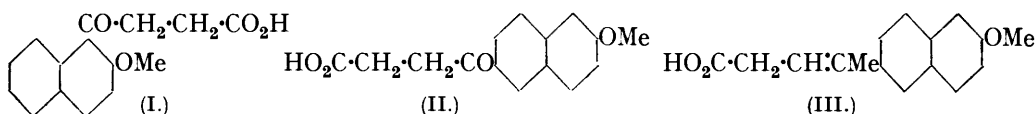


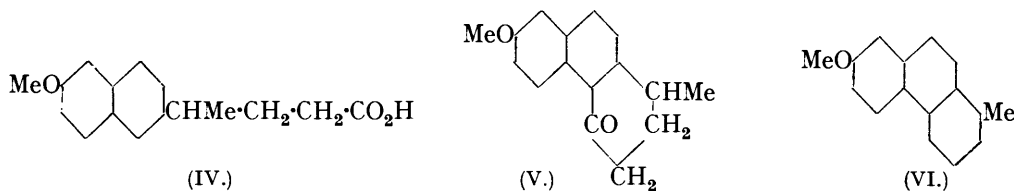
70. *Syntheses in the Phenanthrene Series. Part II. 7-Methoxy-1-methylphenanthrene and a New Route to Phenanthrene.*

By W. F. SHORT, H. STROMBERG, and A. E. WILES.

FIESER and PETERS (*J. Amer. Chem. Soc.*, 1932, **54**, 4351) state that succinic anhydride condenses with  $\beta$ -naphthyl methyl ether in nitrobenzene solution in presence of aluminium chloride to furnish an acid,  $C_{15}H_{14}O_4$ , m. p.  $152^\circ$ , which was presumed to be  $\beta$ -(2-methoxy-1-naphthoyl)propionic acid (I).



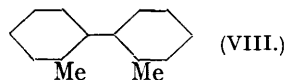
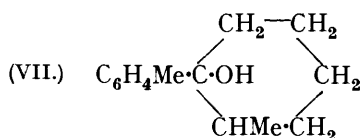
In our hands, these reactants afforded two isomeric ketonic acids,  $C_{15}H_{14}O_4$ , m. p.  $148.5$ — $149^\circ$  and  $136.5$ — $137.5^\circ$ , produced in the approximate ratio of 9 : 1. Oxidation of these acids with alkaline hypochlorite yielded 2-methoxy-6-naphthoic acid and 2-methoxy-1-naphthoic acid respectively, from which it follows that the acid of higher melting point must be  $\beta$ -(2-methoxy-6-naphthoyl)propionic acid (II) and that the acid, m. p.  $136.5$ — $137.5^\circ$ , is  $\beta$ -(2-methoxy-1-naphthoyl)propionic acid (I). The acid (I) is the sole product when the reaction is conducted in carbon disulphide solution. Interaction between the ethyl ester of the acid (II) and methylmagnesium iodide in ether-benzene solution afforded  $\gamma$ -(2-methoxy-6-naphthyl)- $\Delta^8$ -pentenoic acid (III) in 69% yield. On catalytic reduction (platinum oxide and acetic acid at  $80^\circ$ ),  $\gamma$ -(2-methoxy-6-naphthyl)-*n*-valeric acid (IV) was obtained. The dehydration of (IV) with the formation of 4-keto-7-methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (V) could be effected by means of stannic chloride, but much better yields were obtained by using phosphoric oxide (compare Perkin and Robinson, *J.*, 1907, **91**, 1081). Reduction of the cyclic ketone and dehydrogenation with selenium afforded 7-methoxy-1-methylphenanthrene (VI).



Finally, the demethylation of (VI) by means of hydrobromic-acetic acid yielded 7-hydroxy-1-methylphenanthrene, which is identical with the phenol obtained by selenium dehydrogenation of the diterpene alcohol, totarol (to be described in a subsequent communication).

