

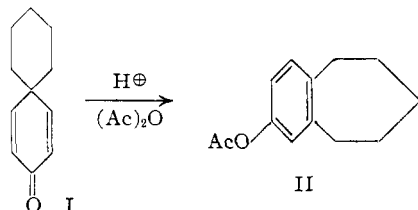
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Dienone-Phenol Rearrangement. IV¹BY S. W. FENTON, R. T. ARNOLD AND H. E. FRITZ²

RECEIVED JUNE 27, 1955

The present work represents an extension of earlier studies in which the dienone-phenol rearrangement is employed to convert spirane derivatives into fused polycyclic compounds. 1,1-Tetramethylene-4-keto-1,4-dihydrophenanthrene has been isomerized to 7,8,9,10-tetrahydro-5-chrysenol, and 4,4-pentamethylene-1-keto-1,4-dihydronaphthalene to 3,4-cyclohepteno-1-naphthol. The latter reaction illustrates a convenient route to certain seven-membered ring compounds.

The recent publication by Burnell and Taylor³ describes the preparation of spiro[5,5]undeca-1,4-dien-3-one (I) and its acid-catalyzed rearrangement in acetic anhydride solution to 2'-acetoxybenzocycloheptane (II)



In the present paper we should like to report two additional examples of dienone-phenol rearrangements one of which is completely analogous to that reported by the English workers in that a new seven-membered ring is formed.

Specifically we have prepared 4,4-pentamethylene-1-keto-1,4-dihydronaphthalene (III) and 1,1-tetramethylene-4-keto-1,4-dihydrophenanthrene (V). These in the presence of acetic anhydride-sulfuric acid at 30° produced spontaneously 3,4-cyclohepteno-1-naphthyl acetate (IV) and 7,8,9,10-tetrahydro-5-chrysenyl acetate (VI).

An abbreviated reaction diagram is given below. This follows the general scheme¹ worked out earlier in this Laboratory.

Several rather orthodox attempts to prove the structure of 3,4-cyclohepteno-1-naphthol (VIII) failed. An independent synthesis of VIII which constitutes a proof of structure was finally achieved. Bromination of 6,6a,7,8,9,10,11,11a-octahydro-5-keto-5H-cyclohepta[a]naphthalene^{4,5} (IX) followed by dehydrobromination gave, as expected, a compound identical with VIII in all respects.

The conversion of 5-acetoxy-7,8,9,10-tetrahydrochrysene (VI) into chrysene (VII) by means of saponification followed by dehydrogenation using palladium-charcoal justifies the formula assigned to VI.

Experimental

Methyl β-(1-Phenyl-2-ketocyclohexyl)-propionate.—2-Phenylcyclohexanone (161 g., 0.925 mole) in dry benzene (200 ml.) was mixed with sodium hydride (1 g.) and the mixture was refluxed for 10 minutes. Freshly distilled methyl acrylate (80 g., 0.93 mole) was added dropwise with

