

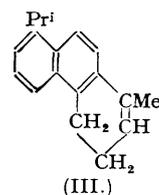
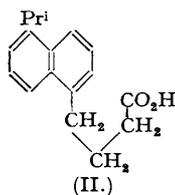
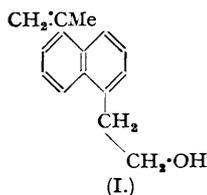
## 204. Syntheses in the Phenanthrene Series. Part XI.\*

## 1-Methyl-8-isopropylphenanthrene.

By W. F. SHORT and H. WANG.

1-Methyl-8-isopropylphenanthrene has been synthesised from 1-naphthoic acid via 5-bromo-1-naphthoic acid,  $\gamma$ -5-isopropyl-1-naphthylbutyric acid, and 1-keto-8-isopropyl-1:2:3:4-tetrahydrophenanthrene. It is identical with the hydrocarbon obtained by the dehydrogenation of totarane.

In attempting the synthesis of 1-methyl-8-isopropylphenanthrene we first prepared 1-bromo-6-isopropenylnaphthalene by the action of acetone on 5-bromo-2-naphthylmagnesium bromide (Fieser and Riegel, *J. Amer. Chem. Soc.*, 1937, 59, 2564) but were unable to obtain an addition product from the unsaturated compound and maleic anhydride. We therefore condensed 1-nitronaphthalene with paraformaldehyde and hydrogen chloride (I.G. Farbenindustrie, B.P. 473,522) and converted the resulting 5-nitro-1-chloromethylnaphthalene into 5-nitro-1-hydroxymethylnaphthalene, 5-nitro-1-naphthaldehyde (Ruggli and Burckhardt, *Helv. Chim. Acta*, 1940, 23, 445), 5-nitro-1-naphthoic acid (Ruggli and Burckhardt, *loc. cit.*), and 5-amino-1-naphthoic acid. Satisfactory conditions for the conversion of the amino-acid into 5-bromo-1-naphthoic acid could not be found, and the bromo-compound was therefore prepared by direct bromination of 1-naphthoic acid (Kerkhof, *Rec. Trav. chim.*, 1932, 51, 747), obtained in 87% yield by the oxidation of 1-naphthyl methyl ketone.



1-Bromo-5-isopropenylnaphthalene, prepared by dehydrating the product of the reaction between methyl 5-bromo-1-naphthoate and methylmagnesium iodide, could not be reduced to the corresponding isopropyl compound owing to preferential removal of the bromine atom. 5-Isopropenyl-1-naphthylmagnesium bromide was therefore brought into reaction with ethylene oxide and the resulting 2-5'-isopropenyl-1'-naphthylethyl alcohol (I) was reduced to 2-5'-isopropyl-1'-naphthylethyl alcohol. The corresponding bromide and ethyl sodiomalonate afforded ethyl 2-5'-isopropyl-1'-naphthylethylmalonate (59%), which was successively hydrolysed to the acid, m. p. 151—152°, and decarboxylated to  $\gamma$ -5-isopropyl-1-naphthylbutyric acid (II), m. p. 120—121°. The acid was dehydrated to 1-keto-8-isopropyl-1:2:3:4-tetrahydrophenanthrene, m. p. 86—87°, by stannic chloride or phosphoric oxide, and the cyclic ketone afforded 1-methyl-8-isopropyl-3:4-dihydrophenanthrene (III), m. p. 72—73°, on successive treatment with methylmagnesium iodide and formic acid. The dihydro-compound was smoothly dehydrogenated by chloranil to 1-methyl-8-isopropylphenanthrene, m. p. 100.5—101°, which is identical with the hydrocarbon obtained by the dehydrogenation of totarane (Short and Stromberg, *J.*, 1937, 519). The consequences of this identity on the structure of totarol are discussed in a forthcoming communication.