The method for the preparation of unsymmetrical derivatives of diphenyl developed by Sherwood, Short, and Stansfield (*J.*, 1932, 1832) may be extended in some cases to the preparation of phenanthrenes and similar condensed ring systems. For instance, 2-methylcyclohexanone and the Grignard compound prepared from *o*-iodotoluene afford 1-*o*-tolyl-2-methylcyclohexanol (VII) in 50% yield, and dehydrogenation with sulphur (2 atoms) at  $180$ — $250^\circ$  furnishes 2 : 2'-dimethyldiphenyl (VIII). When the last substance

is heated more strongly with sulphur, phenanthrene is obtained in good yield (compare Berger, *J. pr. Chem.*, 1932, **133**, 338).



This method is suitable for the synthesis of hydrocarbons, but the introduction of a methoxyl group inhibits the final ring closure; *e.g.*, 4-methoxy-2 : 2'-dimethyldiphenyl was easily obtained by the general scheme starting from 2-methylcyclohexanone and the Grignard compound of 2-bromo-*m*-tolyl methyl ether, but appropriate conditions for conversion into 2-methoxyphenanthrene by dehydrogenation with sulphur or selenium could not be found. For an attempted synthesis of 2-methoxy-1-methylphenanthrene by a similar method, we required 6-bromo-*o*-3-xylene, and the necessary *o*-3-xylene was prepared by the following series of reactions: 2-nitro-*m*-tolyl methyl ether (Gibson, *J.*, 1923, **123**, 1273; Haworth and Lapworth, *ibid.*, p. 2993)  $\longrightarrow$  2-amino-*m*-tolyl methyl ether  $\longrightarrow$  2-bromo-*m*-tolyl methyl ether  $\longrightarrow$  3-methoxy-*o*-xylene  $\longrightarrow$  *o*-3-xylene.

#### EXPERIMENTAL.

$\beta$ -(2-Methoxy-1-naphthoyl)propionic Acid (I).—Aluminium chloride (2.2 mols.) was added in small portions with stirring to a solution of  $\beta$ -naphthyl methyl ether (1 mol.) and succinic anhydride (1 mol.) in carbon disulphide, the mixture then being boiled for several hours and worked up in the usual way. The *keto-acid*, recrystallised from benzene-ligroin, had m. p. 136.5—137.5° (Found: C, 69.8; H, 5.5.  $\text{C}_{15}\text{H}_{14}\text{O}_4$  requires C, 69.8; H, 5.4%). The *ethyl* ester separated from methyl alcohol in colourless plates, m. p. 41—42° (Found: C, 71.0; H, 6.3.  $\text{C}_{17}\text{H}_{18}\text{O}_4$  requires C, 71.3; H, 6.3%). The *keto-acid* (1 g.) and 100 c.c. of alkaline sodium hypochlorite (0.25*M*-NaOCl and 0.5*N*-NaOH) were heated on the water-bath for 20 minutes, then boiled gently for 20 minutes, filtered, and saturated with sulphur dioxide. The precipitated acid, recrystallised from ethyl acetate, melted at 174—175° either alone or after admixture with 2-methoxy-1-naphthoic acid (Fuson, Farlow, and Stehman, *J. Amer. Chem. Soc.*, 1931, **53**, 4101). The methyl esters, prepared by means of diazomethane, melted at 49—49.5° either alone or after admixture. Werner and Seybold (*Ber.*, 1904, **37**, 3661) record m. p. 52°.

