185° at 3 mm., resolidified, m.p. 50°; yield 0.7 g. (71.3%). This was crystallized from ethanol in the cold in fine colorless needles, m.p. 50.5°.

*Anal.** Calc'd for $C_{16}H_{14}$: C, 93.2; H, 6.80.
Found: C, 93.15, H, 6.89.

The *picrate*, prepared in the usual manner (crude m.p. 141–142°), was crystallized as brown-red needles from ethanol, m.p. 143°. Further crystallization failed to raise the m.p. of the substance.

*Anal.** Calc'd for $C_{16}H_{14}{\cdot}C_6H_3N_3O_7$: N, 9.65. Found: N, 9.7.

[*Note:* Lit. (9) reported 50–51° for the m.p. of the hydrocarbon and 143.5° for the picrate. Lit. (10) gave 50–51.5° for the hydrocarbon and 142–143.5° for the picrate.]

Ethyl 4-(β-naphthyl)valerate (V). The aluminum chloride-catalyzed reaction between ethyl allylacetate (15 g.) (prepared through allyl malonate) and naphthalene (15 g.) in 60 cc. of carbon disulphide in the presence of 30 g. of aluminum chloride was carried out by following the conditions applied for the preparation of I. After removal of the solvent the residual liquid was distilled to yield 11 g. of a deep-red viscous liquid (V) at 182–190°/4 mm. For analysis a small part was twice distilled *in vacuo*, giving a light yellow liquid, b.p. 180°/4 mm.; n_D^{24} 1.5587; yield, 40%.

Anal. Calc'd for $C_{17}H_{20}O_2$: C, 79.68; H, 7.8.
Found: C, 79.68; H, 8.09.

4-(β-Naphthyl)valeric acid (VI). Hydrolysis of the above ester (V) (10 g.) with alcoholic potash [prepared from KOH (5 g.), water (3 cc.), and alcohol (110 cc.)] was effected by refluxing for 12 to 13 hours in the usual way; this afforded 7.9 g. of the 2-(β-naphthyl)valeric acid (VI), b.p. 210°/4 mm. Redistillation of the acid under diminished pressure gave 8.5 g. of a light yellow glassy solid, b.p. 210°/4 mm. A portion of this acid (VI) was redistilled to get the analytical sample, when a light yellow, highly viscous liquid, b.p. 210/4 mm., was obtained.

Anal. Calc'd for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02.
Found: C, 78.75; H, 7.16.

Initial attempts to crystallize this acid were not successful. But on standing for a long period (for about eight weeks) the acid solidified and when pressed over a porous tile it gave a fine white solid, m.p. 71°. On crystallization from benzene-petroleum ether (40–60° the melting point rose to 72°. Further crystallization did not raise the m.p.

The *amide* was prepared through the acid chloride (prepared from VI and thionyl chloride) and aqueous ammonia, and was crystallized from a large volume of water, m.p. 98°.

Anal. Calc'd for $C_{15}H_{17}NO$: N, 6.17. Found: N, 6.02.

1-Methyl-4-keto-1,2,3,4-tetrahydrophenanthrene (VII). The mixture of 6 g. of the acid (VI) in 30 cc. of dry ether and 15 drops of dry pyridine was treated with 6 cc. of thionyl chloride. After ½ hour the excess of thionyl chloride and ether was removed under reduced pressure. The residue was dissolved in 60 cc. of dry benzene and treated with 5.5 cc. of stannic chloride. It was allowed to stand for 15 minutes and then hydrolyzed with ice-cold hydrochloric acid. After the usual working up of the mixture with ether, distillation *in vacuo* gave 4 g. (yield, 73%) of 1-methyl-4-keto-1,2,3,4-tetrahydrophenanthrene (VII), b.p. 160°/1 mm. For analysis a small portion was redistilled, when an almost colorless thick liquid, b.p. 160°/1 mm., was obtained.

Anal. Calc'd for $C_{15}H_{14}O$: C, 85.71; H, 6.67.
Found: C, 85.34; H, 7.16.

The *semicarbazone* prepared in the usual way was crystallized from dilute ethanol, m.p. 208° [Lit. (11) m.p. 210–211°]. The *picrate* was prepared in the usual way and crystallized from ethanol in yellow needles, m.p. 92°; further crystallization showed to change in the m.p.