## EXPERIMENTAL.

1-Bromo-6-isopropenylnaphthalene.—A mixture of acetone (6 c.c., 1.6 mols.), ether (15 c.c.), and benzene (6 c.c.) was added to a Grignard solution prepared from 1:6-dibromonaphthalene (15 g.) (Fieser and Riegel, *loc. cit.*), magnesium (1.5 g.), ether (60 c.c.), and benzene (12 c.c.), and the mixture was boiled for an hour. The unsaturated bromo-compound (9.4 g., 73%), b. p. 140—170°/2 mm., was isolated in the usual way and a middle fraction, b. p. 160—165°/3 mm., was analysed (Found: Br, 32.1.  $C_{13}H_{11}Br$  requires Br, 32.4%).

5-Nitro-1-chloromethylnaphthalene.—1-Nitronaphthalene (86.5 g.), paraformaldehyde (37.5 g., 0.55 mol.), anhydrous zinc chloride (37.5 g.), and concentrated hydrochloric acid (15 g.) were stirred at 65—70° for 20 hours, a current of hydrogen chloride being passed into the mixture. The product was poured into water, and the solid was then collected, washed with water to neutrality, pressed to remove oily impurities, and recrystallised twice from carbon tetrachloride, giving 5-nitro-1-chloromethylnaphthalene, m. p. 96—98°, in 57% yield. The preparation was repeated several times, using up to 850 g. of nitronaphthalene per batch, and approx. 1 kg. of the chloromethyl compound was prepared, the

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average yield being 54%. The I.G. Farbenindustrie (B.P. 473,522) records m. p. 96—97° and states that the yield is 74%.

**5-Nitro-1-hydroxymethylnaphthalene.**—The chloromethyl compound was suspended in approximately 2N-sodium carbonate (1.8 mols.) and, after being boiled under reflux for 48 hours, the mixture was cooled, and the solid was washed with water and crystallised from chloroform giving *5-nitro-1-hydroxymethylnaphthalene*, m. p. 128—129° (Found: C, 65.2; H, 4.35.  $C_{11}H_9O_3N$  requires C, 65.0; H, 4.4%). The average yield was 65%. **5-Nitro-1-chloromethylnaphthalene** (10 g.), anhydrous sodium acetate (5 g., 1.3 mols.), and acetic anhydride (50 c.c., 11.5 mols.) were boiled for 3 hours and worked up. Crystallisation of the solid from ethanol afforded *5-nitro-1-acetoxymethylnaphthalene* (67%), m. p. 90° (Found: C, 63.2; H, 4.7; N, 6.15, 5.9.  $C_{13}H_{11}O_4N$  requires C, 63.7; H, 4.5; N, 5.7%).

**5-Nitro-1-naphthaldehyde and 5-Nitro-1-naphthoic Acid.**—(a) A solution of chromic anhydride (2.5 g.; equiv. to 1.5 atoms of oxygen) in hot acetic acid (75 c.c.) was added during 1½ hour to a stirred solution of the preceding alcohol (5 g.) in acetic acid (50 c.c.), the temperature being kept at 65—70° during the addition and for an hour subsequently. The solution was concentrated to 15 c.c. below 80°, and the residue was washed with dilute hydrochloric acid and water. Extraction with dilute aqueous sodium carbonate removed 5-nitro-1-naphthoic acid (1.1 g., 21%), m. p. 235—237°, and crystallisation of the residue from chloroform then gave 5-nitro-1-naphthaldehyde (1.3 g., 27%), m. p. 134—136°. The *semicarbazone* had m. p. 301—304° (decomp.) (Found: N, 22.4.  $C_{12}H_9O_3N_4$  requires N, 21.7%). Ruggli and Burckhardt (*loc. cit.*), who nitrated 1-naphthaldehyde, record 136—137° and 236—237° as the m. p. of the nitro-aldehyde and the nitro-acid, respectively, whilst Ekstrand (*J. pr. Chem.*, 1888, **38**, 241) states that the acid has m. p. 239°. When the alcohol (90 g.) was dissolved in acetic acid (900 c.c.) and oxidised at 65—70° with chromic anhydride (75 g.; equiv. to 2.5 atoms of oxygen) in acetic acid (2250 c.c.) no aldehyde was produced and the yield of nitro-acid, m. p. 237—239°, was 51 g. (53%).