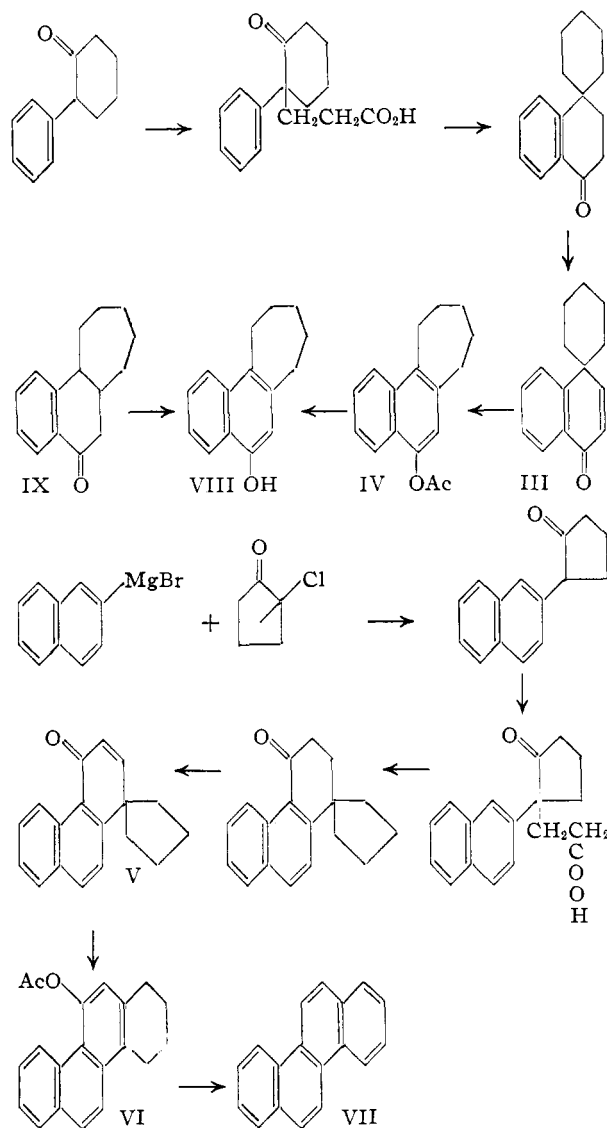
(1) For paper III see R. T. Arnold, J. S. Buckley and R. M. Dodson, *THIS JOURNAL*, **72**, 3153 (1950).

(2) Taken from the Ph.D. thesis of H. E. Fritz submitted to the Faculty, July, 1953.

(3) R. H. Burnell and W. I. Taylor, *J. Chem. Soc.*, 3486 (1954).

(4) C. D. Gutsche, *THIS JOURNAL*, **73**, 786 (1951). We are indebted to Dr. Gutsche of Washington University, St. Louis, Missouri, for a generous sample of this ketone.

(5) D. Ginsburg and R. Pappo, *ibid.*, **75**, 1094 (1953).



stirring during a period of 25 minutes so that a gentle reflux was maintained without external heating. After stirring for two additional hours, the solution was decanted from the residual sodium hydride and washed with five 50-ml. portions of water. The light yellow oil (238 g., 98.9%, n_D^{20} 1.5300) was used directly in the next reaction.

An analytical sample was obtained by distillation: b.p. 160° (0.65 mm.), n_D^{20} 1.5295, n_D^{20} 1.5281.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.98; H, 7.52.

After one year the analytical sample crystallized, but the substance melted from 25 to 51°. Recrystallization of 15 g. of this methyl β-(1-phenyl-2-ketocyclohexyl)-propionate from petroleum ether (15 ml.) gave colorless prisms (8 g.), m.p. 51.5–52.5°.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.90; H, 7.64.

The white semicarbazone was prepared and purified by recrystallization from methanol and ethanol, m.p. 176–177°.

Anal. Calcd. for $C_{17}H_{23}O_3N_3$: C, 64.33; H, 7.32; N, 13.25. Found: C, 64.51; H, 7.52; N, 13.14.

A 2,4-dinitrophenylhydrazone was prepared and recrystallized twice from aqueous methanol and once from methanol. This product was a yellow crystalline solid which melted at 160–161°.

Anal. Calcd. for $C_{22}H_{23}O_6N_4$: C, 59.98; H, 5.50; N, 12.72. Found: C, 60.00; H, 5.57; N, 12.73.

β -(1-Phenylcyclohexyl)-propionic Acid.—A mixture of methyl β -(1-phenyl-2-ketocyclohexyl)-propionate (69 g., 0.265 mole), potassium hydroxide (75 g.), aqueous hydrazine (50 g., 95%) and diethylene glycol (200 ml.) was heated at 123° for two hours. The water and excess hydrazine were distilled very slowly to prevent frothing. In one experiment the reaction evolved nitrogen so rapidly that the entire mixture frothed out of the flask. After 18 hours the temperature was 205°. The mixture was heated under reflux for six hours at this temperature. Water (2 l.) was added, and the ester was hydrolyzed by heating the reaction mixture on a steam-bath for 24 hours. An insoluble silicate was removed by filtration. The filtrate was diluted with water (500 ml.) and acidified with concentrated hydrochloric acid (165 ml.). The precipitated acid was collected and washed with water. The almost white acid (51.4 g., 83.5%) melted at 90–92°. An analytical sample of colorless prisms was obtained by recrystallizing with low recovery twice from ethyl acetate; m.p. 99.5–100.5°.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.70; H, 8.90.