*Anal.** Calc'd for $C_{15}H_{14}O{\cdot}C_6H_3N_3O_7$: N, 9.64. Found: N, 9.8.

1-Methyl-1,2,3,4-tetrahydrophenanthrene (VIII). The ketone (VII) (2.5 g.) was reduced according to Clemmensen's method as used by Bachmann and Edgerton (10) by mixing with amalgamated zinc (25 g.), conc'd HCl (30 cc.), acetic acid (50 cc.), and toluene (10 cc.) and refluxing for 25 hours. The reduced product (VIII) on distillation gave a colorless, mobile liquid, b.p. 130–132°/1 mm.; yield, 2 g. (87%).

Anal. Calc'd for $C_{15}H_{16}$: C, 91.84; H, 8.16.
Found: C, 92.24; H, 8.55.

The *picrate*, prepared in the usual way, was crystallized as orange needles from ethanol, m.p. 102°. After repeated crystallization the melting point remained unchanged.

*Anal.** Calc'd for $C_{15}H_{16}{\cdot}C_6H_3N_3O_7$: N, 9.88. Found: N, 10.10.

1-Methylphenanthrene (IX). The above compound (VIII) (1 g.) was heated with 1 g. of Pd-C (30%) catalyst at 300–320° for 45 minutes. Crystallization of the hydrocarbon, 1-methylphenanthrene (IX), from the solid dehydrogenated product with methanol gave colorless plates, m.p. 118–120°. Yield, 0.73 g. This on further crystallization melted at 121°.

*Anal.** Calc'd for $C_{15}H_{12}$: C, 93.75; H, 6.25.
Found: C, 93.47; H, 6.48.

The *picrate* was prepared in the usual way as deep orange needles, crude m.p. 136°. Crystallization from ethanol raised the m.p. to 138°. Repeated crystallization showed no further rise in the melting point.

*Anal.** Calc'd for $C_{15}H_{12}{\cdot}C_6H_3N_3O_7$: N, 9.98. Found: N, 10.00.

[*Note:* Lit. (12) reported 118° for the melting point of the hydrocarbon and 136° for the picrate, while lit. (13) gives 123° and 139° (corrected) for hydrocarbon and picrate respectively.]

2-(β-Methyl-β-phenylethyl)cyclohexanone (X). (*a*) *Preparation of 2-allylcyclohexanone through the formyl derivative.* The formyl derivative of cyclohexanone was prepared according to the method that Birch and Mukherji (14) employed for the methylation of 3-isopropylcyclohex-2-en-1-one. Cyclohexanone (24 g.) was slowly added through dropping-funnel with stirring and ice-cooling to a mixture of dry sodium ethoxide (from sodium, 6.9 g.) and 200 cc. of dry ether with 21 g. of ethyl formate. A yellow solid immediately formed. The mixture was well shaken and kept overnight. To the orange solid crushed ice and water were added, the dark red aqueous layer was separated, once washed with ether, and acidified with ice-cold hydrochloric acid. The separated oil was taken up with four 50-cc. portions of ether. The ether extracts were combined, washed with water, and dried over Na_2SO_4. The solvent was removed by distillation and the residue on distillation gave a colorless oil, b.p. 63°/5 mm.; yield, 22 g. (70%). (An alcoholic solution of a drop of the liquid gave a deep violet color with ferric chloride solution.)

This oil (22 g.) was added dropwise with swirling to ice-cold dry sodium ethoxide (from sodium, 5.8 g.) in 250 cc. of dry benzene. A yellow solid separated immediately but turned orange on standing. It was thoroughly mixed and kept overnight. Then 37 g. of allyl bromide was slowly added with shaking to the cooled contents of the flask which was allowed to stand for 1½ hours (color gradually fading away), and then refluxed on a water-bath for four hours. The supernatant liquid gave no color with ferric chloride solution. Water was poured in the flask, the benzene layer was separated, and the aqueous layer was extracted twice with benzene. The combined benzene extracts and the main liquid were washed with water and dried over Na_2SO_4. Distillation of the residue after the removal of the solvent yielded a colorless liquid, b.p. 74–85°/5 mm.; yield, 15 g. (50%).