(b) When a solution of potassium permanganate (4.3 g.; equiv. to 2.05 atoms of oxygen) in water (100 c.c.) was gradually added to a boiling suspension of 5-nitro-1-chloromethylnaphthalene (4.4 g.) in 17% aqueous sodium hydroxide (100 c.c.; 26 mols.) the product consisted of 5-nitro-1-naphthoic acid (0.9 g., 21%) and 5-nitro-1-hydroxymethylnaphthalene (1.8 g., 44%).

**5-Amino-1-naphthoic Acid.**—The nitro-acid (7.4 g.) was reduced with a solution of ferrous sulphate heptahydrate (67.5 g., 7.1 mols.) in water (225 c.c.) in the presence of concentrated ammonia (150 c.c.), and the crude amino-acid (5.2 g., 82%) was crystallised from ethanol giving *5-amino-1-naphthoic acid* in orange needles, m. p. 201—202° (Found: N, 7.1.  $C_{11}H_9O_2N$  requires N, 7.4%). The *hydrochloride* separated from alcohol in orange needles, m. p. 278—280° (decomp.; rapid heating) (Found: N, 6.2.  $C_{11}H_{10}O_2NCl$  requires N, 6.3%).

**1-Naphthyl Methyl Ketone.**—The ketone was prepared by adding a solution of aluminium chloride and acetyl chloride in ethylene chloride to a solution of naphthalene in ethylene chloride at 30—35° and stirring the solution at this temperature for 2—3 hours, according to Baddeley's general directions (*J.*, 1949, S 99). Pure 1-naphthyl methyl ketone has m. p. 10.5° (Lock, *Monatsh.*, 1943, **74**, 77), and no ketone melting below 0° was employed in the preparation of 1-naphthoic acid. A fraction of the ketone, b. p. 132—134°/2 mm., usually melted in the range 2—4°, whereas a higher fraction, b. p. 134—136°/2 mm., melted in the range —5° to 0° and contained some 2-naphthyl methyl ketone. If the higher-boiling fraction was not rejected some sodium 2-naphthoate separated during the preparation of 1-naphthoic acid (below). When naphthalene, aluminium chloride, and acetyl chloride were employed in the molecular ratio 1 : 2 : 2, 2600 g. of naphthalene afforded 2014 g. (58%) of ketone having m. p. >0°, and when the ratio was 1 : 1.1 : 1.3, 676 g. of naphthalene gave 574 g. (64%) of ketone of this quality. The yield of ketone, b. p. 134—136°/2 mm. was ca. 10%.

**1-Naphthoic Acid.**—1-Naphthyl methyl ketone was oxidised with alkaline sodium hypochlorite essentially according to the method of Fieser, Newman, and Holmes (*J. Amer. Chem. Soc.*, 1936, **58**, 1055. Compare Newman and Holmes, *Org. Synth.*, 1937, **17**, 65; Coll. Vol. II, 1943, 428). A solution 1.6M. with respect to sodium hypochlorite and 0.54N. with respect to sodium hydroxide was prepared from technical sodium hypochlorite solution (2.6—2.8M.), sodium hydroxide and water, and 3125 c.c. of this solution (containing 5 mols. of sodium hypochlorite and 1.7 mols. of sodium hydroxide) were used for the oxidation of 170 g. of the ketone. A large flask is necessary since there is considerable frothing during the liberation of chloroform, and efficient stirring is essential. Metal stirrers should not be used since they cause decomposition of the hypochlorite and promote the formation of chloronaphthoic acid. An exothermic reaction occurred when the mixture was stirred vigorously at 55° and the temperature was maintained at 60—65° by occasionally cooling in ice-water during this phase (40 minutes). The mixture was stirred at 60—65° for another 30 minutes and excess of hypochlorite was then destroyed by adding aqueous sodium hydrogen sulphite. (If the ketone was contaminated with the 2-isomer a little sodium 2-naphthoate separated on cooling the solution.) The solution was acidified with concentrated hydrochloric acid, and the solid was collected, washed with water, and crystallised once from aqueous ethanol. The 1-naphthoic acid had m. p. 149—152° and was sufficiently pure for use in subsequent operations; the pure acid has m. p. 160°. 1500 G. of 1-naphthoic acid were prepared in this way and the average yield was 87%.