4,4-Pentamethylene-1-keto-1,2,3,4-tetrahydronaphthalene.—A cold, pale yellow solution was obtained when β -(1-phenylcyclohexyl)-propionic acid (23.2 g., 0.1 mole) and thionyl chloride (15 ml.) were mixed. This solution was allowed to stand 24 hours, then the excess thionyl chloride was distilled at room temperature under reduced pressure. To ensure complete removal of the thionyl chloride, anhydrous benzene (20 ml.) was added and this benzene was distilled at room temperature and reduced pressure. Anhydrous benzene (50 ml.) was added and the resulting solution of the acid chloride was cooled in an ice-bath. A solution of stannic chloride (52 g., 0.2 mole) in benzene (20 ml.) was added slowly with stirring. A vigorous reaction resulted with the evolution of heat and the development of a dark brown color. After standing 45 minutes, the solution was treated with ice and hydrochloric acid (50 ml., 10%). The benzene layer was separated, washed once with hydrochloric acid (30 ml., 10%) twice with portions of water (30 ml.), once with sodium hydroxide (30 ml., 5%) and finally five times with water. The solvent was distilled leaving a yellow oil which slowly solidified. 4,4-Pentamethylene-1-keto-1,2,3,4-tetrahydronaphthalene (17.9 g., 83.5%) was obtained as a colorless liquid by distillation through an 8-mm. Vigreux column; b.p. 125–130° (0.25 mm.). This substance crystallized readily, m.p. 64.5–65.5°. An analytical sample obtained by recrystallization from 60–68° petroleum ether melted at 65.5–66°.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.86; H, 8.52.

A semicarbazone was prepared and recrystallized from methanol; m.p. 225–235° with slight decomposition.

Anal. Calcd. for $C_{16}H_{21}ON_3$: C, 70.81; H, 7.80; N, 15.50. Found: C, 71.01; H, 8.11; N, 15.58.

4,4-Pentamethylene-1-keto-2-bromo-1,2,3,4-tetrahydronaphthalene.—4,4-Pentamethylene-1-keto-1,2,3,4-tetrahydronaphthalene (6.9 g., 0.032 mole) was brominated with N-bromosuccinimide (6 g., 0.032 mole) using carbon tetrachloride (40 ml.) as solvent. The colorless reaction mixture was illuminated for two hours with a 100-watt unfrosted incandescent light. In approximately 30 minutes the reaction mixture became colored as if free bromine were present. When the temperature reached approximately 50°, succinimide started to separate on the surface of the reaction mixture. In a previous experiment, azodiisobutyronitrile, $(CH_3)_2C(CN)N=NC(CN)(CH_3)_2$, was added in an attempt to initiate the reaction but no effect was noticed and a slightly lower yield (70%) was obtained. The mix-

ture was allowed to stand two hours. The theoretical amount of succinimide (3.3 g.) was obtained by filtration. The filtrate was washed once with water (30 ml.). The solvent was removed by distillation at room temperature and diminished pressure leaving a crude yellow product (9.5 g., 100%), m.p. 110–116°. Recrystallization from methanol (100 ml.) yielded 7.4 g. (78.9%) of a white crystalline solid, m.p. 116–119°. Evaporation of the solvent gave a second crop (0.7 g.), m.p. 112–114°. The total yield was 8.1 g. (86.4%). An analytical sample was obtained by three more recrystallizations from methanol; m.p. 119–120°.

Anal. Calcd. for $C_{15}H_{17}OBr$: C, 61.44; H, 5.85. Found: C, 61.18; H, 6.12.