This oil (15 g.) was hydrolyzed by refluxing with 15% NaOH solution (100 cc.) for 2 hours and the hydrolyzate was taken up with ether. Distillation gave a colorless, mobile liquid, (2-allylcyclohexanone), b.p. 72°/8 mm.; yield, 8 g. (64%).

The *semicarbazone* was prepared in the usual way and was crystallized from ethanol, m.p. 171°.

*Anal.** Calc'd for $C_{10}H_{17}N_3O$: N, 21.53. Found: N, 21.10.

The *oxime* was prepared by the usual method and was crystallized from ethanol, m.p. 71° [Lit. (15), m.p. 70–70.5°].

(*b*). This 2-allylcyclohexanone (8 g.) was then subjected to anhydrous aluminum chloride-catalyzed reactions with dry, thiophene-free benzene (60 cc.) in the presence of 12 g. of finely powdered aluminum chloride exactly according to the conditions employed for the preparation of (I) when 6.5 g. of 2-(β-methyl-β-phenylethyl)cyclohexanone (X), boiling at 150°/4 mm., was collected. This ketone on redistillation furnished 6 g. of X, a faint yellow liquid, b.p. 150/4 mm., $n_D^{26.5}$ 1.5261; yield, 48%.

Anal. Calc'd for $C_{15}H_{20}O$: C, 83.33; H, 9.26.
Found: C, 82.75; H, 9.08.

The *semicarbazone* was prepared in the usual way and crystallized from ethanol, m.p. 168–169° (mixture m.p. with the semicarbazone of 2-allylcyclohexanone, 152°).

*Anal.** Calc'd for $C_{16}H_{23}N_3O$: N, 15.38. Found: N, 15.00.

2-(β-Methyl-β-phenylethyl)cyclohexanol (XI). The ketone (X) (4.47 g.) in 35 cc. of dry isopropyl alcohol was reduced with the same amount of aluminum isopropoxide used for the preparation of II. Thus 4 g. of 2-(β-methyl-β-phenylethyl)cyclohexanol (XI), a colorless, viscous oil, $n_D^{26.5}$ 1.5277, was obtained by distillation at 138°/3 mm.; yield, 92%.

Anal. Calc'd for $C_{15}H_{22}O$: C, 82.57; H, 10.09.
Found: C, 83.06; H, 6.89.

9-Methyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (XII). The alcohol (XI) (3 g.) was cyclized with conc'd H_2SO_4 (*d.* 1.80, 3 cc.) as for (III) when 2.1 g. of the octahydrophenanthrene (XII), a colorless, mobile liquid boiling at 112°/5 mm. was obtained; n_D^{25} 1.5399, yield, 76.5%.

Anal. Calc'd for $C_{15}H_{20}$: C, 90.00; H, 10.00.
Found: C, 89.66; H, 10.06.

9-Methylphenanthrene (XIII). The cyclized product (XII) (1 g.) was heated with 0.1 g. of Pd-C (30%) catalyst at 240–290° for 2 hours and 9-methylphenanthrene was crystallized from ethanol as fine colorless needles (0.6 g.), m.p. 94°.

*Anal.** Calc'd for $C_{15}H_{12}$: C, 93.75, H, 6.25.
Found: C, 93.49; H, 6.15.

The *picrate* was prepared by the usual method and was crystallized from ethanol, m.p. 154°.

*Anal.** Calc'd for $C_{15}H_{12} \cdot C_6H_3N_3O_7$: N, 9.97. Found: N, 9.63.

[*Note:* Lit (16) reported m.p. 91–92° for the hydrocarbon and 154° for the picrate.]

Acknowledgement. Our grateful thanks are due to Dr. D. K. Banerjee, Professor of Organic Chemistry, College of Engineering and Technology, Jadavpur, Calcutta, for offering us facilities for macro-analysis of some of the compounds.

SUMMARY

A novel and convenient method of synthesis of phenanthrene derivatives such as 1-methyl-, 1,4-dimethyl-, and 9-methyl-phenanthrene has been described.

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