**5-Bromo-1-naphthoic Acid.**—An improved yield of this acid was obtained by modifying Kerkhof's method (*loc. cit.*). A solution of 1-naphthoic acid (200 g.) in glacial acetic acid (500 c.c.) was heated on the steam-bath and stirred during the addition of bromine (60 c.c., 1.01 mols.). A yellow solid separated during the addition (1 hour), and, after being heated and stirred for another 1½ hours and kept overnight at room temperature, the solid was crystallised from acetic acid (2000 c.c.). The average yield in the preparation of 920 g. of bromo-acid was 56% and this product, which melted within the range 252—255°, was used in subsequent experiments. Recrystallisation from acetic acid and methanol raised the m. p. to 256—256.5°; Kerkhof (*loc. cit.*) records m. p. 261°, and Ruggli and Preuss (*Helv. Chim. Acta*, 1941, **24**, 1359), m. p. 245—247°. A complex mixture of bromo-acids was precipitated when the filtrates were diluted with water.

**Methyl 5-Bromo-1-naphthoate.**—(a) Methyl sulphate (240 c.c., 4.2 mols.) was slowly added to a stirred solution of the bromo-acid (150 g.) and sodium hydroxide (30 g., 1.25 mols.) in water (600 c.c.) and

methanol (600 c.c.). The mixture was stirred at room temperature for 3 hours, heated to the b. p. on the steam-bath, cooled, and made alkaline with aqueous sodium carbonate. The solid was collected, and unchanged acid (43%), m. p. 251—254°, was recovered from the alkaline solution. After being washed with water and dried, the crude ester (49%) had m. p. 64—65°, and crystallisation from methanol afforded *methyl 5-bromo-1-naphthoate* in needles, m. p. 66—67° (Found: Br, 30.0.  $C_{12}H_9O_2Br$  requires Br, 30.2%). The ester sublimes readily but can be distilled; b. p. 268—274°/215 mm., 170—175°/3.5 mm. (b) When dry powdered potassium 5-bromo-1-naphthoate (5.8 g.) and methyl sulphate (3 c.c., 1.6 mols.) were heated at 200—210° for 1 hour the yield of ester was 3.3 g. (62.5%), but no acid was recovered.

*1-Bromo-5-isopropenylnaphthalene*.—A solution of methyl 5-bromo-1-naphthoate (265 g.) in ether (1200 c.c.) was added during 1½ hours to an ice-cold solution of methylmagnesium iodide (2.4 mols.), prepared from magnesium (57.5 g.), methyl iodide (148 c.c.), and ether (400 c.c.). After being stirred overnight at room temperature and boiled for 1 hour, the complex was decomposed and the crude product was distilled with powdered potassium hydrogen sulphate (50 g.) giving the crude bromonaphthalene, b. p. 140—150°/3—4 mm. The average yield was 54% and there was occasionally a fraction of higher b. p. which solidified on cooling and consisted of unchanged methyl 5-bromo-1-naphthoate (5—10%). A middle fraction, b. p. 138—140°/2 mm., of the *1-bromo-5-isopropenylnaphthalene* was analysed (Found: C, 62.7; H, 4.5.  $C_{15}H_{11}Br$  requires C, 63.1; H, 4.5%). The *picrate* separated from alcohol in yellow needles, m. p. 94—95° (Found: N, 9.0.  $C_{13}H_{11}Br, C_6H_3O_7N_3$  requires N, 8.8%).