4,4-Pentamethylene-1-keto-1,4-dihydronaphthalene.—4,4-Pentamethylene-1-keto-2-bromo-1,2,3,4-tetrahydronaphthalene (12.3 g., 0.042 mole) was mixed with γ -collidine (75 ml.) which had been purified by distillation from solid potassium hydroxide. On heating, the bromoketone dissolved and the color changed from light yellow to a dark red. The reaction mixture darkened when heated to 167–172° for ten minutes and a considerable amount of crystalline γ -collidine hydrobromide separated. When cooled, the reaction mixture was diluted with approximately 250 ml. of ether and the salt which had precipitated was separated by filtration. A sample of this material was purified by sublimation. This compound, γ -collidine hydrobromide, did not melt below 310°.

The filtrate was washed with five portions of hydrochloric acid (25 ml., 10%), water (25 ml.), saturated sodium bicarbonate (25 ml.) and four times with portions of water (25 ml.). The ether solution was dried over anhydrous magnesium sulfate for 12 hours. The ether was distilled leaving a dark brown oil (9.5 g.) which still had a collidine odor. In a preliminary experiment it was found that the product could be obtained by crystallization from 60–68° petroleum ether, but chromatography resulted in a purer product and in higher yield. The entire residue was adsorbed on activated alumina (155 g.) in a 3 × 18 cm. column. The column was developed with a 1:1 benzene-60 to 68° petroleum ether mixture (2720 ml.) and finally with benzene (3600 ml.) to ensure complete removal of the dienone from the alumina. In the beginning of the development, a sharp band which was fluorescent in ultraviolet light moved down the column. Immediately following this fluorescent band, the dienone was obtained. The dienone obtained by removal of the solvent by distillation weighed 5.65 g. (63.3%), m.p. 78–81°. Recrystallization of this material from 60–68° petroleum ether yielded beautiful colorless prisms, m.p. 82–82.5°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.86; H, 7.54.

3,4-Cyclohepteno-1-naphthyl Acetate.—4,4-Pentamethylene-1-keto-1,4-dihydronaphthalene (2 g., 0.01 mole) was dissolved in acetic anhydride (5 ml.) and a solution of concentrated sulfuric acid (8 drops) in acetic anhydride (6 ml.) was added with thorough mixing. The colorless solution became yellow on mixing and after one minute the yellow color became more intense. After two minutes the color faded to a pale yellow and the temperature of the reaction mixture had risen to approximately 40°. After the mixture had stood 12 hours, distilled water (20 ml.) was added. The reaction mixture was shaken until the acetic anhydride was completely hydrolyzed. The white solid which separated was removed by filtration, washed well with water and then dried over phosphorus pentoxide. The 3,4-cyclohepteno-1-naphthyl acetate (2.2 g., 91.7%) melted at 73.5–74.5°. A sample purified by sublimation at 80° (0.05 mm.) was submitted for analysis; m.p. 78–78.5°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.43; H, 7.17.

3,4-Cyclohepteno-1-naphthol.—A mixture of 3,4-cyclohepteno-1-naphthyl acetate (1.67 g., 0.0066 mole) and sodium hydroxide (20 ml., 10%) was heated on a steam-bath with nitrogen gas bubbling through the mixture to prevent air oxidation of the resulting naphthol. After six hours, the mixture was homogeneous but it was red in color which indicated some oxidation of the product. The solution was extracted twice with portions of ether (20 ml.) which removed all the red coloration from the aqueous layer. The combined ether extracts were washed once with water (20 ml.). The combined aqueous extracts were acidified with 10% hydrochloric acid and only a trace of the naphthol was

obtained. Removal of the ether by distillation yielded 1.34 g. (95.6%) of crude 3,4-cyclohepteno-1-naphthol, m.p. 133–138°. One recrystallization from a small quantity of benzene gave light tan crystals of product, m.p. 134–138°. 3,4-Cyclohepteno-1-naphthol is a weakly acidic substance which was demonstrated above when it was extracted by ether from sodium hydroxide (10%) solution. This compound is precipitated from sodium hydroxide (10%) solution by the addition of concentrated ammonium hydroxide. The compound is readily soluble in carbon disulfide, ether, benzene, ethanol and liquid ammonia but it is sparingly soluble in carbon tetrachloride and petroleum ether. An additional recrystallization from chloroform and petroleum ether (60–68°) yielded a white fluffy electrostatic solid (0.11 g.), m.p. 140–141°. An analytical sample prepared in an analogous manner followed by sublimation melted at 139–140°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.51; H, 7.57.