$\beta$ -(2-Methoxy-6-naphthoyl)propionic Acid.—Succinic anhydride (1.1 mols.) and  $\beta$ -naphthyl methyl ether (1 mol.) were added alternately during  $\frac{1}{2}$  hour to a mechanically stirred solution of aluminium chloride (2 mols.) in nitrobenzene (8 mols.), cooled in a freezing mixture. The whole was stirred for  $\frac{1}{2}$  hour, kept for 100 hours, and then decomposed with ice and hydrochloric acid. Nitrobenzene was removed in steam, and the crude acids isolated with sodium carbonate. The sticky cake was repeatedly extracted with boiling benzene and the extract was recrystallised from methyl alcohol until the m. p. reached *ca.* 135° and then esterified by boiling with 15% alcoholic hydrogen chloride. The crude ester, recrystallised from methyl alcohol, afforded a *solid*, m. p. 107.5—108° (Found: C, 71.3; H, 6.3.  $\text{C}_{17}\text{H}_{18}\text{O}_4$  requires C, 71.3; H, 6.3%), and a *liquid*, which was distilled under diminished pressure. The fraction, b. p. 206—233°/4 mm., was recrystallised from methyl alcohol; it then melted at 41—42° either alone or after admixture with ethyl  $\beta$ -(2-methoxy-1-naphthoyl)propionate (above). The methyl-alcoholic mother-liquors from the recrystallisation of the crude *keto-acids* were esterified; the fraction, b. p. 206—240°/4 mm., furnished a further quantity of the *keto-ester*, m. p. 107.5—108°. The *methyl* ester separated from methyl alcohol in plates, m. p. 98° (Found: C, 70.4; H, 6.1.  $\text{C}_{16}\text{H}_{16}\text{O}_4$  requires C, 70.6; H, 5.9%). Saponification of these esters afforded  $\beta$ -(2-methoxy-6-naphthoyl)propionic acid, m. p. 148.5—149° after recrystallisation from methyl alcohol (Found: C, 69.9; H, 5.5.  $\text{C}_{15}\text{H}_{14}\text{O}_4$  requires C, 69.8; H, 5.4%). This is probably the compound assumed by Fieser and Peters (*loc. cit.*), who record m. p. 152°, to be  $\beta$ -(2-methoxy-1-naphthoyl)propionic acid. Oxidation of the acid with alkaline hypochlorite, under the conditions already specified, afforded 2-methoxy-6-naphthoic acid, m. p. 205°, which did not depress the m. p. of an authentic specimen kindly supplied by Dr. R. D. Haworth. A portion of the acid was converted, through the chloride, into 2-methoxy-6-naphthamide, m. p. 213—215° (Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2835, record m. p. 216°). The total yield of pure ketonic acids was *ca.* 45%.

$\gamma$ -(2-Methoxy-6-naphthyl)- $\Delta^{\beta}$ -pentenoic Acid.—Methylmagnesium iodide (from methyl iodide, 8 g.; magnesium, 0.8 g.; and ether, 40 c.c.) was added during 20 minutes with shaking to an ice-cold solution of ethyl  $\beta$ -(2-methoxy-6-naphthoyl)propionate (5 g.) in benzene (210 c.c.) and a little ether. The mixture was boiled under reflux for 1 hour, decomposed with ice and sulphuric acid, and filtered. The grey solid was dissolved in dilute sodium carbonate solution, reprecipitated by acidification, and recrystallised from glacial acetic acid; m. p. 154—157°. A further quantity was obtained from the benzene solution by extraction with dilute sodium carbonate solution, and successive recrystallisation from acetone and ethyl acetate raised the m. p. to 171—171.5° (Found: C, 75.0; H, 6.2.  $C_{16}H_{16}O_3$  requires C, 75.0; H, 6.25%). The average yield was 69%.

$\gamma$ -(2-Methoxy-6-naphthyl)-*n*-valeric Acid.—Hydrogen was passed under slight pressure into a mechanically stirred solution of the unsaturated acid (9.5 g.) in glacial acetic acid (200 c.c.) at 80° in presence of platinum oxide catalyst (0.1 g.). The theoretical quantity of hydrogen was absorbed in 2 hours; the product, isolated in the usual way, crystallised from ligroin in white microscopic needles, m. p. 121.5° (Found: C, 74.1; H, 7.1.  $C_{16}H_{18}O_3$  requires C, 74.4; H, 7.0%). The yield was 98%.