*2-5'-isoPropenyl-1'-naphthylethyl Alcohol*.—1-Bromo-5-isopropenylnaphthalene is reluctant to react with magnesium, and when methyl iodide or ethyl bromide was used as entrainer, subsequent reaction with ethylene oxide afforded very low yields of the desired alcohol, and hydrocarbons were produced in considerable quantity, analyses suggesting that bromine had been partly replaced by methyl and ethyl, respectively. When Gilman and Kirby's iodine-activated magnesium (*Rec. Trav. chim.*, 1935, 54, 577) was used, a 43% yield of the alcohol was obtained but it was not possible to use a small amount of this activated magnesium to promote reaction of the halide with ordinary magnesium. Much better results were obtained by using preformed ethylmagnesium bromide as catalyst, the reaction being carried out in an atmosphere of dry nitrogen.

A solution of 1-bromo-5-isopropenylnaphthalene (175 g.) in dry ether (700 c.c.) was added during 4 hours to an ice-cold, stirred suspension of magnesium in ethereal ethylmagnesium bromide prepared from magnesium (36 g., 2.1 atoms), ethyl bromide (52.5 c.c., 1 mol.), and ether (440 c.c.). After the mixture had been stirred overnight and boiled under reflux for 1 hour, it was cooled to 0°, and a 25% (w/v) solution of ethylene oxide in dry benzene (520 c.c.; 4.2 mols.) was introduced during 3 hours. The mixture was then boiled under reflux for an hour, the ether was removed by distillation, and the residue, still containing most of the benzene, was cooled and decomposed with ice-cold dilute hydrochloric acid. The alcohol was purified by distillation, the fraction, b. p. 152—158°/1 mm., being collected (average yield, 74%). *2-5'-isoPropenyl-1'-naphthylethyl alcohol* was a colourless, viscous liquid; a fraction, b. p. 153—154°/1 mm., was analysed (Found: C, 83.4, 83.6; H, 7.3, 7.4.  $C_{15}H_{16}O$  requires C, 84.9; H, 7.55%). *2-5'-isoPropenyl-1'-naphthylethyl p-diphenylcarbamate* crystallised from benzene-light petroleum in colourless needles, m. p. 147—148° (Found: C, 82.3; H, 6.2; N, 3.5.  $C_{28}H_{25}O_2N$  requires C, 82.5; H, 6.15; N, 3.4%). Some of the earlier preparations of the alcohol afforded a small fraction, b. p. 165—220°/2 mm., which solidified and afforded crystals, m. p. 183—184°, after crystallisation from alcohol, probably of 5:5'-*disopropenyl-1:1'-dinaphthyl* (Found: C, 92.7; H, 6.5.  $C_{28}H_{24}$  requires C, 92.9; H, 7.0%).

*2-5'-isoPropyl-1'-naphthylethyl Alcohol*.—The unsaturated alcohol (75 g.) was readily reduced when dissolved in methanol (750 c.c.) and shaken with palladium-stromium carbonate (30 g.; 1.2% Pd) in hydrogen at room temperature and atmospheric pressure. Absorption of hydrogen was complete in 5 hours and the average yield of alcohol, m. p. 60—62°, b. p. 158—164°/1.5 mm., was 74%. *2-5'-isoPropyl-1'-naphthylethyl alcohol* separated from light petroleum (b. p. 40—60°) in cubes, m. p. 63—64° (Found: C, 83.7; H, 8.1.  $C_{15}H_{18}O$  requires C, 84.1; H, 8.4%). *2-5'-isoPropyl-1'-naphthylethyl p-diphenylcarbamate* had m. p. 161° (Found: C, 81.6; 81.8; H, 6.5, 6.55; N, 3.7.  $C_{28}H_{27}O_2N$  requires C, 82.1; H, 6.6; N, 3.4%). and *2-5'-isopropyl-1'-naphthylethyl acetate* had b. p. 164—166°/1 mm., m. p. 33—34° (Found: C, 79.4; H, 7.9.  $C_{17}H_{20}O_2$  requires C, 79.7; H, 7.8%).