trans-6,6a,7,8,9,10,11,11a-Octahydro-5-keto-5*H*-cyclohepta[*a*]naphthalene⁴ (0.35 g., 0.0016 mole) was dissolved in carbon tetrachloride (15 ml.) and *N*-bromosuccinimide (0.35 g.) was added. The pink reaction mixture was illuminated with a 100-watt unfrosted bulb for a period of four hours with occasional swirling. Succinimide (0.15 g., m.p. 125–127°) was removed by filtration and was washed twice with portions of carbon tetrachloride (20 ml.). The carbon tetrachloride filtrate was washed with water (20 ml.) and the solvent was removed by distillation at room temperature under diminished pressure. The residual oil was dissolved in redistilled γ -collidine (10 ml.), the air displaced with nitrogen and the solution was heated under reflux (175–185°) for ten minutes. Collidine hydrobromide precipitated in the brown reaction mixture. Ice (*ca.* 15 g.) and ether (50 ml.) were added and after shaking the ether layer was separated. The ether layer was washed three times with hydrochloric acid (10 ml., 10%) and four times with portions of water (10 ml.). The ether was distilled leaving a reddish-brown oil (0.43 g.). The oil was triturated with three portions of sodium hydroxide (20 ml., 10%) and filtered through a sintered glass funnel so that the insoluble oil adhered to the glassware. The clear alkaline solution was extracted with ether (25 ml.). The ether extract was washed twice with portions of water (10 ml.). The ether was distilled leaving a light tan oil (0.15 g., 43%) which crystallized as rosettes. A white solid was obtained by recrystallization from a mixture of chloroform (1 ml.) and petroleum ether (3 ml.); m.p. 139–141°. A mixture of this solid with the 3,4-cyclohepteno-1-naphthol previously obtained by rearrangement melted at 140.5–141.5°. The infrared spectra of the two samples in carbon disulfide and chloroform were identical. The ultraviolet absorption spectra of the two samples (using U.S.P. 95% ethanol as solvent) were identical.

2-(β -Naphthyl)-cyclopentanone.— β -Naphthylmagnesium bromide was prepared from β -bromonaphthalene (100 g., 0.48 mole) and magnesium turnings (14 g., 0.58 mole) in ether (350 ml.). The reaction was initiated readily by the addition of a small quantity of ethylmagnesium bromide in ether. The dark brown ethereal solution of β -naphthylmagnesium bromide was decanted from the unchanged magnesium turnings, diluted with anhydrous toluene (500 ml.) and then cooled in an ice-salt mixture. A solution of freshly distilled 2-chlorocyclopentanone (57 g., 0.48 mole) in anhydrous toluene (150 ml.) was added over a period of ten minutes to the stirred and cooled (0–5°) solution of the Grignard reagent. The color changed to a cherry red and a large quantity of viscous material separated. After this mixture was stirred for 30 minutes, most of the ether was removed by distillation. The reaction mixture was heated on a steam-bath for ten hours and then allowed to stand two days. The greenish-brown mixture contained a considerable quantity of a white solid (presumably magnesium halide) adhered to the flask. The mixture was hydrolyzed with hydrochloric acid (275 ml., 4%). The organic layer was separated and washed four times with water. The solvent was removed by distillation and the residue was distilled under diminished pressure using a Koelsch sausage flask. Impure 2-(β -naphthyl)-cyclopentanone (*ca.* 50 g.) was obtained at 135–200° (6 mm.) as a yellow oil which crystallized readily in beautiful rosettes. Recrystallization from 60–68° petroleum ether (200 ml.) gave 2-(β -naphthyl)-cyclo-

pentanone (27.8 g., 33.2%), m.p. 84–86°. Evaporation of the solvent yielded an additional crop (6 g.), m.p. 82–84°. The total yield was 40.2%. An analytical sample was obtained by further recrystallization from 60–68° petroleum ether; m.p. 85–86°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.68; H, 6.81.