4-Keto-7-methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene.—Phosphoric oxide (5 parts) was added in small portions with vigorous shaking to a solution of the saturated acid (1 part) in boiling benzene (15 parts). After boiling for 3 hours, the mixture was decomposed with ice, and the aqueous layer extracted repeatedly with ether. The extract was washed with dilute sodium carbonate solution, which removed a little unchanged acid, and the ketone, isolated by distillation, was obtained in 80% yield as a viscous oil, b. p. 195°/0.8 mm. The 2 : 4-dinitrophenylhydrazone separated from toluene-ligroin in red needles, m. p. 241° (decomp.) (Found: C, 62.7; H, 5.2; N, 13.4.  $C_{22}H_{20}O_5N_4$  requires C, 62.9; H, 4.8; N, 13.4%).

7-Methoxy-1-methylphenanthrene.—The cyclic ketone was reduced with amalgamated zinc and concentrated hydrochloric acid, and the product dehydrogenated with selenium. The fraction, b. p. 195—200°/0.5 mm., recrystallised from alcohol, formed white plates, m. p. 133.5—134.5° (Found: C, 86.2; H, 6.5.  $C_{16}H_{14}O$  requires C, 86.5; H, 6.3%). The picrate separated from methyl alcohol in red needles, m. p. ca. 142°, but was unstable. The methyl ether was smoothly demethylated by boiling hydrobromic-acetic acid; the resulting 7-hydroxy-1-methylphenanthrene crystallised from benzene in clustered needles, m. p. 190—191° (Found: C, 86.3; H, 5.85.  $C_{15}H_{12}O$  requires C, 86.5; H, 5.7%). The acetate, m. p. 135.5—136° (Found: C, 81.4; H, 5.6.  $C_{17}H_{14}O_2$  requires C, 81.6; H, 5.6%), was oxidised to an orange-yellow quinone, m. p. 202—207° (decomp.) (Found: C, 72.7; H, 4.9.  $C_{17}H_{12}O_4$  requires C, 72.85; H, 4.3%), which afforded a quinoxaline, m. p. 244.5—246.5° (Found: C, 78.65; H, 4.65.  $C_{23}H_{16}O_2N_2$  requires C, 78.4; H, 4.5%).

1-*o*-Tolyl-2-methylcyclohexanol.—*o*-Tolylmagnesium iodide and 2-methylcyclohexanone reacted under the general conditions specified by Sherwood, Short, and Stansfield (*loc. cit.*) to produce the tertiary alcohol, b. p. 153—154°/14 mm., in 50% yield (Found: C, 82.1; H, 9.9.  $C_{14}H_{20}O$  requires C, 82.35; H, 9.8%). Dehydrogenation with sulphur (2 atoms) at 180—250° afforded 2 : 2'-dimethyldiphenyl, m. p. 16—17°, which was compared with a specimen produced by Ullmann's method (*Annalen*, 1904, 332, 38). When 2 : 2'-dimethyldiphenyl (1.4 g.) and sulphur (0.7 g.) were heated in a metal-bath at 270—280°, very little hydrogen sulphide was evolved, but when the temperature was raised so that the mixture distilled, brisk evolution of gas occurred. The distillate solidified immediately and after recrystallisation from alcohol melted at 99° either alone or after admixture with phenanthrene. The picrate, m. p. 145°, caused no depression of the m. p. of phenanthrene picrate. Attempts to convert the carbinol into phenanthrene in one operation by increasing the quantity of sulphur and raising the temperature afforded small yields and the synthesis is most successfully carried out in stages as described above.

6-Bromo-*m*-tolyl Methyl Ether.—The bromination of *m*-cresol is better effected in acetic acid solution as described by Darzens and Levy (*Compt. rend.*, 1931, 193, 292) rather than in chloroform (Huston and Hutchinson, *J. Amer. Chem. Soc.*, 1932, 54, 1504). The yield of pure 6-bromo-*m*-cresol, m. p. 5°, was 55% and 4-bromo-*m*-cresol could not be detected in the product. Methylation with methyl sulphate in 10% sodium hydroxide solution afforded the phenol ether, b. p. 132—135°/25 mm., in satisfactory yield.