*2-5'-isoPropyl-1'-naphthylethyl Bromide*.—Phosphorus tribromide (2.2 c.c., 0.5 mol.) was added to a solution of the alcohol (10 g.) in carbon tetrachloride (10 c.c.) at 50°, and, after being kept at 50—60° for ¼ hour, the solution was poured into ice-water. The *bromide* had b. p. 131—135°/0.2 mm., and separated from light petroleum (b. p. 40—60°) in plates, m. p. 41—42° (Found: C, 65.9, 65.75; H, 6.3, 6.0; Br 29.0.  $C_{15}H_{17}Br$  requires C, 65.0; H, 6.1; Br, 28.9%). The average yield was 50.5%.

*2-5'-isoPropyl-1'-naphthylethylmalonic Acid*.—A solution of ethyl malonate (81 g., 2 mols.) in dry xylene (130 c.c.) was added to a sodium methoxide solution prepared from sodium (7 g., 1.2 atoms) and methanol (100 c.c.), and most of the solvents was removed by distillation under reduced pressure below 80°. A solution of the preceding bromide (70 g.) in xylene (115 c.c.) was then added slowly with stirring, and the temperature was slowly raised to 140—150° (oil-bath). After 16 hours at this temperature the products were isolated; 45% of the ethyl malonate was recovered and the average yield of the substituted malonic ester, b. p. 190—195°/0.5 mm., was 59%. A solution of the malonic ester (10 g.) in methanol (10 c.c.) was added to a solution of potassium hydroxide (8.15 g., 4.4 mols.) in water (10 c.c.), and, when the vigorous reaction had subsided, water (40 c.c.) was added, and the hydrolysis was completed by heating the solution on the steam-bath for 3 hours. The crude malonic acid, m. p. 149—151° (decomp.), was isolated, the average yield being 86%. Recrystallisation of this from acetic acid or benzene afforded *2-5'-isopropyl-1'-naphthylethylmalonic acid* in white plates, m. p. 151—152° (decomp.) (Found: C, 72.3; H, 6.7.  $C_{18}H_{20}O_4$  requires C, 72.0; H, 6.7%).

*γ-5-isoPropyl-1-naphthylbutyric Acid*.—This acid was obtained in 91% yield when the malonic acid was heated at 155—165° for 2 hours and the residue was crystallised from light petroleum (b. p. 60—80°). The pure *acid* crystallised from light petroleum in plates or needles, m. p. 120—121° (Found: C, 78.7, 79.0; H, 7.8, 7.8%; *M*, by titration, 256, 255.  $C_{17}H_{20}O_2$  requires C, 79.7; H, 7.8%; *M*, 256).

1-Keto-8-isopropyl-1 : 2 : 3 : 4-tetrahydrophenanthrene.—(a) The butyric acid (10 g.), phosphoric oxide (50 g., 9 mols.), and benzene (150 c.c.) were heated under reflux for 3 hours, and the product was worked up as described in previous parts of the series. The neutral fraction, b. p. 165—172°/0.3 mm., solidified on cooling giving the crude ketone, m. p. 81—84° (36%), crystallisation of which from light petroleum afforded 1-keto-8-isopropyl-1 : 2 : 3 : 4-tetrahydrophenanthrene in colourless needles, m. p. 86—87° (Found : C, 85.3; H, 7.6.  $C_{17}H_{18}O$  requires C, 85.7; H, 7.6%). The semicarbazone crystallised from alcohol in colourless prisms, m. p. 246—247° (decomp.) (Found : N, 14.2.  $C_{18}H_{21}ON_3$  requires N, 14.2%). The crude ketone isolated from the mother liquors afforded the same semicarbazone, showing that no isomeric ketone is produced in the ring closure. Only a trace of unchanged acid was recovered. (b) A mixture of the butyric acid (3 g.) and stannic chloride (3.9 c.c., 2.8 mols.) was heated at 105—110° for 1½ hours with frequent shaking, cooled, and decomposed with ice-cold dilute hydrochloric acid. After removal of unchanged acid, m. p. 117—119° (15%), the ketone (60%) solidified without distillation and was obtained pure, m. p. and mixed m. p. 86—87°, after one crystallisation from light petroleum.