An oxime was prepared and was purified by three recrystallizations from absolute ethanol. The crystals appeared to decrepitate near 155° and then melt with slight decomposition at 180–181°.

Anal. Calcd. for $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.95; H, 6.86; N, 6.06.

Methyl β -[1-(β -Naphthyl)-2-ketocyclopentyl]-propionate.—A solution of 2-(β -naphthyl)-cyclopentanone (32.5 g., 0.155 mole) in anhydrous toluene (200 ml.) was treated with sodium hydride (0.2 g.) and warmed to 45° for ten minutes. Redistilled methyl acrylate (14 g., 0.163 mole) was added dropwise to the stirred reaction mixture over a period of 30 minutes. The mixture was stirred for an additional hour and the toluene solution was decanted from the unchanged sodium hydride. This solution was washed once with hydrochloric acid (50 ml., 1%) and twice with portions of water (50 ml.). The toluene was distilled leaving a viscous yellow oil (43.8 g., 95%), n_D^{20} 1.5885. This crude methyl β -[1-(β -naphthyl)-2-ketocyclopentyl]-propionate was used in the next experiment. Distillation gave a pure product, b.p. 181–186° (14 mm.), n_D^{24} 1.5891.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 77.0; H, 6.83. Found: C, 76.88; H, 6.75.

The yellow orange *p*-nitrophenylhydrazone which was recrystallized twice from methanol melted at 175.5–176.0°.

Anal. Calcd. for $C_{25}H_{25}O_4N_3$: C, 69.59; H, 5.80; N, 9.74. Found: C, 69.44; H, 5.96; N, 9.74.

The yellow-orange 2,4-dinitrophenylhydrazone was prepared and was purified by two recrystallizations from a chloroform-methanol mixture, m.p. 154–155°.

Anal. Calcd. for $C_{25}H_{24}N_4O_6$: C, 63.01; H, 5.08; N, 11.76. Found: C, 62.8; H, 5.01; N, 11.70.

β -[1-(β -Naphthyl)-2-ketocyclopentyl]-propionic Acid.—Methyl β -[1-(β -naphthyl)-2-ketocyclopentyl]-propionate was prepared from 2-(β -naphthyl)-cyclopentanone (10.5 g., 0.05 mole) and methyl acrylate (4.3 g., 0.05 mole) using the procedure described above. The crude ester was saponified with sodium hydroxide (125 ml., 15%) by heating on a steam-bath for 2.5 hours. The alkaline solution was extracted with ether (50 ml.), treated with charcoal, filtered and then acidified with hydrochloric acid (10%). The solid product was dissolved in ether, and the latter solution was washed twice with water and dried over magnesium sulfate. Removal of the ether by distillation gave a light yellow oil which solidified on cooling; m.p. 94–110°. Recrystallization from a 4:1 water-methanol mixture yielded the acid (4.5 g., 31%), m.p. 111–116°. An analytical sample was obtained by recrystallization from aqueous methanol; m.p. 119.5–120.5°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.54; H, 6.39.

A *p*-nitrophenylhydrazone was prepared. After two recrystallizations from methanol and three from aqueous methanol, it was obtained as a yellow solid, m.p. 184–185°.

Anal. Calcd. for $C_{24}H_{23}O_4N_3$: C, 69.05; H, 5.55. Found: C, 68.79; H, 5.64.

A 2,4-dinitrophenylhydrazone was prepared in the usual manner. After three recrystallizations from a 1:2 chloroform-methanol mixture, this mustard colored product melted at 238–241°.

Anal. Calcd. for $C_{24}H_{22}O_6N_4$: C, 62.33; H, 4.82; N, 12.10. Found: C, 62.08; H, 5.18; N, 11.88.