1-(5'-Methoxy-*o*-tolyl)-2-methyl- $\Delta^1$ -cyclohexene.—The Grignard compound of 6-bromo-*m*-tolyl methyl ether reacted with 2-methylcyclohexanone (1 mol.) at 0° to afford a mixture from which a fraction, b. p. 154—157°/13 mm., could be isolated by fractionation. Analysis showed that this consisted mainly of the unsaturated compound, the carbinol having been dehydrated

during the reaction (Found : C, 81·8; H, 9·1.  $C_{15}H_{22}O_2$  requires C, 76·9; H, 9·4%.  $C_{15}H_{20}O$  requires C, 83·3; H, 9·3%). The yield was 39%. Dehydrogenation with sulphur at 180—240° afforded 4-methoxy-2 : 2'-dimethyldiphenyl in 52% yield. Demethylation could not be effected with hydrobromic acid, but when the crude methyl ether (3 g.) was boiled for 2 hours with hydriodic acid (4 c.c.,  $d$  1·7) and acetic acid (6 c.c.), 4-hydroxy-2 : 2'-dimethyldiphenyl, m. p. 105°, was obtained (Found : C, 84·9; H, 7·25.  $C_{14}H_{14}O$  requires C, 84·9; H, 7·1%). The methyl ether, heated with sulphur or selenium under a variety of conditions, was either unchanged or completely destroyed; no 2-methoxyphenanthrene could be detected in the product.

*2-Bromo-m-tolyl Methyl Ether.*—Sodium hydrosulphite (100 g.) was added during 1½ hours to a boiling mixture of 2-nitro-*m*-tolyl methyl ether (20 g.) (Haworth and Lapworth, *loc. cit.*), alcohol (60 c.c.), and water (100 c.c.). The mixture was then acidified with hydrochloric acid, boiled for 5 minutes, filtered, and made alkaline. Extraction with chloroform furnished 2-amino-*m*-tolyl methyl ether, b. p. 123—130°/18 mm., m. p. 30°, in 67% yield (Gibson, *loc. cit.*, records m. p. 31°). The amine (13·7 g.), dissolved in sulphuric acid (100 c.c.) and water (140 c.c.), was diazotised at 0°, and the solution added to cuprous bromide solution [from copper sulphate 6 g., potassium bromide 6 g., copper powder 3 g., hydrobromic acid ( $d$  1·5) 39 c.c., and water 3 c.c.] at 60°. 2-Bromo-*m*-tolyl methyl ether, obtained in 44% yield, was purified by distillation (b. p. 124°/18 mm.), m. p. 38° (Hodgson and Beard, J., 1925, **127**, 498, record m. p. 35·5—36·5°). A small quantity of 2-hydroxy-*m*-tolyl methyl ether, m. p. 41—42° (Majima and Okazaki, *Ber.*, 1916, **49**, 1482), was isolated as by-product.

*o*-3-Xylenol.—Methyl sulphate (54·5 g.) and ether (150 c.c.) were added during an hour to a Grignard solution prepared from 2-bromo-*m*-tolyl methyl ether (87 g.), magnesium (10·5 g.), and ether (285 c.c.); the mixture was then boiled for an hour and worked up in the usual way. Fractionation of the product afforded 3-methoxy-*o*-xylene, b. p. 85°/18 mm., which was smoothly demethylated by boiling hydrobromic-acetic acid to *o*-3-xylenol, m. p. 73·5—74·5° after crystallisation from alcohol, which did not depress the m. p. of an authentic specimen obtained from the Gesellschaft für Teerverwertung (Duisberg-Meiderich). Bromination of the phenol, dissolved in 10 parts of acetic acid at 0°, furnished 6-bromo-*o*-3-xylenol in 94% yield. This compound melted at 92° as stated by Lockemann and Kuntzmann (*Angew. Chem.*, 1933, **46**, 297) and methylation in 10% alkali solution afforded the methyl ether, b. p. 139—140°/17 mm.

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