1-Methyl-8-isopropyl-3 : 4-dihydrophenanthrene.—A solution of the cyclic ketone (5 g.) in ether (70 c.c.) was added at room temperature to a solution of methylmagnesium iodide (3 mols.), prepared from magnesium (1.5 g.), methyl iodide (4.3 c.c.), and ether (50 c.c.), and, after being boiled under reflux for 3 hours, the product was isolated. The dehydration of the crude carbinol was completed by boiling it for ½ hour with 100% formic acid (10 c.c.) and the crude hydrocarbon, b. p. 165—170°/1 mm., was purified by crystallisation from methanol, giving white plates of 1-methyl-8-isopropyl-3 : 4-dihydrophenanthrene (3.3 g.; 67%), m. p. 72—73° (Found : C, 91.5; H, 8.7.  $C_{18}H_{20}$  requires C, 91.5; H, 8.5%).

1-Methyl-8-isopropylphenanthrene.—A solution of the dihydrophenanthrene (1.5 g.) and chloranil (1.57 g., 1 mol.) in sulphur-free xylene (7 c.c.) was boiled under reflux until no colour reaction for chloranil was obtained (20 hours). The solution was cooled to 0° and filtered from tetrachloroquinol, and the filtrate was diluted with ether, washed with 5% aqueous potassium hydroxide, dried ( $MgSO_4$ ), and evaporated. The residue was crystallised several times from methanol (charcoal) giving 1-methyl-8-isopropylphenanthrene (0.4 g.) in white plates, m. p. 100.5—101° (Found : C, 92.0; H, 7.8.  $C_{18}H_{18}$  requires C, 92.3; H, 7.7%). The material recovered from the mother liquors was distilled from sodium under reduced pressure, and the fraction, b. p. 180—185°/2 mm., which solidified on cooling, was crystallised from ethanol giving 0.51 g. of hydrocarbon, m. p. 99—100° (total yield, 61%). The picrate crystallised from alcohol in orange-yellow needles, m. p. 142—142.5° (Found : C, 62.9; H, 4.4; N, 9.25.  $C_{18}H_{18}, C_6H_3O_7, N_3$  requires C, 62.3; H, 4.5; N, 9.1%), and the styphnate in yellow needles, m. p. 152.5—153° (Found : C, 61.2, 61.1; H, 4.5, 4.4; N, 9.0.  $C_{18}H_{18}, C_6H_3O_8, N_3$  requires C, 60.2; H, 4.4; N, 8.8%). Oxidation of the hydrocarbon (0.2 g.) in acetic acid (3 c.c.) with chromic anhydride (0.26 g. in 0.5 c.c. of water and 1.5 c.c. of acetic acid), the mixture being heated finally on the steam-bath for 10 minutes, afforded 1-methyl-8-isopropylphenanthra-9 : 10-quinone which separated from acetic acid in orange rods, m. p. 163.5—164° (Found : C, 81.4; H, 6.1.  $C_{18}H_{16}O_2$  requires C, 81.8; H, 6.1%). A specimen of the quinone was converted into 1'-methyl-4''-isopropyl-1 : 2 : 3 : 4-dibenzphenazine, which crystallised from ethanol-chloroform in pale yellow rods, m. p. 153.5—154° (Found : N, 8.05.  $C_{24}H_{20}N_2$  requires N, 8.3%).

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