β -[1-(β -Naphthyl)-cyclopentyl]-propionic Acid.—A mixture of methyl β -[1-(β -naphthyl)-2-ketocyclopentyl]-propionate (43.8 g., 0.15 mole), aqueous hydrazine (60 ml., 80%), potassium hydroxide (43 g.) and β,β' -dihydroxydiethyl ether (125 ml.) was heated at reflux temperature (*ca.* 120°) for 2.5 hours. The water and excess hydrazine were removed by distillation over a period of two hours. The red reaction mixture was heated three hours at approximately 200–210°. The solution was diluted with water (900 ml.) and then heated on a steam-bath for one day. The non-

acidic material (ca. 1 g.) was removed by extraction with two portions of ether (250 ml.). The aqueous residue was acidified with hydrochloric acid (10%) and then extracted with three portions of ether (250 ml.). The extracts were combined and washed with four portions of water (100 ml.). The ether was removed by distillation leaving a clear red oil (40.5 g.) which crystallized slowly; m.p. 30–60°. Recrystallization from methanol (1 l.) and water (200 ml.) yielded a light tan solid, m.p. 90–92°. Three additional crops of acid were obtained by successive additions of water. The total yield of acid was 25.9 g. (65%). An analytical sample was obtained by two recrystallizations from 3:1 methanol–water mixture. The white crystals appeared to melt at 89.5–90.5° but then solidified and finally melted at 96.5–97.5°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.38; H, 7.63.

The amide was prepared by treating the acid with thionyl chloride, removing the excess thionyl chloride by distillation, dissolving the residue in benzene and adding this solution to an excess of concentrated aqueous ammonium hydroxide. The colorless analytical sample was obtained by two recrystallizations from aqueous methanol; m.p. 112.5–113°.

Anal. Calcd. for $C_{18}H_{21}ON$: C, 80.86; H, 7.93; N, 5.25. Found: C, 80.64; H, 8.02; N, 5.33.

1,1-Tetramethylene-4-keto-1,2,3,4-tetrahydrophenanthrene.—A solution of β -[1-(β -naphthyl)-cyclopentyl]-propionic acid (25.9 g., 0.1 mole) in benzene (100 ml.) was dried by distilling benzene (50 ml.) from the solution. Thionyl chloride (40 ml.) was added and the solution was heated under reflux for four hours. The benzene and excess thionyl chloride were removed by distillation, the last traces were removed by evaporation at reduced pressure. To ensure complete removal of the thionyl chloride, benzene (100 ml.) was added and distilled from the reaction mixture. The residual oil was dissolved in benzene (200 ml.) and stannic chloride (35 ml.) was added dropwise with stirring over a period of five minutes. The brown reaction mixture was allowed to stand one hour and poured into a mixture of ice (100 g.) and hydrochloric acid (300 ml., 10%). After a black solid (ca. 2–3 g.) was removed by filtration, the layers were separated. The benzene layer was washed with sodium hydroxide (100 ml., 10%) and four portions of water (50 ml.). The benzene was removed by distillation leaving a viscous oil. This product was distilled through an 8-cm. Vigreux column and was obtained as a light brown oil (19.9 g., 82.5%) which crystallized readily; b.p. 175–190° (0.5 mm.), m.p. 51–53°. An analytical sample was obtained with low recovery by recrystallization from 60–68° petroleum ether; m.p. 56.5–57.5°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.27; H, 7.19.

A *p*-nitrophenylhydrazone was prepared in the usual manner. After two recrystallizations from 95% ethanol and one from chloroform–ethanol mixture, the mustard colored solid melted at 176–176.5°.

Anal. Calcd. for $C_{24}H_{23}O_2N_3$: C, 74.78; H, 6.01; N, 10.90. Found: C, 74.94; H, 6.15; N, 10.85.

7,8,9,10-Tetrahydro-5-chrysenyl Acetate.—1,1-Tetramethylene-4-keto-1,2,3,4-tetrahydrophenanthrene (1.60 g., 0.0064 mole) in carbon tetrachloride (6 ml.) was brominated with *N*-bromosuccinimide (1.04 g.). The reaction mixture was illuminated over a period of 3.5 hours with a 100-watt unfrosted incandescent bulb placed approximately 2 mm. from the flask. The succinimide was removed by filtration and washed with carbon tetrachloride. The

filtrate was washed once with water (10 ml.). The carbon tetrachloride was distilled at room temperature under diminished pressure leaving a light brown oil (2.05 g.). This oil was dissolved in redistilled γ -collidine (10 ml.) and heated under reflux (175–185°) for 15 minutes. The cooled brown reaction mixture was diluted with ether and the gray γ -collidine hydrobromide (0.95 g., 82%) was removed by filtration and washed with ether. The filtrate was washed four times with portions of hydrochloric acid (10 ml., 10%) and four times with water. The ether solution was dried over magnesium sulfate. The ether was distilled leaving a light brown oil (1.45 g.). The oil was chromatographed through a column (12 × 260 mm.) of activated alumina (30 g.). A solution of the oil was dissolved in benzene (6 ml.) added to the column, and the column was developed with a 19:1 mixture of 60–68° petroleum ether–benzene (1060 ml.). When benzene (130 ml.) was used as the eluent, 1,1-tetramethylene-4-keto-1,4-dihydrophenanthrene (0.58 g., 40.2%) was obtained as a yellow oil. The dienone was used without further purification.

A solution of concentrated sulfuric acid (0.12 g.) in acetic anhydride (5 ml.) was added to a solution of the above dienone (0.45 g.) in acetic anhydride (5 ml.). The yellow solution was allowed to stand one hour and then the excess acetic anhydride was hydrolyzed by adding an equal volume of water. The pink 7,8,9,10-tetrahydro-5-chrysenyl acetate (0.5 g., 95%) was separated by filtration, washed with water and dried over phosphorus pentoxide; m.p. 101.5–104°. Recrystallization from methanol (8 ml.) gave white needles (0.41 g., 78%), m.p. 110.5–111.5°. A further recrystallization raised the melting point to 111.5–112.5°. A sample was prepared for analysis by sublimation at 95° (0.02 mm.).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.66; H, 6.57.

7,8,9,10-Tetrahydro-5-chrysenol.—A mixture of 7,8,9,10-tetrahydro-5-chrysenyl acetate (0.3 g.), potassium hydroxide (0.6 g.), water (3 ml.) and methanol (10 ml.) was heated under reflux for one hour. The solution was poured into an excess of hydrochloric acid (10%). This mixture was diluted to 50 ml. with water and the light tan solid (0.26 g.) which was separated by filtration, was washed three times with portions of water (5 ml.) and dried over phosphorus pentoxide; m.p. 176–185°. The solid appeared to oxidize while standing exposed to the air. Electrostatic yellow crystals were obtained for analysis by sublimation at 175° (0.02 mm.), m.p. 189–190.5°. The analyses were difficult because the yellow crystals were so electrostatic that they flew from the weighing boat to the combustion tube. A γ -emitting substance did not reduce the electrostatic effect.

Anal. Calcd. for $C_{18}H_{18}O$: C, 87.06; H, 6.50. Found: C, 86.88; H, 6.74.

An aqueous solution of phenyldiazonium chloride gave an orange color when added to the chrysenol in aqueous sodium hydroxide (2%). After five minutes a red coupling product separated.

Chrysene from 7,8,9,10-Tetrahydro-5-chrysenol.—A mixture of 7,8,9,10-tetrahydro-5-chrysenol (40 mg.) and palladium–charcoal (90 mg., 10%) was placed in a glass tube, the air displaced with nitrogen and the mixture heated in a sublimation block (243–268°) for six hours. Colorless plates (ca. 3 mg.) sublimed, m.p. 253–254°. A mixture of sublimed chrysene and the substance obtained melted at 252–254°. The ultraviolet absorption spectra of authentic chrysene and the material were identical.

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